

DISSERTATION

UNLOCKING THE POTENTIAL OF CROSSLINKED POLYMERS:  
FROM DYNAMIC COVALENT BONDS TO RECYCLABLE THERMOSETS

Submitted by

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## ABSTRACT

### UNLOCKING THE POTENTIAL OF CROSSLINKED POLYMERS: FROM DYNAMIC COVALENT BONDS TO RECYCLABLE THERMOSETS

This dissertation describes the development of dynamic covalent chemistries and bond exchange principles in the context of crosslinked polymers demonstrating high performance properties and sustainable end-of-life avenues. Traditional crosslinked polymers, or thermosets, present a significant challenge in meeting the goals of a circular materials economy caused by a strict orthogonality between performance and recyclability. Covalent adaptable networks (CANs) are a developing class of responsive, crosslinked materials that mimic the performance qualities of static thermosets but access flow-state melt processability by triggering crosslink-bond exchange. Several impactful and fundamental advances to this topic and broader sustainable chemistry are discussed herein: demonstration of new dynamic covalent bonds, establishment of intra- and inter-domain exchange principles, orthogonal working/healing exchange conditions for classic thermoset behavior, and upcycling compatibilization of mixed-feed commodity plastics via dynamic crosslinking. The multidisciplinary knowledge developed herein spans the themes of polymer synthesis, catalysis, block copolymers, self-assembly, structure/property relationships, mechanism elucidation, sustainability, materials chemistry, and polymer physics.

Chapter 1 introduces dynamic covalent bonds, sustainable thermoset strategies, and standing challenges impeding wide-scale adoption. Background is also supplied on relevant themes to the following chapters, including pathways for plastics recycling, block copolymer technology, and mechanical reprocessing. Chapter 2 describes the Lewis pair polymerization

(LPP) of renewable indenone to a high  $T_g$  ( $> 300$  °C), optically transparent bio-polymer. Special emphasis is made for the unique upcycling of polyindenone, as well as the Lewis pair polymerization mechanism and methodology which is critical for complex polymer synthesis in Chapters 3 & 4. Chapter 3 discloses the merging of A-B-A triblock copolymer self-assembled thermoplastic elastomer (TPE) *structure* with CAN dynamic bond exchange *function* to establish tethered domain-restriction as an effective strategy to lock out creep deformation during working conditions. We also define the fundamental principles governing inter- and intra-domain exchange and thermomechanical activation of newly established dynamic covalent bonds. Chapter 4 describes our compounded-sequence-control LPP technology applied to produce architecturally and topologically sophisticated cyclic and linear A-B-A-B multiblock copolymers in timely ( $< 10$  min), scalable ( $\sim 40$  g), one-pot two-step processes. Structure/property relationships are meticulously investigated in solution, bulk, and film phase for differentiation of isomeric products. Chapter 5 reports a highly collaborative, multidisciplinary (molecular, material, and computational) study on bis(diazirine) crosslinker molecules with imbedded dynamic covalent bond functionality as universal crosslinking agents for upcycling commodity thermoplastics (polyethylene, etc.) to high-performance, recyclable thermosets. Demonstration of successful crosslinking by C-H insertion, improvements to material performance (tensile pulling, creep-recovery, and thermomechanical durability), and reprocessability are thoroughly discussed. Most critical, we establish the compatibilization of (otherwise immiscible) mixed plastics in dynamically crosslinked polymer blends and examine the phenomenon by molecular modeling and structural characterization. Chapter 6 offers conclusions, remaining challenges, and future opportunities.



## ACKNOWLEDGEMENTS

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## DEDICATION

*To my friends and family,  
& to those who have been so significant in each chapter of my life, but faded away with time.  
I thank and miss you all dearly.*

## TABLE OF CONTENTS

|                                                                                                                                                   |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| ABSTRACT.....                                                                                                                                     | ii  |
| ACKNOWLEDGEMENTS.....                                                                                                                             | iv  |
| DEDICATION.....                                                                                                                                   | vii |
| <br>Chapter 1                                                                                                                                     |     |
| Introduction: The Role of Covalent Adaptable Networks in Next-Generation<br>Recyclable Thermosets.....                                            | 1   |
| References.....                                                                                                                                   | 22  |
| <br>Chapter 2                                                                                                                                     |     |
| Lewis Pair Polymerization of Renewable Indenone to Erythro-Ditactic High- $T_g$<br>Polymers with an Upcycling Avenue                              |     |
| 2.1. Synopsis.....                                                                                                                                | 31  |
| 2.2. Introduction.....                                                                                                                            | 32  |
| 2.3. Results and Discussion.....                                                                                                                  | 35  |
| 2.4. Conclusions.....                                                                                                                             | 49  |
| References.....                                                                                                                                   | 51  |
| <br>Chapter 3                                                                                                                                     |     |
| Thermomechanical Activation Achieving Orthogonal Work/Healing Conditions of<br>Nanostructured Tri-Block Copolymer Thermosets                      |     |
| 3.1. Synopsis.....                                                                                                                                | 57  |
| 3.2. Introduction.....                                                                                                                            | 57  |
| 3.3. Results and Discussion.....                                                                                                                  | 61  |
| 3.4. Conclusions.....                                                                                                                             | 74  |
| References.....                                                                                                                                   | 77  |
| <br>Chapter 4                                                                                                                                     |     |
| Architecturally and Topologically Sophisticated (Meth)Acrylic Multiblock<br>Copolymers: Rapid Scalable Syntheses and Meticulous Differentiations. |     |
| 4.1. Synopsis.....                                                                                                                                | 86  |
| 4.2. Introduction.....                                                                                                                            | 87  |
| 4.3. Results and Discussion.....                                                                                                                  | 91  |
| 4.4. Conclusions.....                                                                                                                             | 108 |
| References.....                                                                                                                                   | 111 |

|                                                                        |                                                               |     |
|------------------------------------------------------------------------|---------------------------------------------------------------|-----|
| Chapter 5                                                              | Dynamic Crosslinking Compatibilises Immiscible Mixed Plastics |     |
| 5.1.                                                                   | Synopsis.....                                                 | 114 |
| 5.2.                                                                   | Introduction.....                                             | 114 |
| 5.3.                                                                   | Results.....                                                  | 116 |
| 5.4.                                                                   | Conclusions.....                                              | 131 |
|                                                                        | References.....                                               | 145 |
| Chapter 6                                                              | Conclusions and Outlook                                       |     |
| 6.1.                                                                   | Conclusions and Outlook .....                                 | 152 |
|                                                                        | References.....                                               | 158 |
| Appendix A – Supplementary Information Corresponding to Chapter 2..... |                                                               | 159 |
|                                                                        | References.....                                               | 180 |
| Appendix B – Supplementary Information Corresponding to Chapter 3..... |                                                               | 181 |
|                                                                        | References.....                                               | 245 |
| Appendix C – Supplementary Information Corresponding to Chapter 4..... |                                                               | 246 |
|                                                                        | References.....                                               | 289 |
| Appendix D – Supplementary Information Corresponding to Chapter 5..... |                                                               | 290 |
|                                                                        | References.....                                               | 406 |

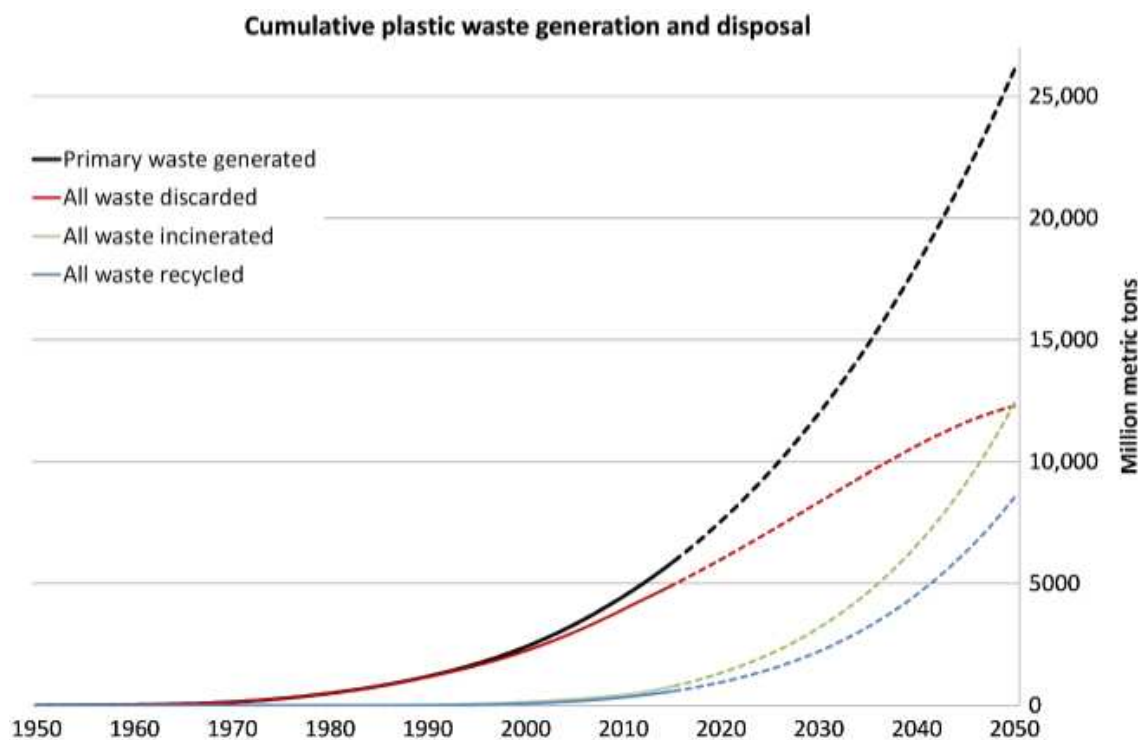
## Chapter 1

### Introduction:

#### The Role of Covalent Adaptable Networks in Next-Generation Recyclable Thermosets

### 1.1 Current Plastics Recycling Overview: Technologies and Opportunities.

The impending 2050 milestone will observe several simultaneous, sobering statistics consequential to seemingly unending demand for commodity plastics: more plastic than fish (by weight) in the ocean, annual plastic production of 1.12 billion tons, and allocation of nearly 20% total petroleum consumption towards production.<sup>1-2</sup> Despite these predictions, and accredited to a growing global population, plastic productions is exponentially increasing in an overwhelming excess, predicted to outcompete scientific and societal actions taken to mitigate the ongoing plastic waste accumulation (Figure 1.1).<sup>3</sup> Linear material economy philosophies have relied on landfilling and incineration as a means to dispose of this waste, which ultimately contributes significantly to rising greenhouse gas emissions and places toxic contaminants into water and soil. Considering the grave implications on human and environmental health if these factors continue to acquiesce with anticipated trends, global polymer research efforts have realigned to emphasize practical end-of-life solutions for a circular materials economy.



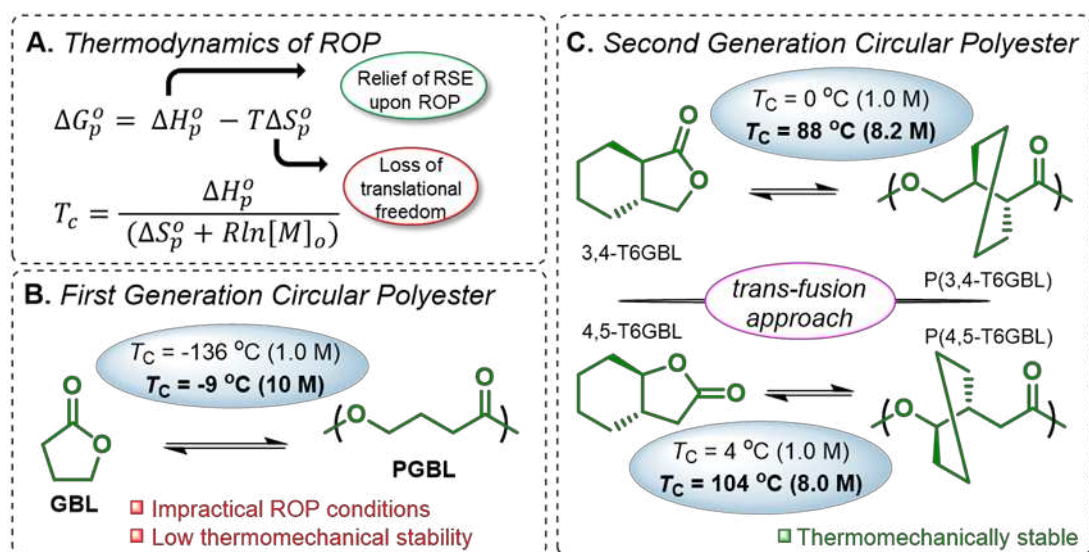
**Figure 1.1.** Cumulative plastic waste generation and disposal (in million metric tons). Solid lines show historical data from 1950-2015; dashed lines show projections of historical trends to 2050. (Source: Geyer, Jambeck, & Law. *Science Advances* 2017)

Practical end of life solutions encompass multiple avenues for recycling or upcycling: biological, chemical, and mechanical – among other less attractive solutions such as pyrolysis for energy recapture.<sup>4</sup> Biological and biodegradable recycling, a microbial strategy to mitigate gross mismanagement of plastics waste discarded into marine and terrestrial environment,<sup>5-7</sup> benefits from avoiding costly collection and purification requirements.<sup>8-10</sup> The emerging field of research has exploited engineered or natural microorganisms to enzymatically break down plastics under ambient conditions, most successfully applied to polyethylene terephthalate (PET).<sup>11-16</sup> This approach, however, remains highly expensive and time-consuming while lacks the retrieval of raw material input for ideal closed-loop circularity.<sup>17</sup> Considering the rapid developments in a short period of time, however, there is high potential for biological recycling to have an important role in ambient plastic degradation.

The development of chemical recyclability, which operates on the closed-loop de-/re-polymerization of virgin-quality polymer and monomer, has afforded the means to hurdle this loss by recapturing and recirculating end-of-life polymers.<sup>18-19</sup> A distinct advantage of chemical recycling over biological alternatives is the quantitative re-collection, and subsequent re-circulation, of primary input raw material. Recalling reported metrics of \$80-120 billion in unrecovered plastic waste value, we emphasize equally substantial economic motivation for recyclable materials. Within this same consideration for energy and economic cost, however, there remains significant challenge in achieving industrial adoption due to the often-overlooked complexity between polymer polymerization and depolymerization.<sup>20</sup> These steps include waste collection, sorting, extrusion, cleaning, decontamination of coloring/plasticizing/antioxidizing agents *before* the purified and isolated polymers can undergo catalyzed depolymerization typically occurring under high vacuum and temperature conditions.

In less than a decade, and despite these daunting impedances, the scope and feasibility of chemically recyclable polymers has expanded tremendously. These platforms rely on the thermodynamic equilibrium principles dictating the catalyzed ring-opening and ring-closing events, separated by ceiling temperature ( $T_C$ ), between a monomer and its corresponding polymer (Figure 1.2a). Manipulation of  $T_C$  through temperature, concentration, and discrete rare-earth metal catalysts – along with redesign of monomer structure and thus RSE for higher enthalpic payout – has afforded a wide breadth of suitable monomer/polymer systems. These include esters/polyesters<sup>21-24</sup> and thioesters/polythioesters,<sup>25</sup> carbonates/polycarbonates,<sup>26-28</sup> acetals/polyacetals,<sup>29</sup> cyclic olefins/cyclic polyolefins,<sup>30-31</sup> and notably emerging polar vinyl acrylic and methacrylic monomer/polymer systems with various synthetic advantages (Figure 1.2b,c and Figure 1.3a-d).<sup>32-35</sup>

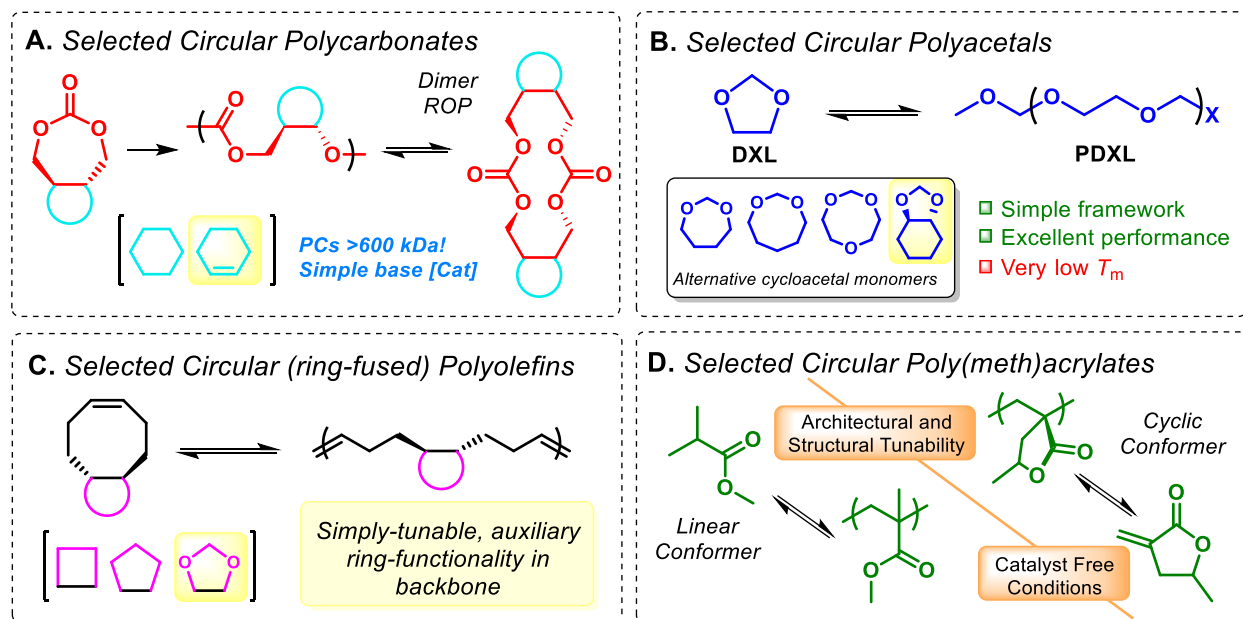




**Figure 1.2.** Evolution of the Intrinsically Recyclable Polymer. (a) Thermodynamic considerations for ROP and variables for tuning ceiling temperature. (b) ROP of low-ring-strain GBL to chemically depolymerizable PGBL. (c) ROP of *trans*-cyclohexyl-fused monomers to significantly enhanced PEs designed on the principles of (b).

The rapid emergence and development of recyclable polymers was sparked from Chen's clever manipulation of thermodynamics to achieve successful ring-opening polymerization (ROP) of historically "non-polymerizable"  $\gamma$ -butyrolactone (GBL) to fully recyclable polyester PGBL (Figure 1.2b).<sup>21</sup> At monomer concentration  $[M]$  1.0 M the  $T_c$  of PGBL was an unreachable  $-136\text{ }^\circ\text{C}$ , but by increasing  $[M]$  to 10 M the  $T_c$  was shifted to a more tangible  $-9\text{ }^\circ\text{C}$ . Recyclable PGBL, however, yielded particularly poor thermal qualities ( $T_m = \sim 60\text{ }^\circ\text{C}$ ) precluding industrial commercialization. Revision of the GBL monomer returned a *trans*-ring-fusion approach to accessing both ambient polymerization and valuable utility (Figure 1.2c). High molecular weight polyesters were produced with favorable thermal and mechanical profiles, including most notably a  $\sim 2\times$  increase in decomposition temperatures.<sup>22,23</sup> Unfortunately, even the impressive advantages of the second-generation polyesters are ultimately challenged by highly brittle character. Thus, from these examples, one can appreciate the compelling obstacles, particularly in merging both valuable sustainability and performance, impeding industrial adoption. Consumer product

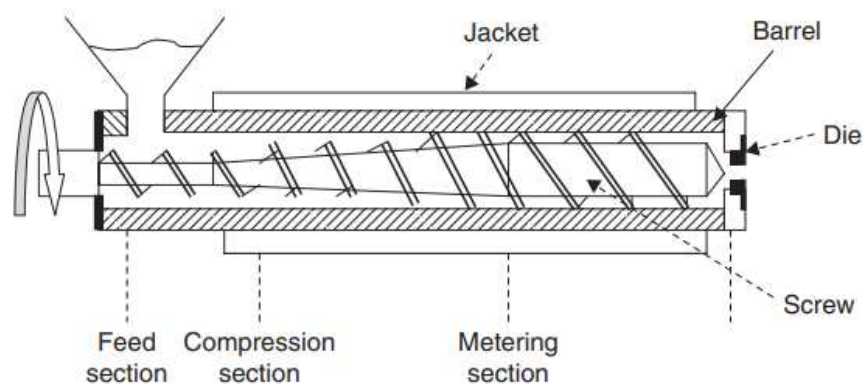
implementation of these technologies will require not only development of more practical synthetic procedures, but more importantly adaptability to current state-of-the-art processing techniques that will require intensive rheological studies on flow and shear character, retained performance with commercial colorants and additives, and high scalability.



**Figure 1.3.** Highlighted Advancements in Chemically Recyclable Polymers from Cyclic Carbonates, Acetals, and Alkenes. (a) Tandem modification-ROP and RCDP of functionalized cyclic carbonates. (b) RD-CROP and depolymerization of cyclic acetals. (c) ROMP and RCM DP of cyclooctene with various *trans*-fused cyclic substituents. (d) RAFT and anionic polymerization of methyl methacrylate (MMA) and  $\alpha$ -methylene- $\gamma$ -methyl-butyrolactone (MMBL).

Most enticing of all presented options is the pathway of mechanical recycling. Mechanical recycling is a classic end-of-life avenue consisting of melt re-processing singular- or mixed-feed thermoplastic waste, side-stepping any need for the high levels of purification as well as the massive energy input for depolymerization to monomer *and* subsequent repolymerization, as the polymer remains in the polymeric phase throughout life-cycling.<sup>36</sup> Traditionally, mechanical recycling is referred to as a downcycling avenue, or a band-aid solution, as present technology faces steep challenges against paralleling degradation of material value over multiple reprocessing cycles and immiscibility between different polymer archetypes when attempting to blend various

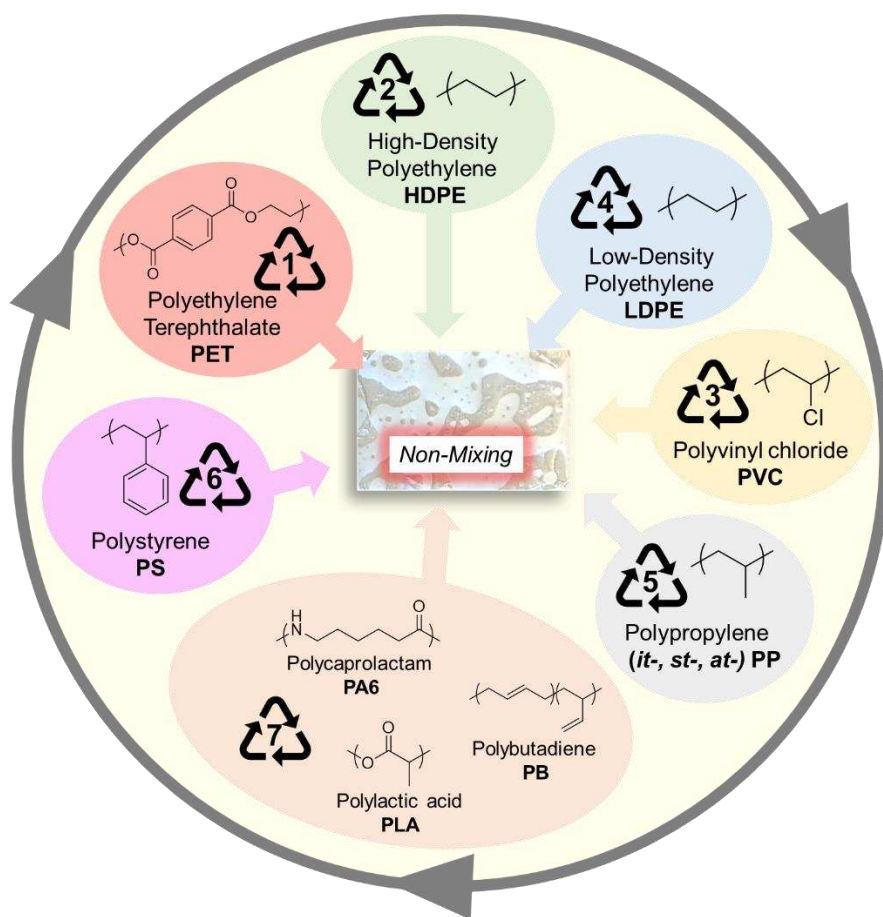
different plastics. Specifically, chain-shortening events caused by extrusion shearing and oxidation such as chain scission, crosslinking, and chain branching can occur during plastics extrusion which leads to a decrease in mechanical and thermomechanical value of the resulting re-processed thermoplastics, eliminating the opportunity for virgin-quality application without the inclusion of some modest percentage of virgin-quality additive (Figure 1.4).<sup>37-39</sup> With prudent extruding parameters, such as tuning the temperature and shearing speed via the screw-spinning, material scientists can regulate the amount of degradation or downcycling for the sample and extend the life-time of consumer items to serve in additional roles, such as lubricants, packaging materials and textiles (Figure 1.4).<sup>40-45</sup>



**Figure 1.4.** Basic structure of a single-screw extruder. (Source: Berk. *Food Processing Engineering and Technology* | Extrusion 2009).

Sorting and purification steps can still remain unavoidable, especially in the cases of multi-layer packaging, when attempting mechanical recycling as, ironically, the world's most-produced plastics are not compatible with one another in the bulk or application stage due to high polarity differences, chain-packing density, or microstructural features (Figure 1.5).<sup>46,47</sup> This, in turn, creates large macrophase-separated interfaces between each component with weak interfacial adhesion and high interfacial stress detrimental to the binary blend's mechanical and thermomechanical integrity (Figure 1.5). Ideally, simultaneous melt reprocessability and

compatibilization of mixed thermoplastic waste could create enormous opportunity in both promoting mechanical recycling practices and lowering energy inputs, as most consumer items on the market are comprised of numerous key players. It is due to this complex inconvenience that the nearly 90 % of plastics which could be mechanically recycled are rather landfilled. Compatibilization as a route for upcycling mixed-plastics thus garners high intrigue as a solution to an over-engineered materials economy, and which if visited with reactive extrusion principles and miscibilizing agents may provide a practical solution.<sup>48</sup>



**Figure 1.5.** Blending immiscibility between the top seven groups of mechanically recyclable post-consumer thermoplastics by melt processing modeled by a polymer blend thin-film highlighting macrophase separation of individual components.

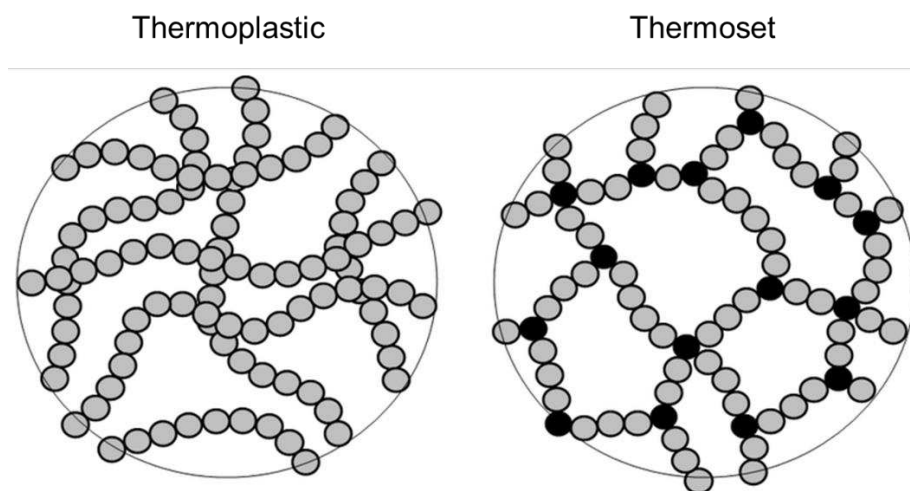
Comparing the simplicity, rationale, and practicality of mechanical recycling over chemical or biological counterparts, the significant environmental and economic impacts that

elevating mechanical recycling technology has is clear. Implementing more practical mechanical recycling requires both optimized extrusion practices as well as the capacity to blend multiple thermoplastic polymer species with compatibilization. These advancements will rely on using structure/property relationships to derive suitable processing conditions to reduce value loss over time and retain performance properties in re-processed materials. Countless valiant, impressive research efforts on extrusion protocols and polymer blend mixing are reported and still underway, though sadly often less highlighted or discussed in lower-impact journals. I applaud and implore the ongoing investigation of these fundamentally critical works, as over time these foundational progressions will serve tremendously to boost plastics recycling by industrially reasonable means.

## **1.2 Thermosets and Performance/Sustainability Trade-Offs.**

The above brief summation on prominent recycling technologies is not universally applicable to all polymeric materials present in today's consumer products. A noteworthy caveat lies in differentiating which materials are appropriate for recycling streams and which are unable to undergo recycling due to inherent design and structural limitations. Take for example thermosets: densely crosslinked polymers which form random, complex networks of covalent bonds forcibly restricting chain mobility (Figure 1.6). While thermoplastics, by definition, have the capacity to melt deform or reprocess, thermoset materials (i.e., rubbers) are unable to be recycled by any practical means. Thermosets are well-understood and regarded as legacy materials due to their resilience to several disposal methods and seemingly infinite life-span in landfills. The dense crosslinking provides several sustainability issues such as: 1) Thermosets cannot be melt reprocessed or re-shaped as the severely restricted chain mobility raises their theoretical melt transition temperatures ( $T_m$ ) far above decomposition, 2) Thermosets cannot be dissolved or

stabilized in solvent as the dense networking precludes penetration by solvent, also precluding biological recycling or enzymatic degradation by microorganisms, 3) Thermosets cannot be depolymerized to starting materials due to the random nature of the covalent crosslinking hindering starting material selectivity or capability for solubility required to introduce catalyzing species.



**Figure 1.6.** Depicted macromolecule architectural distinctions between a linear macromolecule (thermoplastic, left) and a three-dimensional network (thermoset, right). (Source: *Wikipedia: Thermosetting Polymers* 2009).

On the other hand, thermosets are fundamentally fascinating materials and one of the most vital class of polymers in our synthetic arsenal, utilized in thermos-mechanically high-demanding roles. Ironically, it is the same dense networking that defies any recycling or upcycling ability that endows thermosets with such high mechanical performance qualities. The dense networking character allows for significantly higher durability and elasticity than that of thermoplastic analogues to the ends of near-theoretically perfect shape-memory, as deformation or working stress events incurring material strain are recovered upon removal of that stress. The absence of a melt transition or solubility imparts high thermomechanical function and chemical resistance. Most importantly thermosets are most renowned for their lack of creep deformation, a time-dependent deformation caused by the slippage of unlinked chains over long periods of time under

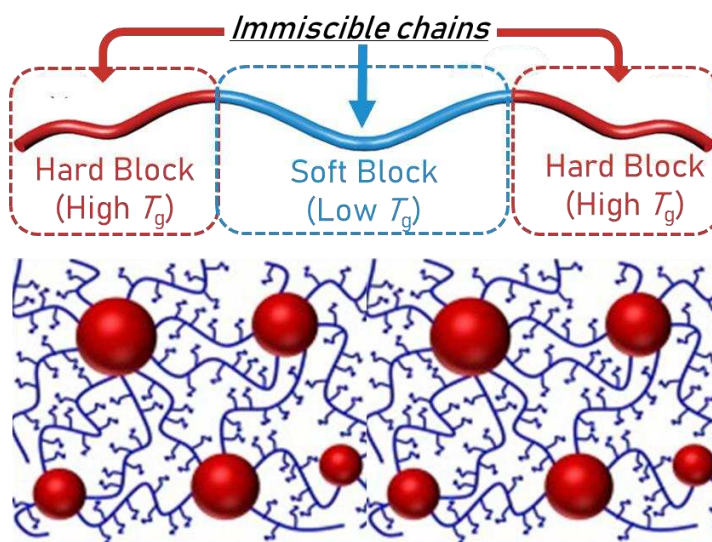
even minimal working stress, a performance nightmare for thermoplastics especially at increasing operating temperatures. These favorable physical properties explain the high production of thermosetting materials for automotive parts (especially car tires), aerospace technology, and rubber applications, among others. This in turn highlights crosslinked polymers as one of the most beautiful examples of structure/property trade-offs when in the context of performance/sustainability.

From a sustainability perspective, thermosets are an obsolete material and do not fit into a circular materials economy as they do not offer any handles for recyclability once the network is locked. While this has naturally motivated green chemists to phase out crosslinked polymers, significant hurdles have made this task seemingly impossible. The challenge lies again in overcoming the stringent performance/sustainability trade-off: in order to access recyclability of some degree there cannot be a permanent covalent network, yet without the permanent covalent network the now sustainable material cannot achieve the same level of performance required to impose industrial adoption. Nonetheless, several stimulating fields of synthetic polymer research have afforded practical strategies to mimic the compelling mechanical behavior of thermosets while imbedding the functionality for convenient mechanical recyclability by melt reprocessing.

One traditional approach relies on microphasic separation-driven self-assembly of A-B-A tri-block copolymers to yield what is referred to as a thermoplastic elastomer (TPE) (Figure 1.7). By predesignating the A- and B- blocks along the same polymer chain to exhibit dramatic immiscibility with one another, thermodynamic separation between the two groups will result in micro-domain formation.<sup>49,50</sup> This is typically incurred by using a high glass transition temperature ( $T_g$ ) repeat unit for the A-block (or the “hard” block) and a low  $T_g$  repeat unit for the B-block (or the “soft” block), where the hard blocks will aggregate as an ambient glassy domain interconnected



by the soft block linkages (Figure 1.7). This phenomenon effectively creates a pseudo-thermoset where the aggregation points act as *physical* crosslinks linked together as a network by the soft domains exhibiting a remarkable toughening impact.<sup>51</sup> Applying heat during melt reprocessing allows sufficient chain mobility to dissociate the aggregates, which re-assemble upon cooling. TPE technology has thus found mild success in industrial application, specifically in the case of polystyrene-*b*-polyisoprene-*b*-PS (PS-*b*-PI-*b*-PS), introduced in the 1960s and still today the single-most manufactured block copolymer material globally.<sup>52</sup> Further adoption by commercial markets is hampered however again by the susceptibility to creep deformation which still occurs due to the absence of covalent linkages. Fundamental insight from the TPE framework has inspired similar thermoset-like, reprocessable materials that exploit extreme domain aggregation by ionized end groups, noted as ionomers.<sup>53,54</sup> One of which, polyethylene-*co*-polysodium methacrylate, has been developed by chemical manufacturer DuPont as hyper-toughened Surlyn. Ionomers also achieve ionic dissociation at high temperatures for reprocessability,<sup>55</sup> though this ultimately limits their thermomechanical performance in a similar manner to non-ionized TPEs counterparts.



**Figure 1.7.** General thermoplastic elastomer network morphology constructed from an A-B-A triblock copolymer represented by classic hard-soft-hard framework, though assembly can be

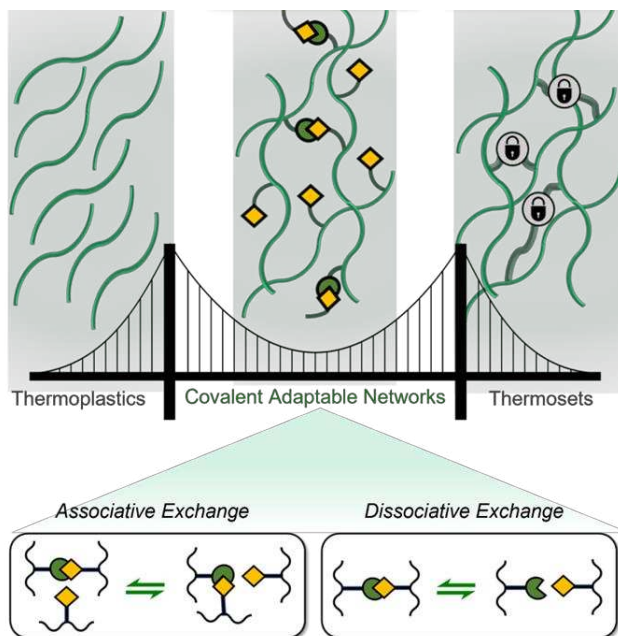


leveraged by crystalline/amorphous, ionic/neutral, intermolecular interacting/non-interacting distinctions between end- and mid- blocks.

### **1.3 Covalent Adaptable Networks: Overview on Dynamic Covalent Chemistry in Reprocessable Crosslinked Polymer.**

More recently, the innovative use of *dynamic* covalent crosslinks inspired by molecular platforms by namely covalent adaptable networks,<sup>56-66</sup> vitrimers,<sup>67-70</sup> and non-covalent self-healing networks<sup>71-78</sup> have emerged as alternative thermoset-inspired recyclable materials. Specifically, covalent adaptable networks (CANs) are thermosets that achieve full reprocessability of network integrity by the imbedded functionality of dynamic covalent crosslink bonds which can undergo stimulus-regulated exchange with neighboring crosslinks or exchange agents (Figure 1.8). The thermodynamic equilibrium nature can be exploited to induce a thermoplastic-like flow-state at high stimulus exposure due to the rapid bond exchanges (healing conditions), while retaining thermoset mechanical performance under minimal or no stimulus exposure when dynamic bond exchange is trace. As the network has a theoretically infinite molecular weight, the degradation consequences of mechanical recycling are neglected via network rearrangement. These materials often rely on privileged crosslinkers, complex post-synthetic modifications, and require exchange agent or catalyst additives to promote flow phase character. Initial observations for dynamic bond interactions within polymer matrices occurred as early as the 1940s during stress relaxation experiments for polysulfide<sup>79</sup> and polysiloxane<sup>80</sup> rubbers, though the impending intense academic intrigue did not surface until the 1990s-2000s with the incorporation of thermally-regulated Diels-Alder and retro Diels-Alder association/dissociation once placed in the context of exploiting the exchange for recyclable and reprocessable crosslinked materials.<sup>81</sup>

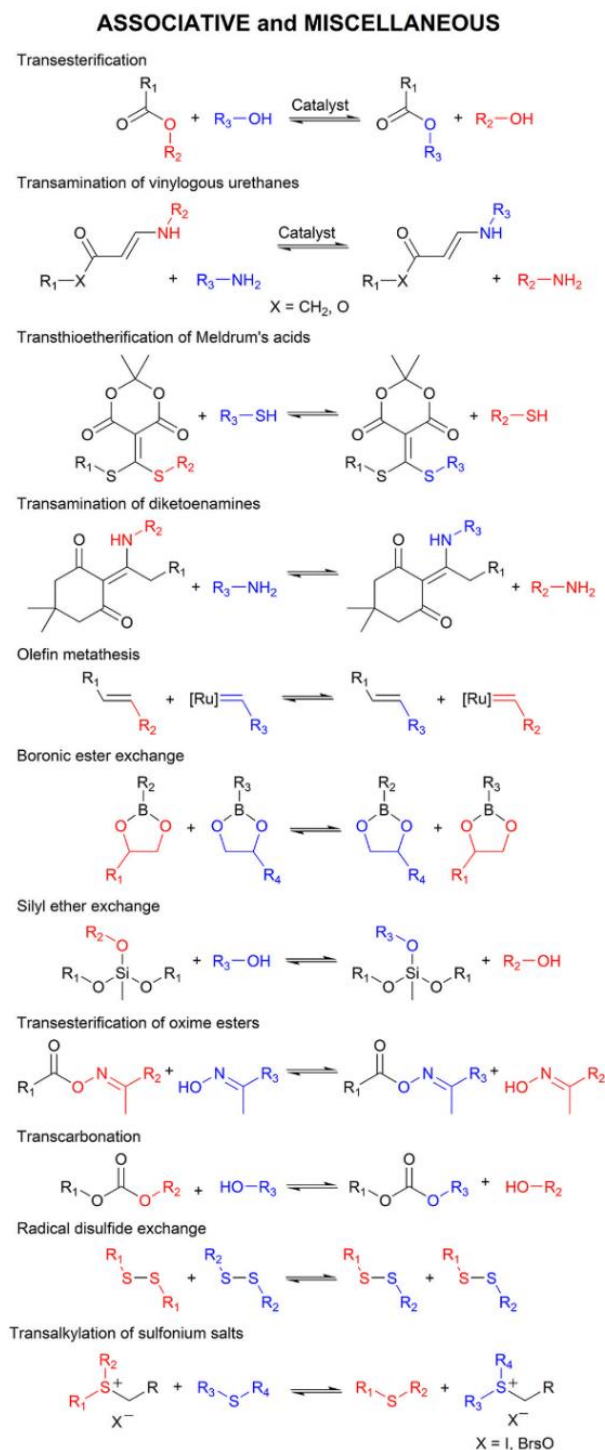
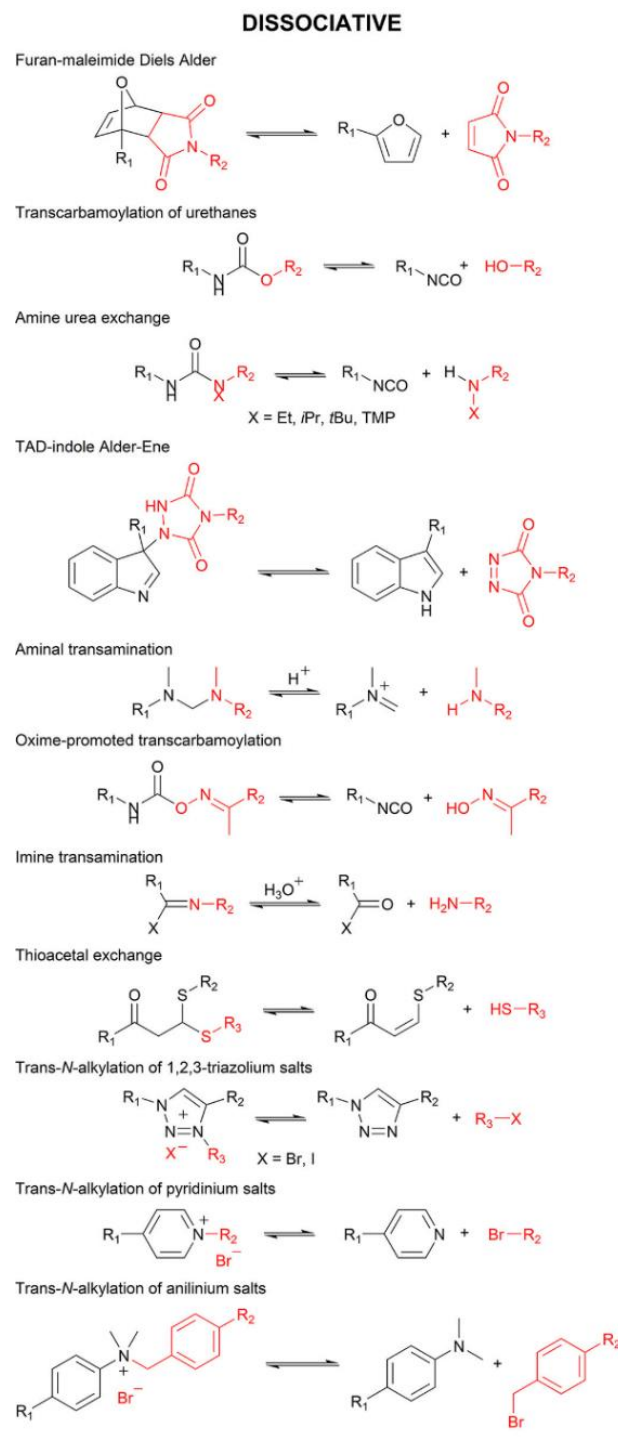
Seminal contributions by Bowman and Liebler regarding covalent adaptable networks (CANs) in 2005 and vitrimers in 2011, respectively, are critical in identifying unique material responses derived from the choice of dynamic functional groups and the exchange mechanism by which they operate upon.<sup>82,83</sup> Two major distinctions in exchange pathway have since been established. The first is *associative* exchange, a process in which a crosslink will exchange with an adjacent crosslink or free exchange agent without any dissociation, thus retaining the total crosslink density of the network across the thermochemical equilibrium. *Dissociative* exchange, on the other hand, proceeds through (increasing) crosslink dissociation to two stable intermediates at high stimulus and re-combination of crosslinks at reduced stimulus, effectively varying the network crosslink density depending on the thermochemical equilibrium conditions (Figure 1.8). Distinctions in the thermomechanical and rheological responses as a result of these two pathways will be discussed in the following section. It is important to note that while through separate means, both of these pathways essentially achieve the same ends of sustainable thermoset materials. Mechanical performance, application, and processing conditions, however, can be tuned or targeted by prudent selection of dynamic covalent bond motif.<sup>84</sup>



**Figure 1.8.** Representation of covalent adaptable networks. (Adapted from Figure 5.1a).

In the short time following, today's CAN technology boasts ubiquitous functional groups, scalability in production, and additive- or catalyst-free exchange pathways. This rapid development is most highlighted by the incorporation of several covalent bonds with facile accessibility and, more importantly, high commercial relevance. Associative exchange mechanisms most prominently encompass transesterification,<sup>83,85,86</sup> transthoesterification,<sup>87</sup> transthoetherification,<sup>88</sup> transalkylation,<sup>89-91</sup> transamination of vinylogous urethanes<sup>92-95</sup> and diketoenamines,<sup>96</sup> boronic ester exchange,<sup>97-99</sup> silyl ether exchange,<sup>100,101</sup> disulfide exchange,<sup>102,103</sup> acid-anhydride<sup>104</sup> and anhydride-anhydride exchange,<sup>105</sup> and olefin metathesis,<sup>106</sup> among others (Figure 1.9). Dissociative exchange mechanisms on the other hand encompass the furan-maleimide Diels-Alder,<sup>81,107</sup> transcarbamylation,<sup>108-111</sup> transamination of imines,<sup>112,113</sup> and trans-*N*-alkylation of 1,2,3-triazolium salts,<sup>114</sup> among others (Figure 1.9). Important to note, some exchange pathways (typically reported as associative) occur through multiple or mixed associative/dissociative mechanisms and are either not entirely understood or are simply

miscellaneous besides non-dissociative. Emergence of broad dynamic covalent bond possibilities is not only significant for progress towards wide application of CAN technology but has further empowered users to exploit the niche differences in bond exchange activation and activation stimulus for control over thermoset viscoelastic behavior.



**Figure 1.9.** Selected dynamic covalent bonds and dissociative (left) and associative (right) exchange reactions exploited as polymer crosslinks that enable malleability in CANs. (Source: Jourdain, Asbai, Anaya, Chehimi, Drockenmuller, & Montarnal. *Macromolecules* 2020).

Worth briefly discussing, while most dynamic crosslink healing processes rely on a thermochemical equilibrium (i.e., heat and/or catalyst) to promote and regulate the rate of bond exchange, selecting specific stimuli outside of simple temperature has become of interest in commanding bond exchange to occur or lie dormant. One of which is photoactivation, primarily used in the exchange of disulfide linkages though disulfide exchange can also be activated by thermal means. Another specialized approach has been reported by Dichtel *et. al.* in which transcarbamoylation exchange was only able to occur under a thermomechanical activation.<sup>111</sup> The authors surmise that restrictive bond angles were relieved upon exerting tensile strain to access favorable interactions, following which exchange was observed. It is now well-understood that CANs exhibit a similar rubbery transition when applied enough energy to the effect of a  $T_g$  when energy input is sufficient, and is highly dependent on the dynamic covalent bond, catalyst loading, and the surrounding polymer matrix environment. This so-called vitrimer activation energy ( $E_a$ ) or vitrification temperature ( $T_v$ ), though considered theoretical as a specific temperature on the basis that exchange can occur across all temperatures within the thermochemical equilibrium, has been tabulated for numerous dynamic covalent bonds via temperature-dependent stress relaxation observations and remains an important handle for tuning viscoelastic behavior.<sup>92</sup>

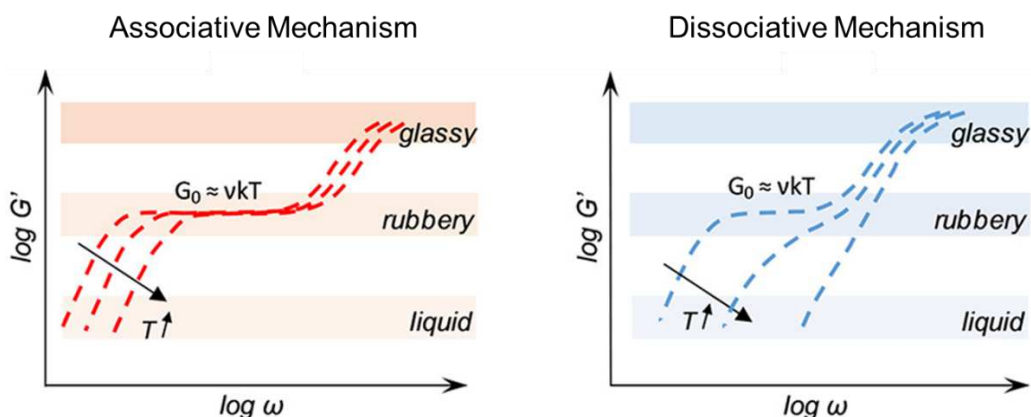
#### **1.4 Mechanical and Viscoelastic Behavior of Covalent Adaptable Networks.**

As CANs, while network architectures, are capable of entering the flow-state at higher energy inputs, they exhibit unique mechanical and viscoelastic profiles. For example, while thermosets do not undergo creep deformation or have flow character, CANs do creep with increasing permanent deformation with paralleled increases in temperature and exhibit shear thinning behavior, i.e., have reduced viscosity as increasing shear force is applied. Liebler in his

pioneering 2010 work compared the Arrhenius-like viscosity deviations with varied temperature of his dynamic thermoset operating on catalyzed transesterification (associative exchange) to that of vitreous silica – thus, “vitrimers”. It has since been observed that some dissociative networks also fit Arrhenius relationships between viscosity, stress relaxation, and temperature.

The viscoelastic behavior is also highly dependent on dynamic covalent bond interaction. In fact, vitrimers and CANs themselves behave quite differently from one another at elevated bond exchange rate, as eluded to in the above discussion, due to the mechanistic distinctions in bond exchange pathways. By using oscillatory rheological measurements to perform high temperature frequency sweeps, an extended frequency curve can be constructed to obtain the transition from the flow state ( $G' < G''$ ), to the rubbery plateau ( $G'' < G'$ ), before entering the glassy region which preferably requires dynamic thermomechanical analysis (DTMA) experiments for further investigation. If these frequency sweeps are constructed at various temperatures, the difference between a CAN and a vitrimer become apparent: 1) A vitrimeric CAN, operating via associative exchange, will retain rubbery plateau storage modulus ( $\Delta G' \sim \text{constant}$ ) while exhibiting an extended flow-state with increasing temperature. 2) A CAN relying on a dissociative exchange mechanism similarly reveals extended flow character with increasing temperature, but the rubbery plateau will reduce in frequency range as well as storage modulus value (Figure 1.10). The underlying reason for the deviation in rubbery plateau response is derived from the net crosslink density in the network during exchange at increasing temperatures. Associative processes do not undergo any form of dissociation, and rather will not exchange without an adjacent crosslink or free exchange agent to interact with, thus retaining net crosslink density throughout temperature variations. Dissociative networks, however, will increasingly reduce crosslink density and yield stable pendant intermediates as temperature increases, though they will reconnect (likely in an

altered rearrangement) upon cooling. This approach has been leveraged in establishing the mechanism of numerous dynamic covalent bonds serving in reprocessable thermoset crosslinks and remains, in tandem with molecular studies, highly conclusive.



**Figure 1.10.** Typical evolutions of storage moduli  $G'$  with angular frequency ( $\omega$ ) and temperature ( $T$ ) for associative networks (left) and dissociative networks (right). (Source: Jourdain, Asbai, Anaya, Chehimi, Drockenmuller, & Montarnal. *Macromolecules* 2020)

It is important to recognize that while these exchange events occur noticeably at higher temperatures to produce rubbery network materials, the thermochemical equilibrium nature of the dynamic covalent bond also implies that trace exchange is still viable even at ambient conditions. This, in turn, creates an enormous conflict in the context of creep deformation when again attempting to match thermoset performance. Essentially, even at working conditions, dynamic bond exchange is capable of reconfiguration of the polymer network to relieve incurred stress or strain, which becomes more dramatic with increasing thermal exposure. As mentioned above, this is a major infraction on producing materials that behave like thermosets. Thus, numerous efforts have been made to understand and control the viscoelastic properties of CANs and vitrimers for future development of mechanically superior, sustainable crosslinked polymers with orthogonal working/healing conditions. To be clear, working conditions are events in which bond exchange should be stringently non-active and unable to proceed, while active bond exchange should only



be reserved or obtainable when the network is undergoing healing or reprocessing. Achieving this orthogonality is paramount for promoting CANs to the commercial rank of existing thermosets.

## **1.5 Conclusion and Outlook.**

This introduction reviews several important concepts that are highly relevant to the dissertation herein: polymer recycling, thermoplastic elastomers, self-assembly, upcycling, covalent adaptable networks, and viscoelastic properties of network materials. With increasing socio-economic and environmental recognition for the value in achieving a circular materials economy, it is crucial that polymer architecture categories beyond that of solely thermoplastics are visited with the end-goal of offering sustainable end-of-life opportunities. The materials discussed throughout this introduction have made invaluable contributions to fundamental principles for designing new healable networks, and while the field is still very young, we must remember that performance qualities of CANs should remain a top focus in order to replace existing single-use thermoset technology. Currently, CANs still fall short of thermosets in several areas: cost-effectiveness, creep-deformation without dictated orthogonality of work/healing exchange events, synthetic feasibility, and a sound understanding of these materials in real-world processing conditions. The following chapters will provide novel insight and opportunities into some of these categories:

- (2) Chapter 2 will discuss the synthesis, optical properties, and end-of-life upcycling of biorenewable vinyl polyindenone. This chapter will also serve as an introduction to Lewis pair polymerization, which is a convenient polymer synthetic tool for the convenient, scalable preparation of vinyl polymers and one-pot discrete multiblock copolymers which will be re-visited in chapters 3 and 4.

- (3) Chapter 3 will discuss the one-pot sequence-controlled Lewis pair polymerization of discrete A-B-A tri-BCPs consisting of (hard) *tert*-butyl acrylate end-blocks and (soft) low- $T_g$  acrylic mid-blocks, as well as the catalyst- and additive-free upgrading to fully-functionalized and self-supplementing covalent adaptable networks with exchange-capable polyacrylic acid and poly acrylic anhydride crosslinked end-blocks. We provide evidence for a novel acid-anhydride exchange mechanism through small-molecule *in-situ* modeling relying on ubiquitous carboxylic acids and anhydrides, while disclosing a mixed associative/dissociative mechanism. Most importantly we explore self-assembly of these tri-BCPs and the resulting TPE nanostructure, from which we define the principles for intra- (non-productive) and inter- (productive) chain exchange events as a way to achieve working/healing orthogonality. This contribution stands as the most progressive work, to the best of our current knowledge, towards thermoset-like performance and thermoplastic-like processability, in this case regulated by thermomechanical activation protocol.
- (4) Chapter 4 will discuss the rapid and scalable sequence-controlled, one-pot, two-step synthesis of linear and cyclic A-B-A-B multiblock copolymers from simple (meth)acrylic monomers. Meticulous differentiation is provided between the compositionally isomeric species, and will serve as the structure/property relationship foundation for future contributions on highly specialized CANs from multiblock copolymer parent polymers.
- (5) Chapter 5 is the cornerstone of this dissertation and discusses a universal crosslinker approach, based on several dynamic molecular crosslinkers, to produce performance-competitive recyclable thermosets from virtually any virgin or upcycled end-of-life C-

H bearing polymer. This includes commodity thermoplastics, such as polyethylene, polypropylene, and various other polyester and vinyl polymers. Remarkably, we report the compatibilization effect of commercial mixed-feed plastic waste, such as that of polyolefins and polyesters, through dynamic crosslinking formation of multiblock copolymers to miscibilize the interfacial tension between the two components. Several novel principles which will likely inspire future fields of research are demonstrated.

Thus this collection of work serves tremendously to further progress the field of dynamic covalent chemistry in the context of recyclable thermosets that overcome staunch traditional barriers between performance/sustainability. Beyond material development, several principles with high fundamental value to the field are defined, while the entire collection of work offers multidisciplinary advancements attractive to many subsets of polymer and physical chemistry.

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## Chapter 2

### Lewis Pair Polymerization of Renewable Indenone to Erythro-Ditactic High- $T_g$ Polymers with an Upcycling Avenue

#### 2.1 Synopsis

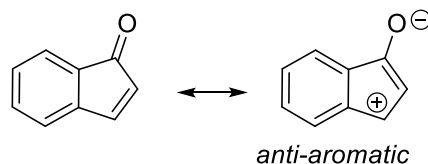
Preparation and storage of biorenewable, monomeric indenone, much less the polymerization to a well-defined, high-molecular-weight polymer, is challenging because of antiaromaticity-driven radical autopolymerization. Herein, we report the successful preparation and subsequent Lewis pair polymerization (LPP) of indenone without autopolymerization side reactions using Lewis pairs consisting of sterically encumbered Lewis acid (LA) catalysts, such as  $B(C_6F_5)_3$  and bis(2,6-*tert*-butyl-4-methylphenoxy)methylaluminum and Lewis base initiators such as silyl ketene acetal and N-heterocyclic olefin nucleophiles. Thus, for the first time, the LPP enabled the synthesis of polyindenone (Pin) with high number-average molecular weight ( $M_n = 1.72 \times 10^5 \text{ g mol}^{-1}$ ) and low dispersity ( $D = 1.13$ ). Observed correlations between the steric bulk of the LA catalyst and diastereoselectivity (57–75%) created the opportunity to model and investigate the relationships between  $\beta$ -substituted monomer motifs, catalyst steric accessibility, and the propagation stereodefining step for ensuing ditactic assignments. Through the increased erythro-diastereoselectivity, semicrystalline materials were produced with remarkably high glass-transition temperatures ( $T_g = 307 \text{ }^\circ\text{C}$ ), high thermal stability ( $T_{d,5\%} = 356 \text{ }^\circ\text{C}$ ), and competitive transmittance ( $T\%$ ) and haziness values ( $T\% = 85\text{--}88\%$ , haze = 11%). Controlled pyrolysis of Pin upconverted it into versatile graphite oxide with 54% conversion, offering an upcycling avenue for Pin at the end of its life.

## 2.2 Introduction

The conjugate-addition polymerization of  $\beta$ -substituted Michael acceptors, which have historically been problematic monomers to polymerize effectively due to their resistance to conventional radical and ionic polymerization methodologies, has been recently re-investigated using more modern polymerization methods.<sup>1,2,3,4,5,6</sup> The challenges associated with such monomers are both thermodynamic and chemoselective in nature, making them good candidates to showcase new polymerization methodologies. These  $\beta$ -substituted monomers add new complexity to the existing field of stereoselective polymerization by including two stereogenic centers at each repeat unit, thus requiring additional control for stereoselectivity to produce *ditactic* polymers. Overall, our interest in  $\beta$ -substituted monomers is twofold: *ditactic* polymers, while much less explored, could offer intriguing or advanced material's properties, and  $\beta$ -substitution is a common motif amongst many naturally occurring, bioderived Michael acceptors, such as crotonates, sorbates, and cinnamates.<sup>7,8,9,10,11,12</sup>

A preference in *linear*  $\beta$ -substituted monomers for disyndiotactic outcomes was generally recognized through a chain-end control mechanism.<sup>13,14,15,16,17,18,19</sup> Chain-end selectivity is derived from chirality at the penultimate repeat unit of the growing polymer chain end. In the two most recently studied examples, methyl crotonate and methyl cinnamate, disyndio-rich polymers were obtained based on chiral influence of the methyl and phenyl groups, respectively.<sup>3,20</sup> Following this logic, we hypothesized that a *cyclic*  $\beta$ -substituted Michael acceptor might exert increased chain-end selectivity due to increased steric hindrance and fewer overall degrees of freedom, thus, fewer possible competing transition states, subsequently bringing about enhanced chain-end control diastereoselectivity.

While considering a number of endocyclic Michael acceptors to test our hypothesis, we found an unlikely candidate, indenone (**M1**). A simple analysis of this monomer revealed several intriguing properties, first and foremost being the *anti-aromatic* resonance structure produced by classical carbonyl activation (Figure 2.1). We reasoned that the additional instability of **M1** due to anti-aromaticity could be used as a driving force for polymerization, as anti-aromatic compounds are known to rearrange/isomerize to relieve instability by achieving an aromatic or non-aromatic structure.<sup>21,22</sup> Likewise, we recognized that conjugate-addition polymerization of **M1** would relieve anti-aromaticity which can thus be used as a driving force, similar to how ring-strain is exploited in ring-opening polymerization of lactones.<sup>23,24,25,26</sup> Indeed, literature examples of **M1** synthesis consistently remarked on the instability of this compound and its predisposition to undergo autopolymerization.<sup>27</sup> In fact, Chandross and Hartless included the statement that “Because of its instability it is not possible to prepare and store indenone” among reported radical copolymerization endeavors.<sup>28</sup>



**Figure 2.1.** Resonance structure displaying the anti-aromatic nature of **M1** ( $2n$   $\pi$ -electrons).

We also found this monomer intriguing because a recent publication on the cationic polymerization of benzofuran, similar in structure to **M1**, revealed especially high glass-transition temperatures ( $T_g = 210$  °C) presumably due to the fused benzene moiety present within that structure.<sup>29</sup> While considering that incorporation of ketones within polymers often increases the  $T_g$ , we hypothesized that polyindenone (Pin) would have a  $T_g$  higher than that of poly(benzofuran), perhaps upwards of 300 °C, making it useful as an engineering plastic. Lastly, we recognized the

reported syntheses of precursor 1-indanone from bio-derived cinnamic acid with heterogeneous catalysts, which serves as an important characteristic of any renewable polymer in order to reduce both CO<sub>2</sub> emissions and dependency on finite petroleum resources (Scheme A1).<sup>30,31,32,33</sup>

Thus, we set out to find appropriate conditions to store indenone and inhibit autopolymerization. Once this task was completed, we sought conditions that would yield a successful and controlled polymerization process by Lewis acid (LA) and Lewis based (LB) pairs, namely Lewis pair polymerization (LPP), by utilizing synergy and cooperativity of the LA and LB sites.<sup>34,35,36,37,38,39</sup> To tame the inherent high reactivity of indenone, we chose LA-mediated group transfer polymerization (LA-GTP) as the silyl enolate LB should render a low energy propagating species compared to that of anionic or radical analogues. Moreover, monomer coordination to a LA would generate a highly reactive anti-aromatic monomer, allowing us to exploit this characteristic as a driving force for polymerization to achieve high degrees of polymerization, shorter reaction times, and lower catalyst loadings. Following the same logic, we also explored the frustrated Lewis pair (FLP) strategy using bulky LA bis(2,6-*tert*-butyl-4-methylphenoxy)methylaluminum (MAD) and bulky *N*-heterocyclic olefin (NHO) 1,3-dimethyl-4,5-diphenyl-2-(propan-2-ylidene)-2,3-dihydro-1H-imidazole as the LB, as such a FLP has been shown to bring out living polymerization of polar conjugated alkenes.<sup>40,41,42,43</sup> Comparatively, the FLP system should exhibit higher activity than the LA-GTP system since frustrated Lewis pair polymerization (FLPP) proceeds through a persistent zwitterionic active species that does not return to a neutral resting state as in LA-GTP. While the persistent zwitterion in FLPP is less stable than the silyl capped enolate present in LA-GTP, there are no obvious termination or transfer pathways foreseeable for indenone that would give reason to protect growing chain. Accordingly, this report presents a full account of our study on the LPP of **M1** by the above described Lewis

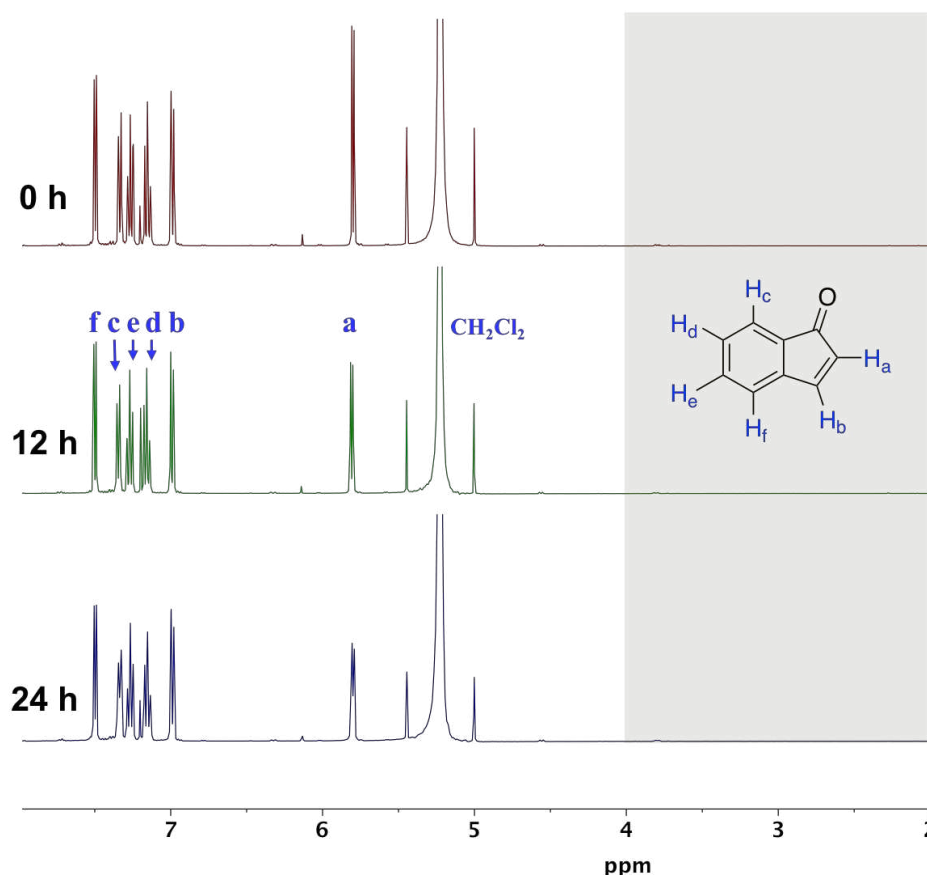
pairs, including the polymerization characteristics, effects of LA sterics on diastereoselectivity, as well as the properties and an end-of-life option (upcycling avenue) of the resulting polymer.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Indenone Preparation, Storage and Autopolymerization Control.

As mentioned above, **M1** readily undergoes autopolymerization to generate an atactic, amorphous Pin (Figure A2). Accordingly, we developed an effective preparation and storage method involving timely **M1** synthesis from indanone (see the SI), dilution to a 0.77 M stock solution in dichloromethane (DCM), and storage at -30 °C, which enabled elimination of autopolymer contaminants in catalyzed samples and longer-term access to monomeric indenone for polymerization studies (Figure A5). To investigate the effectiveness of our indenone storage method over a 7-day period, aliquots were taken every 24 h from the mother stock solution and analyzed by <sup>1</sup>H NMR. In each experiment, there were no signals for the methine protons characteristic of polymer formation between 2.0 – 4.0 ppm (Figure A6). As a control to test autopolymerization of **M1** under the storage concentration, a sample of the monomer solution was stirred (without additives) in a dark, room-temperature (RT, ~ 23 °C) environment within an inert atmosphere. After stirring under such conditions for 24 h, no Pin signals were observed by <sup>1</sup>H NMR (Figure 2.2), indicating that **M1** is stable under dilute, dark conditions, thereby allowing sufficient time to execute LPP experiments without autopolymerization interference. On the other hand, stirring bulk indenone under ambient conditions led to gelation, and this autopolymerized sample as a firm gel was collected after 72 h and analyzed by <sup>13</sup>C NMR (Figure A7) and gel permeation chromatography (GPC) to serve as a comparison to catalyzed Pin samples described below.



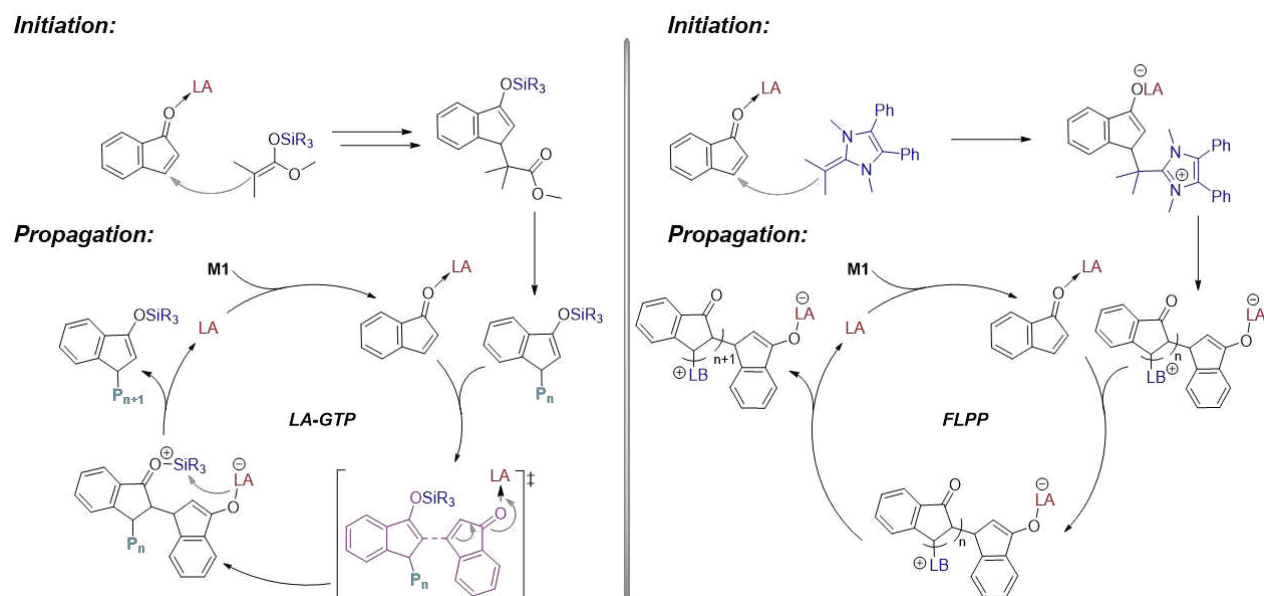


**Figure 2.2.** Overlay of <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of reaction aliquots of additive-free stirring of **M1** stock solution (0.77 M in DCM) under dark, RT, and inert atmosphere conditions as a function of time: 0 h (top), 12 h (middle), and 24 h (bottom), indicating that **M1** is stabilized against auto-polymerization side reactions under such conditions.

### 2.3.2 Polymerization Results and Key Characteristics.

With an autopolymerization-free preparation and storage method established, **M1** was investigated for controlled polymerization to a possibly high molecular weight (MW), functionalized ditactic polymer. Considering the Michael acceptor motif and the highly reactive propagating enolate, we hypothesized that LA-GTP would tame the reactivity of the actively growing chain enolate and inhibit chain-transfer pathways to facilitate a slower, more controlled propagation (Figure 2.3). We began by testing this LA-GTP with sterically encumbered LA B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (FAB) paired with LB/initiator dimethylketene methyl trimethylsilyl acetal (<sup>Me</sup>SKA),

which have been employed to execute GTP on a wide range of Michael acceptor-type monomers.<sup>44,45,46</sup> It should be noted here that background polymerization activity was not observed by either FAB or <sup>Me</sup>SKA, individually, with [M1]/[FAB] or [M1]/[<sup>Me</sup>SKA] = 100/1 at RT for 24 h.



**Figure 2.3.** Outlined initiation and propagation mechanisms for the LPP of M1 by LA/SKA LP via the established LA-GTP (left) and by FLP LA/NHO via the established zwitterionic LPP (right).

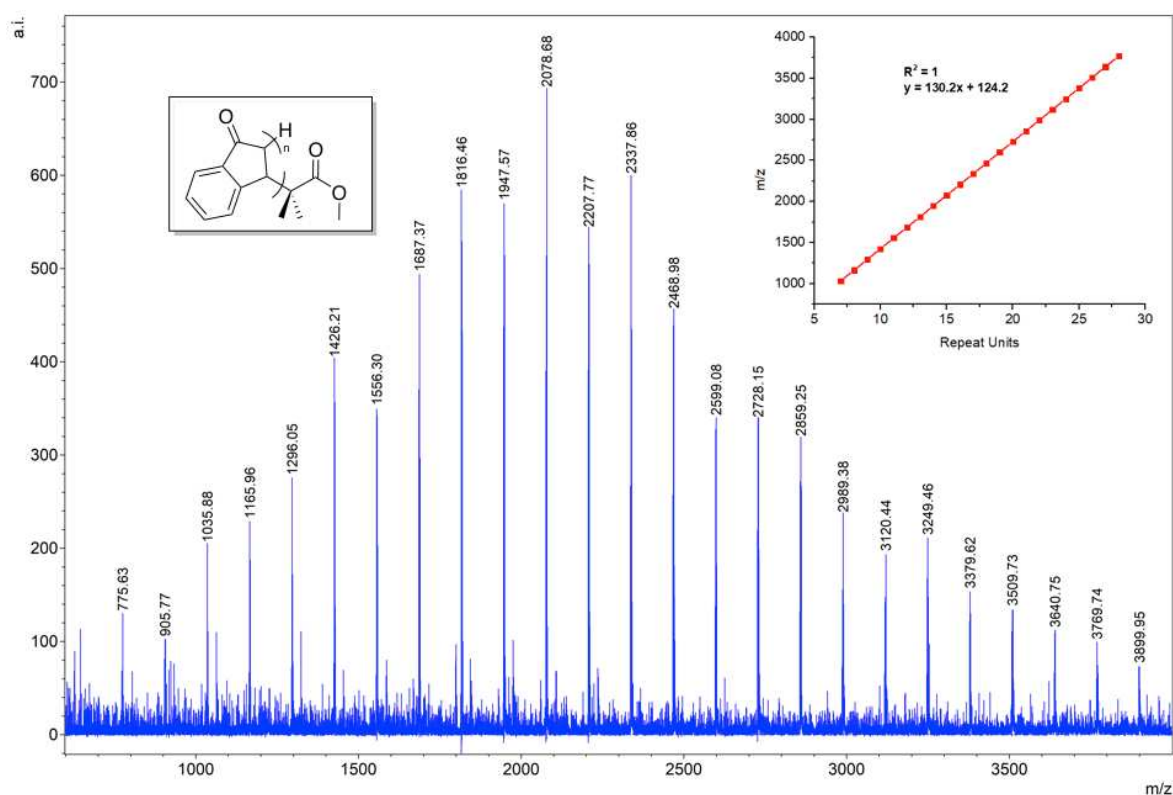
The polymerization reactions were carried out under dark and RT conditions using FAB and <sup>Me</sup>SKA in a 2:1 ratio with catalyst/initiator loadings between 0.1 and 0.6 mol % relative to M1. Each reaction was quenched at either 12 or 24 h, achieving quantitative (>99 %) isolated yields. Isolated polymer samples had  $M_n$  values between  $8.1 \times 10^4$  g mol<sup>-1</sup> and  $1.72 \times 10^5$  g mol<sup>-1</sup> and dispersity  $\bar{D}$  values between 1.13 and 1.23 (Table 2.1, Run 2-3). The low dispersity  $\bar{D}$  values, coupled with a monomodal MW distribution (Figure A8), indicate the absence of parallel autopolymerization, which was verified by our control experiments (*vide supra*). A low MW Pin sample with a theoretical  $M_n$  of  $2.60 \times 10^3$  g mol<sup>-1</sup> was further analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). A near-ideal bell-

curve was observed with the absence of competing peaks related to possible autopolymerization pathways (Figure 2.4). End-group analysis revealed a mass of 124.2 g mol<sup>-1</sup>, which correlates to –Me<sub>2</sub>CO<sub>2</sub>Me (from initiation by initiator <sup>Me</sup>SKA), a proton (from acidic quenching), and a sodium cation (used to ionize the polymer).

**Table 2.1.** Selected Results for LPP of M1<sup>a</sup>

| Run <sup>a</sup> | LA  | LB                | M1:LA:LB | Time (h) | Isolated Yield (%) | <i>M<sub>n</sub></i> <sup>b</sup> (kg mol <sup>-1</sup> ) | <i>D</i> <sup>b</sup> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> ) | <i>T<sub>g</sub></i> <sup>c</sup> (°C) |
|------------------|-----|-------------------|----------|----------|--------------------|-----------------------------------------------------------|-----------------------------------------------------------------------|----------------------------------------|
| 1                | n/a | n/a               | n/a      | 72       | 87                 | 205                                                       | 1.91                                                                  | 269                                    |
| 2                | FAB | <sup>Me</sup> SKA | 300:2:1  | 12       | 99                 | 81                                                        | 1.13                                                                  | 271                                    |
| 3                | FAB | <sup>Me</sup> SKA | 500:2:1  | 12       | 99                 | 172                                                       | 1.23                                                                  | 286                                    |
| 4                | MAD | <sup>Me</sup> SKA | 500:2:1  | 12       | 99                 | <i>d</i>                                                  | <i>d</i>                                                              | 292                                    |
| 5                | MAD | <sup>Me</sup> SKA | 1000:2:1 | 24       | 99                 | <i>d</i>                                                  | <i>d</i>                                                              | 307                                    |
| 6                | MAD | NHO               | 500:2:1  | 1        | 99                 | <i>d</i>                                                  | <i>d</i>                                                              | 303                                    |
| 7                | MAD | NHO               | 1000:2:1 | 2        | 99                 | <i>d</i>                                                  | <i>d</i>                                                              | n/d                                    |

<sup>a</sup> Polymerization conditions: [M1] = 0.77 M (DCM) for Runs 2-7; [M1] = bulk for Run 1, where Run 1 represents autopolymerization beyond gelation without initiator/catalyst additives. Runs 2-7 were performed in dark at RT in an Ar-filled glovebox. NHO was prepared in a toluene stock solution as it slowly decomposes in DCM prior to initiation. n/a = not applicable; n/d = not determined. <sup>b</sup> Absolute *M<sub>n</sub>* and *D* values determined by GPC at 40 °C in CHCl<sub>3</sub> coupled with a DAWN HELEOS II multi(18)-angle light scattering detector and an Optilab TrEX dRI detector. <sup>c</sup> Determined by differential scanning calorimetry. Values were obtained from the second heating scan with at 15 °C/min. <sup>d</sup> Not measured due to stereoselectivity-induced insolubility in common organic solvents



**Figure 2.4.** MALDI-TOF MS spectrum for a low MW Pin sample prepared by  $[M1]/[FAB]/[MeSKA] = 20/2/1$  as well as end-group analysis supporting initiation by the proper  $MeSKA$  LB.

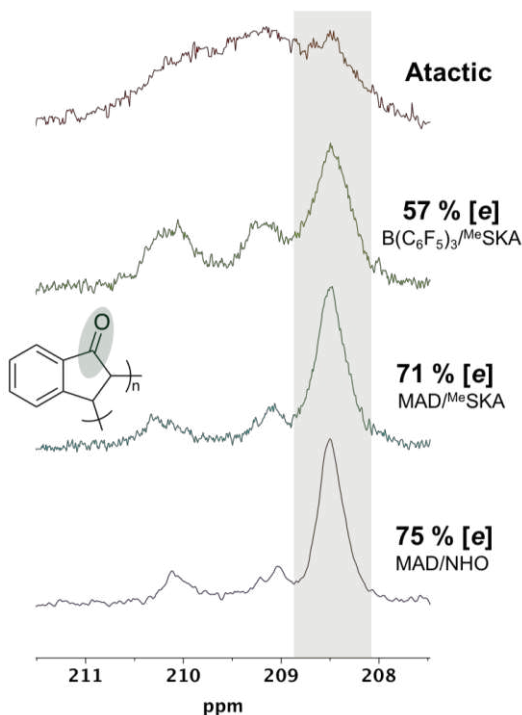
Guided by the hypothesis for LA-mediated chain-end control (*c.f.* Figure 2.3), we further examined the effect of the LA on this LPP by employing a more sterically hindered LA, MAD, which alone did not promote any polymerization (1.0 mol%, RT, 24 h). Polymerizations with  $[M1]/[MAD]/[MeSKA] = 500/2/1$  (run 4) and 1000/2/1 (run 5) afforded Pin materials that are insoluble in common organic solvents ( $CHCl_3$ , DCM, THF, toluene, etc.), precluding GPC analysis for MW information. In fact, the only solvent that would solubilize the MAD-catalyzed Pin was trifluoroacetic acid (TFA), due to enhanced erythro selectivity (71%, *vide infra*). Switching the LB to NHO, the polymerization by the MAD/NHO LP was much faster, achieving quantitative isolated polymer yield in 1 h or 2 h for the run with  $[M1]/[MAD]/[NHO] = 500/2/1$  (run 6) and 1000/2/1 (run 7), respectively. The sterically demanding and acidic-proton-lacking

NHO with  $\alpha,\alpha$ -dimethyl substitution was chosen in particular (apart from other NHOs, NHCs, and conventional LBs) because it forms a truly FLP with MAD and its structure lends itself to predictable reactivity as a potent nucleophile, unlikely to participate in any termination/transfer reactions. Unlike LA-GTP, the NHO/MAD pair facilitates a typical LPP mechanism where the propagating chain would have a cationic initiation end-group and force the polymerization to proceed through a zwitterionic intermediate (Figure 2.3, right column). Thus, this zwitterionic LPP exhibits enhanced activity compared to the LA-GTP mechanism, which is able to escape the zwitterionic intermediate through the silylium recapture (Figure 2.3, left column). On the other hand, this MAD-catalyzed LPP also afforded Pin with the same insolubility in common organic solvents, characteristic of high erythro-selectivity (75%, *vide infra*). Although this insolubility precludes GPC analysis, the possibility of high-MW-induced insolubility was ruled out by MALDI-TOF MS analysis of insoluble Pin oligomers produced by the FLP MAD/NHO. The MALDI spectrum highlights a near-ideal bell curve, while end-group analysis revealed the NHO as the initiator (Figure A9).

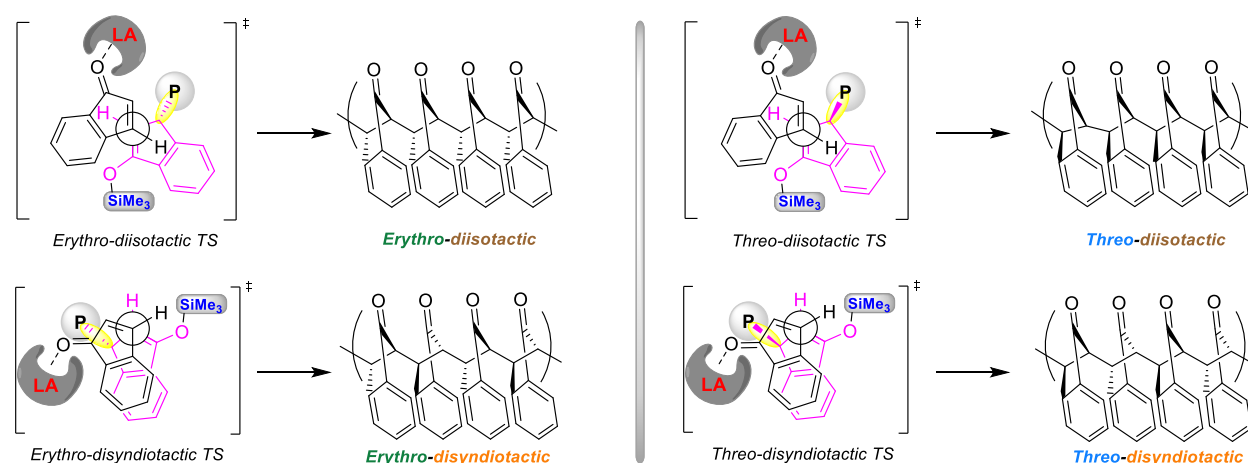
### 2.3.3 Polymerization Stereoselectivity and Polymer Ditacticity Assignments.

The stereoregularity of Pin materials synthesized by LPP using different LPs was ascertained by quantitative  $^{13}\text{C}$  NMR analysis in  $\text{TFA-}d_1$  for solubility reasons. As the carbonyl signal ( $\delta = 208.5$  ppm) is the most sensitive to the stereo-environment, it was chosen for comparison of different Pin materials (Figure 2.5). The full  $^{13}\text{C}$  NMR spectrum of Pin along with peak assignments can be found in Figure A4. As compared to the atactic, amorphous Pin by autopolymerization, the Pin by FAB/ $^{\text{Me}}$ SKA LP showed notable intensity enhancement in the resonance at 208.5 ppm, relative to two other peaks centered at  $\sim 209$  and  $\sim 210$  ppm in the carbonyl

region (Figure 2.5), revealing enhanced stereoregularity (to 57 %). As a new homopolymer without prior reported tacticity assignments by  $^{13}\text{C}$  NMR, Newman projections of the staggered propagation transition states (TSs) were modeled to compare the stereo-defining step. Pin has two stereocenters on each repeat unit, and is thus *ditactic*, where threo-diisotactic, erythro-diisotactic, threo-disyndiotactic, or erythro-disyndiotactic arrangements on the polymer backbone are possible. As the LA-activated **M1** species encounters a growing chain, we postulate that the TS will favor an interaction in which the sterically encumbered LA-activated monomer and the large silyl group will oppose each other spatially to suppress steric interactions (Figure 2.6).



**Figure 2.5.** Expanded carbonyl region of  $^{13}\text{C}$  NMR (125 MHz, TFA- $d_1$ ) spectra of Pin materials produced by autopolymerization and LPP with different LPs as labeled. [e] = erythro-di(iso)tactic.



**Figure 2.6.** Predicted TSs promoting erythro-diastereoselective propagation (left) vs disfavored threo-diastereoselective propagation (right) during LA-mediated GTP. Accompanied are visuals of the four possible stereochemical arrangements for a ditactic Pin.

Of the four possible Newman projections, two (related to threo-diastereoselective outcomes) seem unreasonable because they involve the penultimate polymer repeat unit (and the rest of the chain) pointed in the direction of the incoming monomer. The other two Newman projections, involving the polymer chain pointed back and away from the transition state (highlighted in yellow), are related to erythro-diisotactic and erythro-disyndiotactic units and seem the most reasonable (Figure 2.6). Although we will not speculate on which erythro projection is most favorable, we will point out that erythro-diisotactic is more consistent with thermal analysis and powder X-ray diffraction (pXRD) data as well as solubility observations, discussed below. However, distinguishing between the two possible erythro structures requires further evidence.

Figure 2.5 revealed a large LA effect on the erythro-ditacticity of the resulting Pin. When switching the LA paired with <sup>Me</sup>SKA from FAB to MAD, the selectivity was enhanced from 57% to 71%. Most intriguingly, the Pin with 71% stereoregularity or higher becomes insoluble in common organic solvents tested (*vide supra*), consistent with the increased stereoregularity and/or crystallinity of the polymer. The highest erythro-diastereoselectivity (75%) in this series was

produced by the MAD/NHO LP, revealing less influence by the LB on the selectivity of the resulting Pin. The steric effects of the LA on diastereoselectivity can be ascribed to its influence on the stereochemical defining TSs (whether erythro-diisotactic or -disyndiotactic defining). Referring to the reasoned Newman projections (Figure 2.6), the more sterically encumbered MAD should widen the energy gap between the two competing propagating TSs and thus suppress stereo-errors. In the case of the zwitterionic LPP by the MAD/NHO FLP, the two sterically encumbered LA equivalents are responsible for both activating the free monomer *and* protecting the active enolate chain end. Thus, the ditacticity is enhanced through additional LA steric influence (Figure 2.3), due to further increased energy gap between the competing TSs and suppressed stereo-error. We attempted to further increase the diastereoselectivity by using sterically more demanding LAs including EtAl(BHT)<sub>2</sub> and <sup>i</sup>BuAl(BHT)<sub>2</sub>. However, no noticeable improvement in selectivity was realized by NHO/EtAl(BHT)<sub>2</sub>, while no polymerization activity was observed with NHO/<sup>i</sup>BuAl(BHT)<sub>2</sub>. Therefore, new and more effective catalyst design would be necessary to achieve greater diastereoselectivity. The spectra in Figure 2.5 (with the exception of the atactic Pin) have one large peak accompanied by two smaller peaks. Interestingly, the two minor peaks always share similar integration. Therefore, we hypothesize that the major peak represents the erythro-diastereoselective units while the two minor peaks represent carbonyls at the interface of an erythro-diisotactic/disyndiotactic stereo-error (Figure A10).

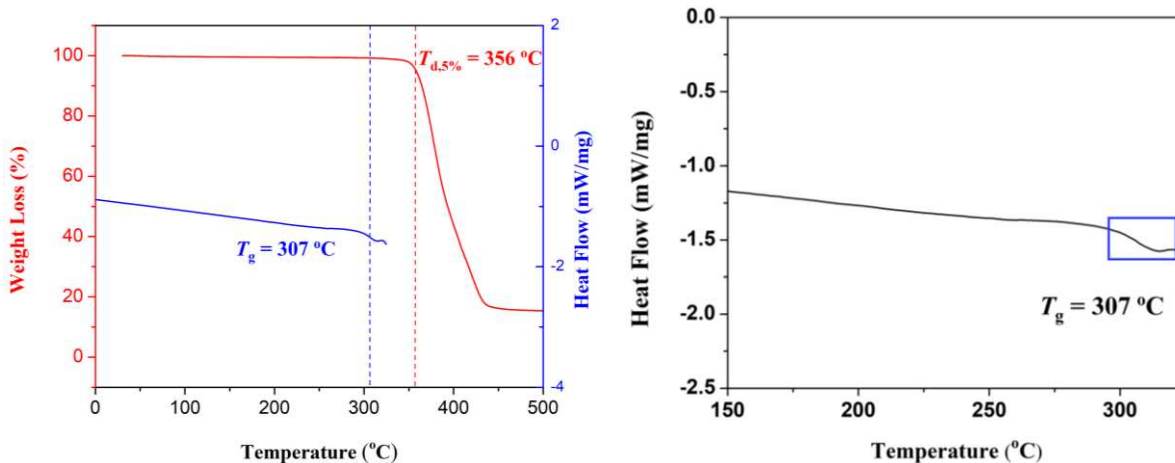
### 2.3.4 Erythro-Ditactic Pin Material's Properties.

Thermal properties of Pin materials with varied erythro-ditactic contents were examined by thermal gravimetric analysis (TGA) as well as differential scanning calorimetry (DSC). All the Pin materials produced by LPs showed nearly identical  $T_{d,5\%}$  (decomposition temperature defined by the temperature at 5% weight loss) values between 354–356 °C (Figure 2.7), while the



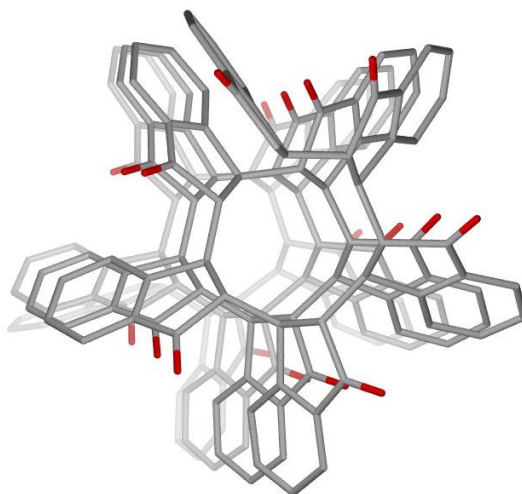
autopolymerized Pin exhibited noticeably lower thermal stability with a  $T_d$  of 329 °C (Figure A10). The overall increased thermal stability for the Pin produced by LPs is presumably due to the enhanced regioselectivity and stereoselectivity through the controlled polymerization via the LPP mechanisms. This reasoning was further supported by the observation that the autopolymerized Pin exhibited a visible shouldering and multi-step decomposition profile (Figure A10), attributable to differences in its head/tail, head/head, and tail/tail linked units (regio-irregularities) by the non-selective radical polymerization process.

DSC traces of the LP-produced Pin showed uniquely high  $T_g$  values but no obvious melting-transition temperature ( $T_m$ ) or crystallization temperature. For example, the Pin produced by the MAD/NHO LP with 71 % stereoregularity had an exceptionally high  $T_g$  of 307 °C (Figure 2.7). The  $T_g$  of other Pin samples with varied MW and diastereoselectivity were in the range of 271 °C and 303 °C (Figures A13 – A18), comparable to that of the autopolymerized Pin (269 °C, Figure A12). Noted, the Pin sample with the highest diastereoselectivity (75%) of the series, coupled with a high theoretical MW of  $M_n = 6.50 \times 10^5$  g mol<sup>-1</sup> displayed no clear  $T_g$ , suggesting that it may be near or above the decomposition temperature ( $T_{d,5\%} = 356$  °C). For the same possible reason, no  $T_m$ , which in theory should be much above  $T_g$ , was observed for all Pin samples.



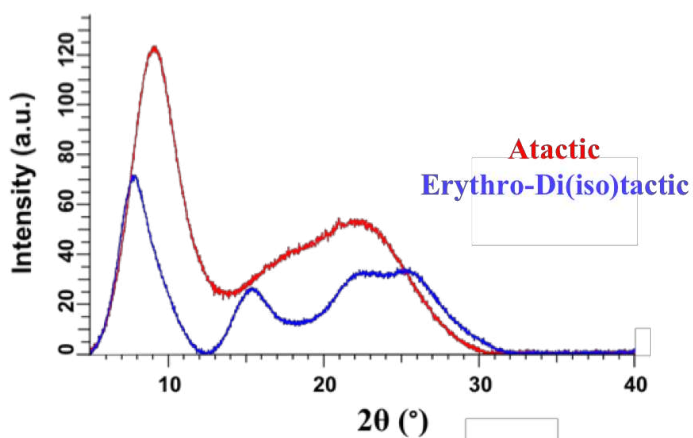
**Figure 2.7.** Left: an overlay of TGA (red curve) and DSC (blue curve) traces for 71 % erythro-ditactic Pin with labeled  $T_{d,5\%}$  and  $T_g$  values, highlighting that the endotherm ( $T_g$ ) on the DSC trace is not due to decomposition. Right: separate DSC curve of the same sample.

To explain the insolubility of the Pin when the erythro-ditacticity reaches about 70%, we hypothesized that at some erythro-ditactic content threshold, Pin may assemble into a secondary structure that increases overall crystallinity and chain rigidity. We probed this hypothesis by modeling a 20-mer of erythro-diisotactic and erythro-disyndiotactic Pin using Molecular Mechanics 2 (MM2, see the SI), which in the case of the former, rearranged to predict a  $5_1$  helical secondary structure (Figure 2.8). Erythro-disyndiotactic conditions led to a random coil architecture. It should be noted here that this computational result solely shows plausibility of helical secondary structures and does not rule out erythro-disyndiotacticity. However, although this does not provide full support for either assignment in our specific sample, it does lead us to surmise that if secondary structures such as helices are produced, an increase in crystallinity and diminished solubility in common organic solvents due to the presence of well-ordered structures would be observed.



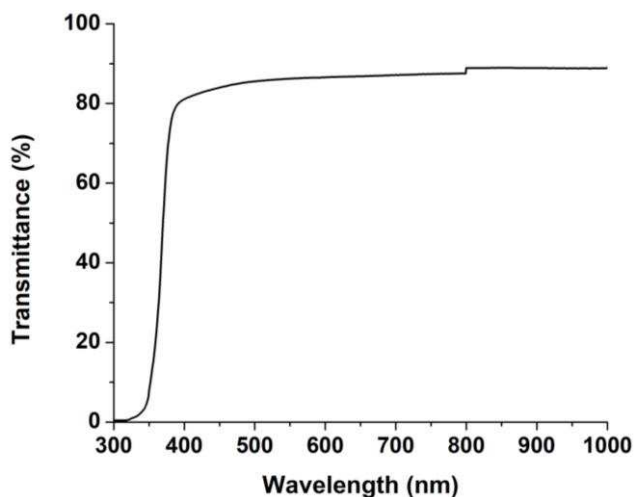
**Figure 2.8.** Predicted  $5_1$  helical secondary structure for erythro-diisotactic Pin by MM2 calculations.

To seek additional evidence for erythro-diisotacticity-induced crystallinity, we performed pXRD analysis on the Pin with 75 % erythro-ditacticity in parallel to the atactic, amorphous autopolymerized Pin. The atactic, amorphous Pin showed only two broad signals at 9.8 and 21.9°, corresponding to  $d$  spacings of 0.90 and 0.41 nm, respectively (Figure 2.9). In contrast, the pXRD patterns of the erythro-ditactic Pin feature four resolved, much sharper diffraction peaks at 7.3, 15.2, 22.5 and 25.3°, corresponding to  $d$  spacings of 1.2, 0.58, 0.39, and 0.35 nm, respectively, which is consistent with the enhanced crystallinity for the diastereoselective Pin. Through pXRD and MM2 models, it is more likely that the TS stereo-defining step produces erythro-diisotactic, helical Pin reflecting heightened crystallinity and suppressed solubility. Collectively, our findings from the analyses of solubility, Newman projections, NMR-derived diastereoselectivity, ordered  $5_1$  helical secondary structure by MM2 calculations, thermal stability and transitions by TGA and DSC, and diffraction patterns by pXRD experiments support the conclusion that the high erythro-diastereoselectivity of the Pin produced by the MAD-based LPs is responsible for its unique material's properties such as insolubility in common organic solvents as well as enhanced thermal stability,  $T_g$ , and crystallinity.



**Figure 2.9.** pXRD plots of autopolymerized Pin (red) and LP-induced Pin with 75% erythro-ditacticity (blue) between 5 – 40 °.

The Pin material with a moderate erythro-ditacticity (57%) produced by the FAB/SKA LP was subjected to optical analysis due to having glassy, transparent character. Employing UV/Vis/NIR spectroscopy on a 160  $\mu\text{m}$  prepared thin film sample, we found transmittance values between 85-89 % in the 400 – 1000 nm region, with no exhibited transmittance in the ultraviolet region due to absorbance by the pendant group chromophores (Figure 2.10). We further obtained a reflectance value of 9.6 % and calculated a haze value of 11.0 % (Figures A20 and A21). This level of transparency is competitive with those of widely used transparent commodity plastics, such as amorphous poly(methyl methacrylate) ( $T_g = 110\text{ }^\circ\text{C}$ ,  $T\% = \sim 90\%$ ) and poly(styrene) ( $T_g = 100\text{ }^\circ\text{C}$ ,  $T\% = \sim 90\%$ ).<sup>47,48</sup> However, Pin fills the gap between high transparency and thermal stability, with a  $T_g$  (286  $^\circ\text{C}$ ) more than 170  $^\circ\text{C}$  higher than that of the commodity transparent plastics. Hence, Pin could serve rational use in solar cell coatings, in which the transparent material coating the solid-state photovoltaics must be able to withstand elevated temperatures from solar energy as well as filter ultraviolet radiation which damages solar cells.<sup>49</sup> It is worth mentioning that Pin's chain rigidity conduces a very brittle material, rendering the preparation of self-supported films thicker than 160  $\mu\text{m}$  challenging.

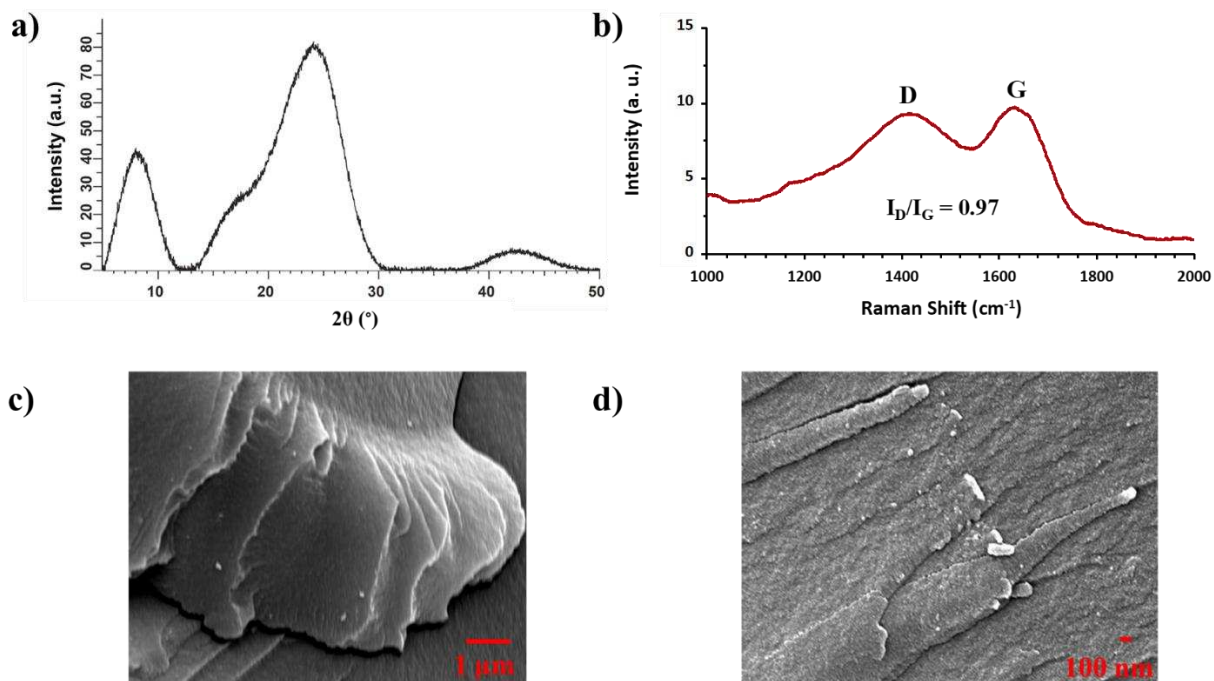


**Figure 2.10.** UV/Vis/NIR spectrum for the total transmittance of 160  $\mu\text{m}$  Pin thin-film ( $M_n = 1.72 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.23$ , erythro-ditacticity = 57%,  $T_g = 286 \text{ }^\circ\text{C}$ ).

### 2.3.5 Upconversion of Pin to Graphite Oxide.

Consistently throughout TGA experiments with Pin, roughly 15 % mass remained after the initial decomposition curve as some carbonaceous material stable up to 700  $^\circ\text{C}$ . We postulated that the ring-fused phenyl group and the ketone functional handle may promote thermal decomposition of Pin into a useful material that could extend this polymer's end of its first life. We collected decomposed Pin upon treatment in a tube furnace at 360  $^\circ\text{C}$  and subjected the material to analysis by pXRD and Raman spectroscopy. pXRD analysis gave 2-theta values of 3.4, 24.8, and 42.3 $^\circ$ , which were converted to  $d$ -spacing multiples of 2.6, 0.36, and 0.21 nm. Comparing these  $d$ -spacing values among indexed material references gave strong evidence for well-ordered carbon-rich materials (Figure 2.11a).<sup>50</sup> Through Raman spectroscopy, we observed only three signals matching the vibrational bands for the out-of-phase  $sp^3$  defect region (D-band; 1390  $\text{cm}^{-1}$ ), the in-phase  $sp^2$  graphitic regions (G-band; 1610  $\text{cm}^{-1}$ ) for graphite oxide (GO), and a very small 2D-band (Figure 2.11b).<sup>51</sup> As further supporting evidence for the formation of GO, we subjected the same samples to scanning electron microscopy (SEM) and found signature layering expected of graphitic lamina (Figure 2.11c,d; 10  $\mu\text{m}$  SEM image shown in Figure A19). Upconversion of Pin was subsequently examined in more detail by varying the Pin erythro content, reaction atmosphere, and pyrolysis temperature (Table A1). Such pyrolysis experiments revealed an inverse correlation between erythro-diastereoselectivity and GO upconversion yield, where atactic Pin yielded 54% GO and the ditactic Pin with the highest erythro-ditacticity yielded only 25 % GO. Decomposition of Pin into GO was an exciting find, not only for the versatile applicability of GO in battery applications,

energy conversion, and coatings,<sup>52</sup> but also because it reveals an upcycling avenue for Pin at its end-of-life.



**Figure 2.11.** (a) pXRD of pyrolyzed Pin carbonaceous material. (b) Raman spectroscopy of GO obtained from pyrolysis of Pin with labeled D-band, G-band, and calculated surface defect ratio ( $I_D/I_G$ ). (c) SEM image of GO at 1 μm scale, highlighting layering characteristic. (d) SEM image of GO at 100 nm scale consisting of grooved layers.

## 2.4 CONCLUSION

This contribution details the preparation and storage of unstable monomeric indenone for the effective polymerization using LPs affording, for the first time, high MW polymers ( $M_n$  up to  $1.72 \times 10^5$  g mol<sup>-1</sup>) with relatively low dispersity values ( $D = 1.13$ - $1.23$ ). Those MW characteristics were measured for the soluble Pin materials with low erythro-diastereoselectivity of 57% produced by the FAB/SKA LP, and it is anticipated the Pin materials with higher erythro-ditacticity of  $\geq 71\%$  produced by MAD-based LPs would be even higher if they can be measured by GPC in common organic solvents. Referring to the predicted propagation transition states, we manipulated the steric

bulk of the LA in the LP and realized tunable diastereoselective bias through a chain-end control mechanism to achieve a range of Pin samples with erythro content between 57 – 75 % and significantly enhanced  $T_g$  and  $T_d$  values of 307 °C and 356 °C, respectively, relative to the non-selective autopolymerized Pin ( $T_g$  = 269 °C and  $T_d$  = 329 °C). Collective evidence pointed to a semi-crystalline material with an ordered  $5_1$  helical secondary structure for Pin with high erythro-di(iso)tacticity. Analysis of the highly stable (to 700 °C) carbonaceous material generated via pyrolysis of Pin at 360 °C by Raman spectroscopy, pXRD, and SEM provided key evidence for the upconversion of Pin into versatile graphite oxide, offering a valuable upcycling avenue to extend this polymer's applicability at end-of-life. Pin also offers valuable applicability as a material with exceptionally high  $T_g$  coupled with good transmittance (> 85 %) and low haziness (11 %).

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## Chapter 3

### Thermomechanical Activation Achieving Orthogonal Work/Healing Conditions of Nanostructured Tri-Block Copolymer Thermosets

#### 3.1 Synopsis

Conventional thermosets, despite their technological significance in today's materials economy, present a modern sustainability challenge because of their lack of end-of-life options for recyclability or reprocessability. Emerging covalent adaptable networks (CANs) offer sustainable alternatives to permanently crosslinked materials, but ideal orthogonal working/reprocessing conditions are hardly achievable by the current thermochemical activation mechanism. Here we report a CAN system of additive/catalyst-free, fully reprocessable, crosslinked, tri-block copolymer (tri-BCP) thermoplastic elastomer networks based on acid-anhydride bond exchange operated on a thermomechanical activation mechanism. The unique functionality of the tri-BCP architecture enables self-assembly into inter-linked, hexagonally packed cylinder nanostructures that preclude any productive inter-cylinder bond exchange (and, thus, creep) without cooperative thermal and mechanical (heating and compression) processing conditions.

#### 3.2 Introduction.

The ever-growing materials economy has recently begun to reevaluate its prioritization of several competing ends. While in the past, factors such as cost, utility, and scalability alone influenced which materials were mass-produced, today's modern perspectives on global sustainability have incentivized the consideration of factors such as renewability, recyclability, reprocessability, and environmental impact.<sup>1-12</sup> Several strategies have been put forth to address these new challenges including, notably, the design of intrinsically recyclable polymers,<sup>13-15</sup>

repurposing or upcycling of post-consumer commodity plastics,<sup>16-20</sup> and enabling reprocessability of crosslinked thermosets by utilizing innovative concepts of vitrimers,<sup>21-28</sup> covalent adaptable networks (CANs),<sup>29-47</sup> and non-covalent self-healing networks.<sup>48</sup> Common requirements for achieving a CAN or vitrimer system include privileged functional groups, multiple synthetic steps, or added catalysts and crosslinkers. Such dynamically crosslinked thermosets can enter their flow state upon activation of covalent bond exchange reactions photo- or thermochemically (with light, or heat and/or catalyst).<sup>30,31,35,42,45,49</sup> An example of polyhydroxyurethane vitrimers via transcarbamoylation activated by mechanical stress was also reported.<sup>50</sup>

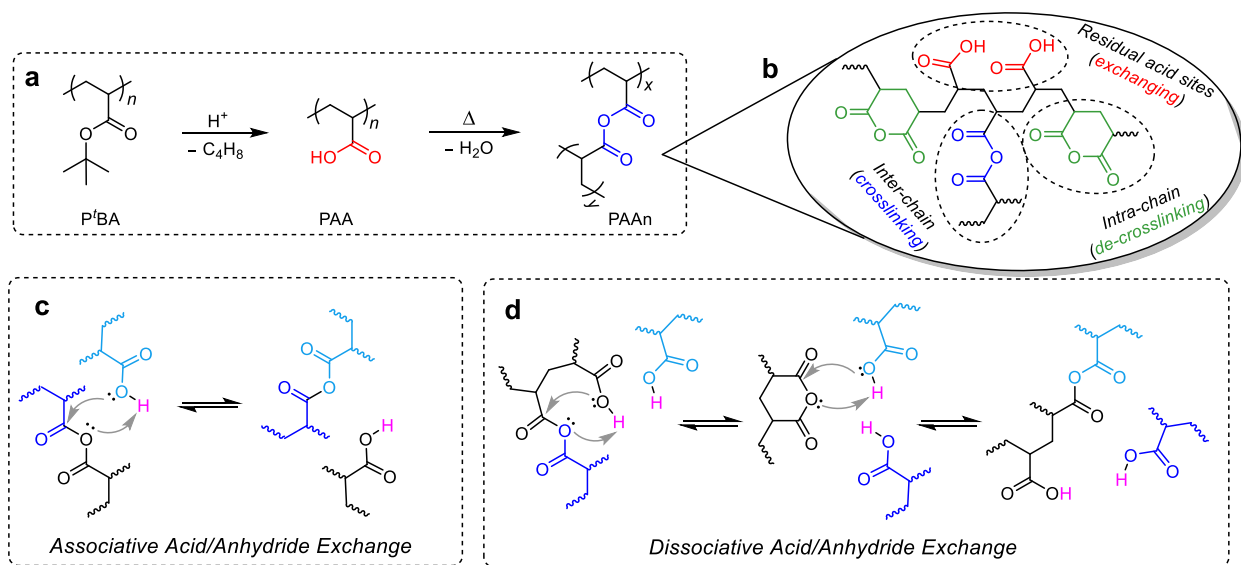
The applications which demand crosslinked materials require resistance to creep (deformation), heat (melting), and solvent (dissolution). Ideal CANs or vitrimers should be capable of resisting dissolution and creep at working temperature and stress, while only entering the flow state during reprocessing conditions. Achieving such ideal *orthogonal* behavior would make CANs sustainable alternatives to conventional thermosets. Creep at working temperature and stress is an important challenge for CANs. Recent efforts sought to improve creep resistance were directed to morphology-tunable block copolymers (BCPs).<sup>51-55</sup> For example, several advantages were reported in a di-BCP system wherein the poly(*n*-butyl methacrylate) (P<sup>*n*</sup>BMA) block exists in domains separated from the vitrimeric domain furnished by poly(2-acetoacetoxyethyl methacrylate) blocks with *added* xylylene diamine cross-linker via dynamic transamination.<sup>21</sup> Most notably, the lamellar phase-separated diblock copolymers exhibited superior resistance to creep compared to random copolymer analogues, which was explained by noting that phase separation localizes crosslinked domains resulting in higher crosslinking density which restricts “network strand diffusion”.

The phase-separated domain morphology provides an ideal platform to test our hypothesis that bond exchange events that occur within one isolated domain is not productive in reconfiguring material shape. In other words, exchange-driven permanent deformation might only be achieved by inter-domain exchange or mixing. To test this, we need to investigate effects of higher block architectures, in particular, an ABA tri-BCP system with crosslinking and exchange points contained within the A-blocks inter-linked by the soft B-blocks. Here, each crosslinking A-domain should be connected to other A-domains generating one continuous macro-network. In contrast, the AB di-BCP system theoretically forms a discontinuous network wherein each hard domain is disconnected from the next. Thus, it is foreseeable that permanent macro-phase deformation can be a source of creep.<sup>56</sup> Recent tri-BCP work utilized a post-functionalized tri-BCP with dynamic bond exchange in localized poly(4-pyridine) terminal domains with the added alkyl dibromide crosslinker by trans-*N*-alkylation, but the creep and reprocessability were not addressed.<sup>57</sup> Combining the two synergistic concepts of ABA-networking and inter-domain exchange, we endeavored to identify an intriguing scenario where neither thermal energy or mechanical force alone is enough to induce creep, but only the collaborative effort of both can achieve productive permanent deformation, as thermal energy is needed to induce dynamic bond exchange while mechanical force is needed to induce inter-domain contact.

To this end, we developed a high-performance, self-assembling and reprocessable tri-BCP network system (Figure 3.1a) by utilizing ubiquitous carboxylic acids and anhydrides of simple acrylic monomers wherein poly(acrylic acid) (PAA) units are crosslinked through a well-known acid/acid condensation of water (forming an anhydride).<sup>58,59</sup> Recognizing the fact that this crosslinking reaction, which occurs at temperatures >150 °C, does not go to completion, we reasoned that the residual carboxylic acid (Figure 3.1b) could serve as an exchange agent by



attacking the anhydride crosslink in poly(acrylic anhydride) (PAA<sub>n</sub>) to eliminate a carboxylate equivalent, thus cleaving the crosslink (Figure 3.1c, d). If supported, this would mean nearly any polymer or copolymer containing acrylic acid units could foreseeably be converted into a covalent adaptable network *without necessity for any additional reagents, catalysts, or crosslinkers*. Since there are already several known methodologies that can produce copolymers of PAA, including the thermal decomposition of poly(*tert*-butyl acrylate) (P<sup>t</sup>BA) to PAA,<sup>60-64</sup> several variations of dynamic materials can be immediately targeted with this concept. For this study, we employed our recently disclosed compound sequence control (CSC) Lewis pair polymerization (LPP) methodology<sup>65</sup> to access high-molecular-weight (MW) all-acrylic ABA tri-BCPs (G1, Figure 3.1a) to study the synergistic self-assembly and discrete networking effects, compared with other CAN architectures, on creep resistance to develop a superior collaborative thermo-mechanical exchange mechanism for orthogonal working/reprocessing conditions in CAN-type materials.



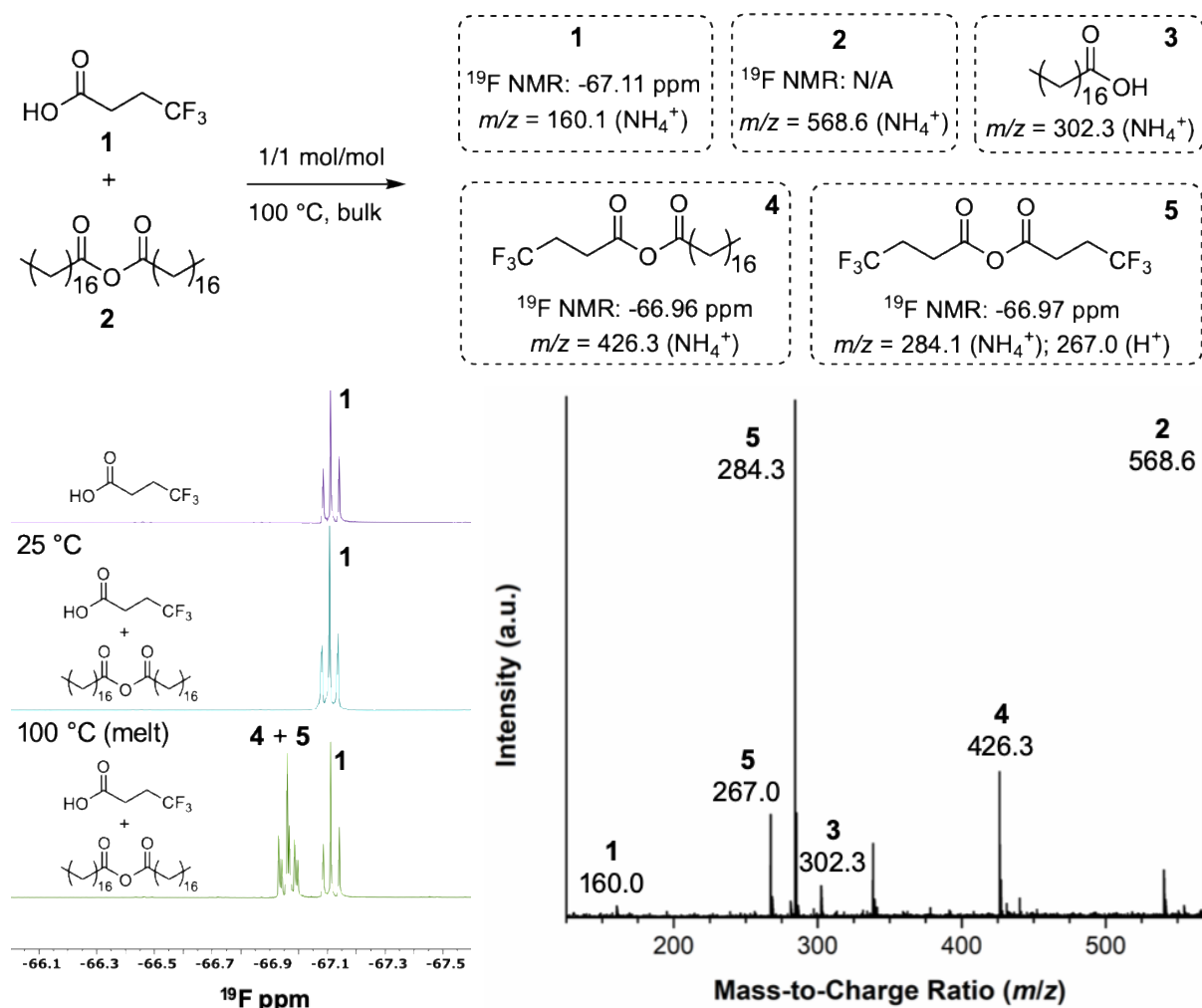
**Figure 3.1. All acrylic ABA tri-BCP CANs via Acid-Anhydride exchange.** **a**, Selective transformation of P<sup>t</sup>BA-containing BCPs (G1) into PAA (G2) and PAA<sub>n</sub> (G3) BCPs. **b**, Possible structures of PAA<sub>n</sub> network polymer. **c**, Postulated inter-chain associative exchange mechanism between residual acid and crosslinked anhydride units. **d**, Postulated intra-chain dissociative exchange mechanism between residual acid and crosslinked anhydride units.

### 3.3 Results and Discussion

#### 3.3.1 Small Molecule Acid-Anhydride Associative Exchange Models.

To provide evidence to support the postulated dynamic exchange between a carboxylic acid and an anhydride, we set out to investigate this possible exchange reaction using small molecule models.<sup>29-39</sup> Using  $^{19}\text{F}$  NMR, we monitored 2-h bulk exchange reactions between 4,4,4-trifluorobutyric acid (TFBA) and stearic anhydride (SAn) at 25 °C, 100 °C, and 150 °C under inert conditions. The evolution of one fluorinated species (triplet) at 25 °C into three, accounting for all exchange products and TFBA (Figure 3.2), beginning at 100 °C supports our postulated exchange mechanism (Figure 3.1c, d). The exchange products were further characterized by quadrupole time-of-flight mass spectrometry (Q-TOF-MS), revealing masses for all expected exchange structures (Figures 3.2, B1-B2).

Conceivably, the dynamic acid-anhydride exchange can either occur as intra-chain between two neighboring acids to form a cyclic anhydride (decrosslinking) or inter-chain to form a linear anhydride (crosslinking) (Figure 3.1c, d).<sup>59</sup> We also considered parallel self-exchange between local anhydrides in the absence of acid groups, which has been previously hypothesized.<sup>66</sup> Using a similar approach, we found successful exchange by Q-TOF-MS between decanoic anhydride and SAn at 100 °C (Figure B3), for which reason we do not rule out the possibility of competing anhydride-anhydride self-exchange.

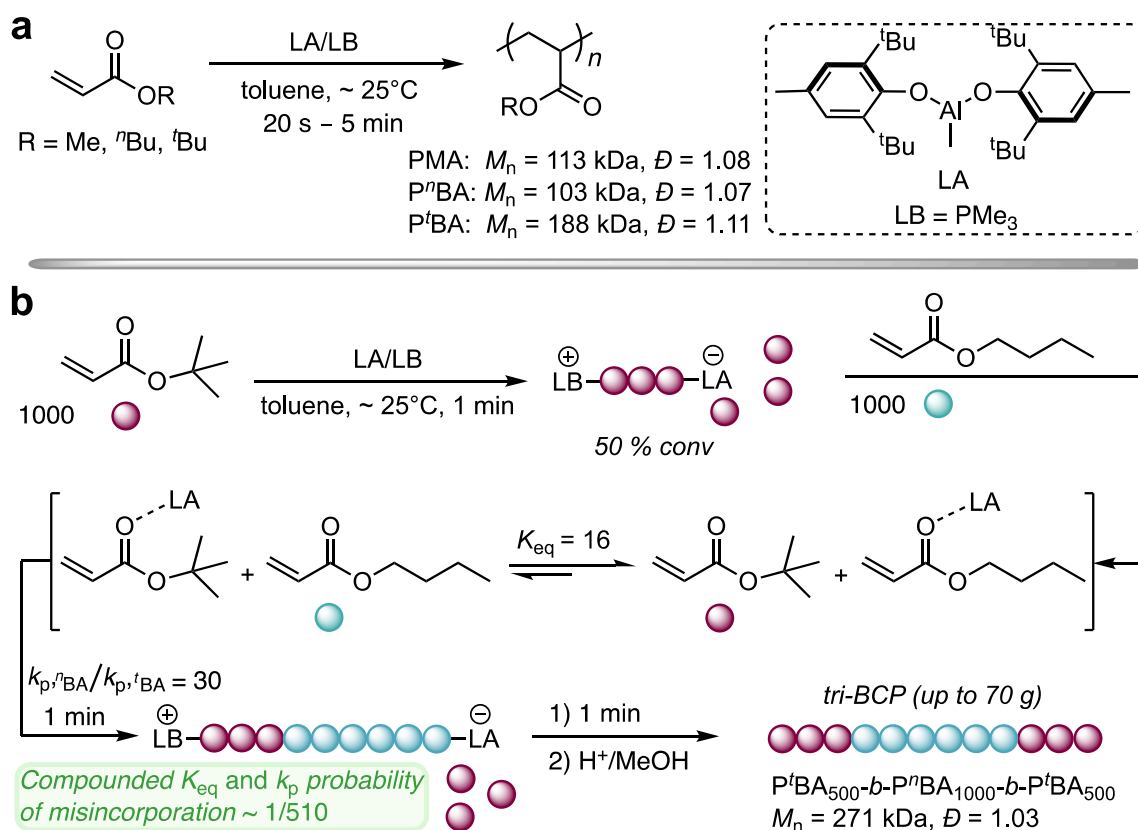


**Figure 3.2. Evidence for acid-anhydride exchange at high temperature.** Depicted results of small molecule proxy experiments for the proposed paralleling acid-anhydride associative and dissociative exchange mechanisms utilizing  $^{19}\text{F}$  NMR and Q-TOF-MS ( $\text{NH}_4^+$ ).

### 3.3.2 Synthesis of All-Acrylic Tri-BCPs and G1-to-G2-to-G3 Evolution.

Our designed hard-soft-hard ABA tri-BCP precursor to thermoplastic elastomer (TPE) CANs has a general structural formula of  $\text{PAA-}b\text{-PAE-}b\text{-PAA}$ , wherein the crosslinkable PAA end-blocks can be readily derived from the selective acid-catalyzed de-*tert*-butylation<sup>67</sup> of P'BA blocks and the middle (soft) block can be a flexible, low glass-transition temperature ( $T_g$ ) poly(acrylic ester) (PAE) such as poly(methyl acrylate) (PMA) or poly(*n*-butyl acrylate) (P<sup>n</sup>BA). We envisioned that such tri-BCPs could be readily synthesized using our recently established CSC-LPP methodology.<sup>65</sup>

We first utilized LPP to synthesize high molecular weight homopolymers for tensile model studies (Figure 3.3a), including: PMA ( $M_n = 1.13 \times 10^5$  g mol<sup>-1</sup>,  $\bar{D} = 1.08$ ); P<sup>n</sup>BA ( $M_n = 1.03 \times 10^5$  g mol<sup>-1</sup>,  $\bar{D} = 1.07$ ); and P<sup>t</sup>BA ( $M_n = 1.88 \times 10^5$  g mol<sup>-1</sup>,  $\bar{D} = 1.11$ ) (Table B1). Next, the model study for transformation of generation 1 (G1) P<sup>t</sup>BA blocks to (G2) PAA blocks, and lastly to G3 crosslinked PAA<sub>n</sub> blocks (i.e., G1-to-G3 tri-BCP transformation) was performed. Specifically, G1 P<sup>t</sup>BA was transformed near-quantitatively into G2 PAA via acid (trifluoroacetic acid, TFA)-catalyzed elimination of isobutene from the <sup>t</sup>Bu-ester (Figure 3.1a).<sup>60,62</sup> Heat treatment of PAA at 150–200 °C results in the condensation of two carboxylic acid units, observable by DSC, to yield an acrylic anhydride in the forms of the intra-chain rigid backbone and inter-chain crosslinker, G3 PAA<sub>n</sub> (Figures 3.1a,b, B23).



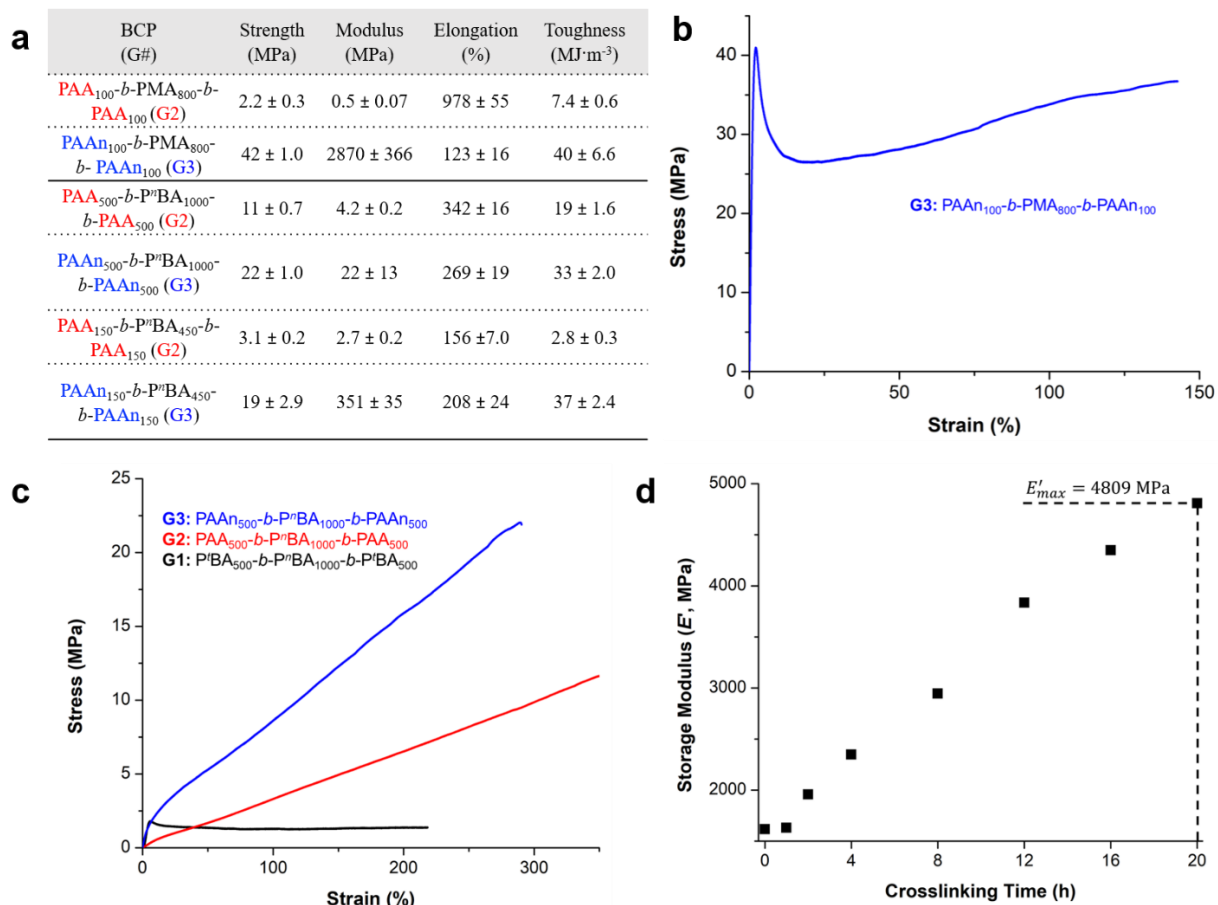
**Figure 3.3. Outlined polymer synthesis by LPP. a,** Synthesis of homopolymer controls. **b,** Synthesis of tri-BCPs (represented by <sup>t</sup>BA and <sup>n</sup>BA).

Using the CSC-LPP method (Figure 3b), we synthesized high MW ( $M_n > 10^5$  g mol<sup>-1</sup>) G1 tri-BCPs in three different hard-soft-hard volume ratios (1:2:1, 1:3:1, and 1:8:1): P'BA<sub>500</sub>-*b*-P''BA<sub>1000</sub>-*b*-P'BA<sub>500</sub> ( $M_n = 2.71 \times 10^5$  g mol<sup>-1</sup>,  $D = 1.03$ ); P'BA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-P'BA<sub>150</sub> ( $M_n = 1.12 \times 10^5$  g mol<sup>-1</sup>,  $D = 1.07$ ); and P'BA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-P'BA<sub>100</sub> ( $M_n = 1.45 \times 10^5$  g mol<sup>-1</sup>,  $D = 1.08$ ) (subscripts note the target degree of polymerization in synthesis, Figures B4-B6). Full synthesis, characterization, and mechanical testing of parent G1 copolymers is discussed in greater detail in the SI (Figures B10-B12, B16-B19, B24-B28, and B32-B33; Table B2).

Following the same G1-to-G3 evolution protocol established for homopolymer P'BA, the above P'BA-containing parent BCPs (G1) were selectively transformed into PAA (G2) and PAA<sub>n</sub> (G3) BCPs. The G1 to G2 transformation was nearly quantitative (98.7 – 99.6%, Figures B34-B36; Table B3), affording G2 PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub>, PAA<sub>500</sub>-*b*-P''BA<sub>1000</sub>-*b*-PAA<sub>500</sub>, and PAA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-PAA<sub>150</sub> tri-BCPs. The G2 BCPs were simultaneously molded into films and crosslinked into G3 network BCPs by compression molding at 200 °C under 5000 psi. As anticipated, all G3 network BCPs are insoluble in common solvents (only swelling), resistant to acids (e.g., 12 M HCl), and soluble/degradable through hydrolysis in 1 M aqueous NaOH, supporting crosslinking by inter-chain anhydrides (Figure B40). Thermal stability of the reprocessable G3 materials was also supported by measuring mass lost during a 1 h isothermal event at 200 °C, which revealed a negligible decline to 99.0 – 99.6 % initial mass (Figures B43-B48). Note here that G3 network BCPs, PAA<sub>n</sub>-*b*-PAE-*b*-PAA<sub>n</sub>, were thermally crosslinked—*without any reagent, linker, or catalyst*—selectively at the PAA domains that were predesignated during the synthesis of the G1 BCPs.

### 3.3.3 Mechanical Properties of G1/G2/G3 Tri-BCPs.

The mechanical properties of G1/G2/G3 tri-BCPs with two different middle soft blocks (PMA and P<sup>n</sup>BA) are summarized in Figure 3.4a and Tables B9-B26, with representative tensile stress-strain curves depicted in Figure 3.4b-c. Additional tensile experiments such as cyclic strain deformation highlighting G2 TPE characteristic elasticity,<sup>68,69</sup> shape memory, and evolution of tensile profiles with tri-BCP generation G1-G3 are described in the SI (Figures B38 and B39; Tables B4-B5). Strips of G3 PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub> films crosslinked for 0 (G2), 1, 2, 4, 8, 12, 16, 20, and 24 h were subjected to dynamic mechanical analysis (DMA) temperature-ramp frequency sweeps (-50 to 150 °C, 5 °C/min, 0.3 % strain, 1 Hz) to track the evolution of mechanical and thermal behavior with crosslinking time (Figure 3.4d). As expected, the uncrosslinked G2 specimen yielded the lowest modulus while failing below 100 °C (Figure B49). Crosslinked G3 specimens exhibited increasing moduli over time to a high modulus maximum of 4.81 GPa (Figure 3.4d and B49, Table B6), indicating drastically increased film hardness. Samples above 20 h of crosslinking time reached a plateau in moduli performance (Figure B50). Each crosslinking time-point sample was also analyzed by Fourier-transform infrared spectroscopy (FTIR), revealing *no observable structural changes or indications of decomposition* (Figure B42). The  $T_g$  values of the PMA block at G2 and each crosslinking time-point were similarly determined through DMA by locating the temperature of the  $\tan \delta_{\max}$ , revealing an immediate jump in  $T_g$  by >14 °C on going from G2 to G3 (Figure B49, Table B6). Additional frequency sweeps to 200 °C revealed a stable rubbery plateau ( $\Delta E' \approx \text{constant}$ ) indicating *thermomechanical stability* at high operating temperatures for thermoset applicability in each of the G3 tri-BCP CANs (Figures B51 and B52).



**Figure 3.4. Tensile properties of G1 – G3 tri-BCPs.** **a**, Tensile profiles of selected G1/G2/G3 tri-BCPs. Values are based on 3–5 averaged dogbone specimens (5 mm/min, ~23 °C; See also Tables S9-S26). **b**, Representative tensile stress-strain curve (5 mm/min, ~23 °C) of G3 network tri-BCP PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub>. **c**, Representative tensile stress-strain curves (5 mm/min, ~23 °C) of tri-BCPs: P<sup>n</sup>BA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-P<sup>n</sup>BA<sub>500</sub> (G1, black), PAA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>500</sub> (G2, red), PAA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>500</sub> (G3, blue). **d**, Relationship between maximum storage modulus ( $E'$ ) over crosslinking time for G3 PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub> by DMA (-50 to 150 °C, 5 °C/min, 0.3 % strain, 1 Hz).

When subjected to tensile tests, the G3 tri-BCPs drastically outperformed the G2 homologs in tensile strength and modulus (Figures 3.4a-c, Table B7). In particular, PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub> exhibited an impressive plastic character with a high Young's modulus  $E \sim 2.9 \pm 0.37$  GPa, ultimate tensile strength  $\sigma_B \sim 42 \pm 1.0$  MPa, and elongation at break  $\epsilon_B \sim 123 \pm 16$  % (Figure 3.4b), reflecting ~5700x, ~20x, and ~5.4x enhancement in modulus, strength, and toughness, respectively, as compared to its G2 homologue (Figure 3.4a). The similar trend, albeit to a lesser

degree, was also observed for the BCPs with P<sup>n</sup>BA as the soft block on advancing to the G3 BCP network (Figure 3.4a,c).

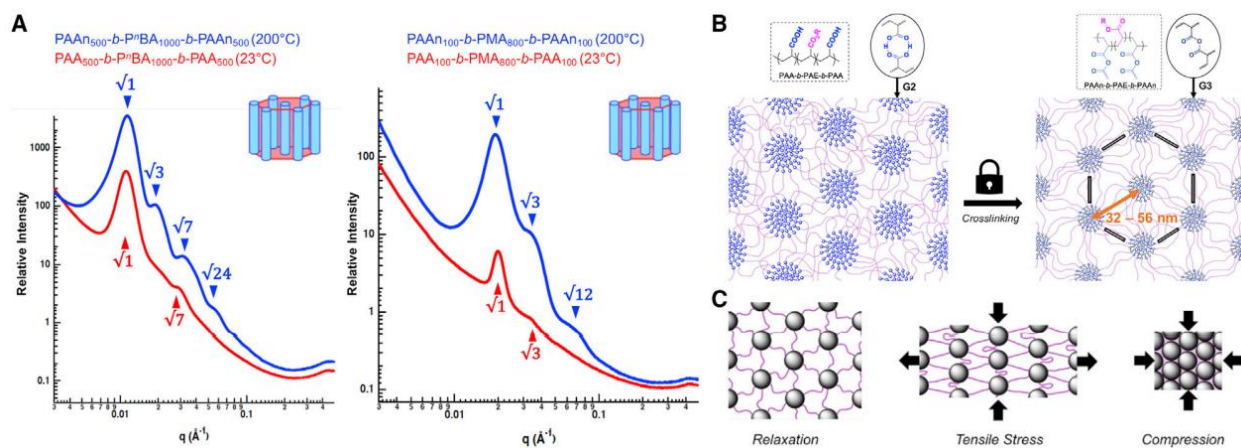
### 3.3.4 Self-Assembly of G2/G3 BCPs and Crosslinked G3 TPE Networks.

Recognizing the advantageous functionality induced by self-assembly into phase-separated nanostructures in various reported BCP systems,<sup>70-72</sup> we envisioned that the presence of the PAA hard blocks in tri-BCPs could effectively utilize H-bonding to self-assemble into discrete acid domains. Flash-heating during compression molding of these G2 BCPs with phase-separated PAA domains could then permanently link into covalently bound tri-BCP PAA<sub>n</sub>-PAE-PAA<sub>n</sub> networks. Accordingly, films of PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub> and PAA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>500</sub> were analyzed by small-angle X-ray scattering (SAXS) to reveal the phase behavior of these BCPs at both ambient (23 °C) and elevated (200 °C) temperatures (Figure 3.5a).

Scattering for each BCP sample was collected at 23 °C and again at 200 °C after 30 min of bulk thermal annealing. Both BCPs exhibited scattering patterns consistent with hexagonally packed cylinder (HPC) self-assembled nanostructures with domain spacings ( $d_{100}$ ) within a range from 32 nm to 56 nm (Figure 3.5b, calculations shown in the SI). This observation infers that at 200 °C, both BCPs retain and improve upon the HPC packing, where the hard domains (PAA, PAA<sub>n</sub>) comprise the cylinders. Noteworthy here is that we did not observe order-disorder transition temperatures at 200 °C, indicating the retention and stability of these complex architectures at reprocessing temperatures. Less intense scattering peaks prior to crosslinking is likely attributed to the non-covalent, looser HPC packing. Figure 5c depicts self-assembled the PMA-containing G3 CAN with inter-cylinder links, connecting each cylinder to its neighbors. Thus, when the HPC structure is relaxed, there can exist a small degree of mobility for each



cylinder due to the flexibility of the soft PMA block. However, when tensile stress is applied, the PMA linkers tighten and immobilize the entire structure. This reasoning can also account for the sizable yield point and high modulus observed for this G3 material (Figure 3.4b).



**Figure 3.5. Self-organizing, crosslinking, and reinforcing.** a, SAXS profiles of tri-BCP films in G2 PAA (red, measured at 23 °C) and G3 crosslinked PAA (blue, measured at 200 °C) HPCs. b, Illustrative nanostructural crosslinking of self-assembled G2 H-bonded PAA sites (left) into covalently linked PAA network BCP domains (right). c, Postulated chain physics of the HPC crosslinked G3 network tri-BCP at relaxation, tensile stress, and compression conditions.

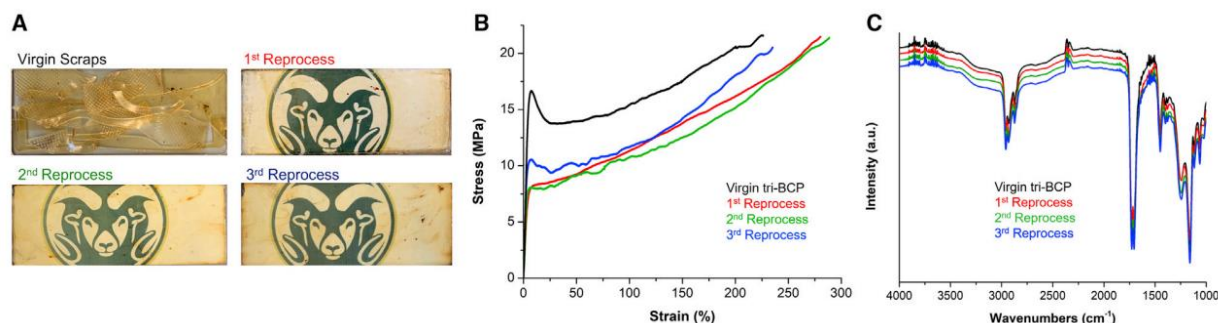
### 3.3.5 Thermomechanical Reprocessability of G3 CANs.

Conventional thermosets seldom permit any reprocessability as a result of the complex, dense network of *random* covalent crosslinks, unless they become dynamically exchangeable under processing conditions, the case of CANs. A consistent compression molding pressure of 5000 psi was chosen for reprocessing G3 BCP scraps, while a temperature of 200 °C was selected in compliance with observed mild endothermic delineation onsets in 3× heating-cycle DSC traces at this temperature (Figure B60).

Accordingly, we added the scraps from the  $\text{PAA}_{150}\text{-}b\text{-P}''\text{BA}_{450}\text{-}b\text{-PAA}_{150}$  tensile tests to the compression mold and subjected them to reprocessing conditions. After reprocessing, what were once deformed scraps had become a homogenous film (Figure 3.6a). Reprocessed G3 CAN

materials exhibited nearly complete, if not superior (within error), mechanical recovery (Table B8). For example, the tensile strength and elongation maintained in the range of 19 to 22 MPa and 208 to 285%, respectively, over the four consecutive reprocessing cycles (Figure 3.6b, Table B8). We also observed that reprocessed G3 CANs exhibited a lower yield strength than the virgin sample, which could be attributed to two possible chemical events occurring during reprocessing conditions. One is the oxidation of anhydride units which would decrease the overall crosslinking density, and the second is the shift in ratio of intra- (decrosslinking) and inter- (crosslinking) molecular anhydrides to the higher-energy cyclic analogue which would similarly decrease the crosslinking density. In either case, FTIR spectra revealed the structural constitution of the TPE CANs, including hydroxyl-region absorption bands, are retained each lifecycle (Figure 3.6c).

As the G3 reconfigurable networks cannot rearrange due to the locked inter-networking of the nanostructure (Figure 3.5b), our remaining hypothesis to explain reprocessability is the *inter-cylinder acid-anhydride exchange*, which allows crosslink-mixing between cylinders (Figure 3.5c). If transformation from G2 to G3 results in a critical maximum number of anhydride bonds, there should be residual acrylic acid units present which should trigger the bond exchange at high temperatures (Figures 3.1c,d). Residual acid units were characterized by FTIR analysis of PAA<sub>n</sub> homopolymer (Figure B41). Exchange within one cylinder would likely be non-productive. Therefore, thermal-*compression* of the HPC-structured G3 network is needed to push exchange-active domains in proximity of colliding with each other (Figure 3.5c) so that acid-anhydride exchange can occur between chains/cylinders.



**Figure 3.6. Reprocessability of Acid-Anhydride CANs.** **a**, Photographed films of (3×) thermo-mechanically reprocessed G3 CAN tensile scraps. **b**, Stress-strain curves (5 mm/min, ~23 °C) of virgin and reprocessed PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> films. **c**, FTIR spectral overlays for virgin and reprocessed PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> films.

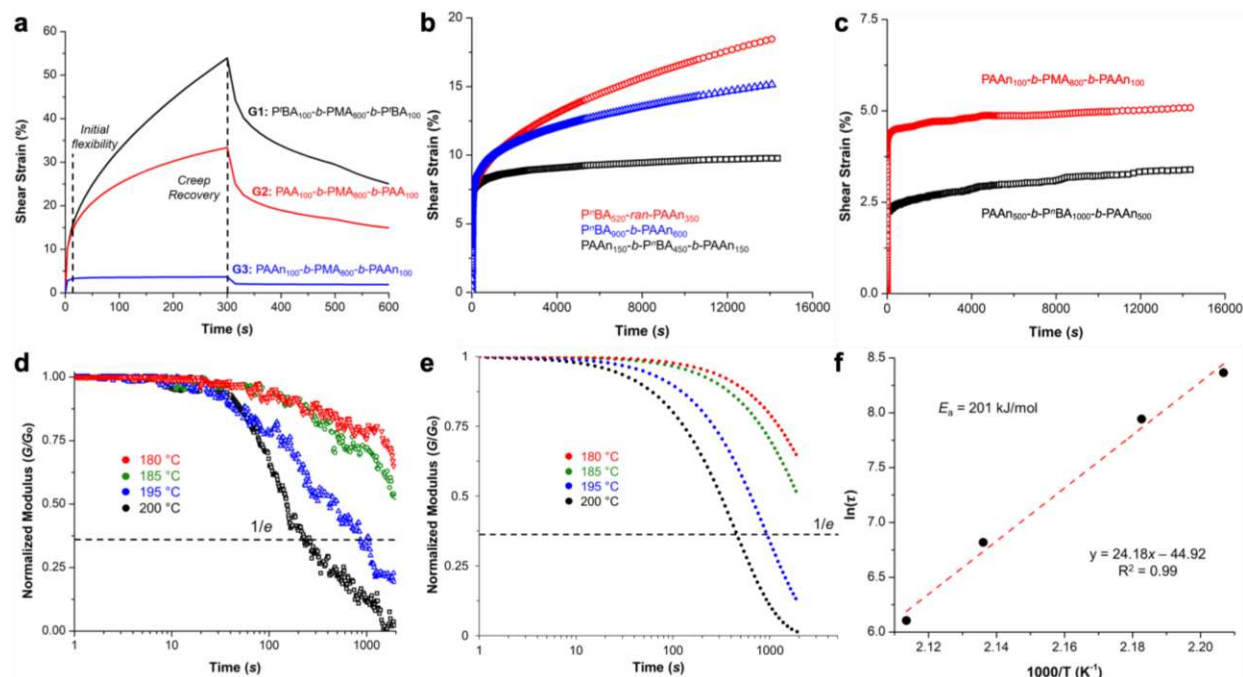
### 3.3.6 Rheological Properties of G3 BCP CANs.

To further probe the recovery nature of the current BCP-based CANs, rheology was employed to observe the material behavior under high-temperature, bulk shearing conditions. We reasoned that, since the G3 inter-linked network architecture requires the unique, cooperative thermal-compression conditions to achieve productive exchange, the tri-BCPs would not be suitable for investigating either prolonged creep or stress relaxation, and thus the acid-anhydride exchange mechanism activation energy. As a result, we utilized non-sequencing LPP to synthesize a random copolymer (RCP), P<sup>n</sup>BA<sub>520</sub>-*ran*-P<sup>n</sup>BA<sub>350</sub> (3:2 for comparison to 1:3:1 tri-BCP,  $M_n = 112$  kDa,  $D = 1.02$ , Figures B7, B13, B20, B29, and B37), which would be unable to assemble into discrete, inter-crosslinked nanostructures and thus experience macro-scale deformation by dynamic bond exchange without thermal-compression events. The RCP, upon advancing to its G3 CAN following the same methods, exhibited excellent reprocessability and full mechanical recovery within 30 minutes of reprocessing, as opposed to the typical 24 h of thermal-compression (Figure B61, Table B8). In absence of the discretely inter-linked exchange domains, the delocalized G3 dynamic crosslinks experience the typical *thermochemical* CAN tradeoff: facile reprocessing, but significantly amplified creep. We explore and establish the *thermomechanical*-

exclusive inter-domain exchange mechanism through creep, frequency sweep, and stress-relaxation experiments, discussed one-by-one below.

Bulk creep/resistance experiments were performed on the acid-anhydride CANs to investigate material integrity over prolonged stress. An initial investigation on evolution of creep displacement (5 kPa, 100 °C for G1-G2 BCPs, 150 °C for G3 BCP), modeled by the PMA-containing tri-BCP set, highlights a significant increase in creep resistance upon advancing G1 to G2 (by 22 %) and G2 to G3 (by 29 %) as a direct result of the respective hydrogen-bonding and crosslinking-network self-reinforcement (Figure 3.7a). Following an initial strain increase accounted for by the material's inherent flexibility, G3 BCP PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub> showed negligible shear creep (< 0.3 %) at 150 °C, whereas the uncrosslinked G1 and G2 homologs exhibited pronounced creep even at a lower temperature 100 °C. Prolonged creep experiments were performed on each G3 CAN over a 4 h period at an elevated temperature of 200 °C (5 kPa), revealing high-performance creep resistance by all G3 tri-BCPs (Figure B55). Specifically, all tri-BCPs exhibited a negligible creep rate between  $2.5\text{--}4.1 \times 10^{-5}$  % shear strain per second and low creep values (< 2 % shear strain over 4 h) excluding the initial spike in strain via intrinsic material flexibility (Figures 3.7a-c, 3.5c). As expected, and in support of our proposed morphology-regulated productive-exchange mechanism, the G3 RCP exhibited noticeably higher creep deformation (11.8 % vs. 1.1 %) and deformation rates ( $5.9 \times 10^{-4}$  vs  $3.4 \times 10^{-5}$  % shear strain per second) over the 4 h stress event compared to its tri-BCP compositional analog (Figure 3.7b). To provide further support for the specific ABA triblock architecture functionality, the authors prepared a compositionally equivalent (3:2, P<sup>n</sup>BA<sub>900</sub>-*b*-P<sup>n</sup>BA<sub>600</sub>,  $M_n = 2.99 \times 10^5$  g mol<sup>-1</sup>,  $\bar{D} = 1.08$ ; Figures B8, B14, B21, and B30) AB di-BCP by CSC-LPP which conceivably should be unable to form an *inter-domain crosslinked* network when crosslinked and, thus, experience deformation in

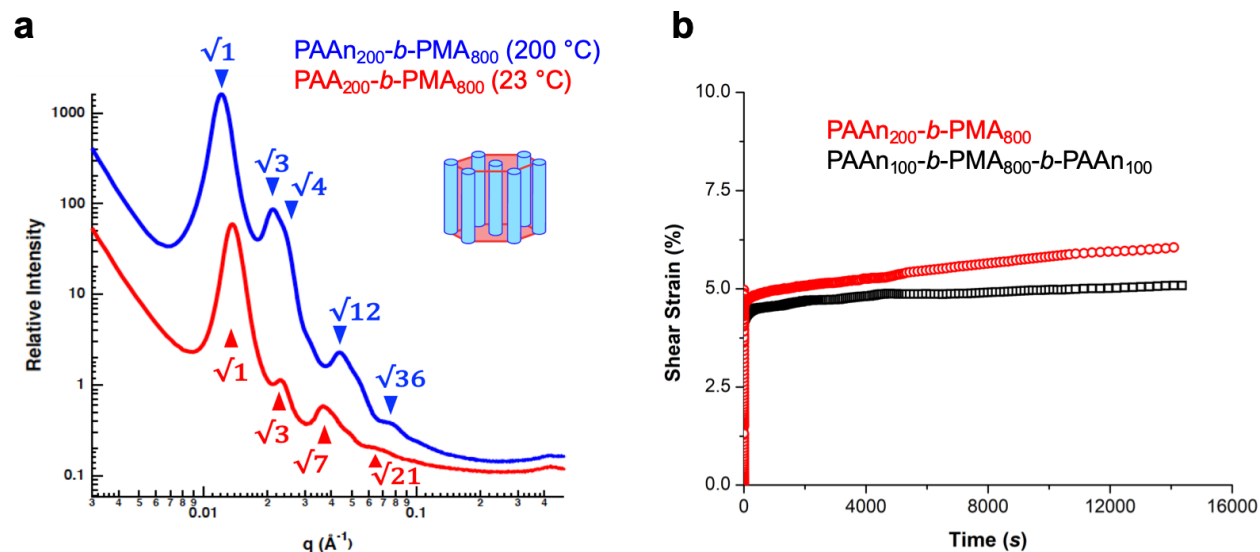
the absence of compression. In agreement, the G3  $P^nBA_{900}$ -*b*- $PAAn_{600}$  di-BCP exhibited pronounced creep (5.5 %) over the 4 h experiment when compared to each of the tri-BCPs, including a noticeably larger creep deformation rate of  $2.5 \times 10^{-4}$  % strain per second (Figure 3.7b,c).



**Figure 3.7. Rheology of G3 CANs.** **a**, Creep experiments (5 kPa, 100 °C for G1 and G2 BCPs, 150 °C for G3 network BCP). **b**, Creep comparison of G3 3:2  $P^nBA/P^rBA$  random, di-BCP, and tri-BCP architectures (4 h, 200 °C, 5 kPa). **c**, Additional G3 tri-BCP creep resistance experiments (4 h, 200 °C, 5 kPa). **d**, Normalized-modulus stress-relaxation curves for  $P^nBA_{520}$ -ran- $PAAn_{350}$  (1 s rise time, 0.3 % shear strain). **e**, Fitted stress-relaxation curves of  $P^nBA_{520}$ -ran- $PAAn_{350}$  used for extrapolating/ deriving the characteristic relaxation values  $\tau$  at  $1/e$  normalized modulus. **f**, Arrhenius relationship plot for the  $E_a$  of the acid-anhydride exchange mechanism.

To directly isolate our unique ABA network as the key component responsible for creep suppression, we prepared another compositionally equivalent PMA-containing AB di-BCP (2:8,  $P^rBA_{200}$ -*b*- $PMA_{800}$ ,  $M_n = 3.86 \times 10^5$  g mol<sup>-1</sup>,  $\bar{D} = 1.14$ ; Figures B9, B15, B22, and B31), which exhibits strong self-assembly at the G2 and G3 stages to HPC nanostructures with *d*-spacing of 47 – 52 nm (Figure 3.8a). In a creep comparison between G3 di-BCP  $PAAn_{200}$ -*b*- $PMA_{800}$  and the tri-BCP analogue ( $PAAn_{100}$ -*b*- $PMA_{800}$ -*b*- $PAAn_{100}$ ), the G3 di-BCP exhibited higher creep (1.1 % vs.

0.6 % shear strain) and creep deformation rates ( $8.0 \times 10^5$  % vs.  $3.2 \times 10^5$  % strain per second) (Figure 3.8b), which is consistent with the P<sup>n</sup>BA-based BCPs creep results and our creep suppression by inter-domain exchange restriction hypothesis.



**Figure 3.8. HPC G3 Di- and Tri-BCP Comparison.** **a**, SAXS profiles of PMA-containing di-BCP films in G2 PAA (red, measured at 23 °C) and G3 crosslinked PAA<sub>n</sub> (blue, measured at 200 °C) HPCs. **b**, Creep comparison of G3 HPC 2:8 PMA/PAA<sub>n</sub> di-BCP and tri-BCP architectures (4 h, 200 °C, 5 kPa).

To further probe the acid-anhydride exchange mechanism, high-temperature frequency sweeps were performed on each G3 CAN at 170, 180, 190, and 200 °C (0.1 to 10 Hz, 0.3 % strain in compliance with linear viscoelasticity probed by initial strain sweeps, Figure B53). All G3 tri-BCPs behaved like characteristic thermosets with constant storage modulus ( $\Delta G' \approx 0$ ) at low frequencies and increased  $G'$  at higher frequencies, while the RCP exhibited an initial increase in modulus at low frequency that was exaggerated with increasing temperature (Figure B54). While the G3 materials establish a near-consistent  $G'$  with increasing frequency, indicative of constant crosslinking density under an associative exchange mechanism (Figure 3.1c), the slight drop in  $G'$  with increasing temperature also supports paralleling dissociative exchange via intra-molecular

anhydride formation (Figure 3.1d) which would ultimately decrease G3 CAN crosslinking density (Figure B54).<sup>46</sup>

Lastly, we subjected the G3 BCP PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> and RCP P<sup>n</sup>BA<sub>520</sub>-*ran*-PAA<sub>n350</sub> analogs to a series of stress-relaxation experiments to derive the activation energy ( $E_a$ ) for the transition to a flow-topology by the exchange mechanism. Once again, in accordance with the lack of compression input available during rheological experiments, and thus no reconfigurability, we did not observe a trend in reduced modulus for the tri-BCP within the experiment time (Figure B58). On the other hand, the compositional analog RCP without compression requirements exhibited characteristic relaxation of induced stress at longer time scales ( $t > 10$ - $100$  s) for temperatures 180, 185, 195, and 200 °C (Figure 3.7d). The normalized modulus for each temperature was fitted to an exponential decay curve and the value  $\tau$  (time at which  $G'/G'_0 = 1/e$ ) was extrapolated under the appropriate assumption (all  $R^2 > 0.9$ ) of a single Maxwell element (Figure 3.7d,e, Figure B56).<sup>73</sup> The obtained Arrhenius plot highlights a linear relationship where the slope of the linear-fit was used to calculate a high  $E_a$  of 201 kJ/mol (48.0 kcal/mol, Figures 3.7f, B57).

### 3.4 Conclusion

Herein, we developed not only a novel class of reprocessable thermosets based on nanostructured, dynamically crosslinked all-acrylic tri-BCP TPEs, but also a new thermomechanical activation mechanism responsible for the observed reprocessability and orthogonal working/reprocessing conditions. Such materials hold potential to provide a more sustainable alternative to non-recyclable or non-reprocessable crosslinked materials. Although we focus herein on a few particular PAA-containing copolymers, we emphasize that virtually any PAA-containing polymer can be converted into similar CANs simply through heat induced

condensation. More importantly, through this self-preparation method we introduce a CAN system that is *independent of external privileged crosslinkers, exchange agents, and catalysts* typically necessary for dynamic bond exchange in reprocessable thermosets.

From a perspective of advanced polymer synthesis methods, our CSC-LPP synthesis of these ABA tri-BCPs is noteworthy in its own right as it is currently the only way to generate such a high MW polymer with such high precision, control, and timely manner at RT. The unique two-step propagation mechanism of LPP that involves bimolecular conjugate addition of a Lewis acid-stabilized enolate chain-end to a Lewis acid-activated monomer provides compounded thermodynamic  $K_{eq}$  and kinetic  $k_p$  differentiation, allowing for precise sequence control over the polymerization of one-pot mixtures of comonomers.<sup>65</sup> Well-defined all acrylic tri-BCPs are challenging to synthesize even at low temperatures and small scale, due to the uncontrollable reactivity, competing termination by facile acid-catalyzed de-*tert*-butylation of *t*BA, and predisposition to the Claisen-type termination of these monomers.<sup>74,75</sup> *The CSC-LPP method facilitates the synthesis of these well-defined tri-BCPs at ambient temperature and relatively large scales (35-70 g products) in a one-pot fashion < 5 mins.*

From a mechanistic point of view, our proposed acid/anhydride inter/intra-chain associative/dissociative dynamic exchange, under the conditions by which we reprocess polymers, was supported by several lines of evidence, including the results obtained from the small molecule model reactions and rheological frequency sweep experiments. Similarly, by rheological testing, we further probed the exchange mechanism by stress-relaxation on an analogue random copolymer to access the standard CAN-type behavior. From these experiments we were able to derive a rather high (composite) activation energy for the acid/anhydride exchange of 201 kJ/mol, which can be attributed to the low nucleophilic character of carboxylic acids.



From a materials performance and reprocessability perspective, crosslinked G3 BCPs exhibit impressive mechanical performance with high modulus, toughness, and creep resistance, as well as repeated reprocessability while maintaining mechanical integrity. The HPC assembly of the materials is credited for modulus and strength increases in going from G2 to the G3 phase, and contributions from the soft acrylic comonomers help give the materials flexibility to avoid the brittleness of many high modulus materials. Our final point is the effect of the BCP self-assembly and the networking effect of the ABA tri-BCP architecture. Crucial to this point is the comparison of the RCP and the AB di-BCPs to the ABA tri-BCP compositional analogues. In the case of the RCP, any associative exchange might be productive in the mending or permanent reshaping of the overall structure since there is no domain spacing to compartmentalize exchange points. Similarly, although exchange points may be compartmentalized in the di-BCP, there is no inter-linked network to restrict productive reprocessing. In stark contrast, the tri-BCP has exchange points that are compartmentalized and thus not in contact with exchange points in other domains. This contrast can be observed in Figure 7b, wherein the RCP showed a  $\sim \times 10$  increase and the di-BCP showed a  $\sim \times 5$  increase in creep over a 4 h shear stress period. This hypothesis is further supported by the direct comparison of G3 di- and tri-BCPs in Figure 8b, where the di-BCP exhibited a roughly  $\sim \times 2$  increase in creep deformation despite having the similarly self-assembled HPC nanostructure. When we consider time-dependent deformation of a domain-separated material, we hypothesize that exchange events occurring within a domain contribute negligibly to the overall creep. Therefore, mechanical force is required to put exchanging domains in contact with each other. This inter-domain exchange requirement provides a means to minimize creep during operating conditions while reserving the option to activate creep with collaborative thermomechanical reprocessing conditions.

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## Chapter 4

### Architecturally and Topologically Sophisticated (Meth)Acrylic Multiblock Copolymers: Rapid Scalable Syntheses and Meticulous Differentiations.

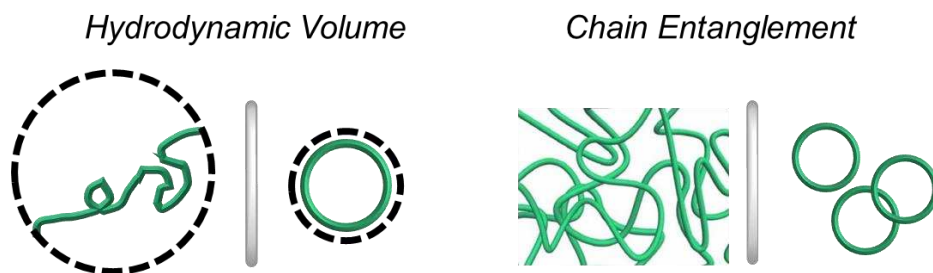
#### 4.1 Synopsis.

Structural deviations between cyclic and linear polymers, through a lack of chain-end groups and the constrained ring-architecture, has rapidly cultivated interest in convenient cyclic polymer syntheses for pursuing behavioral understanding and material application. Moreso, cyclic BCPs are emerging as fascinating materials with unique self-assembly and micro-domain forming properties, though limited in synthetic reach to traditional A-B and A-B-C block sequencing due to severely limited or demanding synthetic techniques. In this report, we leverage our recent compounded-sequence control Lewis pair polymerization technology to conveniently obtain A-B-A-B cyclic multi-BCPs from (meth)acrylic MMA and AIA, the first of its kind, in a one-pot, two-step procedure without the need for sequential addition of monomers, highly diluted conditions, post-synthetic modifications, or post-synthetic ring-closure steps. Our CSC-LPP methodology is able to reach quantitative monomer conversion in < 15 min while yielding polymer up to, but not limited to, 40 g scales. By exploiting the kinetics in a routine A-B di-BCP synthesis, block symmetry of 25/25.5/25/24.5 was realized highlighting incredible synthetic precision. We analyze the unique cyclic MBCP behavior in solution (hydrodynamic volume, viscosity, refractive indices), bulk (thermal), and film (thermomechanical, rheometric, self-assembly) phases while drawing comparisons to a linear A-B-A-B MBCP prepared under similar conditions and with nearly identical MW and block symmetry. We use several analytical methods to differentiate between first) linear and cyclic topology and second) the di-BCP and tetra-BCP architecture, while the comonomer compositions are held constant. Finally, the allylic functional handle was subjected

to thiol-ene click chemistry to exaggerate self-assembly while showcasing the facile post-synthetic modification that may be utilized for producing semi-crystalline, thermoset, ionized, or covalent adaptable network materials with complex cyclic BCP parent polymers.

## 4.2 Introduction.

Cyclic polymers are fundamentally intriguing materials first observed in natural biomacromolecules which contrast their linear counterparts through lack of chain-end functionality, loss of conformational freedom, and reduced chain-entanglement factors. As a result, cyclic polymers are now well understood to exhibit altered macromolecular behavior in solution, film, and bulk setting.<sup>1-6</sup> In solution, cyclic polymers achieve lower viscosity ( $\eta$ ), smaller hydrodynamic volume ( $V_h$ ) and radius of gyration ( $R_g$ ), lower refractive index ( $dn/dc$ ), lower density ( $\rho$ ), and higher elution times when subjected to gel permeation chromatography (GPC) analysis (Figure 4.1). Impacts on thermal properties include higher glass transition ( $T_g$ ) and decomposition ( $T_d$ ) temperatures as well as enhanced rate of crystallization, which coupled with lower melt viscosities than linear analogues by bulk rheology measurements, provide complimentary valuable attributes for material processing and performance. Thus, control over polymer topology presents itself as a modern synthetic handle for fine-tuning material performance qualities. And while not yet achieved, cyclic polymers may achieve practical roles in commodity and biomedical applications upon further behavioral investigation and synthetic command.

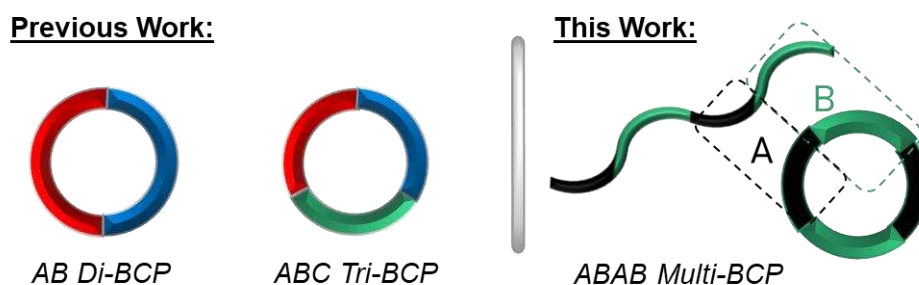


**Figure 4.1.** Intrinsic property differences depicted between linear and cyclic polymer topologies.

Expansion of macromolecular complexity to both cyclic and linear multi-block copolymers (MBCP, those beyond traditional A-B and A-B-C block architectures) has garnered especially high interest for accessing highly functional materials with promising potential in nanotechnology<sup>7,8</sup> and biomedical applications.<sup>9</sup> Increasing the number of blocks along a polymer chain results in a higher degree of inter-domain crossings and chain entanglement anchoring points, thus reducing interfacial tensions and reinforced durability and material performance.<sup>10,11</sup> For example, recently reported linear A-B-A-B tetra-BCPs of polyethylene (PE) and *it*-polypropylene (*i*PP) revealed a dramatic increase in (otherwise immiscible) consumer PE and *it*-PP blend compatibility and mechanical performance over those treated with an A-B di-BCP.<sup>12,13</sup> The conclusions drawn from this work encompass both performance and sustainability, while enticing further general exploration of MBCP materials of which are vastly lacking in behavioral understanding compared to traditional di- and tri-BCPs. Also worth noting, living Lewis pair polymerization was recently utilized with repeated sequential addition of four acrylic monomers, individually, to achieve a record-high linear tripentaconta-BCP ( $n = 53$ ) with moderate  $\bar{D}$  control.<sup>14</sup> To the best of our knowledge, however, there are no reports regarding higher-complexity cyclic MBCPs or their application potentials due to exponentially demanding cyclization protocols, chain-extension requirements during synthesis, monomer incompatibilities, and unintuitive means of differentiating or isolating otherwise identical topology analogues.<sup>15</sup>

Currently, cyclic BCPs are limited to the A-B and A-B-C architecture due to demanding requirements in synthetic approaches, of which few strategies have been reported (Figure 2).<sup>16-24</sup> When obtained, however, cyclic BCPs have revealed an astounding wealth of opportunity in self-assembly behavior and micro-domain formation distinguished from well-studied linear BCPs by

transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS).<sup>25,26</sup> Specifically, well-defined linear and cyclic triblock terpolymer analogues polyisoprene-*b*-polystyrene-*b*-poly(2-vinylpyridine) carefully prepared under low-temperature anionic polymerization, high vacuum, and demanding multi-step post-synthetic functionalization for bimolecular Glaser coupling have been subjected to thorough investigation by Hadjichristidis *et al*, revealing a shift from hexagonally close-packed core-shell cylinders to a rather unique worm-like morphology, respectively.<sup>27</sup> In a separate study, the authors report leveraging cyclic polybutadiene-*b*-polystyrene-*b*-polymethyl methacrylate triblock terpolymer self-assembly for ion etching silica rings as insight to the role of cyclic BCPs for lithographic applications.<sup>28</sup> Further efforts in uncovering crucial, impactful applications in consumer and biomedical fields with cyclic block copolymers will require simple synthetic protocol coupled with high precision and purity.



**Figure 4.2.** Previous work synthesizing A-B and A-B-C cyclic BCPs compared with this work on the synthesis of unique linear and cyclic A-B-A-B MBCPs.

Most recently, our group reported compounded-sequence control Lewis pair polymerization (CSC-LPP) operating under discrete alkyl-sorbate ion-pair initiator species as a convenient strategy to copolymerize mixed-feed homologous polar vinyl monomers to well-defined cyclic di-BCPs in one-pot and one-step, thus eliminating the need for sequential-addition methodology or post-synthetic ring-closure “click” reactions.<sup>29,30</sup> The zeroth-order monomer dependency polymerization kinetics, in compliment to sequential control over even isomeric

monomer mixtures, allows for both spatial and temporal predictability during cyclization to yield highly precise, discrete cyclic BCPs absent of linear contaminants and premature ring-closure events without unfavorable high dilution requirements. In our original cyclic BCP work, high preferential coordination ( $K_{eq}$ ) of encumbered Lewis acid methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) to *n*-butyl acrylate (*n*BA) over methyl methacrylate (MMA) was exploited to remove MMA from the propagation cycle. This effect, coupled with a heavily biased rate of propagation ( $k_p$ ) towards *n*BA, allowed for rapid consumption of “favorable” *n*BA prior to “unfavorable” MMA with infinitesimal margin for misincorporation. We reasoned that we could exploit both kinetic bias and tamed cyclization (in the presence of free monomer) by adding a *second* dose of favorable monomer (A) during some pre-designated consumption of the unfavorable monomer (B), thus immediately shifting coordination ( $K_{eq}$ ) and propagation ( $k_p$ ) back to A to obtain a cyclic A-B-A-B tetra-BCP upon full conversion of both A and B (Figure 4.2). The time-point for addition can be selected with high precision by first preparing and tracking architectural parent di-BCP polymerization kinetics. Such a system would achieve a cyclic MBCP in a remarkably convenient and timely one-pot, two-step fashion.

We now here discuss the results of this cyclic MBCP synthetic strategy while highlighting several behavioral discrepancies between linear and cyclic topological analogues of both the tetra-BCP architecture and the di-BCP parents as a means to distinguish and confirm future material purity and topology. We will individually characterize these materials, of which are nearly identical in  $M_n$  ( $\sim 160$  kg mol<sup>-1</sup>), block DP (A and B =  $\sim 500$  total each), and architectural symmetry, in 2 ways: 1) between linear v. cyclic topology analogues and 2) between di- vs. tetra-BCP compositional analogues. The behavioral contrasting between these constitutionally isomeric BCPs is probed meticulously by solution (viscosity, hydrodynamic volume, refractive index, and

elution time) measurements, and bulk thermal ( $T_g$ , and  $T_d$ ), thermomechanical (dynamic moduli,  $E'$ ) and rheological (bulk viscosity) experiments (linear vs. cyclic). Materials brought to the film stage were visited with SAXS experiments for self-assembly and domain sizing as a key strategy to discriminate BCPs of similar composition yet separate architectures (di-BCP vs. tetra-BCP). We emphasize that these polymer syntheses were conveniently carried out within 15 minutes and were scaled, though not limited by any means, to an impressive ~40 g (quant.) yield in each trial.

## **4.3 Results and Discussion.**

### **4.3.1 Linear and Cyclic MBCP Syntheses, Kinetics, and Spectroscopic Characterization.**

Once more, our synthetic protocol relied and expanded upon notable advancements in the one-pot sequential copolymerization of mixed (meth)acrylic monomer feeds, namely CSC-LPP.<sup>31</sup> Recently, our CSC-LPP technology was further developed to access cyclic A-B di-block copolymers in a one-step and one-pot polymerization, for which the underlying mechanism of the back-biting cyclization on the alkyl sorbate initiator in the absence of free monomer (or full monomer conversion) was revealed shortly thereafter. With this in mind, we envisioned the capacity for CSC-LPP to generate increasingly sophisticated linear and cyclic MBCPs under one-pot and minimal monomer additions while retaining well-defined (high  $M_n$ , low  $\bar{D}$ ) polymer character. The preference to polymerize one “fast” monomer over an adjacent “slow” monomer could be exploited via secondary addition of “fast” monomer to interrupt and separate/split the growing second block with that of a now designated third block (Figure 4.4).

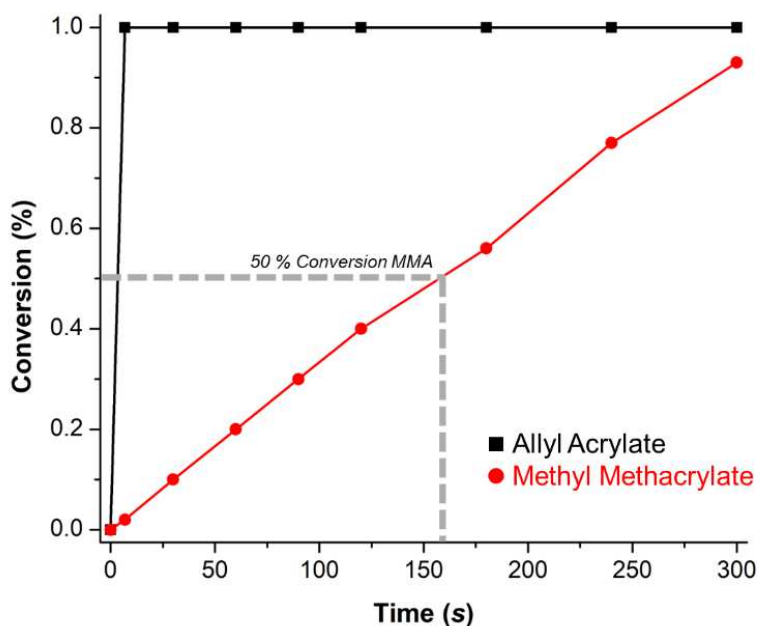
More specifically, we designed two convergent polymerization methods to achieve two compositionally identical cyclic and linear MBCP analogues requiring only a change in the initiating species to designate product topology. In accordance with prior reports, we selected



Lewis base tricyclohexylphosphine (PCy<sub>3</sub>) as the linear polymer initiator and ethyl sorbate/MAD/I<sup>t</sup>Bu-NHC (1:1:1) ion pair **1** as the cyclic polymer initiator. Monomers allyl acrylate (AIA) and methyl methacrylate (MMA) were selected for mixed-feed sequence-controlled copolymerization due to their expected high differentiation by  $K_{eq}$  (for [M1]/[M2]/[LA] coordination equilibrium) and propagation rate ( $k_p$ ). This hypothesis was supported by utilizing high-resolution variable-temperature <sup>1</sup>H-NMR to track the [AIA]/[MMA]/[MAD] equilibrium, where measured at -20 °C, MMA-MAD coordination could not be observed, thus leading us to pronounce the  $K_{eq} > 1000$  for MAD preferential coordination to AIA over MMA (Figure C1). Additionally, the  $k_p$  for AIA was astoundingly fast at  $k_{p,observed} = 8.14 \times 10^4 \text{ [M]} \cdot \text{s}^{-1} \cdot [\text{LA}]_t^{-1} \cdot [\text{LB}]_0^{-1}$ , which is much higher than recently reported  $k_{p,observed} = 3.96 \times 10^2 \text{ [M]} \cdot \text{s}^{-1} \cdot [\text{LA}]_t^{-1} \cdot [\text{LB}]_0^{-1}$  for the LPP of MMA under nearly identical conditions (Figure C2). The heavily biased and compounding kinetic values signal high sequencing control for MAD-catalyzed LPP in mixed-feed, approving advancement into polymerization trials (Figure 4.3). While this sequencing of monomers is highly effective between acrylic and methacrylic homologues, the challenge of sequencing between acrylic-acrylic and methacrylic-methacrylic comonomers adds a layer of complexity and remains an ongoing pursuit to prepare even more diverse ABCD-type MBCPs in ideal one-pot, one-step procedure.

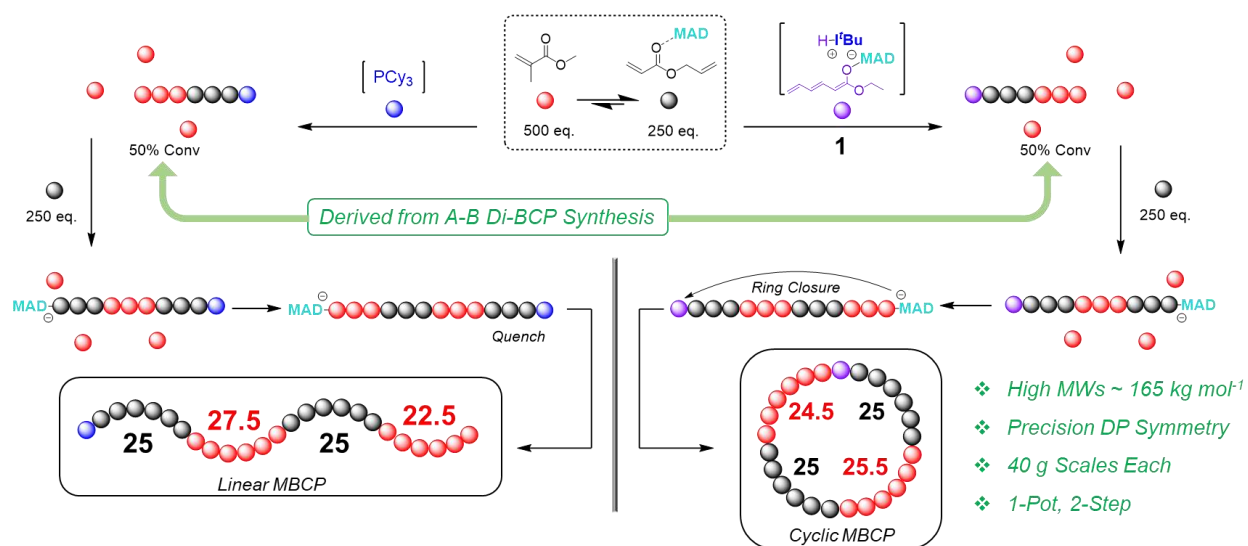
To highlight our ability to exert highly precise block symmetry upon targeted polymers while obtaining high molecular weight materials, we endeavored to achieve linear and cyclic tetra-BCPs near DP = 250/250/250/250 for blocks A1/B1/A2/B2. For this to occur in the fewest possible addition steps, addition of A2 monomer should occur at 50 % conversion of B1, at which point the  $K_{eq}$  will immediately shift to promote polymerization of A2 over B2 (Figure 4.4). Two di-BCPs were synthesized prior to the tetra-BCPs to both model kinetics while simultaneously preparing well-studied di-BCPs for comparing our results and testing methods down the line. The model di-

BCP syntheses were designated at 500/500/10/1, comprised of 22.0 mL of AIA and 18.1 mL of MMA, to closely model *in-situ* conditions and carried out in one-pot where the conversion of the MMA 500 units was modestly slow enough to be monitored by a series of kinetic time-points (Figure C4). We found that the 50 % conversion point of MMA, modeled by the linear di-BCP occurs at 156 s, where AIA was quantitatively consumed before the first post-initiation time-point ( $< 7$  s) (Figure 4.3). Upon full monomer conversion, signaled by characteristic change from a yellow to clear solution, the linear di-BCP was immediately quenched with acidic methanol while the cyclic di-BCP was first left stirring for 24 h per cyclization requirements before similar quenching steps, yielding our two control polymers *c*PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> and *l*PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>. It is worth mentioning that LA MAD coordination between monomers offers a visual handle: coordination to AIA in solution generates a deeper yellow tint, while coordination to MMA generates a lighter yellow tint. Additionally, cyclized solution products exhibit a rose-gold appearance prior to quenching (vs. yellow for linear analogues) as another visual handle for successful cyclization (Figure C3).



**Figure 4.3.** Kinetic conversion vs. time plot tracking the one-pot sequenced copolymerization of AIA<sub>500</sub> and MMA<sub>500</sub>.

The di-BCP parent polymers yielded mid-addition points for our main synthetic endeavor of two analogous linear and cyclic (tetra-) MBCPs. In light of our aforementioned symmetry goal, the initial monomer pool was comprised of 0.5:1 AIA:MMA (250 eq, 11.0 mL:500 eq, 18.1 mL), again expecting the first batch of AIA to have quantitatively consumed before the propagation of MMA occurs (Figure 4.4). Upon injection of the respective initiating species to each concurrently prepared linear and cyclic synthesis, a timer was monitored for the second 0.5 eq (DP 250, 11.0 mL) equivalent of AIA, which was rapidly injected to the stirring mixture causing a noticeable change to a deeper yellow tint for a very short period of time, and then back to light yellow signaling rapid consumption of AIA and subsequent re-propagation of MMA.



**Figure 4.4.** One-pot, two-step sequence-control Lewis pair polymerization of homologous (meth)acrylic monomers to discrete and near-symmetric linear (left) and cyclic (right) ABAB MBCP. (DP = 1000; 500 A total, 500 B total).

At the exact point of AIA (block A2) injection, an aliquot was taken from each polymerization to monitor the exact conversion of the MMA as to assign block compositions. The

resulting aliquot from the cyclic MBCP synthesis revealed extremely precise kinetics as the 2nd batch of AIA was injected at 51 % MMA conversion, yielding a  $c\text{PAIA}_{250}\text{-}b\text{-PMMA}_{255}\text{-}b\text{-PAIA}_{250}\text{-}b\text{-PMMA}_{245}$  with strikingly high block symmetry across the ring upon full monomer conversion (Figure 4.4, Figure C5). The aliquot from the linear MBCP synthesis showed nearly high precision, with the addition of AIA at 55 % MMA conversion to a total  $l\text{PAIA}_{250}\text{-}b\text{-PMMA}_{275}\text{-}b\text{-PAIA}_{250}\text{-}b\text{-PMMA}_{225}$  once at full monomer conversion (Figure 4.4, Figure C6). Once the four species were purified by precipitation and allowed to dry, high-resolution  $^{13}\text{C}$  NMRs were recorded to verify monomer sequencing against random copolymerization. In each case, carbonyl regions revealed well-defined peaks characteristic of unperturbed block sequences of both MMA and AIA, and had sequencing been unsuccessful we would observe noticeable broadness (Figures C11-C14). Additional  $^1\text{H}$  NMRs highlight identical spectra between all products, which is expected for block copolymers of similar monomer compositions (Figures C7-C10).

While these are both not *exactly* equivalent to our 25/25/25/25 model, we emphasize the 1-pot, 2-step process in generating such highly complex polymer architectures unattainable through other reported catalytic approaches. The slight error margins are postulated to have resulted from deviations between the precise amount of LA MAD which is significant in dictating polymerization kinetics at zeroth-order in monomer and first-order in LA. Additionally, the di-BCP synthesis and that of the tetra-BCP, while mirrored in concentration and scale, do not account for the missing 0.5 eq. of AIA in the initial monomer pool which may slow rate of MMA propagation due to increased chain length at higher molecular weight and conversion.

#### **4.3.2.0 Differentiating Between Linear and Cyclic Topology.**

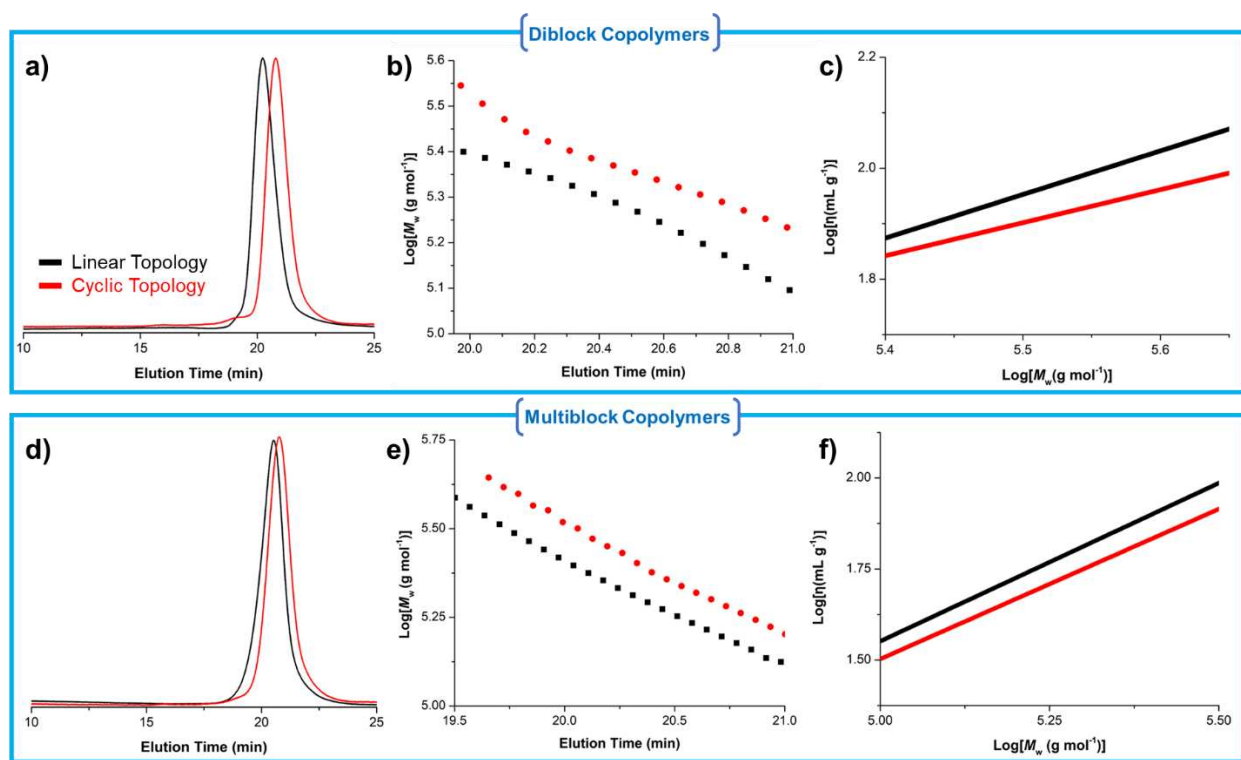
##### **4.3.2.1 Absolute Molecular Weight Measurements and Refractive Indices.**

Once again, the lack of chain ends presented by a cyclic polymer architecture has dramatic implications for solution behavior in contrast to linear counterparts. The degree of chain entanglement for a linear polymer is heavily reduced as intermolecular forces causing entanglement are mediated by solvent, allowing individual chains to undergo uncoiling. On the other hand, cyclic polymers remain confined to the smaller ring architecture regardless of solution or bulk, unable to extend the same physical distance even at the same molecular weight. The resulting differences in hydrodynamic volume afford several advantageous handles for simple differentiation. Here we present several lines of evidence by GPC for near-identical molecular weight complex MBCPs both supporting the sophisticated syntheses and highlighting behavioral differences at such intricate architectures.

First, we aimed to obtain the absolute molecular weights of each sample to ensure we would be making appropriate comparisons across nearly-identical MW species. Refractive indices ( $dn/dc$ ) were thus measured in THF for each of the block copolymers. The linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub> has a higher  $dn/dc$  of 0.0801 mL g<sup>-1</sup> than the cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>250</sub> which is 0.0735 mL g<sup>-1</sup> (Figures C15-C16). This trend for  $dn/dc$  was repeated for the di-BCPs, where the linear PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub> was 0.0783 mL g<sup>-1</sup> and the cyclic analogue was 0.0764 mL g<sup>-1</sup> (Figures C17-C18). These values also serve as handles to support the differences in topology as it is well-reported in other literature examples that cyclic polymers will exhibit a lower refractive index than linear analogues, assumably due again to the smaller size in solution. With these values, we were able to obtain absolute MW values for the linear and cyclic MBCPs as 165 kg mol<sup>-1</sup> ( $\bar{D}$  = 1.25) and 168 kg mol<sup>-1</sup> ( $\bar{D}$  = 1.18) (Figures C19-C20), respectively, and the linear and cyclic di-BCPs as 165 kg mol<sup>-1</sup> ( $\bar{D}$  = 1.21) and 161 kg mol<sup>-1</sup> ( $\bar{D}$  = 1.12), respectively (Figure 4.5a,d; Figures C21-C22).

#### 4.3.2.2 Hydrodynamic Volume Correlations and Solution Viscosity.

It is well-understood that cyclic polymers have a smaller hydrodynamic volume to that of linear polymers.<sup>32,33</sup> When passed through a GPC column, cyclic polymers must navigate additional porous obstacles in contrast to linear polymers which are able to swiftly avoid smaller pore sizes. Thus, cyclic polymers will elute at a higher time. When our MBCPs were examined in this context of fundamental concept, our results agreed: the linear MBCP eluted at 20.4 min and the cyclic MBCP eluted at 20.8 min despite the cyclic tetra-BCP having a slightly higher MW. This is again repeated in the case of the di-BCP samples, where the linear eluted at 20.1 min and the cyclic analogue eluted behind at 20.7 min (Figure 4.5a,d; Figures C19-C22).



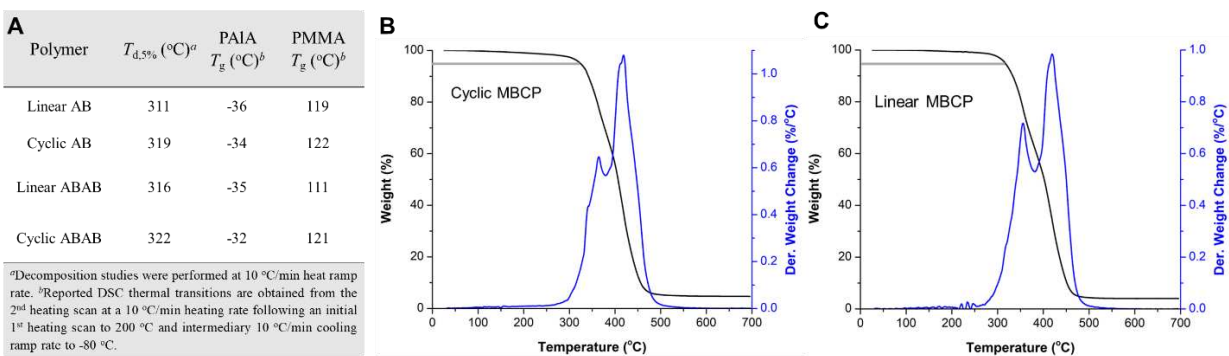
**Figure 4.5. Solution Differentiation of Linear and Cyclic Copolymers.** a) GPC (dRI) traces, b) normalized elution time vs. molecular weight plots, and c) solution viscosity measurements for cyclic and linear diblock copolymers PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub>. d) GPC (dRI) traces, e) normalized elution time vs molecular weight plots, and f) solution viscosity measurements for cyclic tetrablock copolymer PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub> and linear tetrablock copolymer PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub>.

A closer evaluation of the hydrodynamic volume was carried out by recording precise MWs at each time point of elution along the GPC trace. As a cyclic architecture is capable of packing more mass into a smaller ring framework, it should be observed that at the exact same time points, eluted cyclic substrates will exhibit a higher molecular weight. In both the di-BCP and MBCP topology sets, when the molecular weight is logarithmically plotted against standardized elution time, the cyclic architecture has a higher MW, once more supporting the differences in architectural motifs (Figure 4.5b,e). This phenomenon occurs in compliment to the previous analysis on elution time: due to the ring constraint, elution time will be delayed and overlaid MW will inherently be larger.

Finally, we once more differentiate the topology of our complex MBCP products by examining the solution viscosity, which was simultaneously recorded by GPC viscometer. As linear polymers experience a higher degree of intermolecular interactions via friction and chain entanglement, albeit reduced in solution, the solution viscosity should be noticeably higher than cyclic counterparts, assuming a low degree of inter-penetrating catenane structures. When visiting this theory with our linear and cyclic topological isomers, we obtained additional supporting evidence for the structural differences between the two in that the viscosity of the linear MBCP was higher than that for the cyclic at a wide range of MWs (Figure 4.5c,f). The di-BCP samples similarly exhibited the same behavior, the cyclic di-BCP had a lower viscosity per MW compared to the linear di-BCP (Figure 4.5c,f). Overall, considering the exhibited differences in elution time, refractive indices, elution molecular weights, and solution viscosity, we find highly convergent supporting evidence for the differences in topology and affirmation for our convenient synthetic approach to constructing complex linear and cyclic MBCPs.

#### **4.3.2.3 Thermal Properties: Decomposition by TGA and Glass Transitions by DSC.**

We next focused on characterizing the differences in thermal behavior between the linear and cyclic tetrablock copolymers. The chain-end groups in linear polymers are becoming increasingly understood as initiation sites for radical fragmentation events that ignite or expediate further thermal decomposition.<sup>34,35</sup> These labile chain-end groups can be considered as defects in the repeat unit, which not only decrease the temperature for onset decomposition ( $T_{d,5\%}$ ), but contribute to higher complexity decomposition profiles typically observed as broader mass loss events during thermogravimetric analysis (TGA) controlled pyrolysis. Our cyclic polymers have no chain-end sites and structurally uniform (C-C) backbones, thus should demonstrate higher  $T_{d,5\%}$  values and narrowed mass-loss profiles. As there is no differentiation between the bonds comprising the polymer backbone, withholding slight electronics in pendant chain, decomposition will have increased non-selectivity contributing to rapid thermal chain scissions which would otherwise be extended through the lowered temperature required for breaking chain-end bonds. Essentially and theoretically, once enough temperature is applied to disrupt or break the cyclic polymer backbone, decomposition should occur with higher uniformity as the backbone environment is homologous. Worth mentioning, while this theory is well-supported in cyclic homopolymers, the trend has not been thoroughly explored in C-C backbone block copolymers where different pendant group dynamics may influence sequence of block decomposition.



**Figure 4.6.** A) Tabulated glass transition and decomposition temperatures for each BCP specimen by TGA and DSC. B) Recorded mass loss and derivative weight change with temperature ramp



for linear MBCP PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub>, C) and cyclic MBCP PAIA<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>245</sub>.

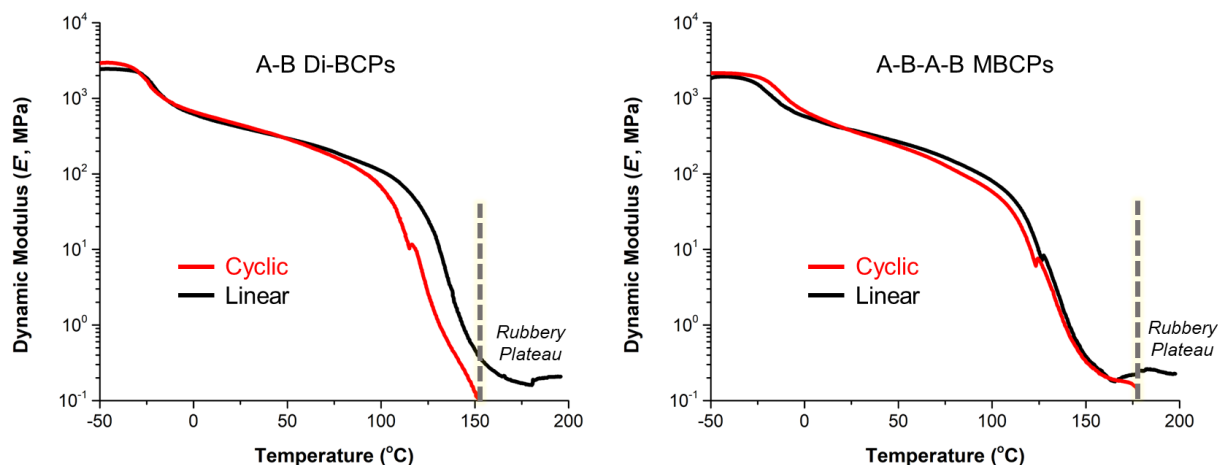
In agreement with the above set of principles, we observed increases in the decomposition temperature for our cyclic A-B and A-B-A-B di- and tetra-BCPs above to those of linear analogues. Specifically, onset decomposition for cyclic PAIA<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>245</sub> occurred at 322 °C, a modest increase to the 316 °C 5 % mass loss for linear PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub> (Figure 4.6a-c; Figures C27 and C29). These results parallel trends for cyclic and linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>, which incur onset decompositions at 319 °C and 311 °C, respectively (Figures C23 and C25). Another intriguing observation from the decomposition curves is the particular broadness or bi-modality presented in the A-B-A-B architecture samples, exaggerated for the linear topology (Figure 4.6b,c). While this may be credible to two distinct comonomers, we hypothesize that the thermally unstable allylic functionality, comprising half of the total polymer pendant groups, may be culprit in early radical formation sabotaging uniformity during pyrolysis.

We also turned to differential scanning calorimetry (DSC) to track thermal transitions in MBCPs upon heating and cooling events. As stated earlier, cyclic polymers typically exhibit increased glass transition temperatures to linear counterparts,<sup>36-38</sup> though this case is not universally supported and may be inversed with specific polymer structure. Nonetheless, our DSC results highlight consistently higher  $T_g$  transitions for cyclic topology in both the A and B block comonomer components. PAIA glass transitions were recorded at -34 °C and -32 °C for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> and PAIA<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>245</sub>, respectively, while the adjacent PMMA transitions were recorded at 122 °C and 121 °C, again respectively (Figures C24 and C26). In contrast, the linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> and PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub> revealed PAIA  $T_g$  values of -36 °C and -35 °C, and PMMA  $T_g$  values of 119 °C and 111

°C, respectively (Figures C28 and C30). These distinctions in temperature are not drastic but do have consistency across topology and most literature present.

#### 4.3.2.4 Thermomechanical Performance by DTMA.

We also performed dynamic thermomechanical analysis tests to probe the temperature-dependent material properties between the cyclic and linear topologies as further differentiating evidence. Previous literature examples have reported that cyclic polymers will exhibit a higher dynamic modulus ( $E'$ , storage modulus) than that of linear analogues.<sup>39</sup> Accordingly, we performed temperature-ramp frequency sweeps (-50 to 200 °C, 5 °C/min, 1 Hz, 0.3 %) for each material and recorded the  $E'_{\max}$  response (Table C1). In the di-BCP set, the linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> achieved  $E'_{\max}$  = 2444 MPa (-50 °C), while the cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> reached a remarkably high 2985 MPa (-50 °C) (Figure 4.7; Figures C31-C32). Paralleling this trend, the linear MBCP revealed  $E'_{\max}$  = 1939 MPa (-50 °C) and the cyclic MBCP was marked at 2153 MPa (-50 °C) (Figure 4.7; Figures C33-C34). We chalk this to the more rigid, locked ring conformation increasing the elasticity of the polymer film.

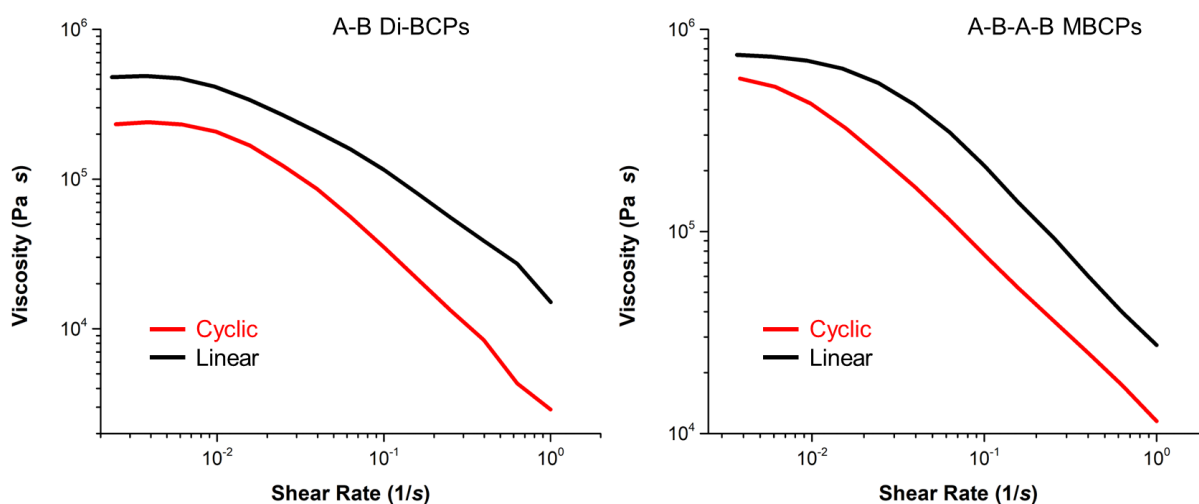


**Figure 4.7.** DTMA temperature-ramp frequency curves for linear (black) and cyclic (right) topological isomers (di-BCPs left, MBCPs right) revealing differences in thermomechanical profiles and performance windows.

This is not the case for the tensile testing, however, as the Young's moduli ( $E$ ) is higher for the linear samples, likely due to differences in elastic v. dynamic moduli test parameters and material response as a result. The DTMA curves also reveal that the linear BCPs are capable of higher thermomechanical durability, as following the second drop in  $E'$  the linear topologies do not fail due to the presence of a rubbery plateau ( $\Delta E' \sim 0$ ) from 150-200 °C (Figure 4.7; Figures C32 and C34). While no crosslinking is present in the system, it is well-understood that high molecular weight amorphous polymers can rely on intensive chain entanglement to retain film performance even above the flow transition for additional working times.

#### **4.3.2.5 Flow Behavior and Melt Viscosity by Oscillatory Rheology.**

Finally, the block copolymers were analyzed by oscillatory shearing rheology to distinguish the flow-phase behavior between linear and cyclic topologies once more. We specifically fixated on the bulk flow profiles, recording polymer viscosity as a function of applied shear rate (175 °C,  $10^{-3}$  to  $1\text{ s}^{-1}$ , 10 rad/s) to obtain the zero-shear viscosities as well as the shear thinning behavior (Table C2). As cyclic polymers are reported to exhibit lower melt viscosities, similar to solution behavior, this is a fundamentally expeditious way to support differences in topology.<sup>40-42</sup> In our case, both cyclic block copolymers (Di-BCP =  $232 \times 10^5\text{ Pa s}$ , MBCP =  $572 \times 10^5\text{ Pa s}$ ) exhibited lower melt viscosity than the linear copolymer comparisons (di-BCP =  $476 \times 10^5\text{ Pa s}$ , MBCP =  $749 \times 10^5\text{ Pa s}$ ) (Figure 4.8; Figures C35-C38; Table C2). Architecturally, it appears that the MBCPs exhibit  $\sim \times 2$  zero-shear viscosity values to that of the di-BCPs, possibly due to increased frictional interactions and inter-domain chain entanglements. This differentiation leads well into the following section where we will present several additional lines of evidence for distinguishing between di- and tetra-BCPs of both linear and cyclic topology as well as identical 50/50 eq. compositions.



**Figure 4.8.** Rheometric shear-thinning flow curves for linear (black) and cyclic (red) di-BCPs (left) and MBCPs (right) highlighting differences in zero-shear viscosity (175 °C,  $10^{-3}$  to  $1 \text{ s}^{-1}$ ,  $10 \text{ rad/s}$ ).

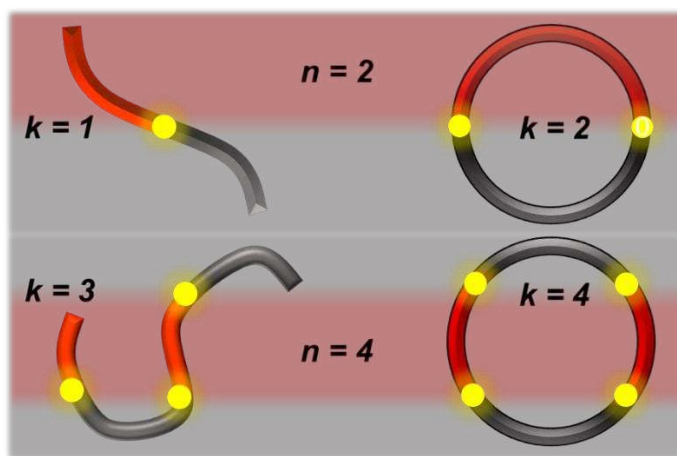
Rate of shear thinning was also evaluated, as we posit that the reduced chain entanglement factors for cyclic polymers may reduce the shear rate required to exhibit a viscoelastic thinning response. Accordingly, we measured the slope of the viscosity curve, following the initial onset of shear thinning. In contrast to our hypothesis, however, the cyclic polymers (di-BCP =  $-1.08x$ , MBCP =  $-0.82x$ ) did *not* have faster rates of shear thinning than the linear polymers (di-BCP =  $-1.08x$ , MBCP =  $-0.80x$ ) (Table C2). Fascinating, however, the rates of shear thinning were found to be nearly identical between the compositionally identical, sequentially split di-BCPs and MBCPs, respectively. Further investigation will be conducted to better understand this phenomenon.

#### 4.3.3.0 Differentiating Between Diblock and Tetrablock Architecture

##### 4.3.3.1 Differentiating Between Compositionally-Identical Di-BCPs and Tetra-BCPs.

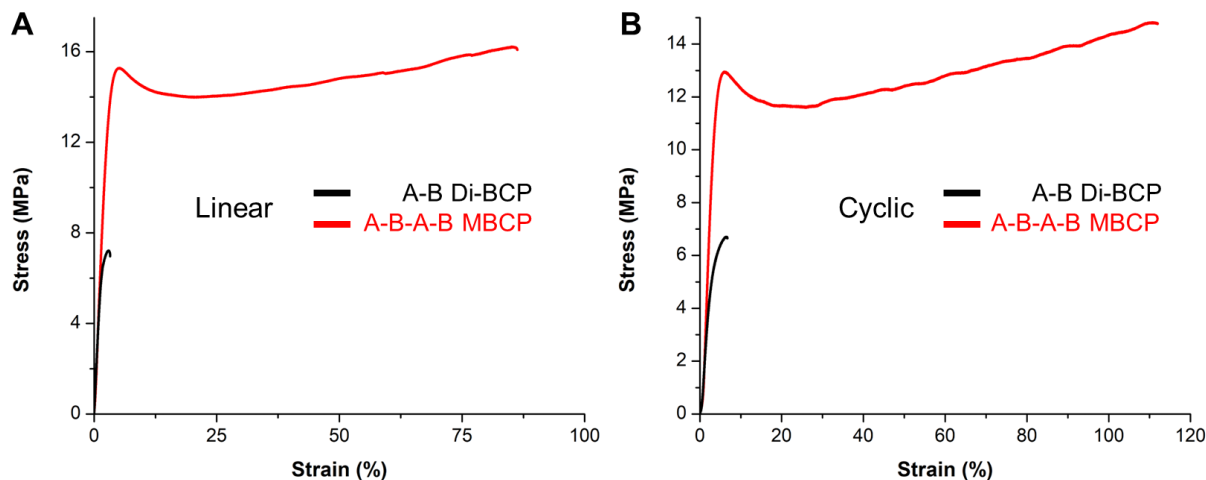
Multi-block architectures are of especially high intrigue due to their untapped potential as high performing materials. The extended capacity for inter-domain crossings in contrast to the

limited ( $k = 1$ ) di-BCP copolymer allows for one MBCP chain to co-entangle across multiple points of domain interfaces ( $k = 3+$ ), acting as anchors for material nanostructure self-reinforcement (Figure 4.9). MBCPs should also be able to embody an improved synergistic mechanical profile to that of the two singular components: while PMMA is a glassy brittle material and PA1A is a viscous liquid, the block architecture of the two is expected to reveal a toughened, ductile thermoplastic.



**Figure 4.9.** Structural features of cyclic and linear A-B di-BCPs and A-B-A-B MBCPs in film phase considering self-assembly and inter-domain chain penetrations. ( $n$  = block count,  $k$  = cross-points).

We thus conducted tensile testing analysis on each of the four materials prepared via melt compression molding with a slow cooling technique to promote self-assembly of the PMMA and PA1A block domains. Considering the above argument, the architectural distinctions in inter-domain crossings and smaller domains should attribute to enhanced thermoplastic character and overall tensile toughness. Stress/strain results were strikingly supportive, as the two di-BCPs performed exceptionally poor with weak (ultimate strength;  $\sigma_B < 8$  MPa), brittle (elongation at break;  $\varepsilon_B < 5 - 10$  %) tensile profiles (Figure 4.10; Figures C39-C40; Table C3). On the other hand, both MBCPs were remarkably improved due to the additional block count, revealing individual yield points consistent with a thermoplastic.



**Figure 4.10.** Tensile stress/strain curves (RT, 5 mm/min) for linear (left) and cyclic (right) di-BCPs (black) and MBCPs (red) revealing dramatic improvements in tensile toughness with increasing architecture complexity.

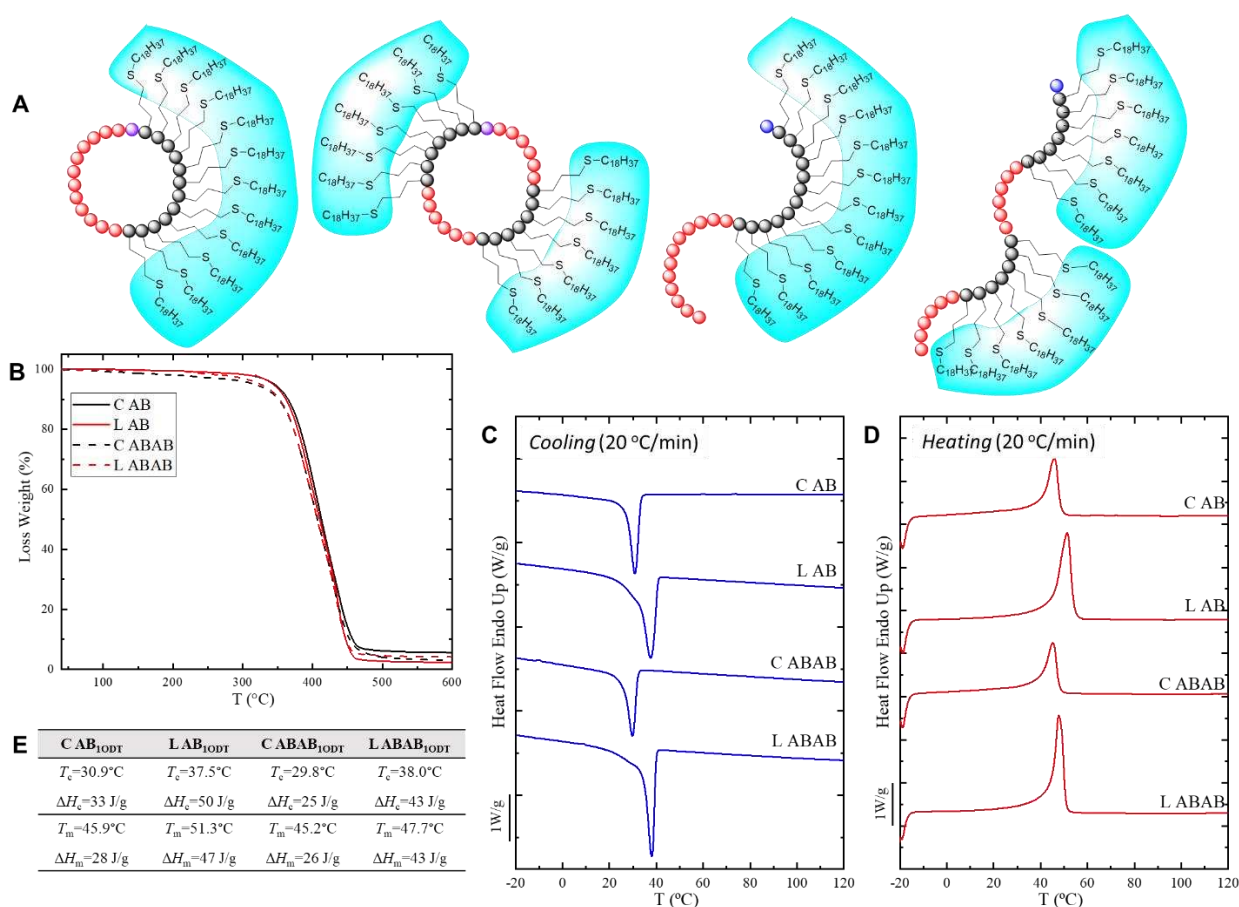
Specifically, the linear MBCP achieved  $\sigma_B = 16$  MPa and an elongation at break of  $\varepsilon_B = 90$  %, while the cyclic MBCP reached an  $\sigma_B = 15$  MPa and  $\varepsilon_B = 110$  % (Figure 4.10; Figures C41-C42; Table C1). We propose that while chain entanglement factors for cyclic polymers are typically reduced, the increased ductility for the cyclic A-B-A-B may be attributed to concatenated rings formed during post-polymerization ring-closure which act as reinforcing, loose crosslink-like, anchors. Though less quantitative, it is worth noting that by physical touch, di-BCPs were noticeably soft and chalky while the MBCPs were strong and flexible, indirectly correlated to their respective measured tensile performances.

#### 4.3.3.2 Self-Assembly, Micro-Domain Formation, and Domain-Sizing for Architectural Discrimination.

By increasing block count from two to four while keeping the composition (50/50 mol eq.) and degree of polymerization ( $DP = 1000$ ) constant, we envisioned that expected self-assembly events would produce ABAB micro-domains with  $\sim$ half the size of the AB BCPs. *We are thus currently exploring the small angle x-ray scattering patterns of these samples and analyzing the*

*1) morphological features and 2) inter-domain spacings between the patterned morphologies. The domain-spacings are anticipated to be roughly halved upon complexifying the BCP architecture from AB to ABAB, though the fitting-derived morphology categories for the same composition are equally anticipated to be the same. This data point will be crucial support for x-ray scattering as a simple strategy to distinguish compositionally-isomeric BCPs of diblock and multiblock architecture.*

To dramatize the effects of self-assembly as well as flex the post-synthetic functionalization power easily accessible through the allylic pendant chain, classic thiol-ene click chemistry was applied (see the SI) to graft 1-octadecanethiol (1ODT;  $C_{18}H_{37}SH$ ) crystalline side chains onto the PAIA units, a procedure well-reported in many previous synthetic cyclic polymer imaging studies (Figure 4.11A).<sup>29,43,44</sup> Prior to imaging and scattering procedures we conducted  $^1H$  NMR spectroscopy to verify a loss in the alkene region, which revealed successful installment of 1ODT side-chains (Figures C43-C44). By initial DSC scans, in all four cases, there was no appearance of a  $T_g$  near the signature  $-35\text{ }^{\circ}C$  for PAIA, as well as notably no melt transition temperature ( $T_m$ ) at  $\sim 30\text{ }^{\circ}C$  which would signal contamination from leftover free 1ODT grafting agent (Figures C45-C49). Additionally, in support of our earlier consideration for the allylic pendant chain causing bimodality in the decomposition profile by TGA, we observed noticeably uniform decomposition in all four 1ODT-grafted BCPs (Figure 4.11B).



**Figure 4.11.** A) Depicted structures for the linear and cyclic di-BCP and MBCP materials obtained from the thiol-ene click reaction with 1-octadecanethiol and highlighted crystalline micro-domain forming side-chains. B) TGA plots for each BCP revealing a singular decomposition pathway in absence of the allylic side chain for PA1A. C) DSC plots with observed  $T_c$  for each crystalline-grafted BCP species. D) DSC plots with observed  $T_m$  for each crystalline-grafted BCP species. E) Tabulated thermal events for each of the four semi-crystalline BCPs (2<sup>nd</sup> heating scan at 20 °C/min, 1<sup>st</sup> cooling scan at 20 °C/min, -20 °C to 120 °C, DSC traces from -80 to 200 °C are found in the SI).

More insightful DSC was also employed to record the melt transition temperatures ( $T_m$ ), crystallization temperatures ( $T_c$ ), enthalpy of crystallization and enthalpy of fusion ( $\Delta H_f$ ) for each of the semi-crystalline materials for comparison between the di-BCP and MBCP architecture sequences (Figure 4.11C,D). In both heating and cooling scans, the linear polymers had higher  $T_m$  and  $T_c$  events than the cyclic counterparts. For the A-B di-BCPs, the linear  $T_m$  and  $T_c$  occurred at 51.3 °C and 37.5 °C, while the cyclic  $T_m$  and  $T_c$  occurred at 45.9 °C and 30.9 °C, respectively. In agreement with this topological correlation, the linear A-B-A-B copolymer  $T_m$  and  $T_c$  were



observed at 47.7 °C and 38.0 °C, higher than the cyclic analogue  $T_m$  and  $T_c$  observed at 45.2 °C and 29.8 °C, respectively (Figure 4.11C-E). Shifting in the  $T_m$  exotherms (blue) and endotherms (red) are clear in the DSC scans and highlight control over the crystallinity with topology.

We surmised that there may be discrepancies spurred by architectural sequence such that the A-B di-BCPs would exhibit larger  $\Delta H_f$  and  $\Delta H_c$  than the A-B-A-B MBCPs due to the larger size of the crystalline domain (Figure 4.11A). This was evident in our experimental results, as integration of both melt and crystallization peaks revealed consistent slight increases in both  $\Delta H_f$  and  $\Delta H_c$  values in the cyclic and linear A-B di-BCPs compared to the smaller crystalline domain cyclic and linear A-B-A-B MBCPs (Figure 4.11E). In the context of topological differences, and in contrast to some literature precedent,<sup>45-47</sup> the  $\Delta H_f$  and  $\Delta H_c$  values of the linear topologies were almost *double* that of the cyclic ones, though this may be due to the side-chain nature of the crystalline groups which do not represent the backbone. Thus, the crystallinity is most dependent on the chain packing capacity, more likely to be disrupted by the cyclic polymer's forced radial constraints.

*This section will also contain TEM imaging and SAXS patterns for these four BCP samples which are still underway. TEM images collected from drop-casted and ultramicrotome-sectioned samples are placed in the supporting information for now (Figures C50-C53), while we will update these figures for main text inclusion with completion of additional experiments and correlation to structural distinctions.*

#### **4.4 Conclusions.**

In summary, though few experiments are still underway, we herein report a facile route to achieving highly complex linear and cyclic multi-BCPs from homologous mixed-feed monomers in a one-pot, two-step polymerization pathway in a timely, high yielding manner. The precision of

this technique is also highlighted by the capacity to receive cyclic A-B-A-B MBCPs with block symmetry of 25/25.5/25/24.5, respectively. Several lines of evidence are reported to support and differentiate the linear and cyclic topology:

- 1) The solution behavior of this cyclic MBCP was compared to that of the linear analogue, revealing classic smaller hydrodynamic volume, lower solution viscosity, longer elution times, and lower refractive indices.
- 2) In bulk, the cyclic MBCP exhibited slightly higher decomposition and glass-transition temperatures than that of the linear MBCP.
- 3) Finally, thermomechanical sweeps revealed that the cyclic MBCP had increased dynamic moduli.

All of these factors are in good agreement with previous literature precedent, while similarly supported alongside differences between in-house furnished linear and cyclic A-B di-BCPs. We also present several lines of evidence useful in differentiating between the di-BCP and tetra-BCP block sequence, while composition of A and B comonomer were held constant at DP = 500 each. These include:

- 4) The MBCP species both exhibited remarkably improved tensile toughness and plasticity over the A-B di-BCPs which were rather weak and brittle.
- 5) Self-assembly by SAXS and TEM imaging, which are still underway in analysis.

Overall, this report presents a highly convenient route to novel cyclic MBCPs and characterizes the behavior against linear counter parts, as well as incorrect di-BCP sequencing, to provide support for our synthetic protocol. We emphasize that CSC-LPP can be leveraged to create much more diverse and complex cyclic multi-BCPs and hope that the synthetic polymer chemistry field

will adopt this technique to further the access and application for cyclic polymers, of which the field remains wide-open for exploration and implementation.

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## Chapter 5

### Dynamic Crosslinking Compatibilises Immiscible Mixed Plastics

#### 5.1 Synopsis

The global plastics problem is a trifecta, significantly impacting environment, energy, and climate<sup>1-</sup>  
<sup>4</sup>. Many innovative closed/open-loop plastics recycling or upcycling strategies have been proposed or developed<sup>5-25</sup>, addressing various aspects of the issues underpinning the achievement of a circular economy<sup>26-30</sup>. Reusing incompatible mixed plastics waste, especially polar/nonpolar polymer mixtures, presents a key challenge in tackling the plastics problem, but many of the existing solutions face their own challenges. Thus, no effective closed-loop solution has emerged<sup>31</sup>. Here, we introduce a compatibilization protocol that installs dynamic crosslinkers to immiscible polymer mixtures. Our combined experimental and modeling studies show that specifically designed classes of dynamic crosslinkers can reactivate mixed plastic "dead" chains, represented here by non-polar polyethylene and polar polyester, and dynamically crosslink them into compatibilized grafted multiblock copolymers. The *in-situ* generated dynamic thermosets exhibit intrinsic reprocessability as well as enhanced tensile strength and creep resistance, relative to virgin plastics. This approach avoids the need for de/reconstruction and thus provides an alternate, facile route towards the recovery of the endowed energy and materials value of the individual plastics.

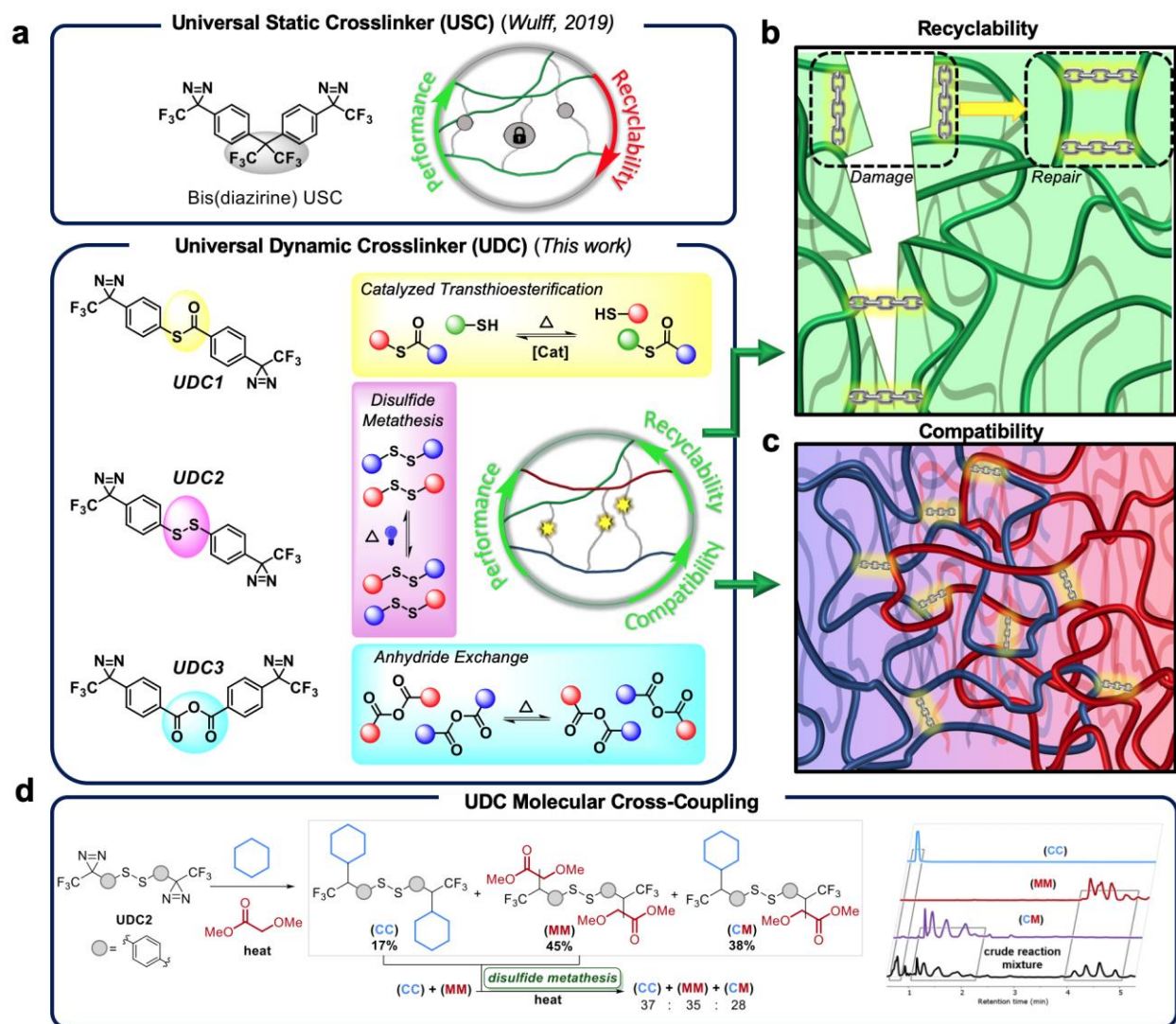
#### 5.2 Introduction

Leibler et al. demonstrated that reversibly crosslinking a polymer to a vitrimer can yield a dynamic thermoset that can be repeatedly reprocessed while maintaining properties.<sup>32</sup> Installation of dynamic<sup>33</sup> and flexible<sup>34</sup> crosslinkers has also been used to increase the adhesion of polymer melts onto polymeric surfaces. Another important concept introduced by Wulff is of universal static (permanent) crosslinkers (USCs) based on symmetric molecular bis(diazirine) precursors

that, upon thermal or light activation, yield highly reactive bis(carbene) species that can crosslink seemingly any polymer bearing a C-H bond through inter-chain double C-H insertion of the carbene (Fig. 1a)<sup>35</sup>. Recognizing that a significant fraction of polymer waste is mixed plastics and most polymer mixtures are immiscible, we further advance these concepts with the goal of reactivating incompatible mixed plastic "dead" chains and dynamically crosslinking them into "living" grafted multiblock copolymers (gMBCPs) using specifically designed universal dynamic crosslinkers (UDCs) (Fig. 1a). Such UDCs incorporate the dynamic nature of vitrimers and the apparent universal crosslinking to compatibilize immiscible polymer mixtures into reprocessable and recyclable thermosets.

The USC-derived permanent network architecture is responsible for enhancing materials performance but deprives the medium to high molecular weight polymers of end-of-life reprocessability. We reasoned that synergistic coupling of USCs and vitrimers by installing dynamic crosslinks commonly found in covalent adaptable networks (CANs)<sup>36-42</sup> into bis(diazirine) universal crosslinkers should yield UDCs capable of exchange reactions within a polymer matrix. This design should enable the effective reconfiguration of network topology, thus allowing the thermoset to access flow-state reprocessing upon exposure to exchange-activating stimuli, while maintaining the desirable thermoset material advantages within the parameterized working conditions (Fig. 5.1a,b). Exchange pathways and crosslink motifs have widely expanded to adapt available functionality in various polymer archetypes, including ubiquitous moieties such as esters<sup>32</sup>, thioesters<sup>43</sup>, boronic esters<sup>33</sup>, disulfides<sup>44</sup>, acids and anhydrides<sup>45</sup> and silyl ethers<sup>46</sup>. Ultimately, merging these two advances in the form of UDCs should enable an optimal strategy for upcycling any mixed plastics by dynamically crosslinking them into value-added thermosets while installing their reprocessability (Fig. 5.1b) and compatibility (Fig. 5.1c).





**Figure 5.1 | Design of universal dynamic crosslinkers (UDCs) and their molecular and macromolecular features.** **a**, Comparisons between the known bis(diazirine)-based universal static crosslinker (USC) scaffold (top) and redesigned UDCs **1-3** imbedded with dynamically exchangeable bonds between the crosslinking sites (bottom). **b**, Illustrated thermoset reprocessability via dynamic bond exchange enabled by UDCs. **c**, Depicted compatibilization effect on otherwise immiscible polymer blend domains rendered by regenerative formation of living, tethered graft multi-block copolymer (gMBCPs) architectures. **d**, Quantified mixed-feed insertion selectivity between cyclohexane and methyl methoxyacetate, molecular models for nonpolar polyolefins (PE etc.) and polar bio-based polymers (PLLA, P3HB, etc.), respectively, and insertion product exchange-mixing to model blend exchange processes.

## 5.3 Results and Discussion

### 5.3.1 Universal Dynamic Crosslinkers (UDCs)

The initial development of UDCs required careful selection of dynamic linkers within the bis(diazirine) framework. They must be inert to the adjacent carbenes during crosslinking yet subsequently capable of dynamic exchange when stimulated; this last aspect is crucial for recyclability (Fig. 5.1b). UDCs **1-3** were prudently equipped with thioester, disulfide, and anhydride moieties, operating on catalyzed thiolate-thioester<sup>43</sup>, disulfide metathesis<sup>44</sup>, and anhydride<sup>45</sup> exchange (Fig. 5.1a), respectively. We envisioned a convergent synthetic approach to these UDCs using 4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzenethiol (TDBT) and commercial 4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzoic acid (TDBA) as key intermediates. TDBT was readily accessed in a multi-step route from commercial materials, allowing preparation on multi-gram scale. The simplicity of UDC derivatization offers scalability and potentially broad access for various undiscovered dynamic linkers. Each UDC derivative exhibits UV-region absorption bands at up to *ca.* 390 nm characteristic of the bis(diazirine) functionality (Figs. D1-D3). Diazirine activation for carbene delivery was monitored through the mass% loss of two N<sub>2</sub> molecules at elevated temperatures by thermogravimetric analysis (TGA) (Figs. SD7-D8). Exotherms further signaling successful carbene formation (113–122 °C) during differential scanning calorimetry (DSC) scans were deemed non-explosive and non-shock sensitive by Yoshida's correlations<sup>47</sup>, supporting safe utility (Figs. D9-D11).

Establishing high crosslinking efficacy without damaging the dynamic linker group is imperative for any UDC derivative prior to polymer application. Cyclohexane was chosen as the model compound to enable isolation and full characterization of crosslinked products (Figs. D4-D6). Thermal activation of UDC**1-3** outperformed photochemical alternatives, inserting in up to 53% yield, which is notably higher than that observed in the USC<sup>35</sup>, likely due to subtle changes in electron density of the resulting trifluoro aryl carbenes as more electron-rich diazirines have

been shown to result in higher C-H insertion yields.<sup>48</sup> Collectively, our experiments demonstrate that UDC1-3 can readily crosslink aliphatic substrates without significant degradation during carbene insertion (Tables D1-D2). Additional control experiments revealed the crosslinking procedure is air and moisture tolerant, simplifying polymer application protocols. Next, cyclohexane and methyl methoxyacetate were chosen as small-molecule models for nonpolar polyolefins and polar polyesters, respectively (Fig. 5.1d). A mixture of the model molecules and UDC2 was incubated at 130 °C and the hetero-crosslinked product (CM) was confirmed by high-resolution mass spectrometry (Figs. D12-D13). More detailed analysis by supercritical fluid chromatography (SFC) further revealed that formation of the mixed-cross-linked CM product is competitive with homo-crosslinking (CC and MM, Fig. 5.1d, Figs. D14-D15). In addition, heating a mixture of the two homocoupling products CC and MM furnished mixed product CM, thus providing evidence for a thermal disulfide metathesis mechanism (Fig. 5.1d, Figs. D16-D17). Furthermore, methyl propionate was used as a small molecule model substrate to probe the regioselectivity of C-H insertion into polyesters. After incubation at 130 °C, insertion into C-H bonds  $\alpha$  to the carbonyl was found predominantly (Fig. D18), a finding that is in agreement with previous reports.<sup>49</sup>

### 5.3.2 Dynamic crosslinking of pure thermoplastics to reprocessable thermosets

To establish crosslinking of relevant thermoplastics, low-molecular-weight polyethylene (LMWPE), low-density PE (LDPE), high-density PE (HDPE), ultra-high-molecular-weight PE, and isotactic polypropylene (*it*-PP), were treated with 0, 5, and 10 wt.% UDC1-3. Reduced enthalpy of fusion ( $\Delta H_{\text{fus}}$ ) and melting temperature ( $T_{\text{m}}$ ) of a semicrystalline thermoplastic verified inserting crosslinks in the melt state<sup>35</sup>. In contrast, the glass-transition temperature ( $T_{\text{g}}$ ) increases (Figs. D19-D33, Tables D3-D9). Crosslinking success was also supported by  $T_{\text{g}}$  increases in

amorphous or semi-crystalline samples, complimented by substantially reduced or eliminated solubility (Fig. D19-D22, D34). Loadings of 5 wt.% UDC**1-3** were selected for scaling, striking a balance between the UDC equivalent and the extent of miscibility.

FTIR analysis of melt-processed thin films of the model LMWPE substrate, pre- and post-UDC treatment, showed no change in polymer structure, mitigating decomposition concerns (Figs. D43-D45). Comparative tensile tests were performed on (un)crosslinked LDPE (melt flow index (MFI) = 21) materials, as the virgin material achieves suitable solubility safely below the carbene activation temperature and, thus, homogeneous UDC dispersion (Fig. D35, Table D11). UDC**3** was selected and compared against the static USC as both crosslinkers operate in the absence of external additives or catalysts. Imbedding LDPE with UDC**3** resulted in films with favorable mechanical performances relative to virgin LDPE, with increased strength at break (13 vs. 11 MPa) and tensile toughness (13 vs. 12 MJ m<sup>-3</sup>) but the same elongation at break (~115 %) (Fig. 5.2a, Figs. D38-D42). LDPE thermosets prepared by USC were inferior in strength (8.9 MPa), ductility (38 %), and toughness (3.0 MJ m<sup>-3</sup>) relative to the virgin and UDC-treated LDPE (Fig. 5.2a). Further distinctions between UDC and USC are emphasized by reprocessing experiments, in which LDPE-UDC**3** exhibited a similarly competitive tensile profile before and after reprocessing, while LDPE-USC lacked reprocessability after single reprocessing, yielding drastic decreases in strength, strain, and toughness by 41%, 82%, and 88%, respectively (Fig. 5.2a, Figs. D36-D37, Table D11).

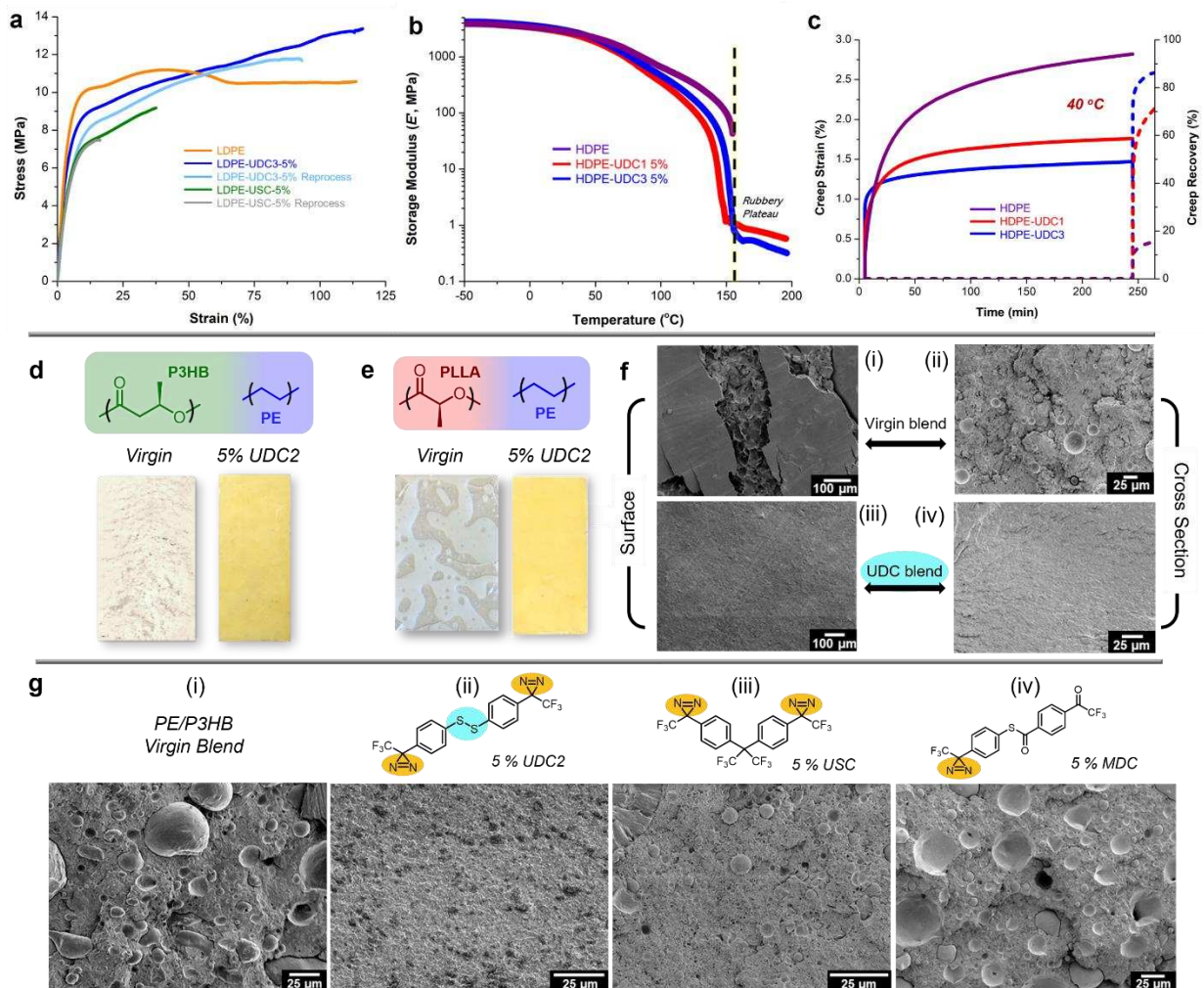
Melt pressed films of UDC**1**- and **3**-imbedded LDPE and HDPE (MFI = 7.6) retained or improved storage modulus ( $E'$ ) values at both -50 °C and 23 °C, relative to the virgin materials. A maximum  $E'$  of 3.2 GPa for LDPE and 4.2 GPa for HDPE were obtained when crosslinked with UDC**3**; these numbers are noticeably higher than the thermosets crosslinked with UDC**1** (Fig. 5.2b,

Table D10). We attribute the superior thermomechanical performances of UDC**3**-crosslinked materials to the stability of the anhydride dynamic linker, which is uncatalyzed and less prone to ambient creep than those derived from UDC**1**. Thermal frequency sweeps revealed the presence of a rubbery plateau ( $E' \sim \text{constant}$ ) above  $T_m$  observed in crosslinked samples, indicating practically advantageous thermomechanical durability of the crosslinked PE materials relative to uncrosslinked analogs (Fig. 5.2b, Fig. D46-D47). For example, at 150 °C the UDC crosslinked HDPE samples have  $E' \sim 0.3\text{-}1$  MPa, depending on the UDC. The plateau modulus of HDPE melts, which is attributable primarily to entanglements, is  $\sim 1$  MPa. The uncrosslinked samples fail under these conditions. Thus, we conclude that the dynamic crosslinks provided by the UDC occur at length scales comparable to the native entanglements but temporally are more persistent and thus provide a measurable modulus. Since it is known that the mean distance between entanglements along the chain contour is  $\sim 50$  monomers, this implies from rubber elasticity that the UDC systems correspond to networks with an elastically active crosslink fraction of 1 vol%. This analysis suggested that only a small fraction ( $\sim 20\%$ ) of the UDC molecules are elastically effective – this could either be due to the high temperature of the measurement, or the likelihood that some crosslinks are intramolecular and hence elastically inactive.

To further demonstrate that the UDC technology can bridge thermoset performance and thermoplastic recyclability, we investigated creep-recovery behavior of crosslinked LDPE and HDPE below their  $T_m$  ( $\sim 30$  °C each) and well-within film operating conditions (Table D12). Virgin-quality LDPE exhibited the most pronounced creep deformation (25.5%) over the course of 10 min at 80 °C in comparison to LDPE reinforced with UDC**1** (9.0%) and UDC**3** (12.4 %), while suffering nearly 30% permanent deformation upon load removal (Fig. D48). Similarly, HDPE films treated with UDC**1** and UDC**3** improved both creep resistance (2.6% and 1.7% less,

respectively) and recovery (+ ~30%) relative to the untreated HDPE film at 110 °C (Fig. D50). Impressively, in a 4-h creep experiment mimicking working conditions at 40 °C and prolonged stress (2 MPa), the creep deformation of HDPE was nearly halved with UDC1 and UDC3 incorporation (1.47% and 1.76%, respectively, vs. 2.82 %) (Fig. 5.2c, Fig. D49). Recovered strain from the 4-h load event was significantly improved from 15 % to over 70 % in both HDPE-UDC specimens, displaying an added elastic character unattainable by HDPE chain entanglement factors alone.

Flow-state mobility and paralleling reconfigurability behavior of UDC crosslinked PEs were characterized by bulk shear oscillatory rheology. Creep-recovery was performed on LDPE at 130 and 140 °C as well as HDPE at 150 and 160 °C, 15 and 25 °C above the respective  $T_m$  values (Table D13). As expected, virgin LDPE (Fig. D51) and HDPE (Fig. 5.3a) thermoplastics experienced extreme creep in the flow state. In comparison, thermosets prepared with UDC1 and 3 exhibited much reduced creep consistent with a viscous material highly influenced by both temperature and dynamic linker exchange pathway (Fig. 5.3d, Figs. D52-D53). We also demonstrated the lack of melt configurability of the statically crosslinked LDPE thermoset by USC (5 wt%) by analyzing the creep at 130 °C and found the least amount of shear strain with nearly full recovery upon removal of shear stress (Fig. D54). Overall, the demonstrated orthogonality – creep suppression below the  $T_m$  and retained creep above the  $T_m$  – is key to the recycling advantages of UDC-crosslinked materials.



**Figure 5.2 | Thermomechanical performance of crosslinked PE and UDC compatibilization of immiscible PE/polyester blends.** **a**, Tensile stress/strain curves (5 mm/min, 25 °C) of LDPE, LDPE thermosets by UDC3 and USC, and reprocessed LDPE thermoset scraps, demonstrating recyclability of UDC-enabled thermosets and non-recyclability of USC-based thermosets. **b**, Storage moduli overlay for HDPE, HDPE-UDC1, and HDPE-UDC3 highlighting crosslinking evidenced by rubbery plateau extension (5 °C/min, 0.3 %, 1 Hz). **c**, Prolong-simulative creep-recovery performance for HDPE at 40 °C against PE-UDC1 and PE-UDC3 (2 MPa, 4 h creep, 30 min recovery). **d**, Photos of immiscible PE-P3HB blend (left) and compatibilized PE-PLLA blend by UDC2 (right). **e**, Photos of immiscible PE-PLLA blend (left) and compatibilized PE-PLLA blend by UDC2 (right). **f**, SEM images of the surfaces (left) and cross sections (right) (3 kV, 10 nm Au coating) of immiscible PE-PLLA blend and compatibilized PE-PLLA blend by UDC2 (5 wt%). **g**, SEM cross-section images of PE-P3HB blends: virgin (i), dynamic UDC (ii), static USC (iii), and mono-diazirine control MDC (iv).

### 5.3.3 Compatibilization of immiscible polyolefin/polyester blends

Nearly all postconsumer plastics exist in mixed-waste streams. Thus, we considered the opportunity to create compatibilized dynamic thermosets by blending incompatible polymer archetypes with the UDCs. Common bio-based poly(L-lactic acid) (PLLA) and poly(3-hydroxybutyrate) (P3HB) were selected for blending trials with LWMPE and LDPE. Average droplet diameter size, tracked by scanning electron microscopy (SEM), serves as the first metric for UDC compatibilization efficacy (Tables D22-D23). As expected, the incompatible LMWPE-PLLA and LMWPE-P3HB blends of heterogeneous films (Fig. 5.2d,e) revealed large PE-polyester domain interfaces with large droplets averaging 29  $\mu\text{m}$  (PLLA) and 32  $\mu\text{m}$  (P3HB) in diameter in the image (Fig. 5.2f,g, Extended Data Figs. 5.1 and 5.2, Figs. D70-D71). Static crosslinking by USC results in the continued presence of droplets, though their average diameters are reduced to 2.1  $\mu\text{m}$  (PLLA) and 1.6  $\mu\text{m}$  (P3HB) (Fig. 5.2g-(iii), Extended Data Figs. 5.4 and 5.9, Table D22). However, the incorporation of UDC**2** or **3** (5 wt%) to either of the blends during mixing improved surface homogeneity so drastically that droplet formation was not observed (Figs. 5.2f-(iii),(iv), 5.2g-(ii); Extended Data Figs. 5.3, 5.7, 5.8; Figs D72-D77), suggesting compatibilized blends. In the case of UDC**1**, droplets still formed but the average droplet diameter was substantially reduced to  $\sim 2.8$   $\mu\text{m}$  (Extended Data Fig. 5.6). The less extent of compatibilization by UDC**1**, relative to UDC**2** or **3**, could be influenced/hindered by the presence of the externally added thiol and base catalyst (required to trigger dynamic exchange). In contrast to the bis(diazirine) counterparts, MDC (a linker with only one functionality) increased the average droplet diameter to 45  $\mu\text{m}$  (PLLA) and 48  $\mu\text{m}$  (P3HB) (Fig. 5.2g-(iv), Extended Data Figs. 5.5 and 5.10).

These microscopy measurements are complemented by small- and wide-angle X-ray scattering (SAXS and WAXS) data that showed that the virgin immiscible LDPE-P3HB (Fig. 5.3e) and LDPE-PLLA (Extended Data Fig. 5.11) blend and the UDC-compatibilized blends have



WAXS patterns that are the linear superposition of the two components. Given that the two constituent polymers are semicrystalline, these results clearly show that each component continues to crystallize in its same native habit even after it is compatibilized by the crosslinker. Fig. 5.3f further illustrates this point through WAXS experiments across a range of temperatures. At a temperature (130 °C) above the  $T_m$  of the LDPE, only the LDPE bands disappeared leaving only the P3HB peaks; subtraction of the 130 °C data from the room temperature data gave only peaks for the LDPE, further supporting these ideas (Fig. D69). The P3HB bands too disappeared at 180 °C, above the  $T_m$  of P3HB, leaving only a broad amorphous halo. The corresponding SAXS peaks showed qualitatively similar features again illustrating that, even though the blends are compatibilized, there is no mixing at the molecular (or even at the domain) level. The spectra observed by subtracting the 130 °C data from the room temperature data showed that the SAXS LDPE peak moves from a wavevector of  $q \sim 0.3 \text{ nm}^{-1}$  (native LDPE) to  $0.4 \text{ nm}^{-1}$  in the UDC blend, which implies a reduction in the LDPE long period from  $\sim 21 \text{ nm}$  to  $16 \text{ nm}$  on compatibilization. This change could be caused by the increased defect content (by crosslinking), a reduction of the equilibrium  $T_m$ , or an increase in  $T_g$  due to the P3HB.

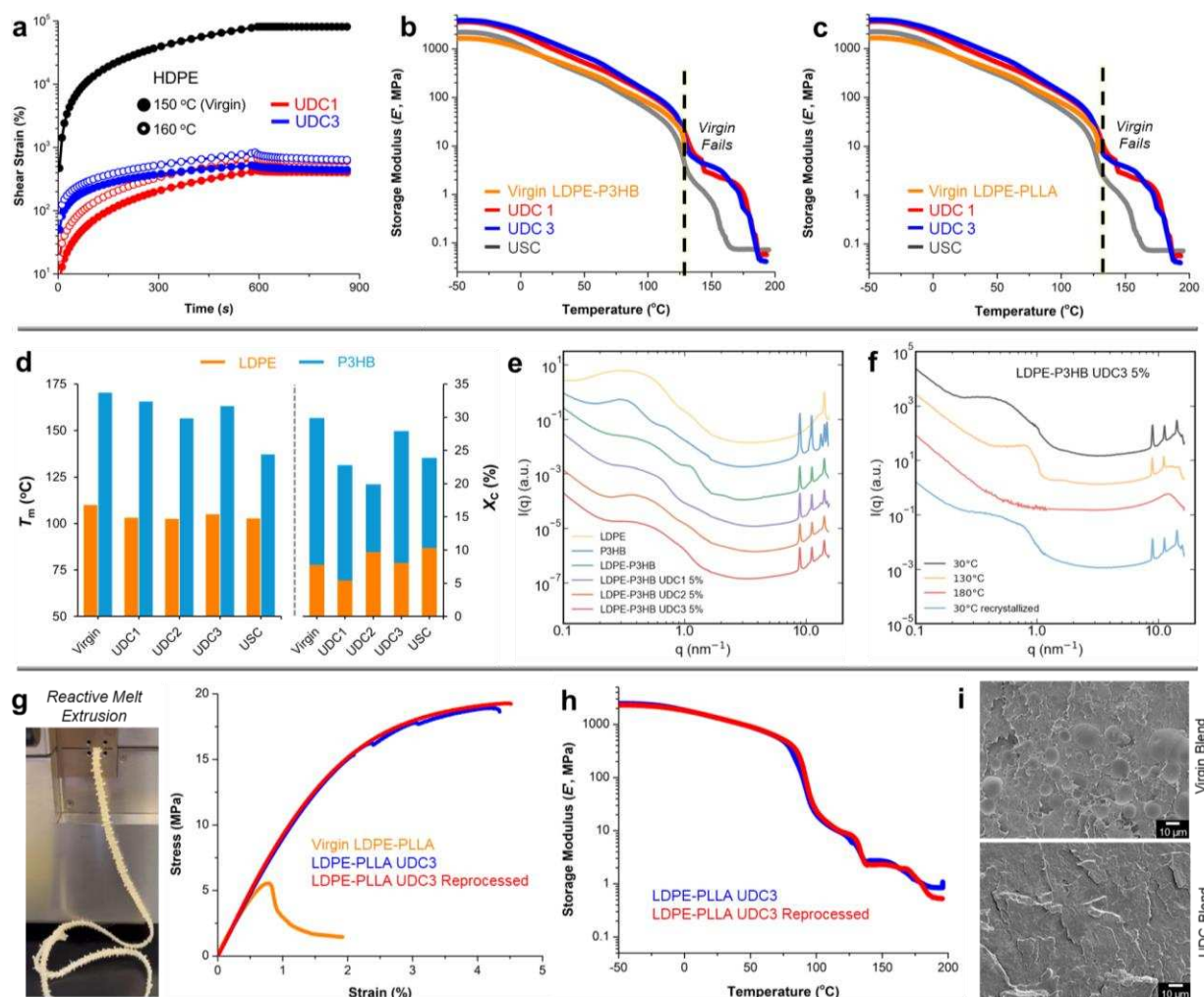
DSC data (Fig. 5.3d) clearly show that the melting points of the both constituents in the compatibilized blends are depressed relative to the pure polymer. The Flory theory of polymer crystallization implies that the melting point can be depressed by the "copolymer effect": -

$$\frac{1}{T_m^{copoly}} - \frac{1}{T_{m0}} = -\frac{R}{h_u} X_b, \text{ where } T_m^{copoly} \text{ is the melting point of the graft copolymers created by the}$$

UDC,  $T_{m0}$  is the melting point of the corresponding pure polymer,  $R$  is the gas constant,  $h_u$  is the enthalpy of melting and  $X_b$  is the crosslinked mole fraction. In the LDPE-P3HB blend the melting point of the pure LDPE is  $T_m = 110 \text{ °C}$ , while that for the LDPE in the UDC systems is  $\sim 104 \pm 1 \text{ °C}$ ; similarly, the pure P3HB has  $T_m = 171 \text{ °C}$ , while the UDC value is  $162 \pm 4 \text{ °C}$ . Both of these

numbers, which have inherently high uncertainties since they were averaged across the different systems, are consistent with the Flory theory with an  $X_b \approx 0.02$ ; this is in reasonable accord with the modulus estimates for the pure HDPE systems discussed above. Thus, the experimentally deduced  $T_m$ 's support with the formation of the *g*MBCP.

Examining the consequences of these crosslinks on the thermomechanical response revealed that the low-temperature modulus of the UDC-compatible blends is larger than the incompatible mixtures (Fig. 5.3b,c). This increased modulus evidently is due to the increased connectivity between the phases through crosslinking which permits for better load transfer. In both UDC-compatible blends there are two drops in moduli with increasing temperature, corresponding to the melting transitions of the two polymers; however, even at the highest temperature the UDC blends have a residual modulus, because the thermoset character imparted by the UDCs is manifesting even in the melt state (Figs. D66-D67). This is similar to the high temperature plateau modulus in the HDPE-UDC system (Fig. 5.2b). Note that the incompatible blends fail at the melting point of the lower  $T_m$  polymer. The measured storage modulus of the UDC-compatible blends at 200 °C is ~0.1 MPa, about an order of magnitude smaller than that found for the HDPE system and the prediction of rubber elasticity theory with the macroscopic crosslinking density anticipated by the UDC concentration. These results likely reflect the fact that, while the addition of the UDC crosslinks certainly reinforces this boundary, regardless, it does so less efficiently than in the bulk homopolymer under the conditions studied. The USC blends showed similar trends (Table D20).



**Figure 5.3 | Reprocessability and recyclability of immiscible polyolefin/polyester blends by UDC.** **a**, Bulk oscillatory shear rheology plots showing dramatic creep-recovery behavioral distinctions between HDPE and dynamic thermosets with UDC1 and UDC3 (10 min creep, 5 min recovery, 2 kPa). **b**, Storage moduli overlay plot for blends of virgin LDPE-P3HB and blends crosslinked with UDC1-3 and USC (5 °C/min, 0.3 %, 1 Hz). **c**, Storage moduli overlay plot for blends of virgin LDPE-PLLA and blends crosslinked with UDC1-3 and USC (5 °C/min, 0.3 %, 1 Hz). **d**, Melting temperatures (left) and crystallinity (right) for individual blend components of virgin LDPE-P3HB and blends crosslinked with UDC1-3 and USC (10 °C/min). **e**, Domain-averaged combination SAXS/WAXS curves for cross-linked LDPE-P3HB blends relative to virgin blend and reference homopolymers. **f**, Effect of temperatures above the component  $T_m$ 's on domain-averaged combination SAXS/WAXS curves for UDC3 compatibilized LDPE-P3HB blend. **g**, Photograph example highlighting reactive melt extrusion of LDPE-PLLA blend embedded with UDC3 in a twin-screw extruder (left) and reprocessability/recyclability of the UDC-crosslinked LDPE-PLLA blend with tensile stress/strain tests (23 °C, 5 mm/min, right) of specimens prepared by reactive extrusion (blue) and extrusion-reprocessed (red) against virgin LDPE-PLLA blend (orange). **h**, Melt extrusion reprocessability by DMA frequency sweeps on UDC-crosslinked LDPE-PLLA dynamic blends at first (blue) and second (red) cycle (5 °C/min, 0.3 %, 1 Hz). **i**, SEM cross-sectional images revealing degree of compatibilization by droplet

analysis for virgin LDPE-PLLA (top) and UDC-compatible LDPE-PLLA UDC3 prepared by melt extrusion (bottom).

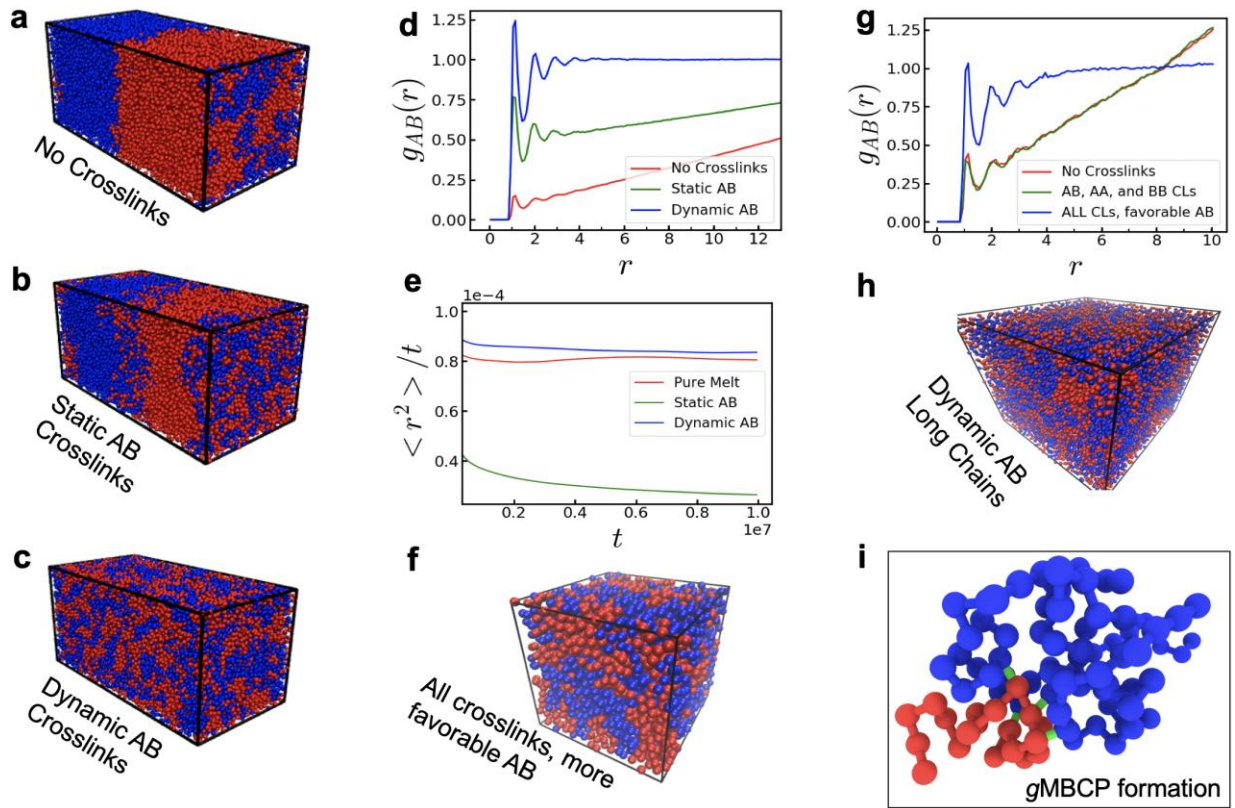
We finally examined the reprocessability and recyclability of the UDC-compatible LDPE-PLLA blend. Upon melt-extrusion by a twin-screw extruder, the virgin blend was macro-phase-separated into two individual parts, while the blend embedded with UDC3 was compounded into continuously homogenous ribbon-like extrudates (Fig. 5.3g, Supplementary Video). The reprocessed specimens are homogenous (Fig. D61), and the compatibilization was confirmed by the absence of droplets in the cross-section imaging, in contrast to the virgin blend (Fig. 5.3i, Fig. D70-D76). The UDC-compatible blend is also recyclable via both tensile testing and DMA analyses (Fig. 5.3g,h, Fig. D68); SAXS data (Fig. 5.3f) also support these conclusions. Noteworthy also is that the UDC blend showed an enhancement of tensile strength, ultimate strain, and toughness by 346%, 268%, and 1850%, respectively, relative to the virgin blend (Figs. D62-D64, Tables D20-D21). Furthermore, as testament of the "living" nature of the system, addition of 50wt% virgin LDPE to the post-tensile specimens of the 50:50 LDPE-PLLA blend compatibilized by UDC3 gave a 75:25 LDPE:PLLA blend (2.5wt% UDC3), which can still be extruded into a homogeneous, reprocessable blend with an enhanced ductility by 220% over the 50:50 blend (Fig. D65).

#### **5.3.4 Molecular dynamics simulations of compatibilization and gMBCP formation**

To establish the underpinning physics of UDC-enabled blend compatibilization, we used the coarse-grained Kremer-Grest bead-spring model<sup>50</sup> in conjunction with the molecular dynamics (MD) method on an incompatible homopolymer blend, whose constituents are termed A and B. Each chain is comprised of  $N = 20$  monomers connected by finite extensible nonlinear elastic (FENE) bonds; some blend simulations also used  $N = 100$ . The interactions between pairs of monomers are described by the Lennard-Jones potential truncated at  $2.5\sigma$  ( $\sigma$  is the monomer

diameter) – thus, attractions between the monomers are included. The strength of the interactions is controlled by the well-depth  $\epsilon_{AA} = \epsilon_{BB} \equiv \epsilon$ . The cross interaction  $\epsilon_{AB} = 0.95\epsilon$  yields an immiscible blend with a relatively sharp interface in the absence of crosslinking (Fig. 5.4a). First, static and dynamic crosslinks are created *only* between pairs of dissimilar (AB) monomers within a predefined cut-off distance,  $r_{bond,c} = 1.3\sigma$  (Fig. 5.4b,c). The corresponding AB radial distribution functions are shown in Fig. 5.4d. These results illustrate the clear transition from an immiscible blend (Fig. 5.4a) to a progressively more miscible one with static crosslinks (Fig. 5.4b) to an almost completely miscible blend with dynamic crosslinks, Fig. 5.4c. This is in agreement with our experimental observations (Fig. 5.3c,d). Longer chain blends ( $N=100$ ) yield qualitatively similar results, Fig. 5.4h. The creation of "living" gMBCPs, which is postulated to be the underpinning driver for the increased miscibility in these cases, is illustrated in Fig. 5.4i – this cluster of one A chain and four B chains is tied together through multiple green bonds (the *dynamic crosslinks*). To make connection to the experiments presented above, we need to have dynamic crosslinks across AA, BB and AB pairs. Introducing AA, BB, and AB crosslinks, while maintaining all of them to be equally likely, does not lead to mixing as indicated in Fig. 5.4g. The creation of "homo" AA or BB crosslinks increases the effective length of the A (B) chains, making them less miscible with each other. while the "hetero" AB crosslinks create living gMBCPs which promotes blend compatibility. Thus, there is a competitive balance between the increased chain length (and hence reduced compatibility) and BCP formation (increased compatibility) – when breaking probabilities,  $p_b = 0.5$  (and also formation probabilities,  $p_f = 0.5$ ) for the AA, BB and ABs are independent of identity then the system remains immiscible. Increasing the life time of the AB crosslinks, relative to the AA and BB crosslinks, by making the  $p_b$  for the AB much smaller (0.06) than for AA and BB (0.5), effectively reduces the free energy of AB crosslinks, which then

yields a compatibilized blend (Fig. 5.4 f,g). It appears that the crosslinks serve as effective attractions between the two monomers that are bridged – when such interactions are more favorable for AB over AA and BB, then the blend is compatibilized. This reduction of bond free energy due to a longer lifetime (smaller bond breaking probability) is illustrated by well-established rate equation ideas: The rate of bond breaking  $p_b \propto e^{-\frac{\delta F}{k_B T}}$ , where  $\delta F$  is the change in free energy of a bond while it goes from an crosslinked to an uncrosslinked state. Thus, the AB bond free energy is reduced by a factor of  $\ln 0.06 / \ln 0.5 \approx 4$  as we change the bond breaking probability from 0.5 to 0.06. This points to the notion that AB crosslinks have to be free energetically favorable relative to the AA and BB bonds to ensure compatibilization.



**Figure 5.4 | Coarse-grained MD simulations of a binary polymer blend,  $N = 20$  unless stated otherwise. **a**, MD snapshot of system with no crosslinks. **b**, MD snapshot of system with 16% AB static crosslinks. **c**, MD snapshot of system with 10% AB dynamic crosslinks of an average lifetime of 20 simulation time-steps. **d**, Radial distribution functions for the systems shown in **a**, **b**, and **c** above. **e**, The chain centre of mass mean square displacement normalized by time in**

a pure melt, binary melt with static AB crosslinks, and binary melt with dynamic AB crosslinks, with the formation and breaking probabilities of  $p_f = p_b = 0.5$ . **f**, MD snapshot with all three types of dynamic crosslinks but AB crosslinks with a longer average lifetime ( $p_b=0.06$  for AB alone while  $p_b = 0.5$  for AA and BB crosslinks, so that AB crosslinks are 10% out of the total 21%). **g**, AB radial distribution functions for a binary melt with no crosslinks, with all three crosslinks, with all three crosslinks with more favourable AB (*i. e.*,  $p_b = 0.5$  for AA and BB but  $p_b = 0.06$  for AB). **h**, MD snapshot of a system of longer chains ( $N = 100$ ) with 13% AB dynamic crosslinks. **i**, MD snapshot of system with one A-type and four B-type polymer chains connected by crosslinkers (green bonds) to form gMBP; red and blue beads are the monomers of two homopolymers.

A final question is why a static crosslinked system yields lower compatibility than the corresponding dynamic system. Fig. 5.4e, which presents mean-squared displacement data (directly related to the diffusion coefficient) of free melt chains, the static crosslinked and dynamically bonded systems in systems with only AB bonds provides a clear indication of the underlying physics. The addition of static crosslinks dramatically reduces the chain diffusivity. Presumably, this is because the gMBPs are localized at the interface between the immiscible blend components, Fig. 5.4b. In contrast, the diffusion coefficient of the system with dynamic bonds is even larger than in the case of a neat melt. An analogy that serves to illustrate this point is a solute diffusing through a polymer. If the solute has no favorable interactions with the polymer, then, it will not dissolve in the melt; in contrast, too strong an interaction between solute and polymer would yield in the solute being localized near a monomer; thus, it no longer diffuses through the system. An intermediate level of attraction that balances solubility and localization typically gives the highest diffusivity. By analogy, the bonds in the dynamically crosslinked systems have sufficient mobility to involve the whole matrix polymer leading to more effective compatibilization. In contrast, the static system localizes the crosslinks and hence minimizes their ability to compatibilize the whole polymer matrix.

The key new insights from the MD study are: (i) the *in-situ* formation of gMBPs leverages their demonstrated ability to compatibilize immiscible blends, while their reconfigurability greatly

facilitates their use through multiple cycles; (ii) the formation of dynamically crosslinked networks, especially those with long lifetimes, slows down the kinetics of blend compatibilization and hence is unfavorable from a processing viewpoint. However, these network constructs dramatically help the temporal stability of the compatibilized blends under lower temperature, in use conditions; and (iii) while we can go from completely immiscible to completely miscible constructs by using our strategy, the creation of *microphase-separated systems* is probably most relevant from an end-use perspective since they retain the unique characteristics of the individual components.

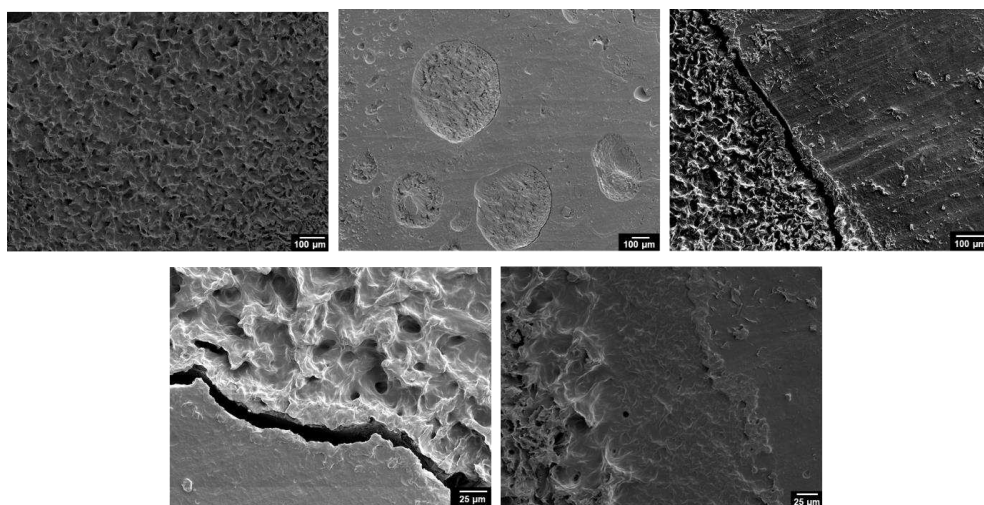
## 5.4 Conclusion

Overall, we credit the enhanced properties, blend compatibilization and reprocessability of mixed polar/nonpolar plastics enabled by UDCs to the synergistic combinations of a) inter-chain crosslinks producing gMBCPs through covalently restrained proximity and b) dynamic bond exchange promoting mixing (and, potentially, network relaxation for large enough UDC concentrations). The inter-chain crosslinking generates rapidly evolving, effectively "living" gMBCPs of otherwise immiscible components *in situ* during processing conditions. This strategy, while relying on the principles of BCP compatibilization, is a clever molecular solution to circumvent the need for *ex-situ* synthesized BCP compatibilizers. Linear or grafted MBCPs can achieve blend stabilization by reducing the interfacial tension between incompatible phases<sup>51-53</sup>. In the scenario of a dynamically crosslinked blend, we leverage rapid crosslink shuffling, which leads to matrix miscibility due to lowered interfacial tensions between the two domains; this is herein attributed to the formation of "living" gMBCP. The capacity for these dynamic tethers to flow during processing (mixing) conditions would then be key to achieve balanced inter-chain linking of A and B and thus stabilization of the binary blend. From these observations we

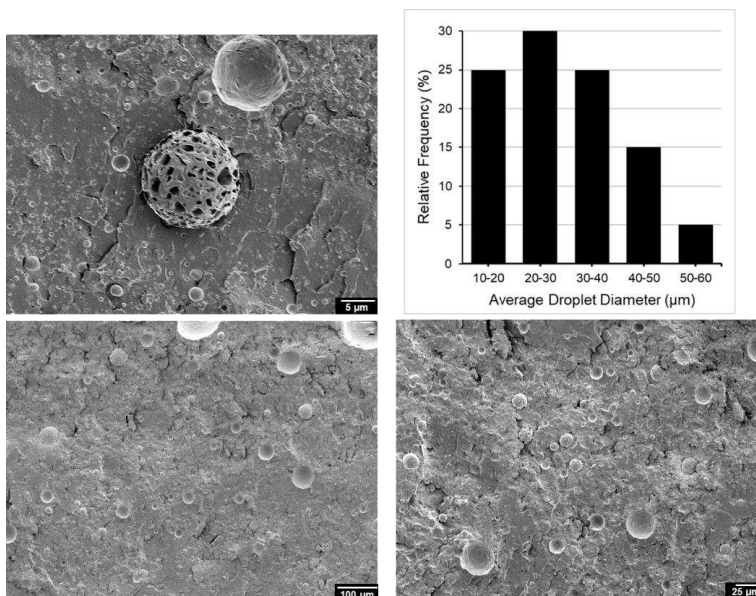


concluded that both melt-processability *and* inter-chain BCP architectures, uniquely accessible by UDCs, are crucial to achieving miscibility between two polar extremes and thus highlight the broader utility of dynamic crosslinking. The universal aspect of UDC carbene C-H insertion and dynamic-crosslinking-induced compatibilization principles introduced here could be leveraged to generate upcycled gMBCPs beyond binary blends.

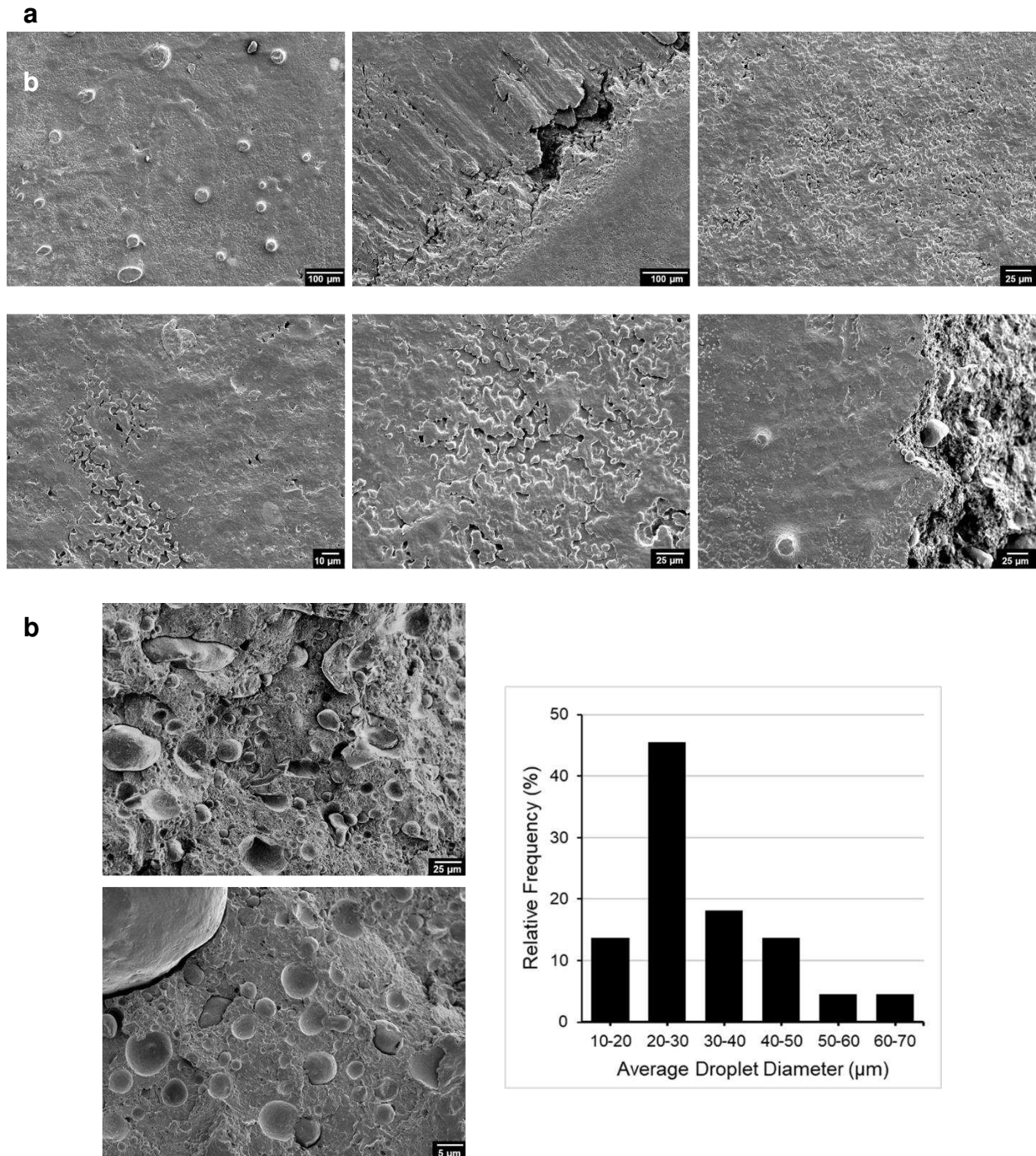
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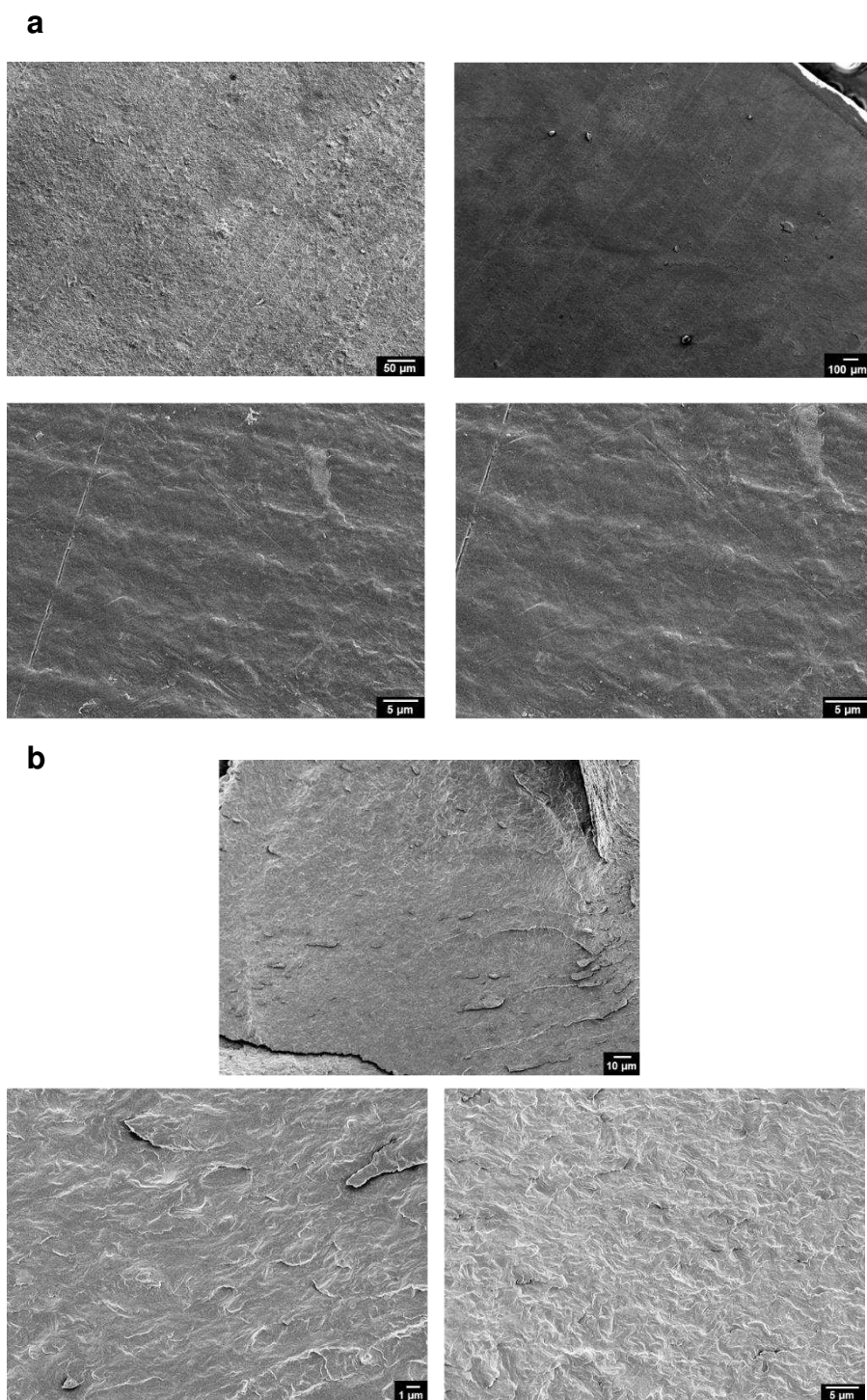
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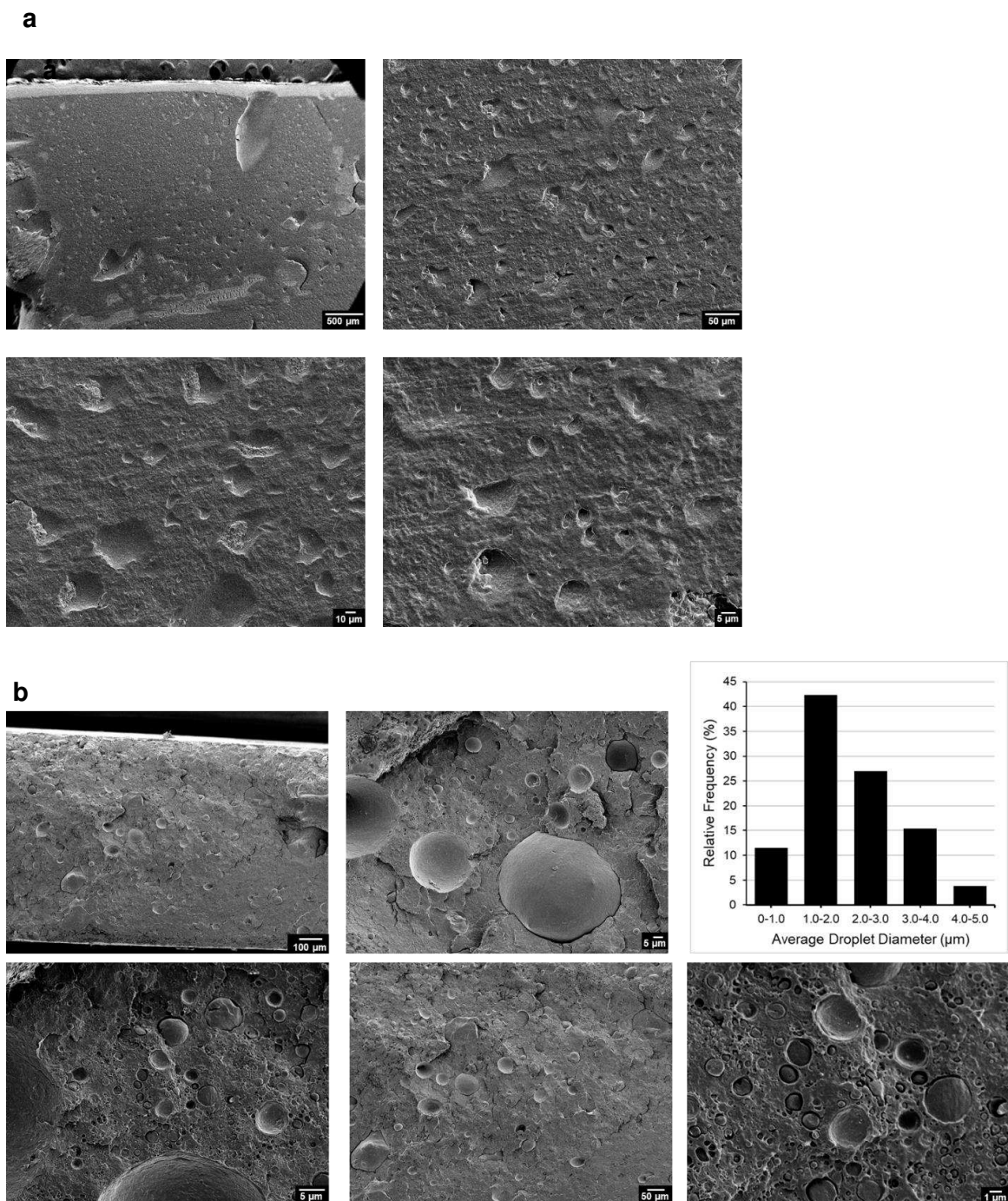
**Extended Data Fig. 5.1 | Additional SEM images.** **a**, Surface images of the virgin 50/50 wt.% LMWPE-PLLA blend. **b**, Cross section images of the virgin 50/50 wt% LMWPE-PLLA blend and cross-section droplet diameter size analysis.



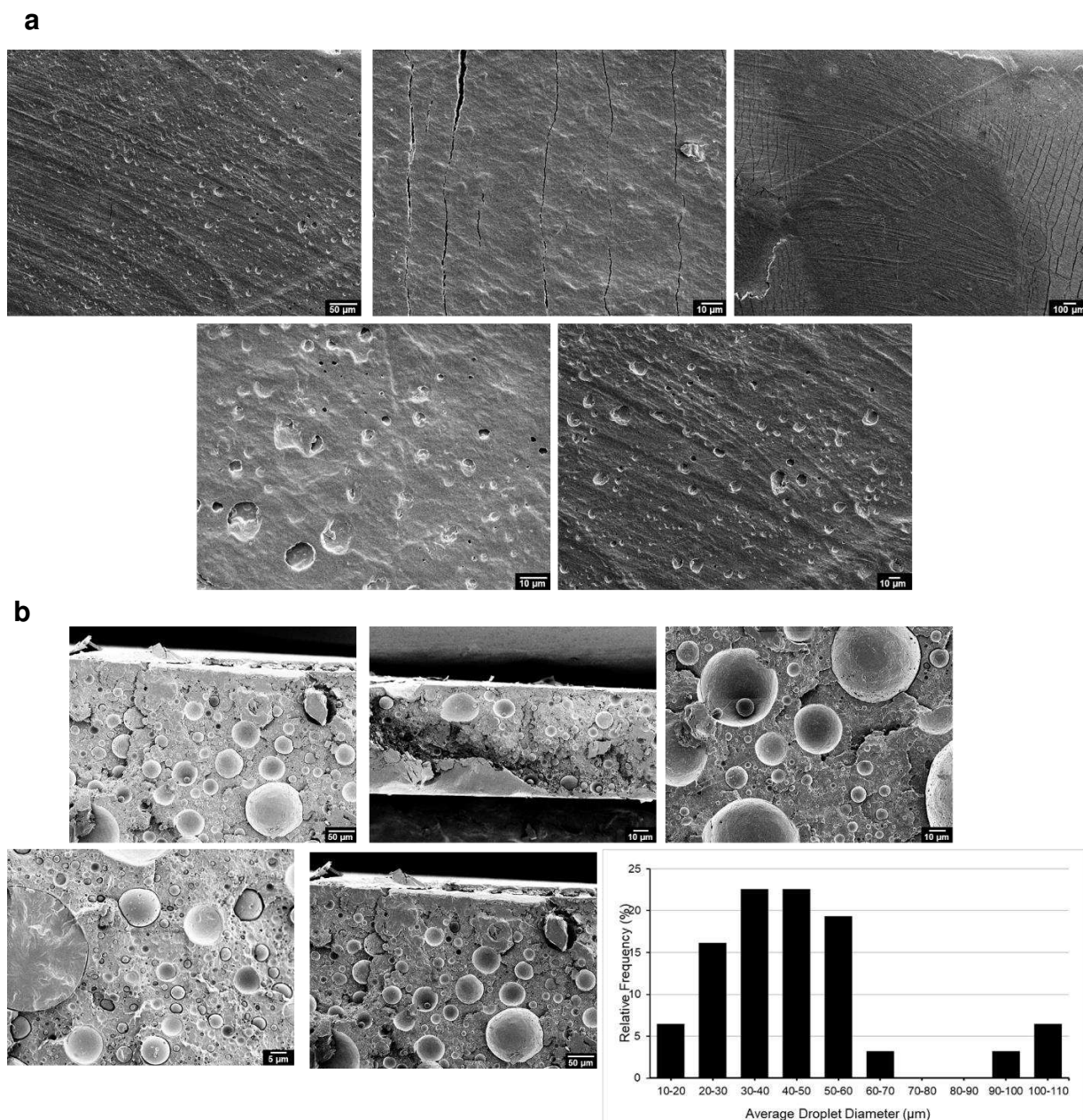
**Extended Data Fig. 5.2 | Additional SEM images. a,** Surface images of the virgin 50/50 wt.% LMWPE-P3HB blend. **b,** Cross section images of the virgin 50/50 wt% LMWPE-P3HB blend and cross-section droplet diameter size analysis.



**Extended Data Fig. 5.3 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-PLLA blend crosslinked with 5 wt.% UDC2. **b,** Cross section images of the 50/50 wt.% LMWPE-PLLA blend crosslinked with 5 wt.% UDC2 and cross-section droplet diameter size analysis.

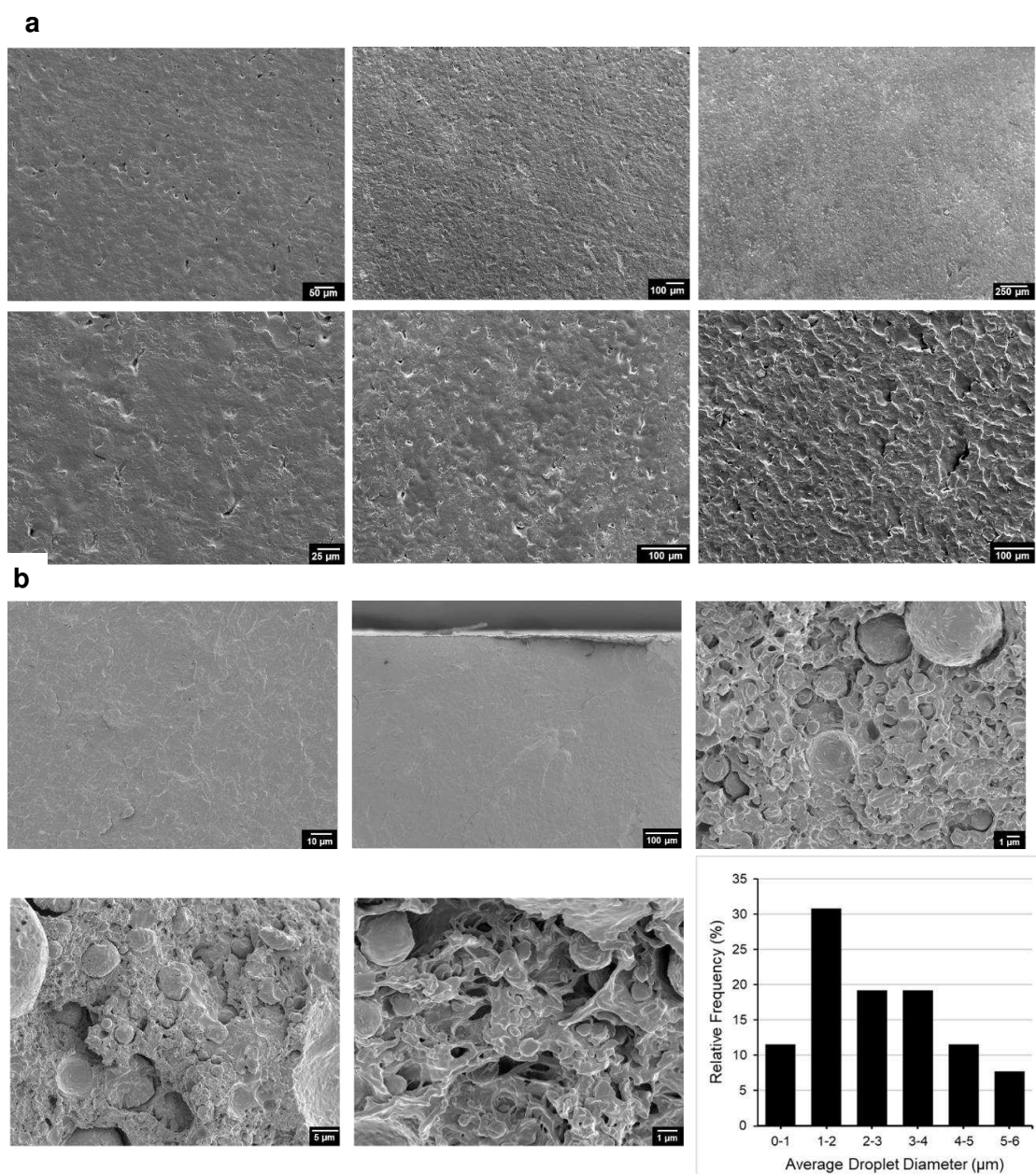


**Extended Data Fig. 5.4 | Additional SEM images. a**, Surface images of the 50/50 wt.% LMWPE-PLLA blend crosslinked with 5 wt.% USC. **b**, Cross section images of the 50/50 wt% LMWPE-PLLA blend crosslinked with 5 wt.% USC and cross-section droplet diameter size analysis.

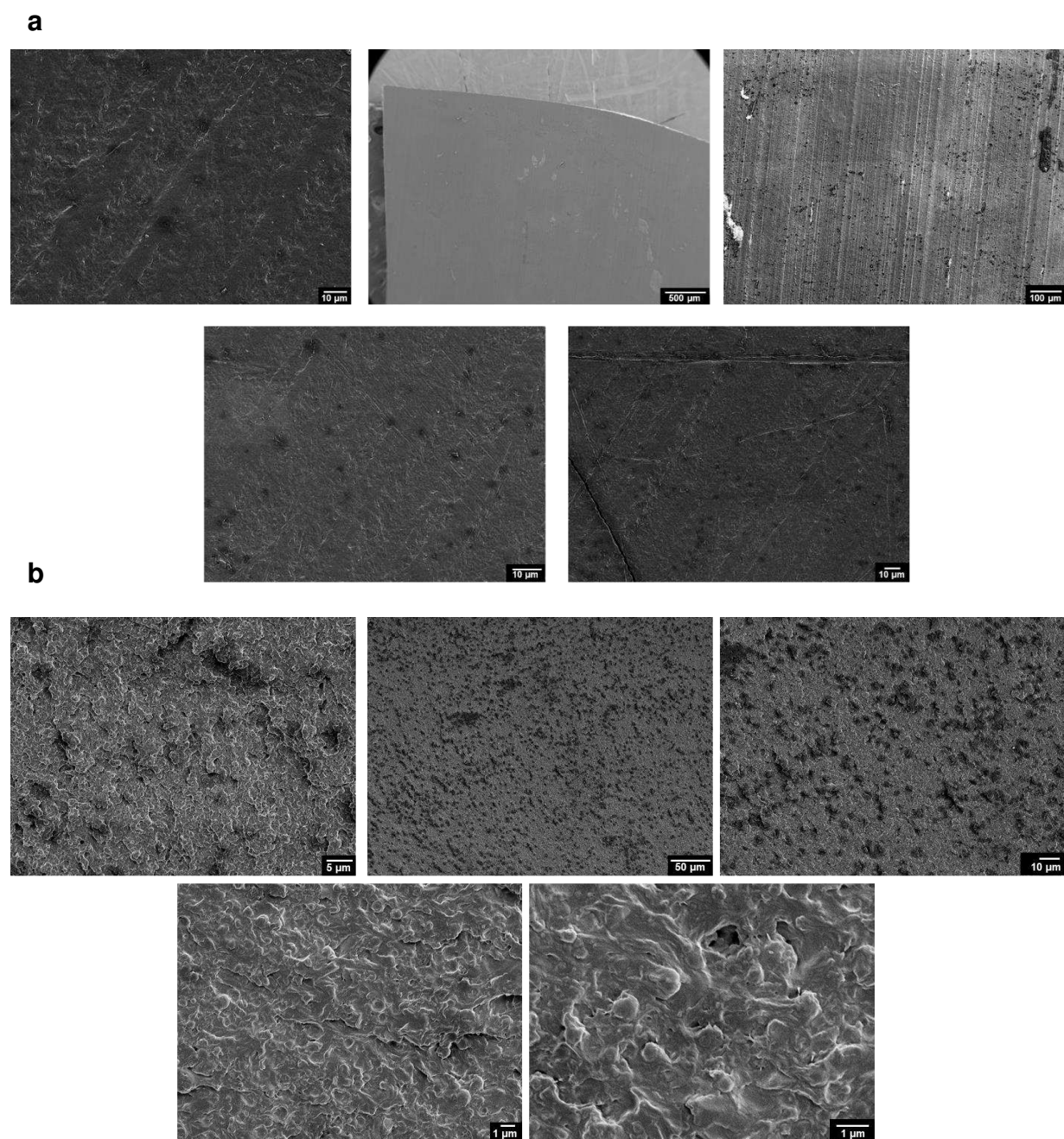




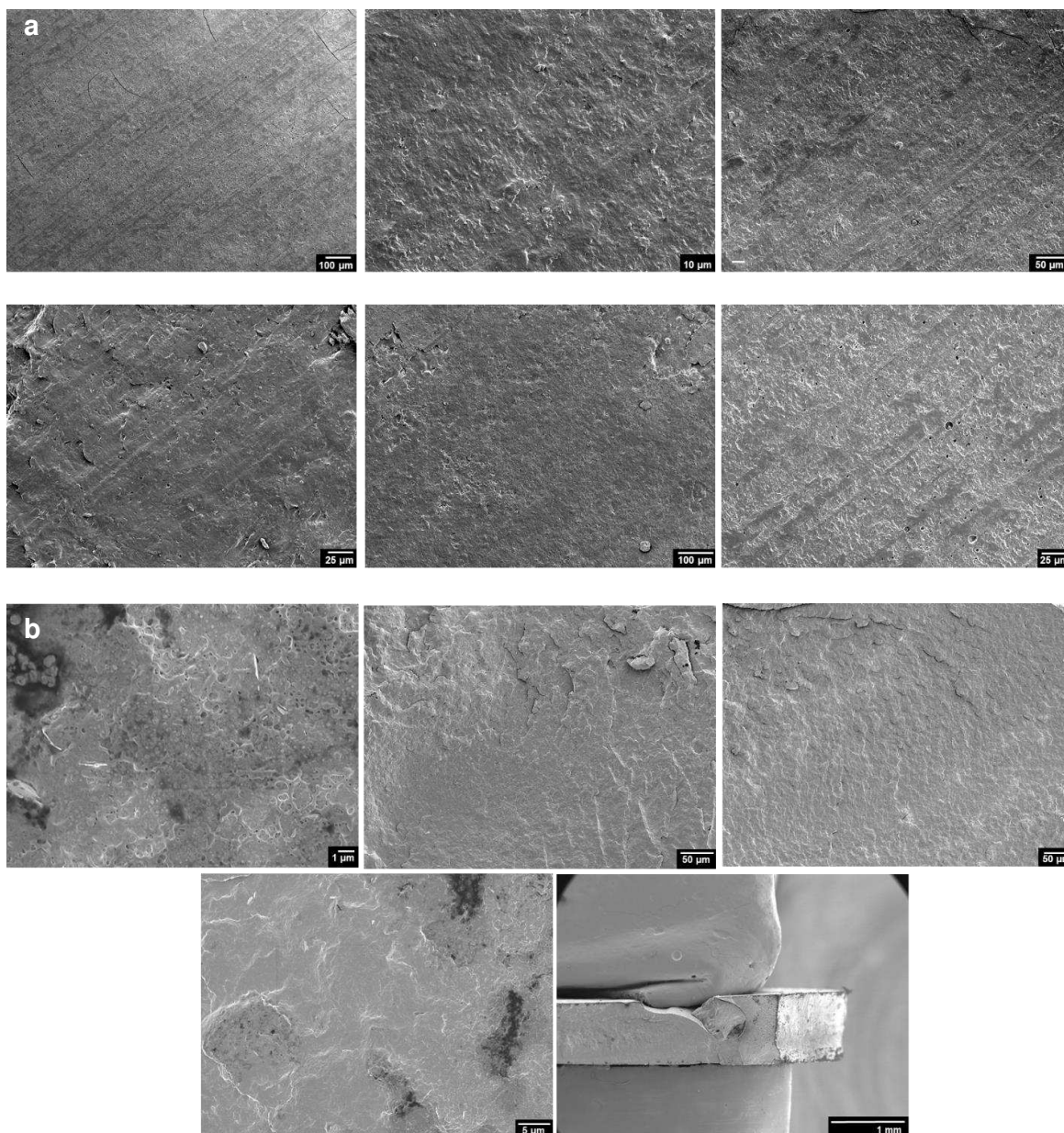
**Extended Data Fig. 5.5 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-PLLA blend crosslinked with 5 wt.% mono-diazirine MDC control. **b,** Cross section images of the 50/50 wt.% LMWPE-PLLA blend crosslinked with 5 wt.% mono-diazirine MDC control molecule and cross-section droplet diameter size analysis.



**Extended Data Fig. 5.6 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% UDC1. **b,** Cross section images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% UDC1 and cross-section droplet diameter size analysis.

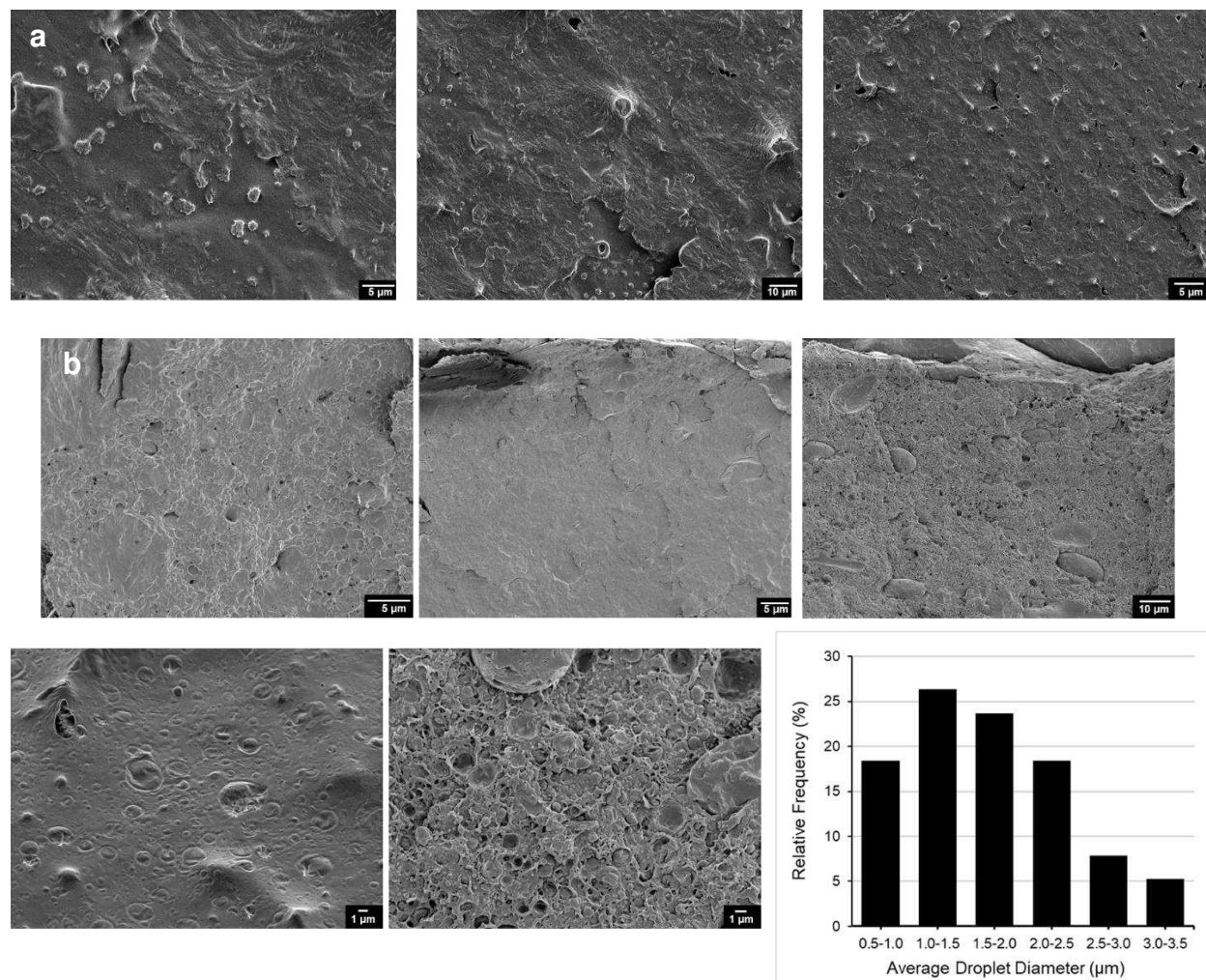


**Extended Data Fig. 5.7 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% UDC2. **b,** Cross section images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% UDC2 and cross-section droplet diameter size analysis.



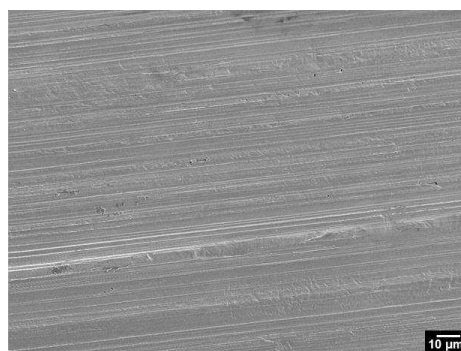
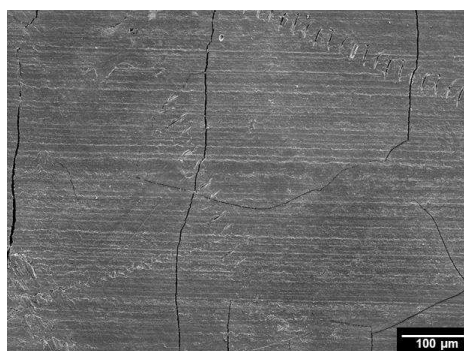
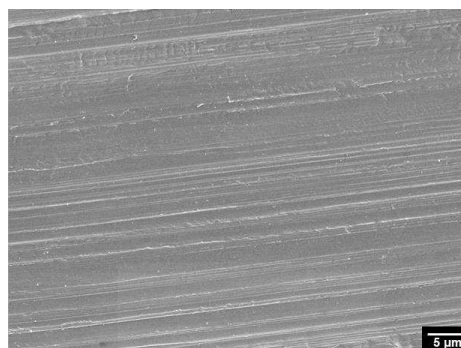
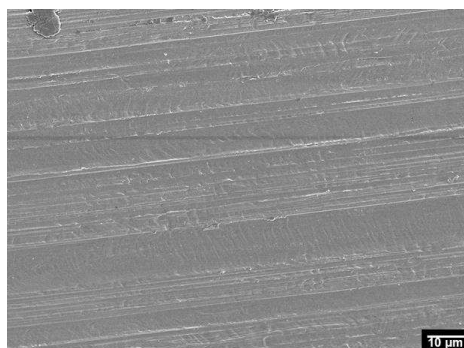


**Extended Data Fig. 5.8 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% UDC3. **b,** Cross section images of the 50/50 wt% LMWPE-P3HB blend crosslinked with 5 wt.% UDC3 and cross-section droplet diameter size analysis.

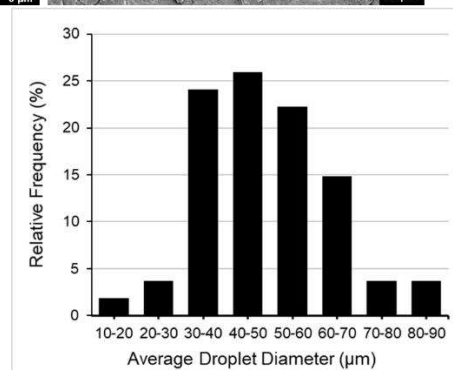
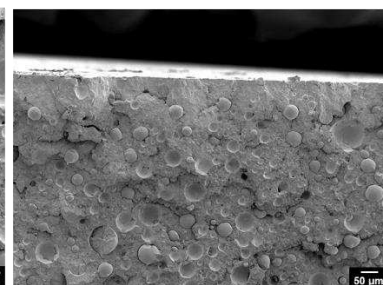
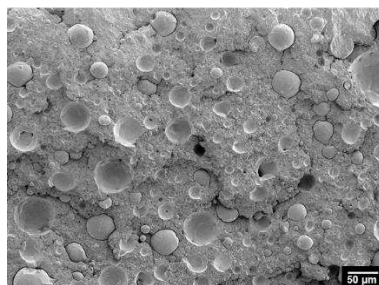
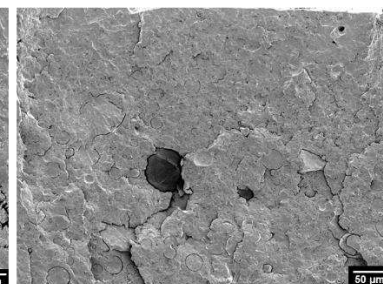
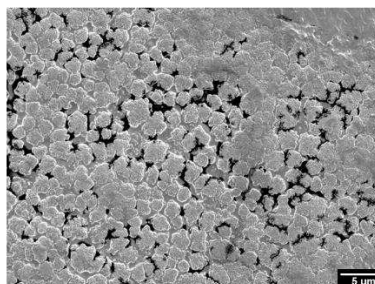
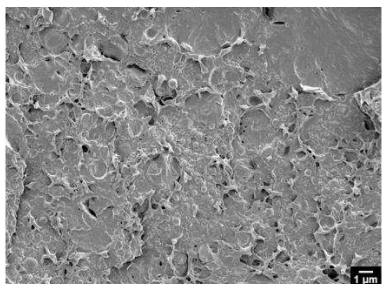


**Extended Data Fig. 5.9 | Additional SEM images. a,** Surface images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% USC. **b,** Cross section images of the 50/50 wt% LMWPE-P3HB blend crosslinked with 5 wt.% USC and cross-section droplet diameter size analysis.

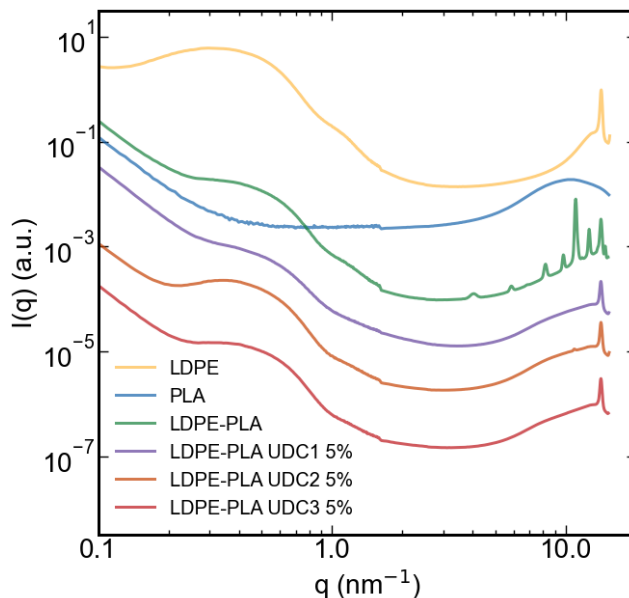
**a**



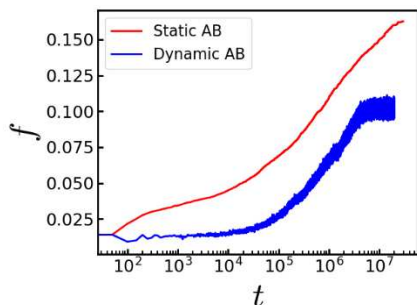
**b**



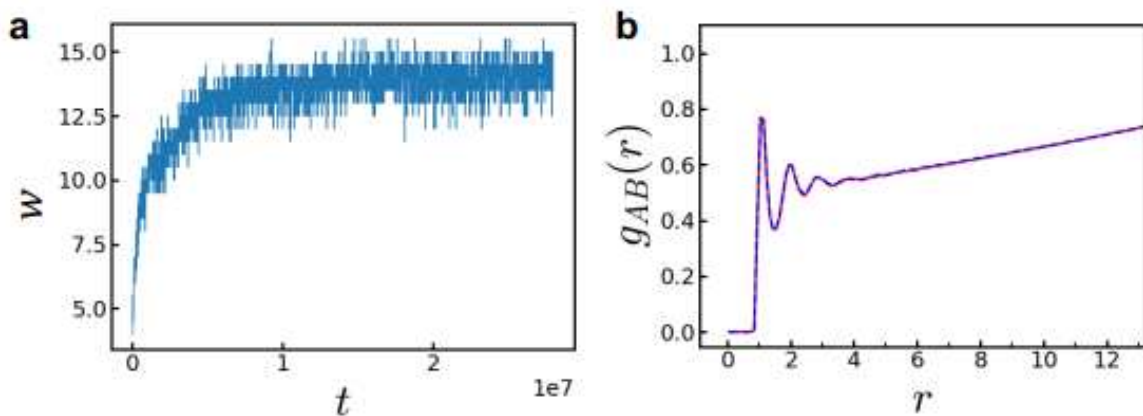
**Extended Data Fig. 5.10 | Additional SEM images.** **a**, Surface images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% mono-diazirine MDC control. **b**, Cross section images of the 50/50 wt.% LMWPE-P3HB blend crosslinked with 5 wt.% mono-diazirine MDC control molecule and cross-section droplet diameter size analysis.



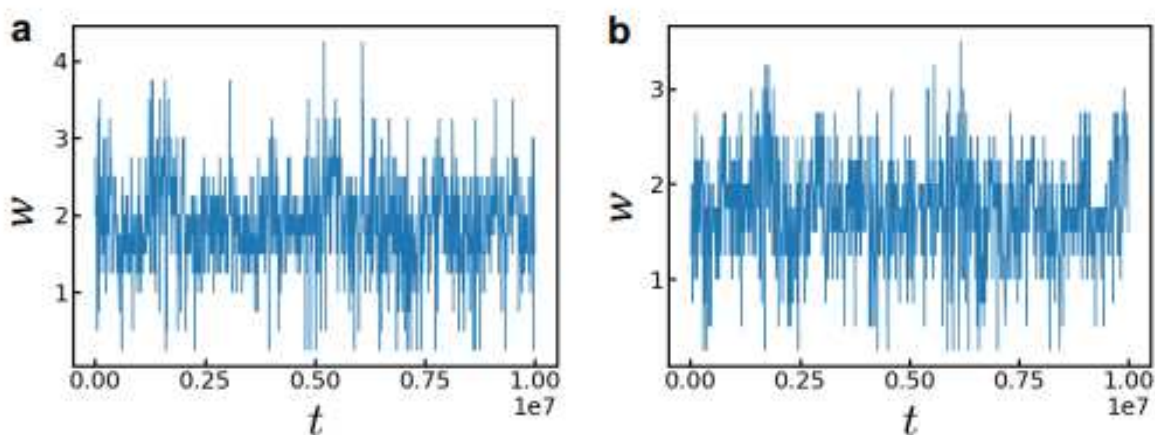
**Extended Data Fig. 5.11 | SAXS/WAXS Profile for LDPE-PLLA Blends.** Domain-averaged combination SAXS/WAXS curves for cross-linked LDPE-PLLA blends relative to virgin blend and reference homopolymers.



**Extended Data Fig. 5.12 | Time evolution of crosslink fraction.** AB crosslink fraction versus time-step for the static (red) and the dynamic (blue) crosslinks. For the static case, the crosslink fraction,  $f$ , monotonically increases and reaches 0.16 whereas for the dynamic case it equilibrates at around 0.10.

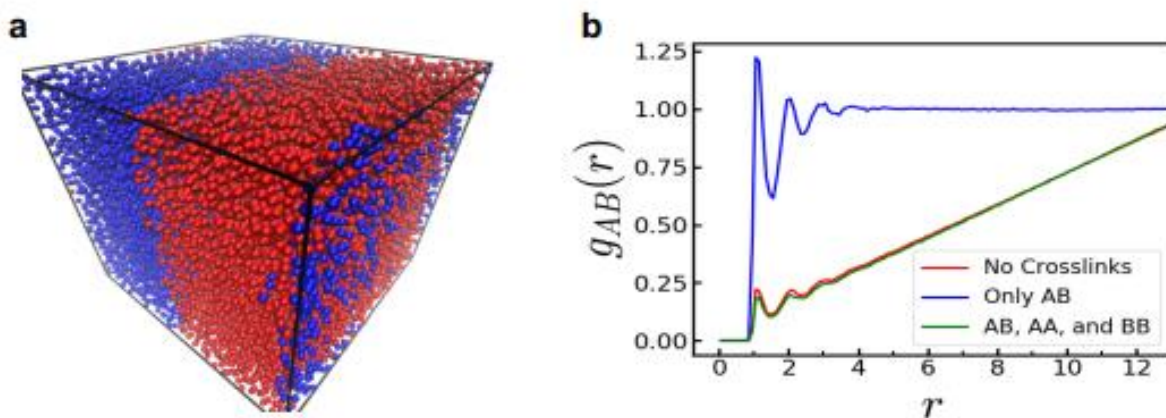


**Extended Data Fig. 5.13 | Stability of the interface with static AB crosslinks.** **a**, The interface width remains stationary at long time showing no further mixing. **b**, Completely overlapping  $g_{AB}(r)$  (at  $t = 23 \times 10^6$  and  $28 \times 10^6$  time-steps), further showing that the interface is stable and there is no more progress in mixing.



**Extended Data Fig. 5.14 | Stability of the interface with all three types of dynamic crosslinks.**

The interface width is stable when all three crosslinks are allowed. **a**, total crosslink fraction = 0.1, (AB fraction = 0.01). **b**, total crosslink fraction = 0.21, (AB fraction = 0.013).



**Extended Data Fig. 5.15 | Mixing binary melts with longer chains,  $N = 100$ .** **a**, MD snapshot of a system with all three types of crosslinks allowed showing no mixing. **b**, Radial distribution functions of three systems – binary melt with no crosslinks (red), and binary melt with all three types of dynamic crosslinks (green) indicate unmixed states, and binary melt with only AB dynamic crosslinks (blue) indicates mixing.

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## Chapter 6

### Conclusions and Outlook

#### 6.1 Conclusions and Outlook

Intensive research efforts are focused on identifying polymers that are either bio-renewable at the beginning-of-life or recyclable at the end-of-life,<sup>1,2</sup> but it is also crucial to hold discussion on the “mid-life” for sustainable polymers. These face substantial competition with petroleum-derived, single-use commodities around which our material economy infrastructure and manufacturing power has been specifically engineered to accommodate for the last 100 years or so. Modernizing away from antiquated linear material economy philosophies will require global cooperation and sacrifice to incentivize the production, collection, upcycling, and recirculation of sustainable materials for the long-term benefit of terrestrial and marine health.<sup>3</sup> The role of material scientists in promoting this initiative centers on matching or exceeding single-use plastics with sustainable alternatives at the beginning, middle, *and* end of life. The individual contributions made throughout each chapter of this dissertation expands our arsenal of tools for designing polymers with merged high performance and practical sustainability avenues via upcycling and/or mechanical recycling. This conclusion will summarize the synthetic and application advancements, as well as new fundamental principles, for sustainable polymer chemistry while pointing to future directions and opportunities made available in their wake.

Many of the biorenewable monomers or raw starting materials obtainable from lignin or biomass feedstocks exist as aromatics,<sup>4</sup> which have not been fully realized as a means to replacing those used in manufacturing high- $T_g$  commodity thermoplastics, such as polystyrene. Furthermore, the C-C backbone is a difficult motif to exercise depolymerization technology upon due to high

ceiling temperature limitations.<sup>5</sup> Indenone is one such example of a biorenewable monomer that can be polymerized to highly transparent and thermally durable ( $T_g = 307\text{ }^{\circ}\text{C}$ ) polyindenone. As depolymerization was infeasible, we turned to pyrolysis as an unconventional means for upcycling. Controlled pyrolysis for one hour in a novice quartz tube furnace under  $N_2$  atmosphere at the exact temperature of decomposition ( $T_{\text{upcycling}} = 36\text{ }^{\circ}\text{C}$ ) yielded 54 % graphene oxide (GO). As GO is an important material in electronics, though considerably expensive and energy-intensive to prepare, this observation yielded a very simple procedure to access bio-based GO with low-temperature formation.<sup>6</sup> We surmised that the ring-fused aromatic is critical in the carbon rearrangement during decomposition, providing a useful end-of-life avenue for an otherwise single-use, renewable polymer. In the few years immediately following, flash pyrolysis has earned headlines as a remarkable tool for upcycling plastics waste from pyrolyzed ash, automotive parts, and other polymers at the end-of-life into graphene and graphene oxide.<sup>7-9</sup> This technique offers significant opportunity for carbon-neutral materials that do not have effective direction for energy or material recapture at post-consumer stage. Thus, further investigation on substrate expansion and optimization of this upcycling technique, which is still very new and unexplored in most renewable polymer systems, is recommended. It is worth mentioning that pyrolysis is a simple method for polymer conversion, and the infrastructure is already in place for scaling.

Mechanical recycling was also visited as a practical means of achieving a circular materials economy in the category of thermosetting polymers. Although thermoplastics are well-known to lose material value after several reprocessing cycles, CANs are capable of retaining virgin quality performance throughout countless cycling. Since the network retains a theoretically infinite molecular weight, chain scission events are inconsequential on the resulting reprocessed mechanical performance. Recyclability of CAN materials is overshadowed, however, by

sabotaged mechanical performance at virgin or reprocessed life-stage due to trace bond exchange causing significant levels of creep during working conditions. Block copolymers exhibiting discrete micro-domain formation via self-assembly effects recently gained attention as a strategy to mitigate creep deformation by restricting network strand diffusion.<sup>10</sup> In the report by Sumerlin, diblock copolymer vitrimers exhibited enhanced creep resistance compared against random copolymers, consistent with this hypothesis. We took this one step further by mimicking the inter-networking architecture of a thermoset with a triblock copolymer assembled into a hexagonally-packed cylinder (HPC) TPE architecture, where the end blocks were inter-chain crosslinked with polyacrylic acid and polyacrylic anhydride units. Providing molecular evidence, we found overwhelming support for acid-anhydride and anhydride-anhydride exchange capabilities which allowed us to reprocess the material during compression molding. Important to note, as acid and anhydride groups are rather ubiquitous in polymer systems, this exchange offers a significantly simple path to producing catalyst- and additive-free CANs in a cost-effective manner. We also observed inability for this network to perform stress relaxation under non-compressive conditions, which led us to realize the principles governing domain-restriction: exchange events occurring within one specific domain (intra-domain) is non-productive towards macroscopic deformation, while exchange events occurring across two isolated domains (inter-domain) is productive for causing macroscopic deformation. Only under thermomechanical activation, or by using heat and compression to force domains within contact, could productive exchange occur. This set of principles is conveniently suitable for separating working (intra-domain exchange; stress, relaxation) and healing (compression) conditions, establishing full orthogonality. This work highlights a strategy to overcome performance/sustainability trade-offs in thermoset-like materials and will undoubtedly be foundational in the future design of creep-resistant block copolymer

CANs. Block copolymers have seemingly limitless tunability by varying block architecture and composition, leaving the door wide open for impactful progress and exploration.

With this in mind, we also report in Chapter 4 the progress of a manuscript in preparation regarding the rapid and scalable synthesis of discrete linear and cyclic multiblock copolymers from methyl methacrylate (MMA) and allyl acrylate (AIA) in one-pot and two-steps by CSC-LPP. It is noteworthy that, to the best of the author's knowledge at the time of writing this dissertation, this report marks the first example of a cyclic block copolymer with complexity beyond the A-B-C ternary stature. Several lines of evidence are presented in support of the cyclic topology against that of the linear analogue, while we draw conclusions on methods for distinguishing the A-B-A-B cyclic architecture against that of a compositionally isomeric A-B diblock copolymer. Interestingly enough, there are also no reports on CANs constructed from cyclic parent polymers. This is surprising as numerous behavioral differences between linear and cyclic polymers could be leveraged for advantageous material properties in cyclic CANs. For example, cyclic polymers have reduced melt viscosity, higher glass transition temperatures, higher storage moduli, and higher decomposition temperatures, among other properties. These properties can be exploited to improve processability, toggle activation energy, and increase thermomechanical durability in recyclable thermosets. As the AIA block contains a pendant allylic group, there are numerous dynamic covalent bond groups that can be installed with simple conditions via thiol-ene click chemistry. We hold high confidence that development of linear and cyclic multiblock copolymers, equipped to flex our domain-restriction principles and thus thermoset-like creep resistance, will aide tremendously in future investigations of rapidly processable, thermally superior recyclable networks.



Finally, our contribution on universal dynamic crosslinkers is hoped to afford a breadth of research opportunities that will expand to numerous polymer-focused groups. There are several categories which will be highly fruitful to investigate: identifying new crosslinkers with increased stability and new core groups, crosslinking of other commodity thermoplastics, and applying the foundational concepts of blend compatibilization to binary (and beyond) blends of other thermoplastic combinations with various performance properties. While we provide the molecular scaffolding for thioester, disulfide, and anhydride exchange, there are several popular dynamic covalent bond motifs that have yet to be implemented and explored for universal dynamic crosslinking. We urge material scientists specializing in specific dynamic functional groups to take on the challenge of incorporating their system into this framework. Beyond polyethylene, polypropylene, polylactic acid, and poly-3-*R*-hydroxybutyrate, UDCs can be expanded to encompass other mass-produced consumer plastics that we did not include, such as polyethylene terephthalate, polystyrene, and polyvinyl chloride, among many other viable candidates for C-H insertion upcycling. Most critically, we hope this contribution will serve to inspire future directions in the realm of polymer blend upcycling via dynamic crosslink compatibilization. As mentioned in multiple lines of this dissertation, mechanical recycling is severely complicated by commodity thermoplastic immiscibility upon mixed-feed melt processing. As such, there are enticing implications for establishing a thorough understanding of binary and multi-component blends consistent with multi-polymer consumer materials that ultimately hinders the true potential of mechanical recycling. We hope that our dynamic crosslinker compatibilization technology will be further investigated alongside our own future efforts to make meaningful progress in mixed-feed waste recirculation.

I end this conclusion with high hopes for the future design and development of recyclable polymers. In the last decade or so, tremendous progress has been made in laying the groundwork for industrial implementation which will undoubtedly accumulate to global adoption with time. This progress is in part due to the fundamentally fascinating chemistry that is offered by working with macromolecules, and the rewarding experience to those who choose to pursue it. I have been fortunate enough to study the physical properties of these materials by means of tensometry, rheology, and microscopy, all very stimulating techniques for material characterization tangential with polymer physics and structure/property relationships. I hope more scientists will take the time to explore the niche field of deformation science and apply the principles therein to processing, performance, and application of recyclable polymers – without rheology expertise, we can only highlight our examples of beautiful chemistry in the frame of academia. I also want to leave off with a favorite quote that I have been lucky enough to read each day on my way to my place of work: “If I have seen further, it was by standing on the shoulders of giants” – Isaac Newton. There is no great contribution that each individual makes on their own, let alone from fully original concept – recognizing this has granted a deep sense of humility and appreciation for the historic strides in scientific innovation that have afforded me the opportunities to pursue my own.

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## Appendix A

### Supplementary Information Corresponding to Chapter 2<sup>g</sup>

#### General Methods

All syntheses and manipulations of air and moisture sensitive materials were carried out in flame dried Schlenk-type glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N<sub>2</sub>)-filled glovebox. HPLC-grade organic solvents for catalyst synthesis and polymerization experiments were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for dichloromethane) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Toluene, hexanes, THF, and benzene-*d*<sub>6</sub> were further dried and purified over Na/K for 24 hours and filtered over a fine-frit filter. Dichloromethane (DCM) and chloroform-*d*<sub>1</sub> were dried over activated calcium hydride for 24 h and vacuum-distilled at 1 atm. All inert solvents were stored over Davidson 4 Å molecular sieves in an inert glovebox. Structural characterizations as well as polymer ditacticity measurements were recorded on either an Agilent (Varian) 400MR (FT 400 MHz, <sup>1</sup>H, 100MHz <sup>13</sup>C), a Bruker AVIII (US) 400 MHz spectrometer (FT 400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C), or an Agilent Inova 500 MHz spectrometer (FT 500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C). Chemical Shifts for <sup>1</sup>H NMR were referenced to internal solvent signals corresponding to 7.26 ppm (chloroform) and 7.16 ppm (benzene) and are reported as parts per million relative to SiMe<sub>4</sub>.

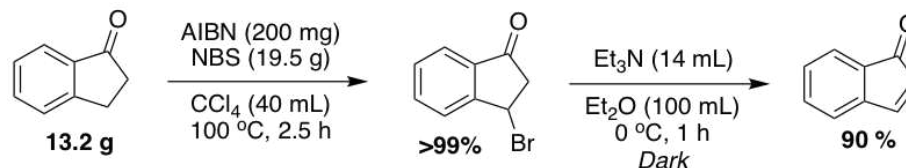
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<sup>g</sup>Taken verbatim from: R. W. Clarke, M. L. McGraw, R. R. Gowda, E. Y.-X. Chen. Lewis Pair Polymerization of Renewable Indenone to Erythro-Ditactic High *T*<sub>g</sub> Polymers with an Upcycling Avenue. *Macromolecules* **53**, 640–648 (2020).

## Materials

1-Indanone was purchased from Beantown Chemical Co. and used as received. Trimethylaluminum, triethylaluminum, triisobutylaluminum, triethylamine, and 2,2-azobisisobutyronitrile were purchased from Aldrich Chemical Co. and used as received. *N*-bromosuccinimide and dimethylketene methyl trimethylsilyl acetal (<sup>Me</sup>SKA) were purchased from TCI Chemicals and used as received. Tris(pentafluorophenyl)borane (FAB) was obtained from Boulder Scientific Co. as a research gift and purified twice by sublimation at 40 °C under vacuum. Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenol) (MAD) and *N*-heterocyclic olefin (NHO) 1,3-dimethyl-4,5-diphenyl-2-(propan-2-ylidene)-2,3-dihydro-1H-imidazole were synthesized according to literature procedures.<sup>1,2</sup>

## Synthesis of indenone



Indenone was synthesized following an adapted procedure at an increased (10x) scale.<sup>3</sup>

### (i) 3-bromo-indan-1-one:

1-Indanone (13.2 g, 0.1 mol) was added into a 100 mL RBF with a stir bar and 40 mL of CCl<sub>4</sub>. *N*-bromosuccinimide (19.5 g, 0.11 mol) and AIBN (200 mg, 1.22 mmol) were added to the reaction vessel and the mixture was refluxed at 100 °C for 2 h under vigorous stirring. The resulting suspension was cooled to room temperature, passed through a celite filter, and concentrated under vacuum (21.0 g, 99.6 %).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.70 (d,  $J$  = 7.8 Hz, 1H), 7.66 (d,  $J$  = 4.1 Hz, 2H), 7.44 (dt,  $J$  = 8.0, 4.0 Hz, 1H), 5.57 (dd,  $J$  = 7.2, 2.7 Hz, 1H), 3.32 (dd,  $J$  = 19.8, 7.2 Hz, 1H), 3.00 (dd,  $J$  = 19.7, 2.7 Hz, 1H).

(ii) Indenone:

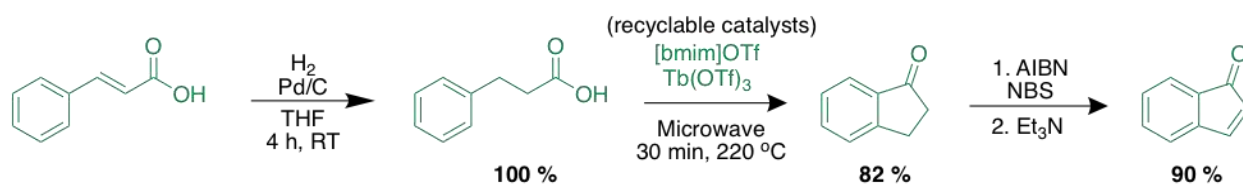
All prior synthesized 3-bromo-indan-1-one compound (99.5 mmol) was dissolved in 100 mL of ether. The flask was covered in foil (to prevent photoinitiated autopolymerization) and cooled to 0 °C. Triethylamine (14 mL, 1.0 eq) was then added dropwise over 10 minutes, producing a yellow precipitate. The mixture was stirred for an additional h before the reaction was quenched with 100 mL of water. The ether layer was separated, washed with 3 x 100 mL water, and washed with brine. Ether was removed under vacuum, and the crude product was purified by flash column chromatography (Hex/EtAcO, 5:1). Indenone was isolated with 90% yield following additional drying over a Schlenk line vacuum to obtain a vibrant orange oil (11.74 g, 90.4 %).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 (d,  $J$  = 6.0 Hz, 1H), 7.42 (d,  $J$  = 7.1 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.22 (t,  $J$  = 7.4 Hz, 1H), 7.05 (d,  $J$  = 7.2 Hz, 1H), 5.88 (d,  $J$  = 5.9 Hz, 1H).

### Storage of indenone

Freshly synthesized indenone was collected and the mass was recorded. A Schlenk flask was separately prepared with activated  $\text{CaH}_2$  and a precise volume of DCM to make a 100 mg/mL (0.77 M) stock solution of indenone. Monomer stock solution was dried over  $\text{CaH}_2$  for 1 h at 0 °C before filtration over a fine-frit filter in an inert glovebox. The dried solution was stored in an amber bottle in an inert glovebox freezer at -30 °C. Monomer was used for polymerization experiments within 1 week of synthesis and storage.

### Synthesis of indanone from cinnamic acid



**Figure A1.** Indenone from renewable feedstock cinnamic acid.<sup>4,5</sup>

(i) Hydrogenation of cinnamic acid:

Cinnamic acid was catalytically hydrogenated by dissolving cinnamic acid (0.25 M) in THF in a 2-neck round bottom flask. The mixture was treated with 0.1 mol % SiliaCat Pd<sup>0</sup> sol-gel-entrapped catalyst (0.05 mmol/g load) and then degassed two times, replacing the voided atmosphere with hydrogen in each attempt. The reaction vessel was then treated with hydrogen gas under hydrogen balloon, room temperature, and vigorous stirring conditions for 2 h. The catalyst was filtered off, rinsed with THF, and the filtrate was collected and concentrated to achieve the hydrogenated product (100 %).

(ii) Friedel-Crafts acylation of dihydro-cinnamic acid to 1-indanone:

A glass vessel was charged with Tb(OTf)<sub>3</sub> (0.1 mmol), [bmim]OTf (0.1 g), and dihydro-cinnamic acid (1 mmol), and the reaction was heated to 220 °C for 30 min under microwave irradiation. After cooling, the product was extracted into diethyl ether (3 x 20 mL). The ether layers were combined and subsequently washed with water (10 mL), Na<sub>2</sub>CO<sub>3</sub> (aq, 2 x 20 mL), brine, and dried over MgSO<sub>4</sub>. The solution was filtered and concentration under reduced pressure to achieve crude 1-indanone. The product was purified by flash column chromatography (hexane 100%, then hexane/ethyl acetate 9:1) (82 %).

(iii) Synthesis of indenone from renewable 1-indanone:

The final step, synthesis of indenone from 1-indanone by Wolf-Ziegler bromination and subsequent elimination, was the same as from the description above (90.4 %).

## General Polymerization Procedures

All polymerizations were carried out in an Ar-filled glovebox at room temperature in either 3-, 5-, or 20 mL scintillation vials charged with a stir-bar and wrapped in aluminum foil to prevent photochemically-initiated autopolymerization. Typical polymerization consisted of the pre-activation of indenone by mixing monomer stock solution (specified in data table) with Lewis acid (LA) and stirring for 5 minutes. The <sup>Me</sup>SKA or NHO initiator was then injected quickly into the LA-coordinated monomer solution. Stock solutions of <sup>Me</sup>SKA (10 μL in 1 mL DCM) were employed where initiator loadings of 0.1 % or below were specified, for accuracy purposes. NHO stock solutions, prepared in toluene to prevent decomposition by DCM, were similarly employed for low initiator loadings. Completed polymerizations were removed from the glovebox and slowly quenched/precipitated/washed with excess acidified methanol (5 % HCl). Polymers achieving high erythro-ditacticity would gel, and upon purification, exhibited insolubility in common organic solvents. In this case, the polymer was dissolved in trifluoroacetic acid and subsequently precipitated by slow addition of excess methanol. Precipitated polymer was filtered over a fine-frit filter and dried in a 60 °C vacuum oven until a constant mass was achieved. Due to overlapping polymer/monomer signals in <sup>1</sup>H NMR spectra, yield % was reported in the place of conversion – where 99 % isolated yield was expected to have achieved full conversion.

## Polymer Characterization

Measurements of polymer absolute weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and molecular weight distributions or dispersity indices ( $\mathcal{D} = M_w/M_n$ ) were performed via GPC. The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and two PL gel 5 μm mixed-C gel permeation columns and coupled with a Wyatt



DAWN HELEOS II multi (18)-angle light scattering detector and a Wyatt Optilab TrEX  $dRI$  detector; the analysis was performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL/min, using Wyatt ASTRA 7.1.2 molecular weight characterization software. The refractive index increment ( $dn/dc$ ) of the poly(indenone) was determined to be 0.1636 mL/g obtained by batch experiments using Wyatt Optilab TrEX  $dRI$  detector and calculated using ASTRA software. Polymer solutions were prepared in chloroform and injected into  $dRI$  detector by Harvard Apparatus pump 11 at a flow rate of 0.25 mL/min. A series of known concentrations were injected and the change in refractive index was measured to obtain a plot of change in refractive index versus change in concentration ranging from 0.5 to 5.0 mg/mL. The slope from a linear fitting of the data was the  $dn/dc$  of poly(indenone).

### **Thermal Analysis.**

Thermal gravimetric analysis (TGA) was used to record the decomposition temperature ( $T_d$ ) on a Q50 TGA Analyzer (TA Instrument). Polymer samples (10 mg) were heated from 25 °C to 700 °C at a 10 °C/min heating rate. The  $T_d$  – labeled on TGA curves – represents the temperature of 5.00% weight loss. Differential Scanning Calorimetry (DSC) was performed on thoroughly dried polymer samples on an Auto Q20 (TA Instrument) in a platinum pan with a platinum lid. DSC plots represent the thermal response to 10 °C/min heating and cooling scans from 0 °C to between 280-360 °C on the second heating scan – once thermal history was removed during the first scan. Glass transition temperature ( $T_g$ ) is labeled on the reported plots.

### **Optimized Pyrolysis of Poly(indenone) for Upconverting to GO**

To achieve the maximal upconversion of Pin to GO, a quartz tube was heated to 150 °C under flowing N<sub>2</sub> (g) for 15 minutes to purge the tubing of any trace water or oxygen. Following the

allotted 15 minutes, a GO-coated boat filled with 500 mg of poly(indenone) is placed into the tube furnace and heated to 360 °C for 1 h. The tube furnace is allowed to cool to room temperature, and the silver/black metallic product is removed from the boat and weighed. (270 mg, 54 %).

### **Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy (MALDI-TOF MS)**

MALDI-TOF MS was recorded for low-molecular weight poly(indenone) samples using an Ultraflex MALDI-TOF mass spectrometer (Bruker Daltonics) operated in positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 kV accelerating voltage. A thin layer of 1% NaI solution was first deposited and dried on the 96-spot target plate, followed by 0.6  $\mu$ L of both poly(indenone) (10 mg/mL in  $\text{CHCl}_3$ ) and matrix (dithranol, 20 mg/mL in  $\text{CHCl}_3$ ). Insoluble Pin samples were deposited onto the spot-plate as a suspension in  $\text{CHCl}_3$ . External calibration was done using a peptide calibration mixture (4 to 6 peptides) on a spot adjacent to the sample. Raw data from was further processed in the FlexAnalysis software (Version 2.4, Bruker Daltonics), and the figures were plotted using the open-access mMass software.

### **Optical Analysis.**

Total transmittance ( $T_t$  %) data was recorded using an Agilent Cary 5000 UV/Vis/NIR spectrophotometer instrument between 300-1000 nm wavelengths. Background subtraction (blanking) was performed using a glass slide cleaned thoroughly with DCM/Acetone. To achieve reflectance, diffusion transmittance, and haziness values, the same Agilent Cary 5000 UV/Vis/NIR spectrophotometer instrument was employed fitted with a DRA (Diffuse Reflectance Accessory) detector. The thin film sample was analyzed between 300-1000 nm, and haziness was calculated from the diffusion transmittance and the total transmittance values, shown in greater detail below.

### **Powder X-Ray Diffraction (pXRD)**

pXRD samples for poly(indenone) with no selectivity and 75 % erythro-ditacticity were prepared by fine-grounding 500 mg of designated polymer, while 1.0 g of 75 % erythro polymer was placed in a quartz tubing and heated to 360 °C by a tube furnace under a steady flow of nitrogen gas. The resulting pXRD spectra were recorded on a Bruker D8 Discover Davinci Powder X-Ray Diffractometer with CuK $\alpha$  radiation and LYNXEYE-XE-T energy discriminating detector.

### **Raman Spectroscopy**

Single reported spectrum was measured in air at room temperature. 532 nm excitation source was directed through a 100x NA0.95 air objective (Olympus PlanFL N100X) and illuminated a 0.7  $\mu$ m-diameter spot at the focal plane. Raman signals were collected and filtered by an Ondax 532 nm THz Raman system, passed through a Horiba iHR550 spectrometer, and then detected by the Synapse CCD detector. Spectrum acquired at power density 1.9 MW/cm<sup>2</sup> for 60 seconds over a spectral range from 10 – 500 cm<sup>-1</sup>. Step size = 1  $\mu$ m. Glass slides were used to “blank” the instrument prior to the experiments.

### **Scanning Electron Microscopy (SEM)**

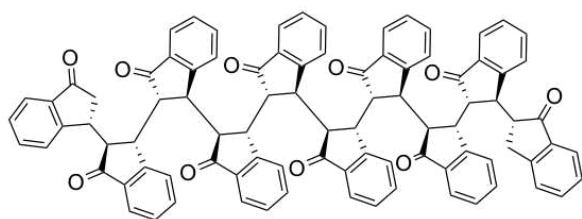
The SEM images were taken from JEOL JSM-6500F scanning electron microscope at a working voltage of 1.0-15 kV. *Sample Preparation 1:* The sample was mounted on the holder using double-sided conductive carbon tape prior to SEM characterization. *Sample Preparation 2:* The sample was coated with a thin layer of gold using a sputter-coater prior to SEM characterization.

### **Thin-Film Preparation**

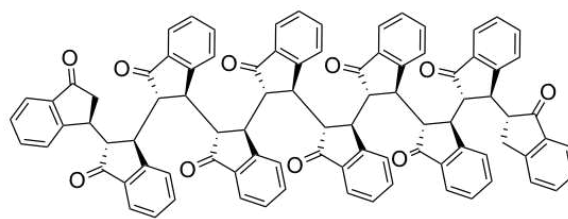
Poly(indenone) (500 mg) was prepared by group transfer polymerization of indenone using  $\text{LA B}(\text{C}_6\text{F}_5)_3$  and  $\text{LB}^{\text{Me}}\text{SKA}$ . The polymer was dissolved in 20 mL of  $\text{CHCl}_3$  at 40 °C and then filtered through a clean, fine-frit filter. The solution was solvent casted to a thin film over a glass surface and layered multiple times until all  $\text{CHCl}_3$  had evaporated. The thin, transparent samples were measured for thickness using micrometer calipers.

## Molecular Mechanics 2

The MM2 calculations provided in the main text as support in discussions on the erythro-diisotactic selectivity, enhanced crystallinity, enhanced thermal properties, and plausible helical conformation taken by highly erythro-diisotactic Pin were generated by the inputting the following ChemDraw 3D structures:



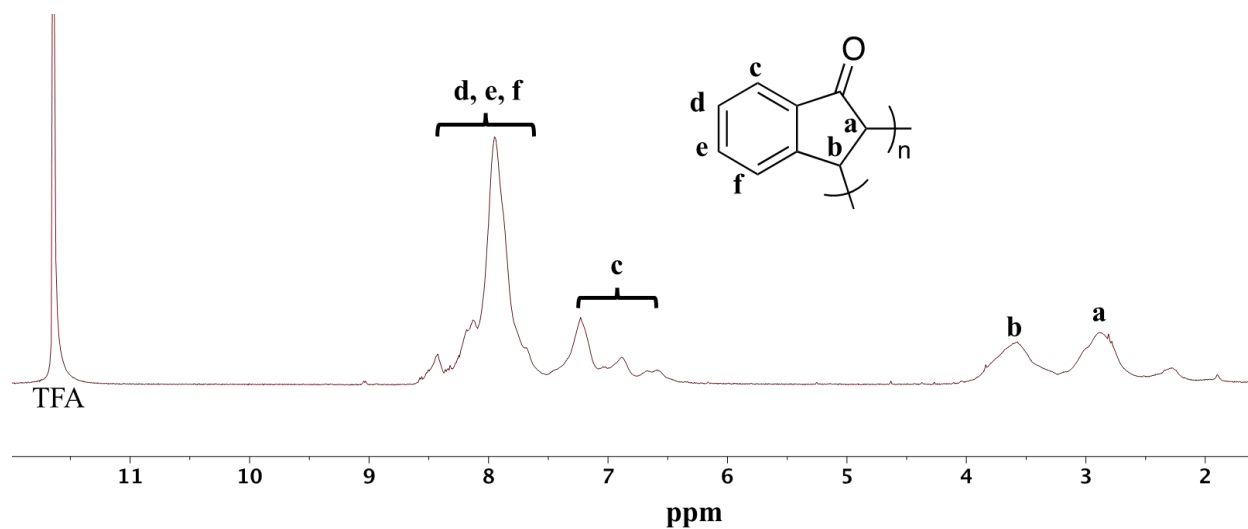
*Erythro-diisotactic*



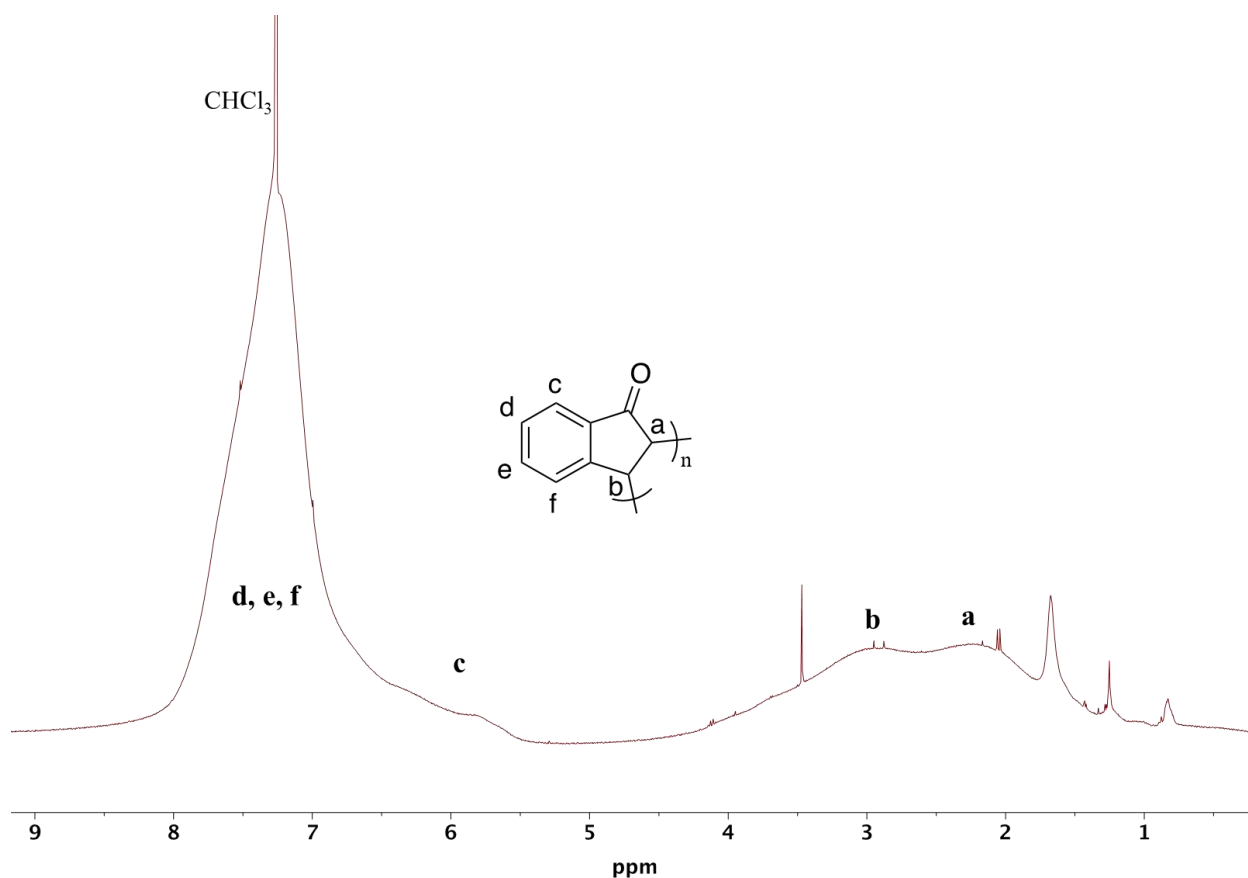
*Erythro-disyndiotactic*

The inputted samples were then modeled to a 3D structure, following the “MM2 Minimize” command adopted the most energetically favorable conformation. The left structure yielded the observed  $5_1$  helices (erythro-diisotactic) while the right yielded a random chain coil (erythro-disyndiotactic). Hydrogen atoms and lone pairs have been removed for clarity.

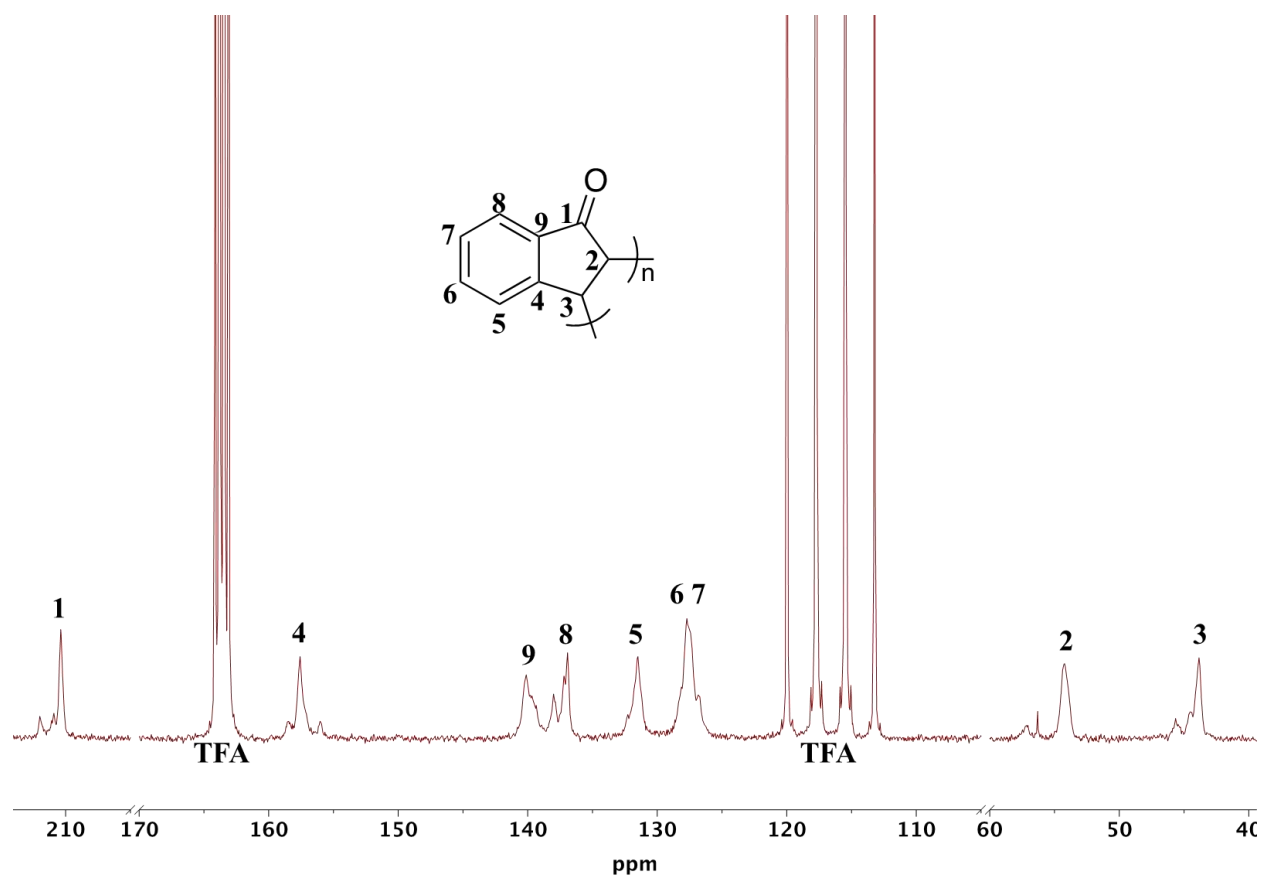
## Supporting Figures



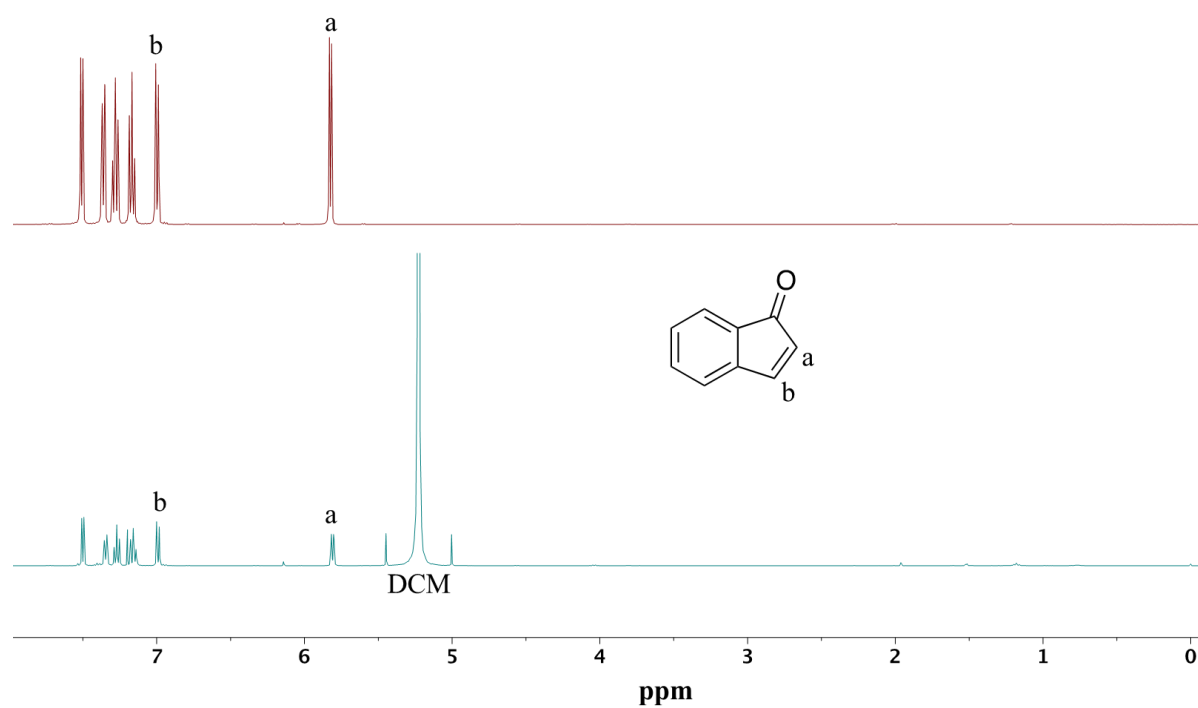
**Figure A2.** Typical  $^1\text{H}$  NMR for 75 % erythro-ditactic poly(indenone) produced by LPP in  $\text{TFA-}d_1$ . Several peaks correlated to a single proton are credited to differing stereochemistry.



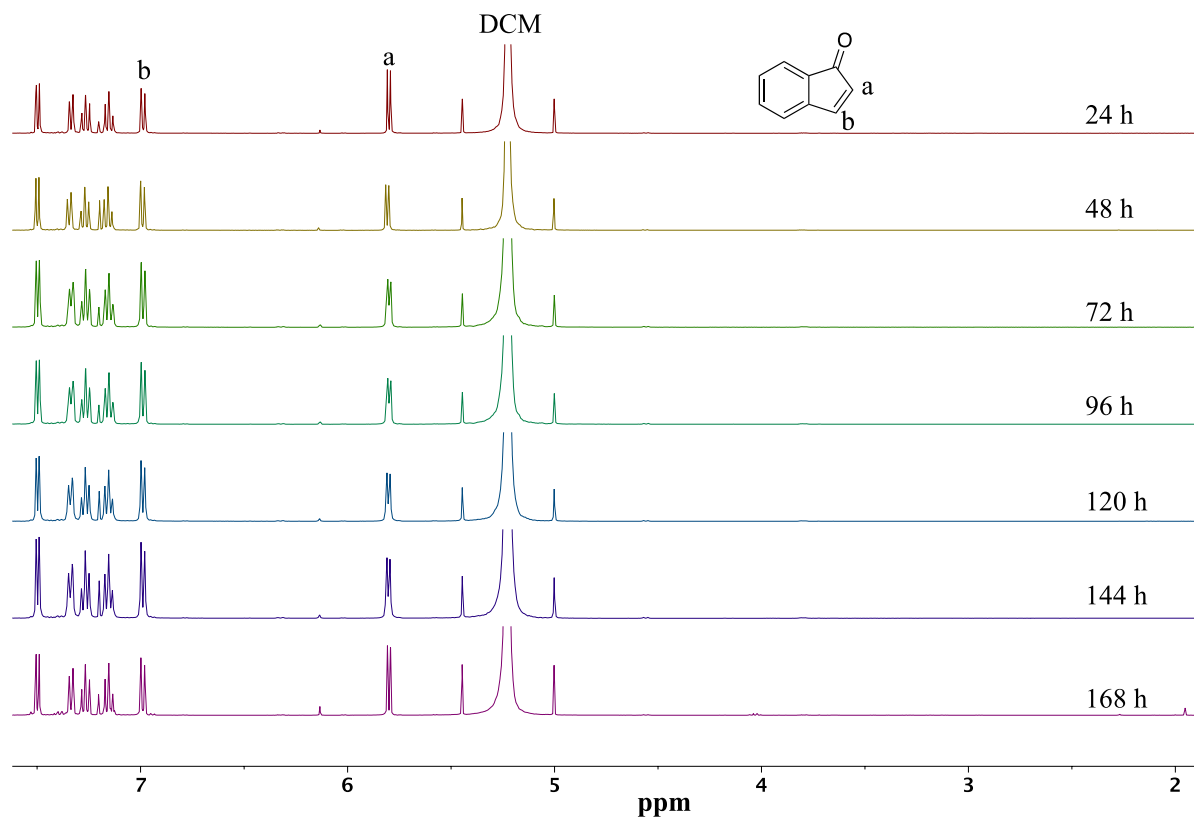
**Figure A3.** Typical  $^1\text{H}$  NMR for atactic, autopolymerized indenone ( $\text{CDCl}_3$ ). Worth highlighting is the intense broadness for each peak, a consequence of sixteen possible stereoisomers.



**Figure A4.** Full-scale  $^{13}\text{C}$  NMR for Pin sample with 75 % erythro-ditactic content (carbonyl; peak 1).

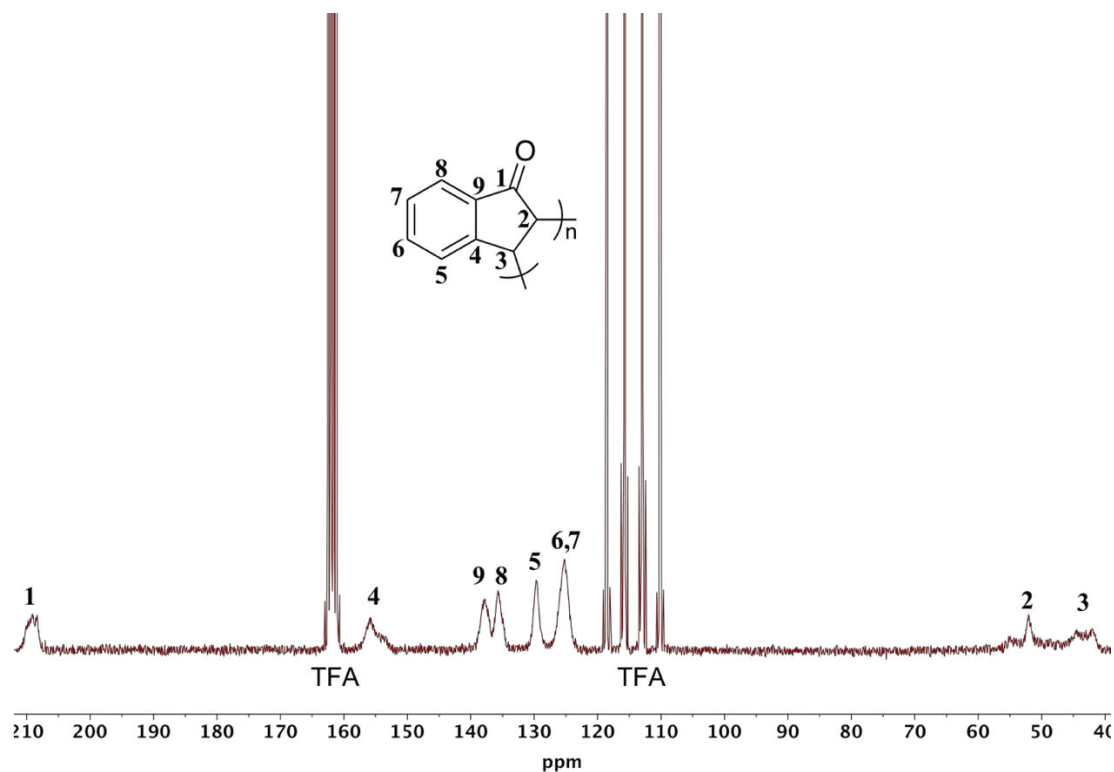


**Figure A5.** Monomeric indenone (top), and 100 mg/mL (DCM) monomer stock solution for polymerization experiments (bottom).

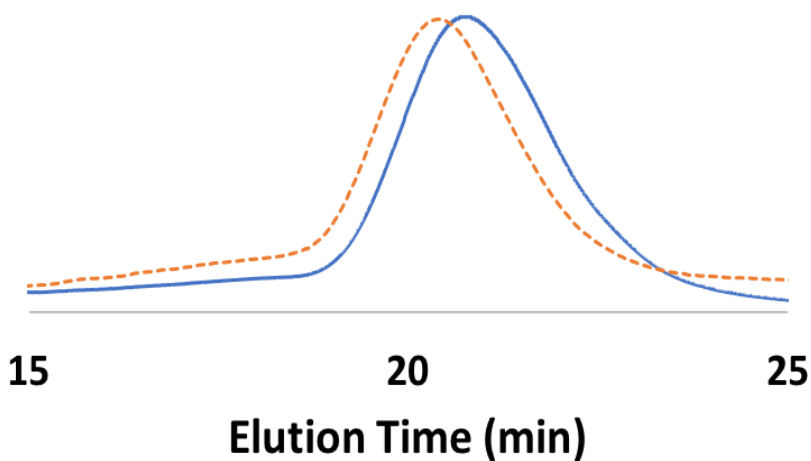


**Figure A6.** Stacked  $^1\text{H}$  NMR spectra of the monomer stock solution over the course of 7 days while stored in an amber bottle at  $-30\text{ }^\circ\text{C}$  to investigate storage method. No autopolymer signals are observed during this period (2.0 – 4.0 ppm) and supports the longer-term usability of indenone for clean polymerizations.

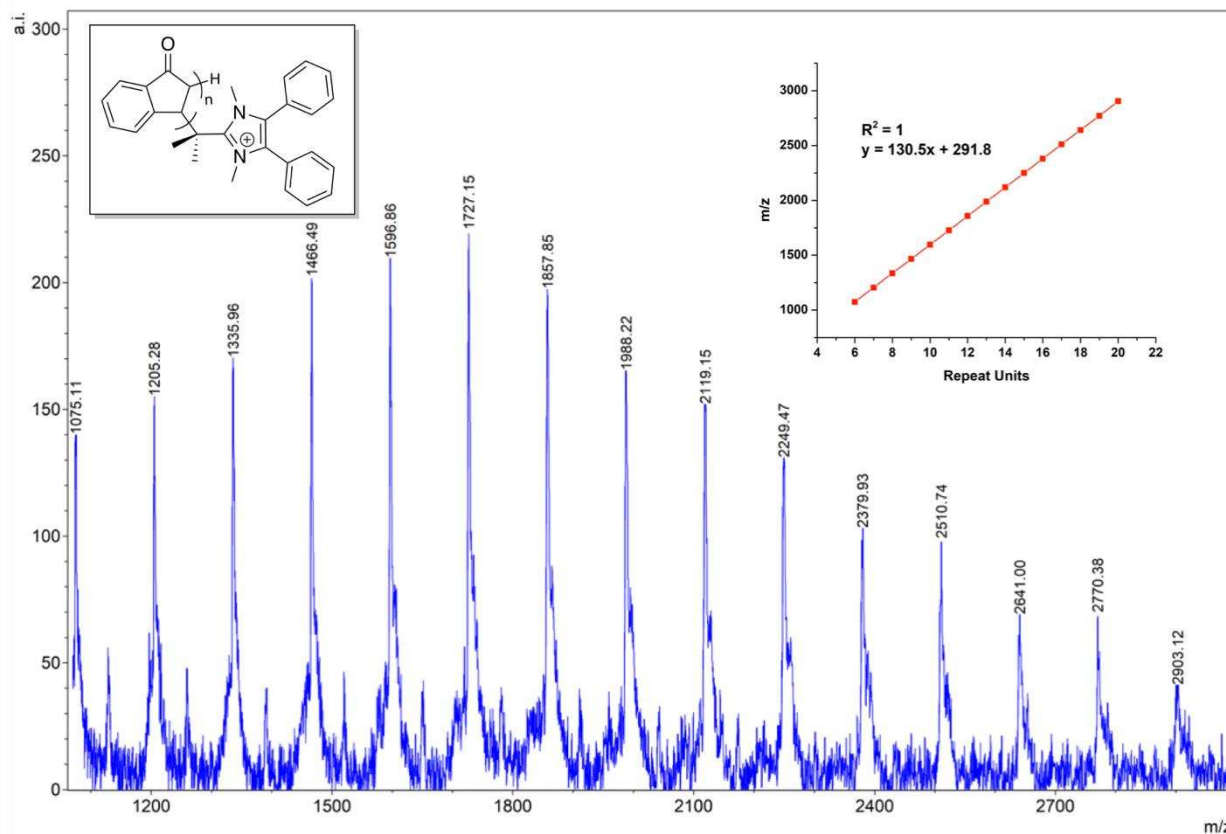




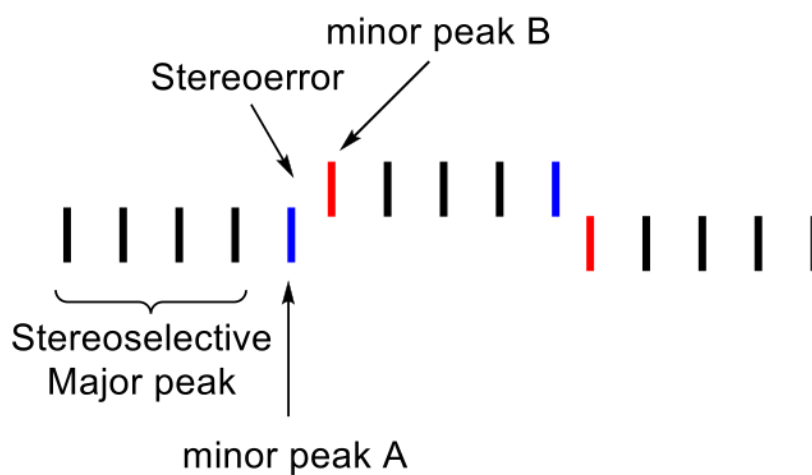
**Figure A7.** Full-scale quantitative  $^{13}\text{C}$  NMR for atactic, autopolymerized Pin sample. Carbonyl **1** signal shows no selectivity in comparison to **Figure B2** (*vide supra*).



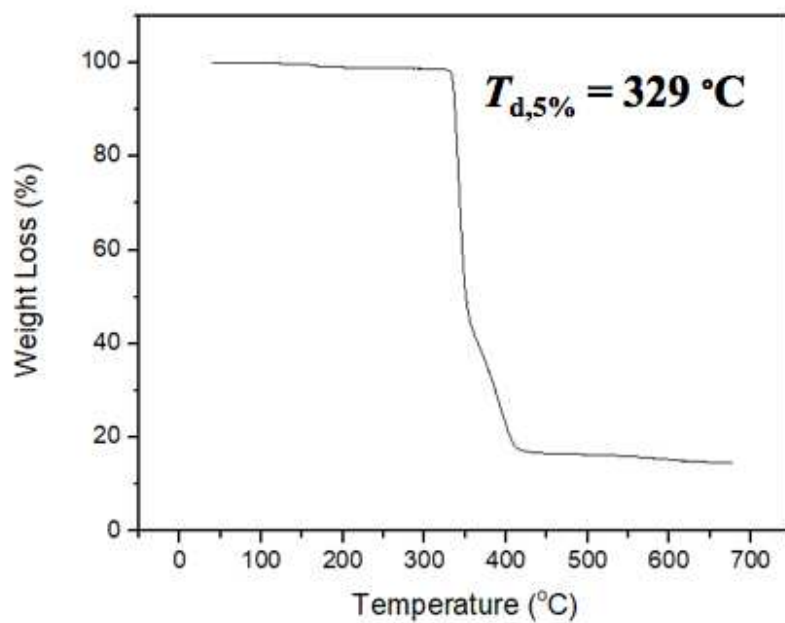
**Figure A8.** Example GPC LS (orange, dash) and RI (blue) traces of Pin with a monomodal MW distribution, obtained by  $[\text{M}]/[\text{FAB}]/[\text{MeSKA}] = 500/2/1$ .  $M_n = 1.72 \times 10^5$  g/mol,  $\bar{D} = 1.23$ . Slightly higher  $M_n$  shouldering in the LS is postulated to be a consequence of high chain rigidity leading to some chain aggregation.



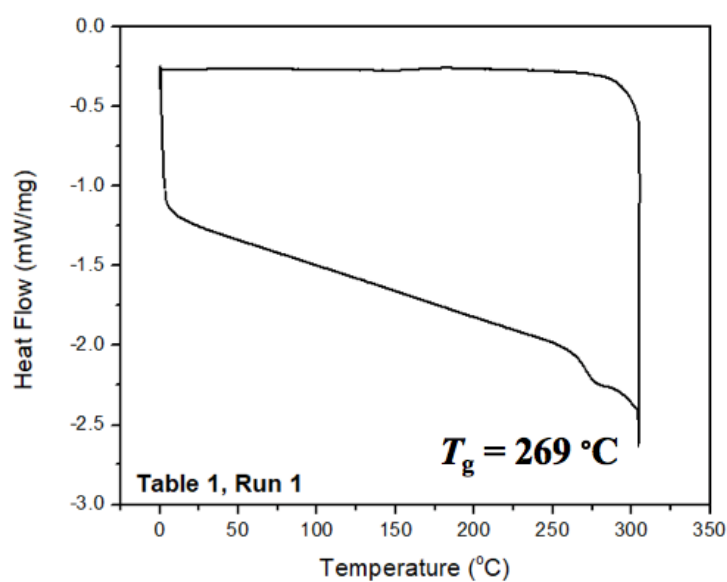
**Figure A9.** MALDI-TOF MS spectrum of a low MW Pin sample prepared with FLPP conditions [M1]/[MAD]/[NHO] as well as end-group analysis supporting initiation by the proper NHO LB.



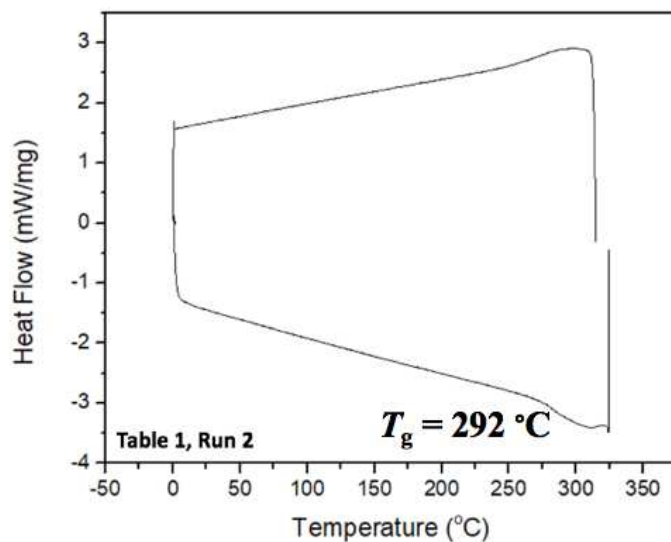
**Figure A10.** Plausible stereo-errors for  $^{13}\text{C}$  peak assignments accounting for the two carbonyl peaks not associated with the main erythro-diastereoselective carbonyl signal (black) and erythro-disyndiotactic (blue and red).



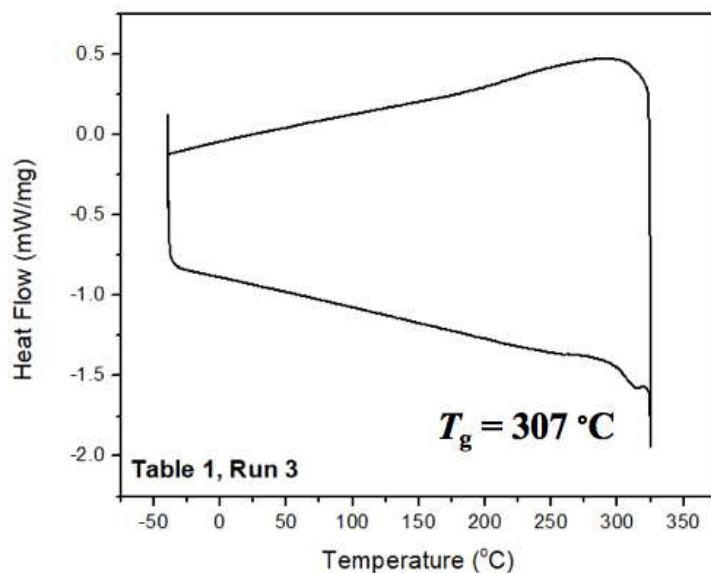
**Figure A11.** TGA curve of an autopolymer ( $M_n = 2.02 \times 10^5 \text{ g mol}^{-1}$ ) showing  $T_{d,5\%} = 329\text{ }^{\circ}\text{C}$ .



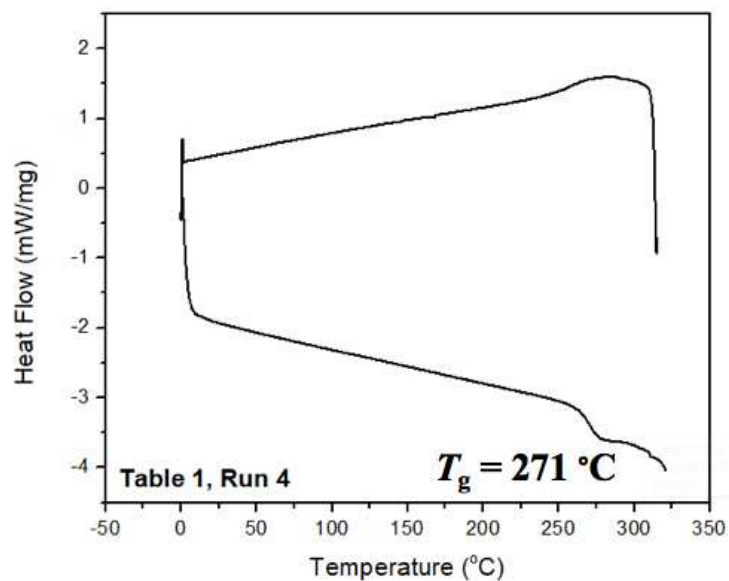
**Figure A12.** DSC trace of autopolymer Pin from the 2<sup>nd</sup> heating scan. A heating rate of 15 °C/min and a cooling rate of 5 °C/min were applied.



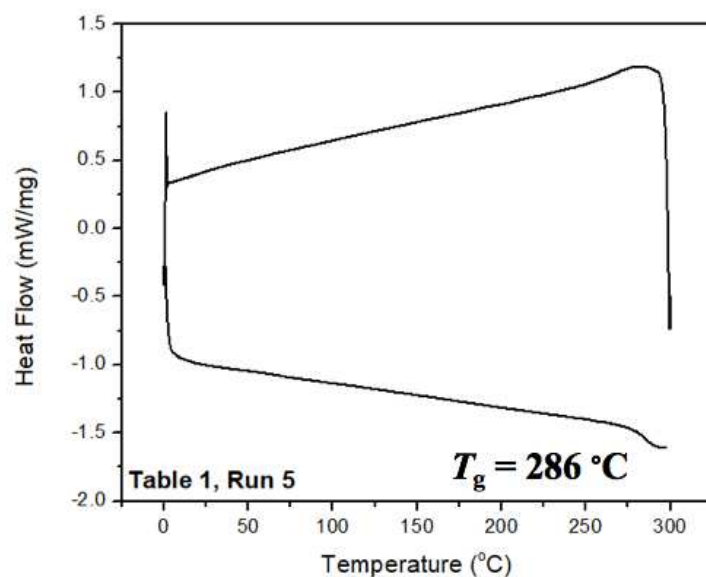
**Figure A13.** DSC trace of 71 % erythro-ditactic Pin ([M1]/[LA]/[LB] = 500/2/1) from the 2<sup>nd</sup> heating scan. A heating rate of 15 °C/min and a cooling rate of 5 °C/min were applied.



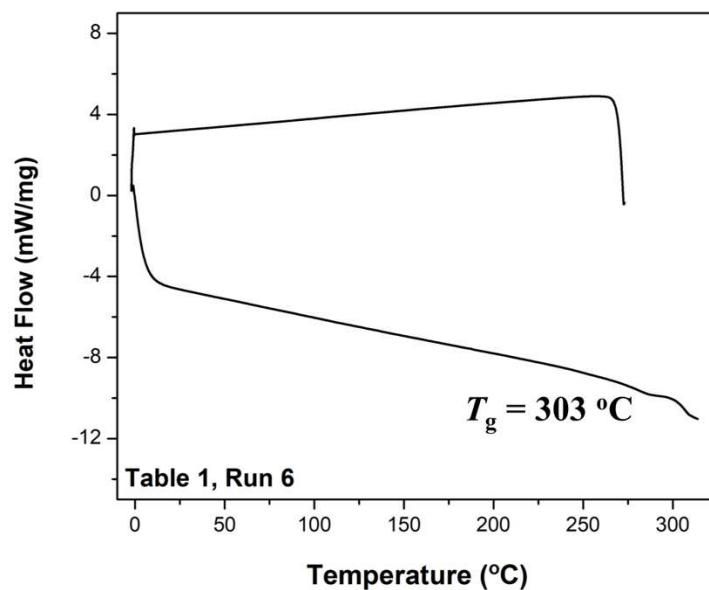
**Figure A14.** DSC trace of 71 % erythro-ditactic Pin ([M1]/[LA]/[LB] = 1000/2/1) from the 2<sup>nd</sup> heating scan. A heating rate of 15 °C/min and a cooling rate of 5 °C/min were applied.



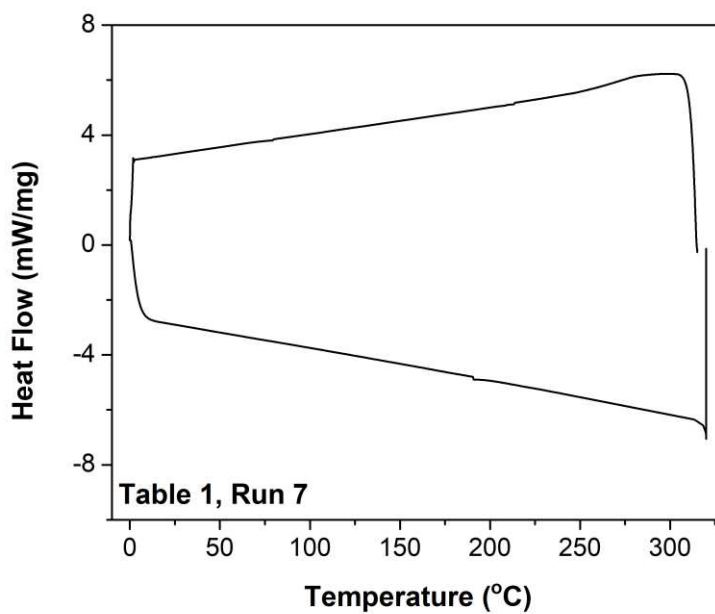
**Figure A15.** DSC trace of 57 % erythro-ditactic Pin ( $[M1]/[LA]/[LB] = 500/2/1$ ) from the 2<sup>nd</sup> heating scan. A heating rate of 15 °C/min and a cooling rate of 5 °C/min were applied.



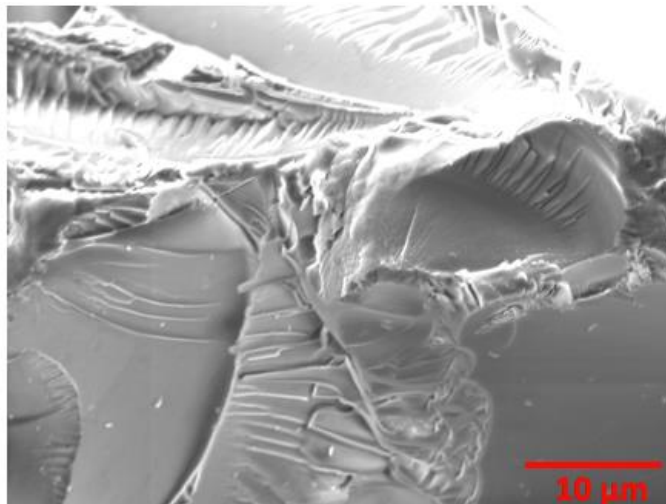
**Figure A16.** DSC trace of 57 % erythro-ditactic Pin ( $[M1]/[LA]/[LB] = 1000/2/1$ ) from the 2<sup>nd</sup> heating scan. A heating rate of 15 °C/min and a cooling rate of 5 °C/min were applied.



**Figure A17.** DSC trace of 75 % erythro-ditactic Pin ( $[M1]/[LA]/[LB] = 500/2/1$ ) from the 2<sup>nd</sup> heating scan. A heating rate of 20 °C/min and a cooling rate of 10 °C/min were applied.



**Figure A18.** DSC trace of 75 % erythro-ditactic Pin ( $[M1]/[LA]/[LB] = 1000/2/1$ ) from the 2<sup>nd</sup> heating scan. A heating rate of 25 °C/min and a cooling rate of 10 °C/min were applied.

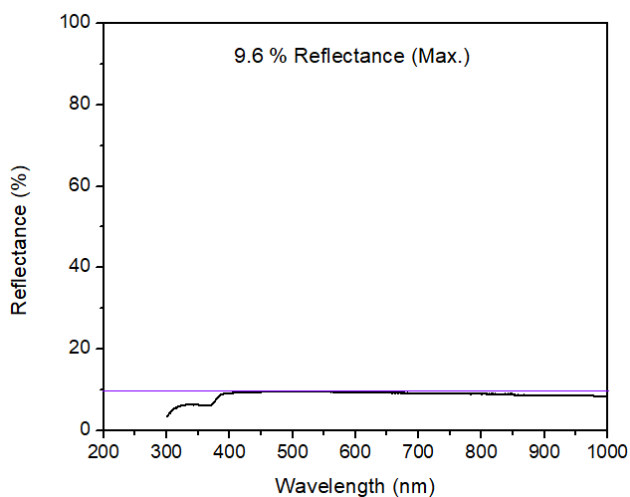


**Figure A19.** SEM characterization of (gold-coated) graphite oxide at 10 micron and 100 nm scale. Both images exhibit a morphology consisting of grooved layers – signature of graphite oxide layers.

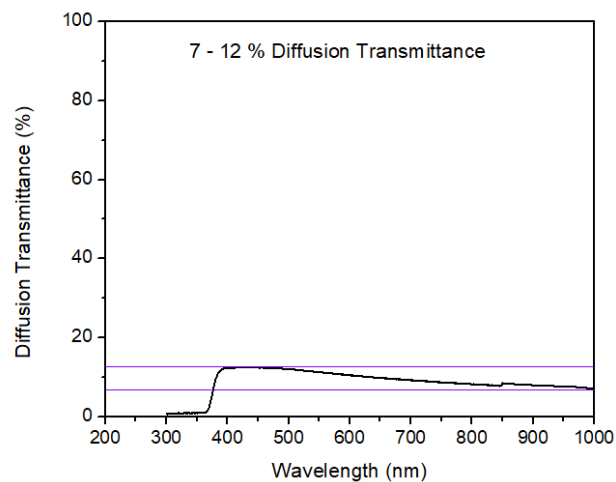
#### Optical Data:

The following graphics exhibit the total transmittance ( $T_t$ ), reflectance (%), diffusion transmittance ( $T_d$ ) and calculated haze (%).

$$\text{Haze} = \text{total transmittance } (T_t) \div \text{diffusion transmittance } (T_d)$$



**Figure A20.** Reflectance properties of the same poly(indenone) sample as in S11.



**Figure A21.** Diffusion Transmittance (%) plot for poly(indenone) thin film (160 micron thick).

$$\text{Haze} = 87.1 \% \div 9.6 \% = 11 \% \text{ Haze Value.}$$

**Table A1.** Upconversion of Pin materials to GO as a function of erythro-diastereoselectivity, pyrolysis atmosphere, and decomposition temperature.

| Run | Erythro Content (%) | Atmosphere     | Heat (°C) | GO Yield (%) |
|-----|---------------------|----------------|-----------|--------------|
| 1   | Atactic             | O <sub>2</sub> | 500       | 14.3         |
| 2   | Atactic             | N <sub>2</sub> | 500       | 23.7         |
| 3   | Atactic             | N <sub>2</sub> | 360       | 53.8         |
| 4   | 57                  | N <sub>2</sub> | 360       | 36.8         |
| 5   | 75                  | N <sub>2</sub> | 360       | 24.9         |



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2. Wang, Q. Y.; Zhao, W. C.; He, J. H.; Zhang, Y. T.; Chen, E. Y.-X. Living Ring Opening Polymerization of Lactones by *N*-Heterocyclic Olefin/ $\text{Al}(\text{C}_6\text{F}_5)_3$  Lewis Pairs: Structures of Intermediates, Kinetics, and Mechanism. *Macromolecules* **2017**, *50*, 123-126.
3. Lu, X.; Schneider, U. Aza-Morita-Baylis-Hillman Reactions Catalyzed by a Cyclopropenylidene. *Chem. Commun.* **2016**, *52*, 12980-12983.
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## Appendix B

### Supplementary Information Corresponding to Chapter 3<sup>h</sup>

#### Materials

HPLC grade organic solvents for catalyst synthesis and polymerization experiments were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Toluene, hexanes, THF, and benzene-*d*<sub>6</sub> for polymerization reactions, catalyst synthesis or purification, and structural confirmation, were further dried and purified by storage under Na/K until passage through a 0.2-μm Nylon VWR syringe filter when required. Chloroform-*d*<sub>1</sub> was dried over activated calcium hydride for 24 h, vacuum-distilled at 40 °C, and stored over Davidson 4 Å molecular sieves in an inert glovebox. Trifluoroacetic acid-*d*<sub>1</sub> was purchased from either Cambridge Isotope Laboratories or Sigma Aldrich and stored in moisture-free containers.

Monomers *n*-butyl acrylate (*n*BA), *tert*-butyl acrylate (*t*BA), and methyl acrylate (MA) were purchased from TCI. All monomers were purified by titration with triethyl aluminum followed by vacuum distillation into a chilled (-78 °C) receiver flask in the absence of light and stored in amber bottles at -30 °C inside an inert glovebox. Trifluoroacetic acid (TFA), 4,4,4-trifluorobutyric acid, decanoic anhydride, and stearic anhydride were purchased from Sigma-Aldrich and used as received. Trimethylphosphine (PMe<sub>3</sub>) was purchased from Alfa Aesar, stored at -30 °C inside an

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<sup>h</sup>Taken verbatim from: R. W. Clarke, M. L. McGraw, B. S. Newell, E. Y.-X. Chen. Thermomechanical Activation Achieving Orthogonal Work/Healing Conditions in Nanostructured Thermosets. *Cell Rep. Phys. Sci.* **2**, 100483 (2021).

inert glovebox, and used as received. Triethylamine was purchased from Fisher Scientific and used as received. Butyryl chloride and decanoic acid were purchased from TCI and used as received. Lewis acids (2,6-di-*tert*-butyl-4-methylphenoxy)diisobutylaluminum (*t*Bu<sub>2</sub>Al(BHT) and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxy) (MAD) were prepared according to literature procedures.<sup>1</sup>

## Instrumentation

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Monomer conversion, small-molecule characterization, acid-anhydride small molecule analysis, as well as structural characterizations of polymers (pre- and post-functionalization) were carried out by either <sup>19</sup>F, <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy (NMR) on an Agilent (Varian) 400MR (FT 400 MHz <sup>1</sup>H, 100MHz <sup>13</sup>C), a Bruker AVIII (US) 400 MHz spectrometer (FT 400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C), and an Agilent Inova 500 MHz spectrometer (FT 500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C). Chemical shifts for <sup>1</sup>H NMR were referenced to internal solvent signals corresponding to 7.26 ppm (chloroform) and 7.16 ppm (benzene) and are reported as parts per million relative to SiMe<sub>4</sub>. Trifluoroacetic acid-*d*<sub>1</sub> (TFA-*d*<sub>1</sub>) was also used as an NMR solvent for obtaining increased solubility of poly(acrylic acid)-containing copolymers (Generation 2).

**Quadrupole Time-of-Flight Mass Spectrometry (Q-TOF-MS).** Ionized acid-anhydride and anhydride-anhydride small molecule model exchange products were characterized on an Agilent 6224 Quadrupole Time-of-Flight Mass Spectrometer equipped with dual ESI source in positive ion mode, run in-house by the Colorado State University Analytical Resource Core – Molecular and Materials Analysis Center (ARC-MMA) staff. Samples were prepared by making separate 0.1

mg/mL solutions of both the fluorinated acid-anhydride exchange reaction products and the anhydride-anhydride exchange products in  $\text{CH}_2\text{Cl}_2$  and subsequently introduced via flow-injection.

**Gel Permeation Chromatography (GPC).** Measurements of polymer absolute weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ) and molecular weight distributions or dispersity indices ( $D = M_w/M_n$ ) were performed via gel-permeation chromatography (GPC). The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and three PL-gel 5  $\mu\text{m}$  mixed-C gel permeation columns running THF as the eluent at 1.0 mL/min at 40 °C. The detectors used were a Wyatt Technology TrEX differential refractometer (dRI) and a Wyatt Technology miniDAWN Treos light scattering detector (MALS). The  $dn/dc$  values were determined experimentally, through analysis of known-concentration samples from 0.5 mg/mL to 5 mg/mL, as 0.0527 mg/mL for poly(*tert*-butyl acrylate), 0.0651 mg/mL for poly(*n*-butyl acrylate), and 0.0480 mg/mL for poly(methyl acrylate). GPC measurements of tri-BCP samples were run using  $dn/dc$  values calculated based on weighted average with respect to co-monomer composition.

**Thermal Analyses (TGA and DSC).** Differential scanning calorimetry (DSC) was performed on selected, thoroughly dried polymer samples on an Auto Q20 in aluminum pans (TA Instruments). DSC plots represent the data obtained from the second heating scan after the thermal history was removed in a previous heating and cooling cycle. The second heating scans were all performed at a heating rate of 15 °C/min and follows cooling scans of 10 °C/min.

Thermal gravimetric analysis (TGA) was similarly performed on selected, thoroughly dried polymer samples on a Q50 TGA Analyzer (TA Instruments). Samples (5-10 mg) were heated

from 25 °C to 700 °C at a rate of 10 °C/min. Thermal stability experiments were performed at 200 °C and held at an isotherm for 1 h.

**Fourier Transform Infrared Spectroscopy (FTIR).** FTIR experiments were carried out on a Bruker TENSOR II FT-IR spectrometer fitted with a Platinum ATR between 4000 and 400  $\text{cm}^{-1}$  wavenumbers. FTIR was run in conjunction with the software OPUS (Bruker).

**Small-Angle X-ray Scattering (SAXS).** SAXS characterization was carried out at the beamline 12-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory. X-rays of wavelength 0.9322 Å (13.3 keV) were used, and the sample to detector distance was calibrated using silver behenate as a standard. Samples were mounted on an XY stage with thermal capabilities. Each sample was exposed to the X-ray beam for 1s. High-temperature SAXS experiments were performed at 200 °C following 30 minutes of thermal soaking time. The scattered X-rays were collected with a Pilatus2M detector located about 2 m downstream from the sample position. The 1D scattering spectra were obtained by radially averaging the images into scattering intensities versus the scattering vector,  $q$ .

**Instron Tensile Testing.** Reported tensile stress-strain curves were obtained on an Instron 5966 universal testing system with a 10 kN load cell and a pulling rate of 5 mm/min at room temperature. Tensile tests were performed on dog-bone-shaped (ASTM D638 standard; Type-V) tensile bar specimens, where the tensile specimens were placed between grips and stretched at constant pull-rates until break. Cyclic deformation experiments, run by repeatedly straining the polymer to 100 % elongation and allowing it to rest for 5 minutes at zeroed strain before re-introducing strain, were performed under similar operating conditions. The mechanical data is an average of three to five specimens measured for each individually reported polymer for material reproducibility. Thickness (varied), grip separation ( $30 \pm 0.2$  mm, screw-tight grip frame) and width (3.18 mm)

were all recorded with micrometer calipers and were necessary for normalization of data by the Bluehill measurement software (Instron). Reported stress-strain curves are an appropriate representation of the data set.

**Dynamic Mechanical Analysis (DMA).** Storage modulus ( $E'$ ), loss modulus ( $E''$ ) and tan delta ( $E''/E'$ ) traces for Generation 2 and Generation 3 triblock vitrimers were measured on a Q800 DMA Analyzer (TA Instruments) in a tension film mode. Temperature-ramp frequency sweep experiments were performed from -50 °C to 200 °C at a heating rate of 5 °C/min and were pulled at 0.3 % strain with a frequency of 1 Hz. Rubbery plateau ( $E' = \text{constant}$ ) analysis for material thermal stability were performed at 170, 180, 190, and 200 °C at a strain of 0.3 % and a frequency of 1 Hz. Film thickness was also measured for normalization of the data by the Q-series measurement software (TA Instruments). Specimens were mounted to screw-tight grips (maximum 7 N for G3, minimum 3 N for G2).

**Oscillatory Shear Rheology.** Oscillatory shear rheology measurements were performed on a Discovery Series HR-2 Hybrid Rheometer (TA Instruments) operating between 100-200 °C under nitrogen gas flow (30 psi) and in conjunction with the TA Instruments TRIOS Software. Samples were loaded between two 8 mm-diameter flat-plate steel electrically heated platen (EHP) loading discs. All experiments were performed within  $0 \pm 0.2$  N of axial force. Further specific experimental details are found in the rheology section of this supporting document.

## Small Molecule Exchange Reaction Procedures

**Acid-Anhydride Molecular Exchange.** The proposed carboxylic acid-to-anhydride CAN exchange co-mechanism was probed by small molecule organic reactions. Fluorine-traced

exchange between 4,4,4-trifluorobutyric acid (1.0 g, 7.1 mmol) and stearic anhydride (3.88 g, 7.1 mmol) is performed by blending both molecules in the melt (100 °C, 150 °C, Argon) in a 250 mL Teflon screw-cap sealed glass pressure reactor for 2 h. Reactors are removed from the heat source and allowed to gently return to room temperature prior to removing the sealant cap. For room temperature experiments, the two molecules are solvated in 50 mL CHCl<sub>3</sub>/THF and stirred for 2 h before drying to a powder at room temperature.

**Anhydride-Anhydride Molecular Exchange.** Our proposed CAN bond exchange co-mechanism between anhydride-anhydride species was carried out using decanoic anhydride and stearic anhydride. To remove any protic impurities that may catalyze the exchange or the hydrolysis of anhydrides, both reagents were dissolved in a 50/50 vol. % THF/DCM and mixed with dried and activated CaH<sub>2</sub> for 24 h. The dried samples were then passed through a fine-fritted filter and all solvent impurities were removed by glovebox vacuum until a constant mass was achieved and solvent signals were no longer visible by NMR. The anhydrides were then similarly blended in the melt (100 °C, 150 °C, Argon) in a 250 mL Teflon screw-cap sealed glass pressure reactor for 2 h. Reactors are removed from the heat source and allowed to gently return to room temperature prior to removing the sealant cap. For room temperature experiments, the two molecules are solvated in 50 mL CHCl<sub>3</sub>/THF and stirred for 2 h before drying to a powder at room temperature.

## Polymer Synthesis and Modification Procedures

**Homopolymerization Procedures.** All polymerizations were carried out in an inert gas (Ar or N<sub>2</sub>)-filled glovebox, following literature procedures.<sup>2</sup> The preparation of homopolymers PMA, P<sup>n</sup>BA, and P<sup>t</sup>BA were previously described and prepared by mixing specified monomer (M) and

the LA (MAD) with toluene.<sup>2</sup> The amount of toluene corresponded to 0.50 mL M per 6 mL of solution, and the  $[M]/[MAD]/[PMe_3]$  ratio was 1000/2/1. Addition of  $PMe_3$  started the polymerization, and the polymerization times varied from 5-20 s for  $^{12}BA$  and MA reactions and 3-5 min for  $^1BA$  polymerization. Their completion was signaled by color change from yellow to clear, at which point polymerizations were quenched under excess acidified methanol (200 mL, 100 ppm benzoic acid) and then an equal volume of water, causing precipitation of polymer. Then, solvents were removed by rotary evaporation until only 10 % solvent volume remained. The polymer stuck to the sides of the flask so that remaining solvent was decanted. For further purification, the polymer can be redissolved in THF or acetone, at which point an equal volume of water can be added. Rotary evaporation of the organic solvent then left majority water, at which point the polymer crashed out and the excess water was decanted. This was the purification method generally used throughout the study. Precipitated homopolymers were further dried in a vacuum oven at 60 °C until a constant mass was achieved.

As a specific example, 21 mL of MA (20 g, -30 °C) was mixed with 230 mL of toluene (RT) and 0.15 g of MAD in a 500 mL round bottom flask equipped with a stir bar. Then, 0.0119 g of  $PMe_3$  (1.0 mL of a 0.156 M stock solution in toluene) was added with vigorous stirring to start the reaction. After about 20 s, the solution changed from yellow to clear, and 200 mL of methanol (100 ppm benzoic acid) was added.

**Mixed Addition Triblock Copolymerization Procedures.** The block copolymerization reactions were carried out by first initiating polymerization on the entire sum of  $^1BA$  followed by addition of  $^{12}BA$  or MA at approximately 50 % conversion of  $^1BA$ , at which point the LPP selects  $^{12}BA$  or MA over  $^1BA$ . Once the  $^{12}BA$  or MA reservoir was depleted, the polymerization returned to the remaining  $^1BA$  to make an A-B-A triblock.



First, toluene, MAD, and  $t$ BA were mixed so that the concentration of total monomer ( $t$ BA +  $\{n$ BA or MA $\}$ ) was 0.50 mL M per 6 mL solution. Then, polymerization of  $t$ BA was initiated by addition of  $\text{PMe}_3$ . The exact time at which this homopolymerization reached completion must be noted independently so that a time point representing 50 % conversion can be acquired. Thus, if the homopolymerization takes 5 min, the analogous triblock polymerization would inject comonomer at 2.5 min. Color change indicated complete conversion, at which point the reaction must be quenched with methanol (200 mL, 100 ppm benzoic acid). At low MAD concentrations, it can be difficult to see this color change, which is another reason why it is important to know the approximate kinetics ahead of time, but it is imperative to quench the reaction shortly after monomer depletion because otherwise the active species and excess MAD would induce side reactions in the absence of monomer.

As a specific example,  $P^t\text{BA-}b\text{-PMA-}b\text{-P}^t\text{BA}$  was synthesized by CSC-LPP by premixing 10 g of  $t$ BA with 470 mL toluene and 0.3747 g of MAD in a 1 L round bottom flask equipped with a stir bar. Then, 0.0302 g of  $\text{PMe}_3$  was added (1.0 mL of a 0.397 M stock solution) with vigorous stirring to start the reaction ( $t$ BA/MAD/ $\text{PMe}_3$  = 200/2/1,  $[t\text{BA}] \sim 0.16$  M). This reaction was found to reach complete conversion (as indicated by color change from yellow to clear) at precisely 2 min. Thus, the same reaction was repeated, except with addition of 26.9 g of MA at precisely 1 min. Complete conversion was observed shortly after 2 min, at which point 200 mL of methanol (100 ppm benzoic acid) was added. Thus, the overall  $t$ BA/MA/MAD/ $\text{PMe}_3$  ratio was 200/800/2/1 to yield a tri-BCP  $P^t\text{BA-}b\text{-PMA-}b\text{-P}^t\text{BA}$  with theoretical DP = 100-800-100 (100 % yield). The same protocol was used to isolate and purify the product as was described in the homopolymerization procedure. GPC analysis gave  $M_n = 1.45 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.08$ , Figure B7).

The same method and procedures were used to prepare two P'BA-*b*-P''BA-*b*-P'BA tri-BCPs with theoretical DP = 500-1000-500 (100 % yield,  $M_n = 2.71 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.03$ , Figure B5) and DP = 150-450-150 (100 % yield,  $M_n = 1.12 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.07$ , Figure B6). The only difference is that with the higher target DP of the 'BA component (cumulative DP = 1000 instead of 200), the 'BA homopolymerization was slower and thus comonomer was added at a different time. For example, when target DP was 500-1000-500, a 'BA/'BA/MAD/PMe<sub>3</sub> ratio of 1000/1000/10/1 was employed. An independent 'BA homopolymerization using these conditions was found to complete in 336 s. Therefore, ''BA was added at 168 s in the triblock polymerization.

**Random Copolymerization Procedure.** The random copolymerization reactions were carried out in a similar, but one-pot, fashion to the synthesis of the P'BA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-P'BA<sub>150</sub>. In this case, non-sequencing Lewis acid diisobutyl(mesityloxy)aluminum [<sup>i</sup>Bu<sub>2</sub>Al(OMes)] is used instead of MAD because it does not exhibit strong enough preferential coordination between comonomers, a key factor for CSC, and thus produces random copolymers from mixed comonomer polymerizations. For this reaction specifically, 9 mL of ''BA was mixed with 6 mL of 'BA and 0.384 g of <sup>i</sup>Bu<sub>2</sub>Al(OMes) and 100 mL of toluene. Then, 0.0389 g of tricyclohexyl phosphine (PCy<sub>3</sub>) was injected quickly as 0.69 mL of a 0.20 M stock solution in toluene. PCy<sub>3</sub> was used instead of PMe<sub>3</sub> in this case as the added steric hindrance helps discourage Claisen-type termination which becomes problematic when <sup>i</sup>Bu<sub>2</sub>Al(OMes) is used instead of MAD. The final ''BA/'BA/<sup>i</sup>Bu<sub>2</sub>Al(OMes)/PCy<sub>3</sub> ratio was 450/300/10/1 and the polymerization was finished in less than 1 min as indicated by color change from yellow to clear and confirmation by H NMR. The polymer product was worked up according to the same procedure used for the triblocks. The random sequencing of the copolymerization process was analyzed by DSC (supported by the

presence of only one glass transition temperature at -19.6 °C and  $^{13}\text{C}$  NMR (low resolution of carbonyl peaks).

**Diblock Copolymerization Procedure.** Diblock copolymers were prepared by a similar method as the random copolymers. The only difference being MAD was used instead of  $t\text{Bu}_2\text{Al}(\text{OMes})$  and  $\text{PMe}_3$  was used instead of  $\text{PCy}_3$ . The two di-BCPs discussed in this work were synthesized from slightly higher monomer ratios of  $n\text{BA}/i\text{BA}/\text{MAD}/\text{PMe}_3 = 900/600/10/1$  and  $\text{MA}/i\text{BA}/\text{MAD}/\text{PMe}_3 = 800/200/10/1$ .

**G1 to G2 Synthesis Procedure.** All G1 BCPs were subjected to TFA treatment (5.0 mol eq. in excess THF) as specified in Table S3. These transformations were performed in 40-60 g scales inside 1 L round bottom flasks equipped with a large stir bar. G1 materials were first dissolved in 500 mL of THF at 50 °C in an oil bath and left overnight. The polymer solution was then cooled in an ice bath to 0 °C, following which, 5.0 mol eq. TFA (to G1) was added over the course of 5 min – as the reaction is exothermic. The reaction was left to stir in the dark for a specified amount of time (Table S3). Once conversion was no longer increasing as monitored by  $^1\text{H}$  NMR, the reaction mixture was voided of solvents under reduced pressure at 50 °C. The polymer was treated with an additional 200 mL of THF after drying for three cycles, and then left in a vacuum oven for 24 h at 50 °C until a constant mass was achieved.

## Film Preparation Procedures

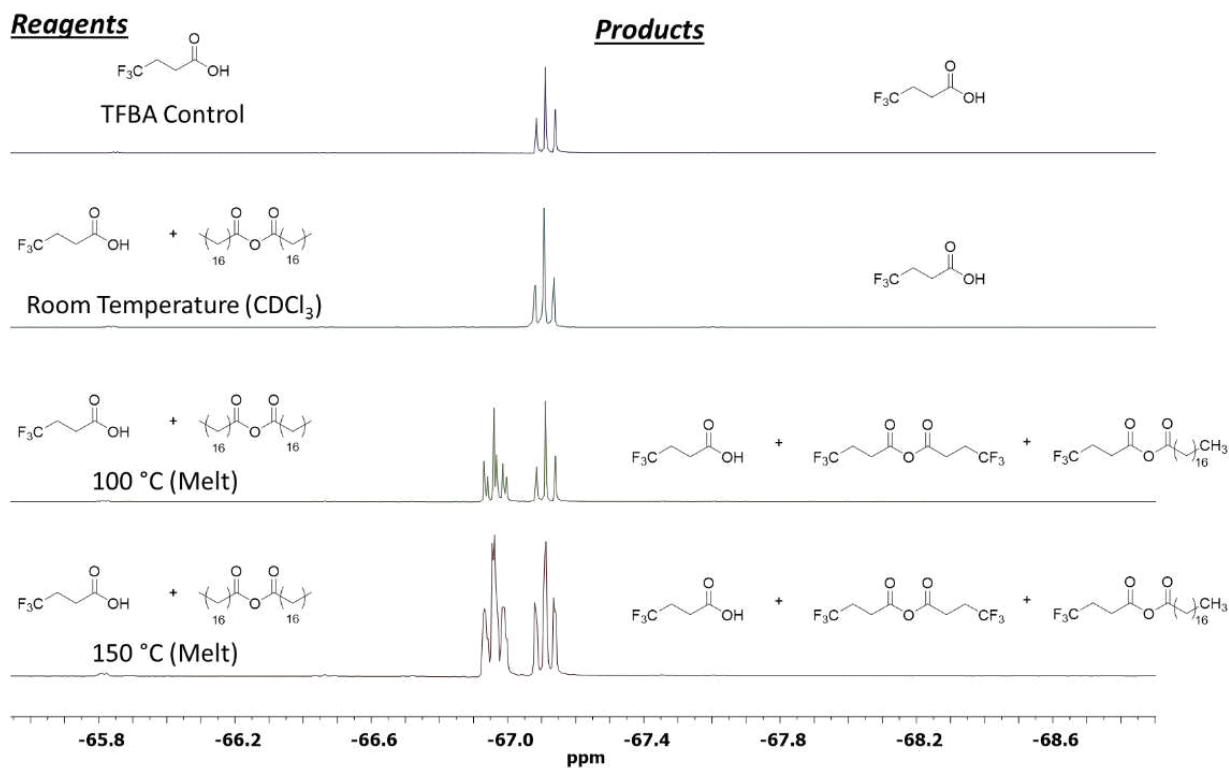
**Compression molding.** Heated compression molding was performed for all polymers (besides G2 copolymers) using a Carver Bench Top Laboratory Press (Carver, Model 3912, Max Force 24000

psi) with programmable plate temperature. Polymer samples prepared for film pressing at G1 and G3 stages were collected into 3-5 g amounts and were loaded between thin, non-stick Teflon sheets into a stainless-steel mold with inset dimensions  $30 \times 73.5 \times 0.87$  mm fabricated in-house and compressed between two 6"  $\times$  6" steel electrically heated plates (EHP) at a set pressure of 5000 psi, with occasional 10,000 psi cycling to remove air-bubble contamination. For G1 P'BA samples, the hydraulic press was heated to 100 °C, while G3 polymer specimens were hot-pressed at 200 °C, including those samples that are reported as reprocessed. G1 films were pressed for 1 h, while G3 materials were pressed for 12 – 24 h as reported, with additional time to cool back to room temperature under constant 5000 psi.

**Solvent Casting.** G2 polymers were not compression molded due to the  $T_g$  of PAA overlapping with the intra/inter-molecular crosslinking temperature. For this reason, G2 polymers were dried completely of TFA and THF by rotovap, and then re-dissolved in THF to be bulk solvent casted. Up to 50 g of G2 polymers were timely, fractionally solvent casted into large crystallization dishes at 10 – 20 g scales of polymer solution at 50 °C, capped with perforated aluminum foil. After 48 h, a homogeneous thin film was carefully removed from the dish and relocated to a vacuum oven to dry overnight at 50 °C. From these dried films, tensile bar specimens were cut to standard dimensions using an ASTM D368-5-IMP cutting die (Qualitest).

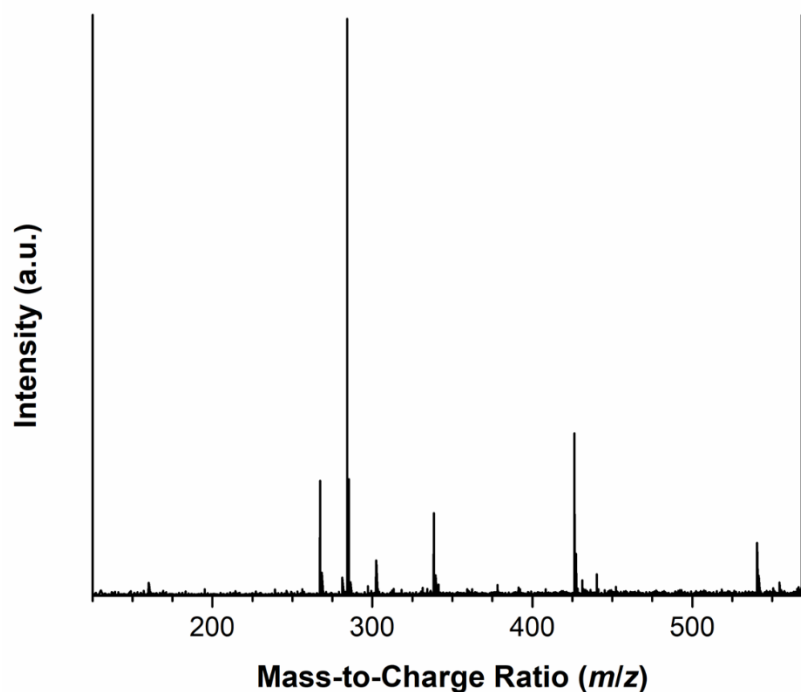
## Supplemental Figures

<sup>19</sup>F NMR:

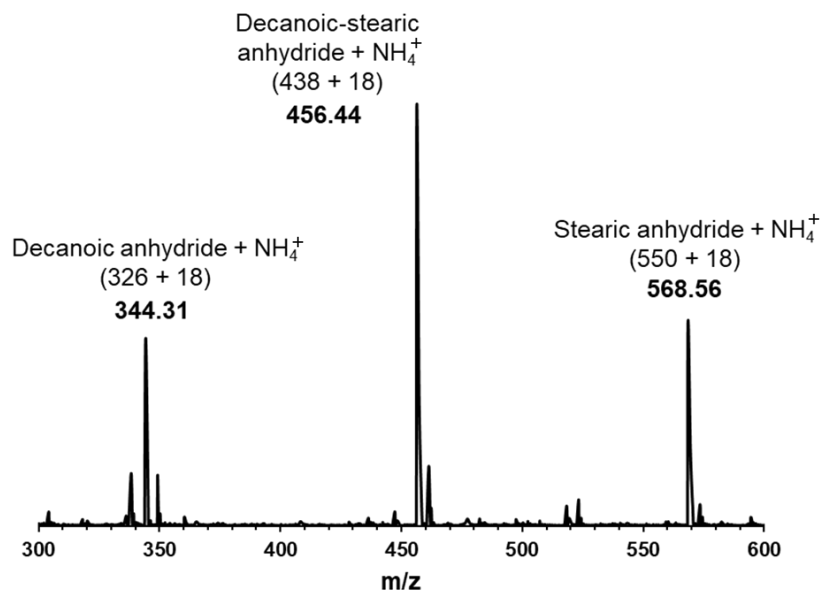


**Figure B1.** <sup>19</sup>F NMR (CDCl<sub>3</sub>) of the acid-anhydride exchange reactions between 4,4,4-trifluorobutyric acid (TFBA) and stearic anhydride (SA) at varied temperatures (Ar, 2 h).

### Mass Spectrometry:



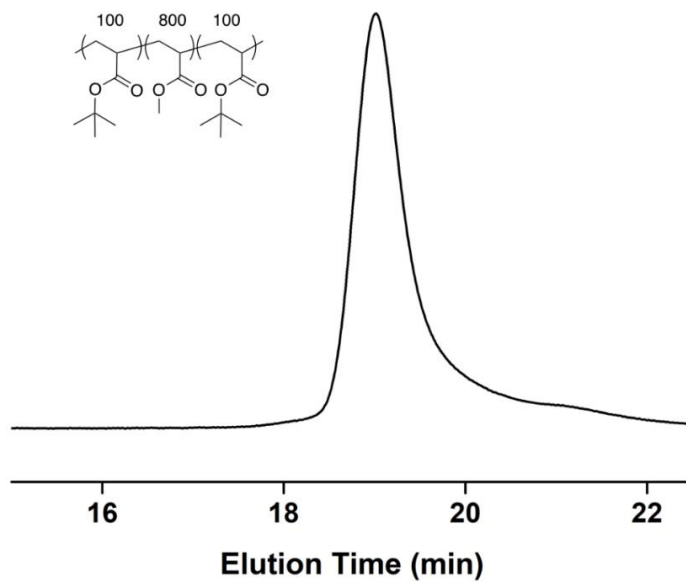
**Figure B2.** Mass spectrum (150 – 600  $m/z$ ;  $z = +1$ ) for the dynamic bond exchange reaction between TFBA and SA at 100 °C for 2 hours.



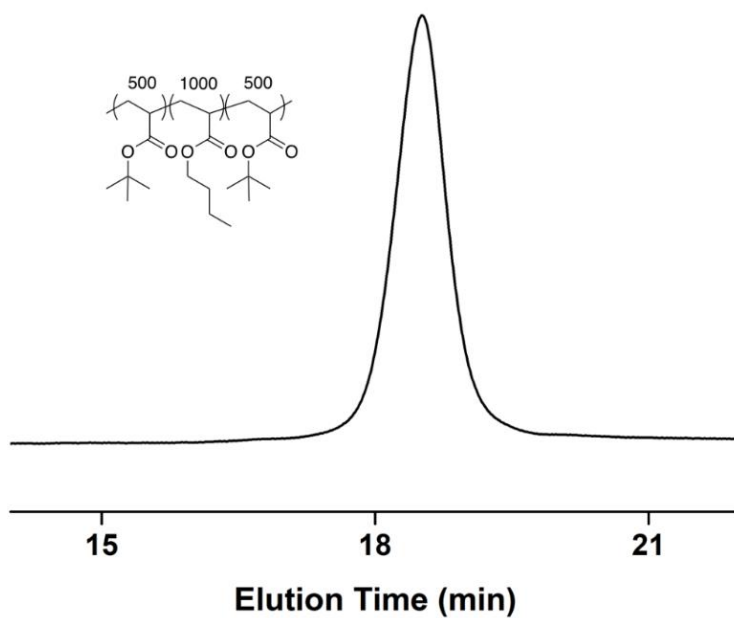
**Figure B3.** Q-TOF-MS full mass spectrum (300-600  $m/z$ ;  $z = +1$ ) for the dynamic bond exchange reaction between decanoic anhydride and SA at 100 °C (Ar, 2 h).

## Homopolymer and G1 Copolymer Characterization

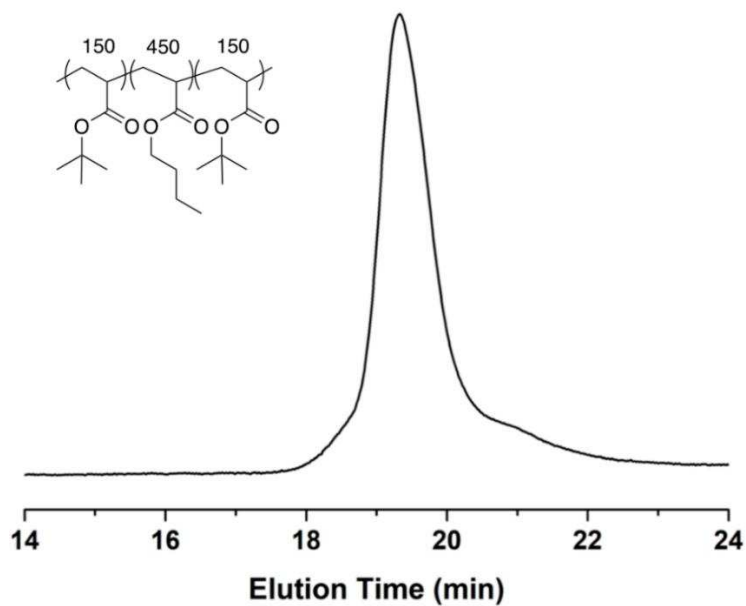
Gel Permeation Chromatography (GPC):



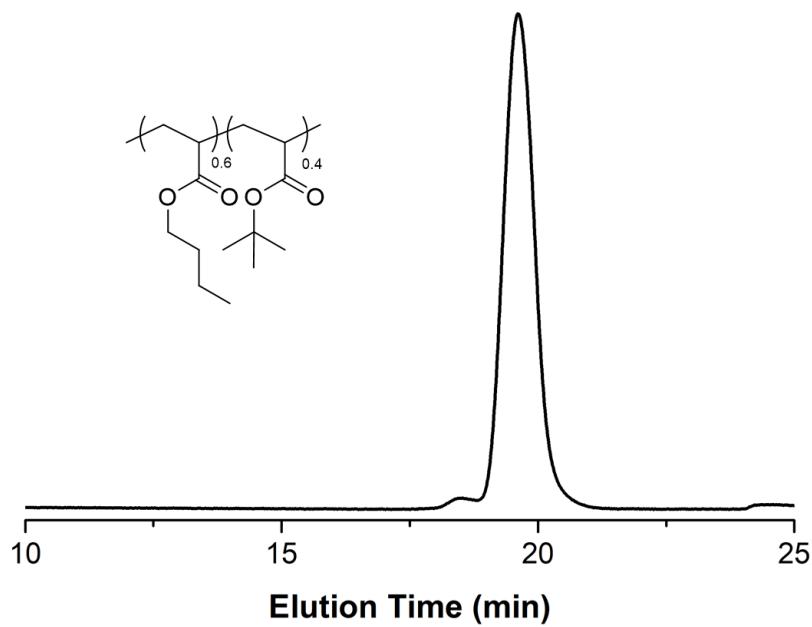
**Figure B4.** GPC trace (dRI) of P'BA<sub>100</sub>-b-PMA<sub>800</sub>-b-P'BA<sub>100</sub> ( $M_n = 1.45 \times 10^5 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.08$ ).



**Figure B5.** GPC trace (dRI) of P'BA<sub>500</sub>-b-P''BA<sub>1000</sub>-b-P'BA<sub>500</sub> ( $M_n = 2.71 \times 10^5 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.03$ ).

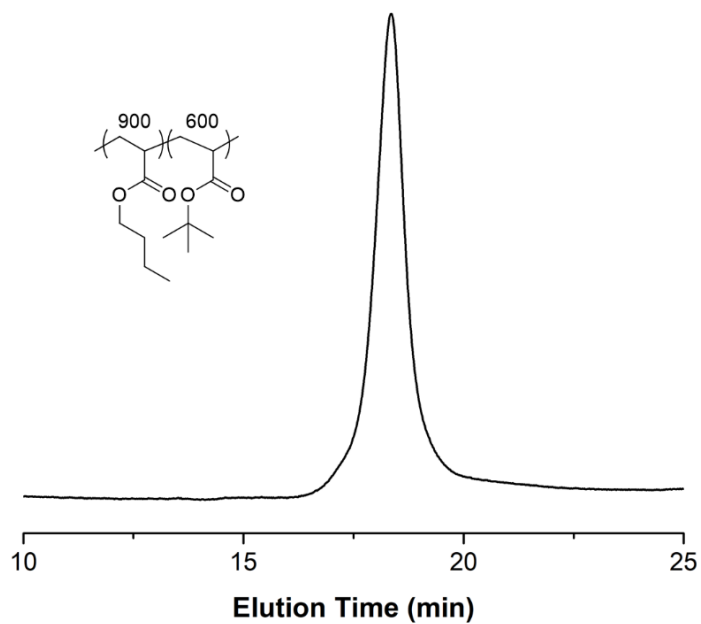


**Figure B6.** GPC trace (dRI) of G1 P'BA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-P'BA<sub>150</sub>. ( $M_n = 1.12 \times 10^5 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.07$ ).

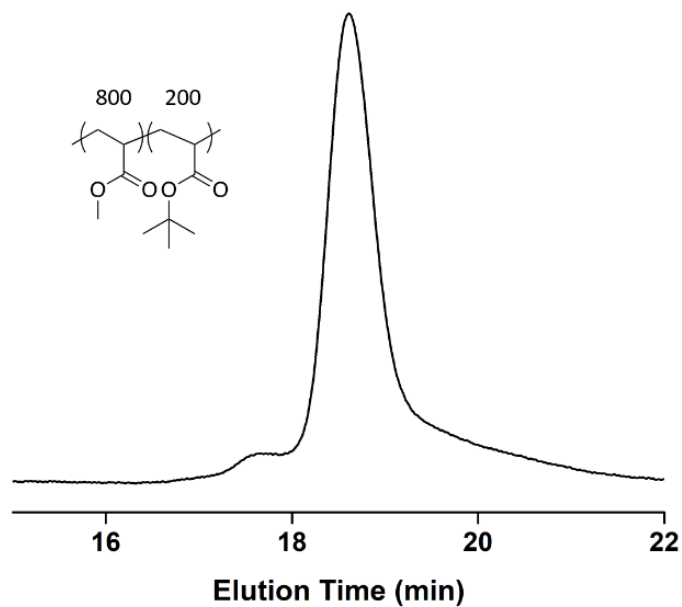


**Figure B7.** GPC trace (dRI) of G1 P''BA<sub>520</sub>-*ran*-P'BA<sub>350</sub>. ( $M_n = 1.12 \times 10^5 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.02$ ).





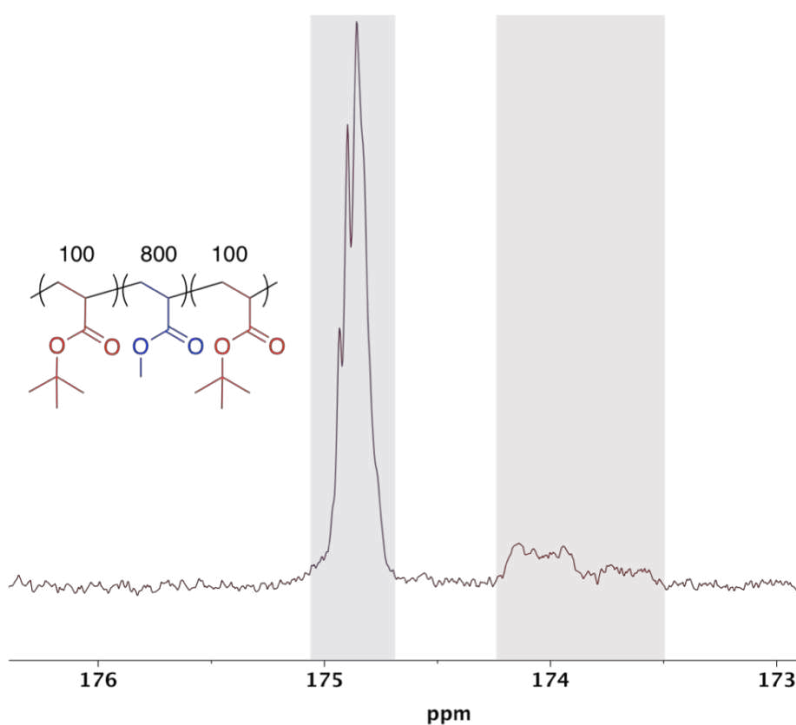
**Figure B8.** GPC trace (dRI) of G1 P''BA<sub>900</sub>-*b*-P'BA<sub>600</sub>. ( $M_n = 2.99 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.08$ ).



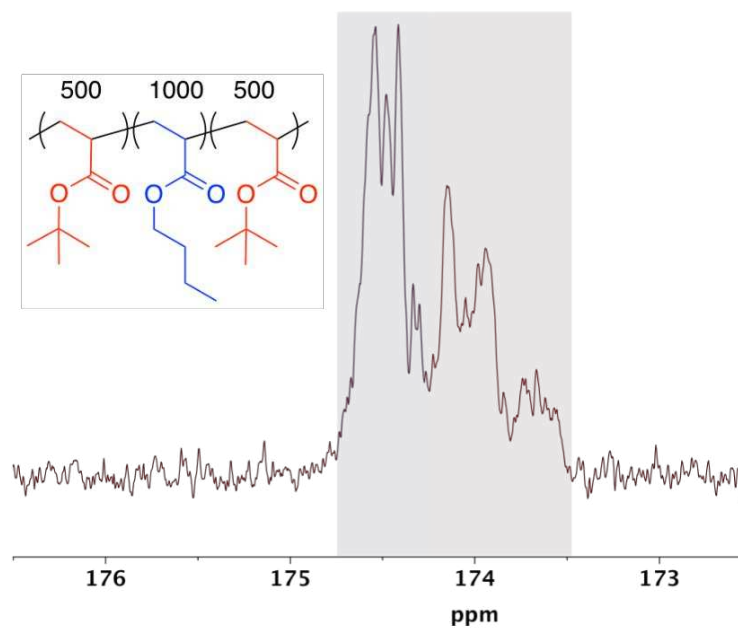
**Figure B9.** GPC trace (dRI) of G1 P'BA<sub>200</sub>-*b*-PMA<sub>800</sub> ( $M_n = 3.86 \times 10^5 \text{ g mol}^{-1}$ ,  $D = 1.14$ ).

$^{13}\text{C}$  NMR:

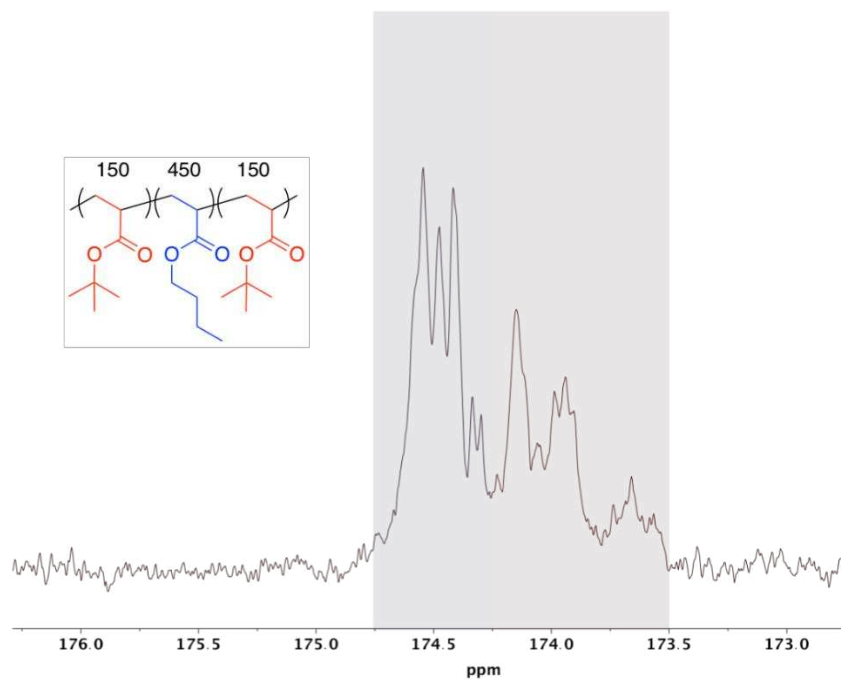
$^{13}\text{C}$  NMR is used to investigate the copolymer architecture at the carbonyl region. In general, well-resolved carbonyl signals support the CSC-LPP mechanism for synthesis of discrete block copolymers, while a poorly resolved carbonyl region supports a lack of sequence control and thus a more random copolymer.



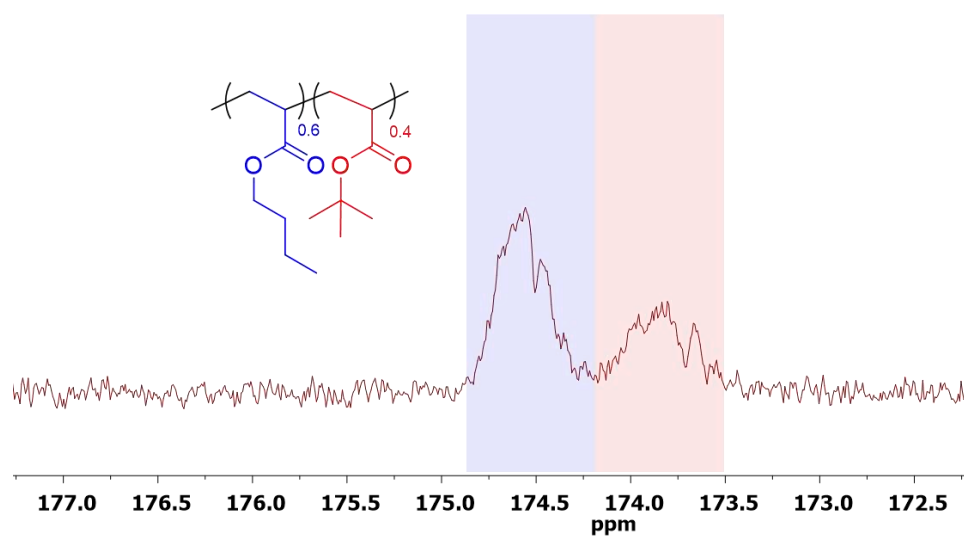
**Figure B10.**  $^{13}\text{C}$  NMR spectrum of the resolved P'BA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-P'BA<sub>100</sub> carbonyl region.



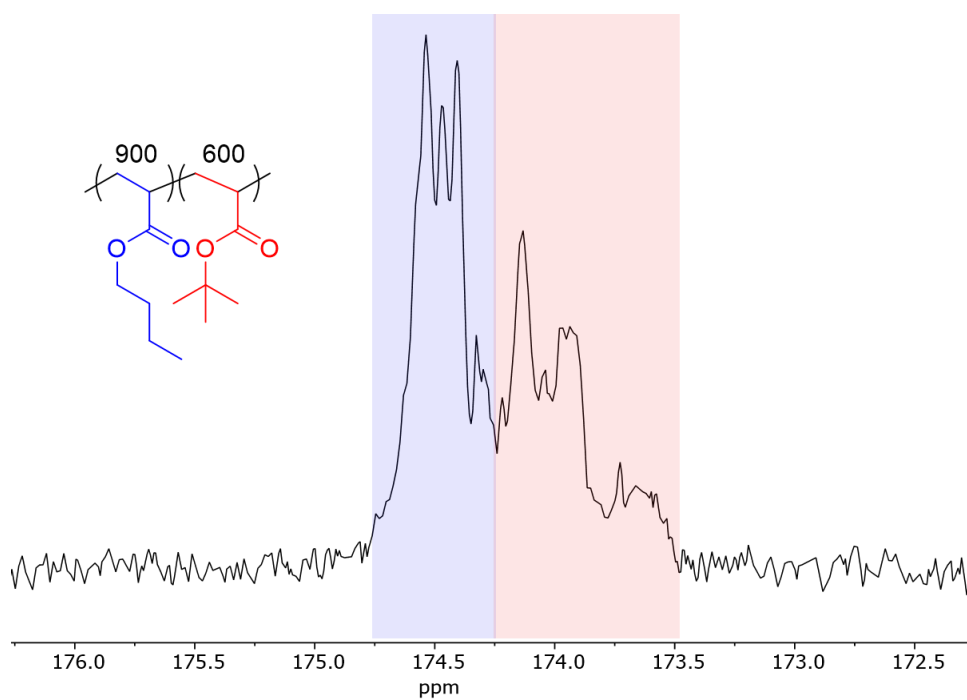
**Figure B11.**  $^{13}\text{C}$  NMR spectrum of the resolved  $\text{P}'\text{BA}_{500}\text{-}b\text{-}\text{P}''\text{BA}_{1000}\text{-}b\text{-}\text{P}'\text{BA}_{500}$  carbonyl region.



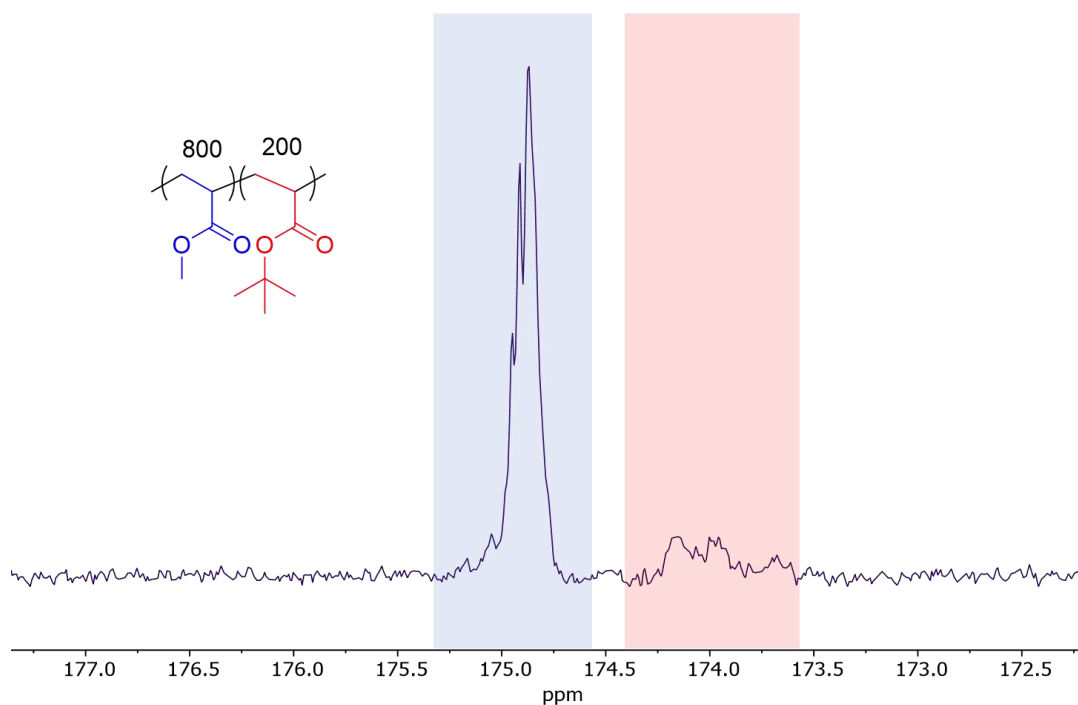
**Figure B12.**  $^{13}\text{C}$  NMR spectrum of the resolved  $\text{P}'\text{BA}_{150}\text{-}b\text{-}\text{P}''\text{BA}_{450}\text{-}b\text{-}\text{P}'\text{BA}_{150}$  carbonyl region.



**Figure B13.**  $^{13}\text{C}$  NMR spectrum of the  $\text{P}^n\text{BA}_{520}\text{-ran-P}^t\text{BA}_{350}$  carbonyl region.



**Figure B14.**  $^{13}\text{C}$  NMR spectrum of the  $\text{P}^n\text{BA}_{900}\text{-b-P}^t\text{BA}_{600}$  carbonyl region.

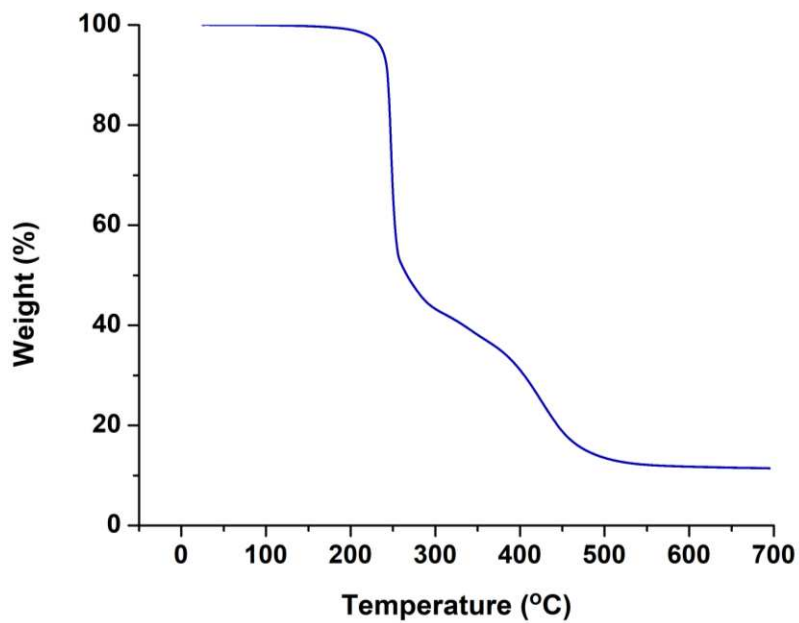


**Figure B15.**  $^{13}\text{C}$  NMR spectrum of the  $\text{P}'\text{BA}_{200}\text{-}b\text{-PMA}_{800}$  carbonyl region.

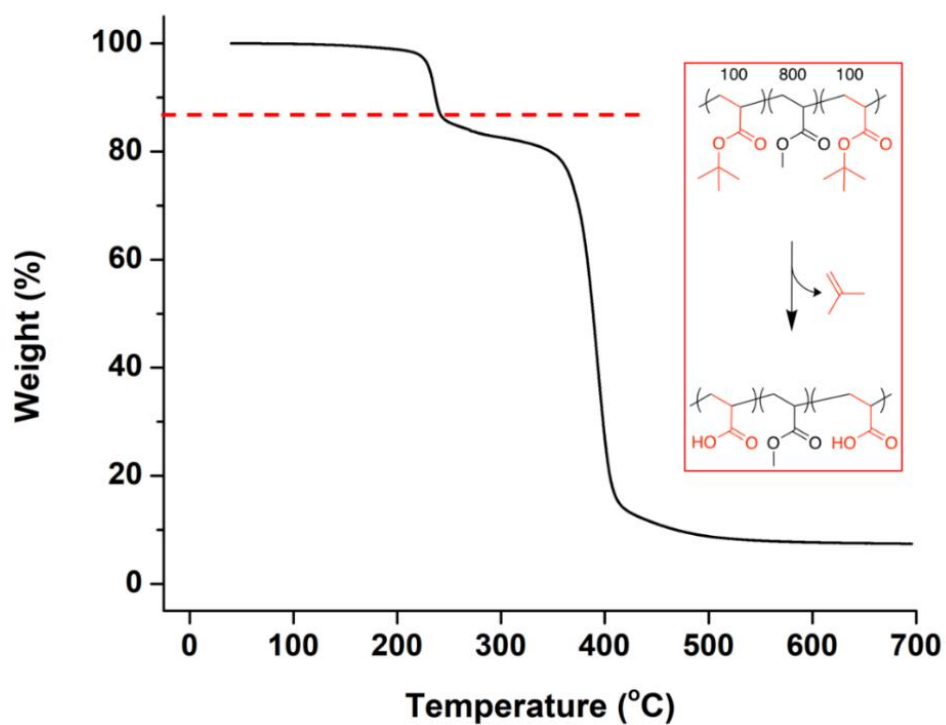
Thermogravimetric Analysis (TGA):

TGA of G1 BCPs was used to characterize and further support the correct composition of *tert*-butyl acrylate amongst homologous acrylate comonomers based on the weight loss during thermal *iso-tert*-butene elimination which is followed by condensation of acrylic acid blocks between 225-250  $^{\circ}\text{C}$ .

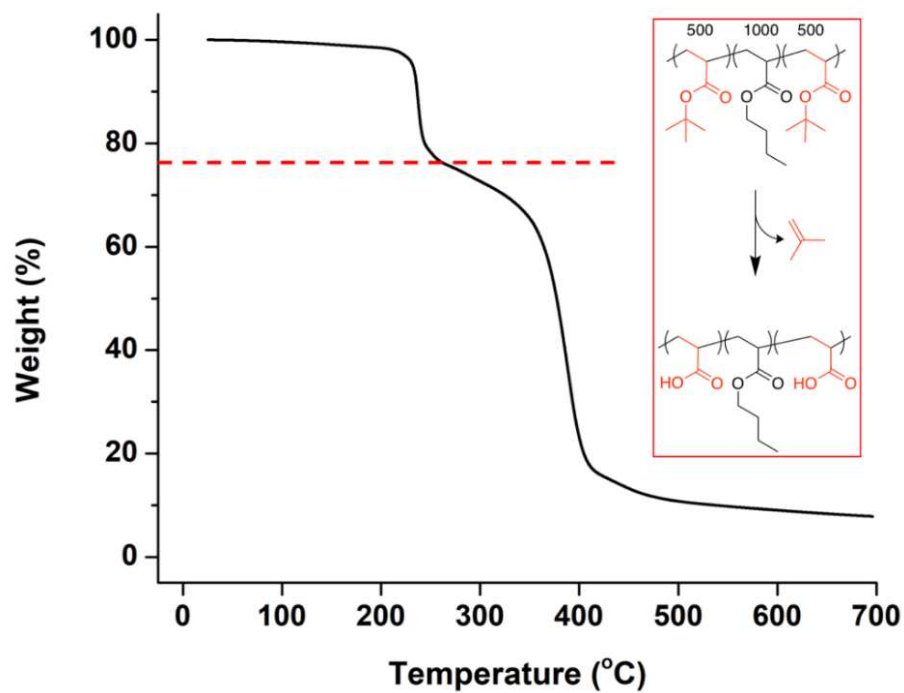
Additional TGA experiments highlighting isothermal high-temperature stability of G3 copolymers are reported below on pages S39-S41.



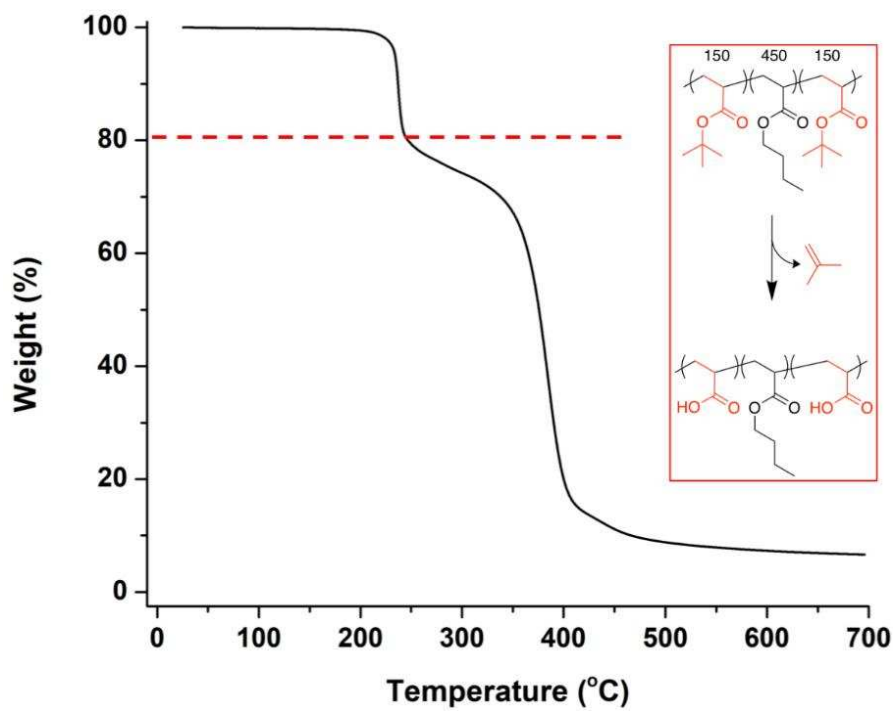
**Figure B16.** TGA curve for P'BA.



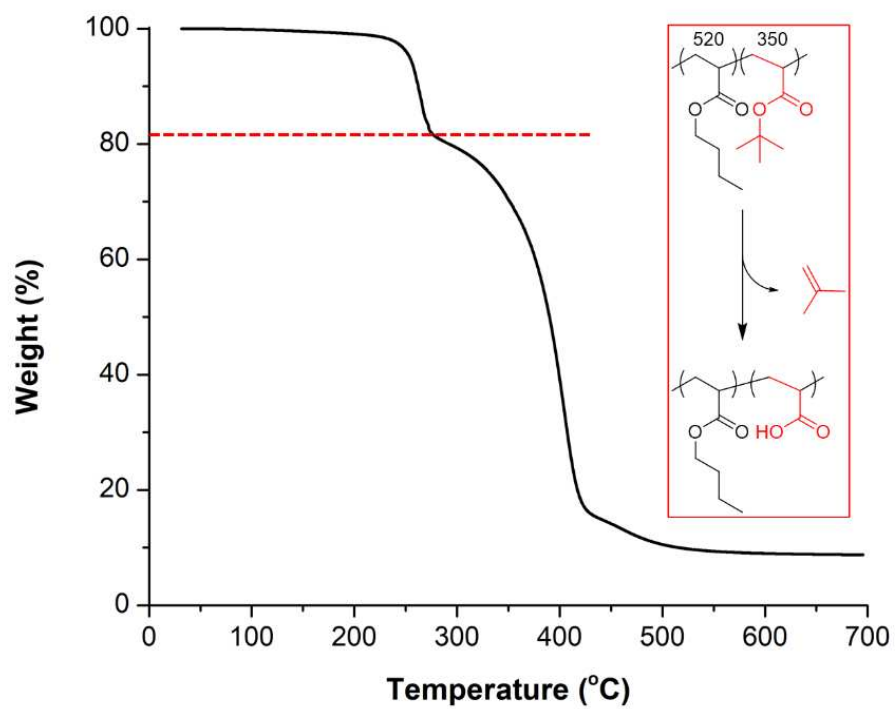
**Figure B17.** TGA curve for P'BA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-P'BA<sub>100</sub>.



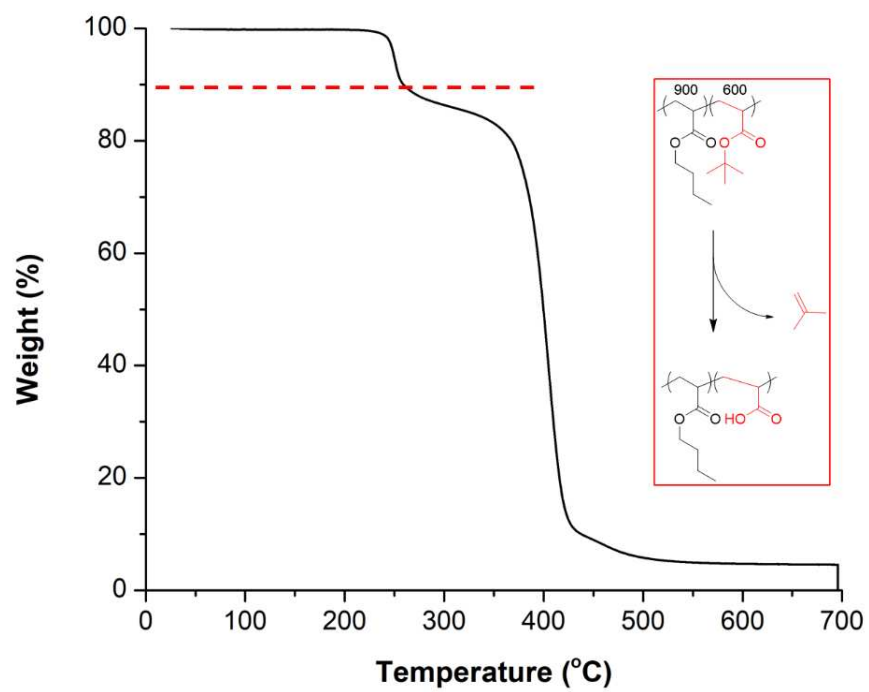
**Figure B18.** TGA curve for  $P'BA_{500}-b-P''BA_{1000}-b-P'BA_{500}$ .



**Figure B19.** TGA curve of  $P'BA_{150}-b-P''BA_{450}-b-P'BA_{150}$ .

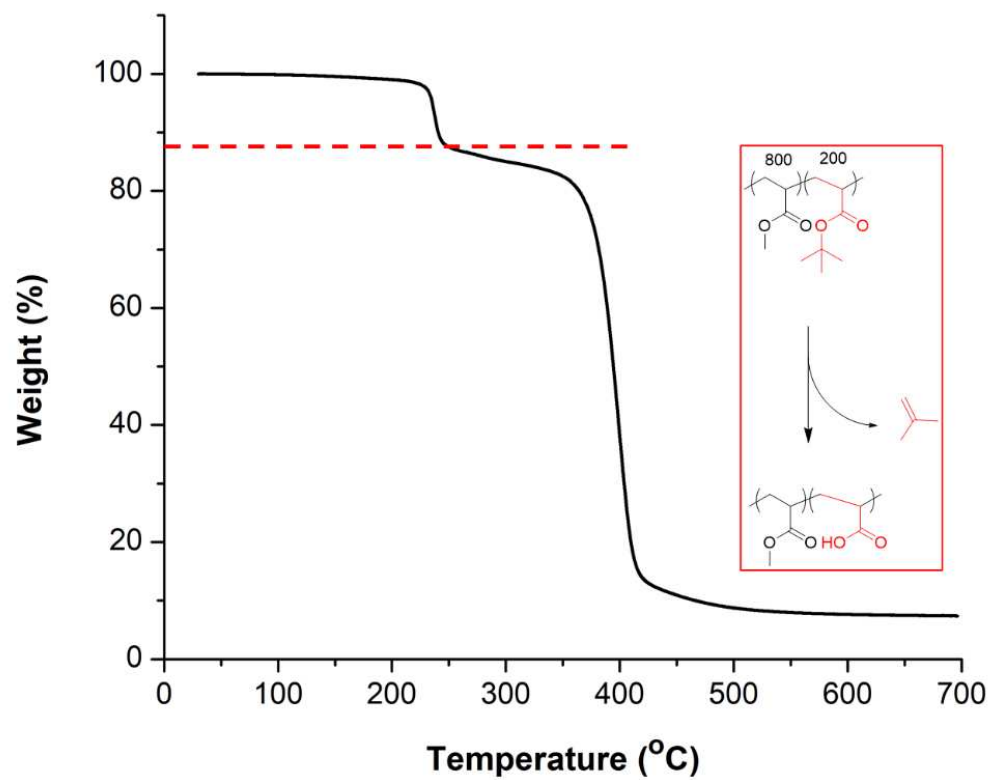


**Figure B20.** TGA curve of  $P''BA_{520}\text{-ran-}P'BA_{350}$ .



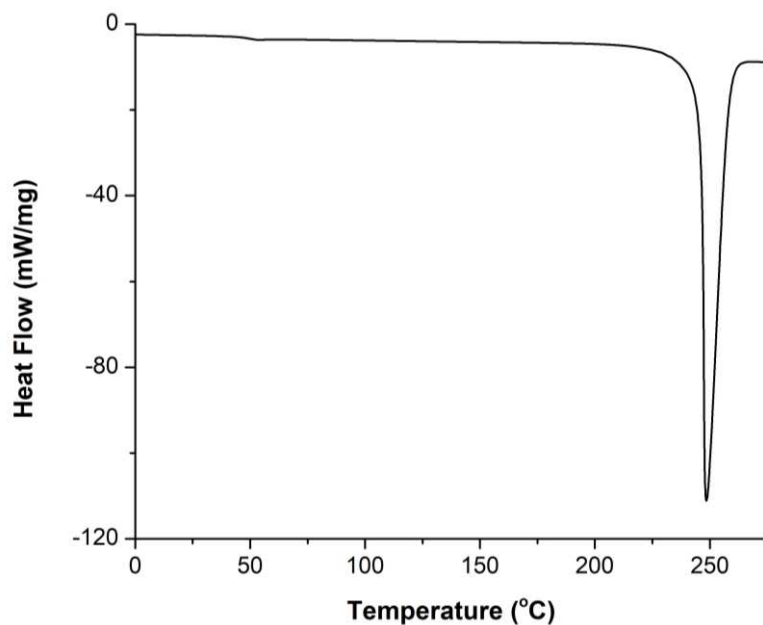
**Figure B21.** TGA curve of  $P''BA_{900}\text{-b-}P'BA_{600}$ .



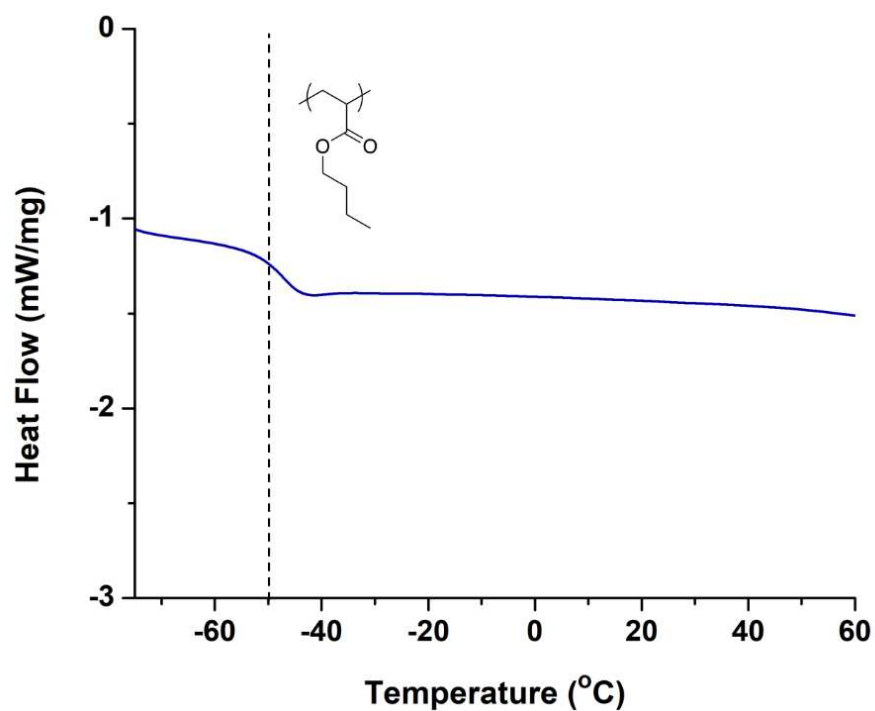


**Figure B22.** TGA curve of P'BA<sub>200</sub>-b-PMA<sub>800</sub>.

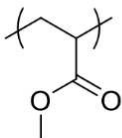
Differential Scanning Calorimetry (DSC):



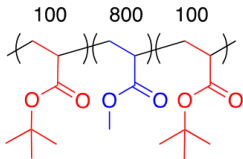
**Figure B23.** DSC trace for the crosslinking reaction that occurs for P'BA homo- and copolymers approaching 250 °C. P'BA  $T_g$  is shown at 50 °C.



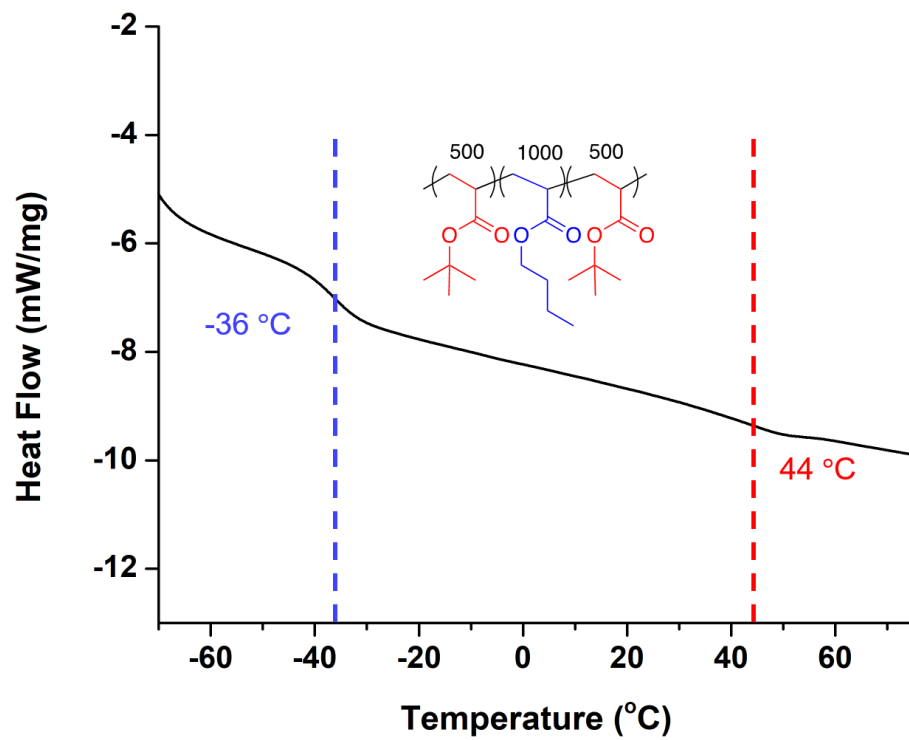
**Figure B24.** DSC trace for P''BA ( $T_g = -50$  °C).



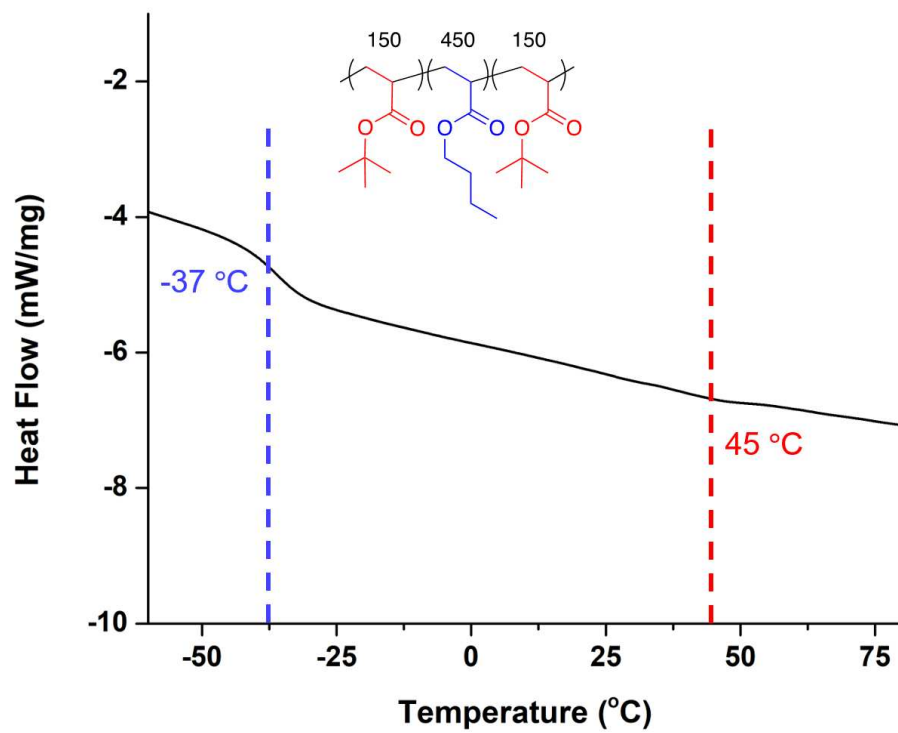
**Figure B25.** DSC trace for PMA ( $T_g = 20\text{ }^{\circ}\text{C}$ ).



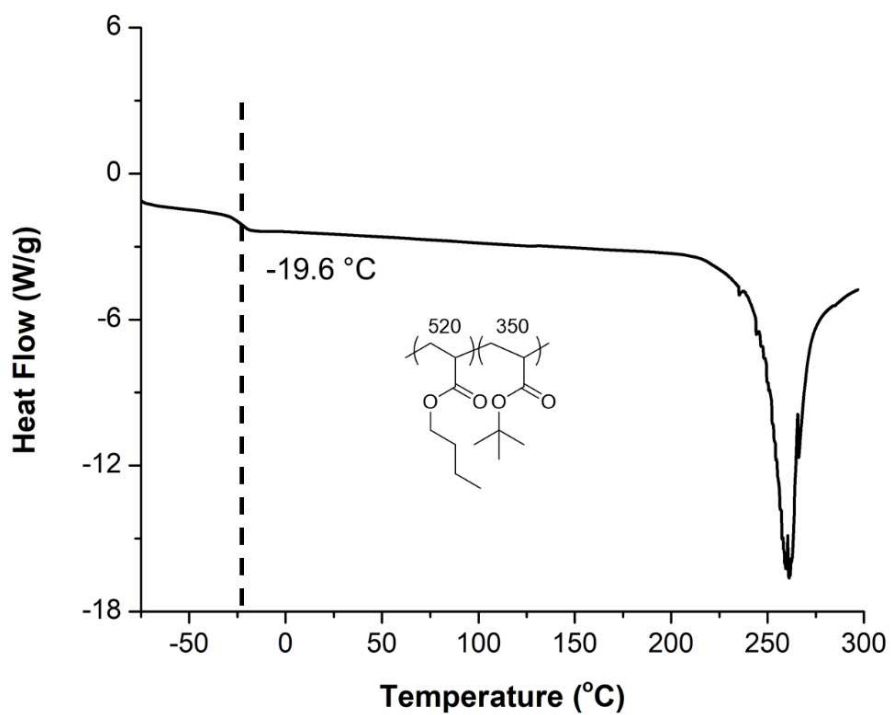
**Figure B26.** DSC trace of P'BA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-P'BA<sub>100</sub>.



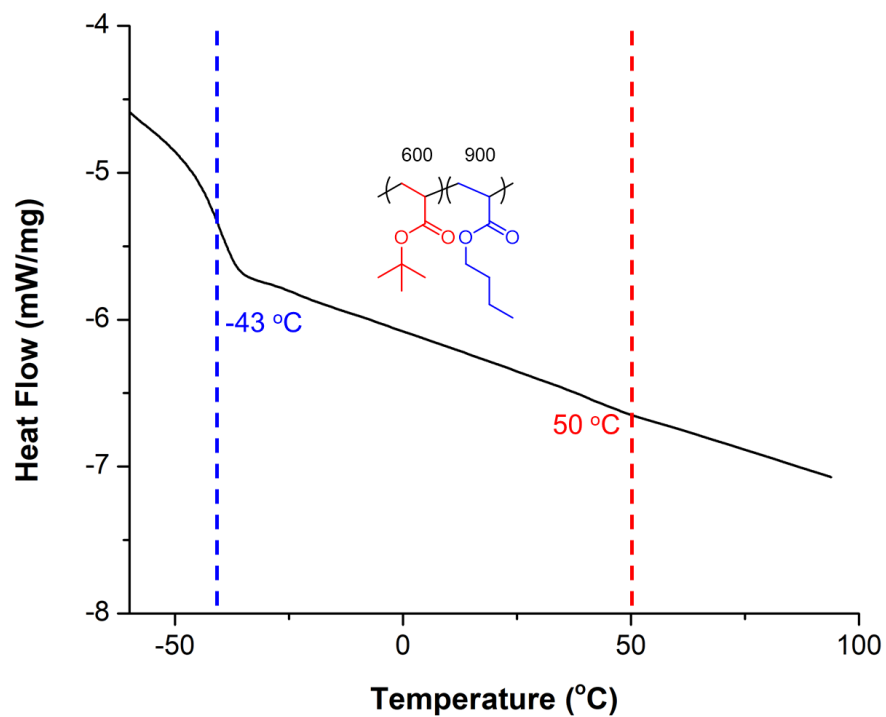
**Figure B27.** DSC trace for G1 P'BA<sub>500</sub>-*b*-P''BA<sub>1000</sub>-*b*-P'BA<sub>500</sub>.



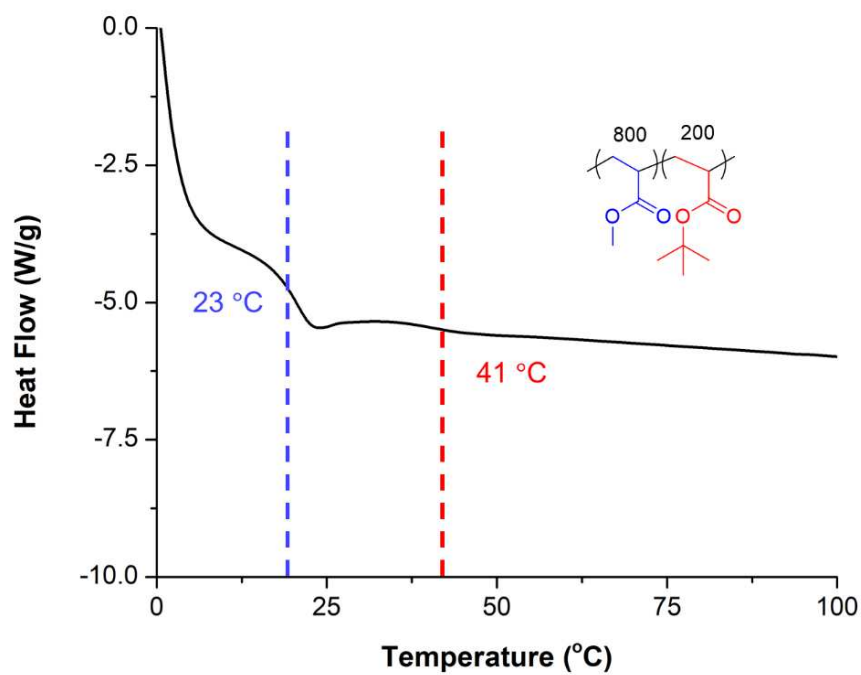
**Figure B28.** DSC trace for  $P'BA_{150}-b-P''BA_{450}-b-P'BA_{150}$ .



**Figure B29.** DSC trace for P<sup>n</sup>BA<sub>520</sub>-*ran*-P<sup>t</sup>BA<sub>350</sub> with single  $T_g$  and thermal de-*tert*-butylation events occurring near -19.6 and 225 °C.

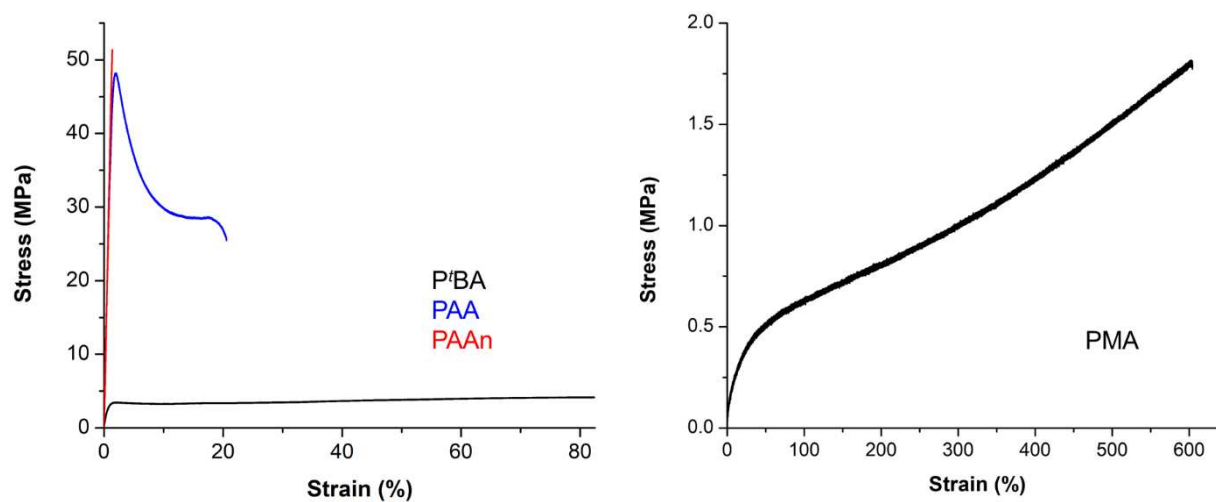


**Figure B30.** DSC trace for P<sup>n</sup>BA<sub>900</sub>-*b*-P<sup>t</sup>BA<sub>600</sub>.



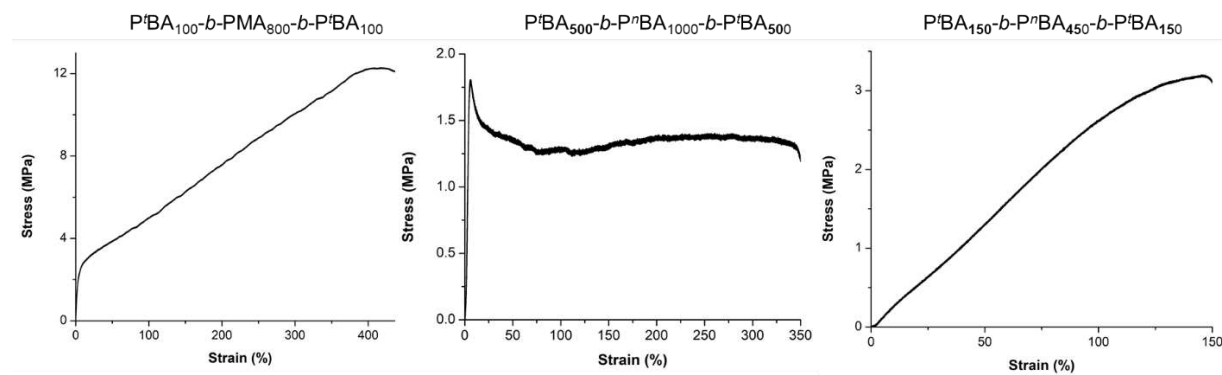
**Figure B31.** DSC trace for P'BA<sub>200</sub>-*b*-PMA<sub>800</sub>.

Homopolymer Tensile Testing:



**Figure B32.** Stress-strain curves for PMA, parent P'BA, G2 PAA, and G3 PAAAn homopolymers (5 mm/min, ~23 °C).

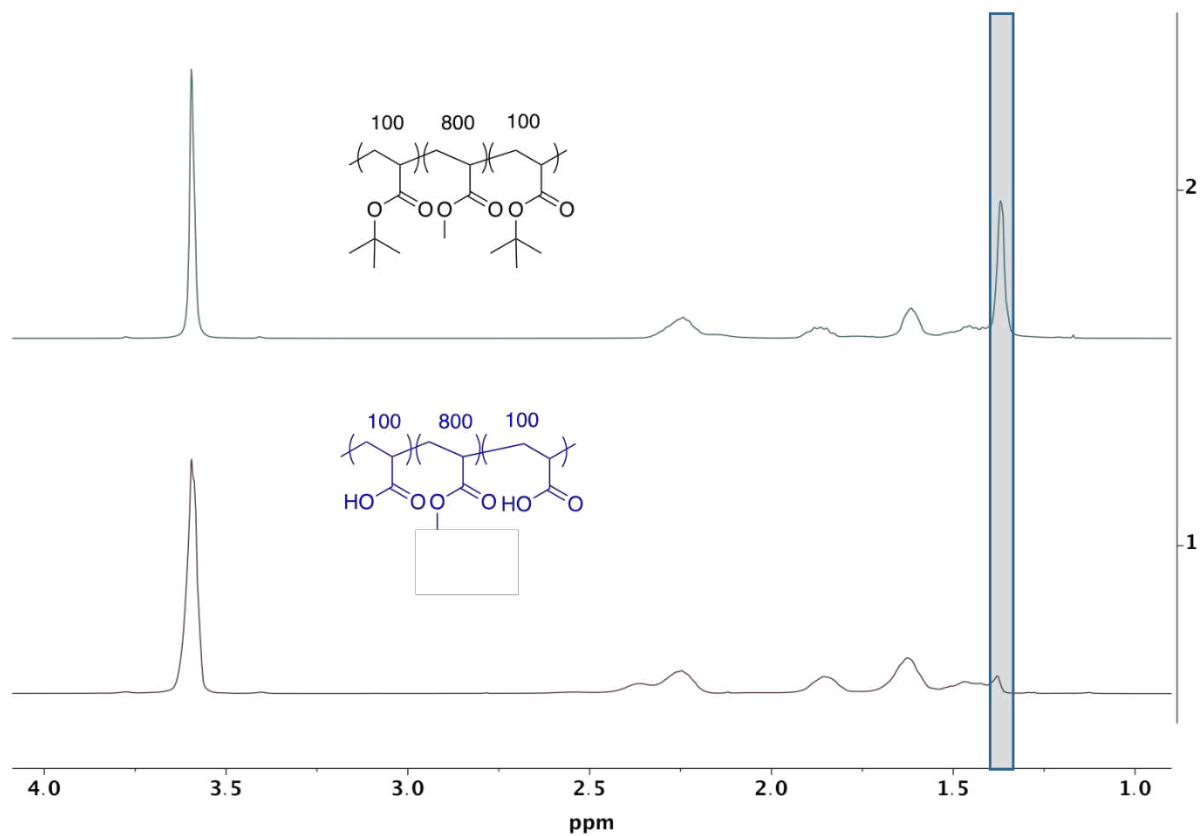
G1 BCP Tensile Testing:



**Figure B33.** Stress-strain curves of G1 triblock copolymers (5 mm/min, ~23 °C).

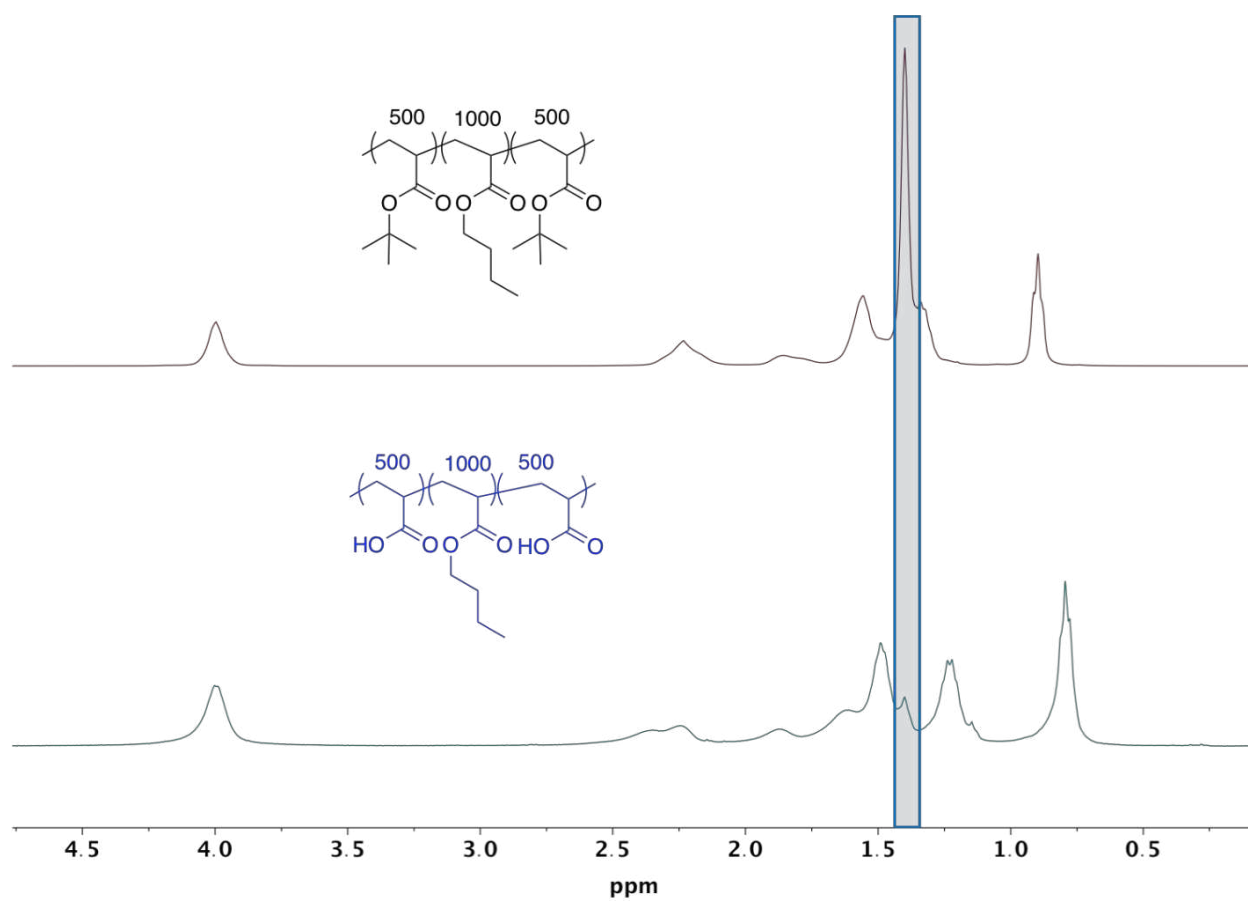
## G2 Copolymer Characterization

$^1\text{H}$  NMR:

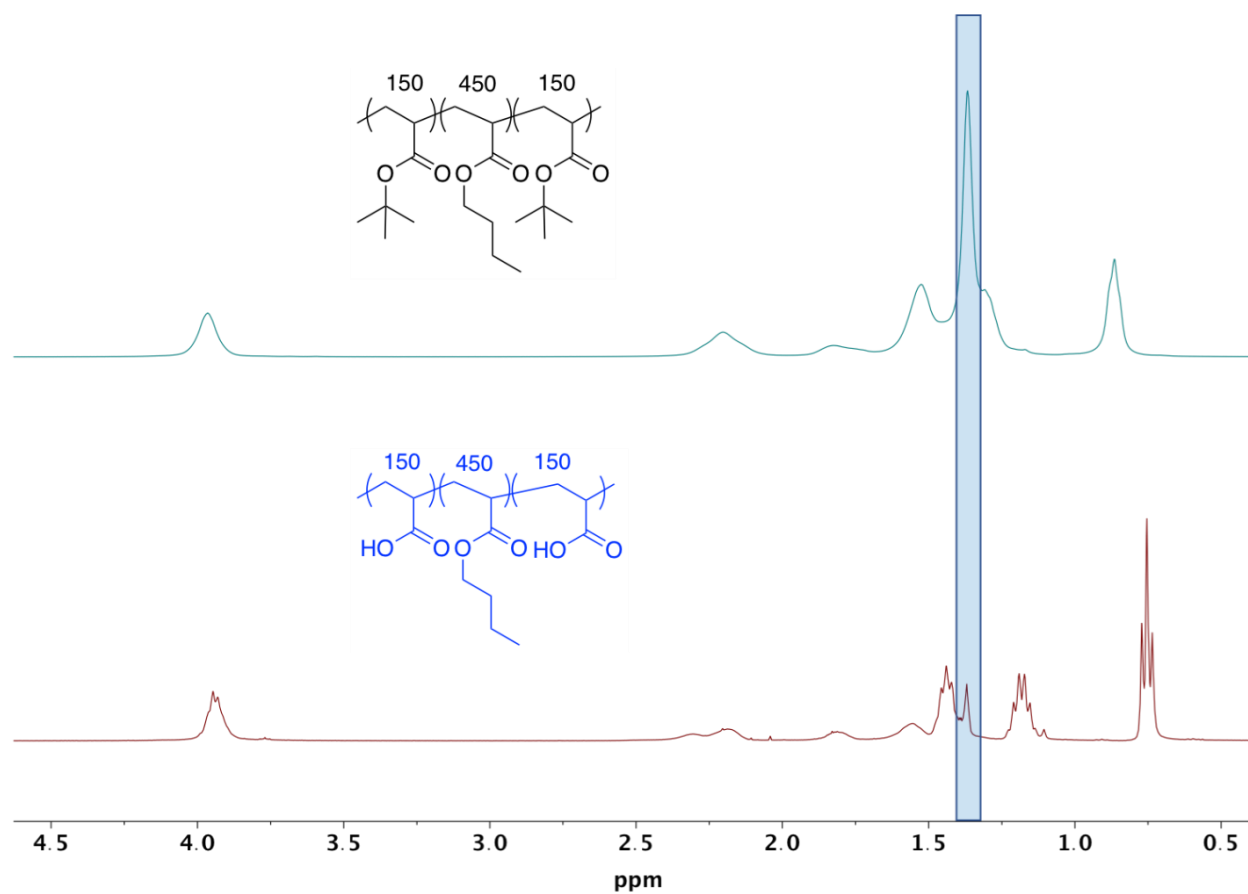


**Figure B34.**  $^1\text{H}$  NMR (TFA- $d_1$ ) spectra for the transformation of  $\text{P}'\text{BA}_{100}\text{-}b\text{-PMA}_{800}\text{-}b\text{-P}'\text{BA}_{100}$  (G1) to  $\text{PAA}_{100}\text{-}b\text{-PMA}_{800}\text{-}b\text{-PAA}_{100}$  (G2).

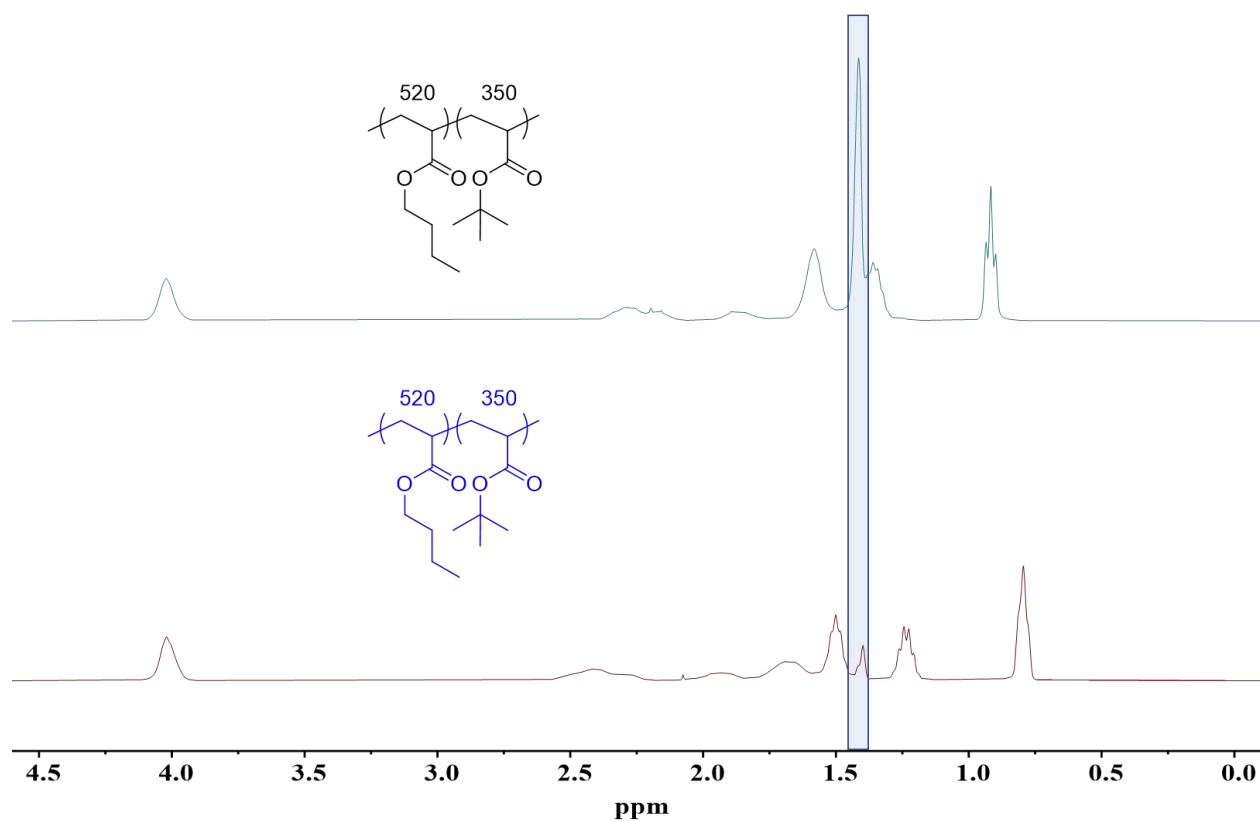




**Figure B35.**  $^1\text{H}$  NMR ( $\text{TFA-}d_1$ ) spectra for the transformation of  $\text{P}'\text{BA}_{500}\text{-}b\text{-P}''\text{BA}_{1000}\text{-}b\text{-P}'\text{BA}_{500}$  (G1) to  $\text{PAA}_{500}\text{-}b\text{-P}''\text{BA}_{1000}\text{-}b\text{-PAA}_{500}$  (G2).

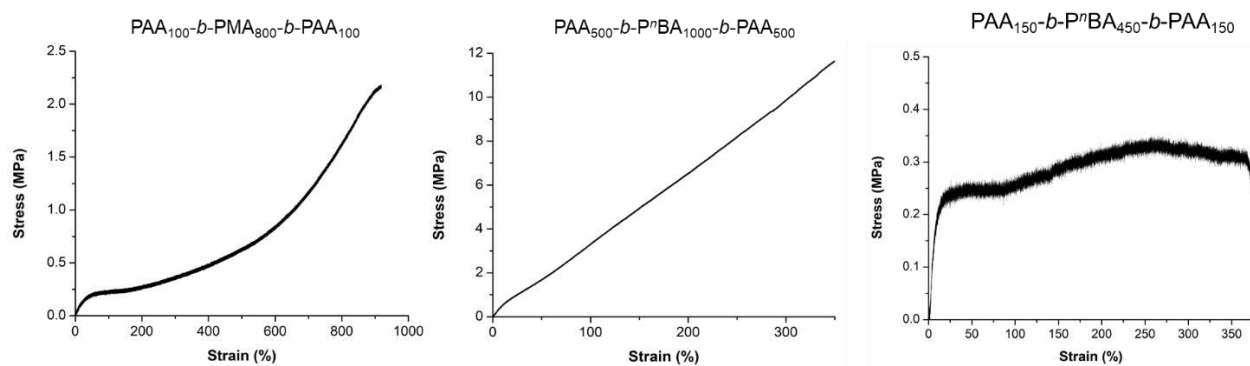


**Figure B36.**  $^1\text{H}$  NMR ( $\text{TFA-}d_1$ ) spectra for the transformation of  $\text{P}'\text{BA}_{150}\text{-}b\text{-}\text{P}''\text{BA}_{450}\text{-}b\text{-}\text{P}'\text{BA}_{150}$  (G1) to  $\text{PAA}_{150}\text{-}b\text{-}\text{P}''\text{BA}_{450}\text{-}b\text{-}\text{PAA}_{150}$  (G2).



**Figure B37.**  $^1\text{H}$  NMR ( $\text{TFA-}d_1$ ) spectra for the transformation of  $\text{P}''\text{BA}_{520}\text{-ran-P}'\text{BA}_{350}$  (G1) to  $\text{P}''\text{BA}_{520}\text{-ran-PAA}_{350}$  (G2).

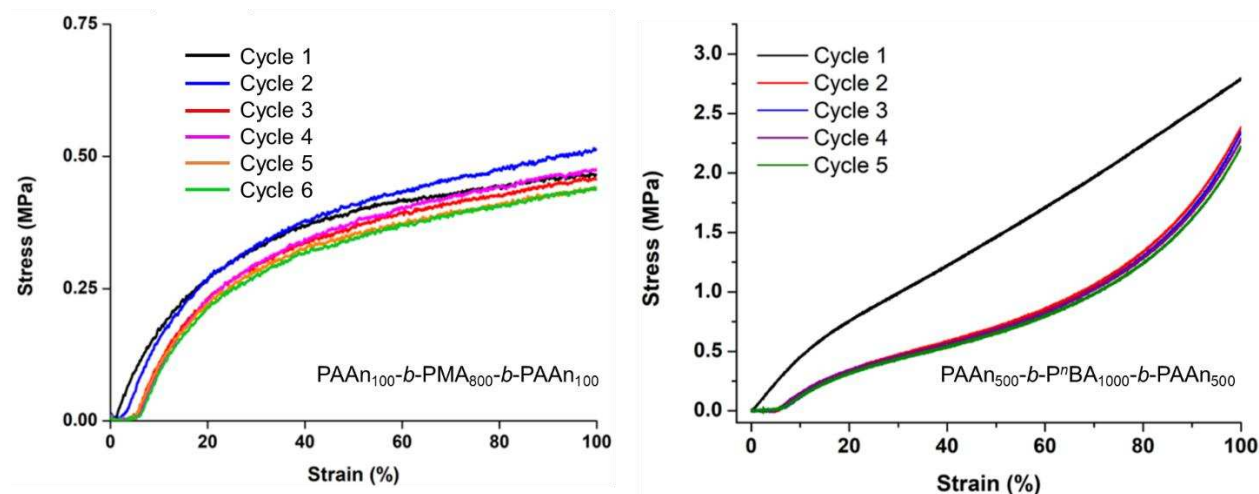
### G2 BCP Tensile Testing:



**Figure B38.** Stress-strain curves of G2 triblock copolymers (5 mm/min,  $\sim 23^\circ\text{C}$ ).

### Cyclic Deformation:

Cyclic strain-recovery experiments were performed on thin films of G2 copolymers PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub> and PAA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>500</sub>. Polymers are strained to 100 % elongation and returned to initial strain (= 0 %) for five minutes before re-straining.

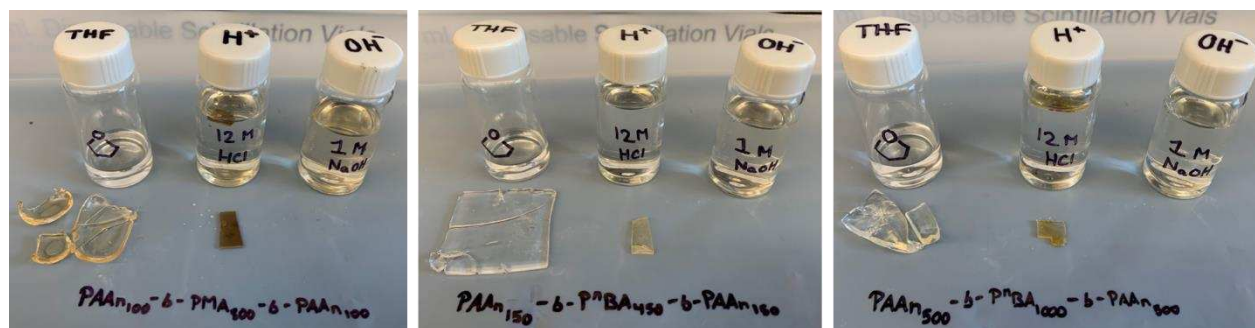


**Figure B39.** Cyclic strain (100 %) of elastic G2 BCPs (5 mm/min, ~23 °C, 5 min rest).

## G3 Copolymer-CAN Characterization

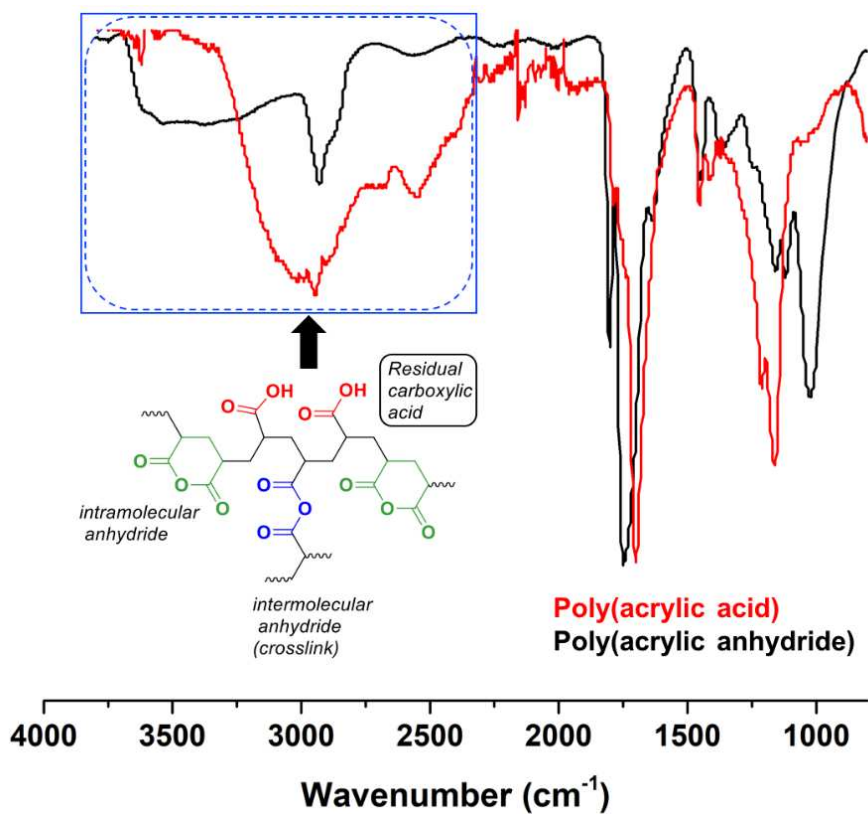
### Solubility Tests:

Film samples of each triblock copolymer CAN were submerged in 1 M HCl, 1 M NaOH, and THF. Crosslinking by anhydride units, as opposed to decomposition products (ketones, etc.), is supported by the significant swelling in THF, acid robustness, and complete solubility in basic aqueous media.

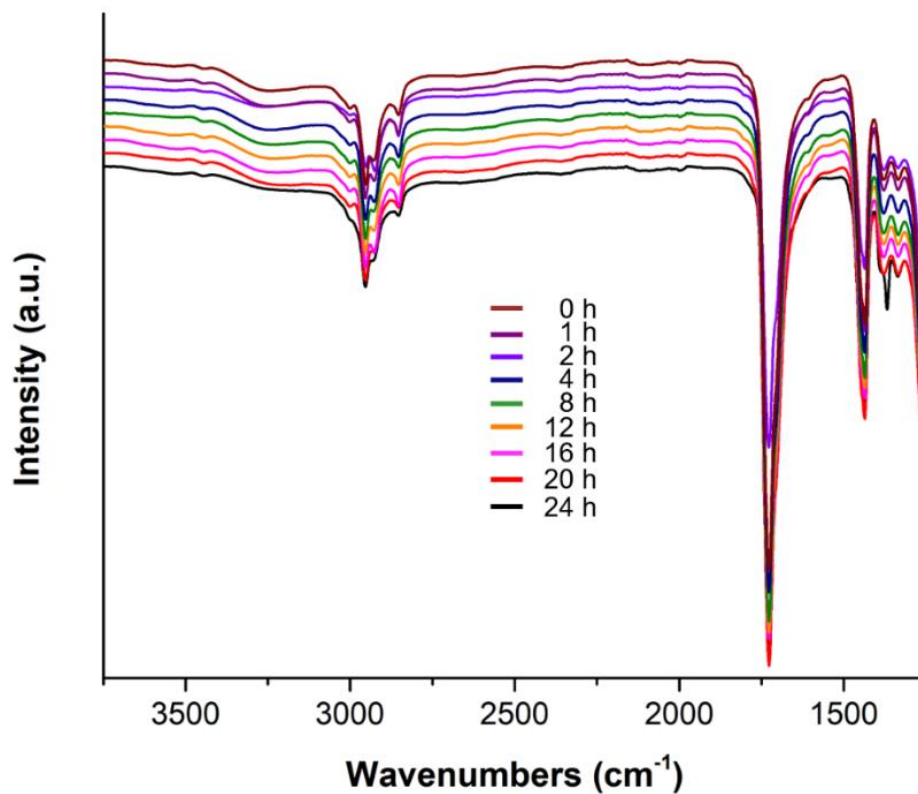


**Figure B40.** Digital images of solubility experiments in THF, 12 M HCl, and 1 M NaOH on each G3 tri-BCP-CAN as labeled.

Fourier-Transform Infrared Spectroscopy (FTIR):



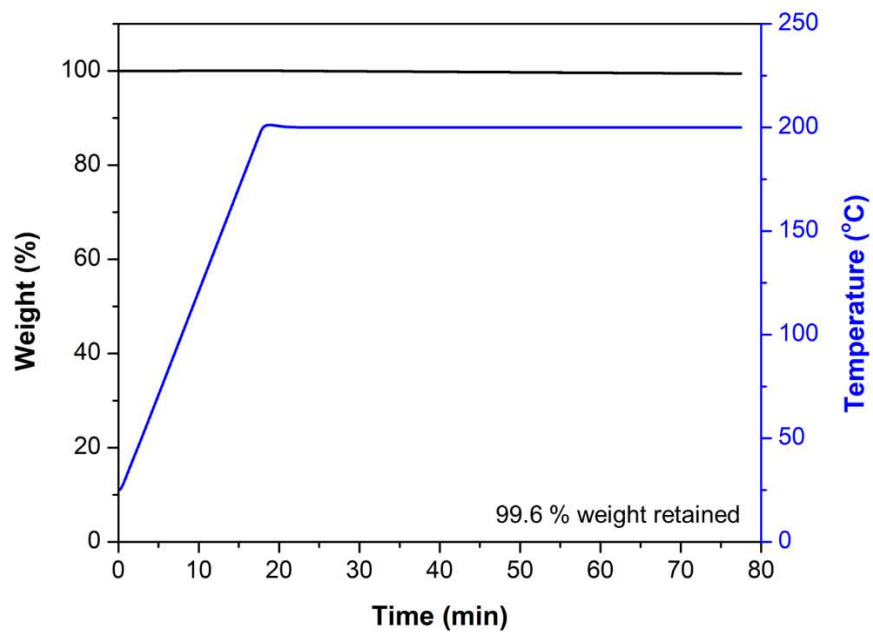
**Figure B41.** FTIR overlay of PAA (red) and synthesized PAA<sub>n</sub> (black) with residual broad hydroxyl signal as evidence for unreacted (exchange-active) acids.



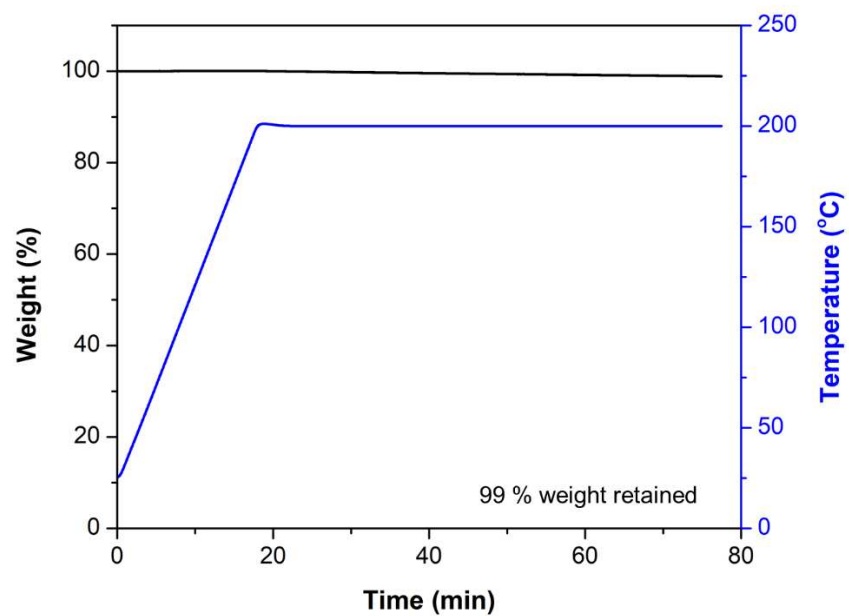
**Figure B42.** FTIR spectral overlay for all crosslinking time-point samples of PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub> between 0 (G2) and 24 h (G3).

*Isothermal High-Temperature Stability (TGA):*

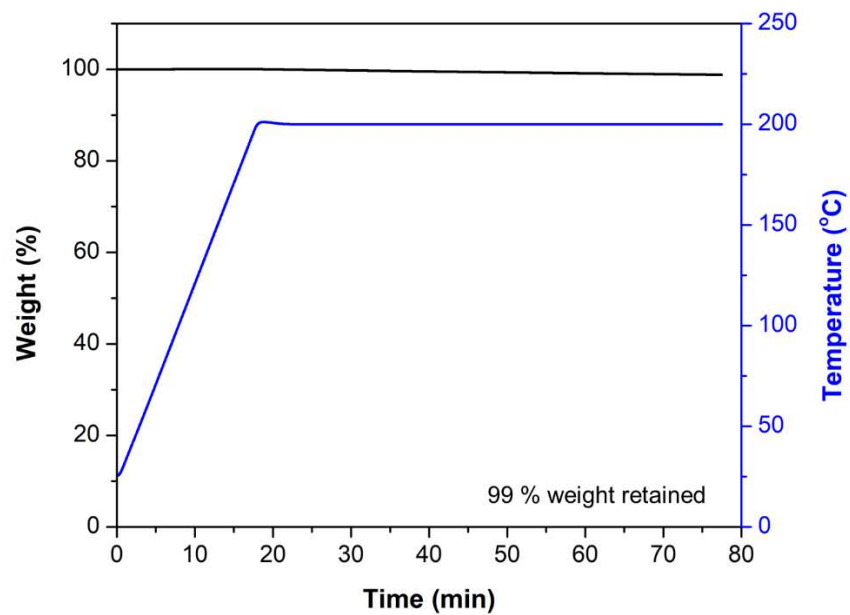
Polymer samples (~ 10 mg) were loaded into a tared platinum TGA pan and elevated to 200 °C under nitrogen. The temperature was held isothermally for 1 h while weight loss was recorded.



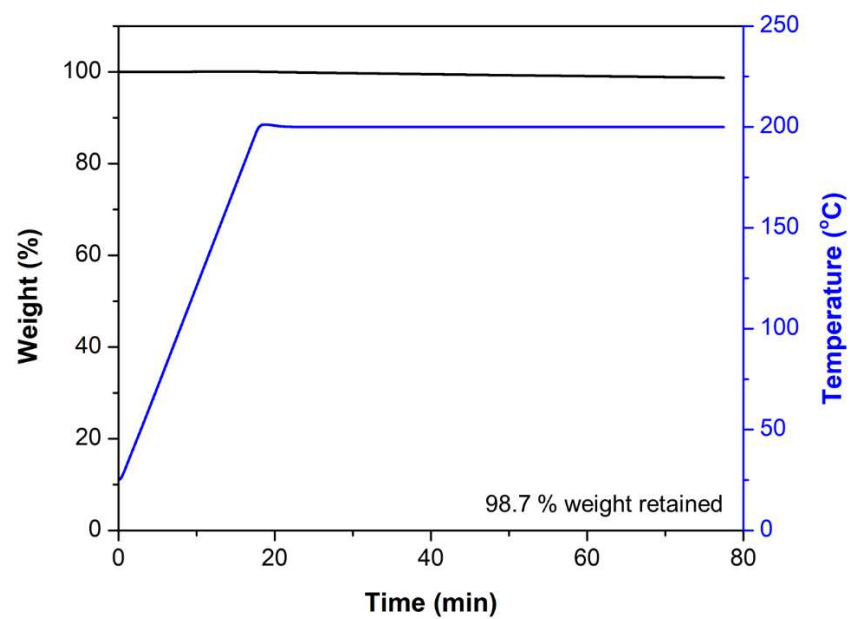
**Figure B43.** TGA isothermal decomposition evaluation of G3 PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub>.



**Figure B44.** TGA isothermal decomposition evaluation of G3 PAA<sub>n500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>n500</sub>.

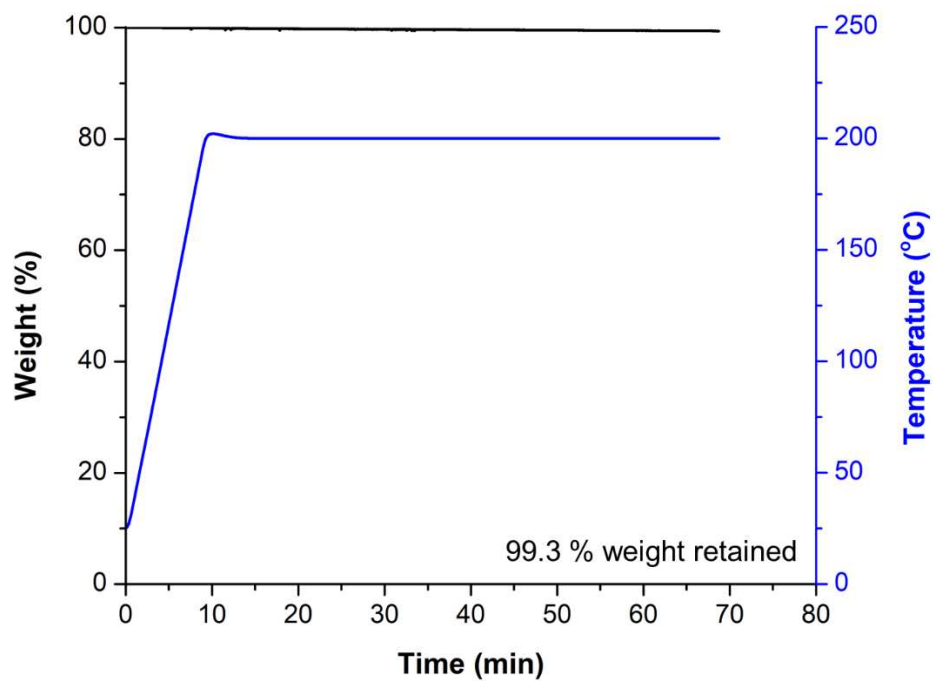


**Figure B45.** TGA isothermal decomposition evaluation of G3 PAA<sub>n150</sub>-b-P''BA<sub>450</sub>-b-PAA<sub>n150</sub>.

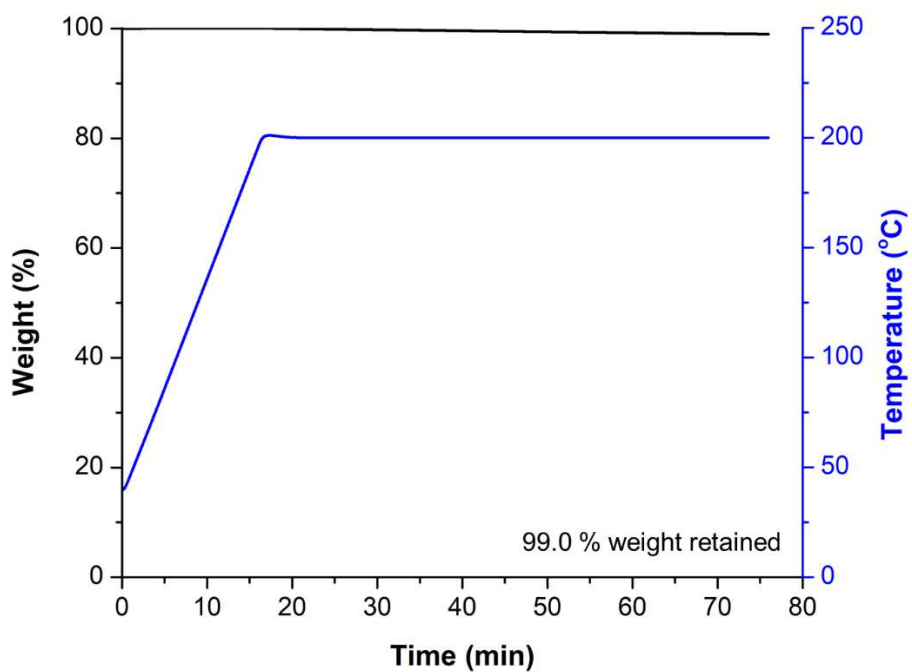


**Figure B46.** TGA isothermal decomposition evaluation of G3 P''BA<sub>520</sub>-ran-PAA<sub>n350</sub>.





**Figure B47.** TGA isothermal decomposition evaluation of G3 P''BA<sub>900</sub>-b-PAA<sub>600</sub>.



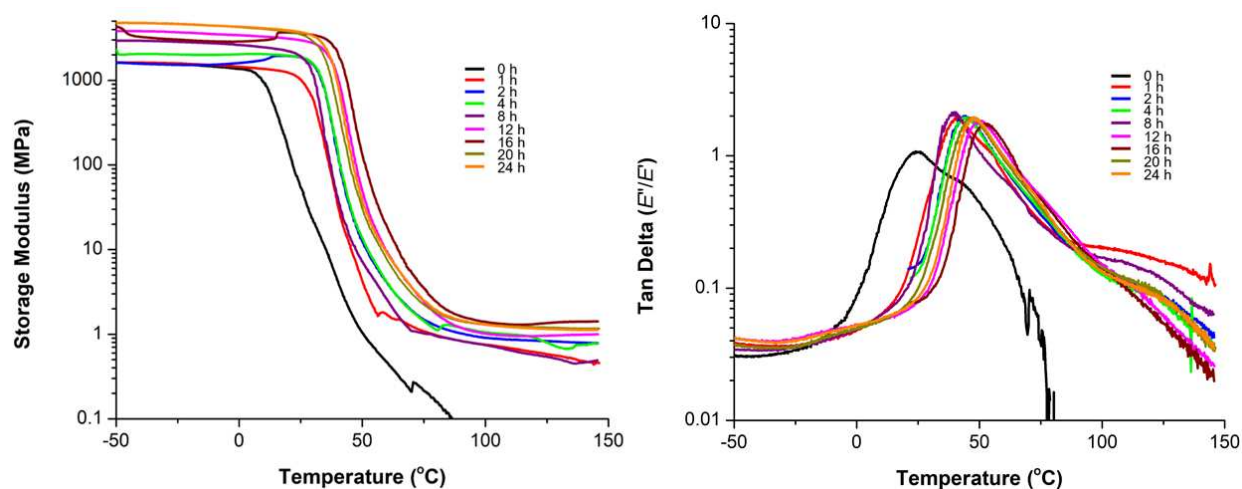
**Figure B48.** TGA isothermal decomposition evaluation of G3 P'BA<sub>200</sub>-b-PMA<sub>800</sub>.

Dynamic Mechanical Analysis (DMA):

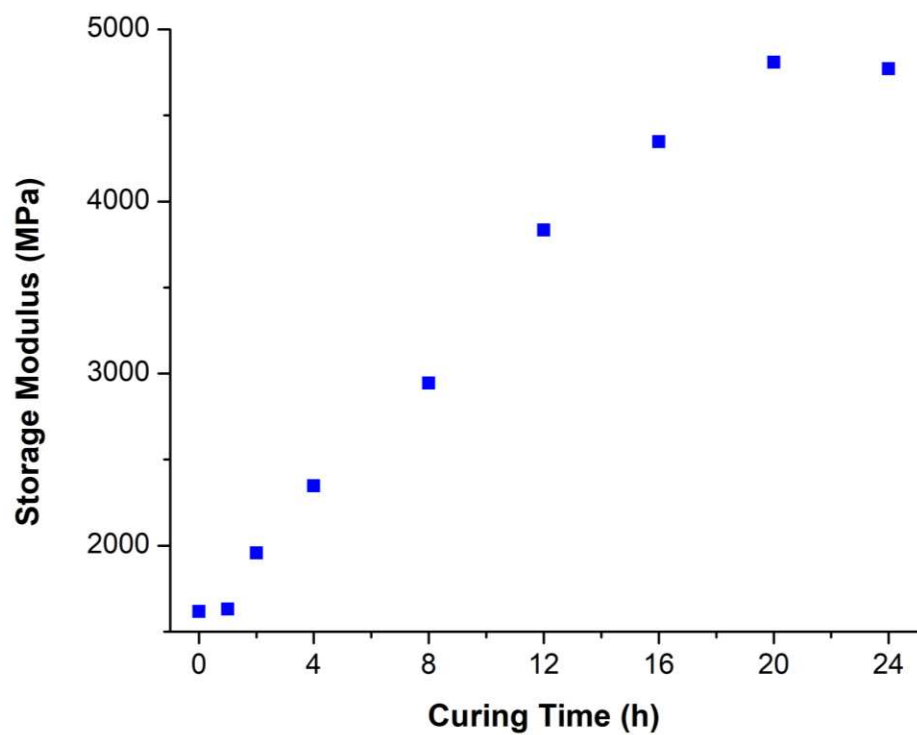
PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n</sub> (G3) samples used for probing storage modulus ( $E'$ ) and tan delta ( $E''/E'$ ) evolution by crosslinking time were prepared by compression-molding a single large film of PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-PAA<sub>100</sub> (G2) at 200 °C under 5 kpsi of compression and cutting DMA strips (two, same width and thickness) at reported time points before returning the remaining majority of the film to the hydraulic press.

*Temperature-ramp frequency sweeps* were performed between -50 to 200 °C with 0.3 % strain and a frequency of 1 Hz. Material integrity up to 200 °C is supported by an unperturbed rubbery plateau ( $E'$  is near-constant). DMA sample holders were tightened to 7 N pressure.

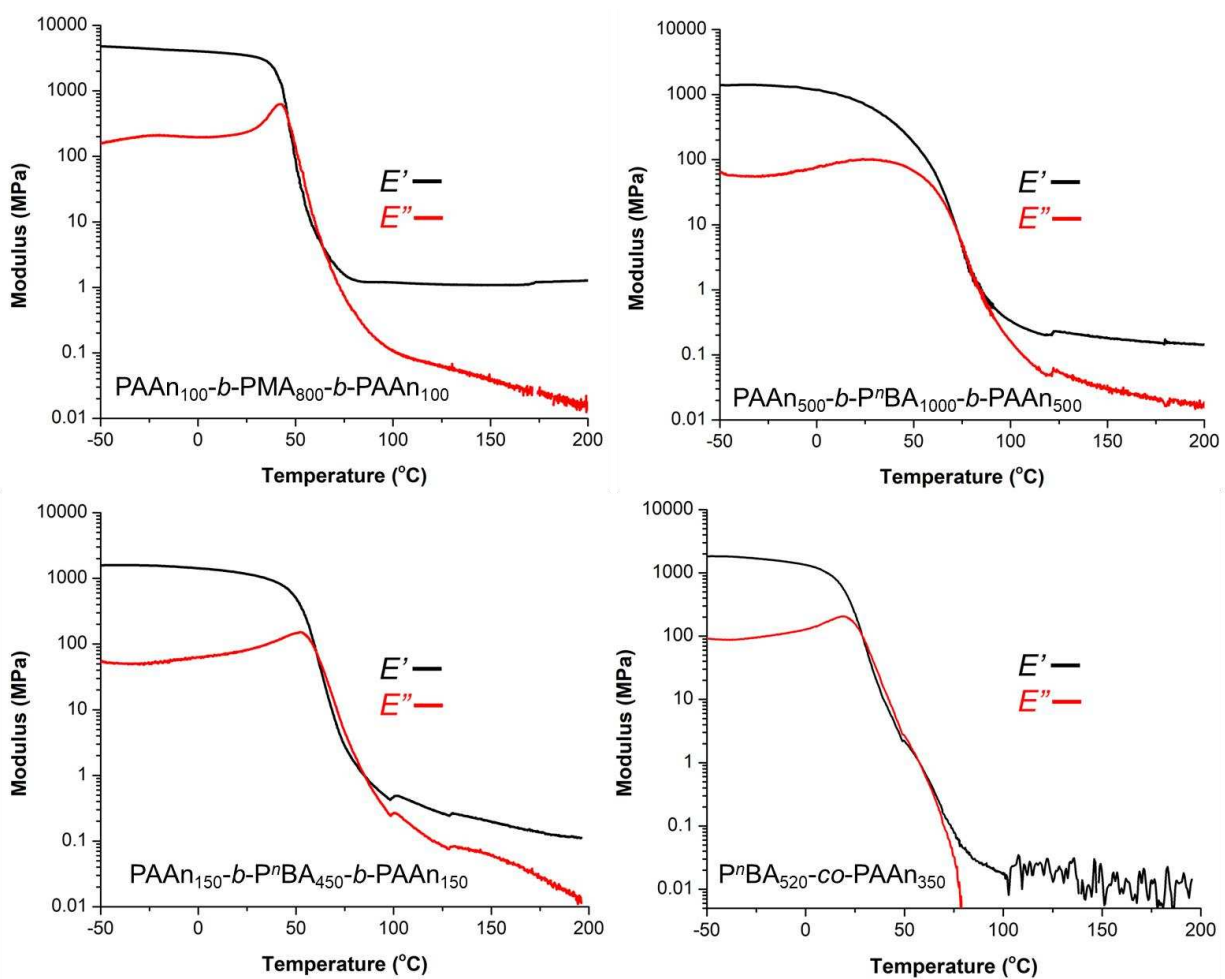
*Isothermal high-temperature frequency sweeps* were performed at a strain of 0.3 % and pulled at frequencies between 0.1 and 10 Hz.



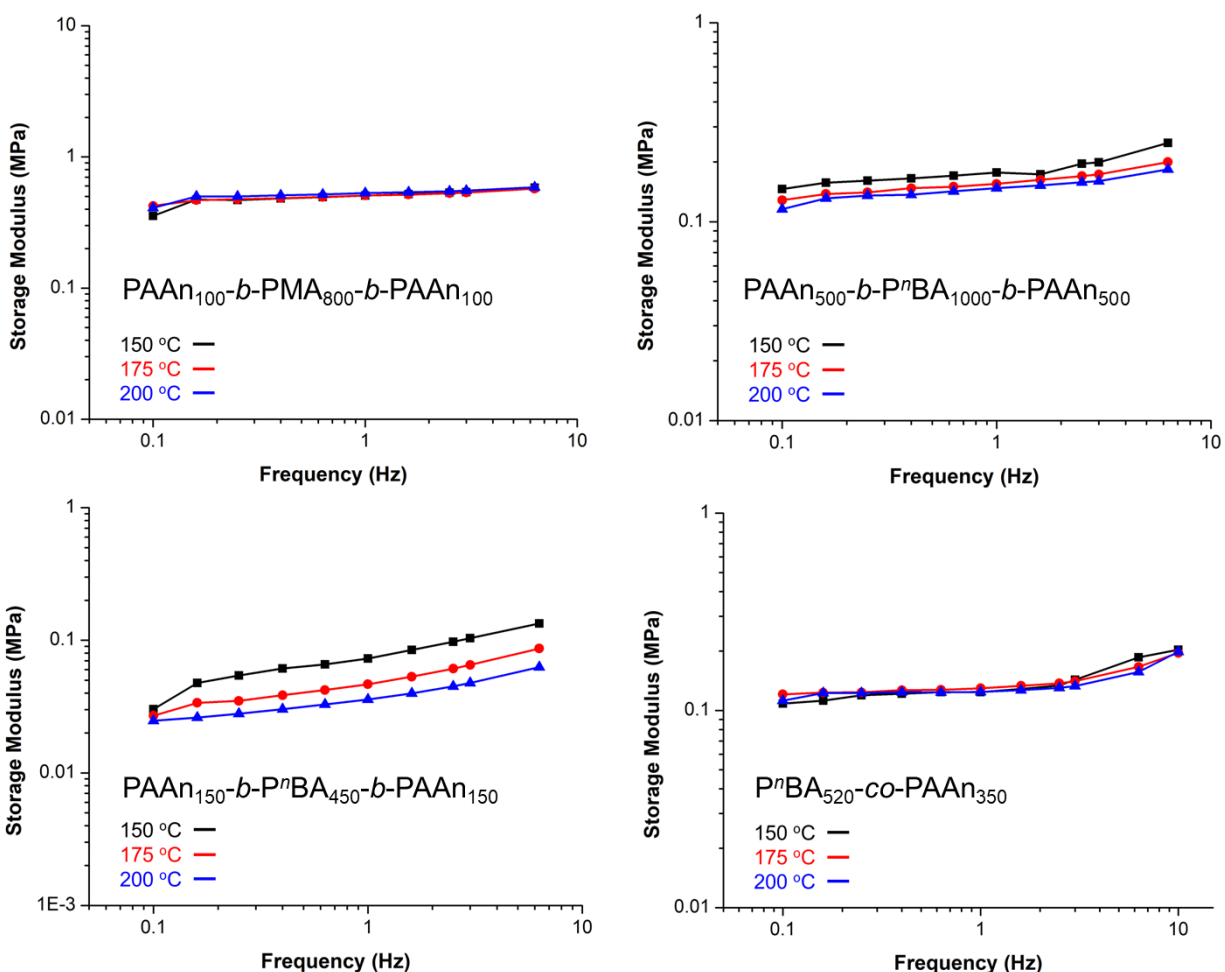
**Figure B49.** Temperature-ramp frequency sweeps (0.3 %, 1 Hz) highlighting the storage modulus ( $E'$ , left) and the tan delta ( $E''/E'$ , right) of PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub> with varied thermal crosslinking time.



**Figure B50.** Evolution of  $E'_{\max}$  for PAA<sub>n100</sub>-b-PMA<sub>800</sub>-b-PAA<sub>n100</sub> by DMA as a function of the crosslinking time. Observed is the plateaued modulus after 20 hours of crosslinking. Values representing  $E'_{\max}$  are at temperatures below RT and the PMA  $T_g$ .



**Figure B51.** Temperature-ramp frequency sweeps ( $E'$ ) of G3 copolymers (5  $^{\circ}\text{C}/\text{min}$ , 0.3 % strain, 1 Hz).

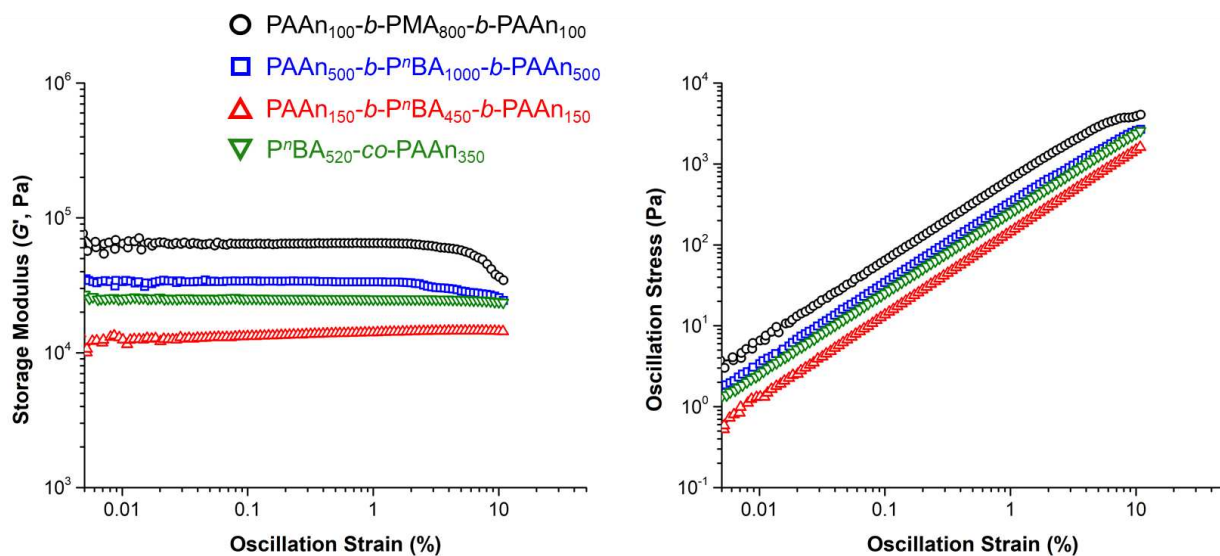


**Figure B52.** Isothermal high-temperature frequency sweeps ( $E'$ ) of G3 copolymers (0.3 % strain).

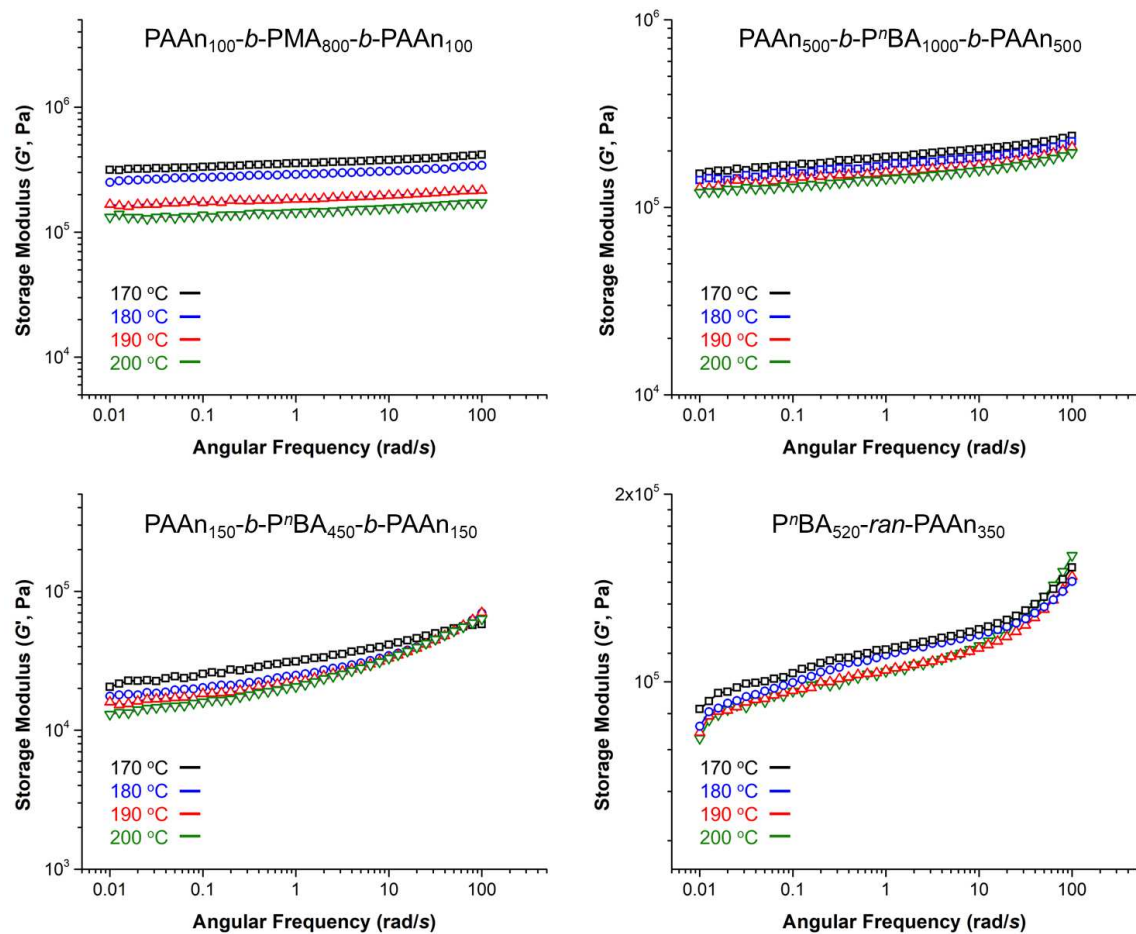
#### Oscillatory Shear Rheology:

Rheology was performed between temperatures of 100 – 200 °C and under controlled axial force of  $0 \pm 0.2$  N. Strain sweeps were conducted to find the strain-limitations of the viscoelastic window, for which all shear rheological testing was performed within. High-temperature frequency sweeps were performed between angular frequencies of 0.01 and 100 rad/s at 0.1 % shear strain. Stress relaxation experiments were performed at 0.3 % shear strain with a controlled

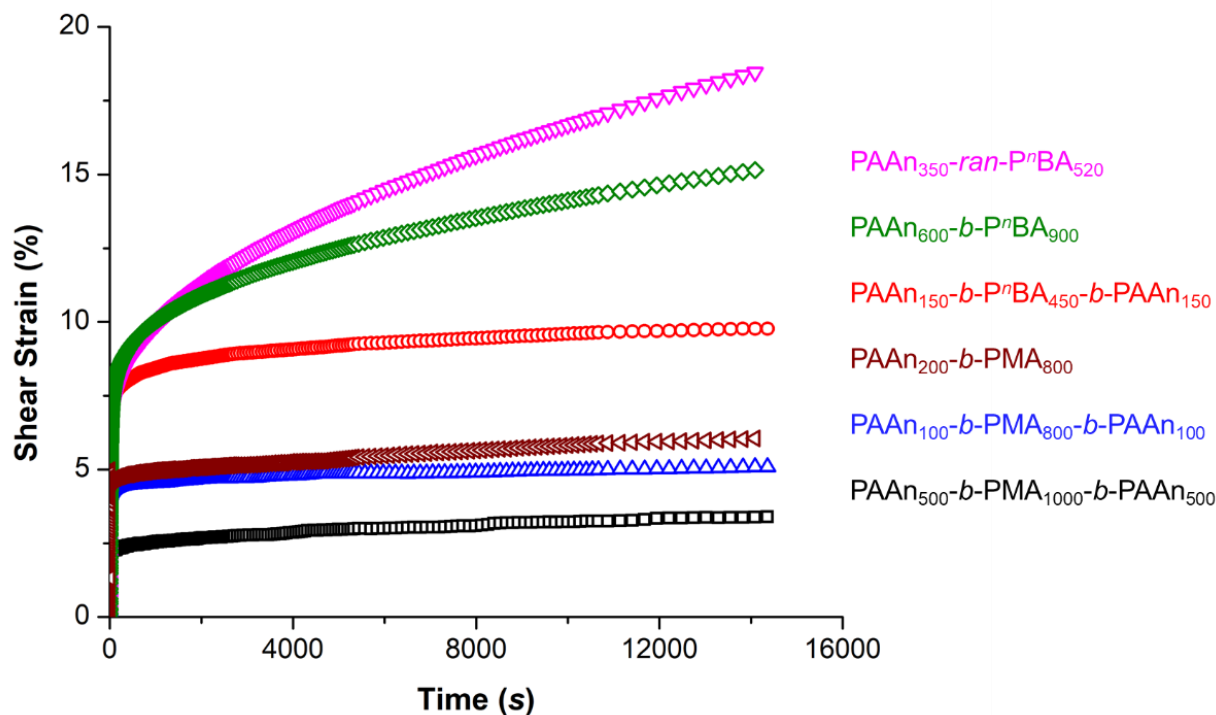
strain-rise time of 1 s. Prolonged creep experiments were performed at 200 °C with 5 kPa of shear stress for 4 hours to mimic long-term deformation.



**Figure B53.** Shear strain sweeps (200 °C, 0.005 – 10 %) highlighting the G3 copolymers' linear viscoelastic window by storage modulus ( $G'$ , left) and oscillation stress (right).



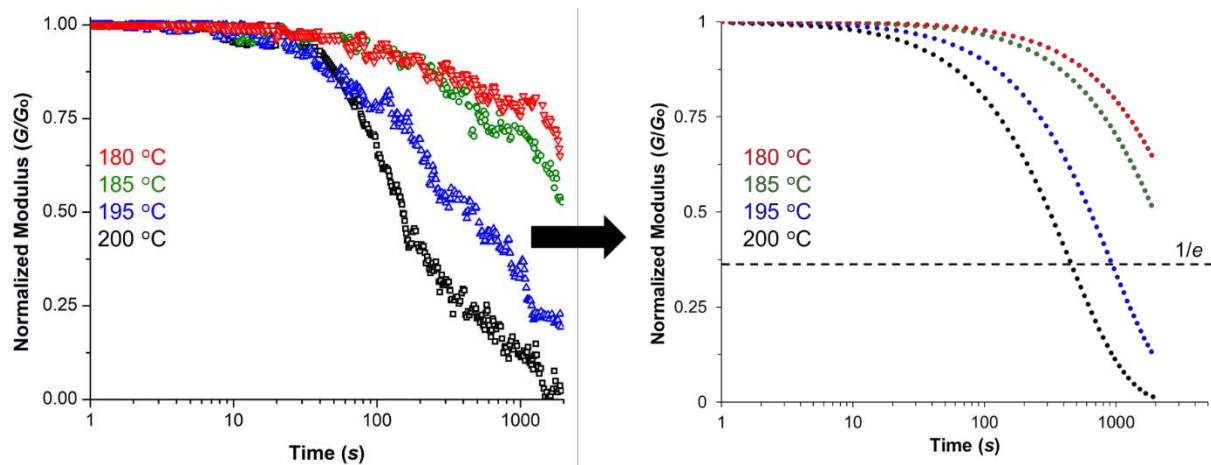
**Figure B54.** High-temperature isothermal frequency sweeps of each G3 copolymer (0.1 % strain).



**Figure B55.** Oscillatory creep experiments for each of the G3 copolymers highlighting the morphology-regulated thermal creep resistance of the ABA-networks compared to random and di-block copolymer analogues (5 kPa, 4 h).

*Stress Relaxation* experiments were performed, as mentioned above, at 0.3 % oscillatory strain with a rise time of 1 s and at the temperatures 180, 185, 195, and 200 °C. The random copolymer, able to exhibit productive exchange over the triblock analogues, was analyzed for the activation energy of the proposed exchange mechanisms.





**Figure B56.** Normalized stress relaxation curves of the G3 P<sup>n</sup>BA<sub>520-co</sub>-PAA<sub>n350</sub> (left) and the normalized fitted stress relaxation curves (right) (0.3 % strain).

Relaxation curves were fitted to an exponentially decaying trendline to generate the following functions:

$$\tau_{(T=180\text{ }^{\circ}\text{C})} = e^{-0.0002314(t)} \quad [\text{Eq. 1}]$$

$$\tau_{(T=185\text{ }^{\circ}\text{C})} = e^{-0.0003530(t)} \quad [\text{Eq. 2}]$$

$$\tau_{(T=195\text{ }^{\circ}\text{C})} = e^{-0.0010866(t)} \quad [\text{Eq. 3}]$$

$$\tau_{(T=200\text{ }^{\circ}\text{C})} = e^{-0.0022165(t)} \quad [\text{Eq. 4}]$$

Where  $t$  is the characteristic relaxation time at which the normalized modulus is  $1/e$  (0.367) assuming a single Maxwell element.<sup>3</sup> Solving each function for  $\tau_{(t = 0.367)}$  yielded the following time constants:

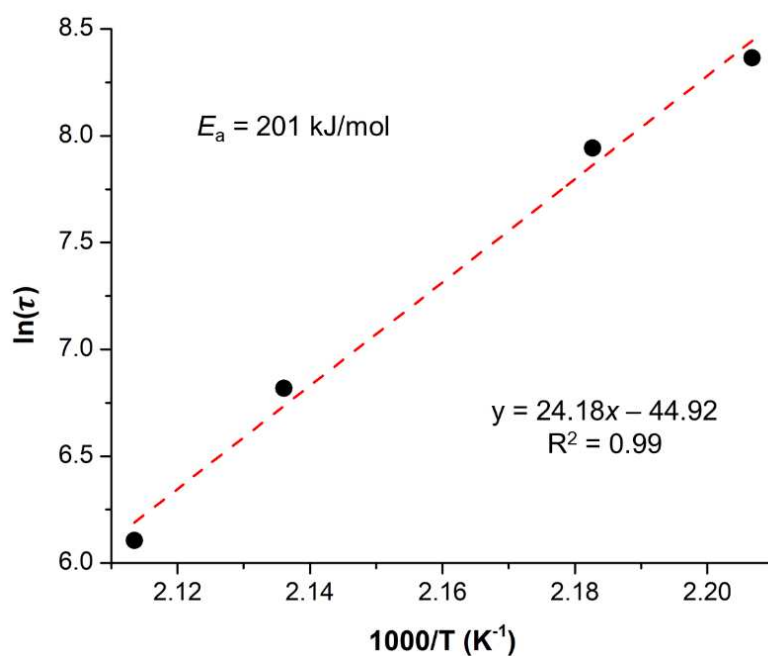
$$\tau_{(T=180\text{ }^{\circ}\text{C})} = 4296; \quad \ln(4296) = 8.37$$

$$\tau_{(T=185\text{ }^{\circ}\text{C})} = 2816; \quad \ln(2816) = 7.94$$

$$\tau_{(T=195\text{ }^{\circ}\text{C})} = 915; \quad \ln(915) = 6.82$$

$$\tau_{(T=200\text{ }^{\circ}\text{C})} = 449; \quad \ln(449) = 6.11$$

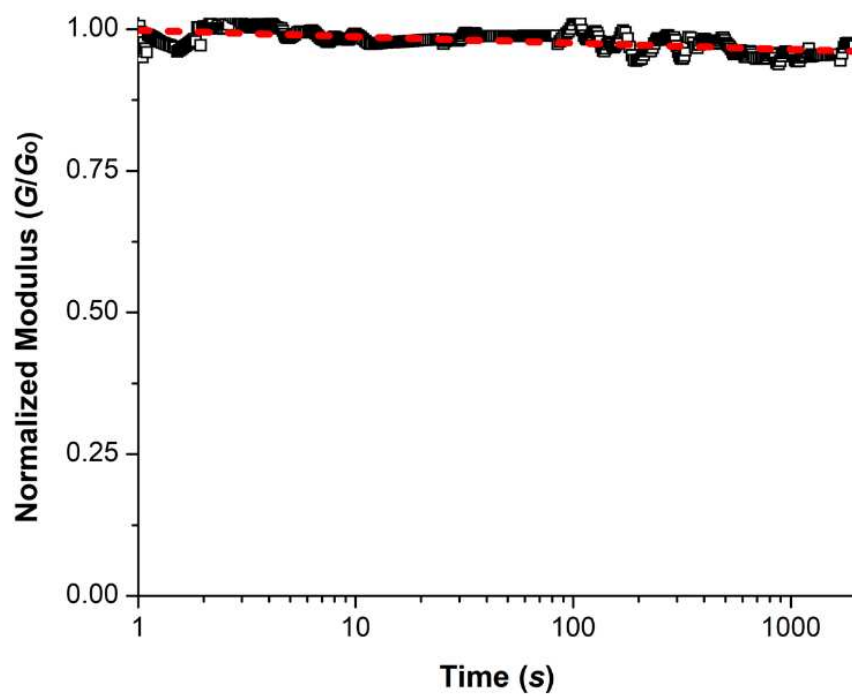
$$\ln(\tau) = \frac{E_a}{RT} + \ln(\tau_0) \quad [\text{Eq. 5}]$$



**Figure B57.** Arrhenius relationship between temperature and the characteristic relaxation time point ( $1/e = 0.367$ , under a single Maxwell element) for the  $\text{P}^n\text{BA}_{520}\text{-co-PAAn}_{350}$ .

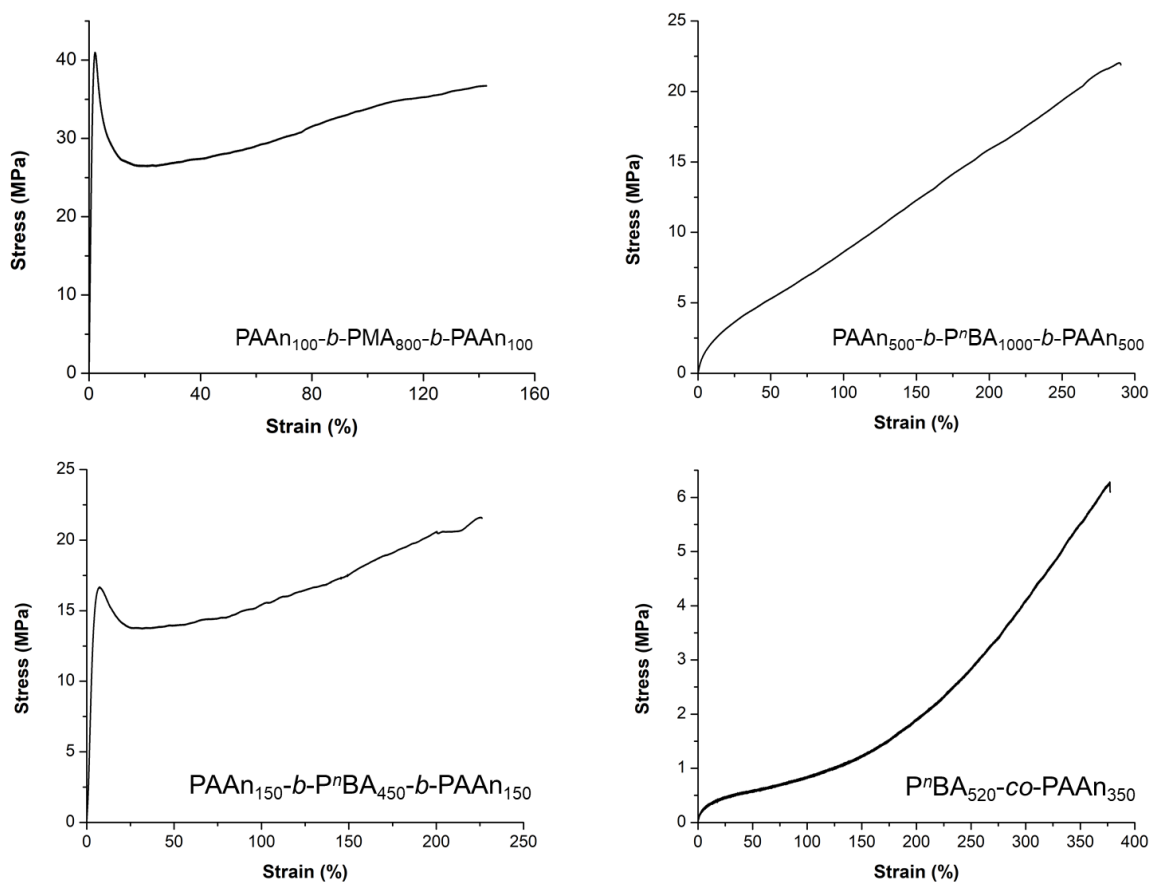
$E_a$  was calculated from the preceding Arrhenius relationship by multiplying the slope to the energy constant  $R$  ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ):

$$E_a \left( \frac{\text{kJ}}{\text{mol}} \right) = 24.18 \times R (\text{kJ}) = 201.0 \frac{\text{kJ}}{\text{mol}}$$



**Figure B58.** Normalized stress relaxation curve of G3 triblock copolymer PAA<sub>n</sub><sub>150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n</sub><sub>150</sub> (0.3 % strain).

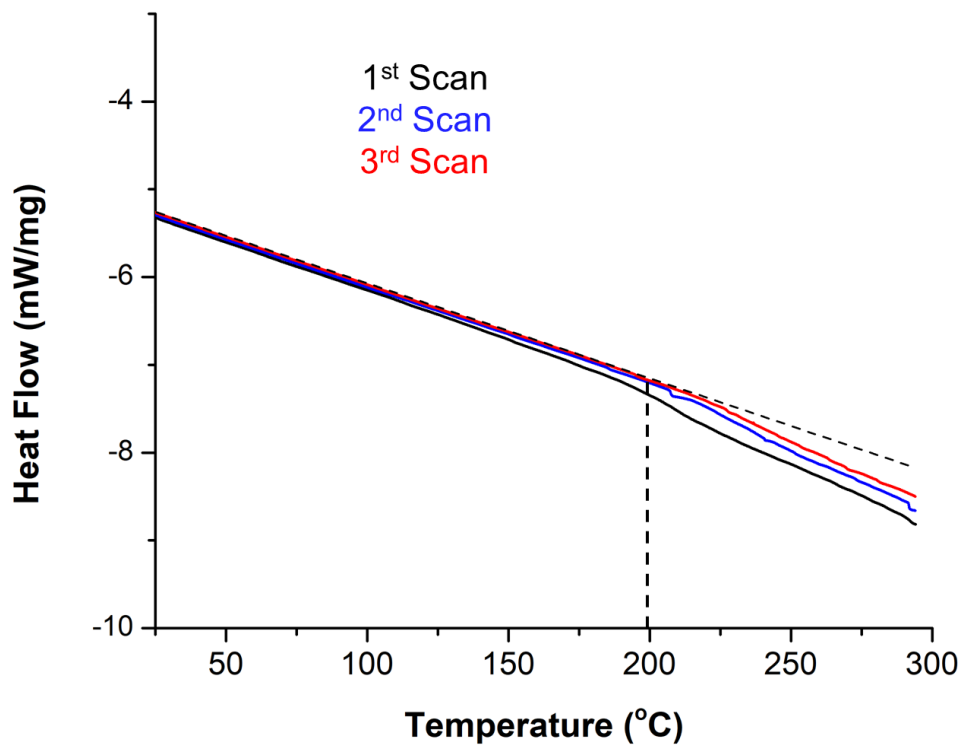
### G3 Copolymer Tensile Testing



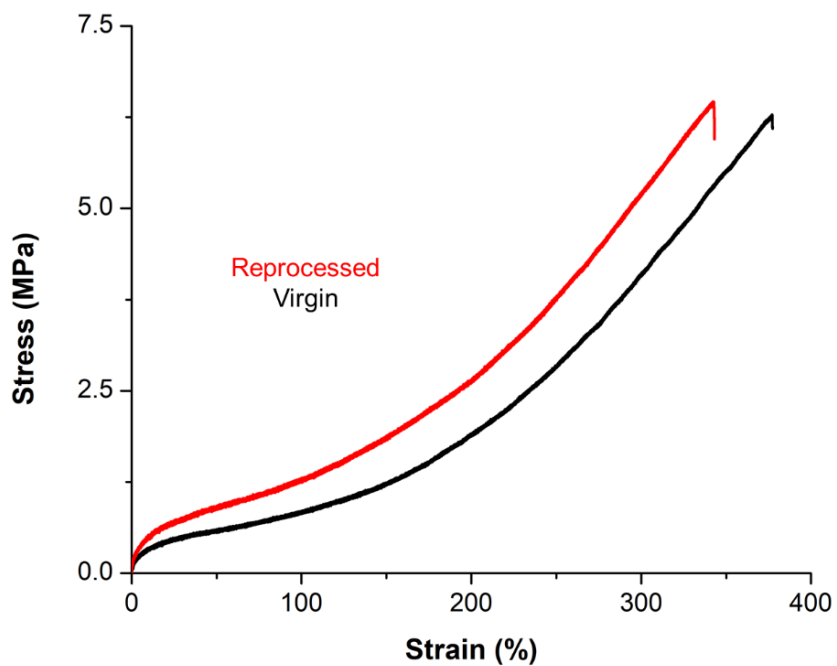
**Figure B59.** Stress-strain curves for G3 copolymers (5 mm/min, ~23 °C).

## Reprocessing

Film reprocessing for G3 triblock copolymers were carried out at 200 °C for 24 h followed by cooling, while the G3 random copolymer was reprocessed at 200 °C for 30 minutes followed by cooling. Thin films were then removed from the mold and cut into ASTM Standard D638-5 tensile bars (“dogbones”) by using the ASTM D638-5-IMP cutting die.



**Figure B60.** DSC trace cycles 1-3 of PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub> with indicated temperature of endothermic delineation (200 °C) from consistent heat flow.



**Figure B61.** Stress-strain curves for virgin (black) and reprocessed (red) tensile bar specimens of CAN P<sup>n</sup>BA<sub>520</sub>-*b*-PAA<sub>n350</sub>.

## Supplemental Tables

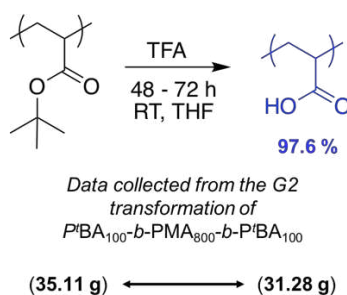
**Table B1.** Tensile strength, tensile strain, and Young's Modulus values for tensile bar specimens of PMA, P<sup>n</sup>BA, PAA, and PAA<sub>n</sub> homopolymers.

| Polymer           | Tensile Strength (MPa) | Modulus (MPa) | Elongation (%) |
|-------------------|------------------------|---------------|----------------|
| P <sup>n</sup> BA | 3.9 ± 1.3              | 392 ± 65      | 96 ± 26        |
| PAA               | 37 ± 11                | 1952 ± 685    | 38 ± 27        |
| PAA <sub>n</sub>  | 33 ± 11                | 2244 ± 360    | 1.7 ± 0.6      |
| PMA               | 1.7 ± 0.6              | 2.2 ± 0.2     | 612 ± 72       |

**Table B2.** Stress-strain experimental results for the parent (G1) tri-BCPs.

| Polymer                                                                                                                     | Tensile Strength (MPa) | Modulus (MPa) | Elongation (%) |
|-----------------------------------------------------------------------------------------------------------------------------|------------------------|---------------|----------------|
| P <sup>n</sup> BA <sub>100</sub> - <i>b</i> -PMA <sub>800</sub> - <i>b</i> -P <sup>n</sup> BA <sub>100</sub>                | 12 ± 1.1               | 50 ± 0.6      | 443 ± 17       |
| P <sup>n</sup> BA <sub>500</sub> - <i>b</i> -P <sup>n</sup> BA <sub>1000</sub> - <i>b</i> -P <sup>n</sup> BA <sub>500</sub> | 1.8 ± 0.1              | 60 ± 3.5      | 373 ± 25       |
| P <sup>n</sup> BA <sub>150</sub> - <i>b</i> -P <sup>n</sup> BA <sub>450</sub> - <i>b</i> -P <sup>n</sup> BA <sub>150</sub>  | 0.3 ± 0.04             | 4.7 ± 0.8     | 389 ± 11       |

**Table B3.** Remaining *tert*-Butyl Ester Content Following G1 to G2 Transformation.



| Polymer                                                                                                                     | Time (h) | <i>tert</i> -butyl content (%) | Theoretical $M_n$ (kg mol <sup>-1</sup> ) |
|-----------------------------------------------------------------------------------------------------------------------------|----------|--------------------------------|-------------------------------------------|
| P <sup>n</sup> BA <sub>500</sub> - <i>b</i> -P <sup>n</sup> BA <sub>1000</sub> - <i>b</i> -P <sup>n</sup> BA <sub>500</sub> | 72       | 1.3                            | 211                                       |

|                                                                                      |    |     |      |
|--------------------------------------------------------------------------------------|----|-----|------|
| P'BA <sub>150</sub> - <i>b</i> -P''BA <sub>450</sub> - <i>b</i> -P'BA <sub>150</sub> | 72 | 1.1 | 98.0 |
| P'BA <sub>100</sub> - <i>b</i> -PMA <sub>800</sub> - <i>b</i> -P'BA <sub>100</sub>   | 48 | 0.4 | 136  |
| P''BA <sub>520</sub> -co-P'BA <sub>150</sub>                                         | 96 | 0.3 | 92.0 |

**Table B4.** Stress-strain experimental results for G2 tri-BCPs.

| Polymer                                                                             | Tensile Strength (MPa) | Elongation (%) | Modulus (MPa) |
|-------------------------------------------------------------------------------------|------------------------|----------------|---------------|
| PAA <sub>500</sub> - <i>b</i> -P''BA <sub>1000</sub> - <i>b</i> -PAA <sub>500</sub> | 11 ± 0.7               | 342 ± 16       | 4.2 ± 0.2     |
| PAA <sub>100</sub> - <i>b</i> -PMA <sub>800</sub> - <i>b</i> -PAA <sub>100</sub>    | 2.2 ± 0.1              | 1128 ± 337     | 0.5 ± 0.05    |
| PAA <sub>150</sub> - <i>b</i> -P''BA <sub>500</sub> - <i>b</i> -PAA <sub>150</sub>  | 3.1 ± 0.2              | 156 ± 7.0      | 2.7 ± 0.2     |

**Table B5.** Results for Cyclic Deformation Experiment (PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub>).

| Strain Cycle       | Tensile Strength (MPa) | Elongation (%) | Modulus (MPa) |
|--------------------|------------------------|----------------|---------------|
| Virgin             | 0.501                  | 100            | 2.13          |
| Cycle 1            | 0.553                  | 100            | 1.76          |
| Cycle 2            | 0.487                  | 100            | 1.71          |
| Cycle 3            | 0.512                  | 100            | 1.69          |
| Cycle 4            | 0.478                  | 100            | 1.60          |
| Cycle 5            | 0.476                  | 100            | 1.56          |
| Average            | 0.501                  | 100            | 1.742         |
| Standard Deviation | 0.029                  | 0              | 0.204         |

**Table B6.** Recorded Storage Modulus by DMA and Calculated  $T_g$  by Tan Delta for PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub> at various crosslinking times.

| Crosslinking Time | Storage Modulus ( $E'$ ) (MPa) | $T_g$ (C) |
|-------------------|--------------------------------|-----------|
| 0                 | 1614                           | 25.8      |
| 1                 | 1630                           | 40.2      |
| 2                 | 1958                           | 44.3      |

|    |      |      |
|----|------|------|
| 4  | 2348 | 44.9 |
| 8  | 2944 | 40.4 |
| 12 | 3834 | 50.3 |
| 16 | 4348 | 52.3 |
| 20 | 4809 | 45.9 |
| 24 | 4771 | 47.5 |

**Table B7.** Tensile stress-strain results for G3 crosslinked tri-BCPs.

| Polymer                                                                                           | Tensile Strength (MPa) | Elongation (%) | Modulus (MPa) |
|---------------------------------------------------------------------------------------------------|------------------------|----------------|---------------|
| PAA <sub>n500</sub> - <i>b</i> -P <sup>n</sup> BA <sub>1000</sub> - <i>b</i> -PAA <sub>n500</sub> | 21 ± 1.9               | 264 ± 19       | 19 ± 13       |
| PAA <sub>n100</sub> - <i>b</i> -PMA <sub>800</sub> - <i>b</i> -PAA <sub>n100</sub>                | 41 ± 0.8               | 123 ± 16       | 2870 ± 366    |
| PAA <sub>n150</sub> - <i>b</i> -P <sup>n</sup> BA <sub>450</sub> - <i>b</i> -PAA <sub>n150</sub>  | 18 ± 2.9               | 208 ± 24       | 351 ± 35      |

**Table B8.** Tensile test results for reprocessing of PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> (131TB) and P<sup>n</sup>BA<sub>520</sub>-*b*-PAA<sub>n350</sub> (RCP).

| Polymer              | Tensile Strength (MPa) | Modules (MPa) | Elongation (%) |
|----------------------|------------------------|---------------|----------------|
| Virgin 131TB         | 18 ± 2.9               | 351 ± 35      | 208 ± 24       |
| 131TB Reprocessed 1x | 19 ± 2.2               | 388 ± 73      | 262 ± 17       |
| 131TB Reprocessed 2x | 21 ± 2.6               | 210 ± 27      | 285 ± 44       |
| 131TB Reprocessed 3x | 22 ± 3.3               | 411 ± 37      | 238 ± 48       |
| RCP                  | 6.2 ± 0.2              | 397 ± 17      | 3.4 ± 0.6      |
| RCP Reprocessed 1x   | 6.8 ± 0.5              | 380 ± 27      | 2.6 ± 0.5      |



### **Tabulated Tensile Stress-Strain Data of Selected G1 – G3 Polymer Samples**

This section contains all compiled data for selected tensile bars used for tensile stress-strain analysis. Each table contains individual specimen tensile strength (MPa), tensile strain (%), and Young's modulus (MPa or GPa). Similarly, averages and standard deviations as reported in the text are displayed.

**Table B9. P'BA.**

| <b>Specimen</b>    | <b>Tensile Strain (%)</b> | <b>Tensile Strength (MPa)</b> | <b>Modulus (MPa)</b> |
|--------------------|---------------------------|-------------------------------|----------------------|
| 1                  | 128                       | 4.2                           | 406                  |
| 2                  | 107                       | 3.4                           | 468                  |
| 3                  | 70                        | 5.5                           | 382                  |
| 4                  | 80                        | 2.5                           | 310                  |
| Average            | 96                        | 3.9                           | 392                  |
| Standard Deviation | 26                        | 1.2                           | 65                   |

**Table B10. PMA.**

| <b>Specimen</b>    | <b>Tensile Strain (%)</b> | <b>Tensile Strength (MPa)</b> | <b>Modulus (MPa)</b> |
|--------------------|---------------------------|-------------------------------|----------------------|
| 1                  | 661                       | 1.8                           | 2.4                  |
| 2                  | 604                       | 1.8                           | 2.5                  |
| 3                  | 513                       | 1.4                           | 1.9                  |
| 4                  | 668                       | 1.7                           | 2.1                  |
| Average            | 612                       | 1.7                           | 2.2                  |
| Standard Deviation | 72                        | 0.2                           | 0.2                  |

**Table B11. PAA.**

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 30                 | 26                     | 1434          |
| 2                  | 21                 | 48                     | 2857          |
| 3                  | 23                 | 45                     | 2110          |
| 4                  | 78                 | 28                     | 1409          |
| Average            | 38                 | 37                     | 1953          |
| Standard Deviation | 27                 | 11                     | 685           |

**Table B12.** PAA<sub>n</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 1.4                | 39                     | 2770          |
| 2                  | 2.5                | 41                     | 2026          |
| 3                  | 1.7                | 37                     | 2178          |
| 4                  | 1.2                | 16                     | 2000          |
| Average            | 1.7                | 33                     | 2244          |
| Standard Deviation | 0.6                | 12                     | 360           |

**Table B13.** P'BA<sub>500</sub>-*b*-P''BA<sub>1000</sub>-*b*-P'BA<sub>500</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 406                | 1.7                    | 58            |
| 2                  | 351                | 1.9                    | 65            |
| 3                  | 378                | 1.7                    | 58            |
| 4                  | 356                | 1.8                    | 57            |
| Average            | 373                | 1.8                    | 60            |
| Standard Deviation | 25                 | 0.1                    | 3.7           |

**Table B14.** PAA<sub>500</sub>-*b*-P''BA<sub>1000</sub>-*b*-PAA<sub>500</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 351                | 11.7                   | 3.6           |
| 2                  | 329                | 10.7                   | 3.5           |
| 3                  | 360                | 10.5                   | 3.2           |
| 4                  | 328                | 10                     | 3.2           |
| Average            | 342                | 11                     | 3.4           |
| Standard Deviation | 16                 | 0.7                    | 0.2           |

**Table B15.** PAA<sub>n500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>n500</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 291                | 22                     | 11            |
| 2                  | 257                | 21                     | 37            |
| 3                  | 260                | 23                     | 18            |
| Average            | 269                | 22                     | 22            |
| Standard Deviation | 19                 | 1.0                    | 13            |

**Table B16.** P'BA<sub>100</sub>-*b*-PMA<sub>800</sub>-P'BA<sub>100</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 461                | 10.1                   | 48            |
| 2                  | 439                | 12.4                   | 51            |
| 3                  | 421                | 11.7                   | 59            |
| 4                  | 449                | 12.3                   | 43            |
| Average            | 443                | 12                     | 50            |
| Standard Deviation | 17                 | 1.1                    | 6.7           |

**Table B17.** PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub>.

| Specimen | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|----------|--------------------|------------------------|---------------|
|----------|--------------------|------------------------|---------------|

|                    |      |     |      |
|--------------------|------|-----|------|
| 1                  | 943  | 2.4 | 0.55 |
| 2                  | 919  | 2.2 | 0.52 |
| 3                  | 1027 | 1.8 | 0.40 |
| 4                  | 1024 | 2.2 | 0.50 |
| Average            | 978  | 2.2 | 0.5  |
| Standard Deviation | 55   | 0.3 | 0.07 |

**Table B18.** PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 118                | 41                     | 3010          |
| 2                  | 143                | 41                     | 3220          |
| 3                  | 128                | 43                     | 2360          |
| 4                  | 104                | 41                     | 2890          |
| Average            | 123                | 42                     | 2870          |
| Standard Deviation | 16                 | 1.0                    | 366           |

**Table B19.** P'BA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-P'BA<sub>150</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 373                | 0.35                   | 3.8           |
| 2                  | 387                | 0.35                   | 4.3           |
| 3                  | 403                | 0.29                   | 4.3           |
| 4                  | 390                | 0.39                   | 5.9           |
| 5                  | 391                | 0.31                   | 5.1           |
| Average            | 389                | 0.3                    | 4.7           |
| Standard Deviation | 11                 | 0.04                   | 0.8           |

**Table B20.** PAA<sub>150</sub>-*b*-P''BA<sub>450</sub>-*b*-PAA<sub>150</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 148                | 3.2                    | 2.9           |
| 2                  | 164                | 2.9                    | 2.5           |
| 3                  | 152                | 3.2                    | 2.8           |
| 4                  | 158                | 3.0                    | 2.6           |
| Average            | 156                | 3.1                    | 2.7           |
| Standard Deviation | 7.0                | 0.2                    | 0.2           |

**Table B21.** PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 227                | 17                     | 372           |
| 2                  | 181                | 22                     | 370           |
| 3                  | 216                | 17                     | 311           |
| Average            | 208                | 19                     | 351           |
| Standard Deviation | 24                 | 2.9                    | 35            |

**Table B22.** Reprocessed PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> Cycle 1.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 252                | 18                     | 462           |
| 2                  | 252                | 18                     | 385           |
| 3                  | 281                | 22                     | 317           |
| Average            | 262                | 19                     | 388           |
| Standard Deviation | 17                 | 2.3                    | 73            |

**Table B23.** Reprocessed PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> Cycle 2.

| Specimen | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|----------|--------------------|------------------------|---------------|
| 1        | 325                | 24                     | 188           |

|                    |     |     |     |
|--------------------|-----|-----|-----|
| 2                  | 290 | 21  | 240 |
| 3                  | 239 | 19  | 203 |
| Average            | 285 | 21  | 210 |
| Standard Deviation | 43  | 2.5 | 27  |

**Table B24.** Reprocessed PAA<sub>n150</sub>-*b*-P<sup>n</sup>BA<sub>450</sub>-*b*-PAA<sub>n150</sub> Cycle 3.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 290                | 25                     | 411           |
| 2                  | 194                | 19                     | 448           |
| 3                  | 231                | 21                     | 373           |
| Average            | 238                | 22                     | 411           |
| Standard Deviation | 48                 | 3.0                    | 38            |

**Table B25.** P<sup>n</sup>BA<sub>520</sub>-*b*-PAA<sub>n350</sub>.

| Specimen           | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|--------------------|--------------------|------------------------|---------------|
| 1                  | 389.3              | 6.29                   | 2.84          |
| 2                  | 385.1              | 6.43                   | 4.12          |
| 3                  | 415.6              | 6.02                   | 3.36          |
| Average            | 397                | 6.2                    | 3.4           |
| Standard Deviation | 17                 | 0.2                    | 0.6           |

**Table B26.** P<sup>n</sup>BA<sub>520</sub>-*b*-PAA<sub>n350</sub> Reprocessing Cycle 1.

| Specimen | Tensile Strain (%) | Tensile Strength (MPa) | Modulus (MPa) |
|----------|--------------------|------------------------|---------------|
| 1        | 406.9              | 7.21                   | 2.88          |
| 2        | 352.3              | 6.97                   | 2.89          |

|                    |       |      |      |
|--------------------|-------|------|------|
| 3                  | 380.1 | 6.29 | 2.01 |
| Average            | 380   | 6.8  | 2.6  |
| Standard Deviation | 27    | 0.5  | 0.5  |

## Calculation of SAXS Signals for HPC Self-Assembled G2 and G3 Films

### 1. PAA<sub>500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>500</sub>

$$q_0 = 0.012170$$

$$q_1 = 0.021138$$

$$\frac{q_1}{q_0} \approx 2.6 \approx \sqrt{7}$$

### 2. PAA<sub>n500</sub>-*b*-P<sup>n</sup>BA<sub>1000</sub>-*b*-PAA<sub>n500</sub>

$$q_0 = 0.011209$$

$$q_1 = 0.018896$$

$$q_2 = 0.031066$$

$$q_3 = 0.054766$$

$$\frac{q_1}{q_0} \approx 1.7 \approx \sqrt{3} \quad \frac{q_2}{q_0} \approx 2.77 \approx \sqrt{7} \quad \frac{q_3}{q_0} \approx 4.89 \approx \sqrt{24}$$

### 3. PAA<sub>100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>100</sub>

$$q_0 = 0.019536$$

$$q_1 = 0.033080$$

$$\frac{q_1}{q_0} \approx 1.7 \approx \sqrt{3}$$

#### 4. PAA<sub>n100</sub>-*b*-PMA<sub>800</sub>-*b*-PAA<sub>n100</sub>

$$q_0 = 0.018896$$

$$q_1 = 0.032667$$

$$q_2 = 0.065014$$

$$\frac{q_1}{q_0} \approx 1.7 \approx \sqrt{3}$$

$$\frac{q_2}{q_0} \approx 3.4 \approx \sqrt{12}$$

#### 5. PAA<sub>200</sub>-*b*-PMA<sub>800</sub>

$$q_0 = 0.013451$$

$$q_1 = 0.023059$$

$$q_2 = 0.035870$$

$$q_3 = 0.063413$$

$$\frac{q_1}{q_0} \approx 1.7 \approx \sqrt{3}$$

$$\frac{q_2}{q_0} \approx 2.66 \approx \sqrt{7}$$

$$\frac{q_3}{q_0} \approx 4.71 \approx \sqrt{21}$$

#### 6. PAA<sub>n200</sub>-*b*-PMA<sub>800</sub>

$$q_0 = 0.012170$$



$$q_1 = 0.021138$$

$$q_2 = 0.023700$$

$$q_3 = 0.042596$$

$$q_3 = 0.073662$$

$$\frac{q_1}{q_0} \approx 1.7 \approx \sqrt{3} \quad \frac{q_2}{q_0} \approx 2 \approx \sqrt{4} \quad \frac{q_3}{q_0} \approx 3.5 \approx \sqrt{12} \quad \frac{q_4}{q_0} \approx 6 \approx \sqrt{36}$$

The HPC domain spacings ( $d_{100}$ ) (calculated from the primary peak  $q_{100}$  value from SAXS using the equation  $d_{hkl} = 2\pi / q_{hkl}$ ) for each of the four samples are within a comparable range from 32 nm to 56 nm.

## References

- 
- <sup>1</sup> Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. Sterically Hindered Aryloxide-Substituted Alkylaluminum Compounds. *Organometallics* **1988**, 7, 409–416.
- <sup>2</sup> McGraw, M. L.; Clarke, R. W.; Chen, E. Y.-X. Compounded Sequence Control in Polymerization of One-Pot Mixtures of Highly Reactive Acrylates by Differentiating Lewis Pairs. *J. Am. Chem. Soc.* **2020**, 142, 5969–5973.
- <sup>3</sup> Goodwin, J. W.; Hughes, R. W.; Rheology for Chemists: An Introduction. *Royal Society of Chemistry*. **2008**, 95-100.

## Appendix C

### Supplementary Information Corresponding to Chapter 4<sup>i</sup>

#### Materials, Reagents, and Methods.

All syntheses and manipulations of air- and moisture-sensitive chemicals were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N<sub>2</sub>)-filled glovebox. High-performance liquid chromatography (HPLC)-grade organic solvents used for polymerization or catalyst synthesis were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina [for dichloromethane (DCM)] followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Dried toluene for polymer synthesis was additionally dried over sodium/potassium alloy for 24 h and subsequently vacuum-distilled into a dry 1 L round-bottom flask prior to immediate storage in an inert-atmosphere glovebox. Toluene-*d*<sub>8</sub> was dried over sodium/potassium alloy and vacuum-distilled, whereas CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> were dried over activated Davison 4 Å molecular sieves.

Monomers allyl acrylate (AIA), methyl methacrylate (MMA), and ethyl sorbate (ES) were all purchased from TCI and were dried under CaH<sub>2</sub> and distilled under heat and vacuum prior to storage at -30 °C in inert atmosphere. *N*-heterocyclic carbene (NHC) 1,3-di-*tert*-butylimidazolium-2-ylidene (tBu) was purchased from TCI and used as received. Tricyclohexylphosphine (PCy<sub>3</sub>) was purchased from Alfa Aesar and used as received. 1-octadecanethiol (1ODT) and 2,2-

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<sup>i</sup>Taken from: R. W. Clarke, M. R. Caputo, K. A. Franklin, L. T. Reilly, M. L. McGraw, A. J. Müller, E. Y.-X. Chen. Architecturally and Topologically Sophisticated (Meth)Acrylic Multiblock Copolymers: Rapid Scalable Syntheses and Meticulous Differentiations. (Manuscript in Preparation, 2022).

Dimethoxy-2-phenylacetophenone (DMPA) were purchased from TCI and Sigma Aldrich, respectively, and used as received. Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was synthesized according to literature procedures.<sup>1</sup>

### **Analytical Methods.**

**NMR Spectroscopy.** Monomer conversion, characterization of catalysts and polymers, polymerization kinetics, and polymer block architecture were carried out by <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments using either a Varian Inova 400 MHz (FT 400 MHz <sup>1</sup>H; 100 MHz <sup>13</sup>C) or a Bruker AVIII 400 MHz spectrometer (400 MHz <sup>1</sup>H; 100 MHz <sup>13</sup>C). Variable-Temperature <sup>1</sup>H NMR experiments were used to obtain Van't Hoff plots and subsequent  $K_{eq}$  values using an Agilent Inova 500 MHz spectrometer (500 MHz <sup>1</sup>H NMR, 125 MHz <sup>13</sup>C). Chemical shifts were referenced to internal solvent resonances corresponding to 7.26 ppm (CHCl<sub>3</sub>) and 7.16 (C<sub>6</sub>D<sub>6</sub>) and reported as parts per million, relative to SiMe<sub>4</sub>.

**Gel Permeation Chromatography (GPC).** Measurements of diblock copolymer and tetrablock copolymer absolute weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and molecular weight distributions or dispersity indices ( $D = M_w/M_n$ ) were performed via GPC. The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and two PL<sub>gel</sub> 5  $\mu$ m mixed-C gel permeation columns (Polymer Laboratories; linear range of molecular weight = 1000-3,000,000) and coupled with a Wyatt Technology miniDAWN Treos light scattering detector (MALS), a Wyatt Technology TrEX dRI detector, and a Wyatt Viscostar III viscometer. The experiments were performed at 40 °C using THF as the eluent at a flow rate 1.0 mL min<sup>-1</sup> and the analyses were performed using Wyatt ASTRA 7.1.2 software. Refractive index ( $dn/dc$ ) values for absolute molecular weight measurements as well as distinction between

block copolymer samples with linear (diblock copolymer = 0.0783 mL g<sup>-1</sup>, tetrablock copolymer = 0.0801 mL g<sup>-1</sup>) and cyclic (diblock copolymer = 0.0764 mL g<sup>-1</sup>, tetrablock copolymer = 0.0735 mL g<sup>-1</sup>) topology were determined experimentally by batch experiments through the Wyatt Technology TrEX dRI detector and calculated via the ASTRA 7.1.2 software. Four series of polymer solutions with four or five precise concentrations (1.0 – 5.0 mg mL<sup>-1</sup>) were prepared in THF and injected into the dRI detector by a Harvard Apparatus Pump 11 at a flow rate of 1.0 mL min<sup>-1</sup>. The refractive index was then recorded and plotted against concentration to obtain a universal calibration curve. The slope from a linear fitting (All  $R^2 \geq 0.999$ ) was the  $dn/dc$  of the polymer.

#### **Thermal Characterizations:**

**Thermogravimetric Analysis (TGA).** TGA was performed on all four thoroughly dried polymer samples (5-10 mg) on a Q50 Analyzer (TA Instrument). Polymer samples were heated from 25 °C to 700 °C at a 10 °C/min heating ramp rate. Decomposition temperatures ( $T_d$ ) represent the temperature of 5.00% initial weight loss. Maximum decomposition temperatures ( $T_{max}$ ) represent the peak maxima from the derivative curve for weight loss. Data analysis was performed using the publicly available Universal Analysis software (TA Instruments).

**Differential Scanning Calorimetry (DSC).** DSC was performed on all four thoroughly dried polymer samples (5-10 mg) on an Auto Q20 (TA Instrument). All DSC plots represent the data obtained from a second heating scan after the thermal history was removed on the first heating scan (10 °C/min). The second heating scan was performed at a heating rate of 10 °C/min, following a cooling scan at a rate of 10 °C/min. Data analysis was performed using the publicly available Universal Analysis software (TA Instruments).

#### **Polymer Film Processing.**

**Melt Compression Molding.** Selected polymers (*l*PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub>, *c*PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub>, *l*PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub>, and *c*PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>) were melt-compression molded into suitable films using a Carver Auto Series Plus Laboratory Press S4 (Carver, Model 3889.1PL1000, Max Force 15 ton) with programmable electrically-heated platen (EHP) temperature, complimented by air- and water-circulatory cooling control. Polymer substrates (~5 g) are placed between two non-stick Teflon sheets in a stainless-steel, rectangular (30 × 73.5 × 0.87 mm) mold and compressed between two 6" × 6" EHPs at 7000 psi for roughly 30 minutes. All four specimens were melt processed at 150 °C and cooled over the course of 2–3 h while remaining under compression.

### **Mechanical Analysis.**

**Tensile (Stress/Strain) Pulling Tests.** Thin films (*vide supra*) suitable for tensile stress/strain testing were sectioned to ASTM-D638 Type-V standard tensile bar specimens (cross-section  $w = 3.18$  mm) and analyzed on an Instron 5966 Universal Tensometer Testing System (TA Instruments) equipped with a 10 kN load cell and operated at room temperature (~23 °C). Individual sample thicknesses (~0.87 mm) were recorded prior to the start of testing using a Fowler 0-6" IP67 Pro-Max Model S electronic digital caliper set. Tensile bars were clamped tightly between two sets of textured grips (separated by ~28 mm) and pulled at a constant strain rate of 5 mm/min until sample failure. Reported measurements are obtained from the Instron readout in cooperation with BlueHill Universal software (TA Instruments) normalizing force/displacement response to stress/strain, and reported curves were generated from an average of a minimum of ~4 individual samples for reproducibility, with error margins included accordingly. Young's modulus ( $E$ , MPa), ultimate strength ( $\sigma_B$ , MPa), yield strength (MPa), and elongation at break ( $\epsilon_B$ , %) were obtained from software analysis.

**Dynamic Thermomechanical Analysis (DTMA).** Storage modulus ( $E'$ ), loss modulus ( $E''$ ) and tan delta ( $E''/E'$ ) traces for reported polymers were measured on a Q800 DTMA Analyzer (TA Instruments) in a tension film mode. Film width was set to 5.45 mm, and thickness was measured before testing for normalization of the data by the Q-series measurement software (TA Instruments). Specimens were mounted to screw-tight grips (3-7 N). Temperature-ramp frequency sweep experiments were performed from -50 °C to 200 °C at a heating rate of 5 °C/min at 0.3 % strain and a frequency of 1 Hz.

**Oscillatory Rheology.** Oscillatory rheology measurements were performed on a Discovery Series HR-2 Hybrid Rheometer (TA Instruments) operating under nitrogen gas flow (30 psi) and in conjunction with the publicly available TRIOS software (TA Instruments). Samples were loaded between two 25 mm-diameter flat-plate steel electrically heated platen (EHP) loading discs and trimmed to radial fit. Bulk melt viscosity measurements were performed at 175 °C from  $10^{-3}$  to  $1\text{ s}^{-1}$  at 10 rad/s. Zero-shear viscosity values were recorded at the point of lowest applied shear rate, while shear thinning rates were obtained by measuring the slope of viscosity decline between onset shear thinning and final viscosity measurement.

## **Micro-Domain and Morphology Analysis**

### **X-Ray Scattering and Micro-Domain Morphological Assignments.**

*This section will be updated once experiments are completed.*

### **Transmission Electron Microscopy (TEM)**

*This section will be updated once experiments are completed.*

## **Experimental Details.**

## General Polymerization Procedures:

### 1. Diblock Copolymerization

*This section is awaiting completion from M. L. McGraw*

### 2. Tetrablock Copolymerization

*This section is awaiting completion from M. L. McGraw*

## Characterization of AIA/MMA/MAD Equilibrium

In a nitrogen filled glove box, toluene- $d_8$  0.27 M stock solutions were prepared of AIA, MAD, and MMA. Into four J-Young NMR tubes, the following samples were prepared: (1) MAD alone (0.6 mL of 0.27 M MAD stock), (2) MAD + AIA (0.3 mL of 0.27 M MAD stock + 0.3 mL of 0.27 M AIA stock), (3) MAD + MMA (0.3 mL of 0.27 M MAD stock + 0.3 mL of 0.27 M MMA stock), (4) MAD + AIA + MMA (0.2 mL of 0.27 M MAD stock + 0.2 mL of 0.27 M AIA stock + 0.2 mL of 0.27 M MMA stock). Each sample was sealed and analyzed by  $^1\text{H}$  NMR at  $-20\text{ }^\circ\text{C}$ . The equilibrium was quantified via peak integration of the MAD Al- $\text{CH}_3$  signal representative of coordination to AIA and MMA in spectra 4, with peak assignments for each environment coming from spectra 2 and 3, respectively.

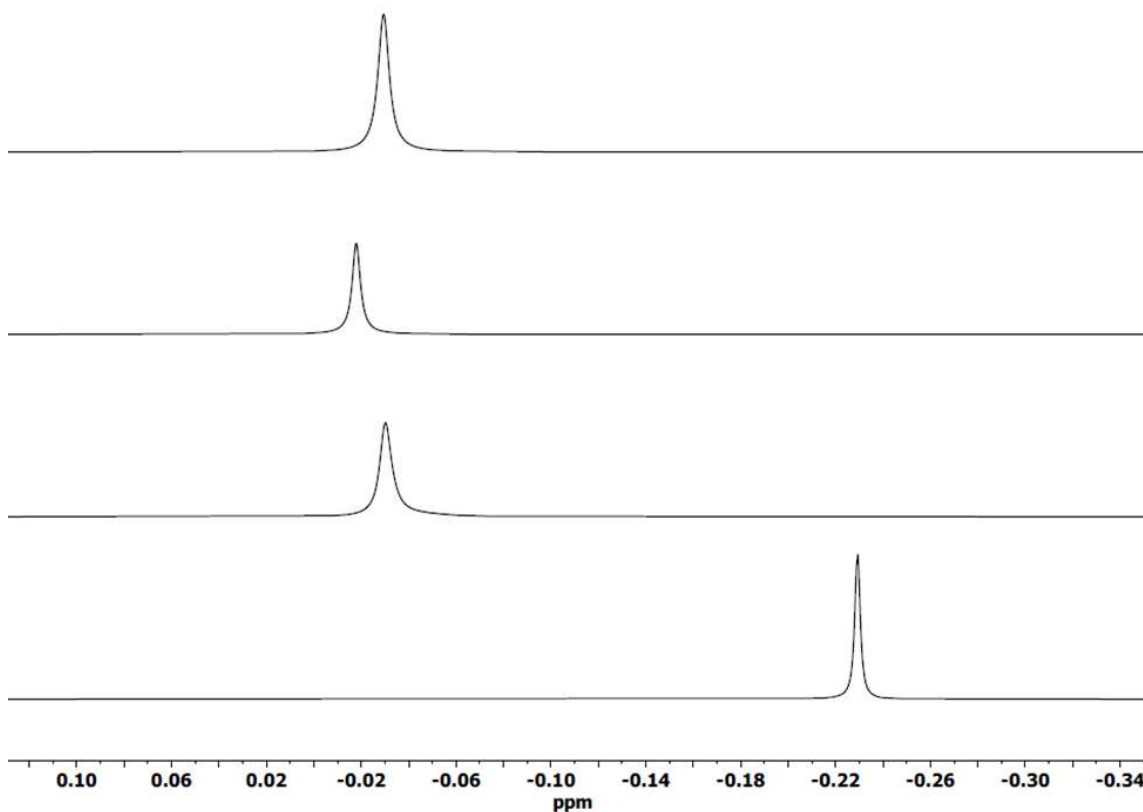
## Thiol-Ene Click Grafting Procedure for PAIA-BCPs with 1ODT

In an argon filled glovebox, a glass 500 mL high-pressure reactor was charged with 5.0 g of all four reported BCPs, 5 eq. (at 50 % AIA composition; ~10 g) of octadecane thiol, 0.2 g of DMPA (2,2-dimethoxy-2-phenylacetophenone), a stir bar, and 300 mL of anhydrous toluene. The reactor was sealed and placed inside a photoreactor equipped with a stir plate. The mixture was irradiated with UV wavelengths for 8 h under vigorous mixing conditions. The crude product was concentrated, precipitated with cold ( $-30\text{ }^\circ\text{C}$ ) ethyl acetate, placed under vacuum until a precipitate

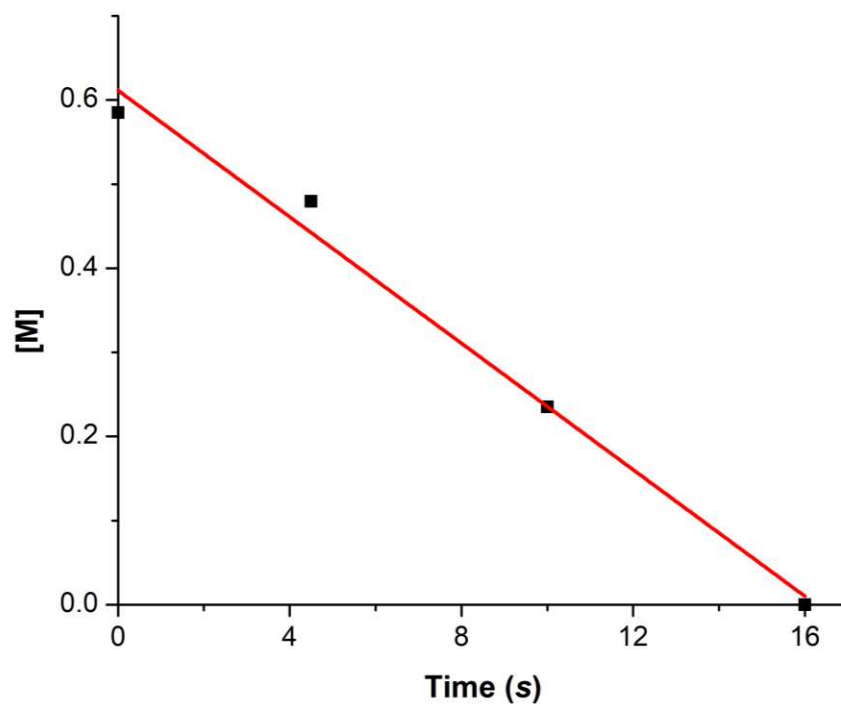


was formed from additional concentration and chilling, and finally filtered. The solid product was carefully washed three times with 50 mL of cold (-30 °C) ethyl acetate or THF and dried in a vacuum oven at 60 °C until a constant mass was achieved.

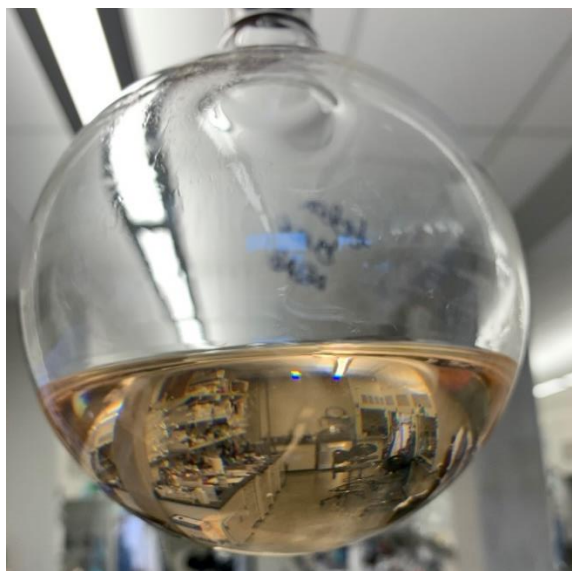
### Supplemental Figures



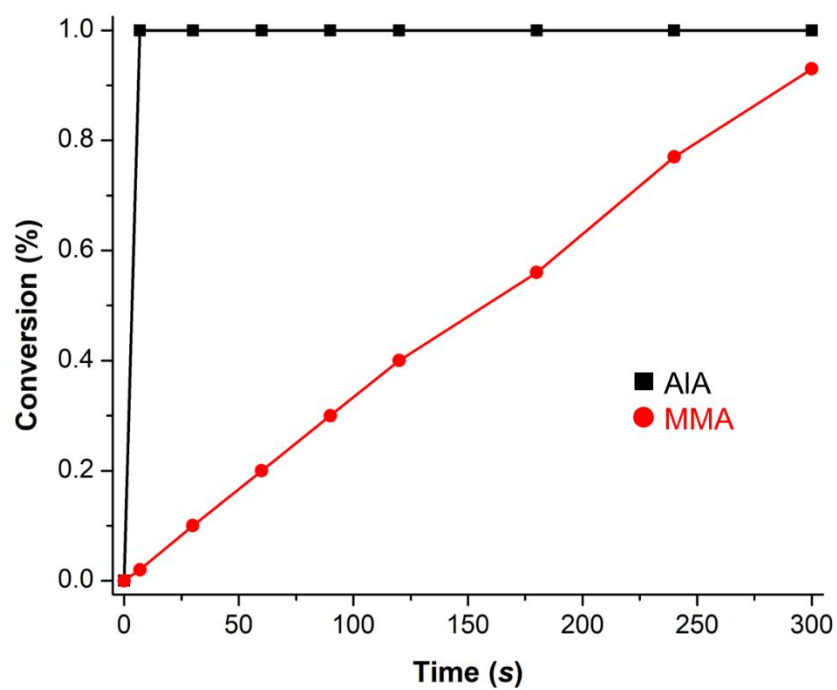
**Figure C1.** <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, -20 °C) equilibrium study of MMA vs. AIA LA affinity with MAD. From bottom to top: (1) MAD; (2) MAD:AIA = [1]:[1]; (3) MAD:MMA = [1]:[1]; (4) MAD:AIA:MMA = [1]:[1]:[1].



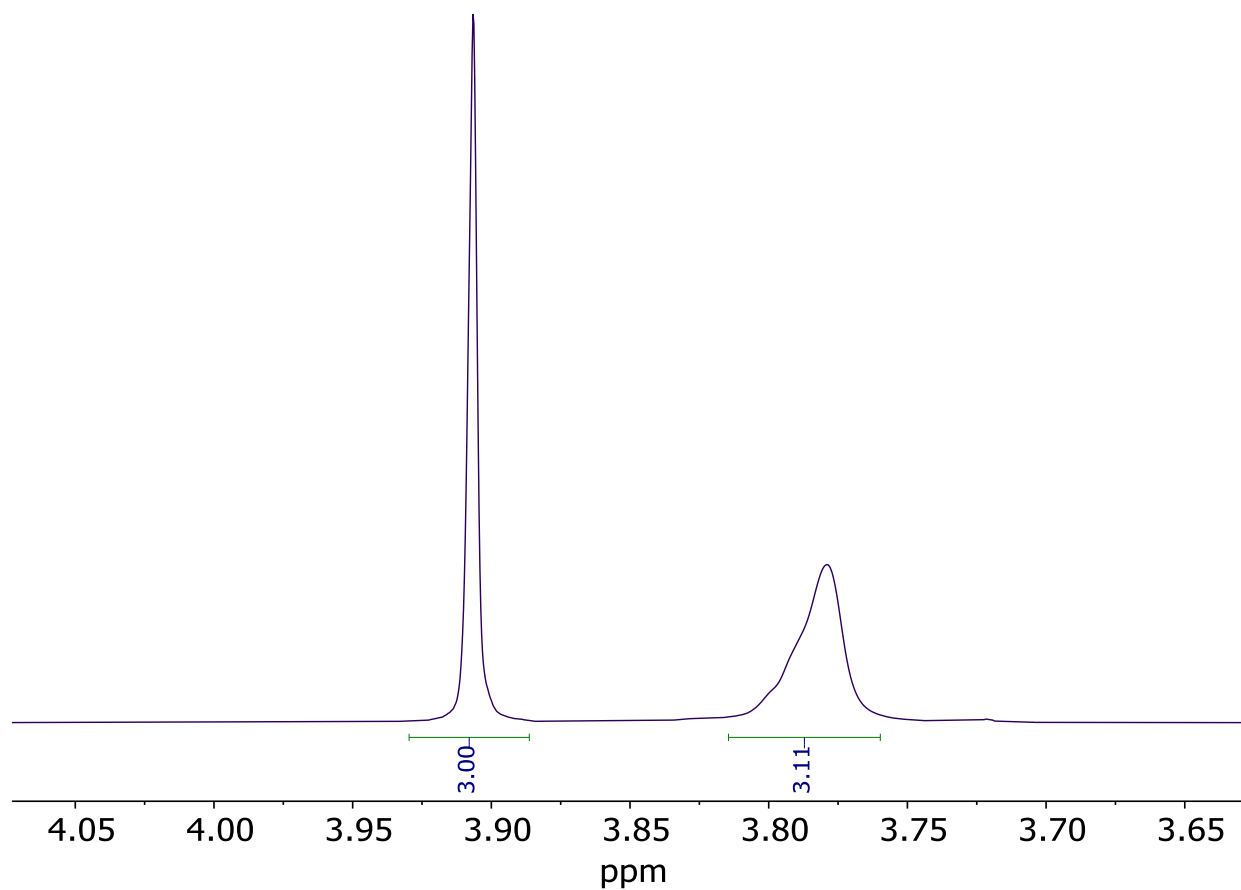
**Figure C2.** Polymerization kinetics for deriving  $k_p$  of AIA.



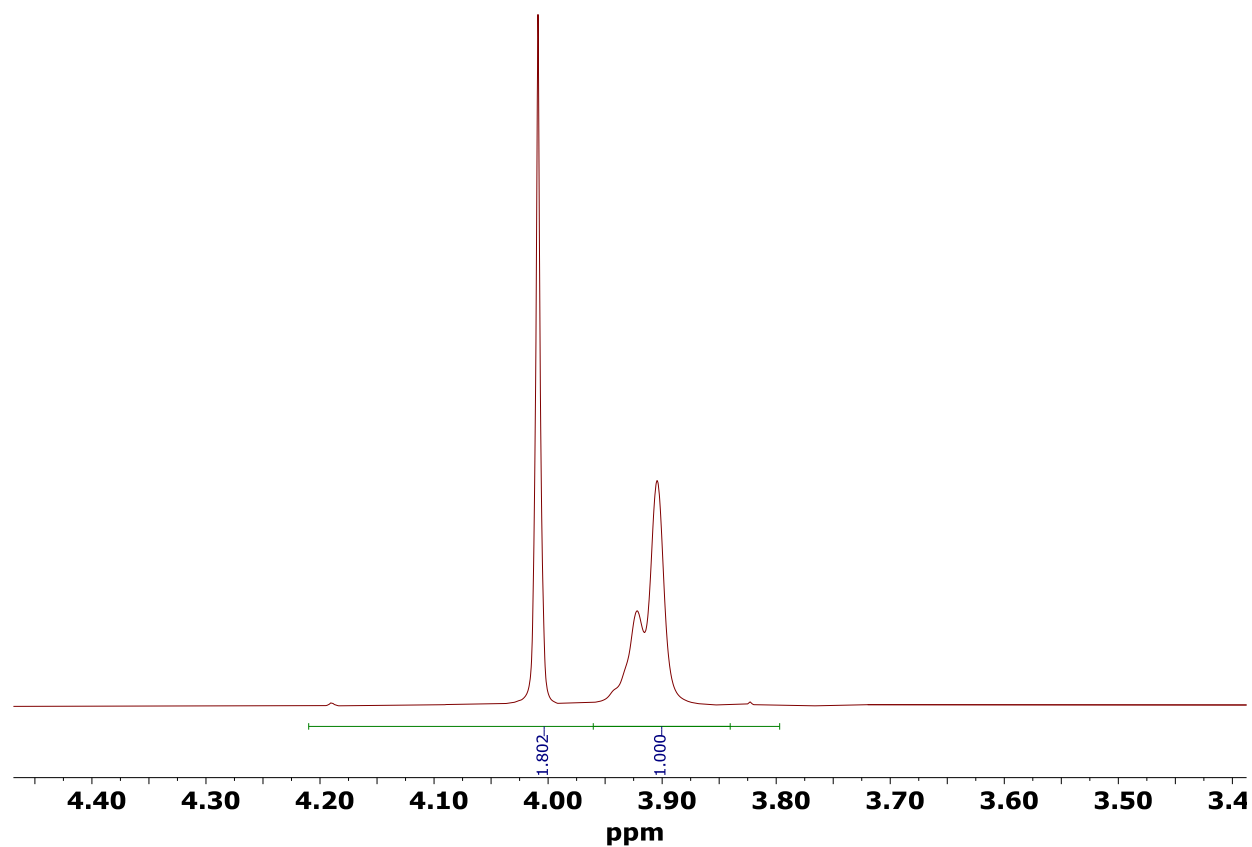
**Figure C3.** Digital images of cyclic  $\text{PAIA}_{250}\text{-}b\text{-PMMA}_{255}\text{-}b\text{-PAIA}_{250}\text{-}b\text{-PMMA}_{245}$  exhibiting a distinct rose-gold characteristic of cyclized polymer prior to quenching or precipitation.



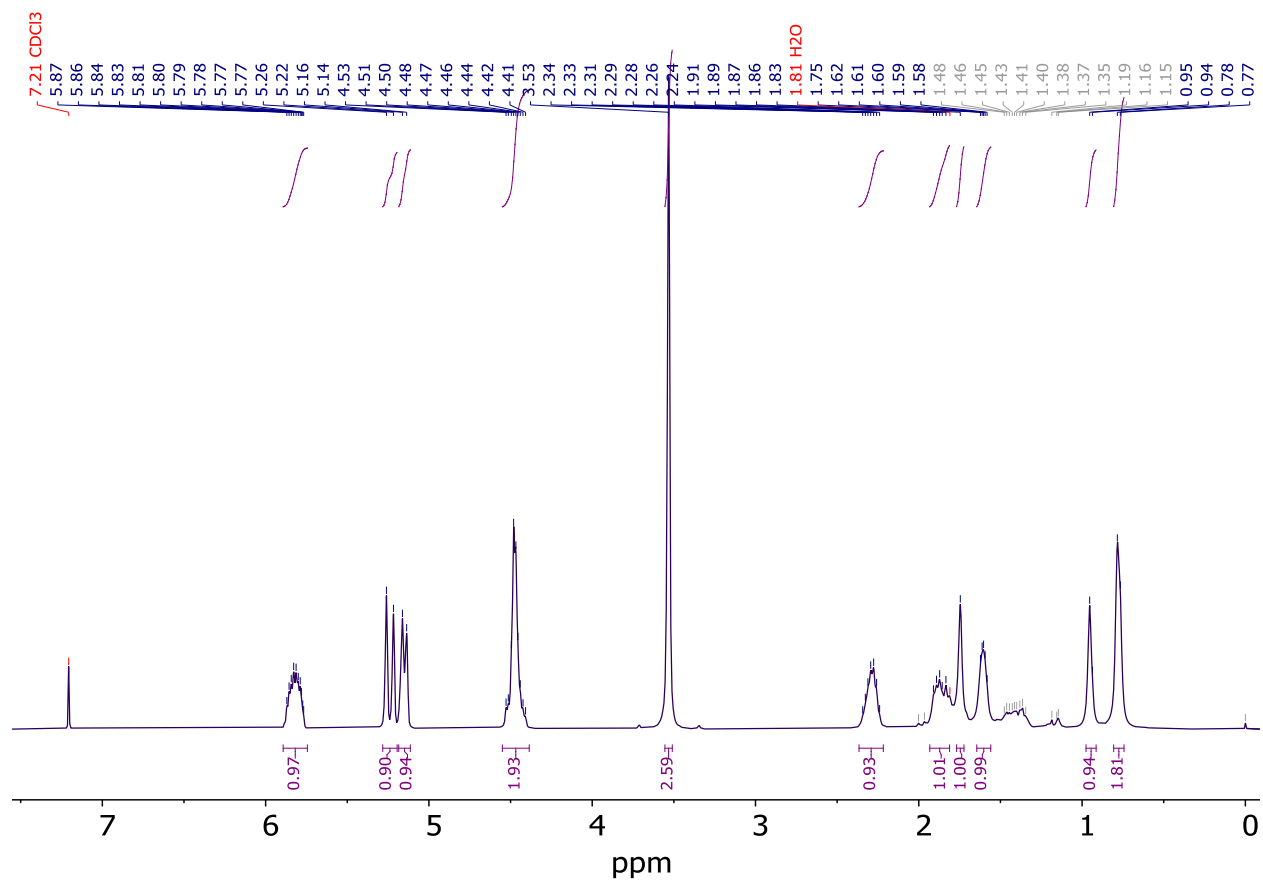
**Figure C4.** Conversion time points for the kinetics of linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> synthesis, from which 50 % MMA was derived to occur at 156 s.



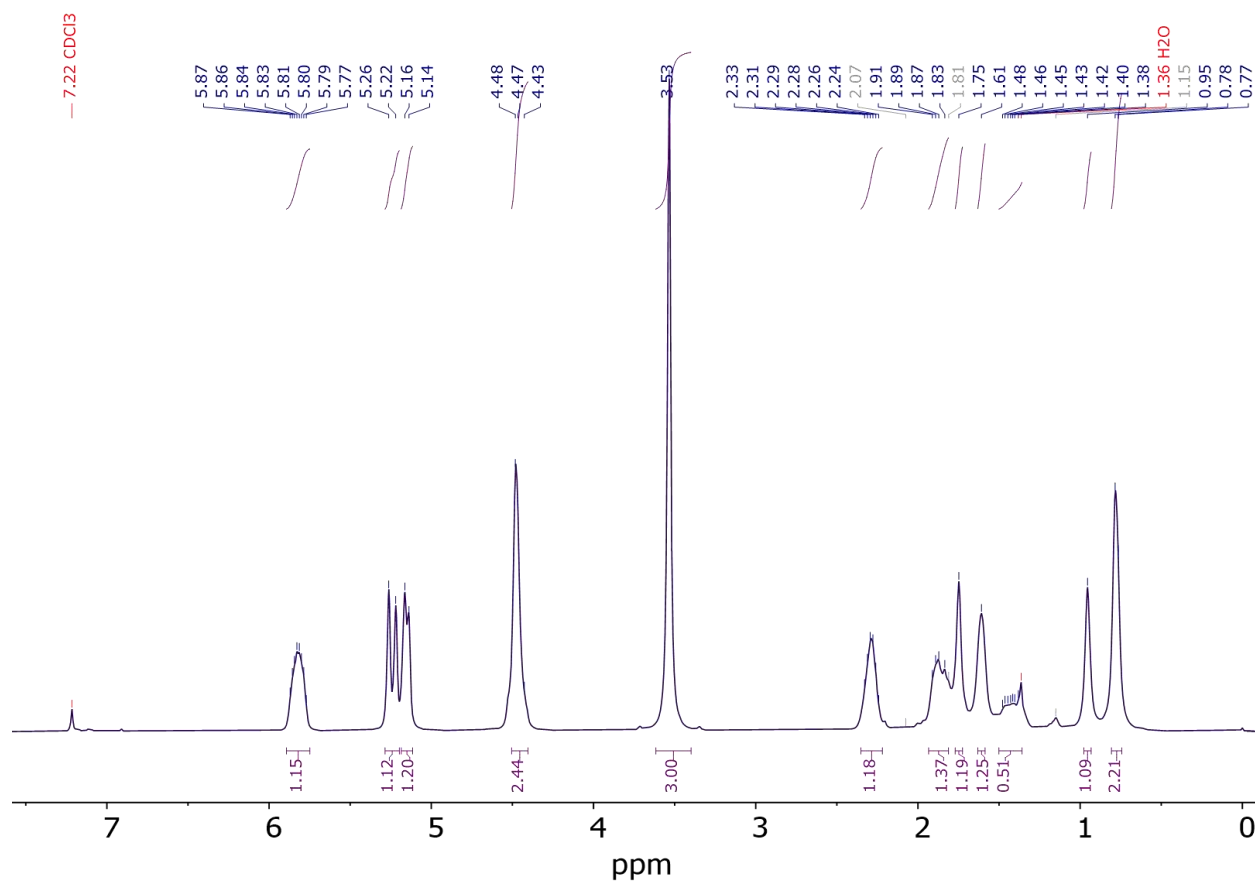
**Figure C5.**  $^1\text{H}$  NMR for the simultaneous time-point taken during the addition of the second 0.5 eq. (250 units, 11.0 mL) of AIA at 50 % MMA conversion (156 s) for the cyclic tetrablock copolymer.



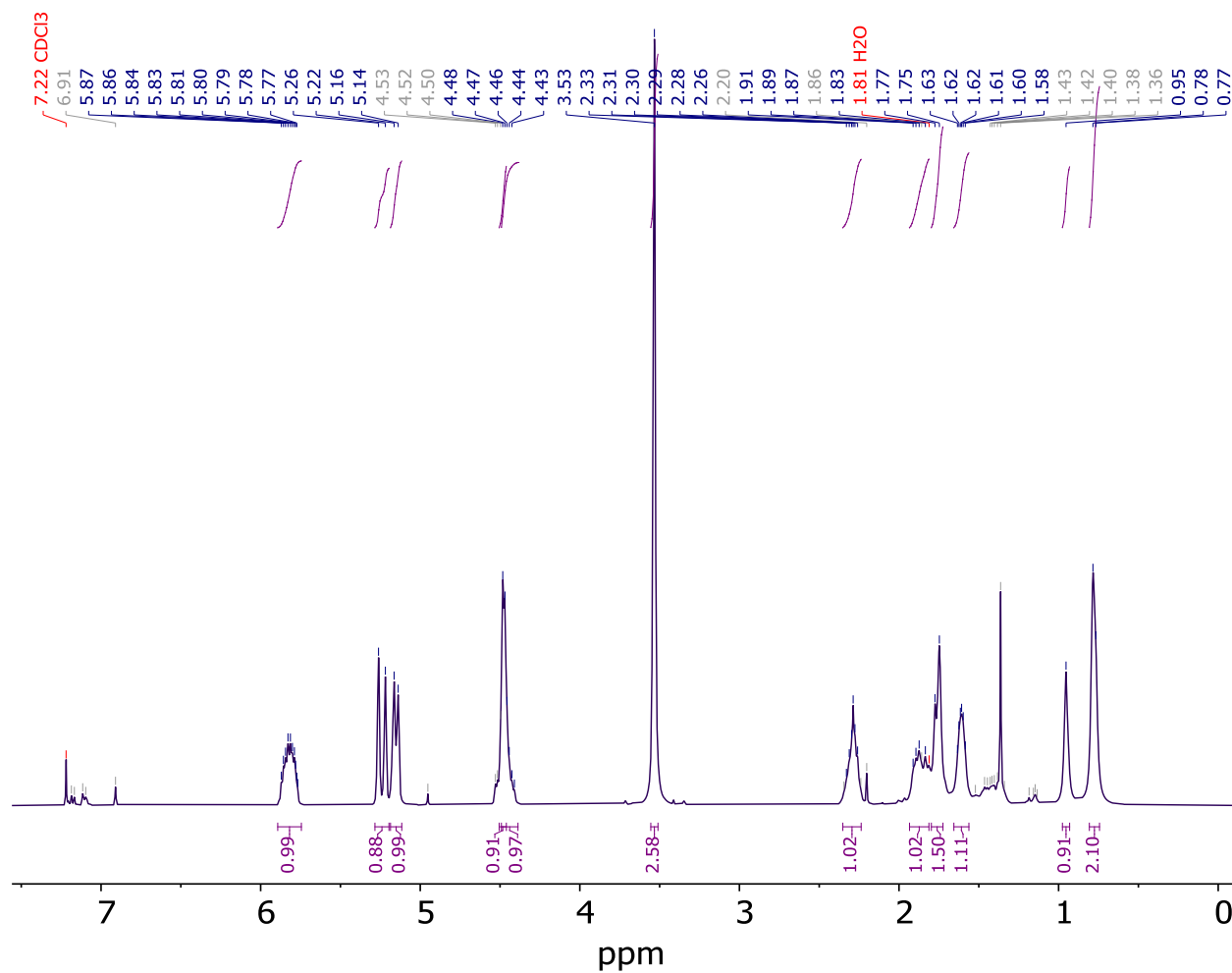
**Figure C6.**  $^1\text{H}$  NMR for the simultaneous time-point taken during the addition of the second 0.5 eq. (250 units, 11.0 mL) of AIA at 50 % MMA conversion (156 s) for the linear tetrablock copolymer.



**Figure C7.** <sup>1</sup>H NMR for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> (CHCl<sub>3</sub>).

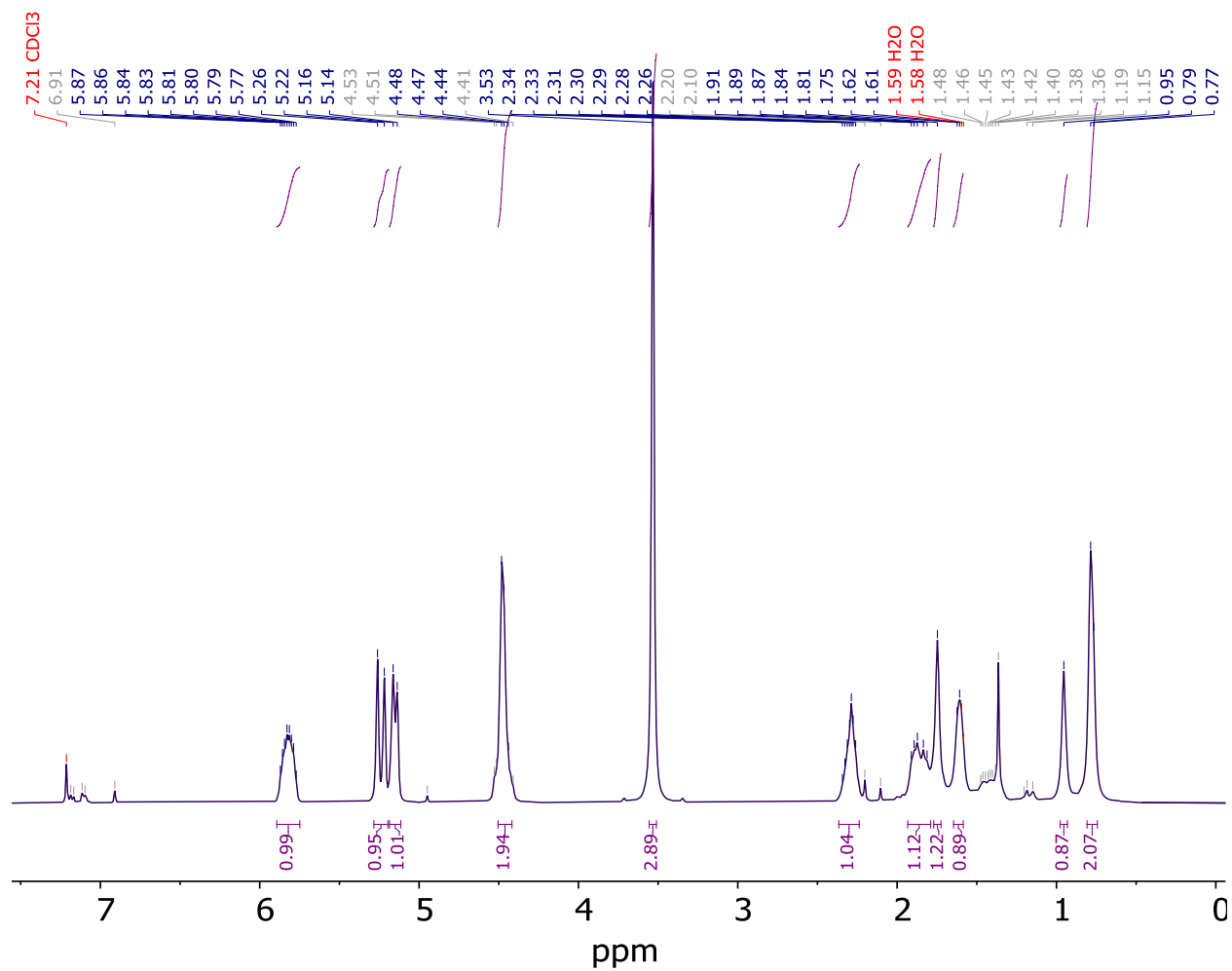


**Figure C8.** <sup>1</sup>H NMR for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub> (CHCl<sub>3</sub>).

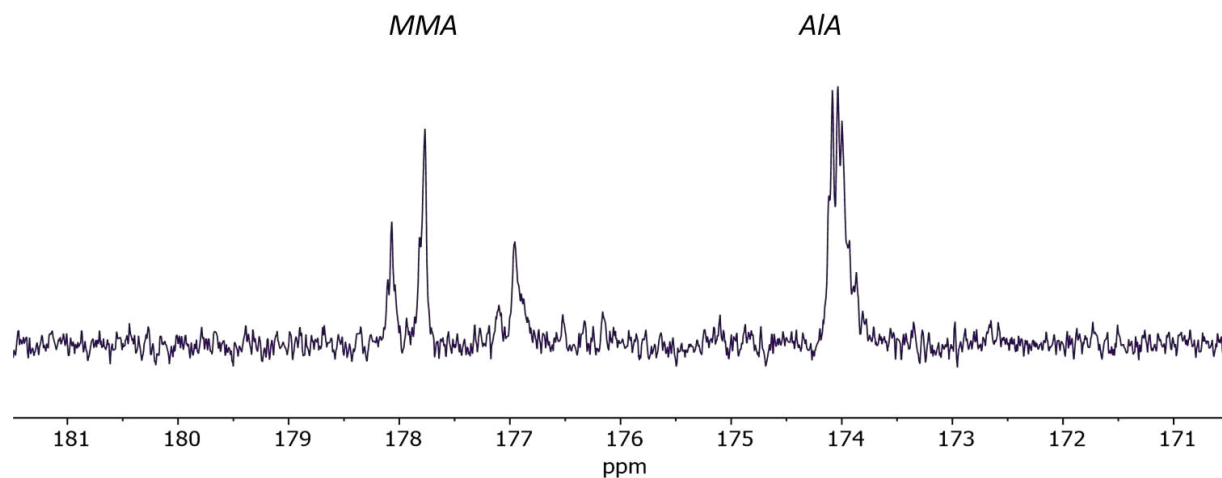


**Figure C9.** <sup>1</sup>H NMR for linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> (CHCl<sub>3</sub>).

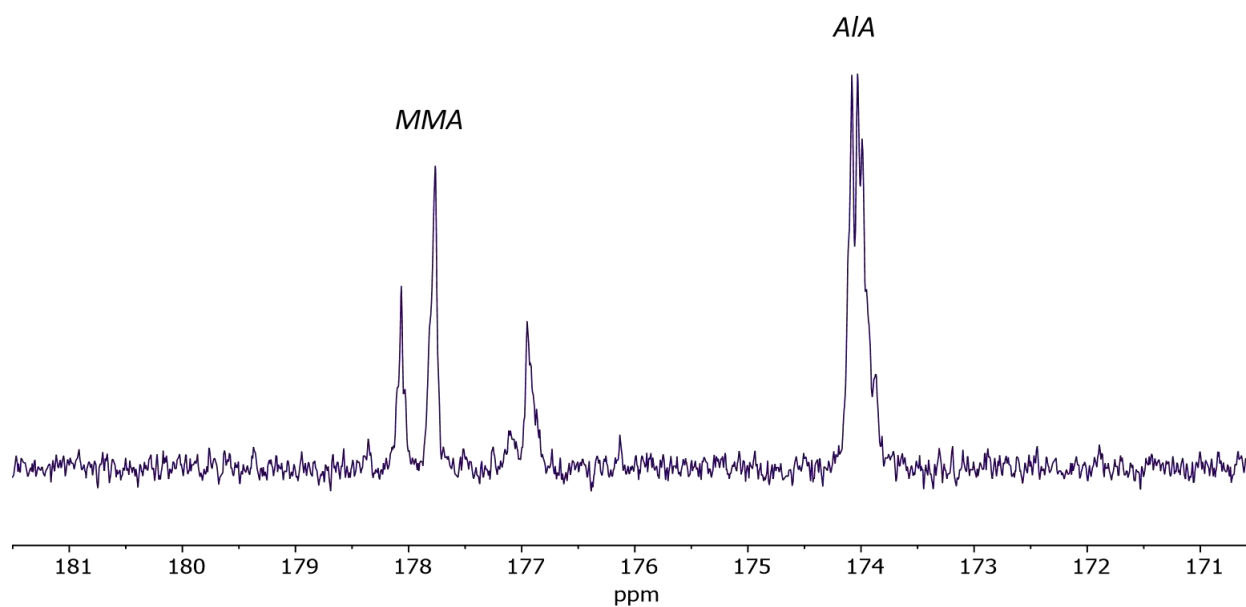




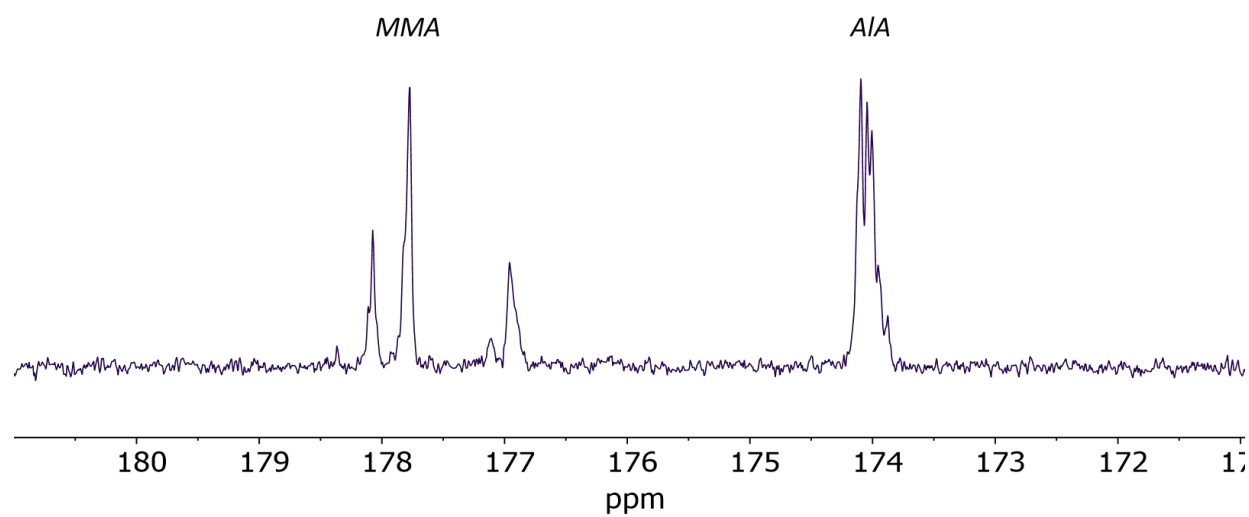
**Figure C10.** <sup>1</sup>H NMR for linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub> (CHCl<sub>3</sub>).



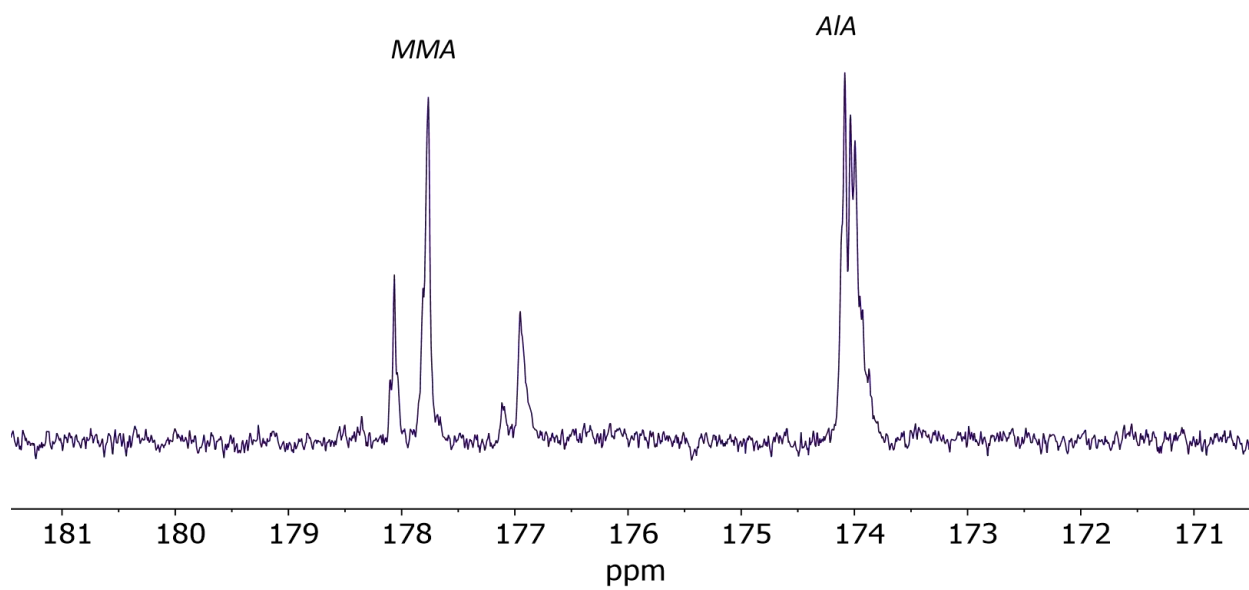
**Figure C11.**  $^{13}\text{C}$  NMR for cyclic  $\text{PAIA}_{500}\text{-}b\text{-PMMA}_{500}$  ( $\text{CHCl}_3$ ).



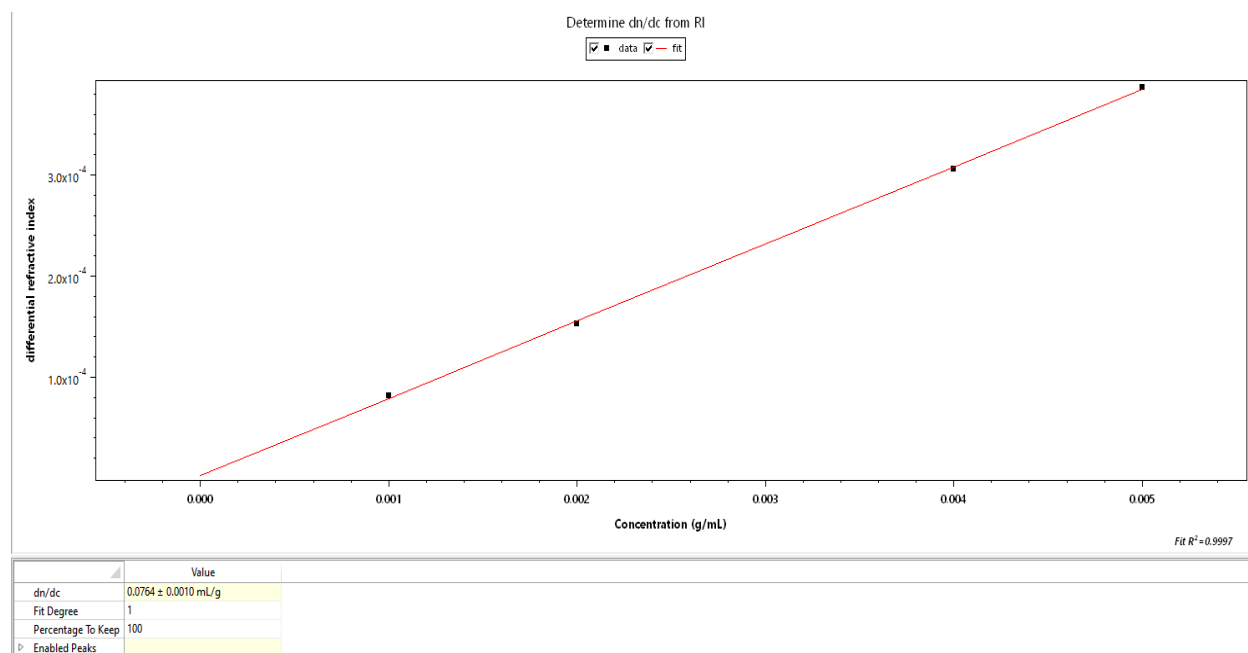
**Figure C12.**  $^{13}\text{C}$  NMR for cyclic  $\text{PAIA}_{250}\text{-}b\text{-PMMA}_{255}\text{-}b\text{-PAIA}_{250}\text{-}b\text{-PMMA}_{245}$  ( $\text{CHCl}_3$ ).



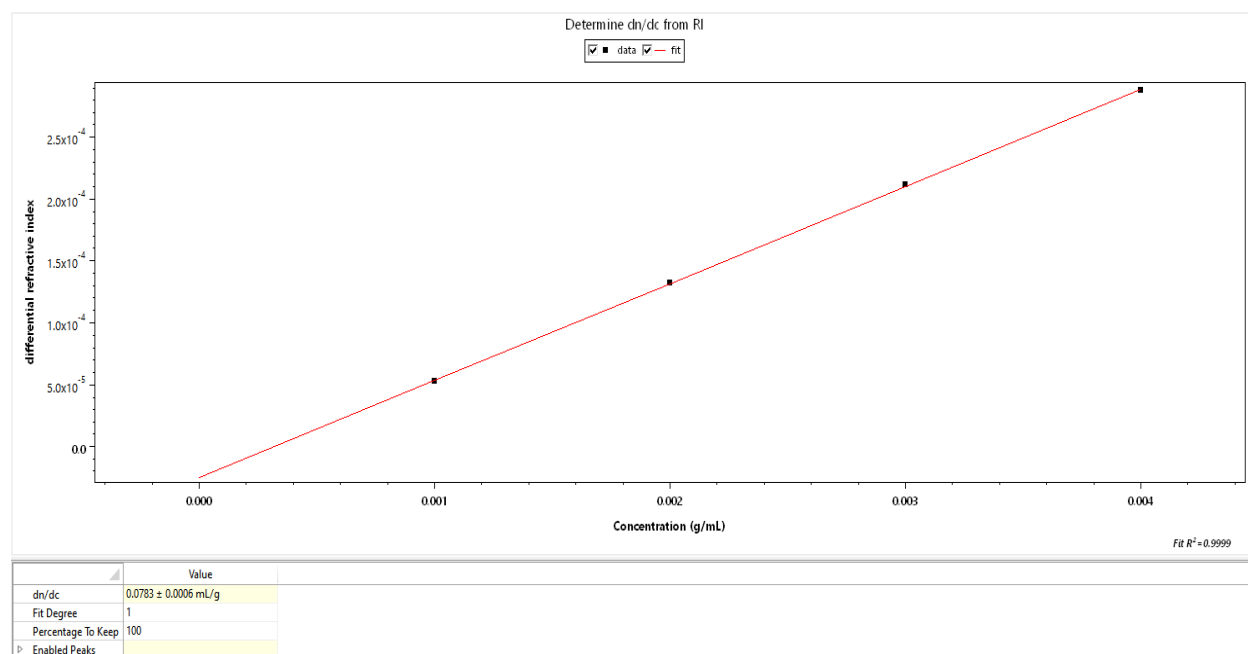
**Figure C13.**  $^{13}\text{C}$  NMR for linear  $\text{PAIA}_{500}\text{-}b\text{-PMMA}_{500}$  ( $\text{CHCl}_3$ ).



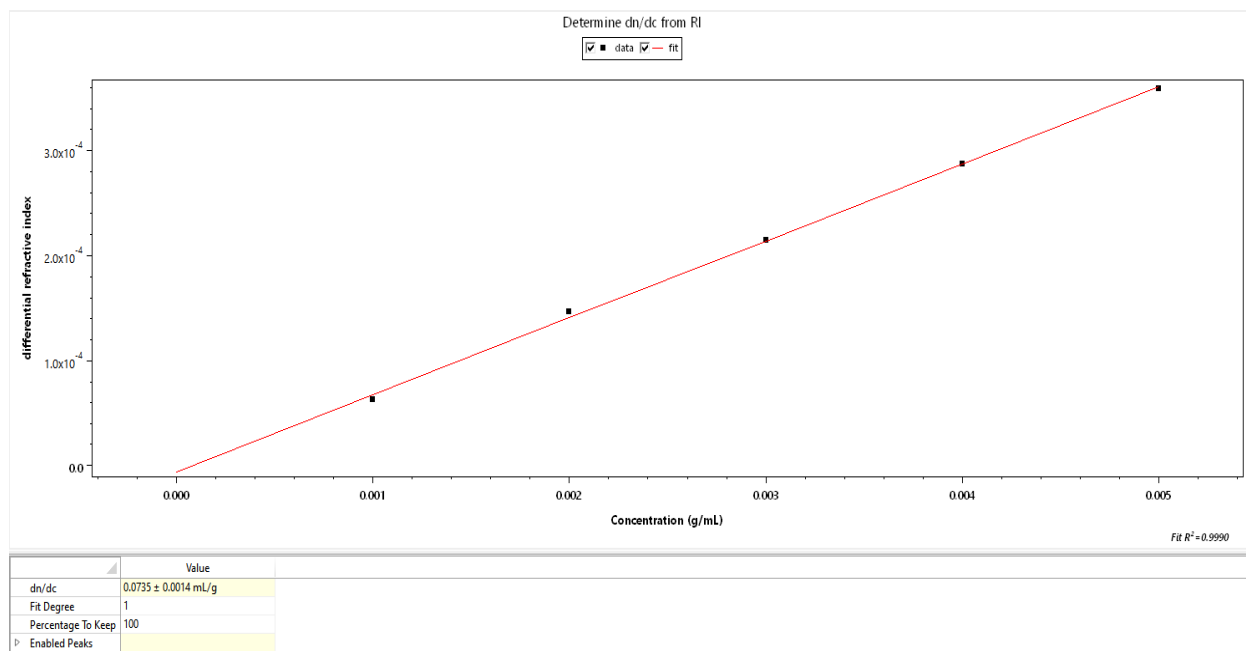
**Figure C14.**  $^{13}\text{C}$  NMR for linear  $\text{PAIA}_{250}\text{-}b\text{-PMMA}_{275}\text{-}b\text{-PAIA}_{250}\text{-}b\text{-PMMA}_{225}$  ( $\text{CHCl}_3$ ).



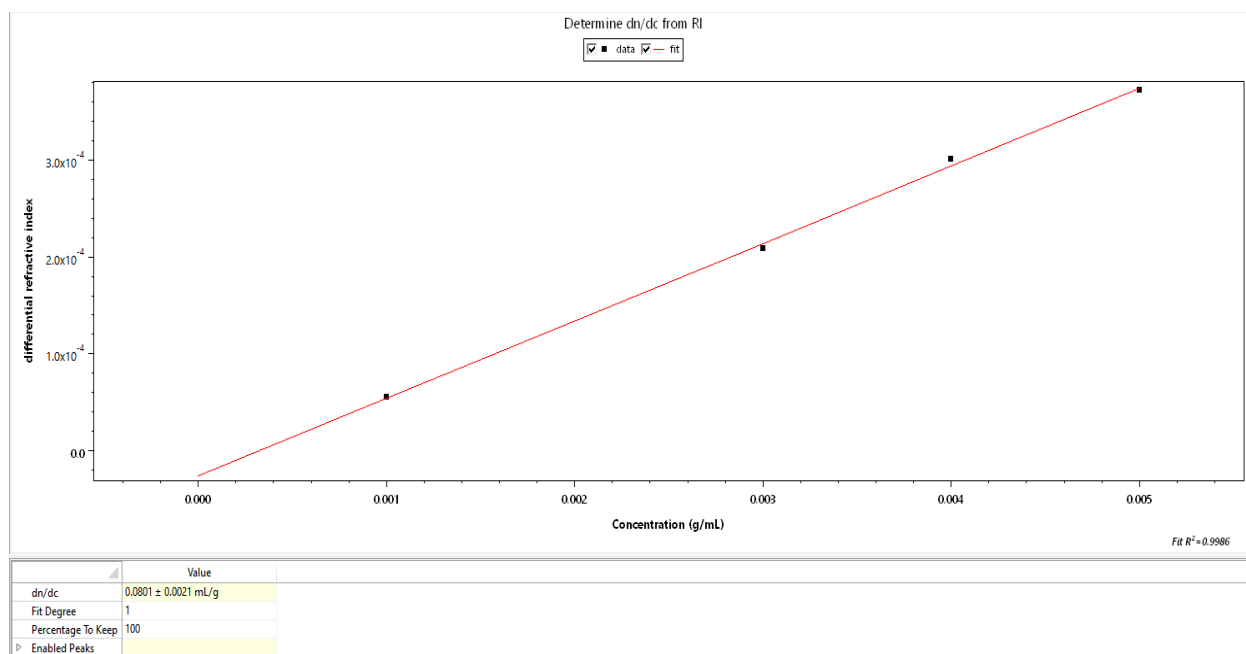
**Figure C15.** Batch  $dn/dc$  measurement results and line-fitting for cyclic PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub> in CHCl<sub>3</sub>.



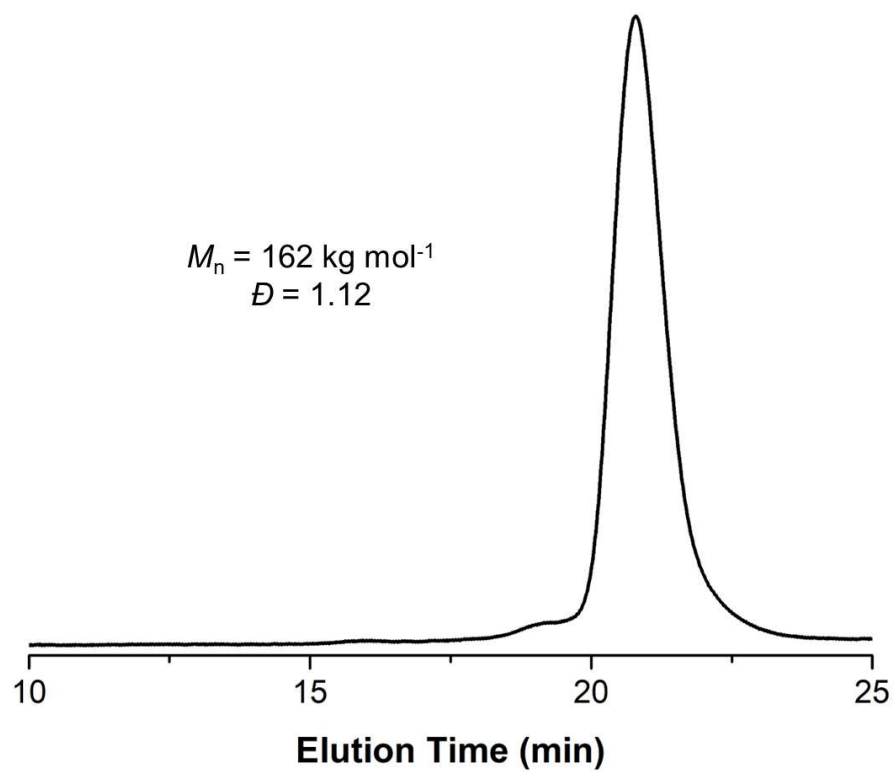
**Figure C16.** Batch  $dn/dc$  measurement results and line-fitting for linear PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub> in THF at 1.0 mL min<sup>-1</sup>.



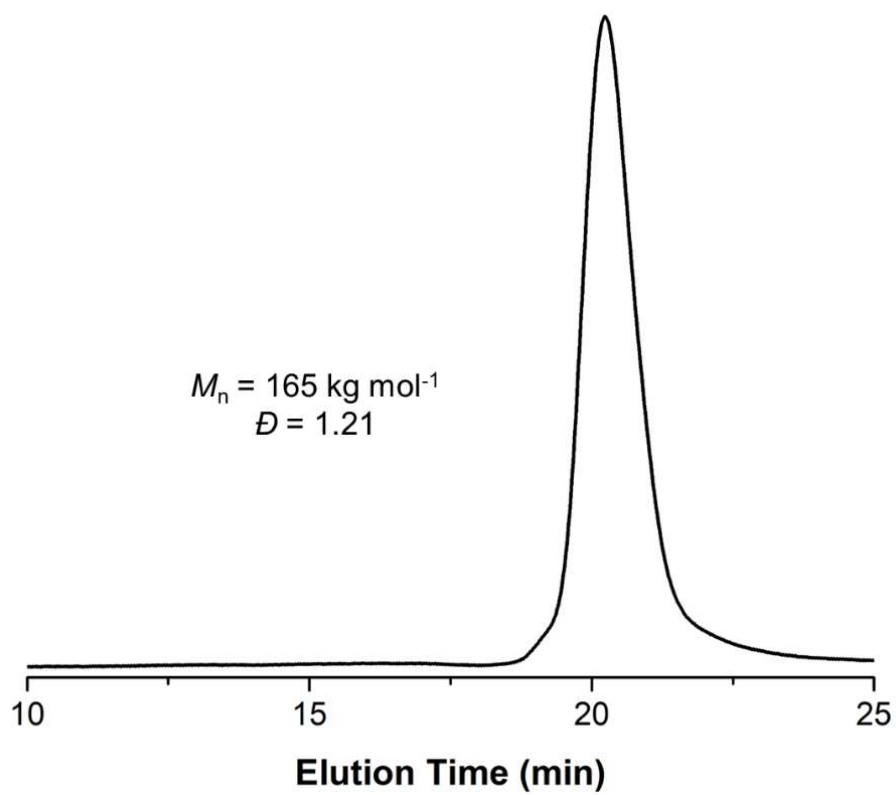
**Figure C17.** Batch  $dn/dc$  measurement results and line-fitting for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub> in THF at 1.0 mL min<sup>-1</sup>.



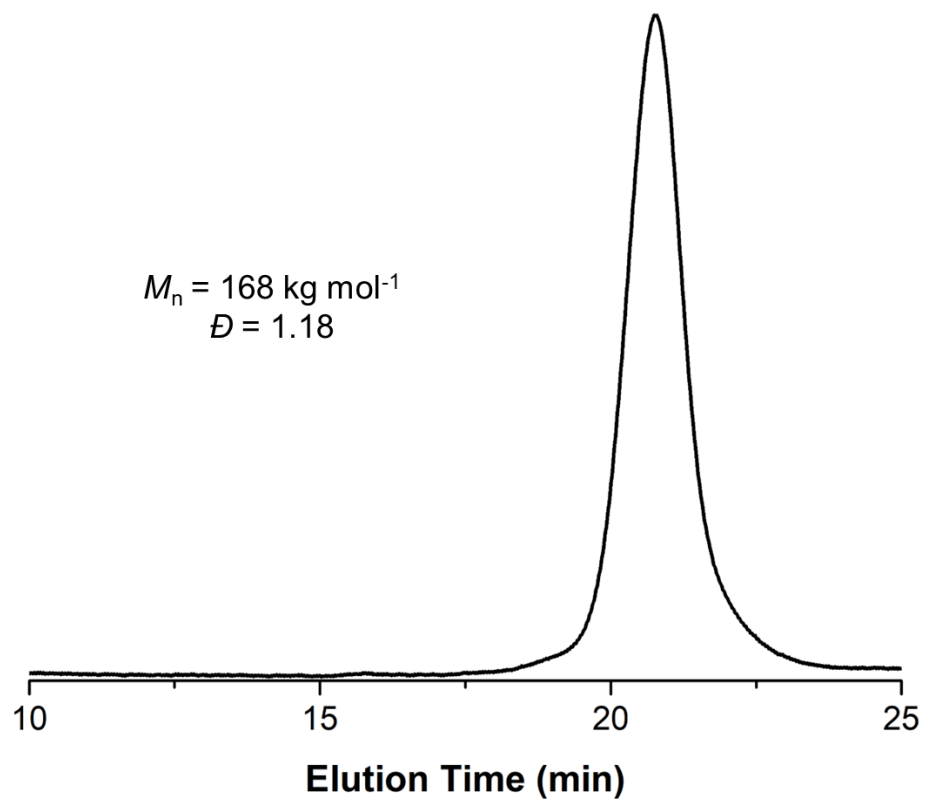
**Figure C18.** Batch  $dn/dc$  measurement results and line-fitting for linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub> in THF at 1.0 mL min<sup>-1</sup>.



**Figure C19.** GPC dRI trace for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub> (CHCl<sub>3</sub>).

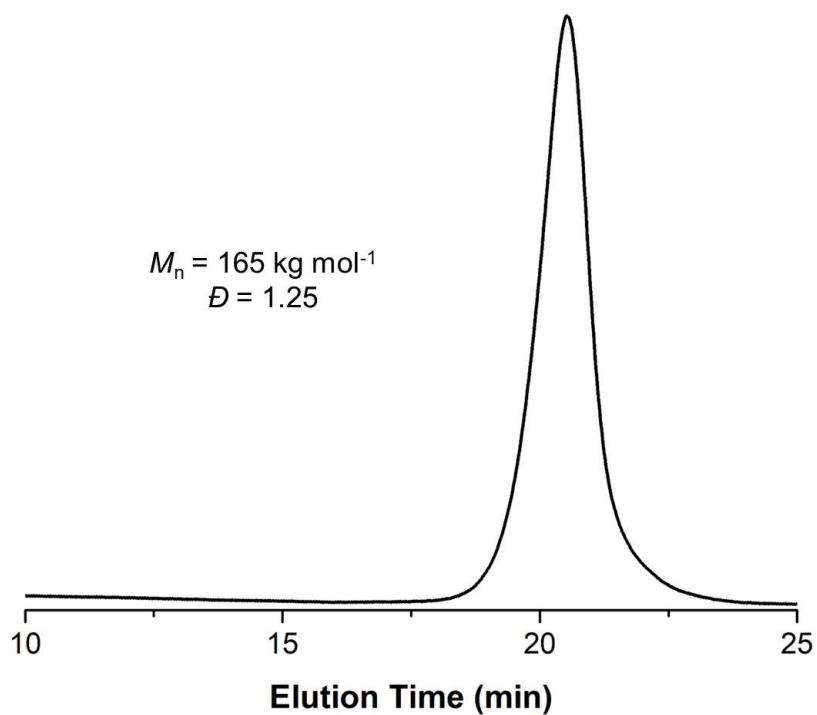


**Figure C20.** GPC dRI trace for linear PAI A<sub>500</sub>-*b*-PMMA<sub>500</sub> (CHCl<sub>3</sub>).

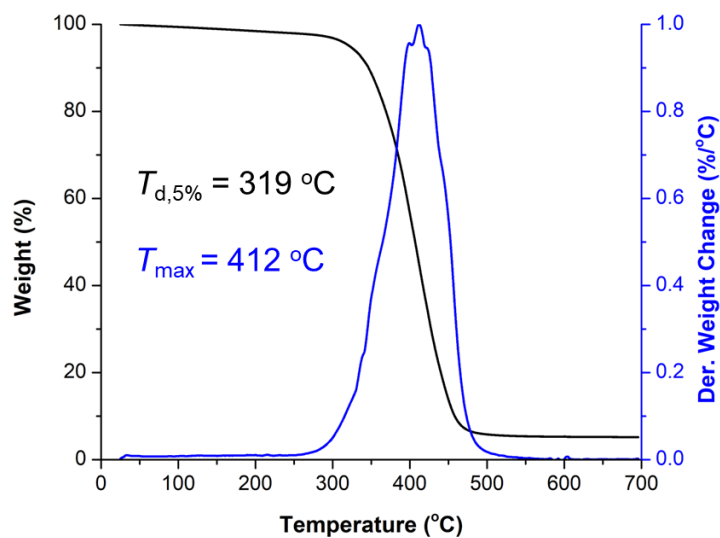


**Figure C21.** GPC dRI trace for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub> (CHCl<sub>3</sub>)

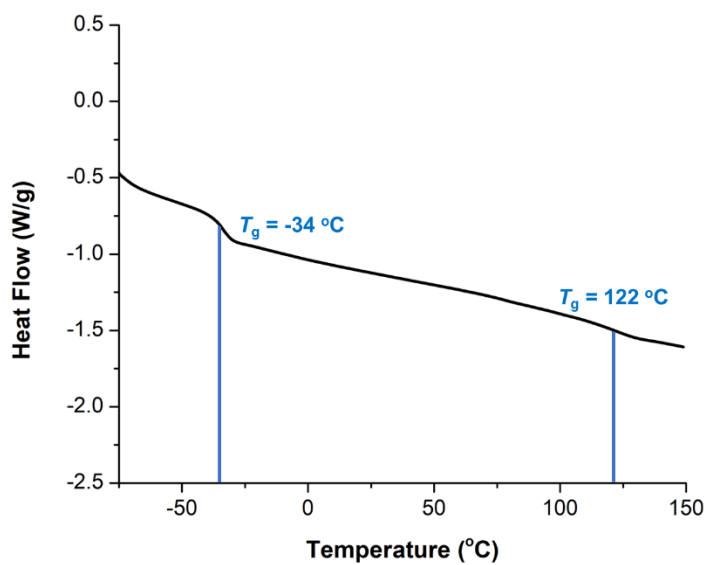




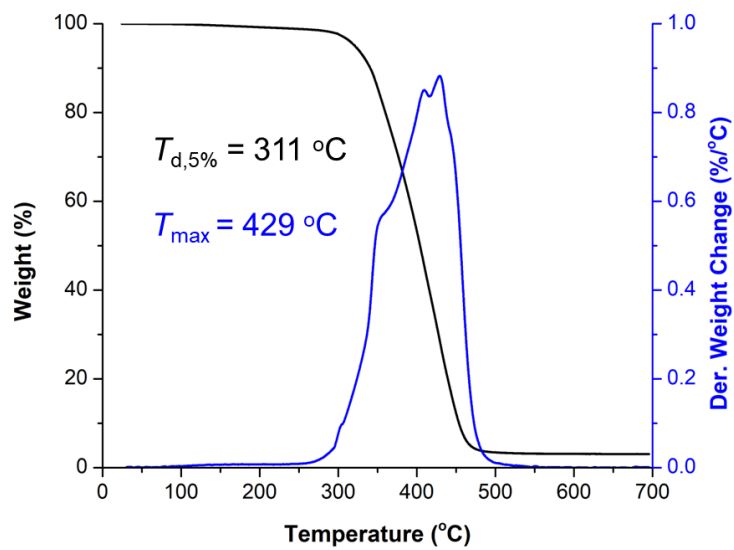
**Figure C22.** GPC dRI trace for linear PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub> (CHCl<sub>3</sub>).



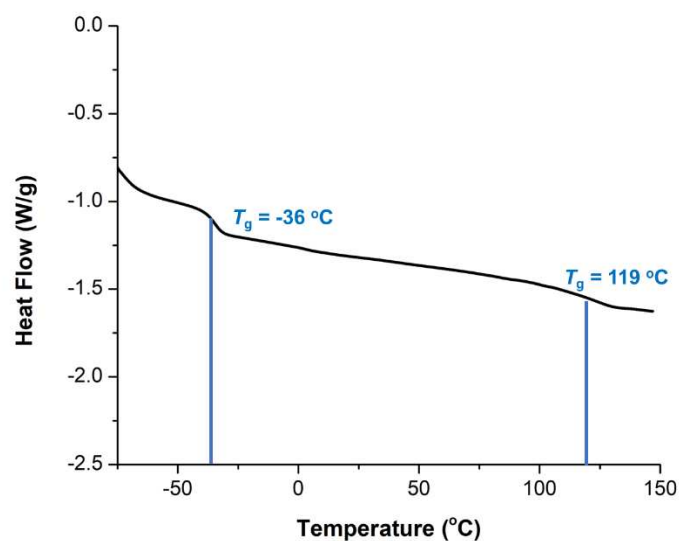
**Figure C23.** TGA plot (10 °C) for the thermal decomposition of cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>.



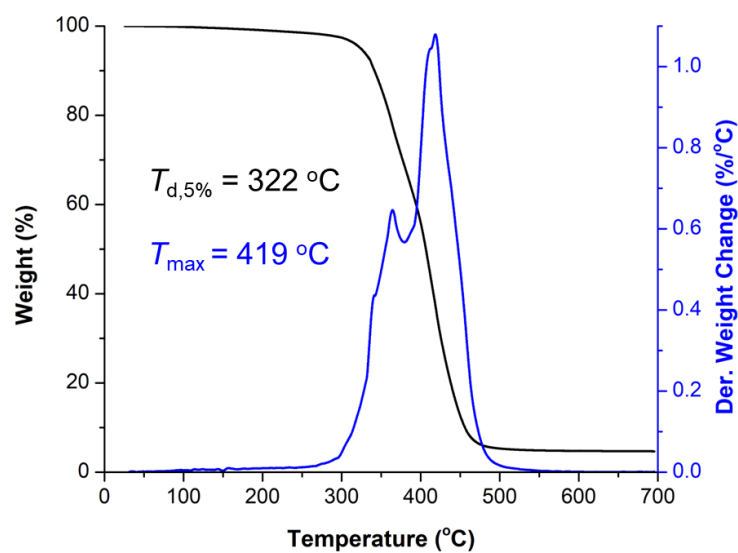
**Figure C24.** DSC plot (2<sup>nd</sup> heating scan; 10 °C/min) for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>.



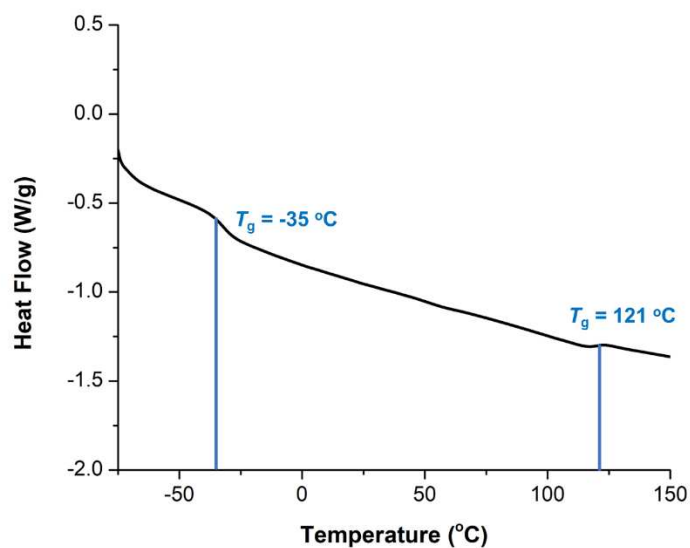
**Figure C25.** TGA plot (10 °C/min) for the thermal decomposition of linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>.



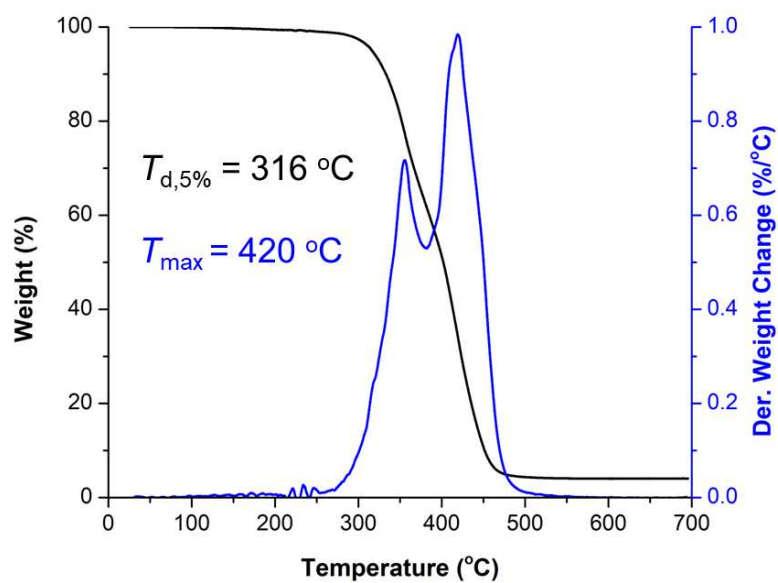
**Figure C26.** DSC plot (2<sup>nd</sup> heating scan; 10 °C/min) for linear PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub>.



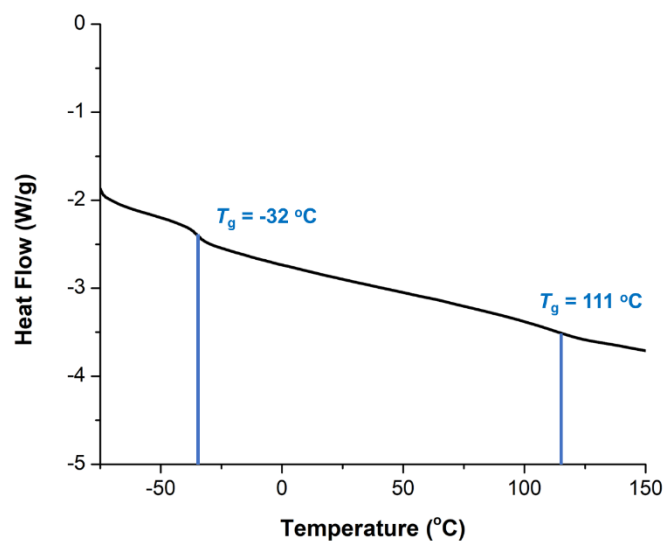
**Figure C27.** TGA plot (10 °C) for the thermal decomposition of cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>.



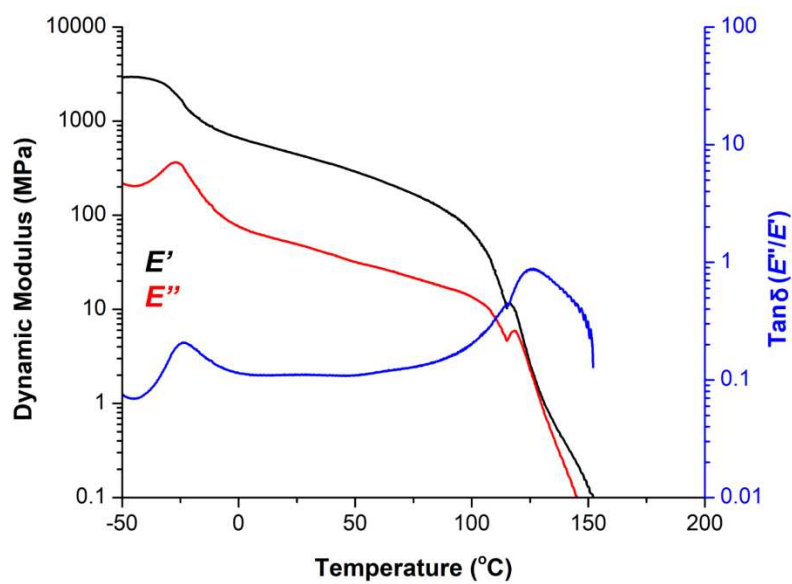
**Figure C28.** DSC plot (2<sup>nd</sup> heating scan, 10 °C/min) for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>.



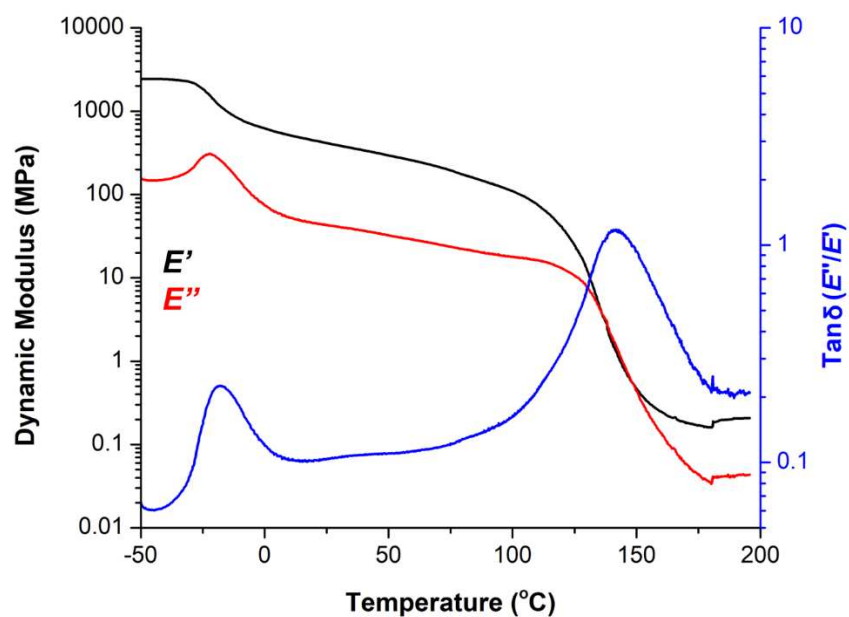
**Figure C29.** TGA plot (10 °C) for the thermal decomposition of linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub>.



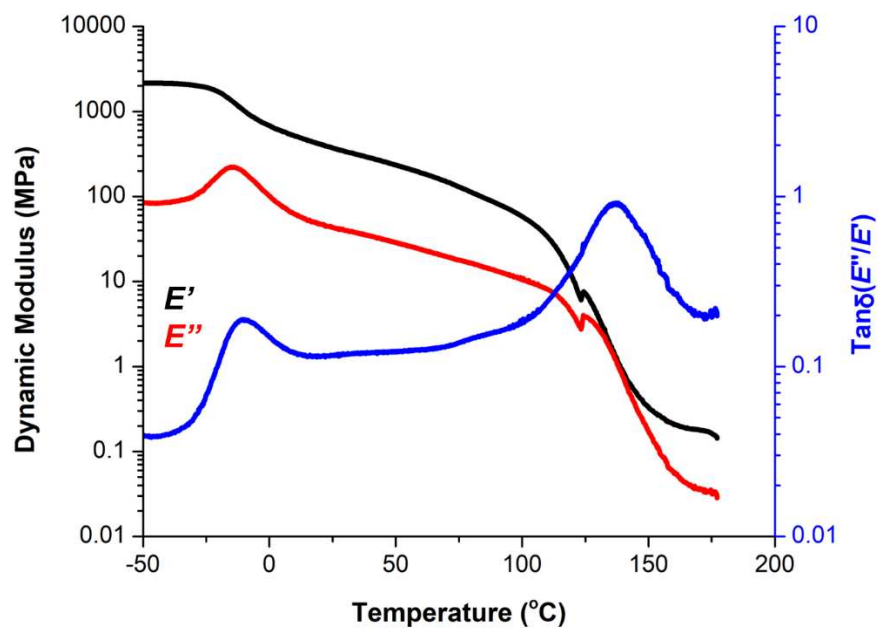
**Figure C30.** DSC plot (2<sup>nd</sup> heating scan; 10 °C/min) for linear PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub>.



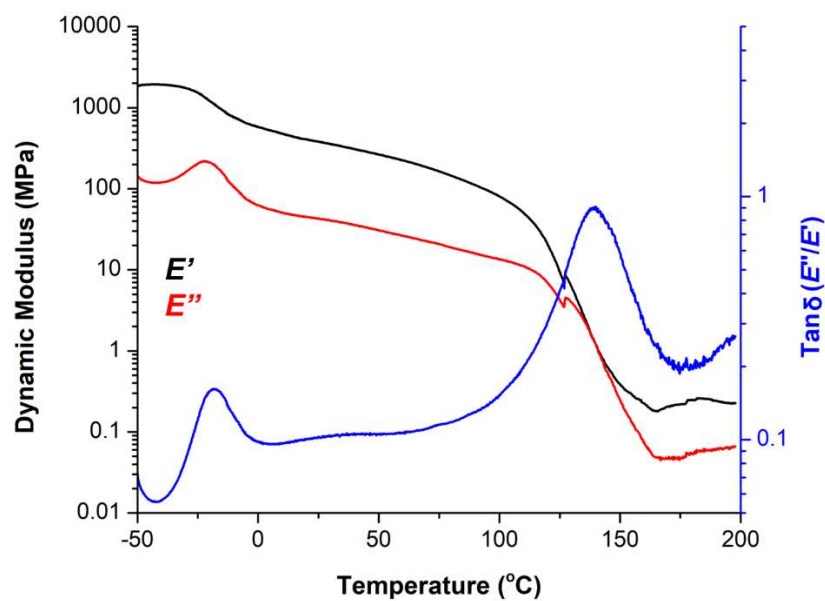
**Figure C31.** DTMA temperature-ramp frequency sweep (-50 to 150 °C, 1 Hz, 0.3 %, 5 °C/min) for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>.



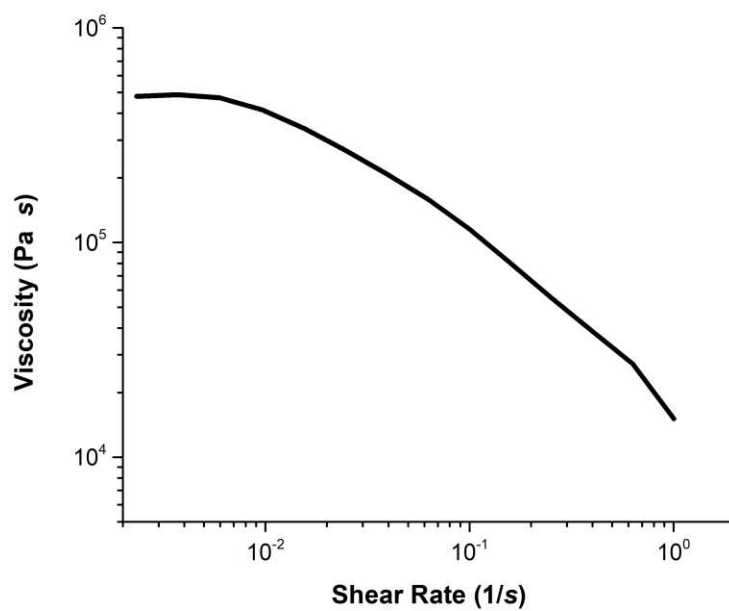
**Figure C32.** DTMA temperature-ramp frequency sweep (-50 to 150 °C, 1 Hz, 0.3 %, 5 °C/min) for linear PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub>.



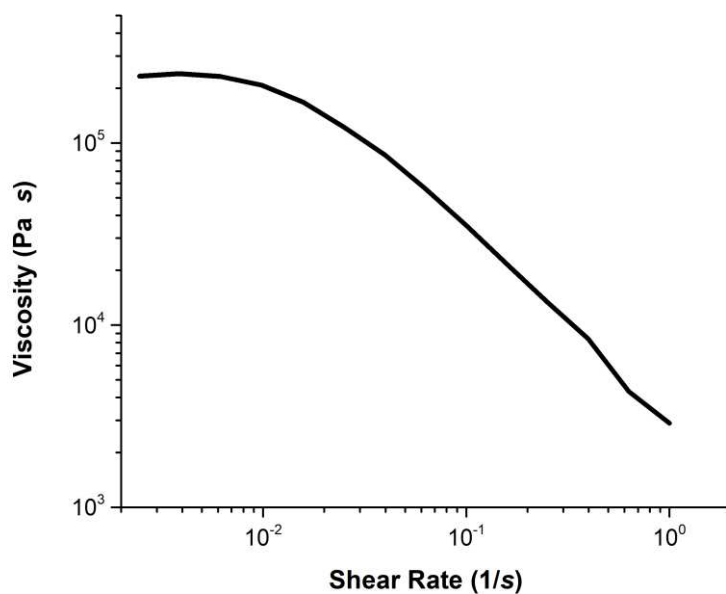
**Figure C33.** DTMA temperature-ramp frequency sweep (-50 to 150 °C, 1 Hz, 0.3 %, 5 °C/min) for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>.



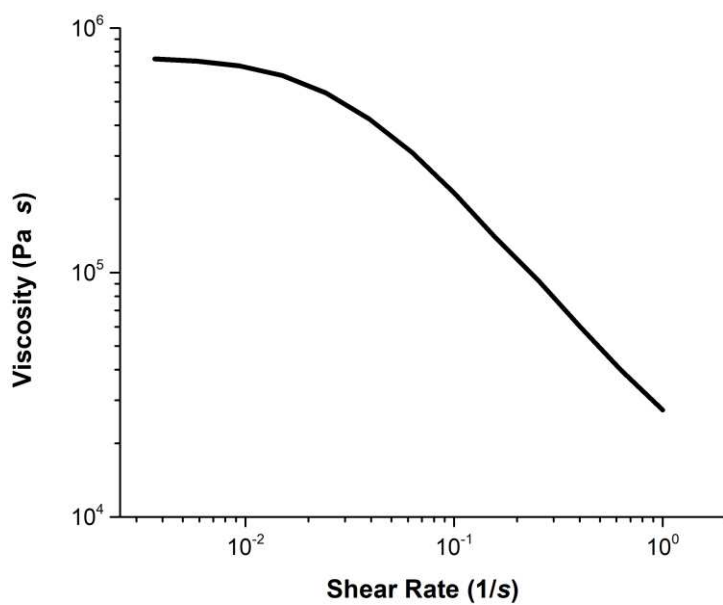
**Figure C34.** DTMA temperature-ramp frequency sweep (-50 to 150  $^{\circ}\text{C}$ , 1 Hz, 0.3 %, 5  $^{\circ}\text{C}/\text{min}$ ) for linear  $\text{PAI}A_{250}\text{-}b\text{-PMMA}_{275}\text{-}b\text{-PAI}A_{250}\text{-}b\text{-PMMA}_{225}$ .



**Figure C35.** Rheometric flow curve for linear  $\text{PAI}A_{500}\text{-}b\text{-PMMA}_{500}$  (0.001 to 1  $\text{s}^{-1}$ , 10  $\text{rad}/\text{s}$ , 175  $^{\circ}\text{C}$ ).

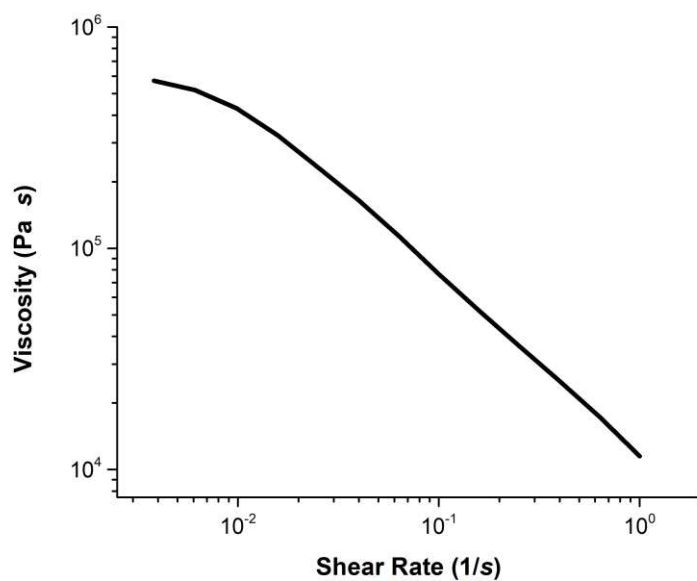


**Figure C36.** Rheometric flow curve for cyclic PA1A<sub>500</sub>-*b*-PMMA<sub>500</sub> (0.001 to 1 s<sup>-1</sup>, 10 rad/s, 175 °C).

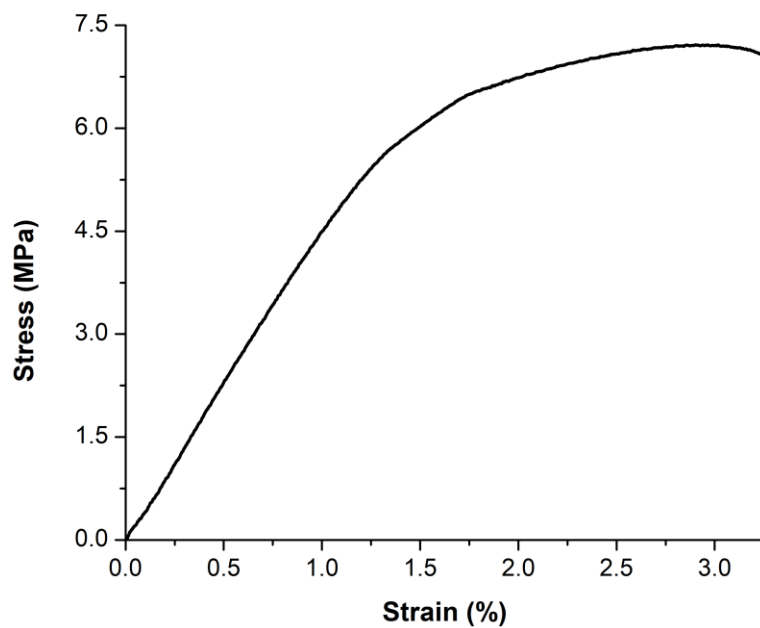


**Figure C37.** Rheometric flow curve for linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub> (0.001 to 1 s<sup>-1</sup>, 10 rad/s, 175 °C).

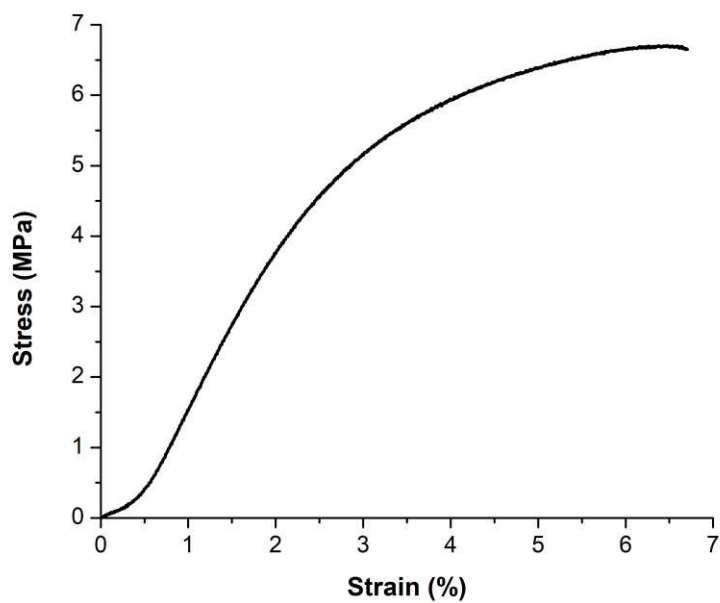




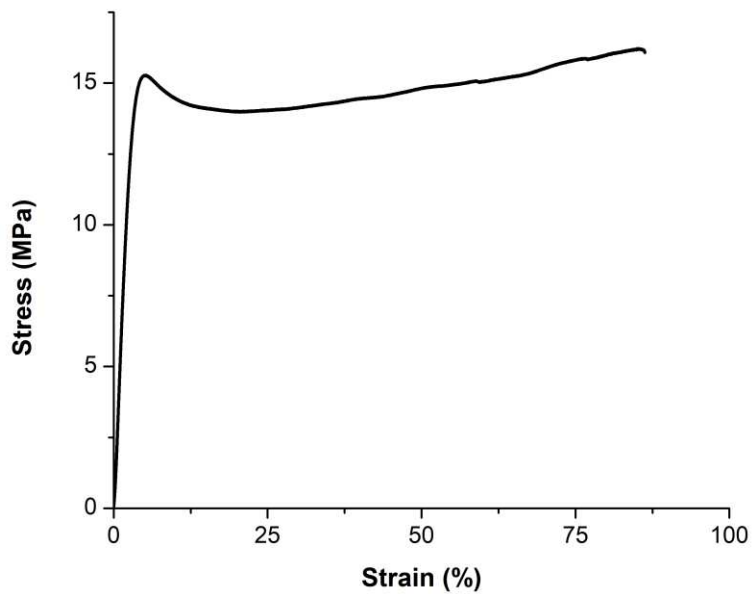
**Figure C38.** Rheometric flow curve for cyclic PAIA<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>245</sub> (0.001 to 1 s<sup>-1</sup>, 10 rad/s, 175 °C).



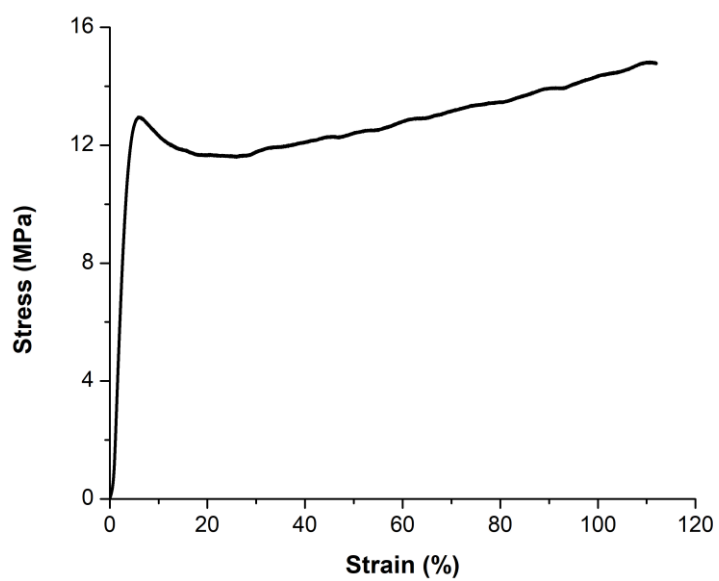
**Figure C39.** Averaged tensile stress/strain test for linear PAIA<sub>500</sub>-*b*-PAMA<sub>500</sub> (RT, 5 mm/min).



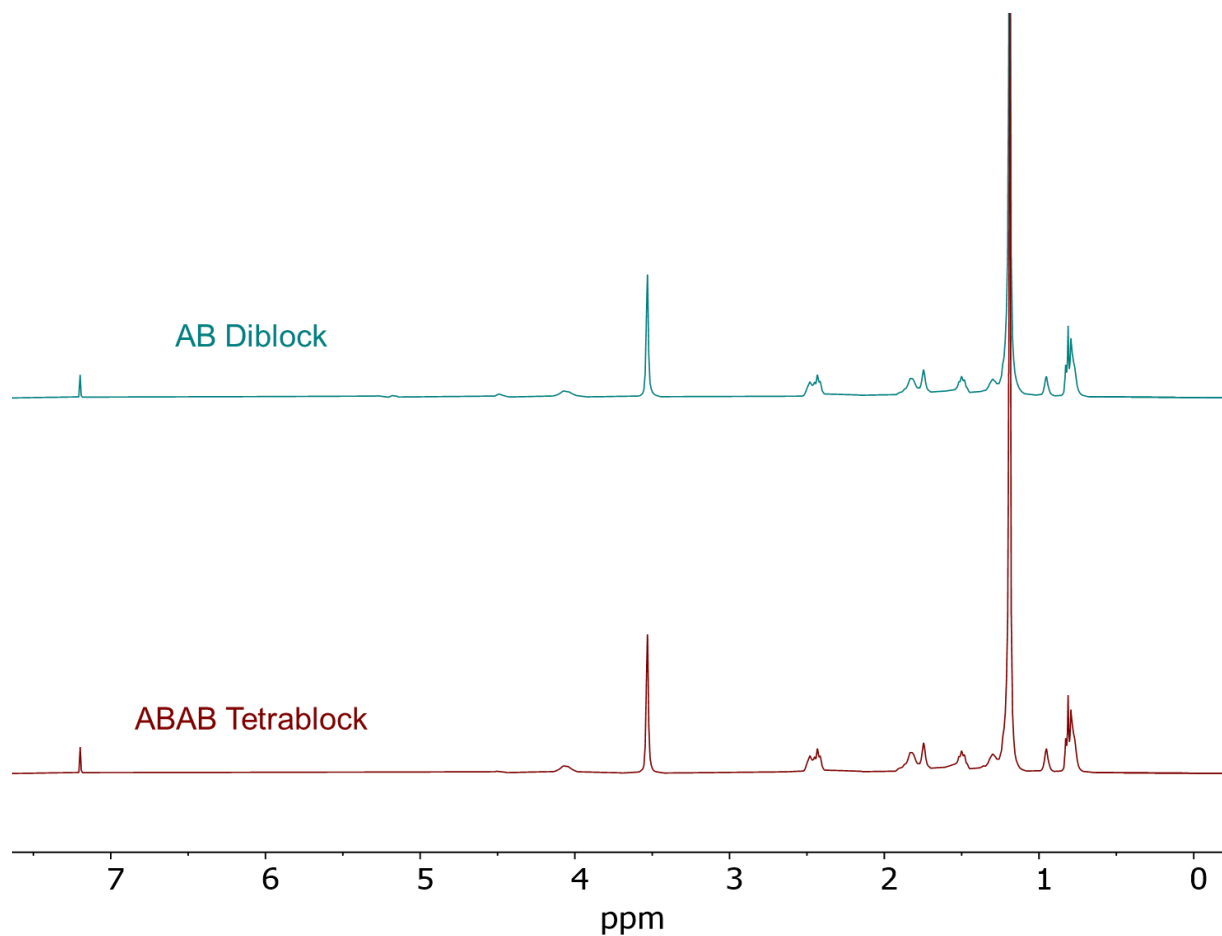
**Figure C40.** Averaged tensile stress/strain test for cyclic PA1A<sub>500</sub>-*b*-PAMA<sub>500</sub> (RT, 5 mm/min).



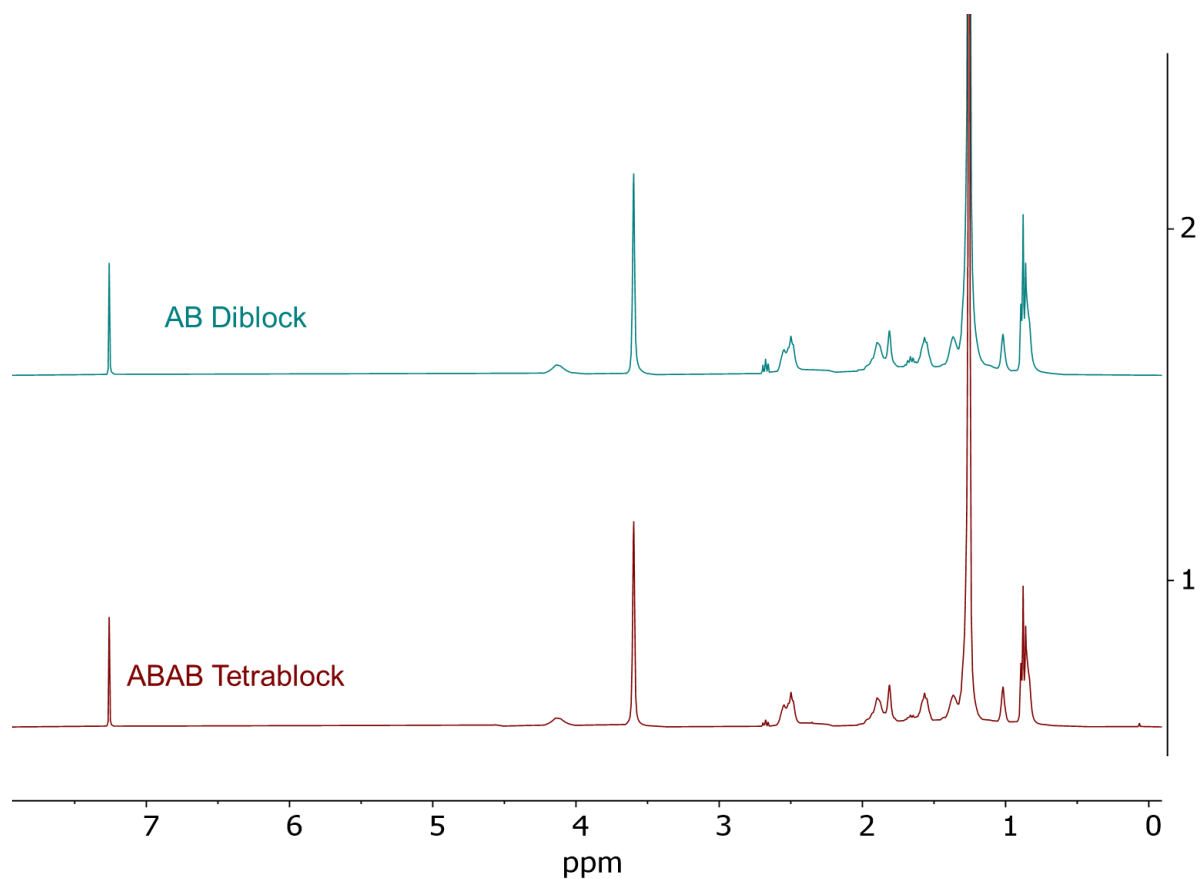
**Figure C41.** Averaged tensile stress/strain test for linear PA1A<sub>250</sub>-*b*-PAMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub> (RT, 5 mm/min).



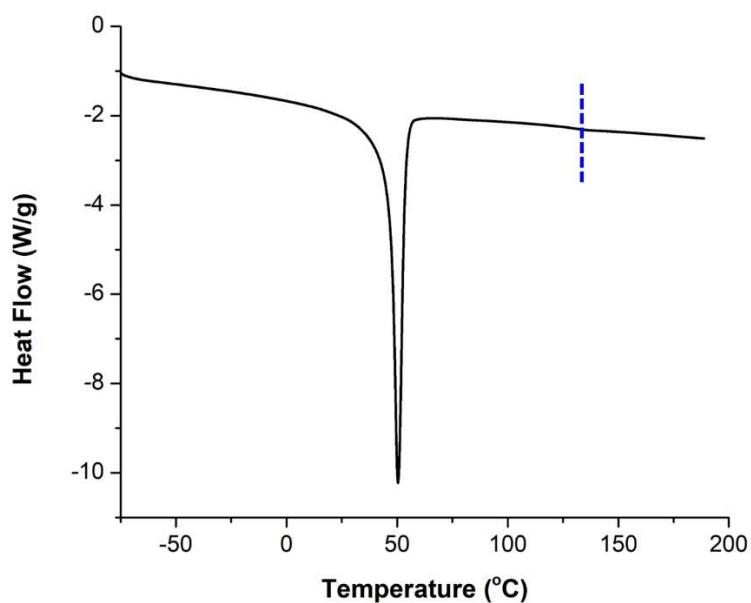
**Figure C42.** Averaged tensile stress/strain test for cyclic PA1A<sub>250</sub>-*b*-PAMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub> (RT, 5 mm/min).



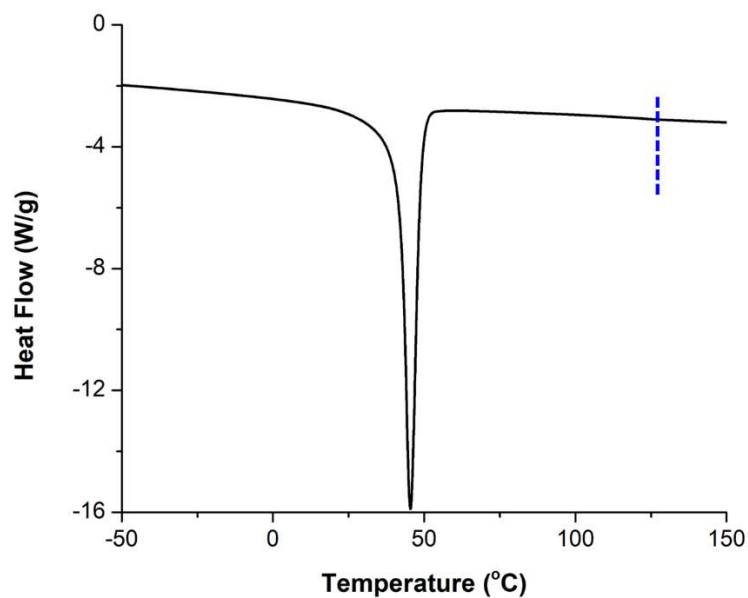
**Figure C43.** <sup>1</sup>H NMR spectra overlays for linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT and PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub>-*g*-1ODT, with little no alkene presence signaling successful installment of 1ODT by thiol-ene click functionalization.



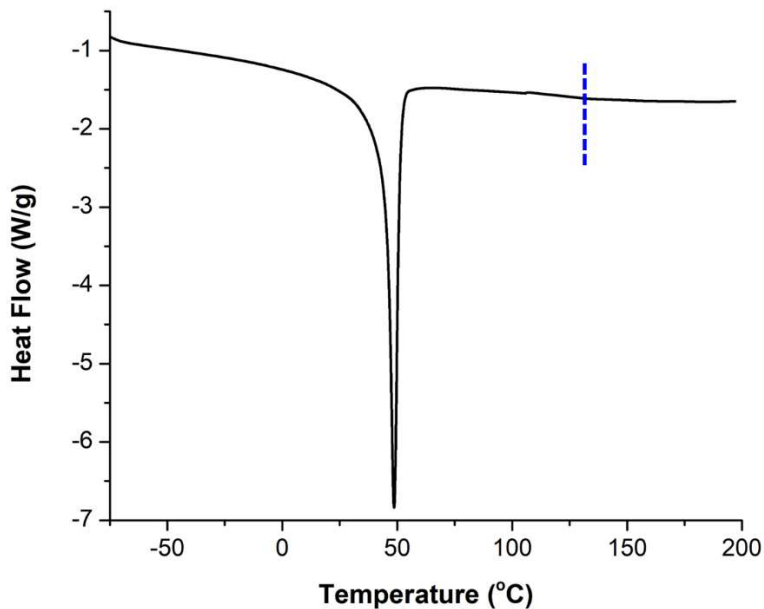
**Figure C44.** <sup>1</sup>H NMR spectra overlays for linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT and PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub>-*g*-1ODT, with little no alkene presence signaling successful installment of 1ODT by thiol-ene click functionalization.



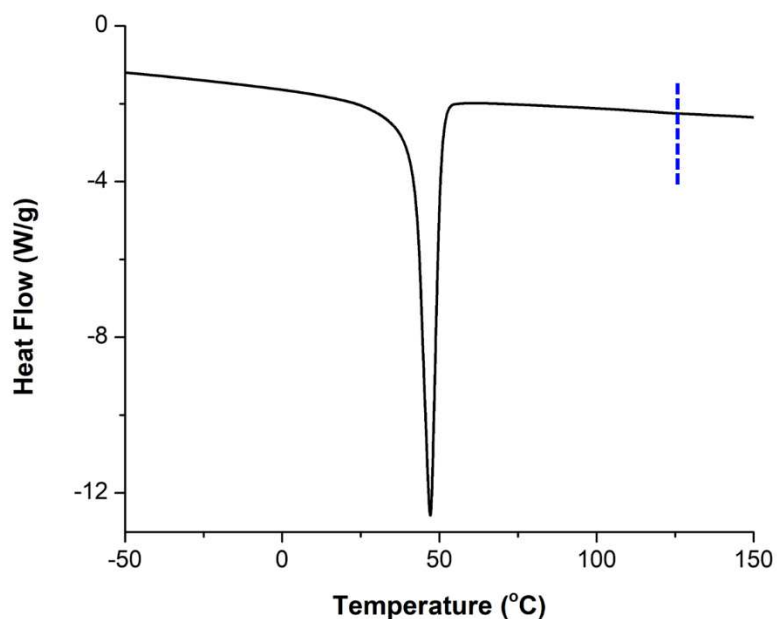
**Figure C45.** DSC trace (2<sup>nd</sup> heating scan; 10 °C/min) for linear PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT highlighting the loss PAIA  $T_g$  (-35 °C), appearance of 1ODT-grafted  $T_m$ , and retained PMMA  $T_g$  (~120 °C).



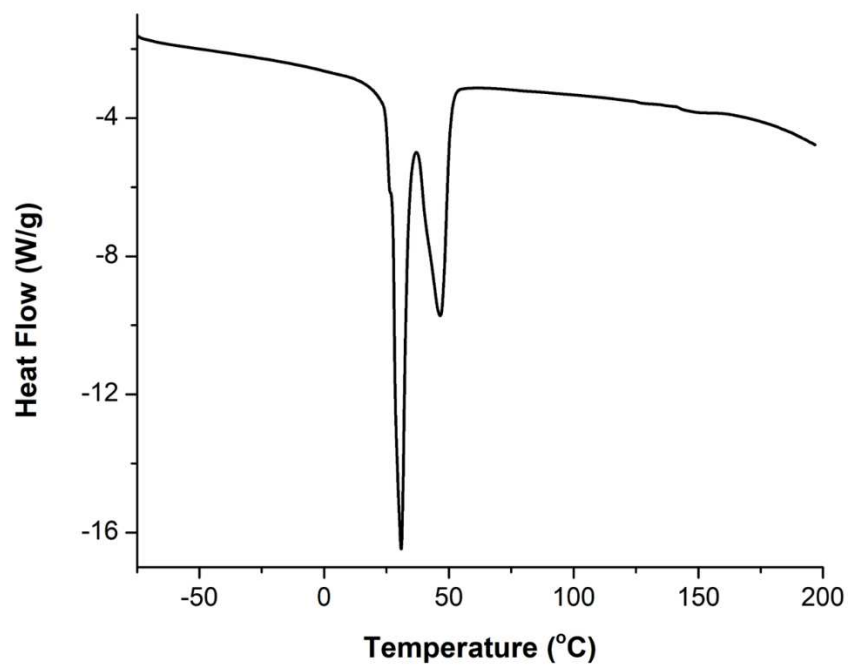
**Figure C46.** DSC trace (2<sup>nd</sup> heating scan; 10 °C/min) for cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT highlighting the loss PAIA  $T_g$  (-35 °C), appearance of 1ODT-grafted  $T_m$ , and retained PMMA  $T_g$  (~120 °C).



**Figure C47.** DSC trace (2<sup>nd</sup> heating scan; 10 °C/min) for linear PA1A<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>225</sub>-*g*-1ODT highlighting the loss PA1A  $T_g$  (-35 °C), appearance of 1ODT-grafted  $T_m$ , and retained PMMA  $T_g$  (~120 °C).

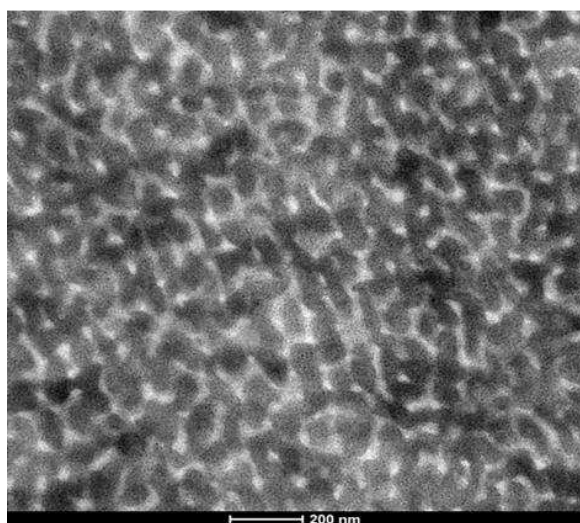
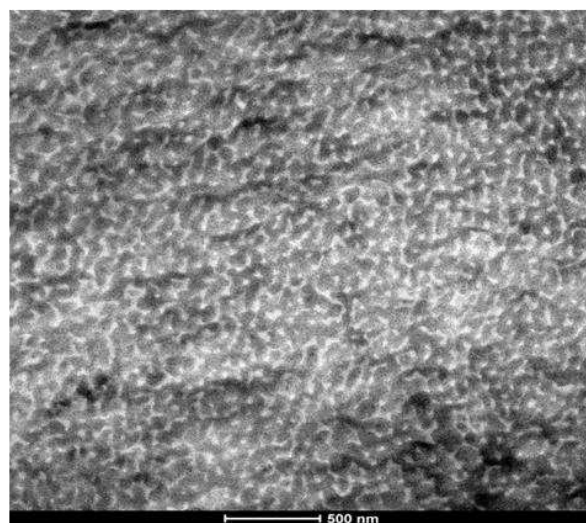
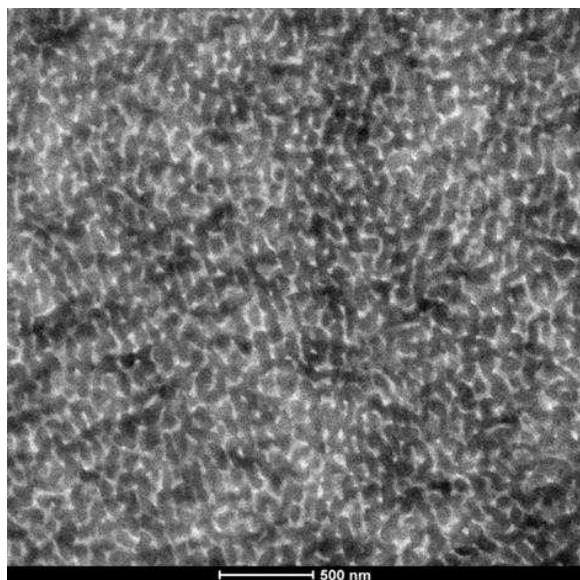


**Figure C48.** DSC trace (2<sup>nd</sup> heating scan; 10 °C/min) for cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>-*g*-1ODT highlighting the loss PA1A  $T_g$  (-35 °C), appearance of 1ODT-grafted  $T_m$ , and retained PMMA  $T_g$  (~120 °C).

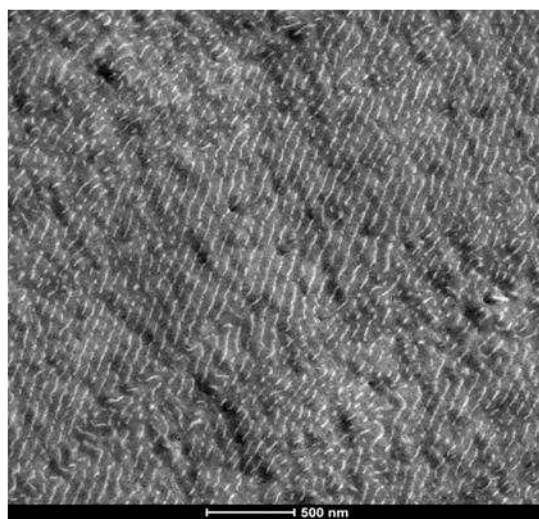
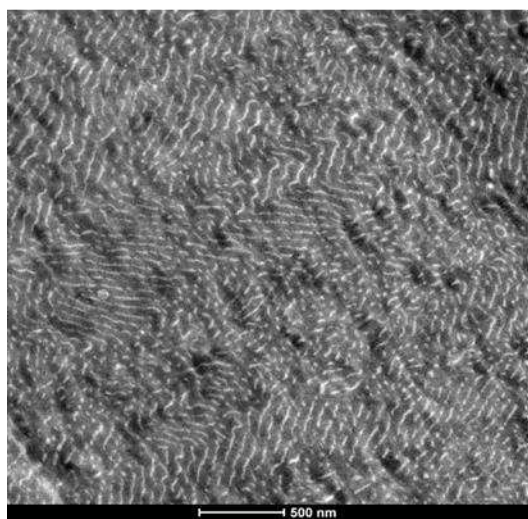
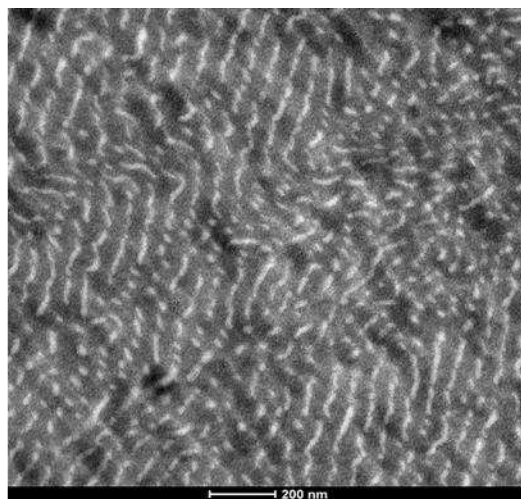
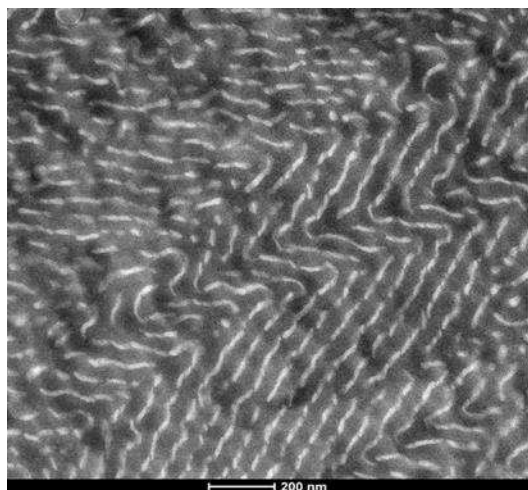


**Figure C49.** DSC trace (2<sup>nd</sup> heating scan; 10 °C/min) for cyclic PAIA<sub>500</sub>-*b*-PAIA<sub>500</sub>-*g*-1ODT spiked with 1 mol. eq of free 1ODT grafting agent to display the separate  $T_m$  (~30 °C) observable when samples are not properly purified.

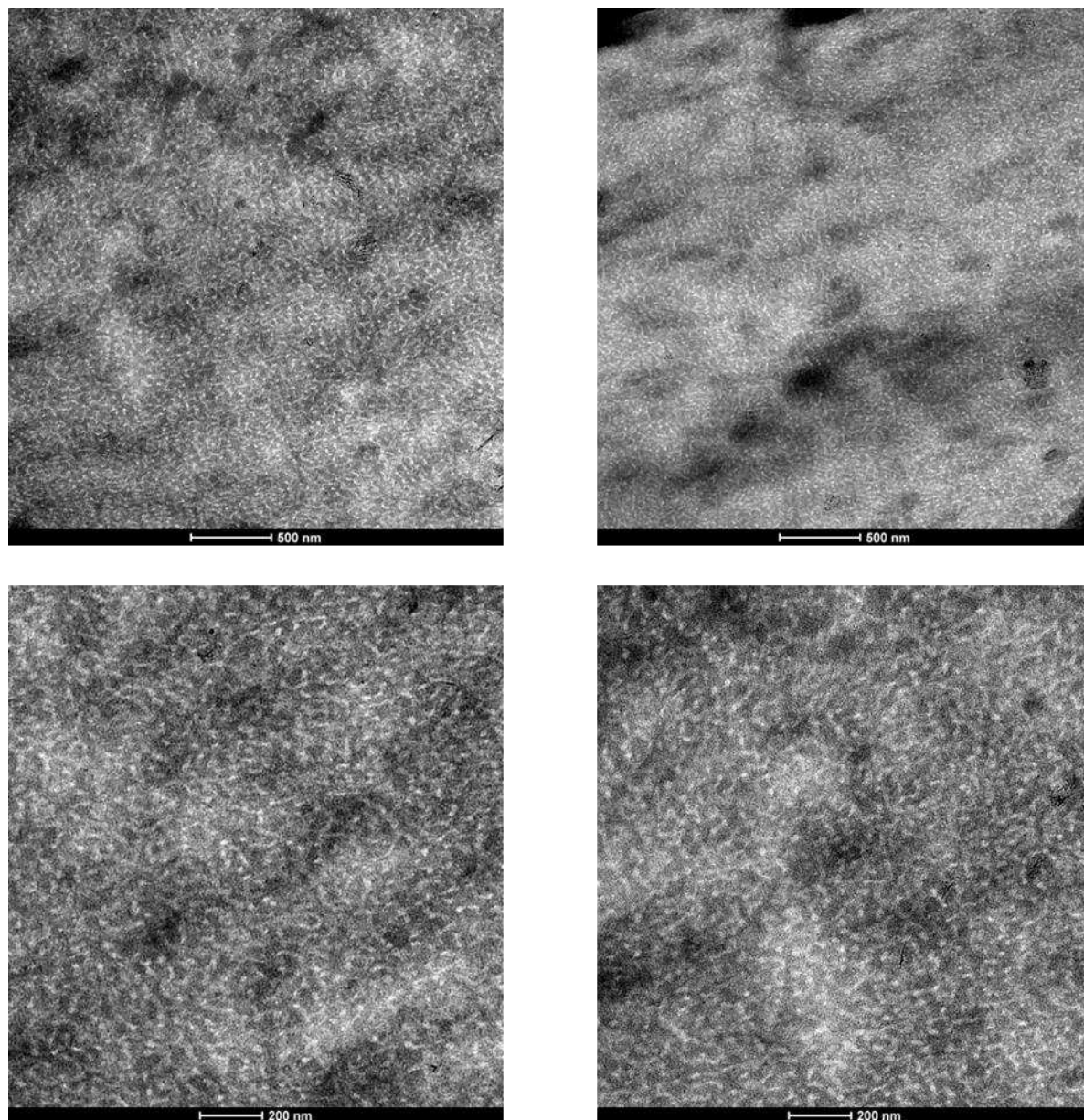




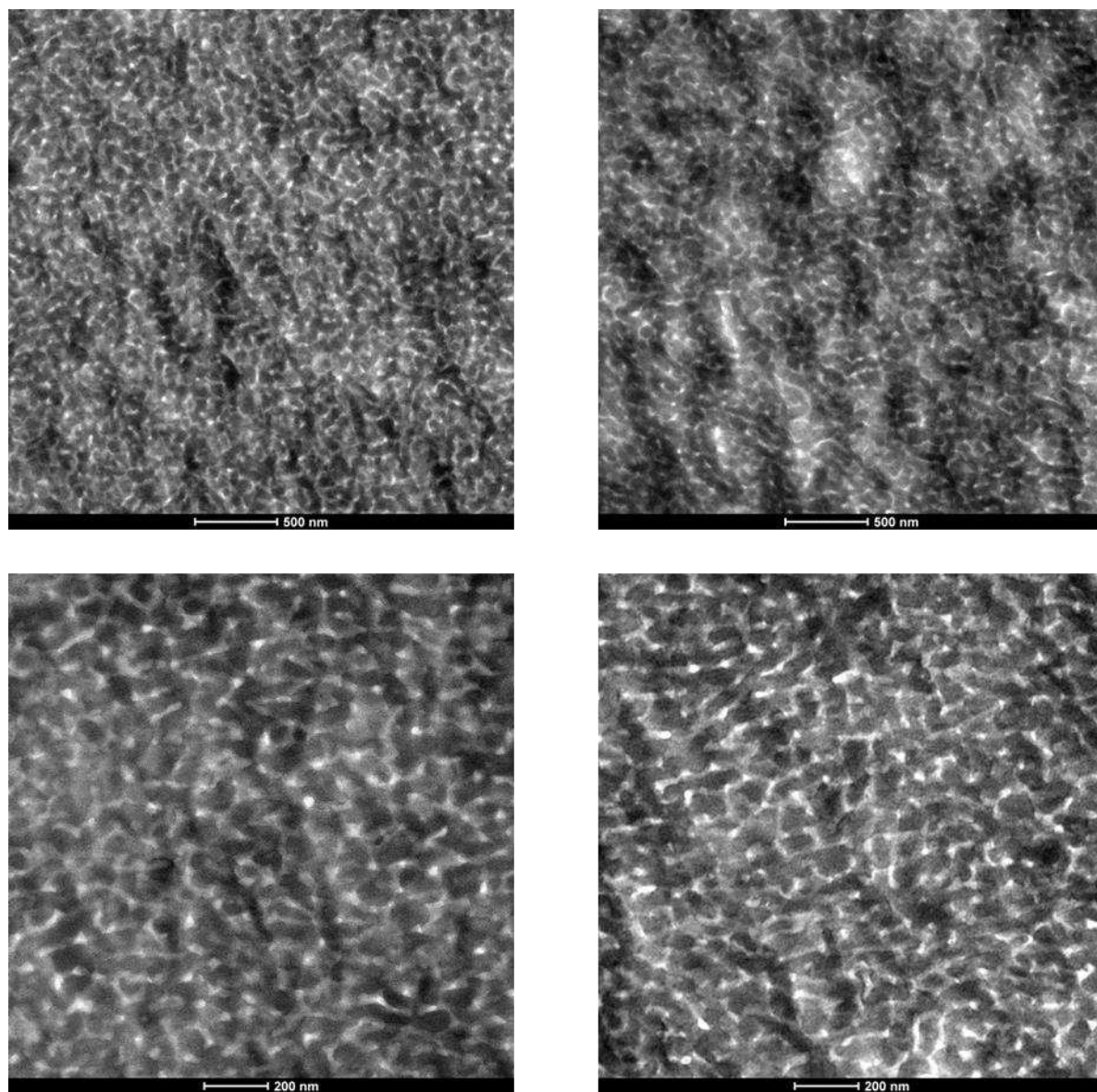
**Figure C50.** Supplemental TEM images for annealed, ultramicrotome-sectioned thin films of linear PAI<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT.



**Figure C51.** Supplemental TEM images for annealed, ultramicrotome-sectioned thin films of cyclic PAIA<sub>500</sub>-*b*-PMMA<sub>500</sub>-*g*-1ODT.



**Figure C52.** Supplemental TEM images for annealed, ultramicrotome-sectioned thin films of linear PAIA<sub>250</sub>-*b*-PMMA<sub>275</sub>-*b*-PAIA<sub>250</sub>-*b*-PMMA<sub>225</sub>-*g*-1ODT.



**Figure C53.** Supplemental TEM images for annealed, ultramicrotome-sectioned thin films of cyclic PA1A<sub>250</sub>-*b*-PMMA<sub>255</sub>-*b*-PA1A<sub>250</sub>-*b*-PMMA<sub>245</sub>-*g*-1ODT.

## Supplemental Tables.

**Table C1.** DTMA temperature-ramp frequency sweep data for selected polymer specimens (-50°C to 200 °C, 5 °C/min, 0.3 %, 1 Hz).

| Polymer                | $E'_{\max}$ (MPa) | $E''_{\max}$ (MPa) | Tan $\delta s_{\max}$ ( $E'/E'$ ) |       |
|------------------------|-------------------|--------------------|-----------------------------------|-------|
| Cyclic AB Diblock      | 2985              | 365.6              | -23.6                             | 126.4 |
| Cyclic ABAB Tetrablock | 2153              | 220.7              | -10.3                             | 137.0 |
| Linear AB Diblock      | 2444              | 306.9              | -18.8                             | 141.7 |
| Linear ABAB Tetrablock | 1939              | 222.4              | -18.5                             | 139.9 |

**Table C2.** Rheometric flow analysis table for selected polymer specimens (175 °C,  $10^{-3}$  to  $1\text{ s}^{-1}$ , 10 rad/s).

| Polymer                | Zero Shear Viscosity (Pa·s) | Shear Thinning Slope |
|------------------------|-----------------------------|----------------------|
| Cyclic AB Diblock      | 232255                      | -1.076x              |
| Cyclic ABAB Tetrablock | 572070                      | -0.8195x             |
| Linear AB Diblock      | 479591                      | -1.076x              |
| Linear ABAB Tetrablock | 748978                      | -0.795x              |

**Table C3.** Tensile (stress/strain) testing averaged data for selected polymer specimens (RT, 5 mm/min).

| Polymer                | Stress (MPa)  | Strain (%)    | Modulus (MPa) |
|------------------------|---------------|---------------|---------------|
| Cyclic AB Diblock      | $6.5 \pm 0.5$ | $6.5 \pm 1.4$ | $235 \pm 14$  |
| Cyclic ABAB Tetrablock | $15 \pm 0.1$  | $112 \pm 5.8$ | $436 \pm 14$  |
| Linear AB Diblock      | $7.4 \pm 1.6$ | $3.2 \pm 1.2$ | $382 \pm 38$  |
| Linear ABAB Tetrablock | $16 \pm 0.8$  | $73 \pm 15$   | $564 \pm 9.0$ |

## References

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- <sup>1</sup> A. P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins, S. Ittel. *Organometallics* **7**, 409-416 (1988).

## Appendix D

### Supplementary Information Corresponding to Chapter 5<sup>j</sup>

#### Materials

4-Bromobenzenethiol, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), anhydrous ammonia (lecture bottle, 170 g), and 4-(trifluoroacetyl)benzoic acid were purchased from Sigma-Aldrich. 4-[3-(Trifluoromethyl)-3H-diazirin-3-yl]benzoic acid (TDBA) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purchased from TCI America. All reagents were used as received. Poly(methyl methacrylate) (PMMA, powder,  $M_n = 120 \text{ kg mol}^{-1}$ , 182230), isotactic polypropylene (*it*-PP, 5 mm gran.,  $M_n = 97.0 \text{ kg mol}^{-1}$ , 427861), low-molecular-weight polyethylene (LMWPE, powder,  $M_n = 1.7 \text{ kg mol}^{-1}$ , 42772) and poly-3-hydroxybutyrate (P3HB, powder, natural origin, 363502) were purchased from Sigma-Aldrich. Low-density polyethylene (LDPE, 5 mm gran., MFI = 21, Product Code ET31-GL-000105), high-density polyethylene (HDPE, 2 – 4 mm gran., MFI = 7.6, Product Code ET32-GL-000110), and poly(L-lactic acid) (PLLA, 3 – 5 mm gran., MFI = 8, Product Code ME34-GL-000120), were purchased from Goodfellow. Ultra-high molecular weight polyethylene (UHMWPE, powder, 43951-30) was purchased from Alfa Aesar. All polymers were used as received.

#### Instruments and Characterization

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<sup>j</sup>Taken from: R. W. Clarke, T. Sandmeier, K. A. Franklin, D. Reich, X. Zhang, N. Vengallur, T. K. Patra, R. J. Tannenbaum, S. Adhikari, S. K. Kumar, T. Rovis, E. Y.-X. Chen. Dynamic Crosslinking Compatibilises Immiscible Mixed Plastics. *Nature* (In Peer Review, 2022)

Nuclear magnetic resonance (NMR) data were recorded on a Bruker 400 MHz or 500 MHz spectrometer at 298 K. Chemical shifts ( $\delta$ ) are reported in ppm with the solvent resonance employed as the internal standard (chloroform at 7.26 ppm for  $^1\text{H}$ -NMR and 77.16 ppm for  $^{13}\text{C}$ -NMR spectroscopy; acetone- $\text{d}_6$  at 2.05 ppm for  $^1\text{H}$ -NMR and 29.8 for  $^{13}\text{C}$ -NMR spectroscopy). Signals are reported as integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad signal), coupling constant(s) in Hz, assignment. For diastereomeric mixtures only signals belonging to the major diastereomer are reported, unless stated otherwise.

High resolution mass spectrometric (HRMS) analyses were performed at the Mass Spectrometry Core Facility at Columbia University. Measurements were conducted on a Waters high-resolution Xevo G2-XS Q-ToF mass spectrometer coupled with an Acquity UPLC H-Class in positive electrospray ionization mode (ESI). Infrared spectra (IR) were measured neat as thin films or solids on a Perkin Elmer Spectrum Two FT-IR spectrometer. Only major peaks are reported as absorption maxima ( $\text{cm}^{-1}$ ).

Super critical fluid chromatography (SFC) was carried out on a Waters low resolution SQD2 quadrupole mass spectrometer equipped with a UPC2 SFC inlet, a photodiode array UV-vis detector, and a dual ESI/APCI probe in positive ionization mode at the Mass Spectrometry Core Facility at the Columbia University chemistry department. Separation was performed on a Waters BEH (1.7  $\mu\text{m}$ , 2.1 x 100 mm) analytical column using  $\text{CO}_2$ /acetonitrile gradient elution. Thermogravimetric Analysis (TGA) was performed on UDCs and dried polymer samples (5 – 10 mg) on a Q50 TGA Analyzer (TA Instruments). Polymer samples were placed in a weight-tared aluminum pan and heated from 25  $^\circ\text{C}$  to 700  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C}/\text{min}$ . UDCs were similarly, individually prepared and heated from 25  $^\circ\text{C}$  to 200  $^\circ\text{C}$ . A constant flow of  $\text{N}_2$  was flushed through



the furnace at 40.00 mL/min, and the mass loss was quantified as a percentage of the initial mass with increased temperature. Thermal stability and weight loss measurements were analyzed on Universal Analysis (TA).

Differential Scanning Calorimetry (DSC) was performed on dried samples (3 – 5 mg) on an Auto Q20 in aluminum pans and hermetic lids against an identical, empty reference pan/lid (TA Instruments). The oven was constantly flushed with 40.00 mL/min of N<sub>2</sub>. UDC sample analysis (0 to 200 °C) was performed on the 1<sup>st</sup> heating scan, where single-event exothermic signals for carbene formation were recorded at a heating rate of 5 °C/min. On the other hand, DSC plots for polymer species show the 2<sup>nd</sup> heating scan and 1<sup>st</sup> cooling scan (-40 or -50 to 200 °C). Initial (1<sup>st</sup>) heating scans were operated at a ramp rate of 10 °C/min, followed by cooling at 10 °C/min and a 2<sup>nd</sup> heating scan at 10 °C/min. Thermal transitions by DSC were characterized by Universal Analysis (TA). Explosivity and shock sensitivity values for UDC**1**, **2**, and **3** were obtained by DSC measurements and Yoshida's correlation calculations, discussed in the supporting figures.

Fourier Transform Infrared Spectroscopy (FTIR) experiments were carried out on a Bruker TENSOR II FT-IR spectrometer fitted with a Platinum ATR between 4000 – 400 cm<sup>-1</sup>. FTIR data was acquired and analyzed through the software OPUS (Bruker).

SAXS/WAXS experiments were performed on dried samples using a lab-scale instrument (SAXSlab, Amherst, MA) with a beam cross section of 200 × 200 μm and wavelength  $\lambda = 0.154$  nm for variable sample-to-detector distances covering a  $q$  range of 0.05-12 nm<sup>-1</sup>. Samples were ~1mm thick and cut down to ~0.25 cm<sup>2</sup> in area. The data were background subtracted and reported as scattered intensity as a function of momentum transfer,  $q$ . 9 spots were rastered across each sample to provide areally averaged data. Temperature control was provided via a Linkam stage (Linkam Scientific, Redhill, UK). Temperature protocol involved taking data at 30 °C for

reference, heating at 10°C/min up to 120 °C, then 130°C and 180 °C prior to cooling back to 30 °C for sample recrystallization. Samples were held at each temperature for 1.5 h with data collected in 5-min exposures to track progression at each temperature. Data presented in Figure 3 represents the final exposure at each temperature.

Film processing (melt compression molding) was performed for all polymers using a Carver Auto Series Plus Laboratory Press (Carver, Model 3889.1PL1000, Max Force 15 ton) with programmable electrically heated platen (EHP) temperature, and air-/water-controlled cooling. Polymer samples prepared for film processing (3-5 g) were sandwiched between thin, non-stick Teflon sheets in a stainless-steel mold with inset dimensions 30 × 73.5 × 0.87 mm fabricated in-house and compressed between two 6" × 6" EHPs at a set pressure of 7000 psi for 30 – 60 min. LMWPE and LDPE samples were heated to 110 °C. HDPE, UHMWPE, and PMMA samples were heated to 150 °C. Blends containing PLLA or P3HB were heated at 175 °C. All samples were cooled in ~10 minutes by air- and water-circulation attachments while under the 7 kpsi of compression.

Melt extrusion processing and reactive blending of LDPE-PLLA were conducted using a Thermo Fisher Scientific HAAKE™ Minilab 3 Micro-Compounder (Twin Screw Extruder) in the manual mode. The compounder was operated at 180 °C with inert gas (Ar) flowing through the chamber. The screws were set to 50 rpm with care that the torque was not above 5 Nm. The material was then added through a hopper and pushed down to the barrel. The compounder was set to flush mode, and material was directly extruded through the standard flat filament die over 10-15 minutes. Extruded material was then compression molded for mechanical testing or directly taken for imaging.

Tensile stress/strain tests were performed on ASTM D-638 Standard Type-V tensile bar ("dog-bones";  $w = 3.18$  mm;  $t = 0.5 - 1.0$  mm) specimens on an Instron 5966 (TA Instruments) universal testing system equipped with a 10 kN load cell and operated at room temperature. Selected samples were tightly placed between textured grips, with a grip separation of  $\sim 28$  mm, and pulled at a constant strain-rate of 5 mm/min until break. Reported curves and values were averaged from 3-4 individual trials of each sample for reproducibility, and error margins are supplied accordingly. Force/displacement values were recorded and normalized to stress/strain by the Bluehill Universal Software (TA). Young's modulus ( $E$ , MPa), ultimate strength ( $\sigma_B$ , MPa), yield strength (MPa), and elongation at break ( $\epsilon_B$ , %) are obtained from the software analysis. Toughness values ( $U_T$ ; MJ m<sup>-3</sup>) were obtained by manual calculation (integration) of the area under the stress/strain curve.

Dynamic mechanical analysis (DMA) was performed on a Q800 DMA Analyzer (TA Instruments). Samples for DMA were prepared under similar conditions ( $w = 5.40$  mm,  $t = 0.5 - 1.0$  mm) with length measured within the grips by the Q-series measurement software (TA) before each trial. Grips were judiciously tightened between 3 – 7 lbs-in accordance with the sample's modulus. Temperatures below ambient were probed by a liquid-nitrogen GCA tank attachment (TA).

Bulk flow experiments by oscillatory shear rheology were performed on a Discovery Series Hybrid 2 (DHR-2) Rheometer (TA Instruments) between 130 – 160 °C in step-transient creep-recovery testing mode. Circular discs (25 mm) of polymer films were loaded between two 25 mm steel parallel-plate EHP geometries under N<sub>2</sub> (30 psi) gas flow and allowed to soak at specified temperatures for a minimum of 5 min. Rheometer control and data analysis were performed with

the TA Instruments TRIOS Software. Further details can be found in the rheology supplementary figures section.

Scanning electron microscopy (SEM) was employed for surface analysis and imaging of UDC-treated and non-treated polymer blends and carried out on a JEOL JSM-6500F scanning electron microscope at an electron voltage of 3 kV, as described in image captioning. Electron current was set to 7, and the working distance was set to 10 mm. Samples were coated with a thin layer (10 nm, 33 seconds) of gold using a plasma sputter-coater under argon (Desk II). Coated films were inserted into the microscope on an aluminum mount, secured with double-sided carbon tape and copper tape. Image processing was conducted using the publicly available tool ImageJ2 (NIH).

## Synthesis and spectra

Detailed procedures and spectra for the synthesis of the UDCs as well as the USC and MDC controls are provided in the respective section of the Supplementary Information.

## MD modeling

Polymer chains are modeled as the standard bead-spring chains where each bead is of mass  $m$  and diameter  $\sigma$ , and the intramolecular bond potential is given by the finitely extensible nonlinear elastic potential.

$$U = -\frac{k}{2} R_{max}^2 \log \left[ 1 - \left( \frac{R}{R_{max}} \right)^2 \right]$$

where  $k$  is the spring constant and  $R_{max}$  sets the upper bound for the bond length<sup>54</sup>. In addition to the bond potential, each bead interacts with every other bead through the Lennard-Jones (LJ) potential with well depth  $\epsilon$  and length scale parameter  $\sigma$ . Following the standard Kremer–Grest

parametrization, we set  $k = \frac{30\epsilon}{\sigma^2}$  and  $R_{max} = 1.5 \sigma$  for the bond potential and the cutoff distance for the LJ potential is set at  $2.5 \sigma$ . The intrinsic Molecular Dynamics unit of time is  $\tau = \sigma \sqrt{\frac{m}{\epsilon}}$ . This coarse-grained model has been used successfully for over three decades to describe various aspects of the dynamics and thermodynamics of polymeric systems<sup>304-307</sup>. The degree of chemical mismatch between the two polymers can be varied by changing the parameter of the three possible LJ interactions (AA, BB, and AB) between the two types of monomers. We set  $\epsilon_{AA} = \epsilon_{BB} = 1$  and  $\epsilon_{AB} = 0.95$  so that it results in immiscible melts for both the chain lengths we consider,  $N = 20$  and  $N = 100$ . Assuming a coordination number of 6 yields  $\chi \approx 0.3$  (Flory Huggins chemical mismatch parameter), which is well above the critical value for phase separation  $\chi_c = 0.1$  for  $N = 20$  and  $\chi_c = 0.02$  for  $N = 100$ . The equations of motion are integrated in the isothermal-isobaric (NPT) ensemble at  $T^* = \frac{k_B T}{\epsilon} = 1$  and  $P^* = \frac{P \sigma^3}{\epsilon} = 0$  using the molecular dynamics simulation package LAMMPS<sup>58</sup>. Simulations are carried out in a box with periodic boundary conditions in all three orthogonal directions. The temperature and pressure are maintained by a Nose-Hoover thermostat and barostat, respectively. We set the simulation timestep at  $0.005 \tau$ .

Creation and breaking of crosslinks are achieved by using LAMMPS' 'fix react' package. Inter- and intrachain crosslinks between monomers are allowed to be formed with a predefined probability,  $p_f$ , when two atoms are located closer than a threshold distance from each other ( $r_{threshold} = 1.3 \sigma$ ). Also, an existing crosslink can break at any time step with a predefined probability  $p_b$ . The probability that a bond breaks after  $n$  simulation time steps is  $P_n = (1 - p_b)^{n-1} p_b$ . If the simulation timestep is  $\delta t$ , then the average bond lifetime,  $\tau_X$ , is  $\tau_X = \delta t \frac{\sum_{n=1}^{\infty} n P_n}{\sum_{n=1}^{\infty} P_n} = \frac{\delta t}{p_b}$ . Since we allow bond creation and breaking only  $N_{every}$  time steps, replacing

$\delta t$  by  $N_{every}\delta t$ , we get  $\tau_X = \frac{N_{every} \delta t}{p_b}$ . So, the average lifetime of the crosslinks can be varied by varying  $p_b$  or  $N_{every}$ . For the results in Fig. 4 of the main text we take  $N_{every}=10$ ,  $p_f=0.5$  and  $p_b=0.5$  unless stated otherwise. The evolution of crosslink fraction with time is shown in Extended Data Fig. 12.

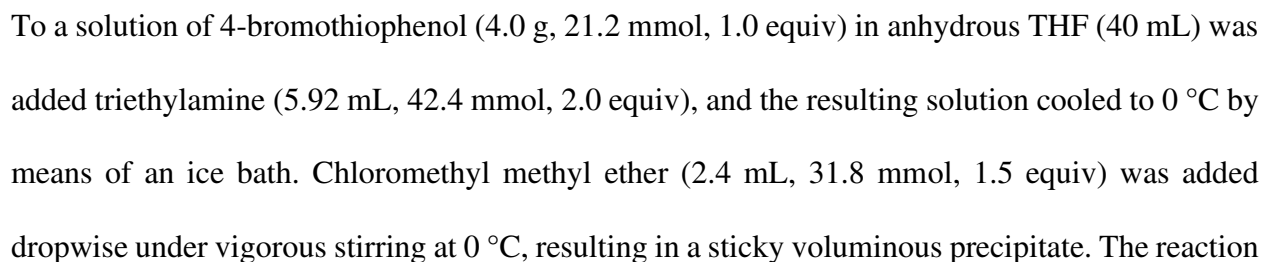
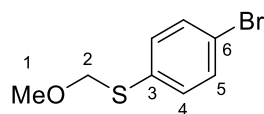
The stability of the interface with only AB static crosslinks and all three types of dynamic crosslinks was investigated. The interface width,  $w$ , is characterized by the full width at half maxima of  $\rho_A(z) \times \rho_B(z)$  versus  $z$  curve, where  $\rho_A$  and  $\rho_B$  denote monomer number densities of A and B polymers, respectively, and  $z$  is the distance across the simulation box normal to the interface of the two polymer melts. In the case of static AB crosslinks, Extended Data Fig. 13a, as the chains lying near the interface start to form crosslinks and mix with each other, the interface broadens for some time, then it becomes stable indicating no further progress in mixing. The completely overlapping radial distribution functions from two different simulation times in Extended Data Fig. 13b also demonstrate no further mixing. Similarly, Extended Data Fig. 14a,b illustrate the evolution of  $w$  when all AB, AA, and BB crosslinks are equally probable. As there are not enough AB crosslinks for mixing, the interface width,  $w$ , remains stable in both cases shown.

In a binary melt with chain length  $N = 100$ , mixing occurs when only AB crosslinks are allowed as shown in Fig. 4h in the main text. Extended Data Fig. 15a shows no mixing when all three dynamic bonds are allowed, the same observation as in the case of  $N = 20$  in the main text. The radial distribution functions in Extended Data Fig. 15b quantify the miscibility of the systems with only AB dynamic crosslinks, all three types of dynamic crosslinks, and no crosslinks. A detailed exploration of the miscibility behavior of a binary melt in the parameter space of  $(\epsilon_{AB}, \tau_X)$  is currently undergoing.

## Supplementary Synthetic Methods

All reactions were performed in flame-dried glassware under an atmosphere of N<sub>2</sub>, unless stated otherwise. Reactions were stirred magnetically and monitored by analytical thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F<sub>254</sub> TLC glass plates and visualized with 254 nm light and aqueous potassium permanganate followed by heating. Crude products were absorbed into silica and purified by flash column chromatography on SiliaFlash, SiliCycle Silica Gel P60, 230-400 mesh, 40-63 μm particle size and analytical grade hexane, ethyl acetate, dichloromethane, and methanol as eluents at 0.3-0.5 bar overpressure. Preparative thin-layer chromatography (PTLC) was carried out on SiliCycle 1000 μm 20x20 cm TLC plates and visualized with a low intensity 365 nm UV-lamp. Concentration under reduced pressure (*in vacuo*) was performed by rotary evaporation at 40 °C at the appropriate pressure unless otherwise noted. The yields given refer to the purified products, unless otherwise stated. For larger scale synthesis, 4-[3-(trifluoromethyl)-3H-diazirin-3-yl]benzoic acid (TDBA) was prepared following a known literature procedure.<sup>1</sup>

### Synthesis of (4-bromophenyl)(methoxymethyl)sulfane<sup>2</sup>:





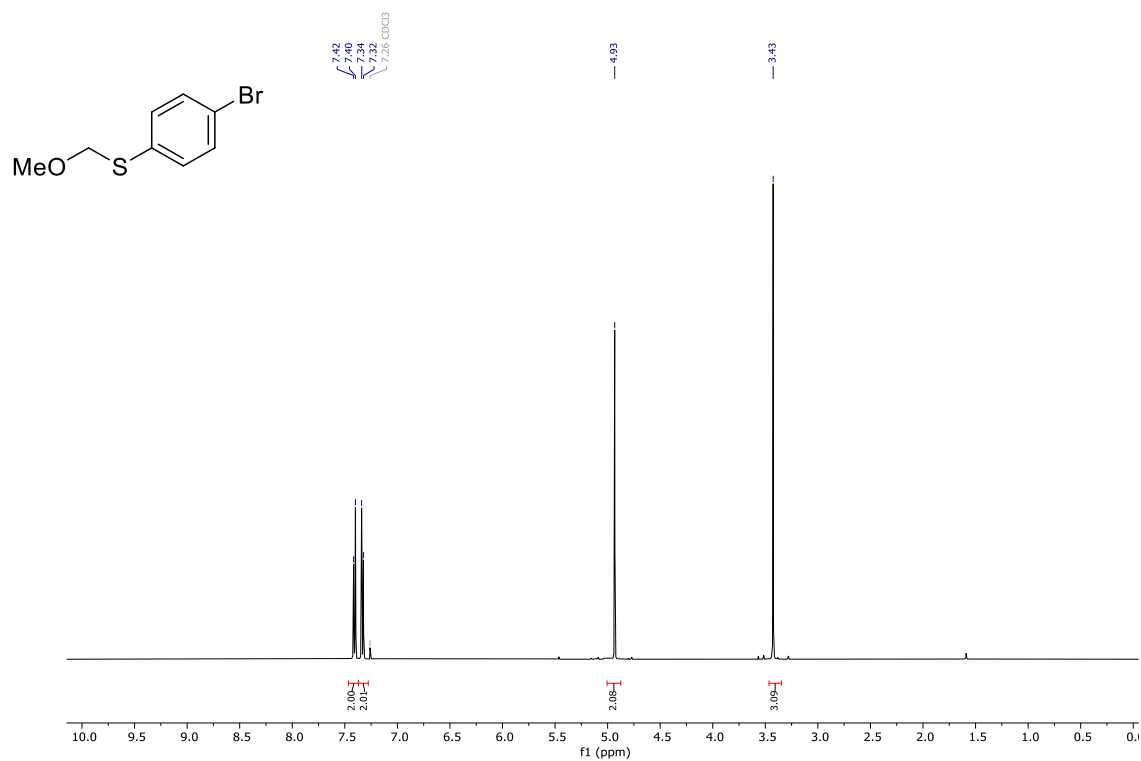
mixture was stirred for 2 h at 0 °C, after which the mixture was diluted with water and the aqueous phase extracted with ethyl acetate (3x). The combined organic phases were dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. The resulting crude mixture was purified by silica flash column chromatography (eluent: 2% ethyl acetate in hexanes), yielding the title product (4.79 g, 20.5 mmol, 97%) as colorless oil. R<sub>f</sub> (20% ethyl acetate in hexanes): 0.58, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.41 (2 H, d, *J* = 8.6 Hz, H<sub>4</sub>), 7.33 (2 H, d, *J* = 8.6 Hz, H<sub>5</sub>), 4.93 (2 H, s, H<sub>2</sub>), 3.43 (3 H, s, H<sub>1</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 135.3 (C<sub>3</sub>), 132.1 (2 C, C<sub>4</sub>), 131.8 (2 C, C<sub>5</sub>), 120.9 (C<sub>6</sub>), 77.8 (C<sub>2</sub>), 56.2 (C<sub>1</sub>); *m/z* HRMS ASAP+ found [M{<sup>79</sup>Br}+H]<sup>+</sup> 231.9548, found [M{<sup>81</sup>Br}+H]<sup>+</sup> 233.9525, C<sub>8</sub>H<sub>10</sub><sup>79</sup>BrOS<sup>+</sup> requires 231.9557, C<sub>8</sub>H<sub>10</sub><sup>81</sup>BrOS<sup>+</sup> requires 233.9537.

**Improved synthesis of (4-bromophenyl)(methoxymethyl)sulfane:**

A solution of 4-bromothiophenol (0.527 g, 2.65 mmol, 1.0 equiv.) and triethylamine (0.74 mL, 5.3 mmol, 2.0 equiv.) in THF (5.0 mL) was cooled to 0 °C. Chloromethyl methyl ether (2.92 mmol, 1.1 equiv.) in THF (1.0 mL) was added resulting in the formation of a white precipitate. The suspension was stirred at 0 °C for 2 h. Additional THF (5.0 mL) was added to dilute the viscous mixture and the reaction was stirred at room temperature for 2 h. The reaction was diluted with water and extracted with EtOAc (3 times). The organic phases were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude mixture was analyzed by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The yield of (4-bromophenyl)(methoxymethyl) sulfane was determined to be 94% (2.49 mmol).

*Note: Technical-grade chloromethyl methyl ether was used for this experiment. The purity of the reagent was determined by <sup>1</sup>H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard prior to use.*

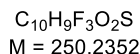
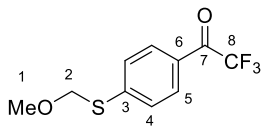
$^1\text{H}$  NMR of (4-bromophenyl)(methoxymethyl)sulfane (500 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of (4-bromophenyl)(methoxymethyl)sulfane (126 MHz,  $\text{CDCl}_3$ , 300 K)

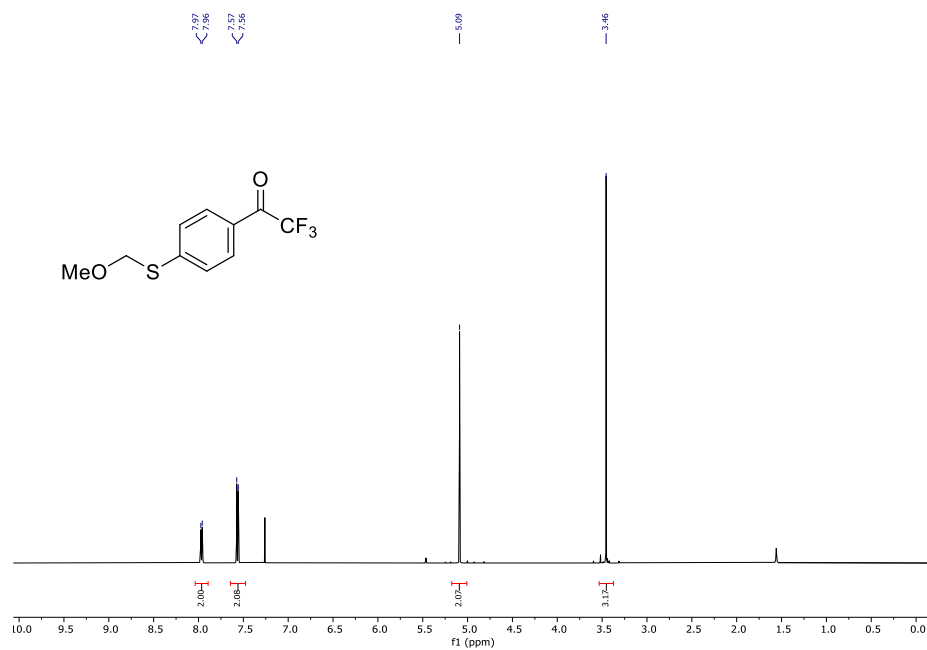


### Synthesis of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one:

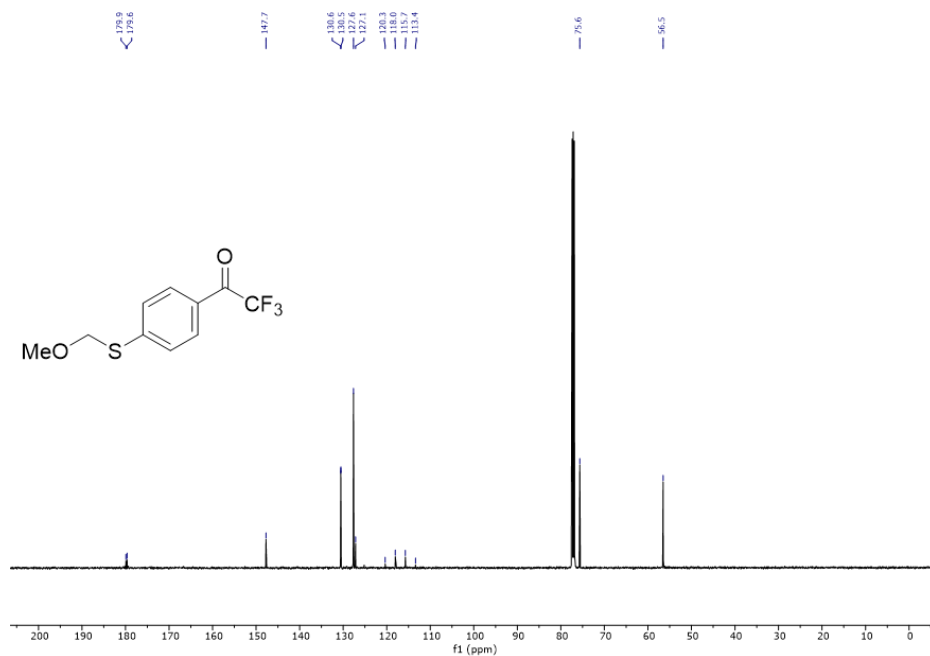


A solution of (4-bromophenyl)(methoxymethyl)sulfane (4.79 g, 20.5 mmol, 1.0 equiv) in anhydrous THF (100 mL) was cooled to  $-78\text{ }^{\circ}\text{C}$ . A solution of *n*-BuLi (2.5 M in hexanes, 9.48 mL, 24.6 mmol, 1.2 equiv) was added dropwise with stirring and the resulting solution was stirred for 1 h at  $-78\text{ }^{\circ}\text{C}$ . Ethyl trifluoroacetate (2.93 mL, 24.6 mmol, 1.2 equiv) was then added dropwise at  $-78\text{ }^{\circ}\text{C}$ . After complete addition, the cooling was removed, and the reaction mixture stirred for 14 h at room temperature. The mixture was quenched by addition of saturated ammonium chloride solution and the resulting biphasic mixture was extracted with ethyl acetate (3x). The combined organic phases were dried ( $\text{MgSO}_4$ ), filtered and concentrated in vacuo. The resulting crude oil was purified by silica flash column chromatography (eluent: 3% ethyl acetate in hexanes), yielding the title product (3.40 g, 13.6 mmol, 66%) as a colorless oil.  $R_f$  (15% ethyl acetate in hexanes): 0.46 (diffuse);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.96 (2 H, d,  $J = 8.8$  Hz,  $\text{H}_4$ ), 7.56 (2 H, d,  $J = 8.8$  Hz,  $\text{H}_5$ ), 5.09 (2 H, s,  $\text{H}_2$ ), 3.46 (3 H, s,  $\text{H}_1$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 179.8 (q,  $^2J = 34.8$  Hz,  $\text{C}_7$ ), 147.7 ( $\text{C}_3$ ), 130.5 (2 C,  $\text{C}_4$ ), 127.6 (2 C,  $\text{C}_5$ ), 127.2 ( $\text{C}_6$ ), 116.9 (q,  $^1J = 291.3$  Hz,  $\text{C}_8$ ), 76.7 ( $\text{C}_2$ ), 56.5 ( $\text{C}_1$ );  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-70.4$ ;  $m/z$  HRMS ASAP+ found  $[\text{M}+\text{H}]^+$  251.0359,  $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2\text{S}^+$  requires 251.0354.

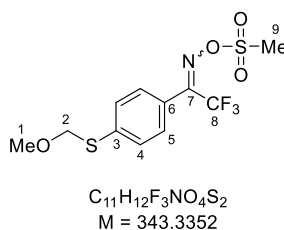
$^1\text{H}$  NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (500 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (126 MHz,  $\text{CDCl}_3$ , 300 K)



**Synthesis of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime:**



*Step 1: Oxime formation*

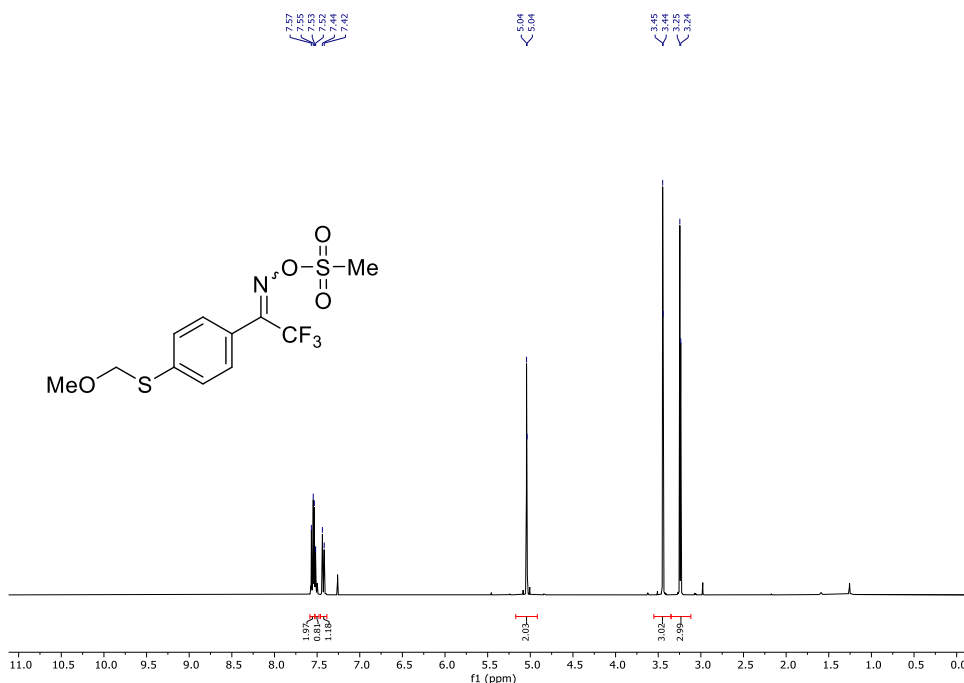
2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (3.40 g, 13.6 mmol, 1.0 equiv), hydroxylamine hydrochloride (4.25 g, 61.2 mmol, 4.5 equiv) and sodium hydroxide (2.44 g, 61.2 mmol, 4.5 equiv) were dissolved in anhydrous ethanol (50 mL). The vessel was sealed under nitrogen and the mixture stirred vigorously at 80 °C for 18 h. The suspension was allowed to cool to room temperature and subsequently diluted with ethyl acetate, washed with dilute aqueous hydrochloric acid (0.1 M, 3x) and brine. The organic phase was then dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The crude oxime was obtained as a clear oil and used directly in the next step.

*Step 2: Mesylation*

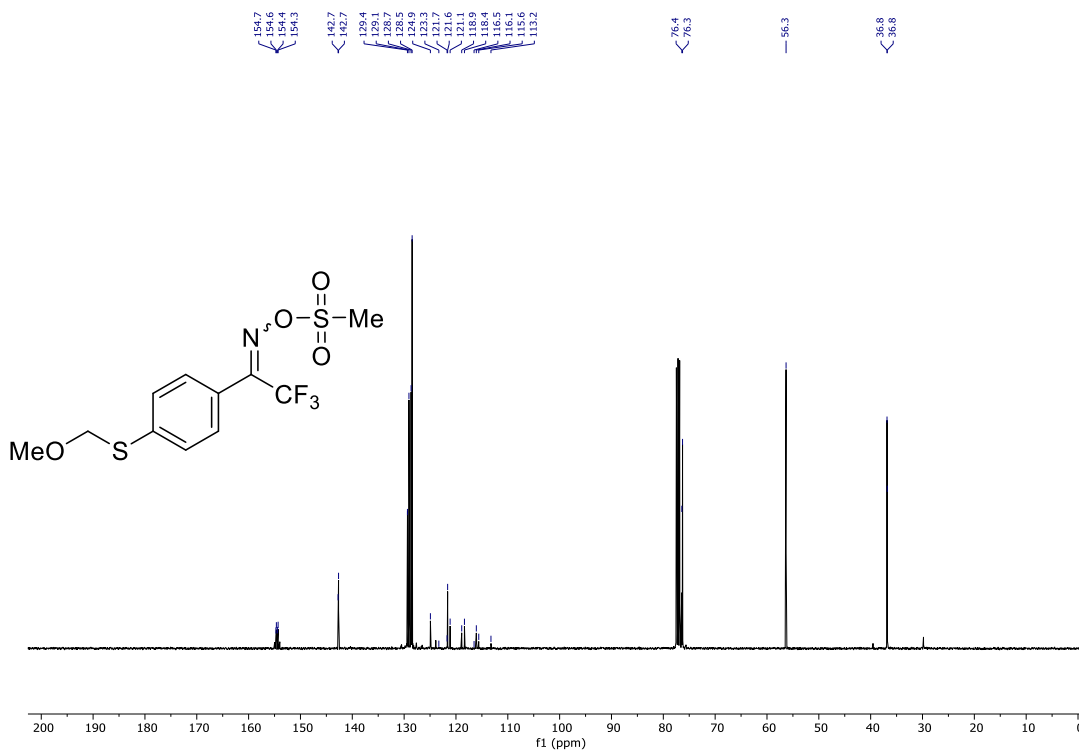
The crude oxime obtained from step 1 was dissolved in anhydrous dichloromethane (40 mL) and the resulting solution cooled to 0 °C by means of an ice-bath. Triethylamine (3.03 mL, 21.8 mmol, 1.6 equiv) was added dropwise to the stirred solution at 0 °C, followed by dropwise addition of methanesulfonyl chloride (1.05 mL, 13.6 mmol, 1.0 equiv). The cooling was then removed, and the reaction mixture stirred at room temperature for 14 hours. Equal parts of water and saturated aqueous ammonium chloride solution were then added, and the resulting biphasic mixture extracted with diethyl ether (3x). The combined organic phases were dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The residue was purified by silica flash column chromatography (eluent:

100% dichloromethane), yielding the title product (3.97 g, 11.6 mmol, 85%, d.r. = 1.5 : 1) as a pale yellow oil that solidifies on standing.  $R_f$  (100% dichloromethane): 0.64;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.58–7.48 (3 H, m,  $\text{H}_{4,5}$ ), 7.45–7.37 (1 H, m,  $\text{H}_{4,5}$ ), 5.044 (2 H, s,  $\text{H}_2$ , *major*) [5.037 (2 H, s,  $\text{H}_2$ , *minor*)], 3.45 (3 H, s,  $\text{H}_1$ , *major*) [3.44 (3 H, s,  $\text{H}_1$ , *minor*)], 3.25 (3 H, s,  $\text{H}_9$ , *major*) [3.24 (3 H, s,  $\text{H}_9$ , *minor*)];  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.5 (q,  $^3J_F = 33.7$  Hz,  $\text{C}_7$ , *major*) [154.6 (q,  $^2J_F = 32.6$  Hz,  $\text{C}_7$ , *minor*)], 142.65 ( $\text{C}_3$ , *major*) [142.74 ( $\text{C}_3$ , *minor*)], 129.1 ( $\text{C}_{4/5}$ , *major*) [129.4 ( $\text{C}_{4/5}$ , *minor*)], 128.4 ( $\text{C}_{4/5}$ , *major*) [128.7 ( $\text{C}_{4/5}$ , *minor*)], 121.6 ( $\text{C}_6$ , *major*) [124.9 (*minor*)], 119.7 (q,  $^1J_F = 278.2$  Hz,  $\text{C}_8$ , *major*), [117.4 (q,  $^1J_F = 283.6$  Hz,  $\text{C}_8$ , *minor*)], 76.3 ( $\text{C}_2$ , *major*) [76.4 ( $\text{C}_2$ , *minor*)], 56.3 ( $\text{C}_1$ ), 36.8 ( $\text{C}_9$ , *major*) [36.9 ( $\text{C}_9$ , *minor*)];  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : –66.21 (*major*) [–61.4 (*minor*)].  $m/z$  HRMS ESI+ found  $[\text{M}+\text{H}]^+$  344.0242,  $\text{C}_{11}\text{H}_{13}\text{F}_3\text{NO}_4\text{S}_2^+$  requires 344.0238.

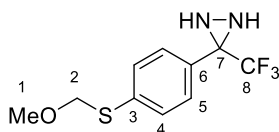
$^1\text{H}$  NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (400 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (101 MHz,  $\text{CDCl}_3$ , 300 K)



### Synthesis of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine:



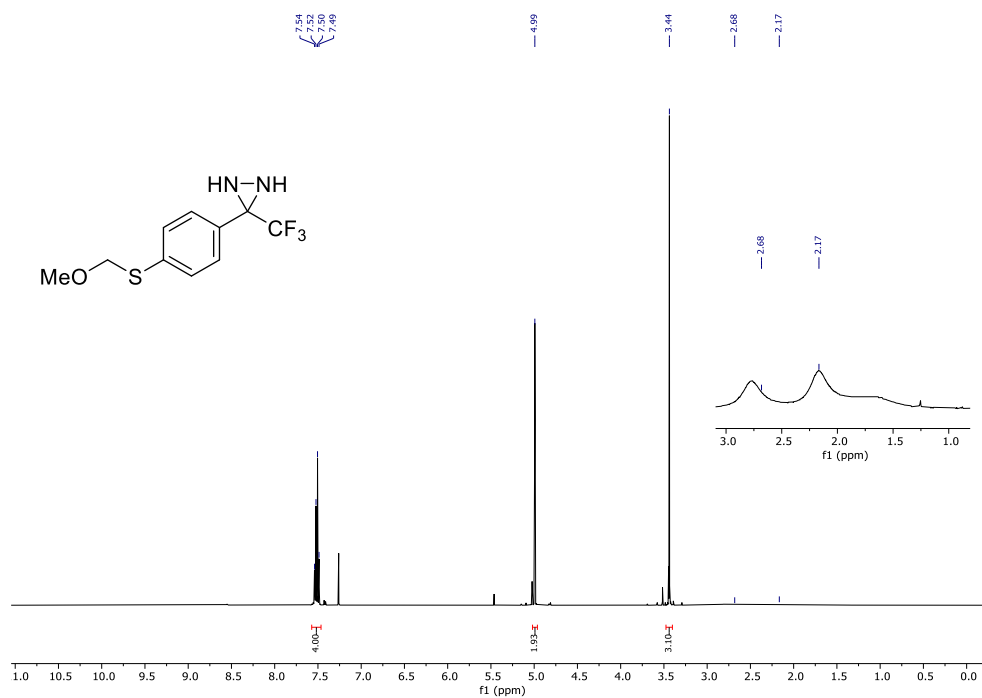
$\text{C}_{10}\text{H}_{11}\text{F}_3\text{N}_2\text{OS}$   
 $M = 264.27$

Anhydrous ammonia was condensed (approx. 15 mL) into a pre-cooled flask at  $-78\text{ }^\circ\text{C}$  using a dry-ice acetone cold finger. To the stirred liquid ammonia, a solution of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (3.79 g, 11.6 mmol, 1.0 equiv) in anhydrous dichloromethane (9 mL) was added dropwise at  $-78\text{ }^\circ\text{C}$ . The solution was

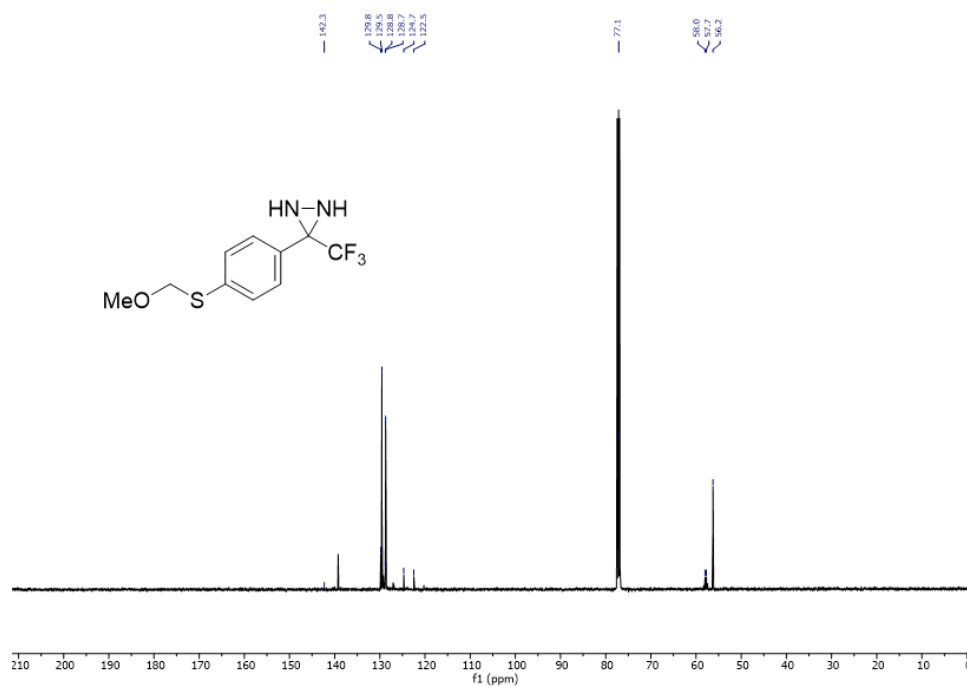
stirred for 1 h at  $-78\text{ }^{\circ}\text{C}$  and then gradually warmed to room temperature over the course of 12 h, while allowing excess ammonia to vent. To the residue, water (40 mL) was added, and the resulting solution was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with brine, then dried ( $\text{MgSO}_4$ ), filtered and concentrated in vacuo. The resulting crude oil was purified by silica flash column chromatography (gradient elution: 25% dichloromethane in hexanes to 100% dichloromethane), yielding the title product (2.29 g, 8.67 mmol, 75%) as a colorless oil.  $R_f$  (100% dichloromethane): 0.29;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.55–7.47 (4 H, m,  $\text{H}_{4,5}$ ), 4.99 (2 H, s,  $\text{H}_2$ ), 3.44 (3 H, s,  $\text{H}_1$ ), 2.68 (1 H, br s, NH), 2.17 (1 H, br s, NH);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.3 ( $\text{C}_3$ ), 129.8 ( $\text{C}_6$ ), 129.5 ( $\text{C}_{4/5}$ ), 128.7 ( $\text{C}_{4/5}$ ), 123.5 (q,  $^1J_{\text{F}} = 278.3\text{ Hz}$ ,  $\text{C}_8$ ), 77.1 ( $\text{C}_2$ ), 57.9 (q,  $^2J_{\text{F}} = 36.3\text{ Hz}$ ,  $\text{C}_7$ ), 56.2 ( $\text{C}_1$ ).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-74.59$ ;  $m/z$  HRMS ESI+ found  $[\text{M}+\text{H}]^+$  265.0635,  $\text{C}_{10}\text{H}_{12}\text{F}_3\text{N}_2\text{OS}^+$  requires 265.0623.



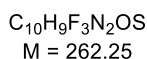
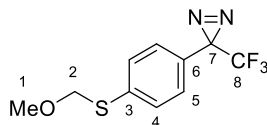
$^1\text{H}$  NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (500 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (126 MHz,  $\text{CDCl}_3$ , 300 K)

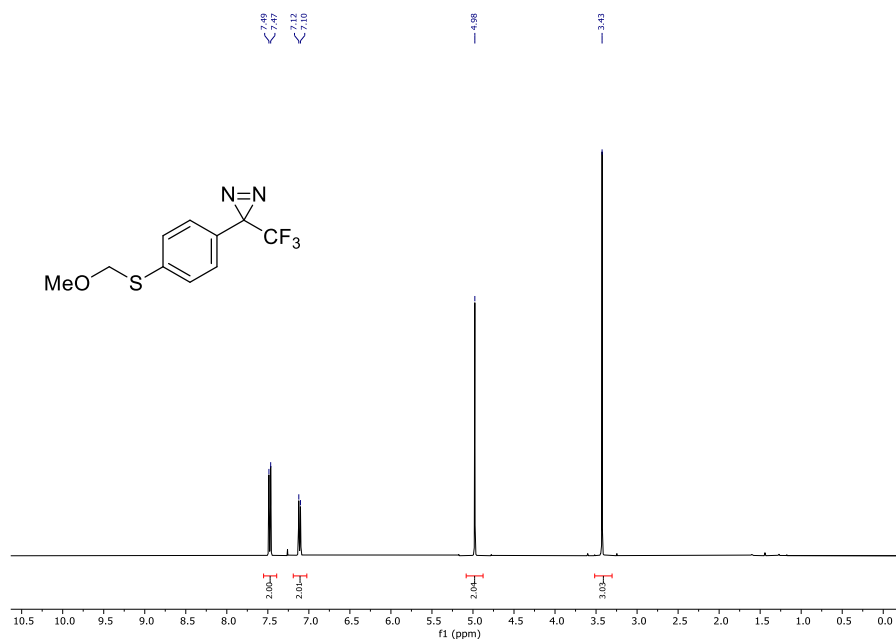


### Synthesis of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine:

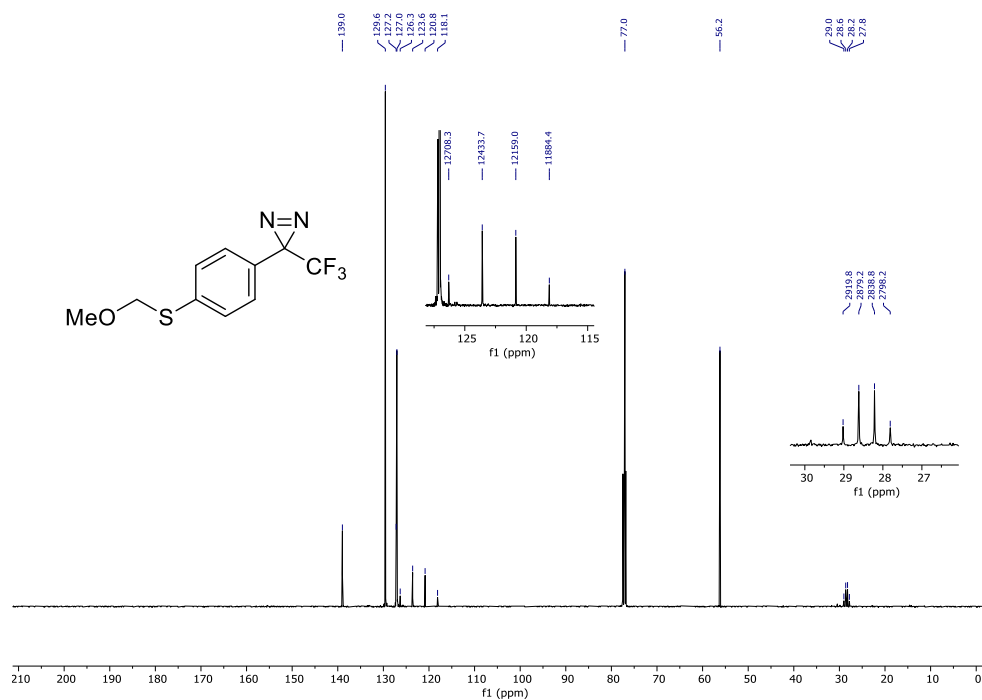


To a solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (2.29 g, 8.67 mmol, 1.0 equiv) in methanol (60 mL) was added triethylamine (3.62 mL, 26.0 mmol, 3.0 equiv) followed by portion-wise addition of iodine (6.60 g, 26.0 mmol, 3.0 equiv) with vigorous stirring at room temperature. The resulting dark solution was stirred for 14 h at room temperature under the exclusion of ambient light (tin foil) and subsequently quenched via addition of 10% aqueous sodium thiosulphate solution (60 mL). The almost colorless biphasic mixture was extracted with diethyl ether (3 x), and the combined organic phases dried ( $\text{MgSO}_4$ ), filtered, and concentrated under reduced pressure. The residue was purified by silica flash column chromatography (elution: 25% dichloromethane in hexanes), yielding the title product (1.92 g, 7.32 mmol, 84%) as a pale yellow oil.  $R_f$  (50% dichloromethane in hexanes): 0.62;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.48 (2 H, d,  $J = 8.7$  Hz,  $\text{H}_{4/5}$ ), 7.11 (2 H, d,  $J = 8.7$  Hz,  $\text{H}_{4/5}$ ), 4.98 (2 H, s,  $\text{H}_2$ ), 3.43 (3 H, s,  $\text{H}_1$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 139.0 ( $\text{C}_3$ ), 129.6 (2 C,  $\text{C}_{4/5}$ ), 127.2 ( $\text{C}_6$ ), 127.0 (2 C,  $\text{C}_{4/5}$ ), 122.2 (q,  $^1J_{\text{F}} = 274.7$  Hz,  $\text{C}_8$ ), 77.0 ( $\text{C}_2$ ), 56.2 ( $\text{C}_1$ ), 28.4 (q,  $^2J_{\text{F}} = 28.4$  Hz,  $\text{C}_7$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -65.40.

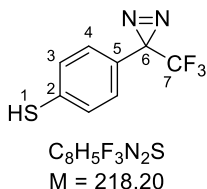
$^1\text{H}$  NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (400 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (400 MHz,  $\text{CDCl}_3$ , 300 K)



### Synthesis of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol<sup>3</sup>:

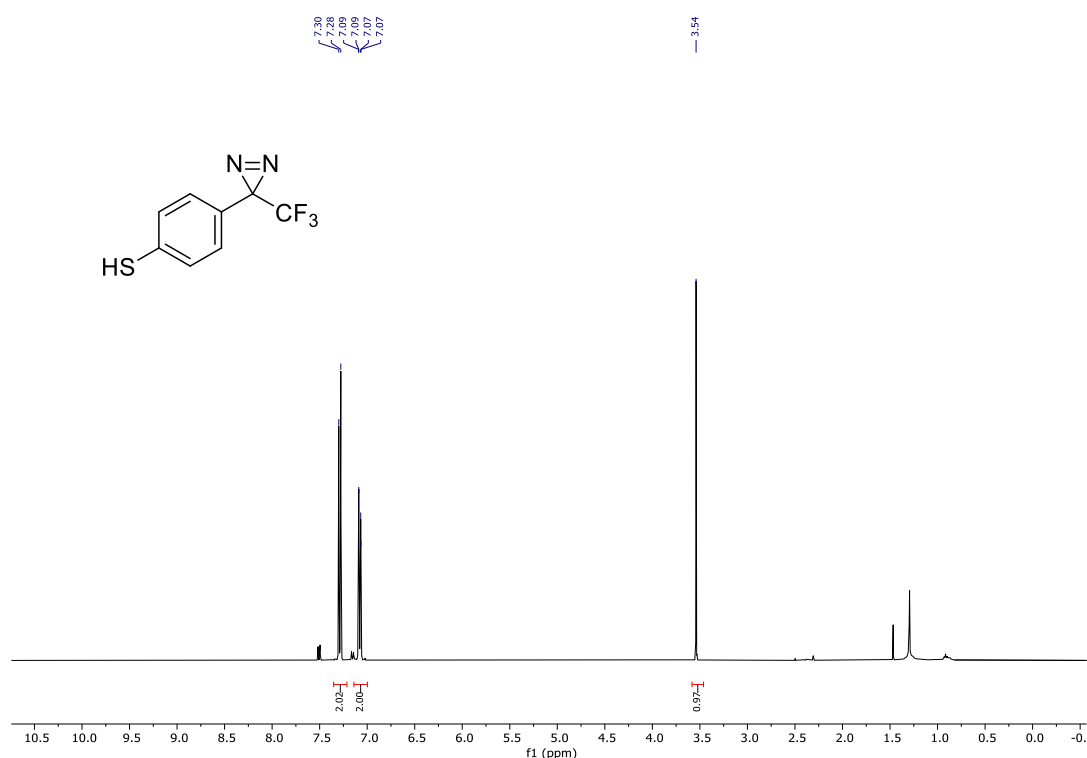


A solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (4.00 g, 15.3 mmol, 1.0 equiv) in anhydrous ethanol (450 mL, degassed by sparging with  $\text{N}_2$  for 20 min) was heated to 55 °C and silver nitrate (3.11 g, 18.3 mmol, 1.2 equiv) was added in one portion with vigorous stirring. The mixture was stirred at 55 °C for 2 h, during which the reaction mixture became considerably more viscous followed by the formation of a voluminous precipitate. At this point silver nitrate (778 mg, 4.58 mmol, 0.25 equiv) was added and stirring was continued at 55 °C for 1 h. All volatiles were removed in vacuo using a rotary evaporator. The reaction flask was evacuated and backfilled with  $\text{N}_2$  three times, and 6 M aqueous hydrochloric acid (380 mL, degassed by sparging with  $\text{N}_2$  for 20 min) was added via cannula. The resulting suspension was stirred for 30 min before dichloromethane (160 mL, degassed by sparging with  $\text{N}_2$  for 20 min) was added via cannula. The mixture was vigorously stirred for 1.0 h at room temperature. The reaction mixture was diluted with dichloromethane, and the organic phase washed with water and brine. The organic phase was dried ( $\text{MgSO}_4$ ), filtered and concentrated in vacuo.

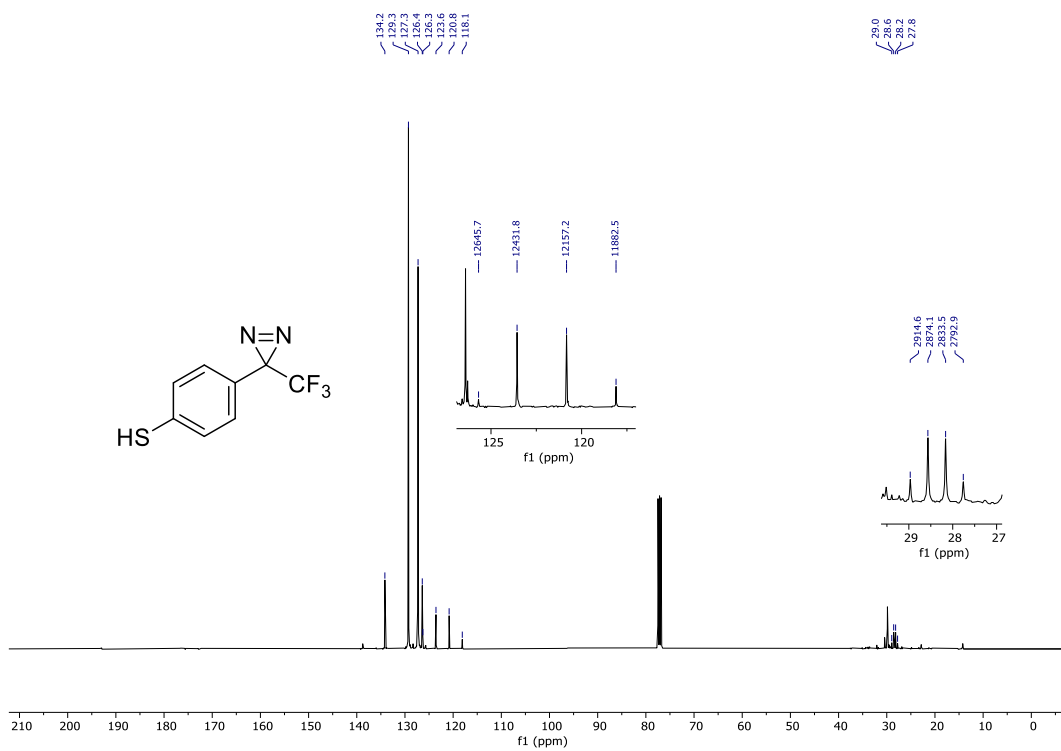
TLC and  $^1\text{H}$ -NMR analysis of crude reaction mixture indicated the presence of disulfide UDC2. Hence, the crude mixture was dissolved in acetonitrile (180 mL) and water (20 mL) was added. To the resulting solution tris(2-carboxyethyl)phosphine (TCEP, 1.09 g, 3.83 mmol, 0.25 equiv) was added in one portion. The mixture was stirred at room temperature for 20 min diluted with water (200 mL) and extracted with diethyl ether (3 x 150 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. Purification by silica flash column

chromatography (elution: 0.2% diethylether in hexanes) yielded the title product (122 mg, 559  $\mu\text{mol}$ , 73%) as a volatile pale yellow oil.  $R_f$  (10 % diethylether in hexanes): 0.28;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.29 (2 H, d,  $J = 8.6$  Hz,  $\text{H}_3$ ), 7.08 (2 H, d,  $J = 8.6$  Hz,  $\text{H}_4$ ), 3.54 (1 H, s,  $\text{H}_1$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 134.2 ( $\text{C}_2$ ), 129.3 (2 C,  $\text{C}_4$ ), 127.3 (2 C,  $\text{C}_3$ ), 126.4 ( $\text{C}_5$ ), 122.2 (q,  $^1J = 274.6$  Hz,  $\text{C}_7$ ), 28.4 (q,  $^2J = 40.5$  Hz,  $\text{C}_6$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-65.4$ .

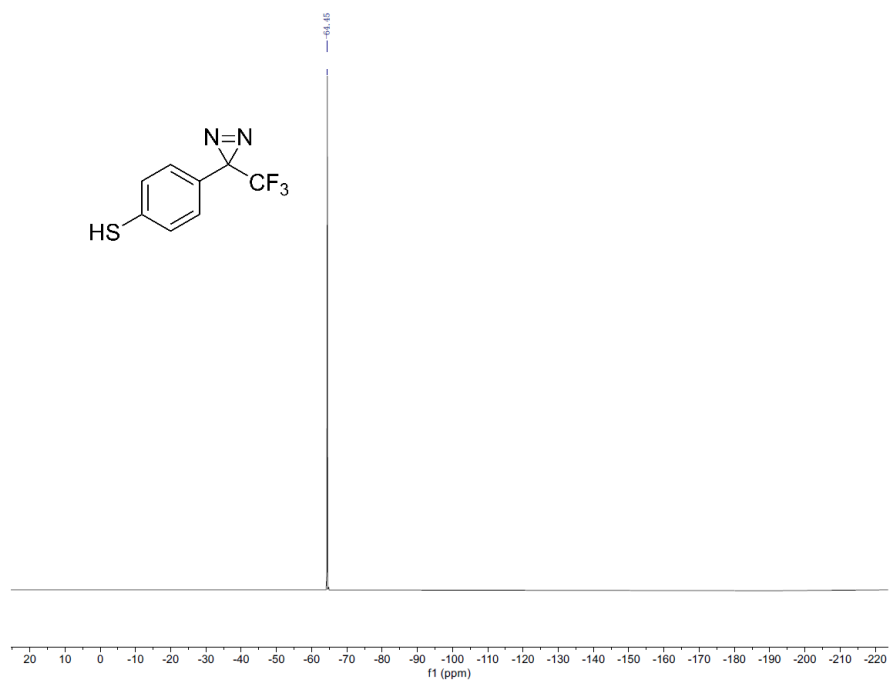
$^1\text{H}$  NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (400 MHz,  $\text{CDCl}_3$ , 300 K)



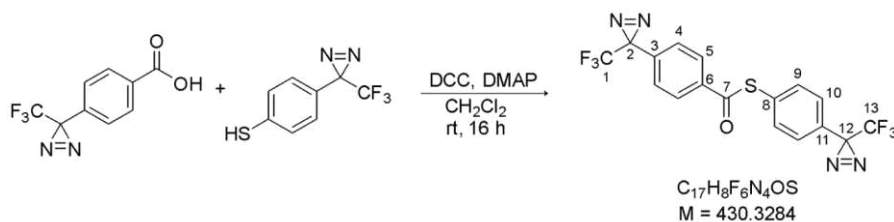
$^{13}\text{C}$  NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (101 MHz,  $\text{CDCl}_3$ , 300 K)



<sup>19</sup>F NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (376 MHz, CDCl<sub>3</sub>, 300 K)

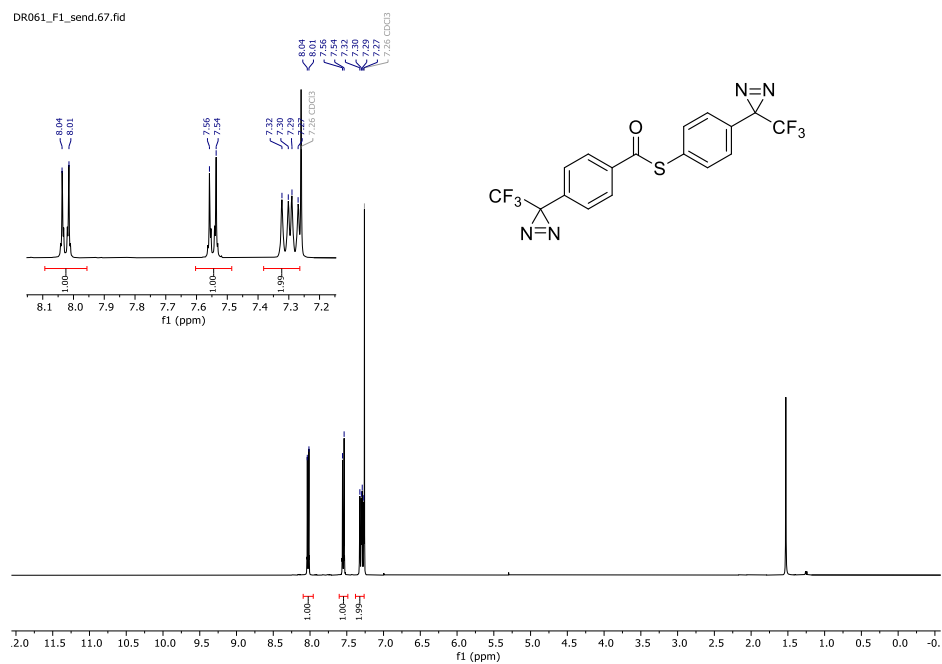


**Synthesis of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzothioate (UDC1):**

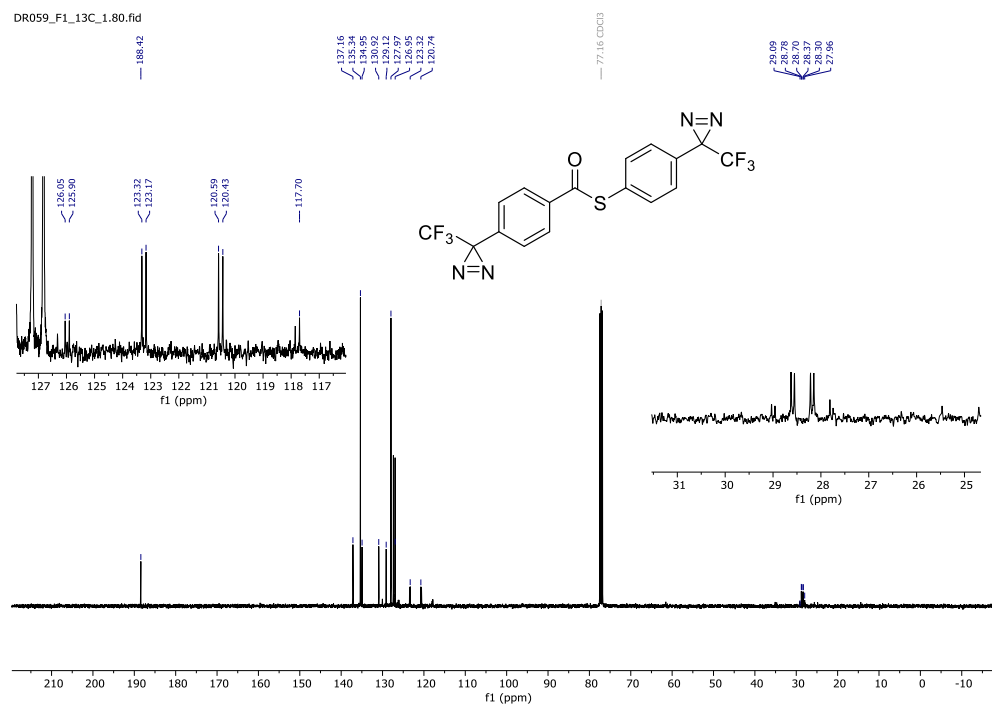


A 50 mL Schlenk flask was charged with 4-(3-trifluoromethyl)-3*H*-diazirin-3-yl)benzoic acid (TDBA) (2.0 g, 8.69 mmol, 1.0 equiv), DCC (2.15 g, 10.4 mmol, 1.2 equiv) and DMAP (425 mg, 3.48 mmol, 0.4 equiv), sealed and backfilled with nitrogen (3 x). A solution of 4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzenethiol (TDBT) (1.90 g, 8.69 mmol, 1.0 equiv) in anhydrous dichloromethane (29 mL) was added via syringe, and the resulting mixture stirred at room temperature for 16 h. The reaction mixture was filtered through celite, the filter cake washed with diethyl ether, and the filtrate concentrated in vacuo. The residue was purified by silica flash column chromatography (gradient elution: hexanes then 8% dichloromethane in hexanes), yielding the title product (3.51 g, 8.16 mmol, 94%) as a colorless waxy solid.  $R_f$  (10 % diethyl ether in hexanes): 0.63;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (2 H, d,  $J = 8.7$  Hz,  $\text{H}_5$ ), 7.55 (2 H, d,  $J = 8.7$  Hz,  $\text{H}_4$ ), 7.31 (2 H, d,  $J = 8.2$  Hz,  $\text{H}_{9/10}$ ), 7.28 (2 H, d,  $J = 8.2$  Hz,  $\text{H}_{9/10}$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 188.4 ( $\text{C}_7$ ), 137.2 ( $\text{C}_6$ ), 135.3 (2 C,  $\text{C}_9$ ), 134.9 ( $\text{C}_3$ ), 130.9 ( $\text{C}_{8/11}$ ), 129.1 ( $\text{C}_{8/11}$ ), 128.0 (2 C,  $\text{C}_5$ ), 127.4 (2 C, q,  $^4J = 1.5$  Hz,  $\text{C}_{10}$ ), 127.0 (2 C, q,  $^4J = 1.8$  Hz,  $\text{C}_4$ ), 122.1 (q,  $^1J = 274.9$  Hz,  $\text{C}_{1/13}$ ), 121.9 (q,  $^1J = 274.9$  Hz,  $\text{C}_{1/13}$ ), 28.6 (q,  $^2J = 40.9$  Hz,  $\text{C}_{2/12}$ ), 28.5 (q,  $^2J = 40.9$  Hz,  $\text{C}_{2/12}$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -64.0, -64.2 IR (film)  $\nu_{\text{max}}$ : 3198, 2927, 1722, 1699, 1253, 1179, 1128, 905.

# <sup>1</sup>H NMR of UDC1 (400 MHz, CDCl<sub>3</sub>, 300 K)

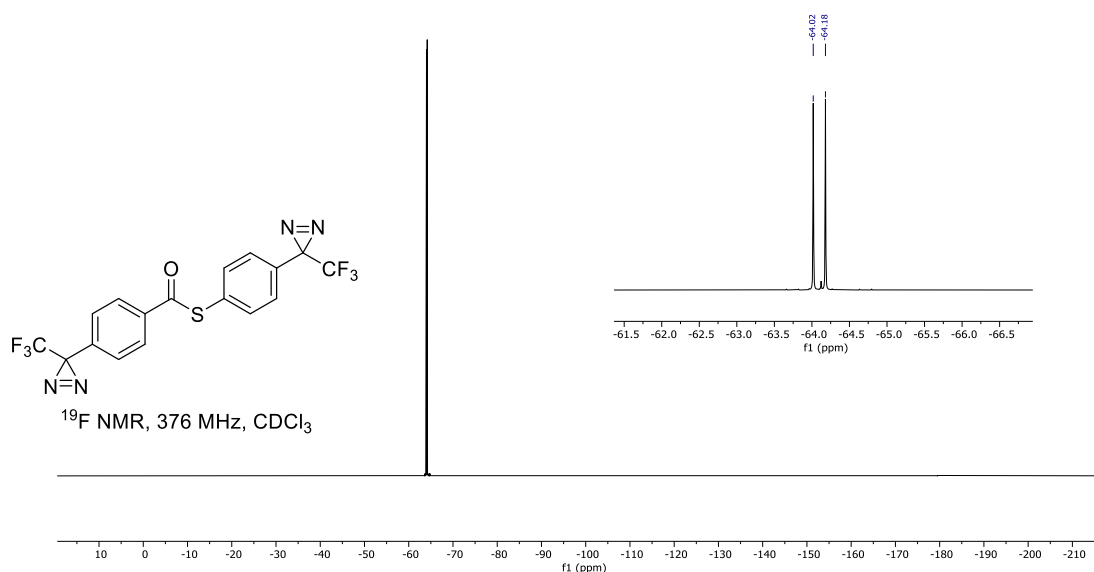


# <sup>13</sup>C NMR of UDC1 (101 MHz, CDCl<sub>3</sub>, 300 K)

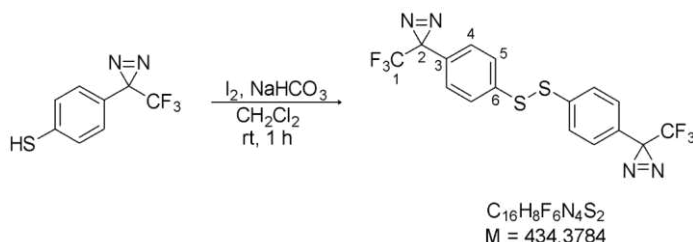




$^{19}\text{F}$  NMR of UDC1 (376 MHz,  $\text{CDCl}_3$ , 300 K)



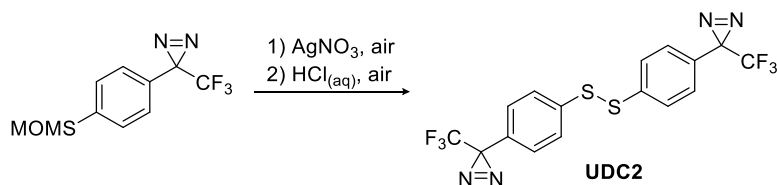
**Synthesis of S-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl) 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethioate (UDC2):**



A 250 mL round-bottom flask was charged with 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (1.00 g, 4.58 mmol, 1.0 equiv) and anhydrous dichloromethane (57 mL).  $\text{NaHCO}_3$  (481 mg, 5.73 mmol, 1.25 equiv) was added in one portion and the resulting suspension was stirred at room temperature for 15 min. Iodine (1.74 g, 6.87 mmol, 1.5 equiv) was added portion was and the resulting dark purple mixture was stirred for 40 min. Half-saturated aqueous sodium thiosulfate

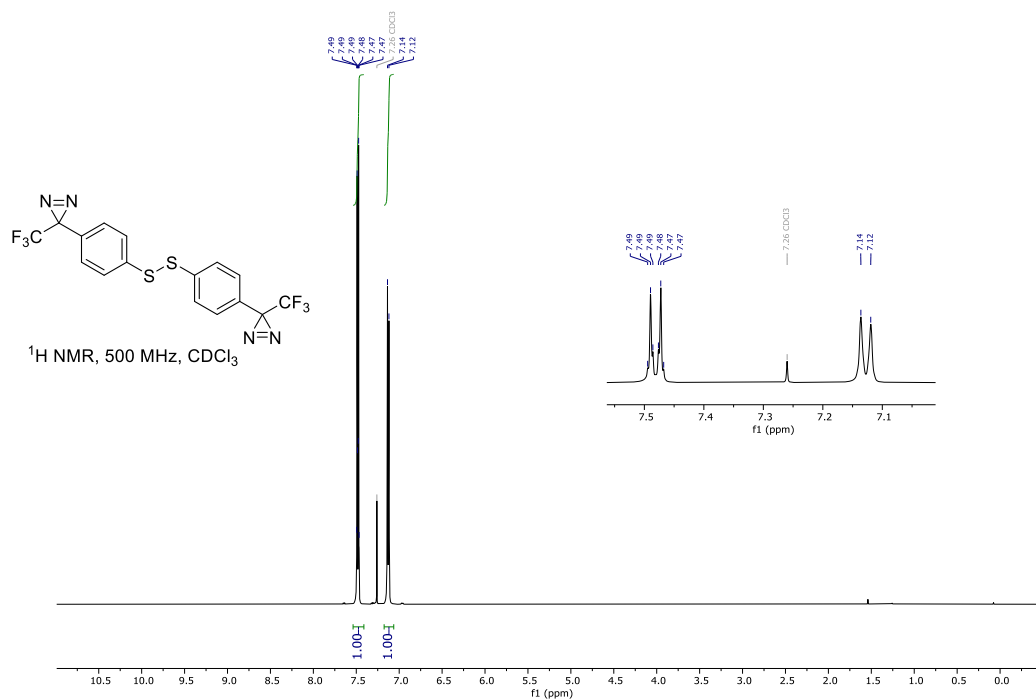
(50 mL) was added and the biphasic mixture was stirred vigorously until all excess iodine had been consumed as evidenced by full discoloration of the organic phase (approximately 30 min). The phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Purification by flash column chromatography (hexanes) furnished the title product (886 mg, 2.29 mmol, 89%) as a pale yellow oil (melting point ~20 °C). *R<sub>f</sub>* (hexanes): 0.39; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.50–7.45 (4 H, m, H<sub>5</sub>), 7.13 (4 H, d, *J* = 8.3 Hz, H<sub>4</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 138.8 (2 C, C<sub>6</sub>), 128.3 (2 C, C<sub>3</sub>), 127.4 (4 C, C<sub>4</sub>), 127.2 (4 C, C<sub>5</sub>), 122.1 (2 C, q, <sup>1</sup>*J* = 274.7 Hz, C<sub>1</sub>), 28.4 (q, <sup>2</sup>*J* = 40.8 Hz, C<sub>2</sub>), <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ: – 64.3; HRMS ASAP+ found [M+H]<sup>+</sup> 435.0166, C<sub>16</sub>H<sub>8</sub>F<sub>6</sub>N<sub>4</sub>S<sub>2</sub><sup>+</sup> requires 435.0173; IR (film) ν<sub>max</sub>: 2990, 1715, 1341, 1181, 1148, 936, 814, 696.

**Synthesis of UDC2 from 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine:**

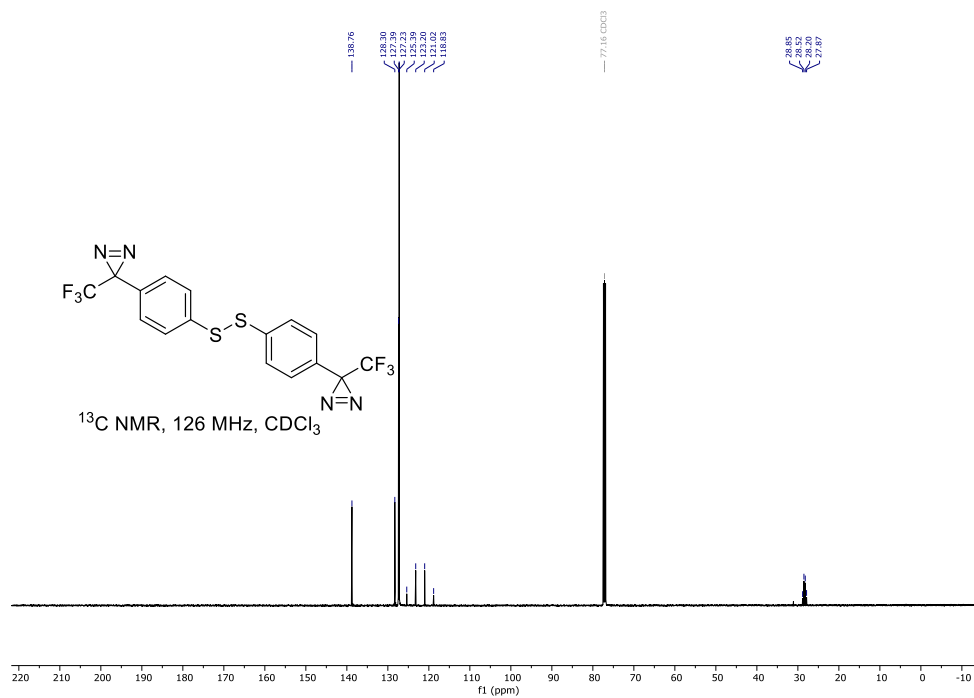


A solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (2.00 g, 7.63 mmol, 1.0 equiv) in anhydrous ethanol (240 mL) was stirred open to air at 55 °C. Silver nitrate (1.55 g, 9.15 mmol, 1.2 equiv) was added in one portion with vigorous stirring. The mixture was stirred at 55 °C for 2 h, during which a white precipitate was formed, rendering the reaction highly viscous. All volatiles were removed in vacuo using a rotary evaporator. 6 M aqueous hydrochloric acid (218 mL) was added to the crude mixture and the reaction was stirred at ambient temperature open to air for 1.5 h. Dichloromethane (100 mL) was added and stirring was continued for 1 h. The biphasic mixture was filtered and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> filtered and concentrated in vacuo. Purification by silica flash column chromatography (elution: hexanes) yielded the title product (1.36 g, 3.13 mmol, 82%) as a volatile pale-yellow oil that solidified at lower temperatures. Analytical data were identical to those reported above for UDC2.

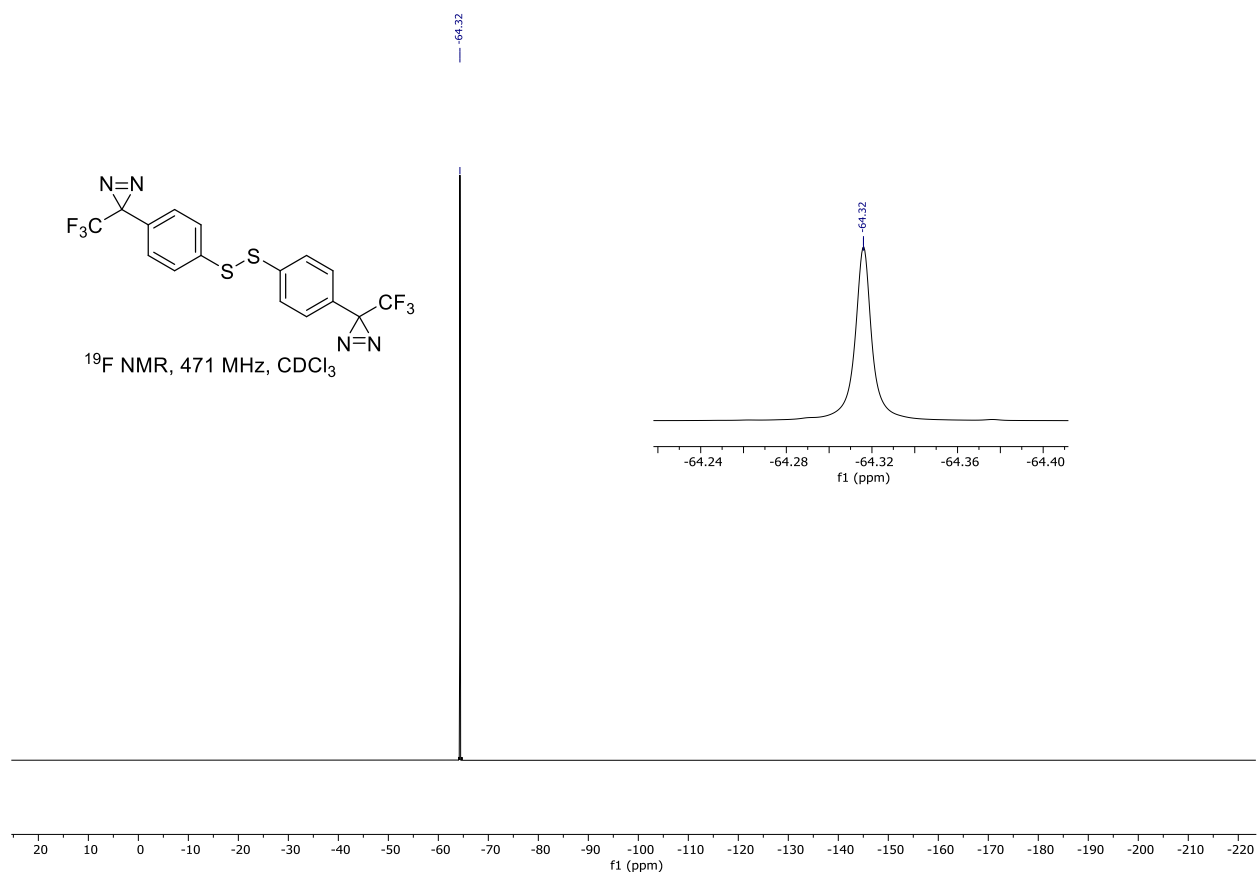
$^1\text{H}$  NMR of UDC2 (500 MHz,  $\text{CDCl}_3$ , 300 K)



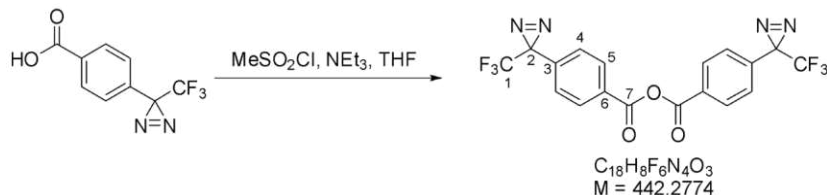
$^{13}\text{C}$  NMR of UDC2 (126 MHz,  $\text{CDCl}_3$ , 300 K)



$^{19}\text{F}$  NMR of UDC2 (126 MHz,  $\text{CDCl}_3$ , 300 K)



### Synthesis of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoic anhydride (UDC3):

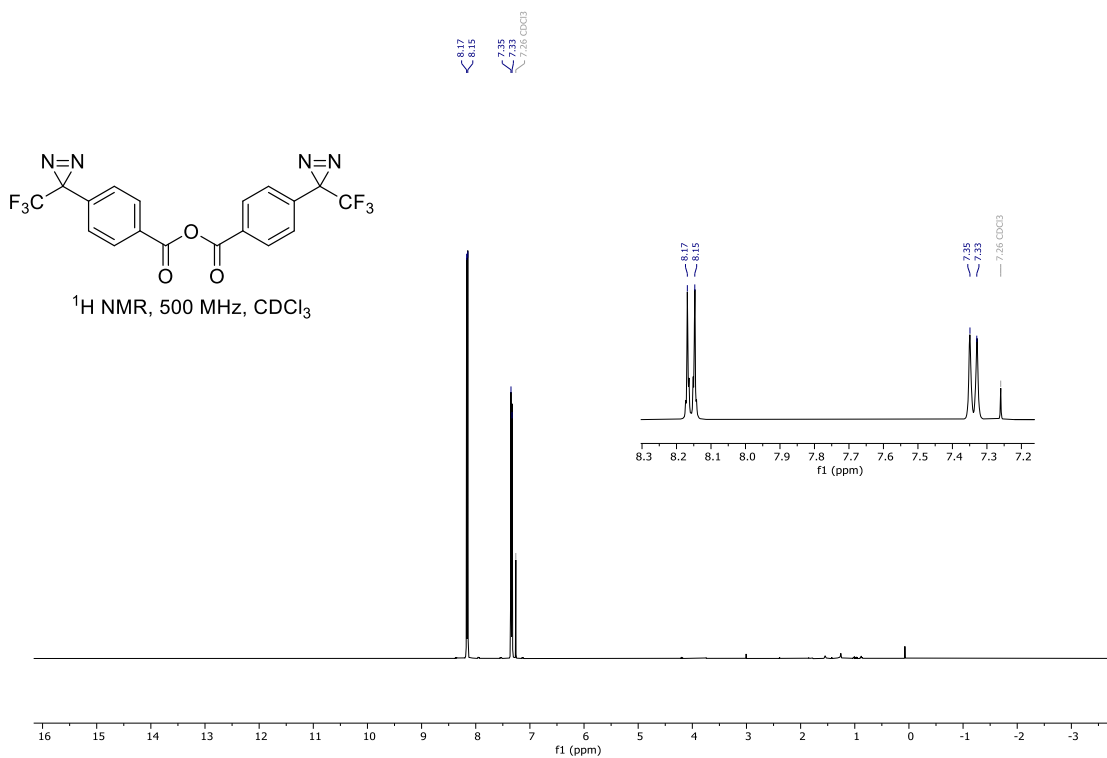


A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoic acid (1.50 g, 6.52 mmol, 1.0 equiv) in anhydrous THF (20 mL) was cooled to 0 °C, and MeSO<sub>2</sub>Cl (277 μL, 3.58 mmol, 0.55 equiv) was added dropwise. The resulting pale-yellow solution was stirred for 5 min at 0 °C before triethylamine (1.55 mL, 11.2 mmol, 1.7 equiv) was added dropwise resulting in the formation of a white precipitate. After stirring for 1 h at 0 °C, the ice bath was removed and the reaction mixture was allowed to warm to room temperature for 10 min. The mixture was concentrated (rotary evaporation at 40 °C) and directly purified by column chromatography (10% dichloromethane in hexanes containing 1% (v/v) HCl (2 M in Et<sub>2</sub>O), to 25% dichloromethane in hexanes containing 1% (v/v) HCl (2 M in Et<sub>2</sub>O)) to give the title compound as a white, crystalline solid (1.38 g, 3.12 mmol, 96%). *R<sub>f</sub>* (25% dichloromethane in hexanes + 1% (v/v) HCl (2 M in Et<sub>2</sub>O)): 0.41; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.16 (4 H, d, *J* = 8.6 Hz, H<sub>5</sub>), 7.13 (4 H, d, *J* = 8.3 Hz, H<sub>4</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 161.1 (2 C, C<sub>7</sub>), 135.9, (2 C, C<sub>6</sub>), 131.0 (4 C, C<sub>5</sub>), 129.7 (2 C, C<sub>3</sub>), 127.0 (4 C, C<sub>4</sub>), 121.9 (2 C, q, *J* = 274.8 Hz, C<sub>1</sub>), 28.6 (2 C, q, *J* = 41.0 Hz, C<sub>2</sub>); <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ: − 64.8; HRMS ESI+ found [M+Na]<sup>+</sup> 463.0416, C<sub>18</sub>H<sub>8</sub>F<sub>6</sub>N<sub>4</sub>NaO<sub>3</sub><sup>+</sup> requires 465.0398; IR (film) ν<sub>max</sub>: 2991, 2898, 2677, 1688, 1346, 1290, 1202, 1184, 1153, 942, 736.

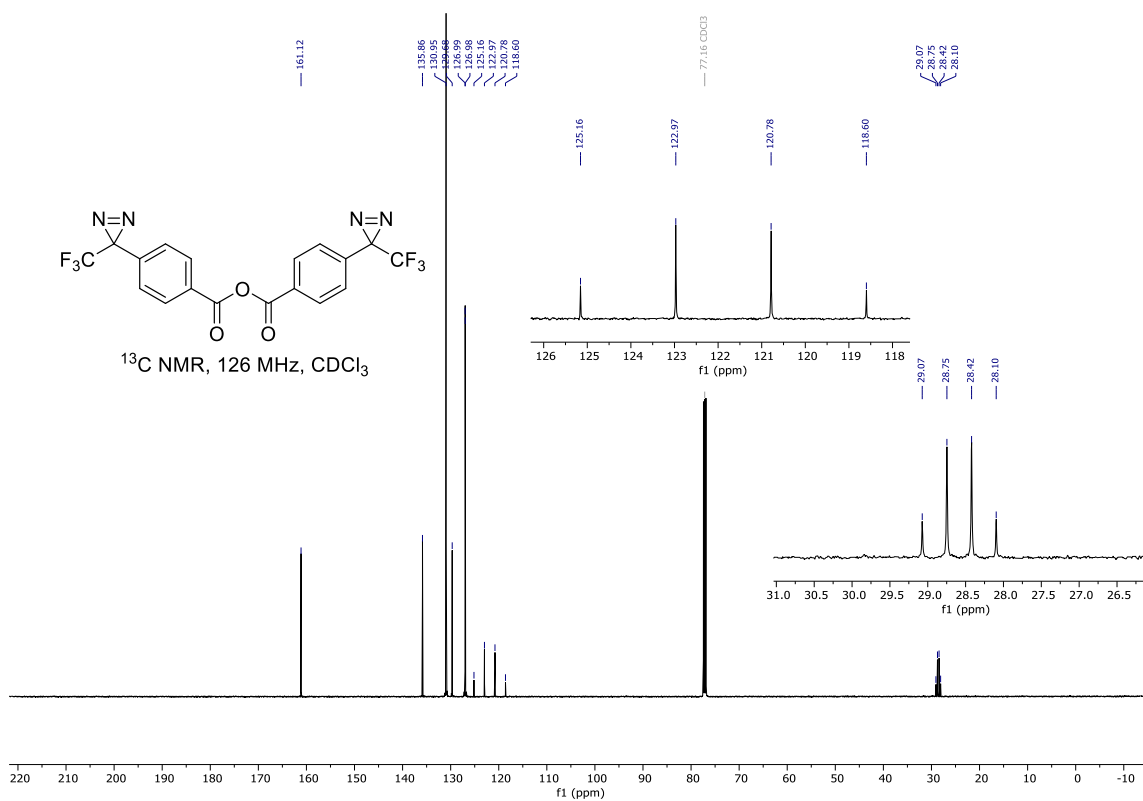
*Note: UDC3 was found to be stable towards ambient moisture and even aqueous workup. However, UDC3 hydrolyzes readily on neutral or basic silica. Hence, acidification of silica prior to and during column chromatography is required in order to obtain high yields. Commercially*

available solutions of *HCl* in diethyl ether or dioxane were found to furnish the best results.  
 Acidification using acetic or formic acid leads to undesired cross-anhydride products.

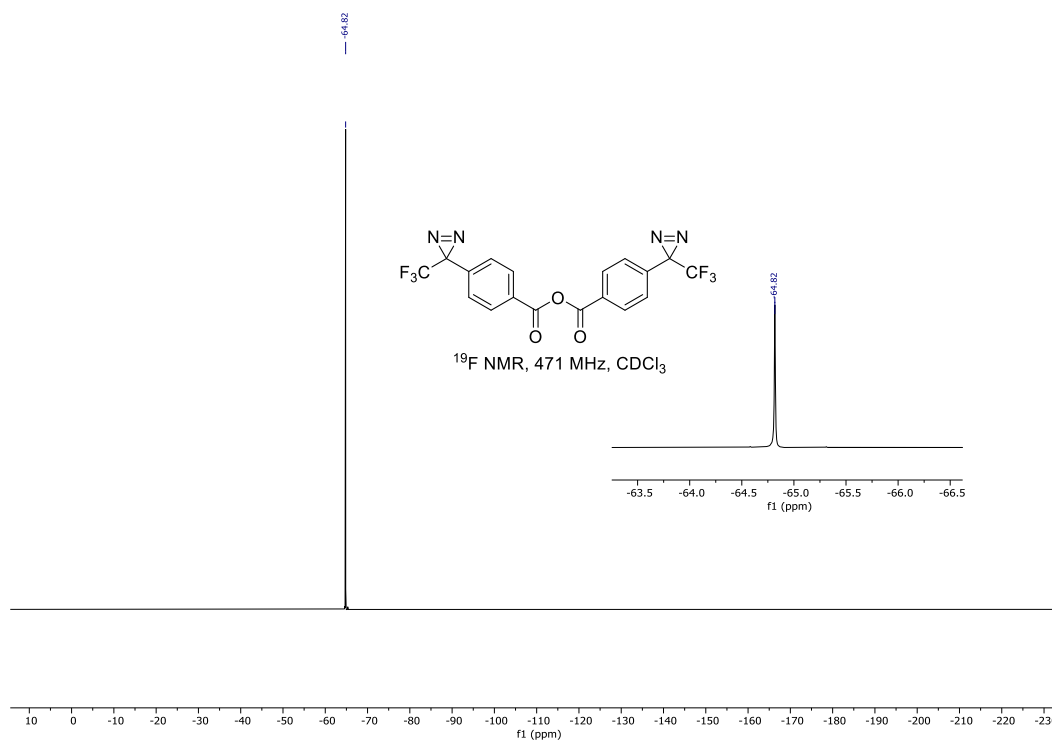
$^1\text{H}$  NMR of UDC3 (500 MHz,  $\text{CDCl}_3$ , 300 K)



$^{13}\text{C}$  NMR of UDC3 (126 MHz,  $\text{CDCl}_3$ , 300 K)

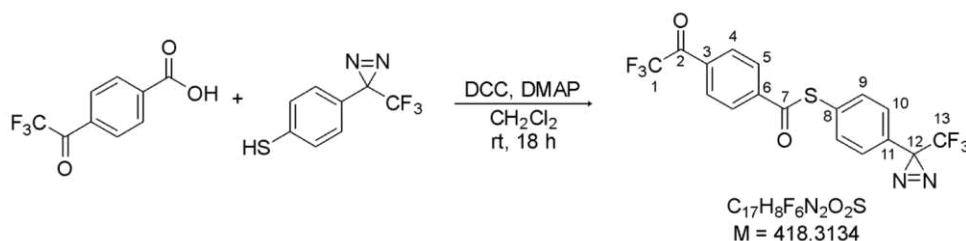


$^{19}\text{F}$  NMR of UDC3 (471 MHz,  $\text{CDCl}_3$ , 300 K)



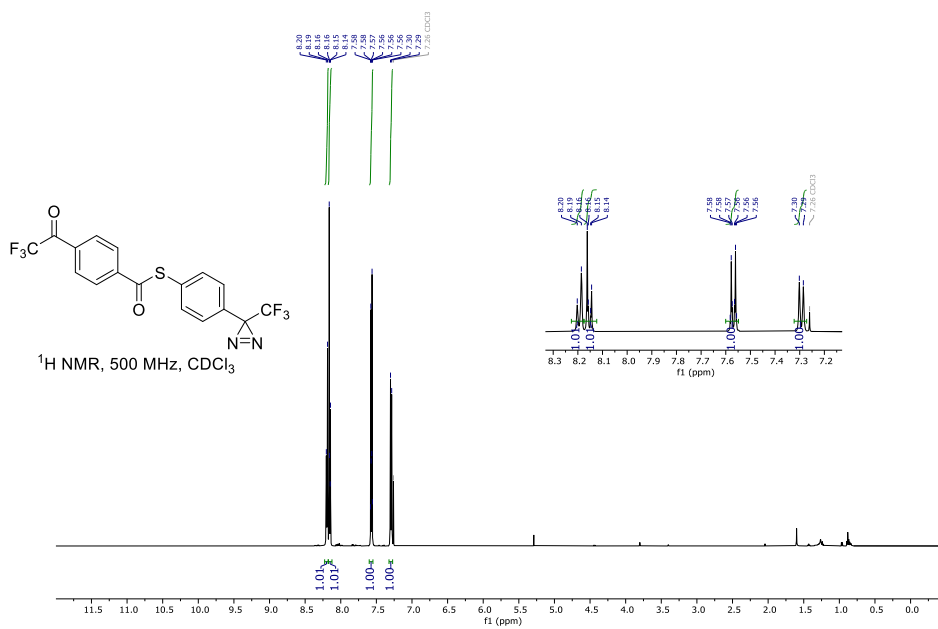


**Synthesis of S-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzoate:**

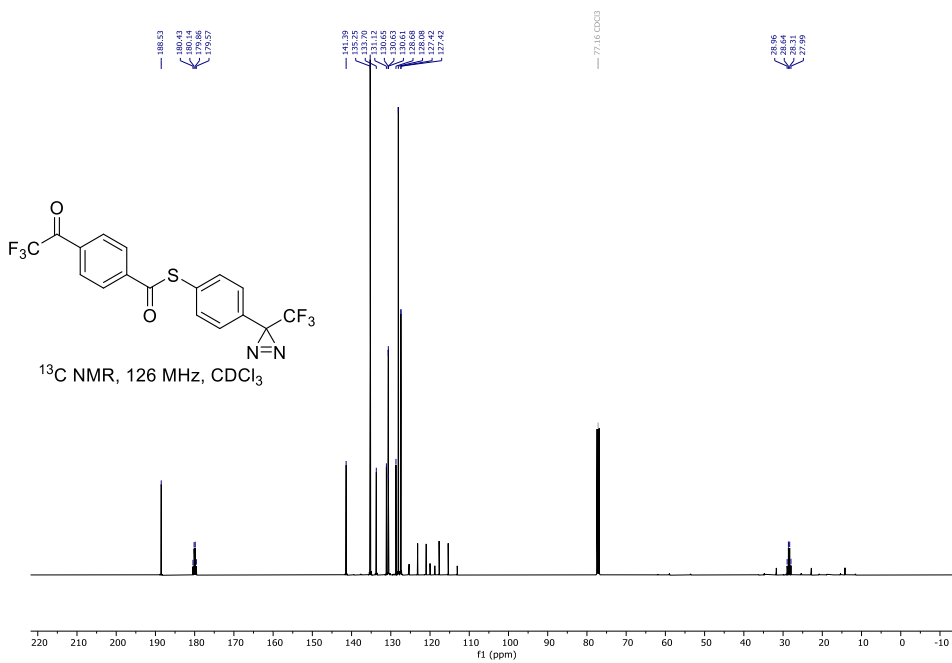


A 50 mL Schlenk flask was charged with 4-(2,2,2-trifluoroacetyl)benzoic acid (960 mg, 4.40 mmol, 1.2 equiv), DCC (1.06 g, 5.13 mmol, 1.4 equiv) and DMAP (202 mg, 1.65 mmol, 0.45 equiv), sealed and backfilled with nitrogen (3 x). A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (800 mg, 3.67 mmol, 1.0 equiv) in anhydrous dichloromethane (13 mL) was added via syringe, and the resulting mixture stirred at room temperature for 18 h. The reaction mixture was filtered through celite, the filter cake washed with diethyl ether, and the filtrate concentrated in vacuo. The residue was purified by silica flash column chromatography (gradient elution: hexanes then 10% dichloromethane in hexanes), yielding the title product (1.02 g, 2.44 mmol, 67%) as a colorless oil  $R_f$  (10 % diethyl ether in hexanes): 0.53;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (2 H, d,  $J = 8.4$  Hz,  $\text{H}_{4/5}$ ), 8.17 – 8.13 (2 H, m,  $\text{H}_{4/5}$ ), 7.61 – 7.54 (2 H, m,  $\text{H}_{10}$ ), 7.29 (2 H, d,  $J = 8.2$  Hz,  $\text{H}_9$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  188.5 ( $\text{C}_7$ ), 180.00 (q,  $J = 36.0$  Hz,  $\text{C}_2$ ), 141.4 ( $\text{C}_6$ ), 135.3 (2 C,  $\text{C}_9$ ), 133.7 ( $\text{C}_3$ ), 131.1 ( $\text{C}_{8/11}$ ), 130.6 (2 C, q,  $J = 2.0$  Hz,  $\text{C}_{10}$ ), 128.7 ( $\text{C}_{8/11}$ ), 128.1 (2 C,  $\text{C}_5$ ), 127.4 (2 C,  $\text{C}_4$ ), 122.06 (q,  $J = 274.7$  Hz,  $\text{C}_{12}$ ), 116.5 (q,  $J = 291.0$  Hz,  $\text{C}_1$ ), 28.5 (q,  $J = 40.7$  Hz,  $\text{C}_{12}$ );  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$ : -64.1 (s,  $\text{F}_3\text{C}-1$ ), -70.9 (s,  $\text{F}_3\text{C}-13$ );

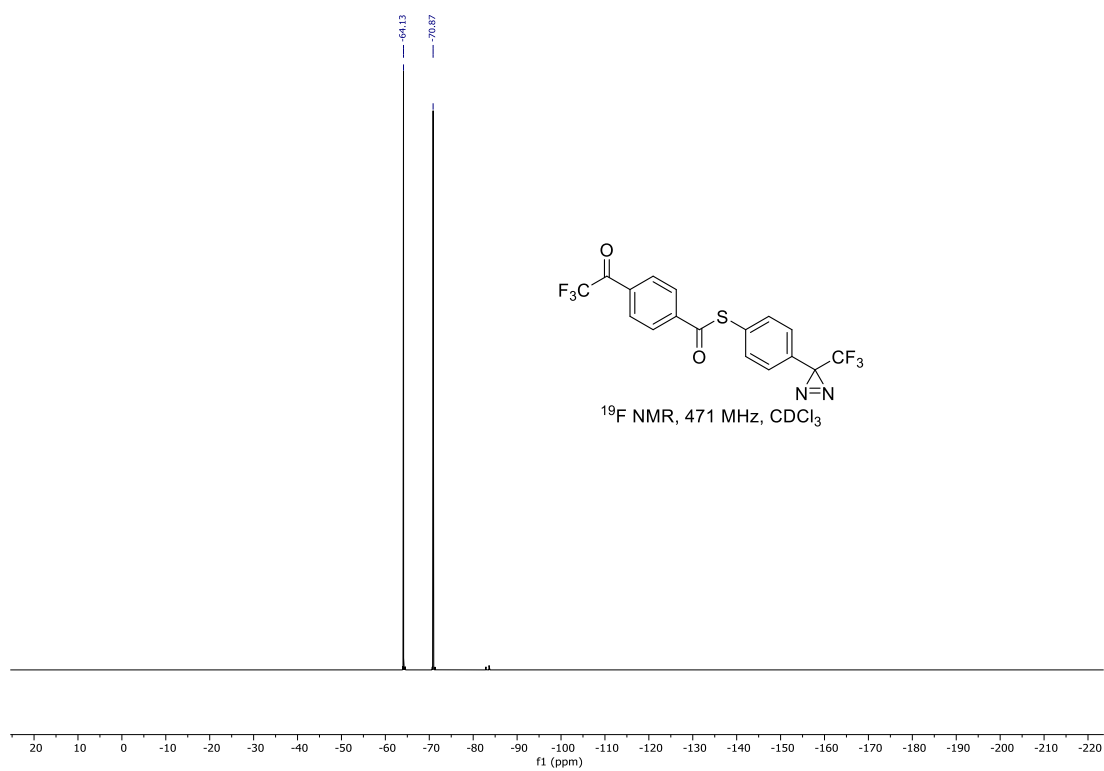
<sup>1</sup>H NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (500 MHz, CDCl<sub>3</sub>, 300 K)



<sup>13</sup>C NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (126 MHz, CDCl<sub>3</sub>, 300 K)

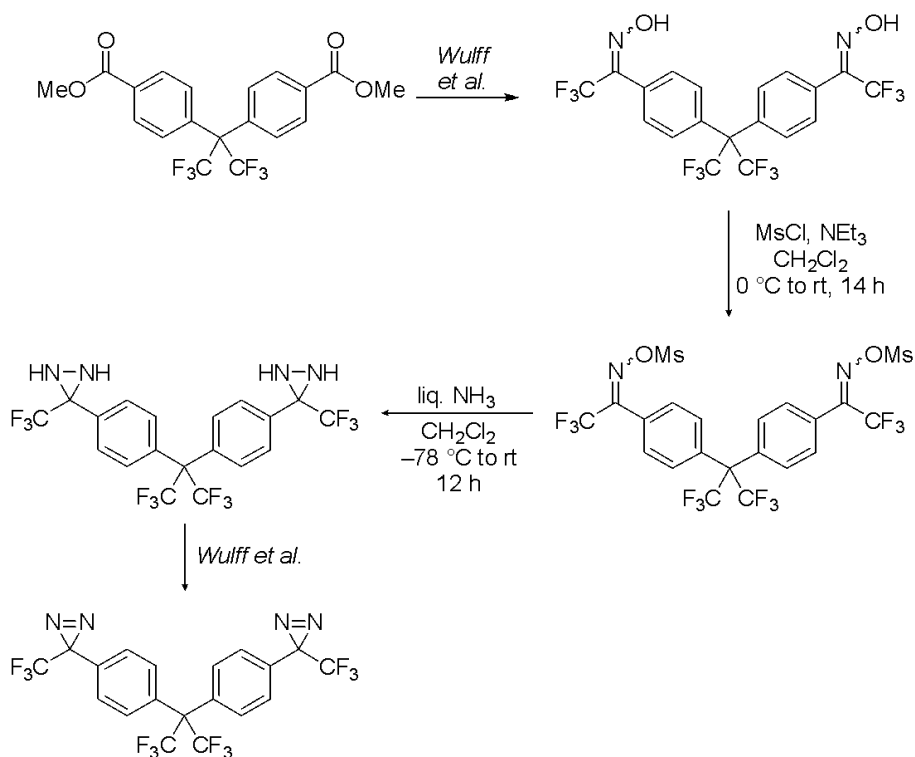


$^{19}\text{F}$  NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (471 MHz,  $\text{CDCl}_3$ , 300 K)

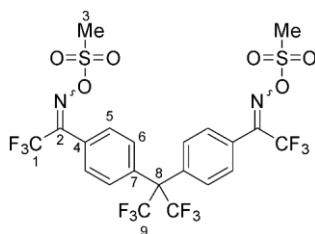


**Synthesis of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3*H*-diazirine)<sup>4</sup> (USC):**

This compound was synthesized following the route established by Wulff *et al.*<sup>4</sup> with two slight deviations: The bis-oxime synthesized by Wulff and co-workers was mesylated instead of tosylated and then treated with liquid ammonia.



**Synthesis of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime:**

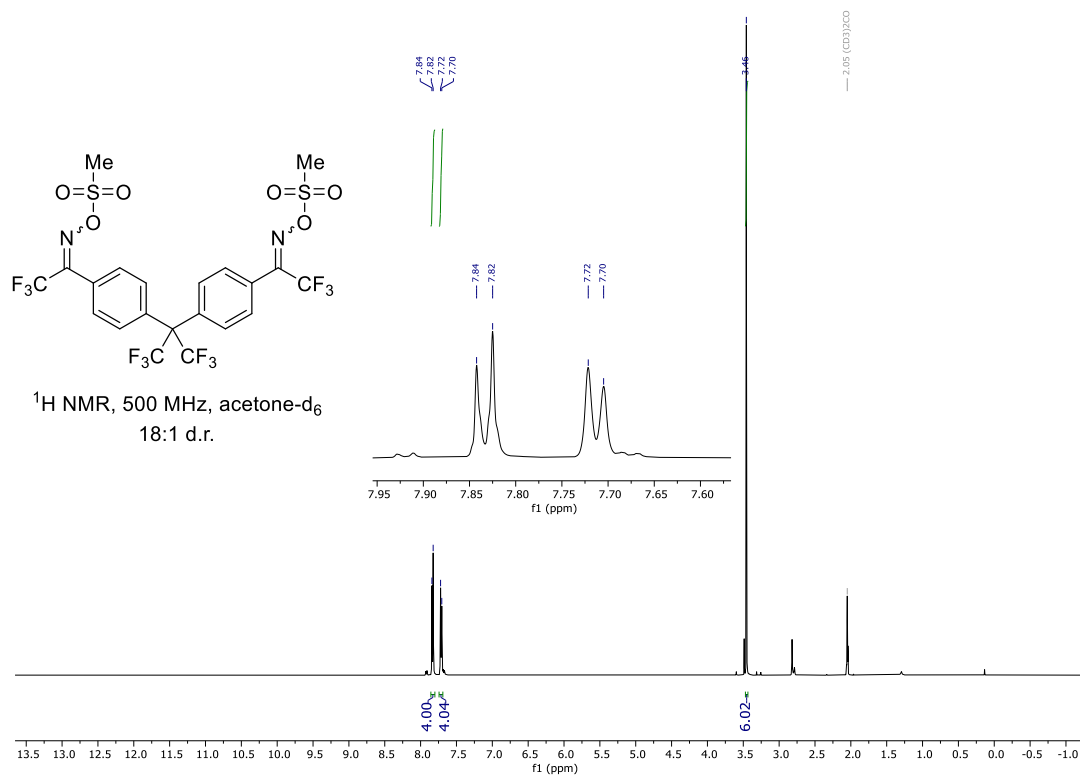


A solution of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime (4.89 g, 9.29 mmol, 1.0 equiv) in anhydrous dichloromethane (48 mL) was cooled to 0 °C, triethylamine (4.14 mL, 29.7 mmol, 3.2 equiv) was added dropwise followed by MsCl (1.58 mL, 20.4 mmol, 2.2 equiv). The reaction was allowed to warm to room temperature overnight (approximately 15 h) and then quenched by addition of sat. aq.  $\text{NH}_4\text{Cl}$  (50 mL). Water (15 mL) was added to dissolve the resulting precipitate. The mixture was extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The resulting crude solid was purified by silica flash column chromatography (gradient elution: hexanes to 25% ethyl acetate in hexanes), yielding the title product (4.83 g, 7.08 mmol, 76%) as a colorless solid.

The title compound was isolated as a 18:1 mixture of diastereomers. Only signals corresponding to the major diastereomer are reported:  $R_f$  (25% ethyl acetate in hexanes): 0.23;  $^1\text{H}$  NMR (500 MHz, acetone)  $\delta$  7.83 (4 H, d,  $J$  = 8.7 Hz,  $\text{H}_5$ ), 7.71 (4 H, d,  $J$  = 8.3 Hz,  $\text{H}_6$ ), 3.46 (6 H, s,  $\text{H}_2$ );  $^{13}\text{C}$  NMR (126 MHz, acetone)  $\delta$ : 153.8 (2 C, q,  $J$  = 33.8 Hz,  $\text{C}_2$ ), 136.8 (2 C,  $\text{C}_4$ ), 131.6 (4 C,  $\text{C}_5$ ), 130.1 (4 C,  $\text{C}_6$ ), 127.0 (2 C,  $\text{C}_7$ ), 124.8 (2 C, q,  $J$  = 288.1 Hz,  $\text{C}_9$ ), 120.7 (2 C, q,  $J$  = 276.5 Hz,  $\text{C}_1$ ), 65.6 (app q,  $J$  = 51.8 Hz,  $\text{C}_8$ ), 37.3 (2 C,  $\text{C}_3$ );  $^{19}\text{F}$  NMR (471 MHz, acetone)  $\delta$  -63.1 (s,  $\text{F}_3\text{C}$ -9), -66.7 (s,  $\text{F}_3\text{C}$ -1); HRMS ESI+ found  $[\text{M}+\text{Na}]^+$  705.0001,  $\text{C}_{21}\text{H}_{14}\text{F}_{12}\text{N}_2\text{NaO}_6\text{S}_2^+$  requires 704.9994 IR (film)  $\nu_{\text{max}}$ : 3030, 1702, 1381, 1249, 1187, 1142, 971, 892, 814, 756, 674, 518, 487.

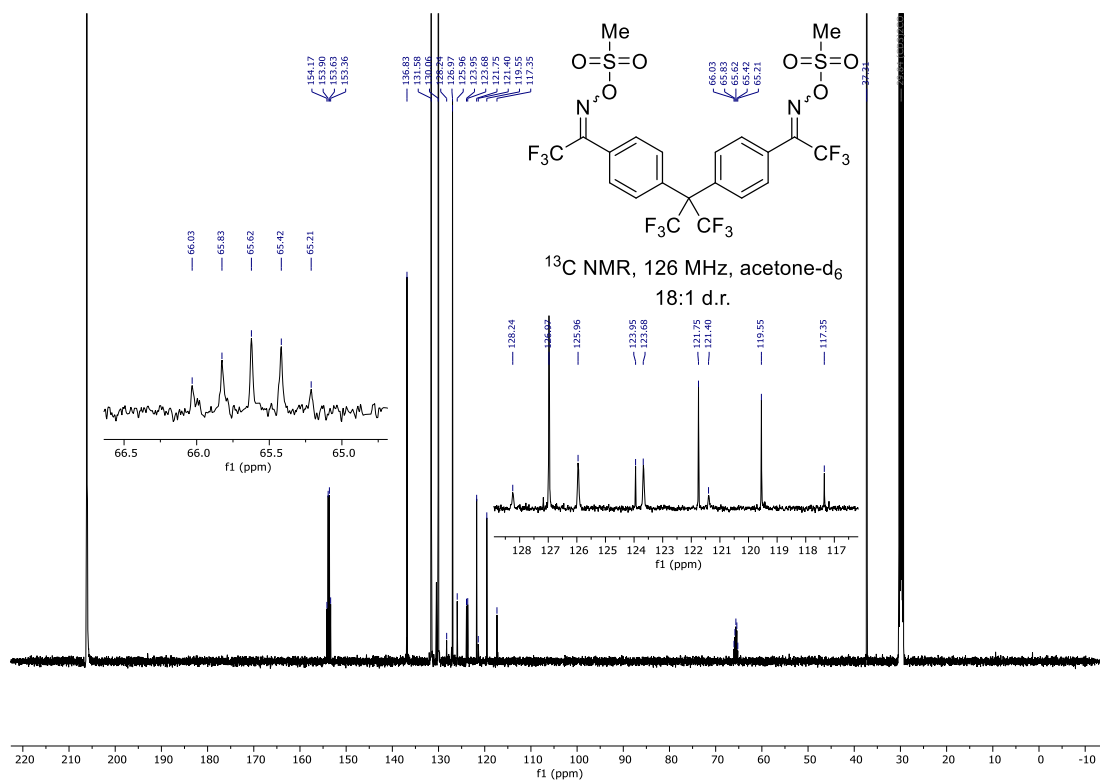
$^1\text{H}$  NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one)

O,O-dimethylsulfonyl dioxime (500 MHz, Acetone- $d_6$ , 300 K)

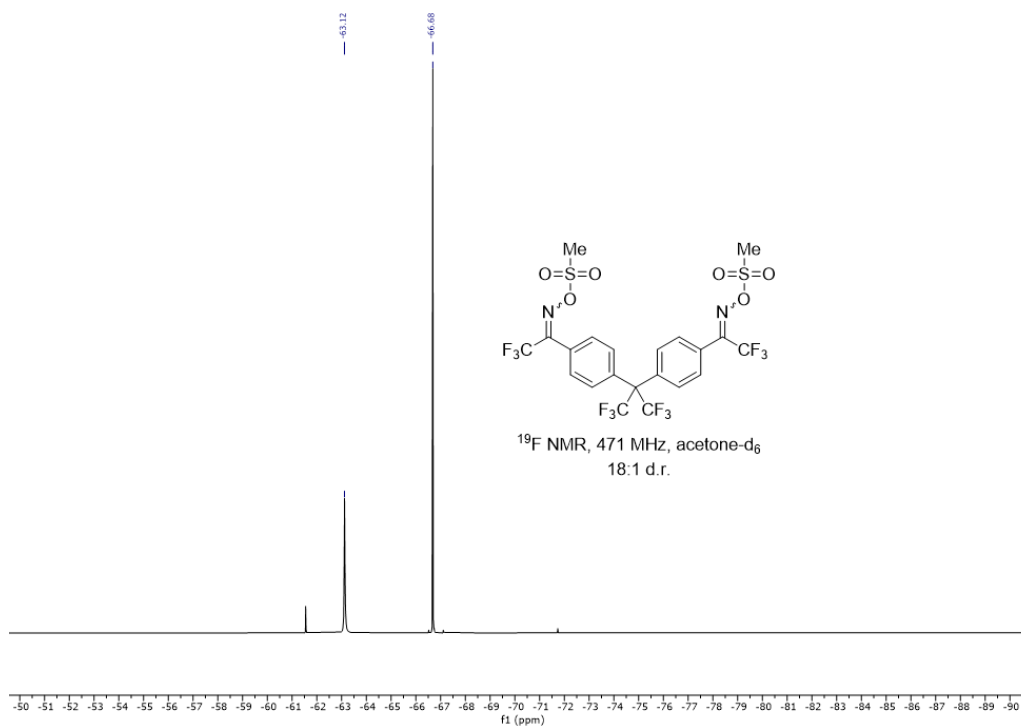


$^{13}\text{C}$  NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one)

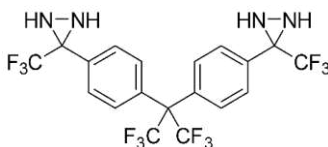
O,O-dimethylsulfonyl dioxime (126 MHz, Acetone- $d_6$ , 300 K)



<sup>19</sup>F NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime (126 MHz, Acetone-d<sub>6</sub>, 300 K)



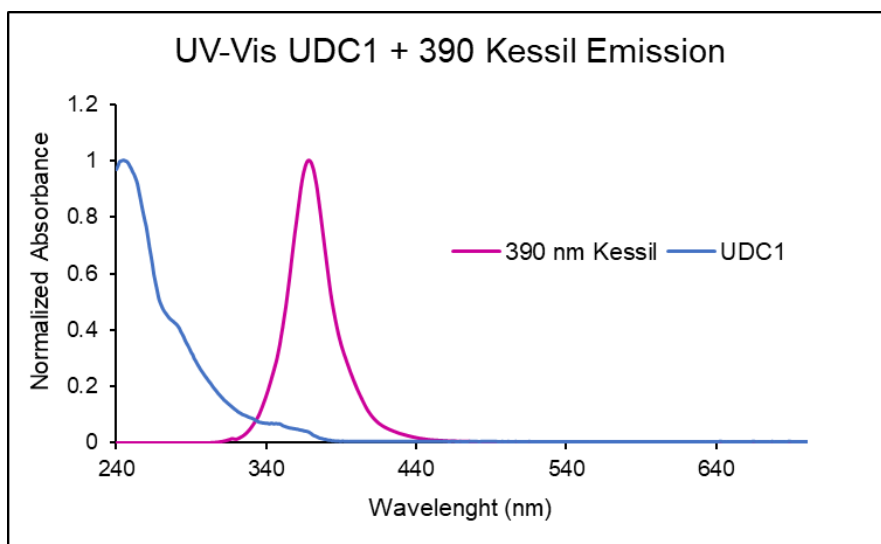
**Synthesis of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine):**



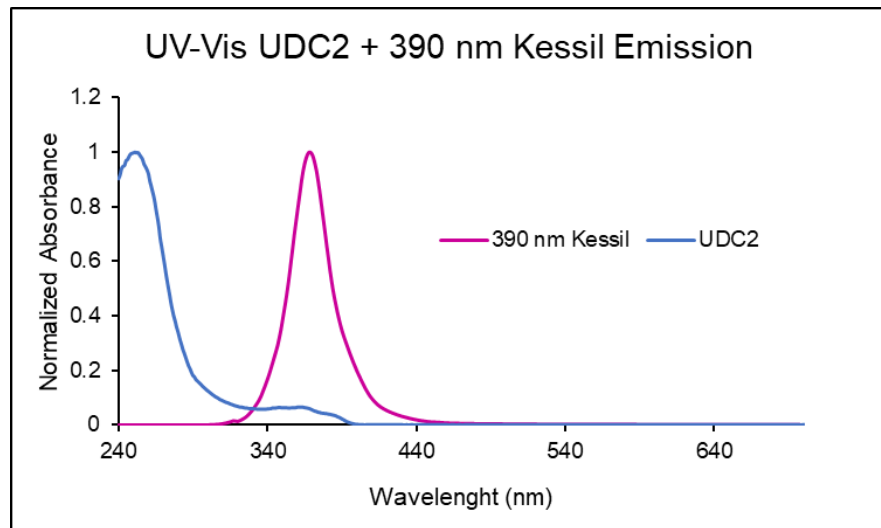
Anhydrous ammonia was condensed (approx. 40 mL) into a pre-cooled Schlenk flask at  $-78\text{ }^{\circ}\text{C}$  using a dry-ice acetone cold finger. To the stirred liquid ammonia, a solution of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethyl sulfonyl dioxime (4.80 g, 7.03 mmol, 1.0 equiv) in anhydrous tetrahydrofuran (40 mL) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The solution was stirred for 1 h at  $-78\text{ }^{\circ}\text{C}$  and then gradually warmed to room temperature over the course of 15 h, while allowing excess ammonia to vent. Nitrogen was bubbled through the resulting suspension for 10 min to remove residual ammonia. The resulting suspension was concentrated and dichloromethane (200 mL) was added. The resulting mixture was washed with sat. aq.  $\text{NH}_4\text{Cl}$  (150 mL). The phases were separated, and the aqueous phase was extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The resulting crude solid was purified by silica flash column chromatography (gradient elution: 50% dichloromethane in hexanes to dichloromethane to 10% ethyl acetate in dichloromethane), yielding the title product (3.03 g, 5.78 mmol, 82%) as a colorless solid. Analytical data agreed with values reported by Wulff and co-workers.<sup>4</sup>



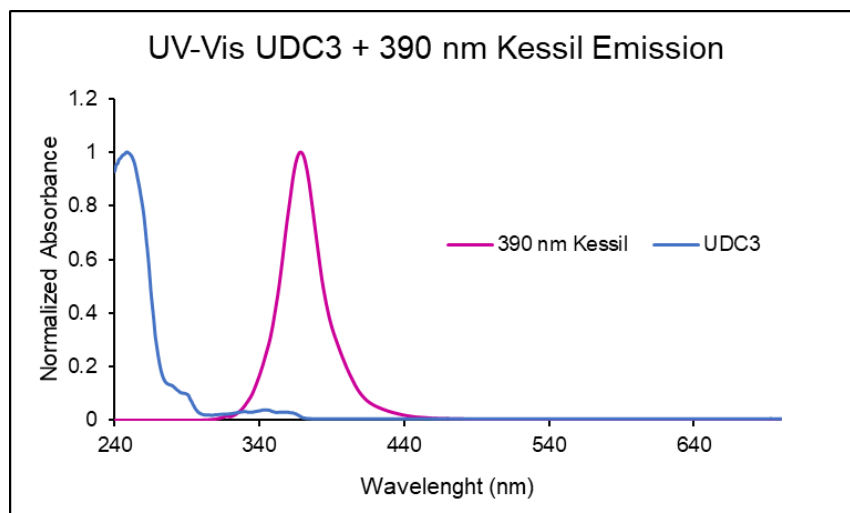
## Supplementary Figures



**Figure D1.** UV-Vis absorption profile for UDC1 (5 nM in MeCN) overlaid with 390 nm Kessil emission.



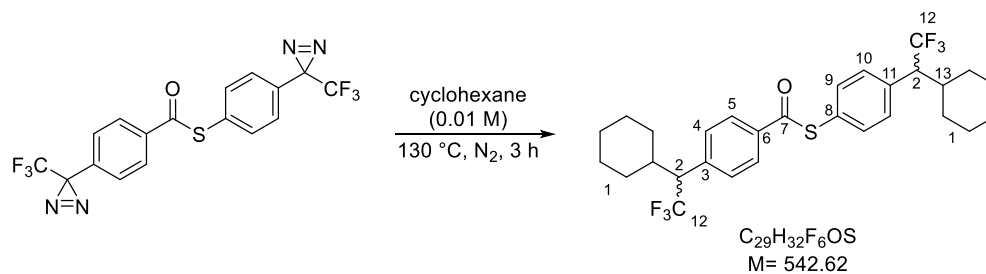
**Figure D2.** UV-Vis absorption profile for UDC2 (5 nM in MeCN) overlaid with 390 nm Kessil emission.



**Figure D3.** UV-Vis absorption profile for UDC3 (5 nM in MeCN) overlaid with 390 nm Kessil emission.

### Modeled Carbene Activation and Insertion Crosslinking on Cyclohexane by UDC1, 2, and 3.

#### UDC1



#### Thermal Protocol

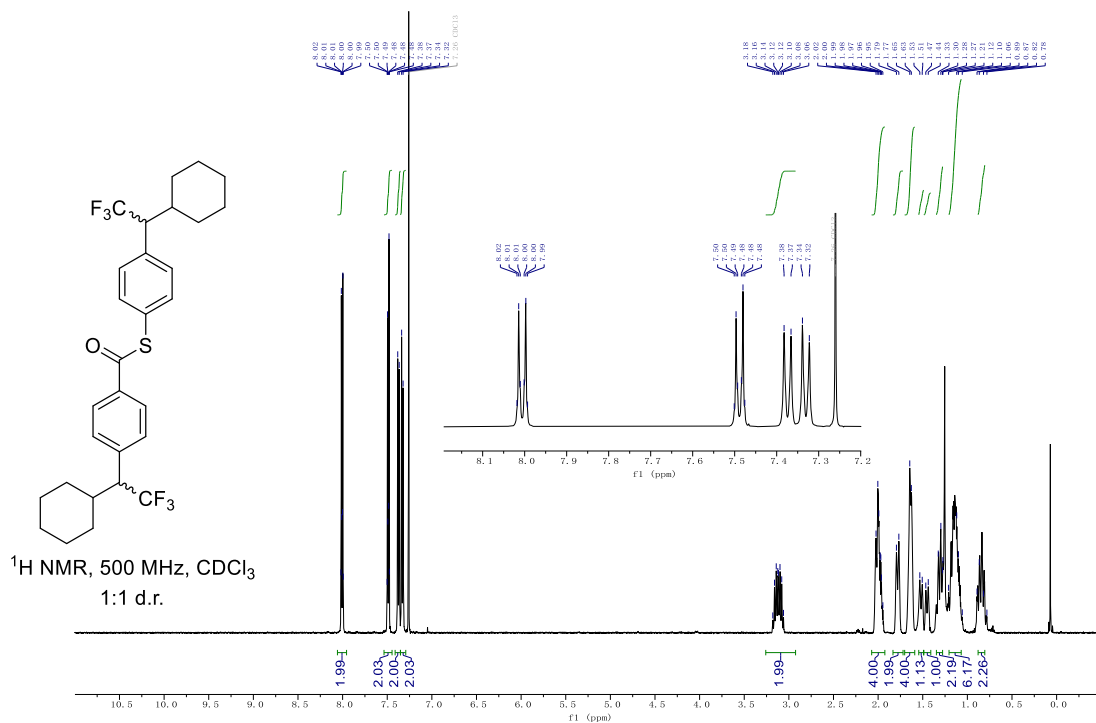
A pressure tube was charged with **UDC1** (90 mg, 0.21 mmol) under nitrogen and cyclohexane (21 ml) was added. The tube was sealed and heated to 130 °C (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the reaction mixture was concentrated. The crude reaction mixture was purified by column chromatography (12%

dichloromethane in hexanes, to 20% dichloromethane in hexanes containing to give the title compound as a colorless oil (11.2 mg, 20.6  $\mu\text{mol}$ , 10%) as a 1:1 mixture of diastereomers.

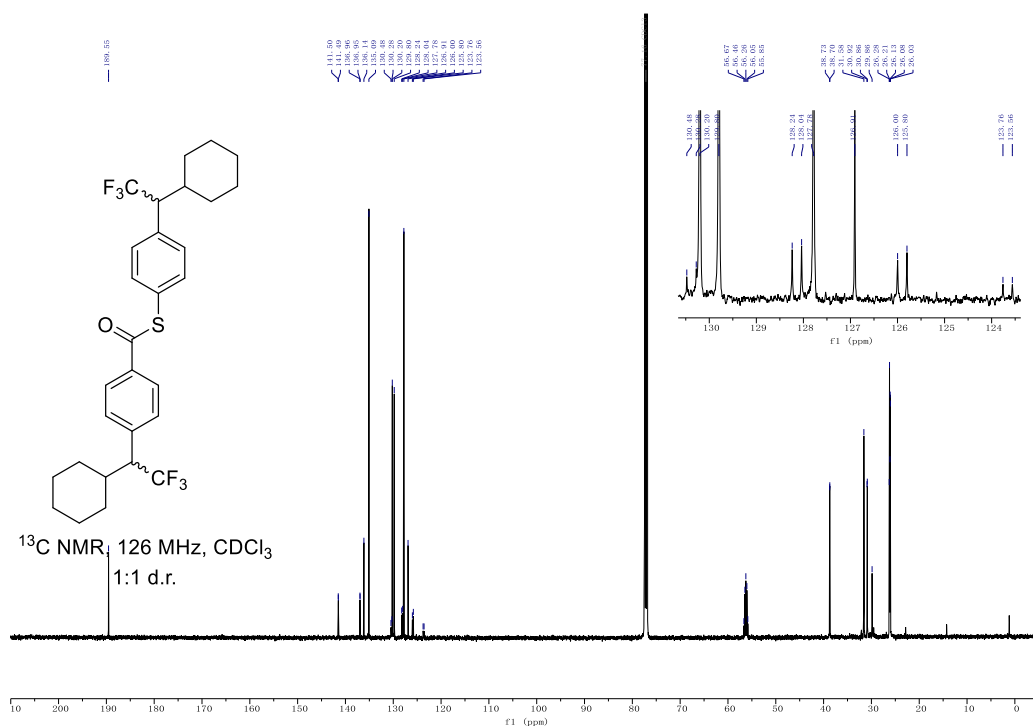
A similar experiment was carried out using **UDC1** (12.9 mg, 30.0  $\mu\text{mol}$ ) in 3.0 mL cyclohexane at 130 °C for 3h. After cooling to room temperature, 1,4-dinitrobenzene was added as an internal standard for quantification. The crude reaction mixture was concentrated and then analyzed by  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectroscopy. A yield of 3.3 mg (6.07  $\mu\text{mol}$ , 20%) of the crosslinked product was determined.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 7.99 (2H, m,  $\text{H}_5$ ), 7.50 – 7.47 (2H, m,  $\text{H}_4$ ), 7.37 (2 H, d,  $J$  = 8.3 Hz,  $\text{H}_{9/10}$ ), 7.33 (2 H, d,  $J$  = 8.3 Hz,  $\text{H}_{9/10}$ ), 3.19 – 3.04 (2H, m,  $\text{H}_2$ ), 2.07 – 1.91 (4H, m,  $\text{H}_{1/13}$ ), 1.83 – 1.74 (2H, m,  $\text{H}_{1/13}$ ), 1.69 – 1.60 (4H, m,  $\text{H}_{11/13}$ ), 1.52 (1 H, d,  $J$  = 13.5 Hz,  $\text{H}_{1/13}$ ), 1.45 (1 H, d,  $J$  = 13.8 Hz,  $\text{H}_{1/13}$ ), 1.37 – 1.27 (m, 2H,  $\text{H}_{1/13}$ ), 1.21 – 1.06 (6H, m,  $\text{H}_{1/13}$ ), 0.92 – 0.74 (2H, m,  $\text{H}_1$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.6 ( $\text{C}_7$ ), 141.5 (q,  $^3J$  = 2.2 Hz,  $\text{C}_3$ ), 137.0 (q,  $^3J$  = 2.2 Hz,  $\text{C}_{11}$ ), 136.1 ( $\text{C}_6$ ), 135.1( $\text{C}_5$ ), 130.2 ( $\text{C}_{4/10}$ ), 129.8 ( $\text{C}_{4/10}$ ), 127.8 ( $\text{C}_9$ ), 127.1 (q,  $^1J$  = 281.6 Hz), 126.9 (q,  $^1J$  = 281.6 Hz), 126.9 ( $\text{C}_8$ ), 56.7 – 55.8 (m, 2C,  $\text{C}_{13}$ ), 38.7 ( $\text{C}_1$ ), 38.7 ( $\text{C}_1$ ), 31.6 ( $\text{C}_1$ ), 30.9 ( $\text{C}_1$ ), 30.9 ( $\text{C}_1$ ), 29.9 ( $\text{C}_1$ ), 26.3 ( $\text{C}_1$ ), 26.2 ( $\text{C}_1$ ), 26.13 ( $\text{C}_1$ ), 26.08 ( $\text{C}_1$ ), 26.0 ( $\text{C}_1$ );  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  –62.17 (d,  $J$  = 9.8 Hz), –62.27 (d,  $J$  = 9.9 Hz); HRMS ASAP+ found  $[\text{M}+\text{H}]^+$  543.2170,  $\text{C}_{29}\text{H}_{33}\text{OSF}_6^+$  requires 543.2156.

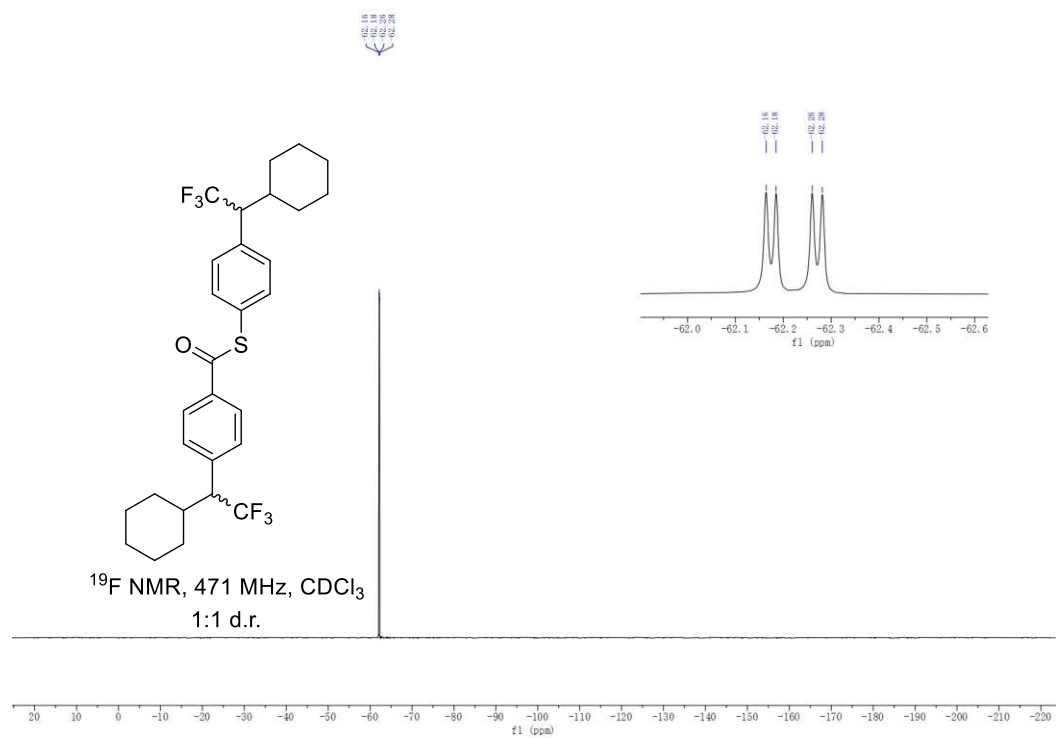
$^1\text{H}$  NMR of UDC1-crosslinked cyclohexane (500 MHz,  $\text{CDCl}_3$ , 300 K)

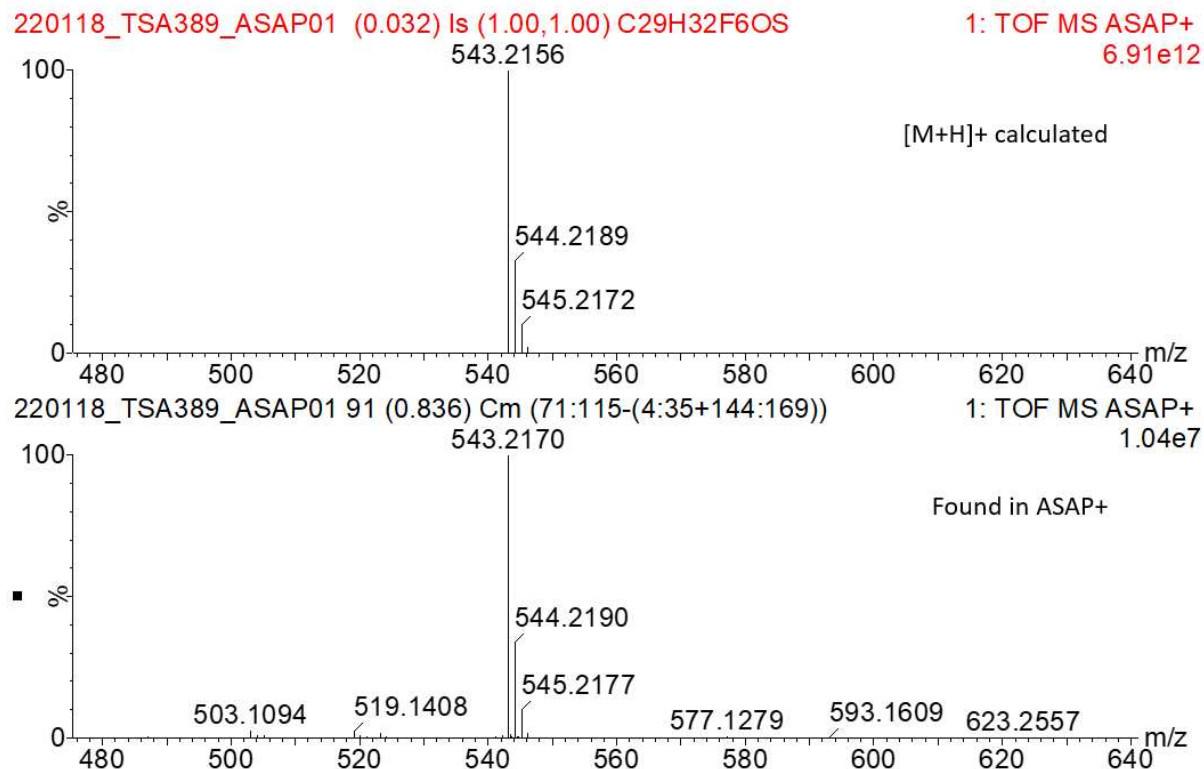


$^{13}\text{C}$  NMR of UDC1-crosslinked cyclohexane (126 MHz,  $\text{CDCl}_3$ , 300 K)



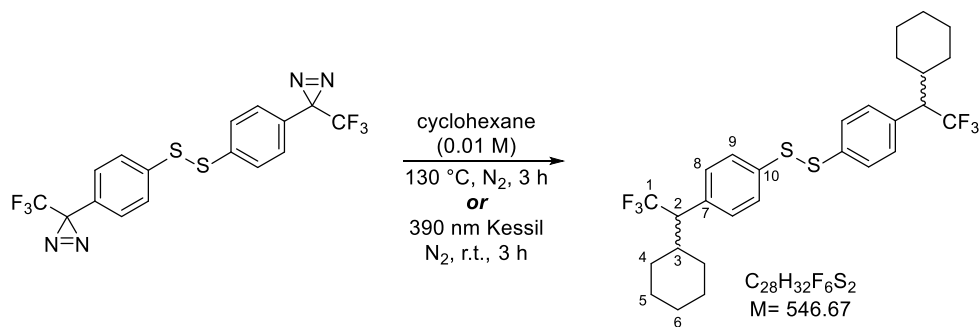
$^{19}\text{F}$  NMR of UDC1-crosslinked cyclohexane (471 MHz,  $\text{CDCl}_3$ , 300 K)





**Figure D4.** Mass spectrum revealing products of UDC1 thermal-initiated C-H insertion for cyclohexane.

## UDC2



### UV-Irradiation protocol

A 1.5 dram vial was charged with UDC2 (17.4 mg, 40.0  $\mu$ mol) under nitrogen and cyclohexane (4 ml) was added. The vial was sealed tightly and irradiated with a 390 nm Kessil lamp for 3 h. The reaction mixture was concentrated and 1,4-dinitrobenzene was added as an internal standard

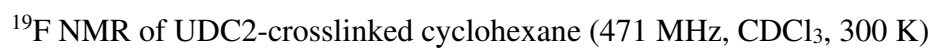
for quantification. The crude reaction mixture was then analyzed by  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectroscopy.

To obtain isolable quantities of the C-H insertion product, the protocol outlined above was set up 8 times in parallel (139 mg, 320  $\mu\text{mol}$  of UDC2 in total). Upon completion of the reactions, the crude mixtures were combined, concentrated, and purified by flash column chromatography (hexanes) to give the desired addition product (19.1 mg, 34.9  $\mu\text{mol}$ , 11%) as a colorless oil and a 1:1 mixture of diastereomers.  $R_f$  (hexanes): 0.61;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.38 (4 H, m,  $\text{H}_9$ ), 7.23 – 7.14 (4 H, m,  $\text{H}_8$ ), 3.02 (2 H, p,  $J = 10.1$  Hz,  $\text{H}_2$ ), 2.04 – 1.88 (4 H, m), 1.81 – 1.72 (2 H, m), 1.68 – 1.58 (4 H, m), 1.47 (2 H, d,  $J = 12.7$  Hz), 1.36 – 1.24 (2 H, m), 1.21 – 1.03 (6 H, m), 0.80 (2 H, qd,  $J = 12.1, 3.4$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  136.7 (4 C,  $\text{C}_{10}$ ), 134.5 (2 C, q,  $J = 2.7$  Hz,  $\text{C}_7$ ), 130.1 (4 C,  $\text{C}_9$ ), 127.5 (4 C,  $\text{C}_8$ ), 127.17 (2 C, q,  $J = 281.5$  Hz,  $\text{C}_1$ ), 55.9 (2 C, q,  $J = 25.1$  Hz,  $\text{C}_2$ ), 38.7 (2 C,  $\text{C}_3$ ), 31.6 (2 C,  $\text{C}_4$ ), 30.8 (2 C,  $\text{C}_4'$ ), 26.3 (2 C,  $\text{C}_{5/6}$ ), 26.2 (2 C,  $\text{C}_{5/6}$ ), 26.1 (2 C,  $\text{C}_{5/6}$ );  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.45, -62.47; HRMS ASAP+ found  $[\text{M}+\text{H}]^+$  547.1914,  $\text{C}_{28}\text{H}_{33}\text{S}_2\text{F}_6^+$  requires 547.1928; IR (film)  $\nu_{\text{max}}$ : 2926, 2854, 1493, 1251, 1135, 1098, 813, 731, 518.

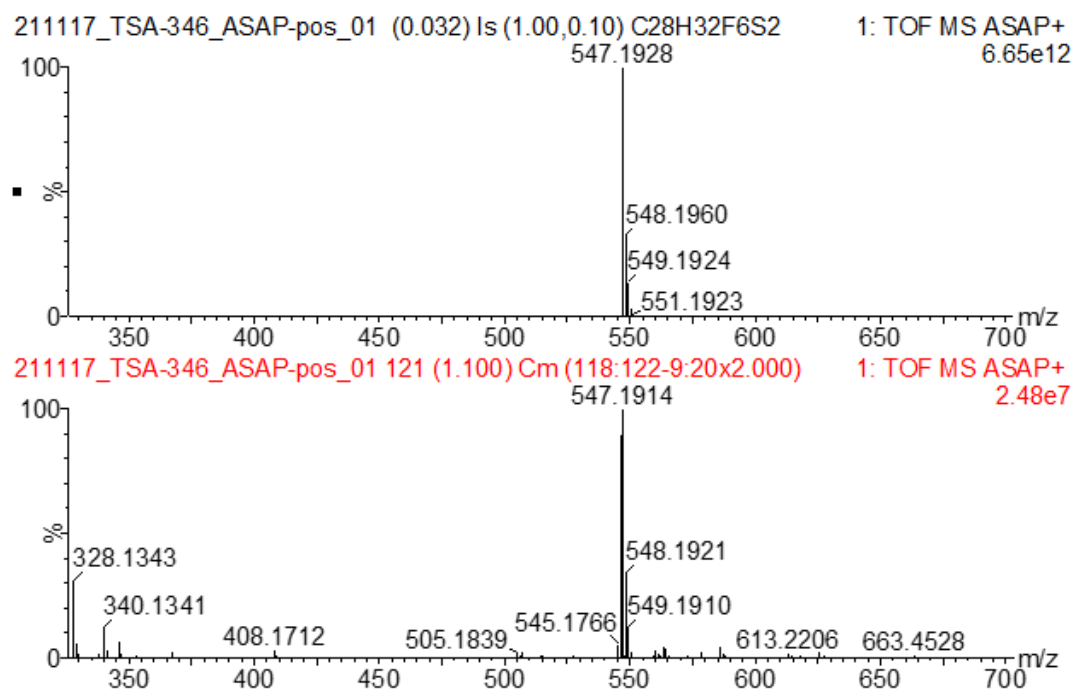
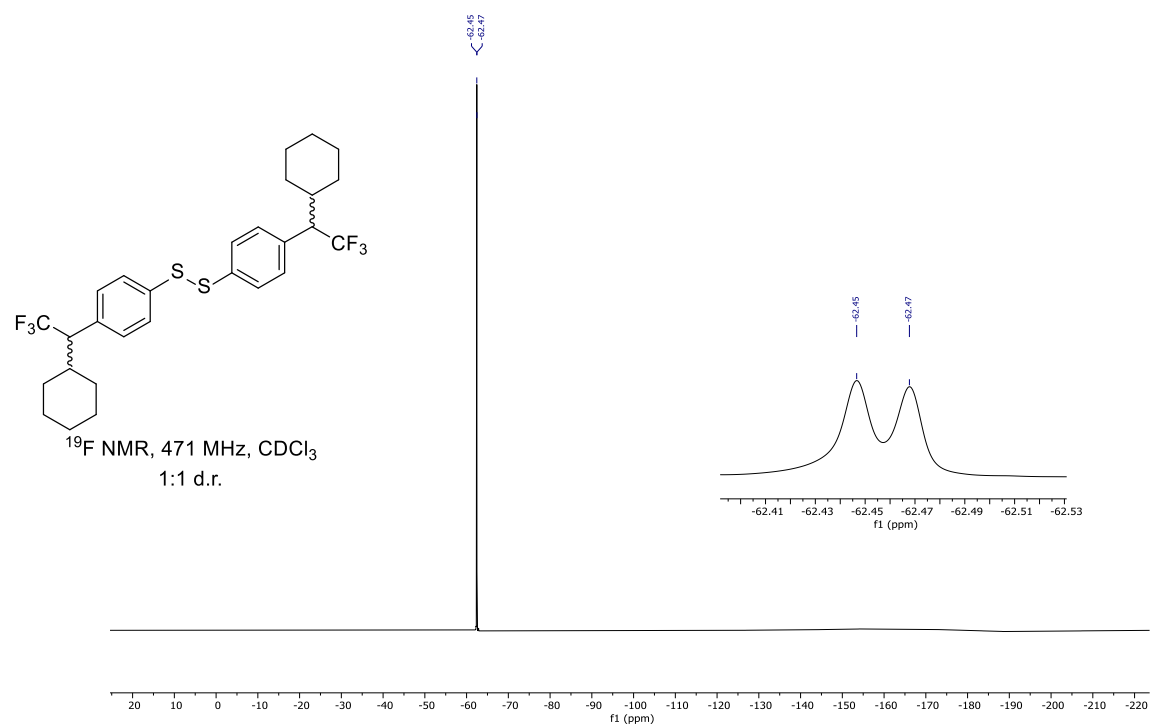
#### Thermal Protocol

A pressure tube was charged with (8.2 mg, 20.0  $\mu\text{mol}$ ) under nitrogen and cyclohexane (2 ml) was added. The tube was sealed and heated to 130  $^\circ\text{C}$  (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. 1,4-Dinitrobenzene was added as an internal standard for quantification and the crude reaction mixture was then analyzed by  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectroscopy.

$^1\text{H}$  NMR of UDC2-crosslinked cyclohexane (500 MHz,  $\text{CDCl}_3$ , 300 K)

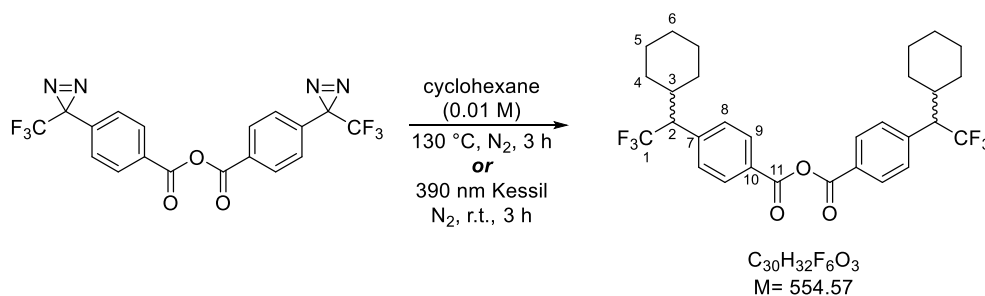






**Figure D5.** Mass spectrum revealing products of UDC2 thermal-initiated C-H insertion for cyclohexane.

UDC3



### UV-Irradiation protocol

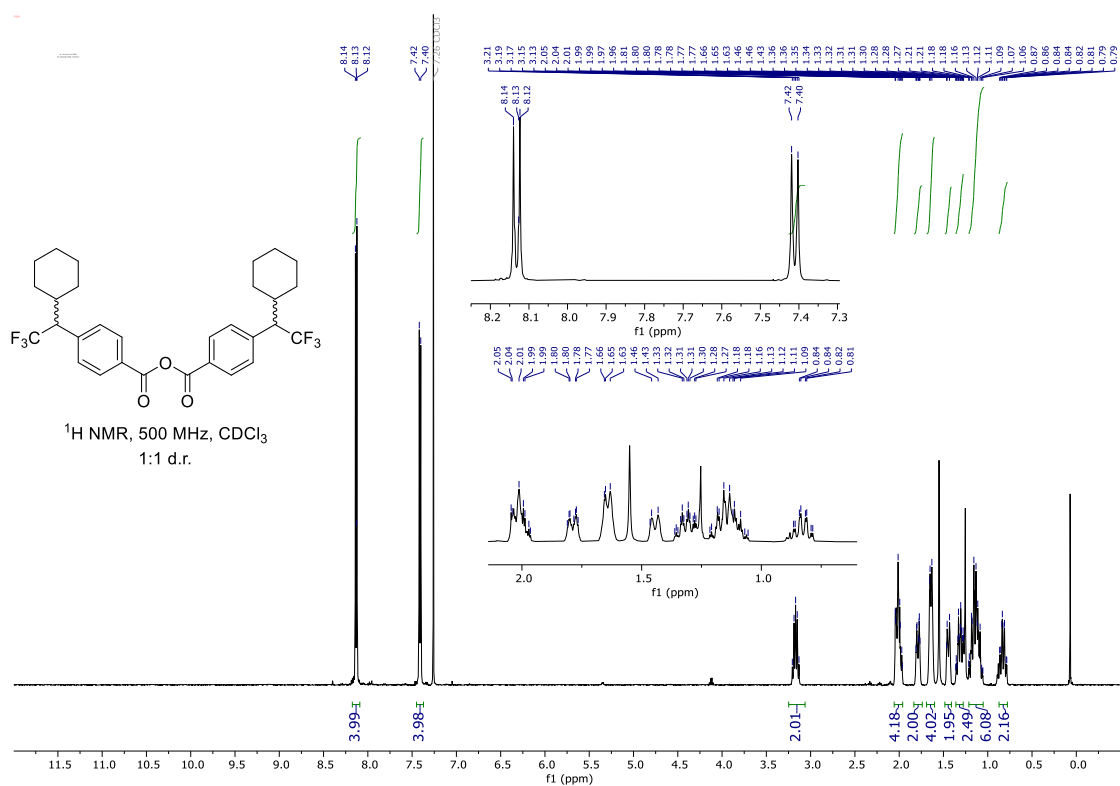
A 1.5 dram vial was charged with UDC3 (8.9 mg, 20.0  $\mu\text{mol}$ ) under nitrogen and cyclohexane (2 mL) was added. The vial was sealed tightly and irradiated with a 390 nm Kessil lamp for 3 h. The reaction mixture was concentrated and 1,4-dinitrobenzene was added as an internal standard for quantification. The crude reaction mixture was then analyzed by  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectroscopy.

### Thermal Protocol

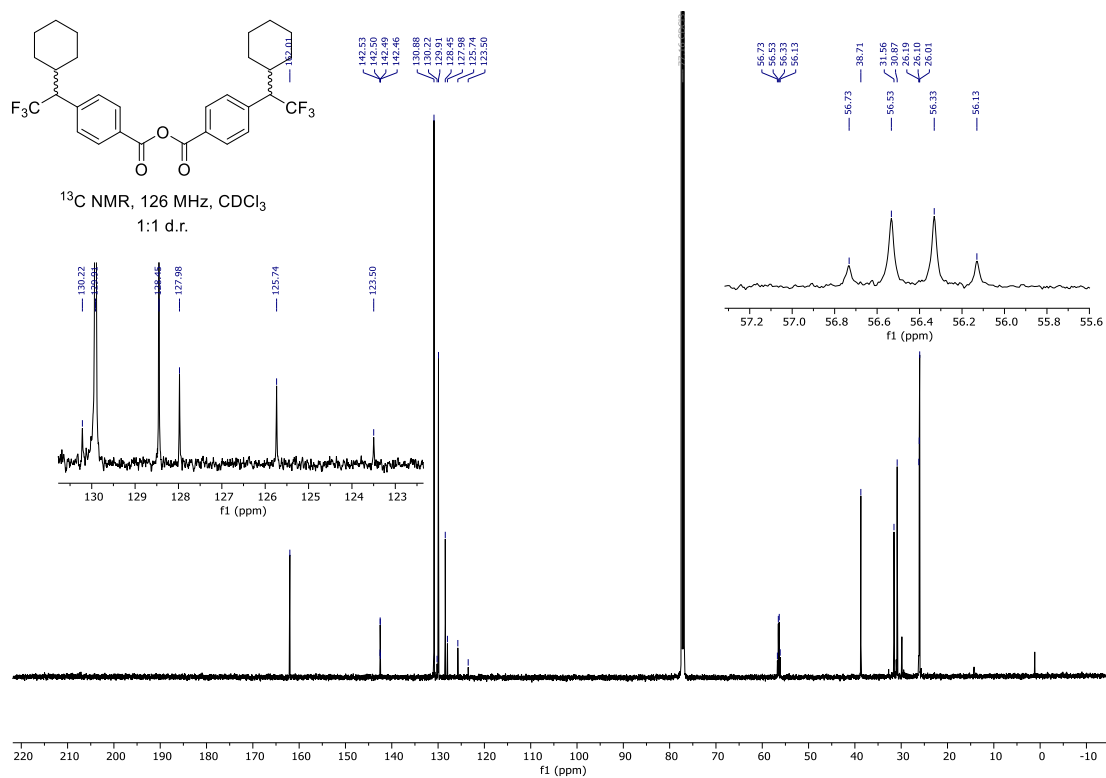
A pressure tube was charged with (102 mg, 230.0  $\mu\text{mol}$ ) under nitrogen and cyclohexane (23 mL) was added. The tube was sealed and heated to 130  $^{\circ}\text{C}$  (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude reaction mixture was purified by column chromatography (1% ethyl acetate in hexanes containing 1% (v/v) HCl (2 M in  $\text{Et}_2\text{O}$ ), to 2.5% ethyl acetate in hexanes containing 1% (v/v) HCl (2 M in  $\text{Et}_2\text{O}$ )) to give the title compound as a colorless oil (9.1 mg, 21.0  $\mu\text{mol}$ , 9%) as a 1:1 mixture of diastereomers.  $R_f$  (3% ethyl acetate in hexanes + 1% (v/v) HCl (2 M in  $\text{Et}_2\text{O}$ )): 0.36;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 – 8.11 (4 H, m,  $\text{H}_9$ ), 7.41 (4 H, d,  $J = 8.3$  Hz,  $\text{H}_8$ ), 3.17 (2 H, p,  $J = 9.8$  Hz,  $\text{H}_2$ ), 2.06 – 1.95 (4 H, m), 1.83 – 1.75 (2 H, m), 1.68 – 1.60 (4 H, m), 1.48 – 1.41 (2 H, m), 1.32 (2 H, qt,  $J = 12.5, 2.9$  Hz), 1.22 – 1.05 (6 H, m), 0.83 (2 H, qd,  $J = 12.4, 3.4$  Hz);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (2 C,  $\text{C}_{11}$ ), 142.49 (2 C, q,  $J = 2.8$  Hz,  $\text{C}_7$ ),

130.9 (4 C, C<sub>9</sub>), 129.9 (4 C, C<sub>8</sub>), 128.5 (2 C, C<sub>10</sub>), 126.9 (2 C, q,  $J = 281.6$  Hz, C<sub>1</sub>), 56.4 (2 C, q,  $J = 25.1$  Hz, C<sub>2</sub>), 38.7 (2 C, C<sub>3</sub>), 31.6 (2 C, C<sub>4</sub>), 30.9 (2 C, C<sub>4'</sub>), 26.2 (2 C, C<sub>5/6</sub>), 26.1 (2 C, C<sub>5/6</sub>), 26.0 (2 C, C<sub>5/6</sub>); <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -62.12, -62.14; HRMS ESI+ found [M+Na]<sup>+</sup> 577.2161, C<sub>30</sub>H<sub>32</sub>O<sub>3</sub>NaF<sub>6</sub><sup>+</sup> requires 577.2153; IR (film)  $\nu_{\text{max}}$ : 2934, 2857, 1790, 1728, 1612, 1252, 1221, 1003, 707.

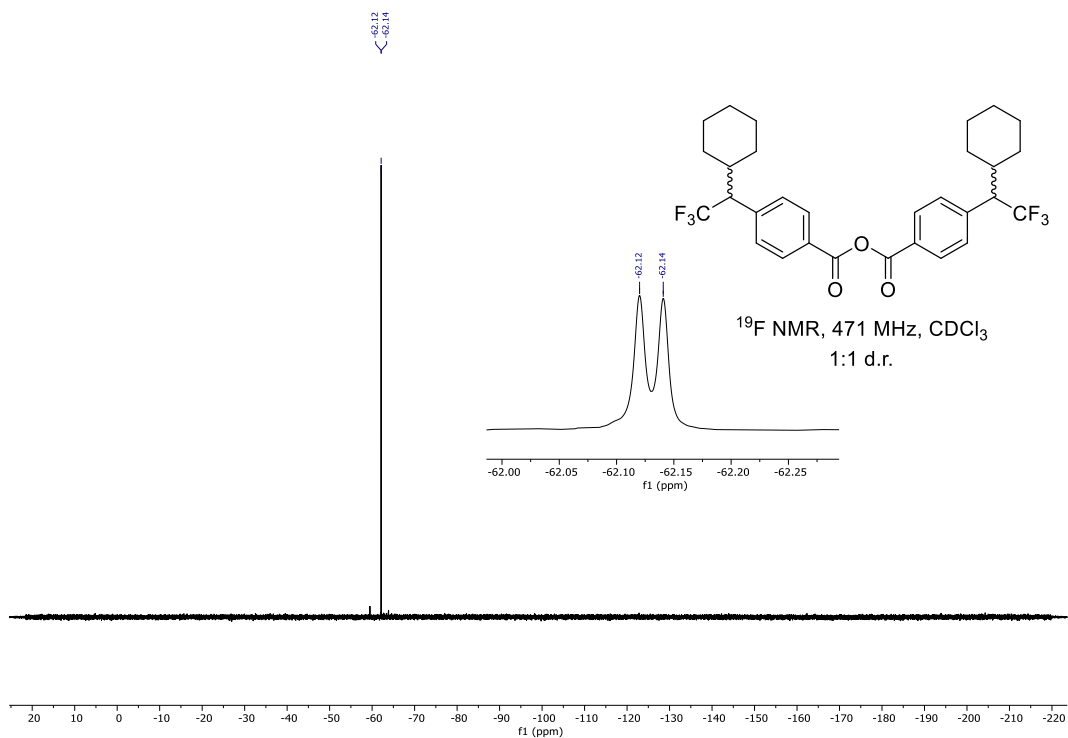
<sup>13</sup>C NMR of UDC3-crosslinked cyclohexane (126 MHz, CDCl<sub>3</sub>, 300 K)

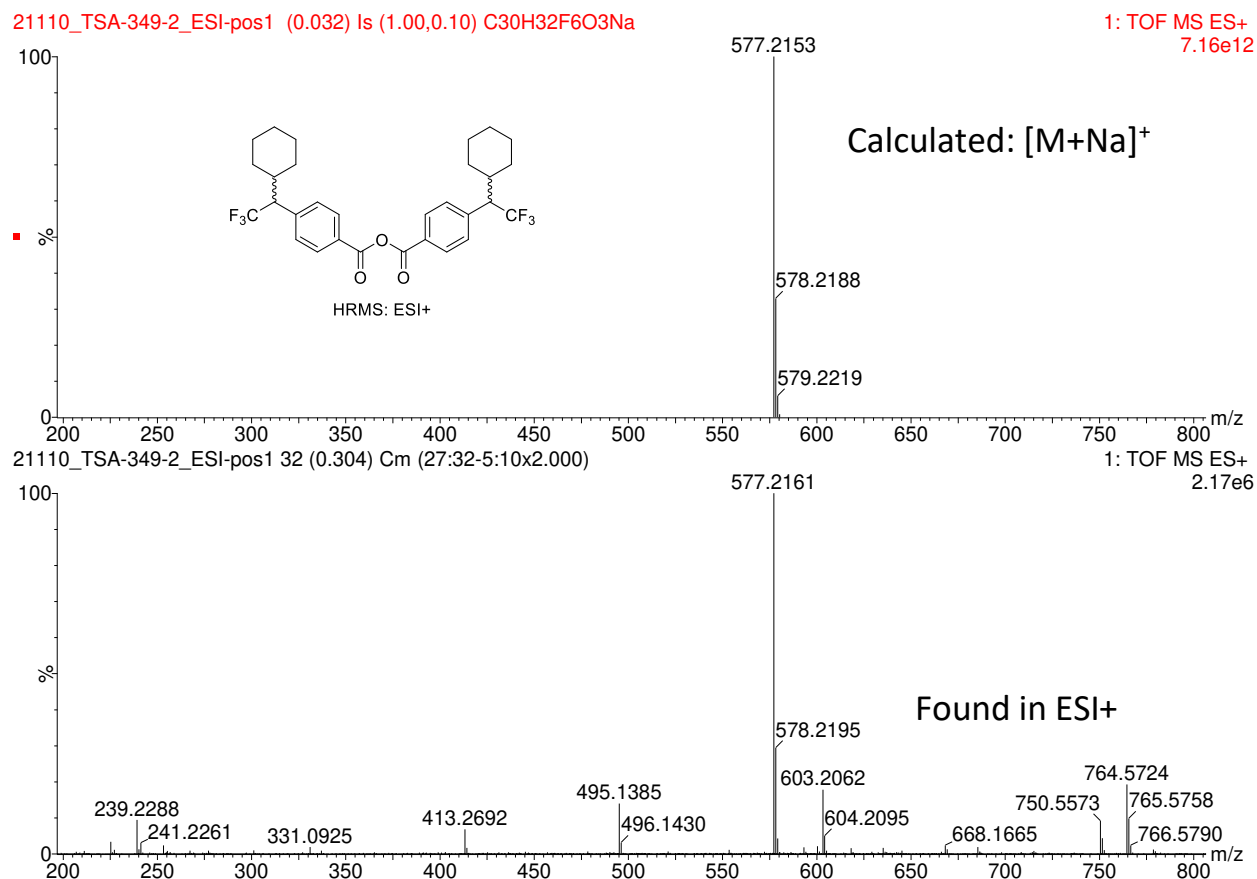


<sup>13</sup>C NMR of UDC3-crosslinked cyclohexane (126 MHz, CDCl<sub>3</sub>, 300 K)



$^{19}\text{F}$  NMR of UDC3-crosslinked cyclohexane (471 MHz,  $\text{CDCl}_3$ , 300 K)

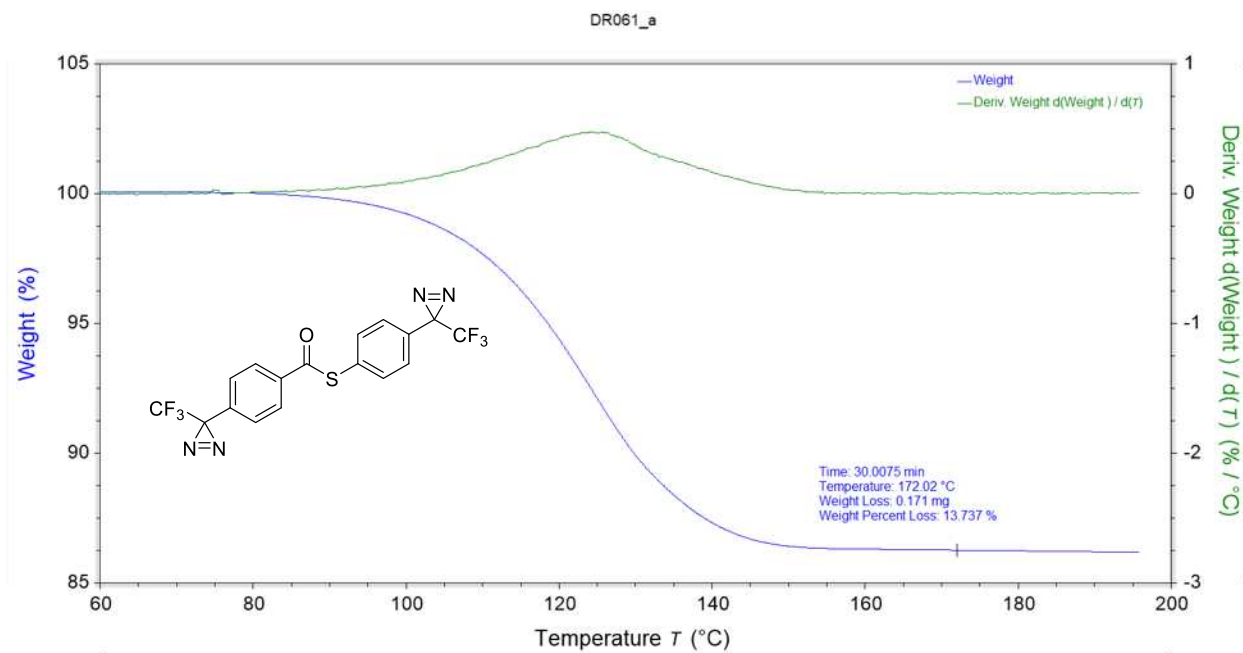




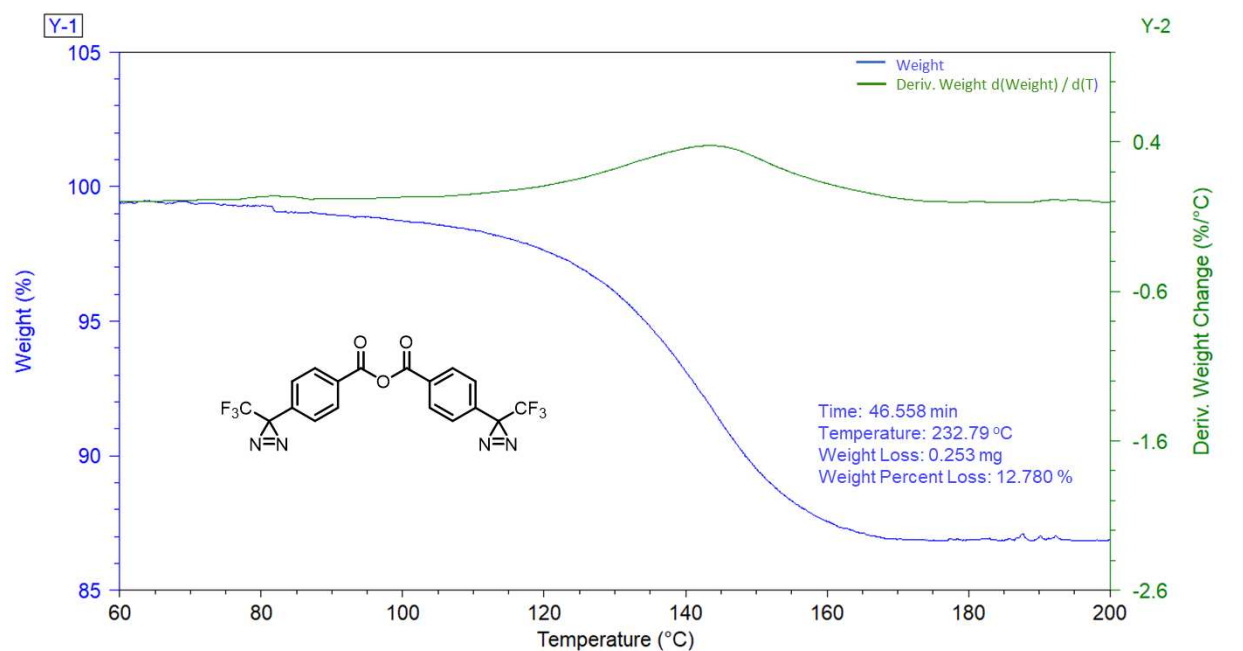
**Figure D6.** Mass spectrum revealing products of UDC3 thermal-initiated C-H insertion for cyclohexane.

### Carbene Formation and N<sub>2</sub> Loss by TGA

The singular thermal degradation profile of UDC2 was not investigated, as mass loss approaching 100-110 °C led to a pungent gas escaping the TGA equipment, and thus the sample was deemed not suitable for continuing the experiment.



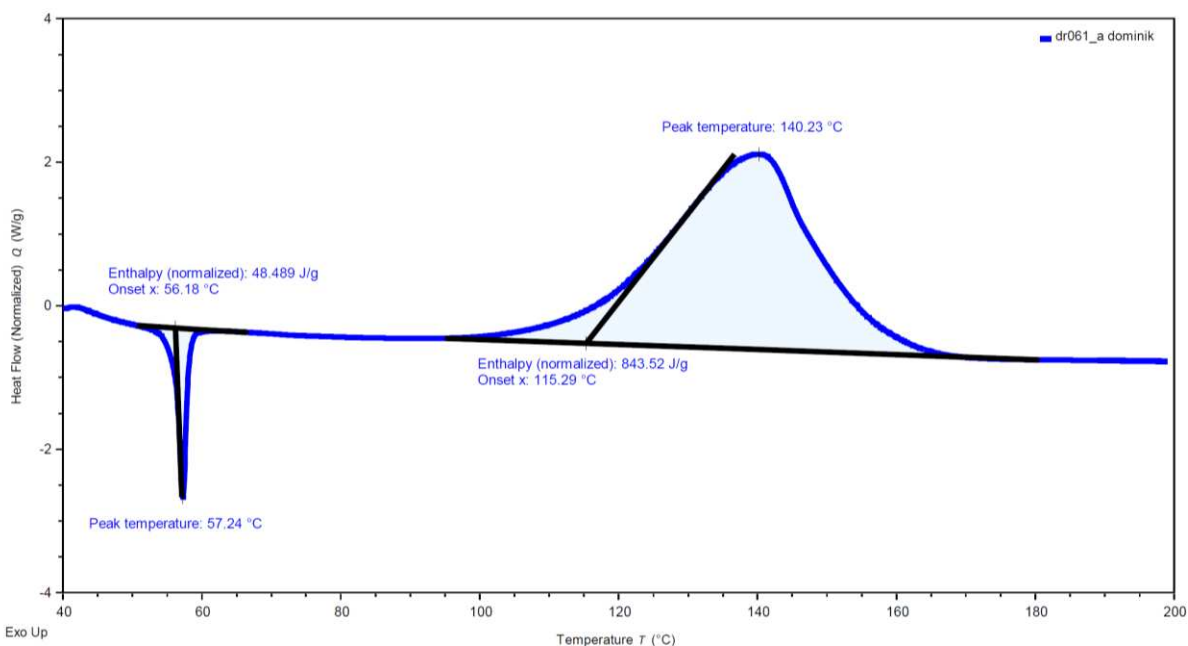
**Figure D7.** Weight percent loss [loss of 2 molecules of nitrogen] upon heating UDC1. Calc: 13.0 %, found 13.74 %. (n = 1).



**Figure D8.** Weight percent loss [loss of 2 molecules of nitrogen] upon heating UDC3. Calc: 12.7 %, found 12.78 %. (n = 1).

**Yoshida's Correlations by DSC:**

Calculations for UDC1, 2, and 3 explosivity and shock sensitivity. Note, a positive SS and EP value signify explosivity and shock sensitivity:



**Figure D9.** DSC trace for UDC1. Sample size: 0.92 mg; 40 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

$$\text{Shock sensitivity (SS)} = \log ( Q_{\text{DSC}} ) - 0.72 \times \log ( T_{\text{onset}} - 25 ) - 0.98$$

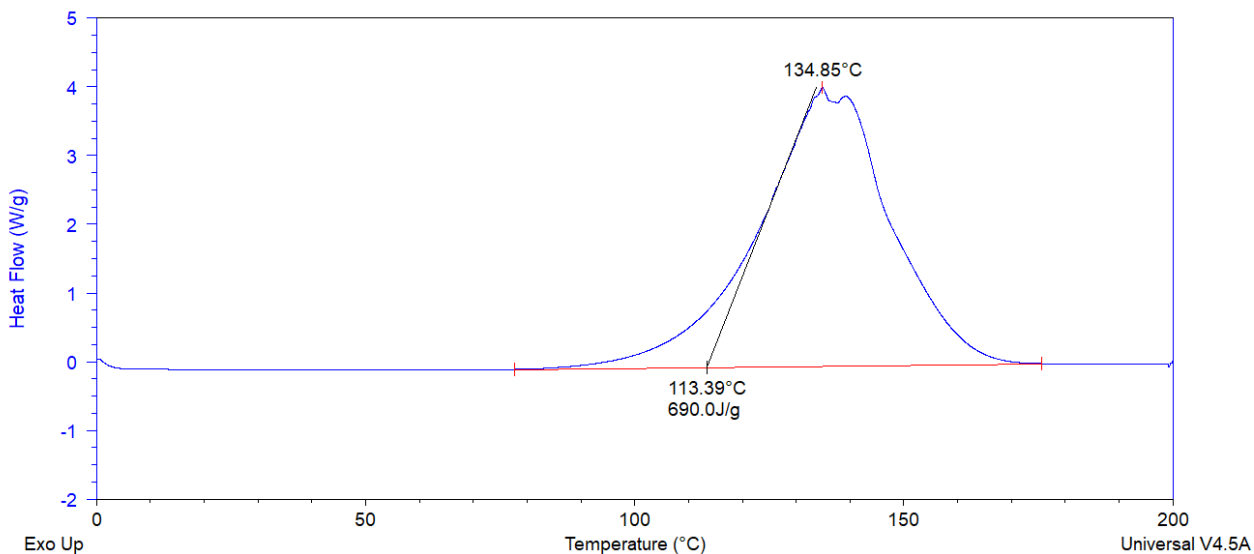
$$\text{Explosive propagation (EP)} = \log ( Q_{\text{DSC}} ) - 0.38 \times \log ( T_{\text{onset}} - 25 ) - 1.67$$

$$\text{SS}_{(1)} = -0.084$$

$$\text{EP}_{(1)} = -0.109$$

In case of  $\text{SS} < 0$  no shock sensitivity is expected. In case of  $\text{EP} < 0$  no explosion propagation is expected.

Compound UDC1 is **NOT LIKELY** to be explosive or shock sensitive.



**Figure D10.** DSC trace for UDC2. Sample size: 10.11 mg; 0 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

$$\text{Shock sensitivity (SS)} = \log ( Q_{\text{DSC}} ) - 0.72 \times \log ( T_{\text{onset}} - 25 ) - 0.98$$

$$\text{Explosive propagation (EP)} = \log ( Q_{\text{DSC}} ) - 0.38 \times \log ( T_{\text{onset}} - 25 ) - 1.67$$

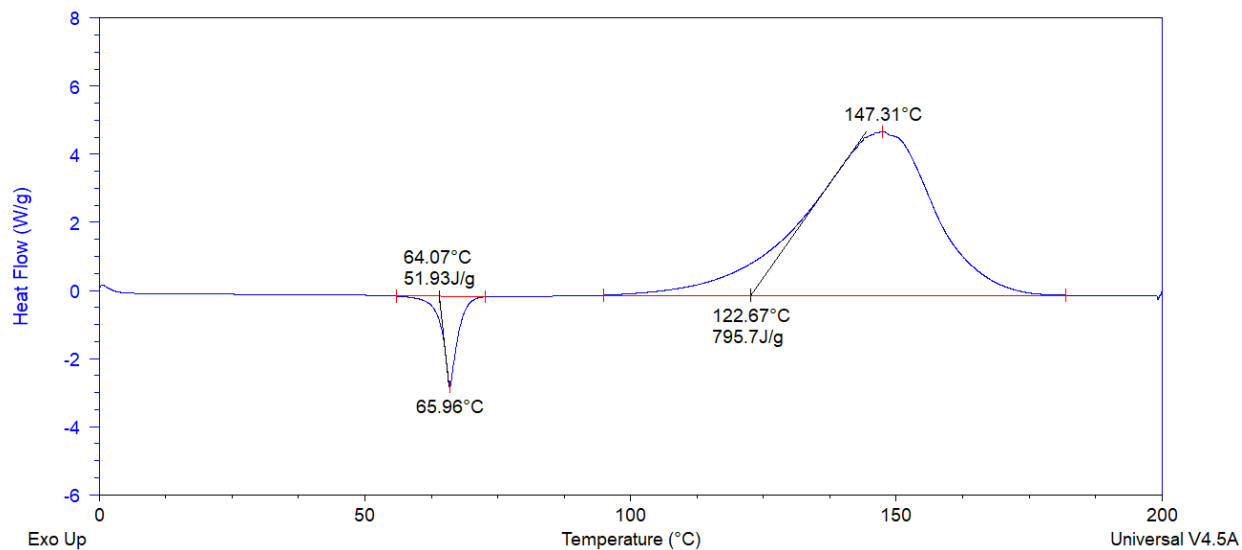
$$\text{SS}_{(1)} = -0.164$$

$$\text{EP}_{(1)} = -0.193$$

In case of  $\text{SS} < 0$  no shock sensitivity is expected. In case of  $\text{EP} < 0$  no explosion propagation is expected.

Compound UDC2 is **NOT LIKELY** to be explosive or shock sensitive.





**Figure D11.** DSC trace for UDC3. Sample size: 5.20 mg; 0 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

$$\text{Shock sensitivity (SS)} = \log ( Q_{\text{DSC}} ) - 0.72 \times \log ( T_{\text{onset}} - 25 ) - 0.98$$

$$\text{Explosive propagation (EP)} = \log ( Q_{\text{DSC}} ) - 0.38 \times \log ( T_{\text{onset}} - 25 ) - 1.67$$

$$\text{SS}_{(1)} = -0.134$$

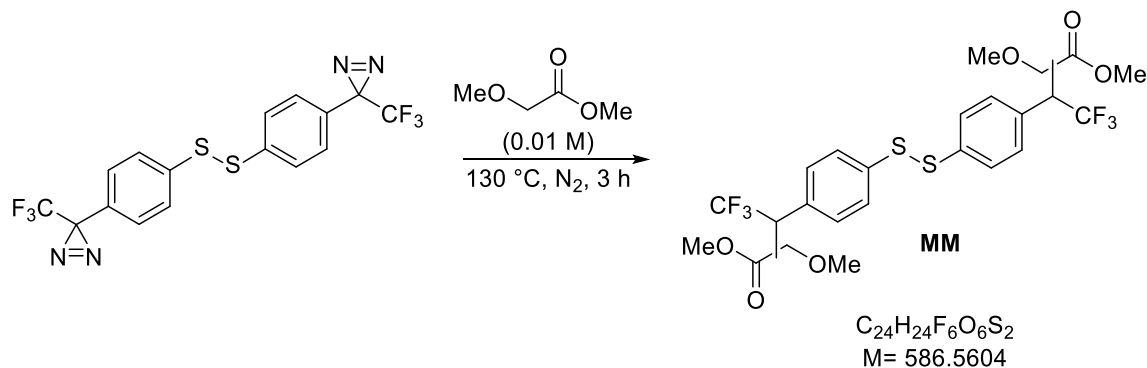
$$\text{EP}_{(1)} = -0.147$$

In case of  $\text{SS} < 0$  no shock sensitivity is expected. In case of  $\text{EP} < 0$  no explosion propagation is expected.

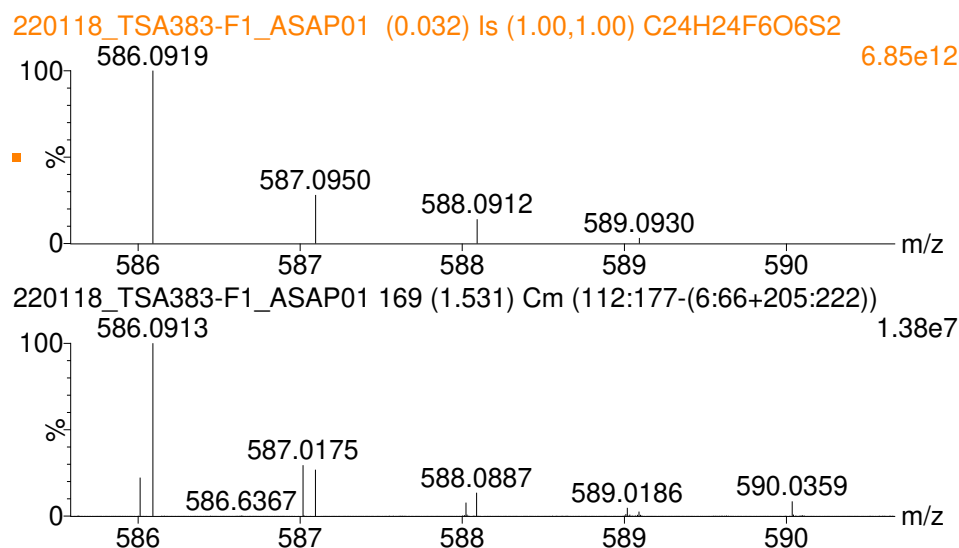
Compound UDC3 is **NOT LIKELY** to be explosive or shock sensitive.

## Molecular Trials for Blend Compatibilization and Mixing

Crosslinking of methyl methoxyacetate by UDC2 (reference compound)

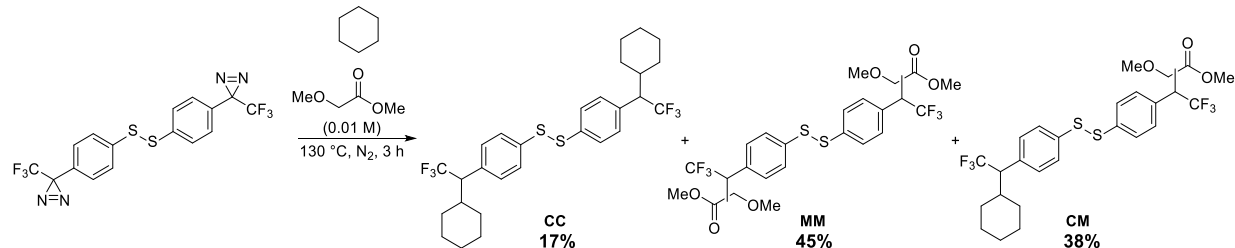


A pressure tube was charged with (17.4 mg, 40.0  $\mu\text{mol}$ ) of **UDC2** under nitrogen and methyl methoxyacetate (4.0 ml) was added. The tube was sealed and heated to 130  $^\circ\text{C}$  (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude reaction mixture consisted of a complex mixture of regio- and diastereomers. The crude mixture was purified by preparative thinlayer chromatography (30% ethyl acetate in hexanes). All fractions were analyzed by  $^1\text{H}$ -,  $^{19}\text{F}$ -NMR, and HRMS. The desired product (MM) was unambiguously identified by HRMS: ASAP+ found  $[\text{M}]^+ 586.0913$ ,  $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}_2\text{F}_6^+$  requires 586.0919.



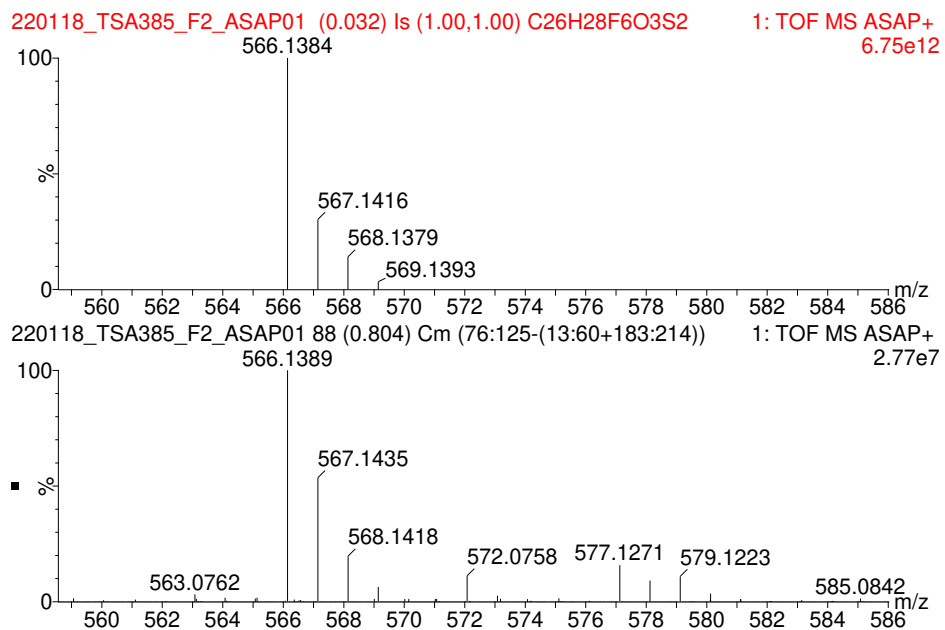
**Figure D12.** Mass spectrum revealing products of UDC2 thermal-initiated C-H insertion for methyl methoxyacetate.

## Crosslinking of cyclohexane/methyl methoxyacetate by UDC2

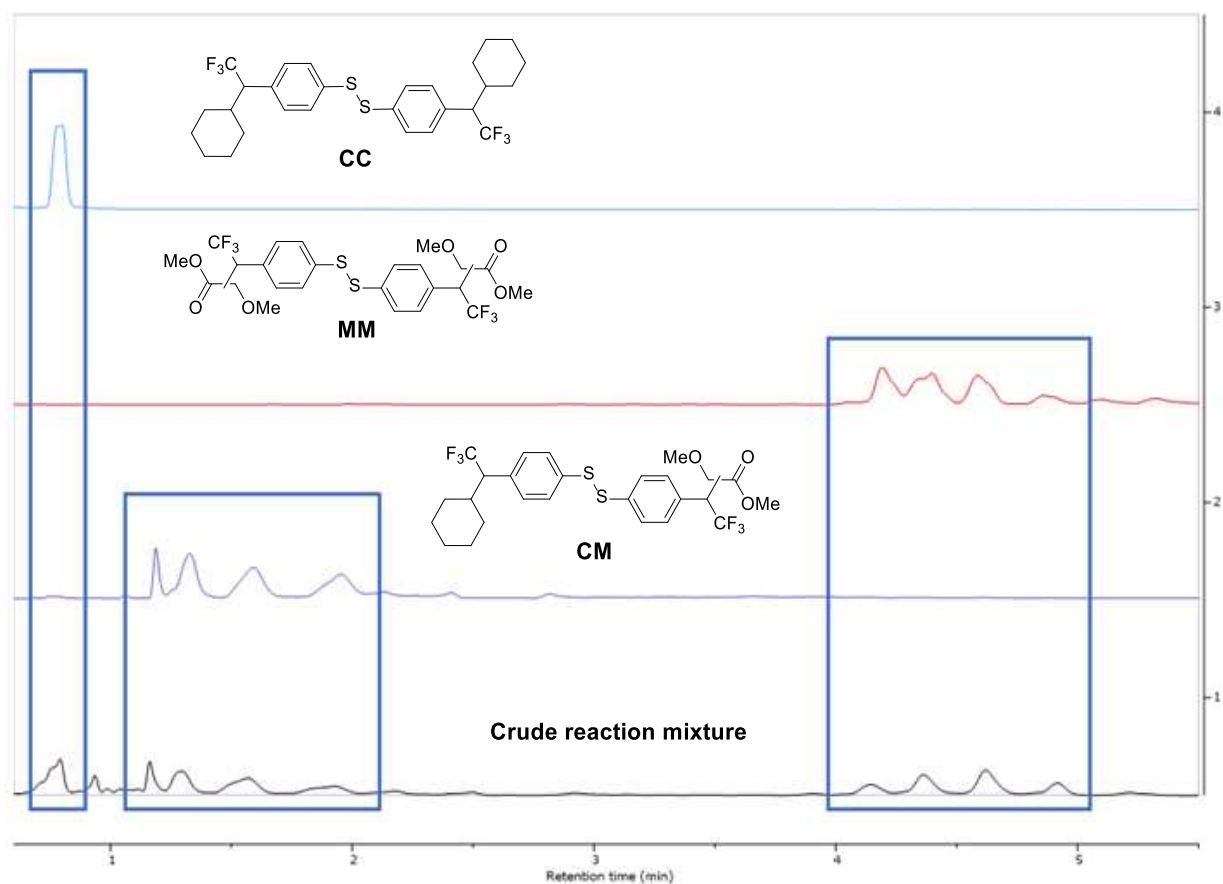


A pressure tube was charged with (17.4 mg, 40.0  $\mu\text{mol}$ ) of **UDC2** under nitrogen. Cyclohexane (2.0 mL) and methyl methoxyacetate (4.0 mL) were added. The tube was sealed and heated to 130 °C (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude mixture was purified by preparative thinlayer chromatography (20% ethyl acetate in hexanes). All fractions were analyzed by  $^1\text{H}$ -,  $^{19}\text{F}$ -NMR, and HRMS. The fractions containing the mixed-crosslinked product (**CM**) were unambiguously identified by HRMS: ASAP+ found  $[\text{M}]^+$  566.1389,  $\text{C}_{26}\text{H}_{28}\text{O}_3\text{S}_2\text{F}_6^+$  requires 566.1384.

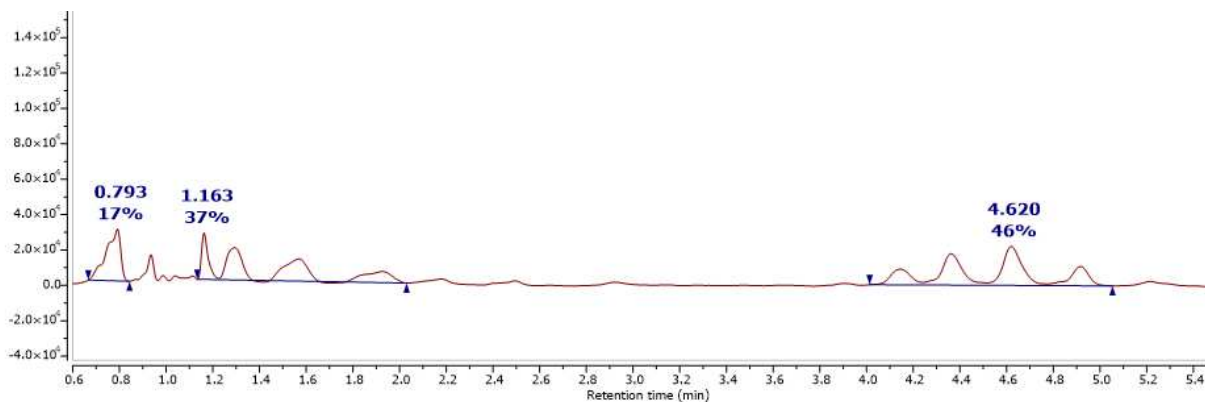
The reaction protocol outlined above was repeated and the crude reaction mixture was analyzed by SFC-MS using authentic samples of **CC**, **MM**, and **CM** (see above) as reference compounds. (SFC conditions: Water BEH (Ethylene Bridged Hybrid) column, gradient elution, 0% MeCN to 5% MeCN in  $\text{CO}_2$  over 10 min, 1.2 mL/min, 40 °C). The following relative yields were determined: **CC**: 17%, **MM**: 45% and **CM**: 38%.



**Figure D13.** Mass spectrum revealing intermolecular-mixed products of UDC2 thermal-initiated C-H insertion for cyclohexane and methyl methoxyacetate.

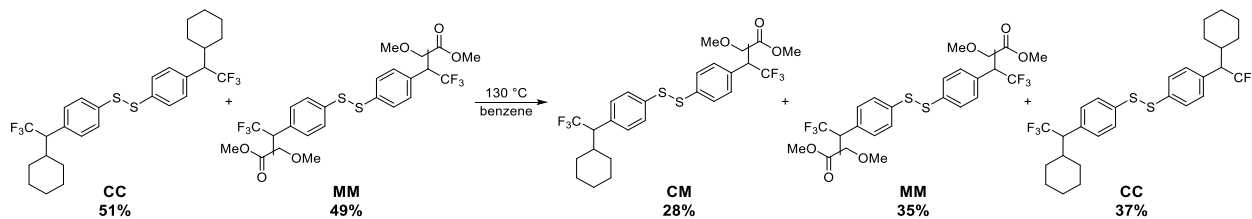


**Figure D14.** SFC Chromatograms of cyclohexane/methyl methoxyacetate mixed crosslinking experiments.

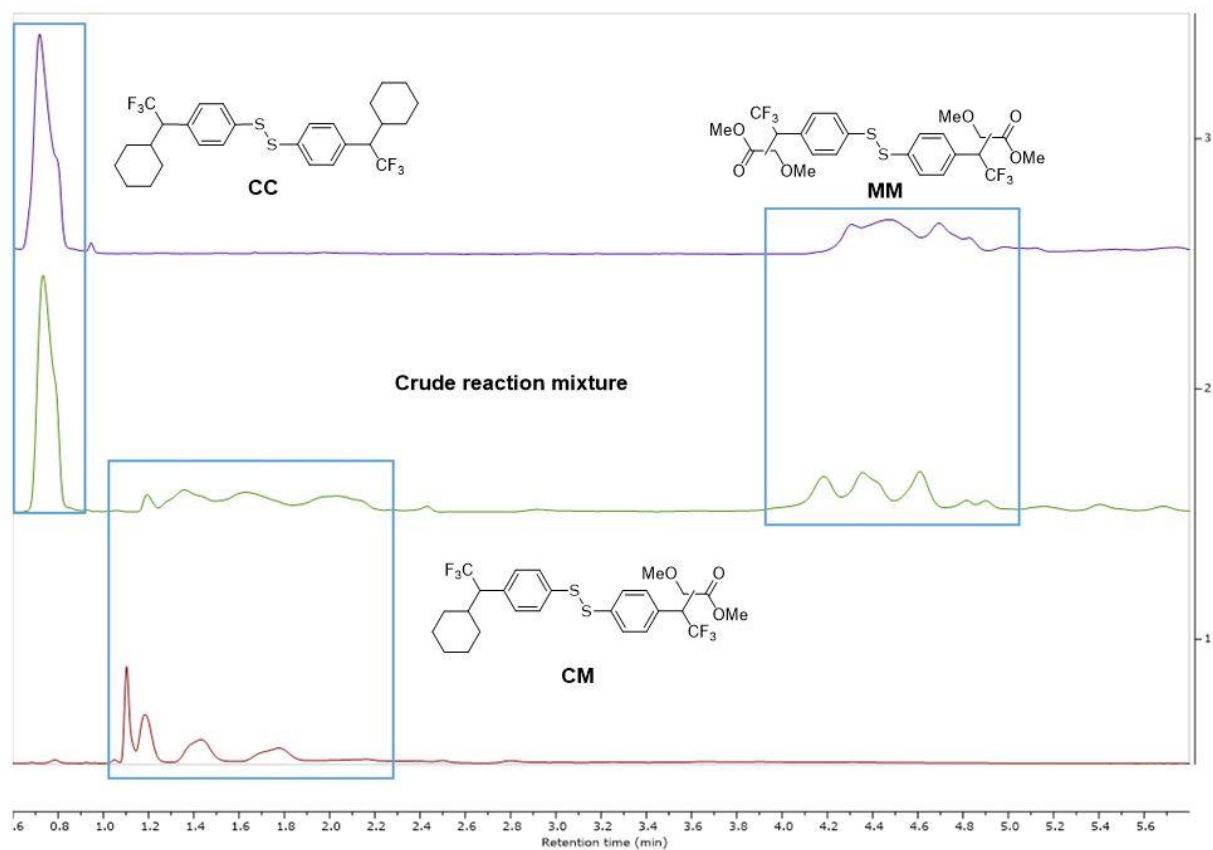


**Figure D15.** Quantification of cyclohexane/methyl methoxyacetate mixed crosslinking experiments by SFC-MS.

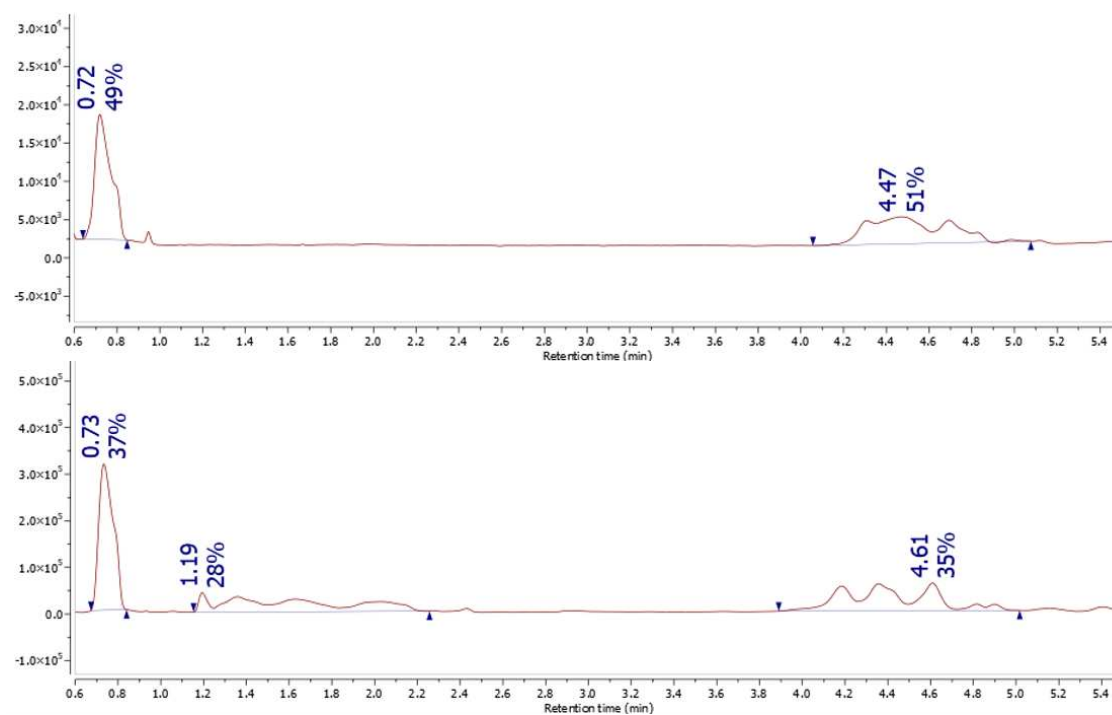
#### Disulfide exchange experiments



A small pressure tube was charged with **CC** (5.0 mg, 9.15  $\mu\text{mol}$ ) and **MM** (5.6 mg, 9.15  $\mu\text{mol}$ ) benzene (0.1 mL, 0.09 M) was added under argon. The vessel was sealed and heated to 130 °C for 24 h. The reaction mixture was concentrated and analyzed by SFC-MS. The following relative product distribution was determined: **CC**: 37%, **MM**: 35% and **CM**: 28%.



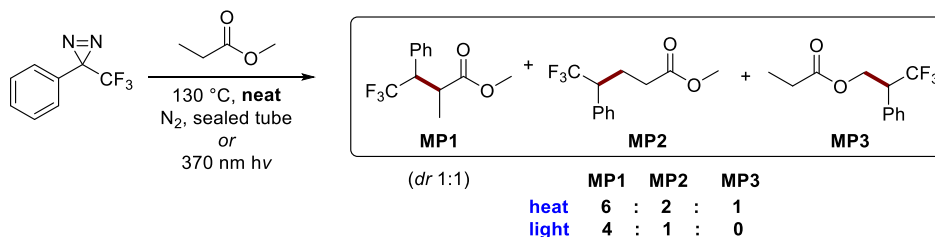
**Figure D16.** SFC Chromatograms of disulfide-metathesis experiments.



**Figure D17.** Quantification of disulfide-metathesis experiments by SFC-MS.

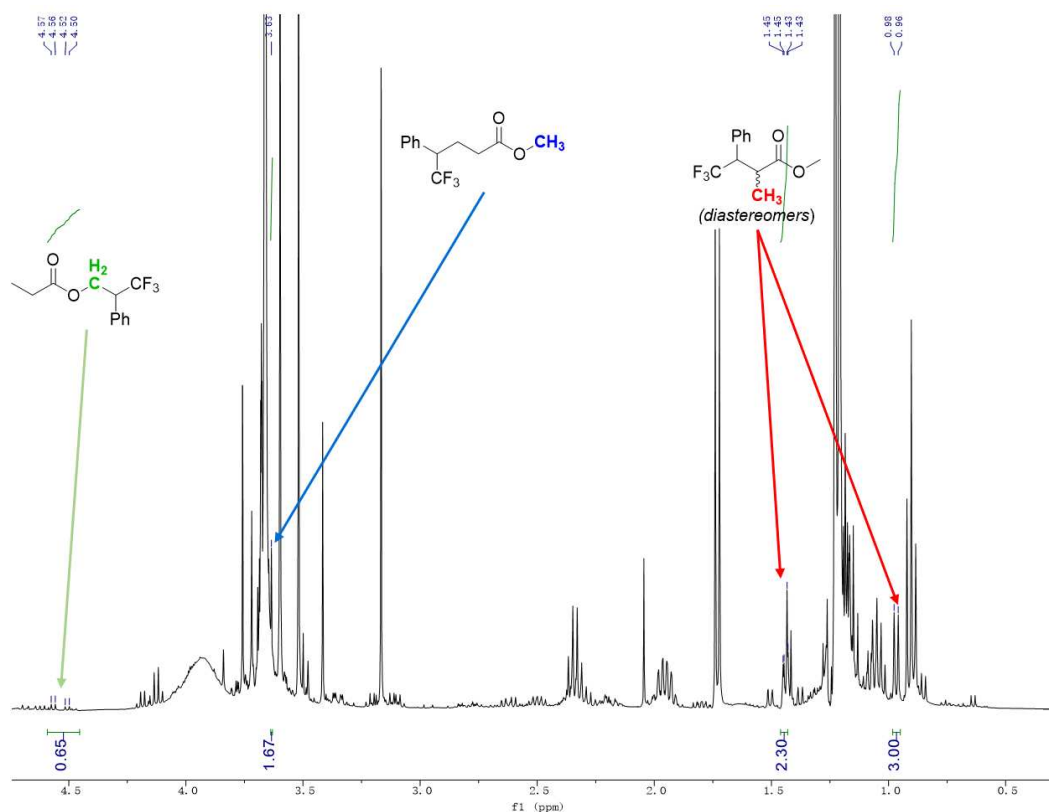
### Determination of C-H insertion selectivity for polyesters

Methyl propionate was used as a model substrate to investigate the regioselectivity of the C-H insertion of aryl-trifluoro diazirines into polyesters.



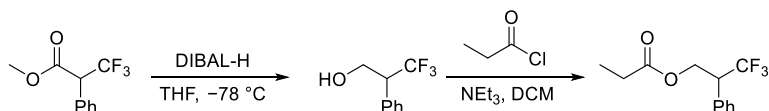
A small pressure tube was charged with commercially available 3-phenyl-3-(trifluoromethyl)-3H-diazirine (7.2  $\mu$ l, 7.5 mg, 40.0  $\mu$ mol) and methyl propionate. (4.0 mL, 0.01 M). The vessel was sealed and heated to 130 °C for 3 h. The reaction mixture was cooled to room temperature and the volatiles were removed by rotary evaporation. The thus obtained crude mixture was analyzed by <sup>1</sup>H-NMR spectroscopy. **MP1**<sup>5</sup> and **MP2**<sup>6</sup> are literature-known compounds. An authentic sample of **MP3** was obtained through chemical synthesis (*vide infra*). Using NMR spectroscopic data and reference spectra, a ration of **MP1:MP2:MP3** of **6:2:1** was determined. This is in agreement with earlier literature reports<sup>7</sup> concluding preferential insertion of phenyl-trifluoro diazirine-derived carbenes into  $\alpha$ -carbonyl C-H bonds of ethyl acetate.





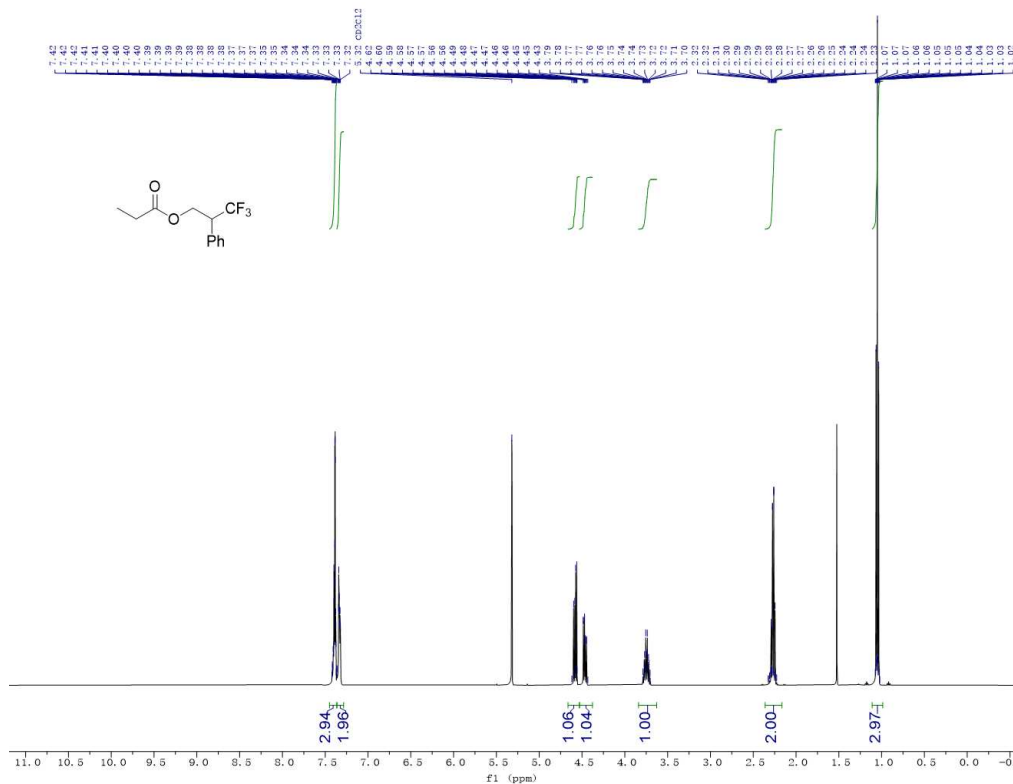
**Figure D18.** Quantification of disulfide-metathesis experiments by SFC-MS.

### Synthesis of 3,3,3-trifluoro-2-phenylpropyl propionate (MP3, reference compound)

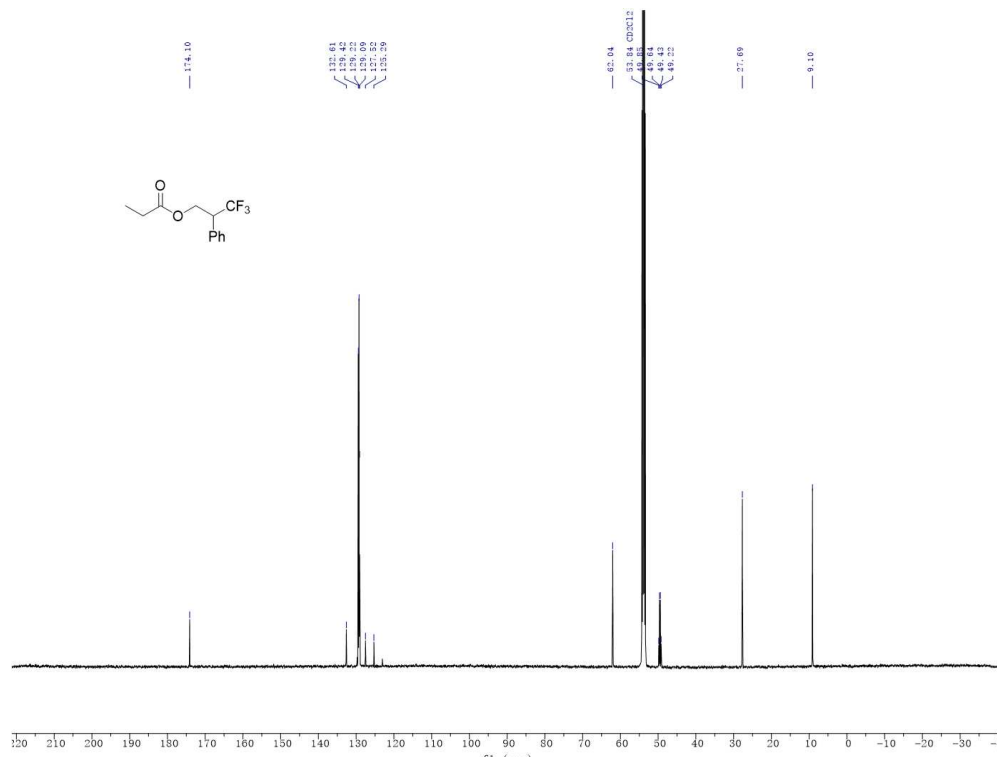


Methyl 3,3,3-trifluoro-2-phenylpropanoate (150 mg, 0.67 mmol, 1.0 equiv.) was dissolved in THF (5 mL) under nitrogen and cooled to  $-78^\circ\text{C}$ . DIBAL-H (1.0 M in DCM, 3.30 mL, 3.30 mmol, 5.0 equiv.) was added dropwise. The reaction mixture was allowed to stir at room temperature for 3h and then cooled to  $-78^\circ\text{C}$ . MeOH (0.48 mL) was added dropwise followed by aq. NaOH (1 M, 0.42 mL). The mixture was allowed to warm to room temperature and stirred overnight. The thus obtained suspension was filtered through Celite® to obtain crude 3,3,3-trifluoro-2-phenylpropan-1-ol which was directly used in the subsequent step.

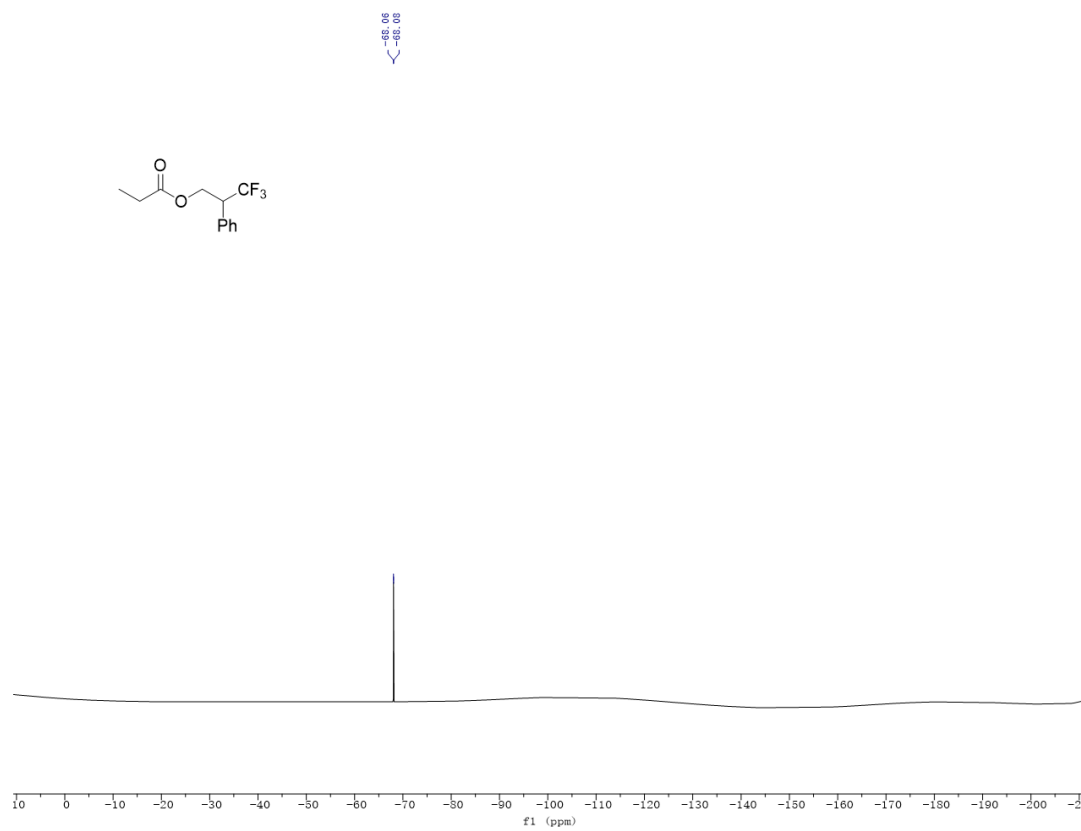
A 10 mL flask was charged with crude 3,3,3-trifluoro-2-phenylpropan-1-ol (126 mg, 0.66 mmol, 1.0 equiv.), CH<sub>2</sub>Cl<sub>2</sub> (3.3 mL, 0.2 M), and triethylamine (120 μL, 0.86 mmol, 1.3 equiv.). The reaction mixture was cooled to 0 °C and a solution of propionyl chloride (88 μL, 0.99 mmol, 1.5 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL) was added dropwise. The mixture was stirred at 0 °C for 40 min and then allowed to warm to room temperature overnight. The reaction was quenched by addition of sat. aq. NaHCO<sub>3</sub> (6.6 mL) and diluted with CH<sub>2</sub>Cl<sub>2</sub> (6.6 mL). The layers were separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 6.6 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash column chromatography (5% EtOAc in hexanes) to give 3,3,3-trifluoro-2-phenylpropyl propionate (55.8 mg, 34%) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 4.58 (dd, *J* = 11.6, 6.8 Hz, 1H), 4.50 – 4.43 (m, 1H), 3.75 (qt, *J* = 9.2, 6.9 Hz, 1H), 2.33 – 2.22 (m, 2H), 1.05 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 174.10, 132.61, 129.42, 129.22, 129.09, 126.41 (q, *J* = 280.0 Hz), 62.03 (d, *J* = 3.1 Hz), 49.53 (q, *J* = 26.6 Hz), 27.69, 9.10; <sup>19</sup>F NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -68.07 (d, *J* = 9.2 Hz).

<sup>1</sup>H NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (500 MHz, CD<sub>2</sub>Cl<sub>3</sub>, 300 K)

<sup>13</sup>C NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (126 MHz, CD<sub>2</sub>Cl<sub>3</sub>, 300 K)



$^{19}\text{F}$  NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (470 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K)



## **General Polymer Crosslinking Procedures/Considerations**

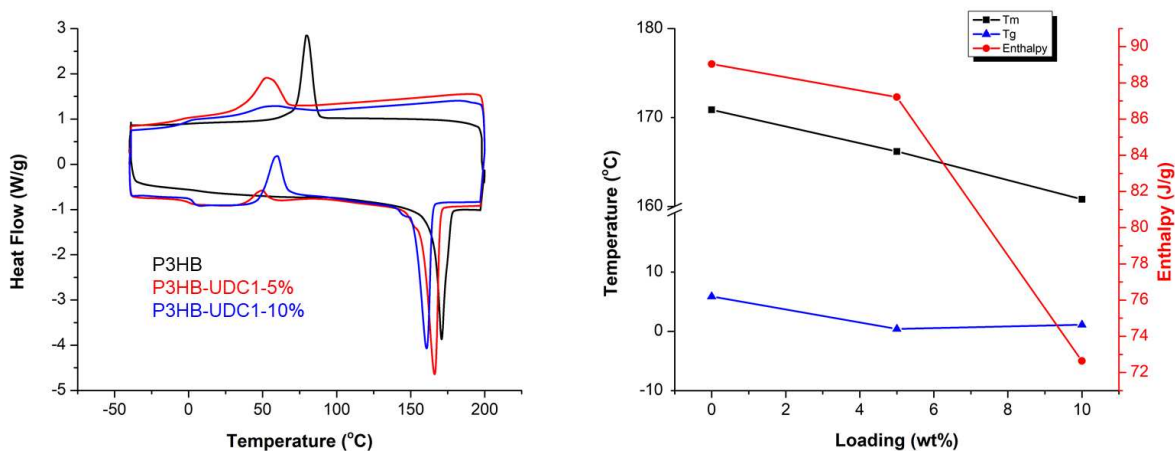
Typical polymer crosslinking by UDC1, 2, and 3 was performed on the dissolved target polymer in a suitable solvent (toluene or  $\text{CHCl}_3$ ) at or below 85 °C in a round bottom flask. Selected UDC (5 wt. %) was added to the polymer mixture in a toluene solution and allowed to mix briefly before being removed from heat and cooled in an ice bath (0 °C). Careful monitoring of temperature is critical to avoiding pre-mature UDC activation. Solvent was removed under vacuum, which yielded a white powder which was placed in a vacuum oven at 50 °C until a constant mass was achieved. The powder was moved into an oven at 125 °C for 3 h, during which time the polymer was crosslinked by activated carbenes, visibly confirmed by powder yellow tint. The following strategy, based on discussed thermal/solubility/performance results among similar literature precedent, was deemed effective for homogeneous dispersion of and crosslink by UDC. This procedure was the full requirement for UDCs 2 and 3. UDC1 CANs were further diluted (swelled) in heated (85 °C) toluene for 4 h. Then 3 % base catalyst (DBU) and free tetra-thiol source PETMP (equimolar to UDC) was added to the mixture and stirred briefly, after which the sample was cooled using an ice bath (0 °C) and the toluene was removed under vacuum at 60 °C. Polymer-UDC1 was then dried in a 60 °C vacuum oven overnight or until a constant mass was achieved. Dried samples were stored in sealed containers at ambient conditions. Small-scale initial trials were performed at 50 mg polymer loading, while large-scale trials were performed at 5.0 g polymer loading. Procedure deviations for blended samples are discussed in the supplemental materials and tables.

### **Example Homopolymer Small-Scale Crosslinking Procedure (0, 5, 10 wt. % UDC)**

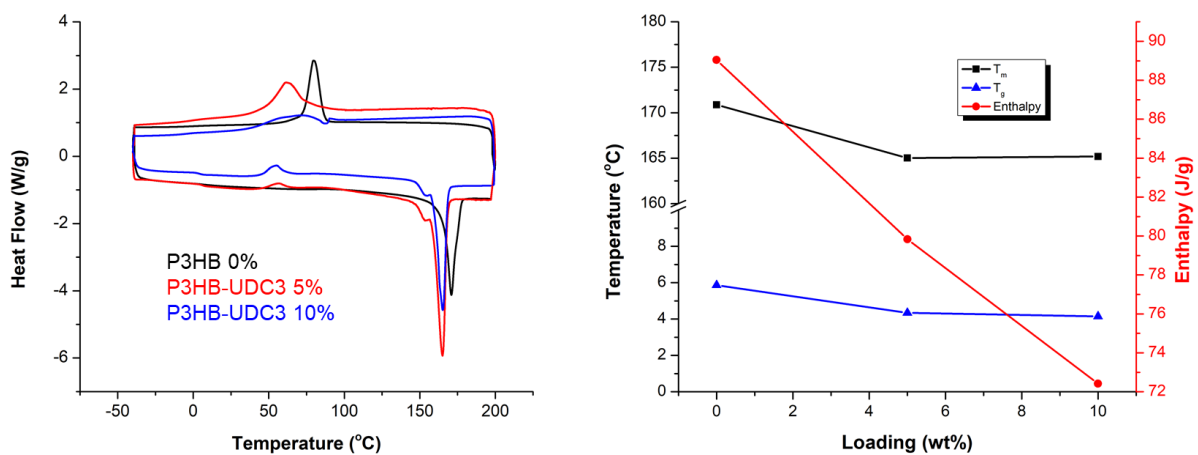
#### **Applicable Polyesters:**

PLA, P3HB

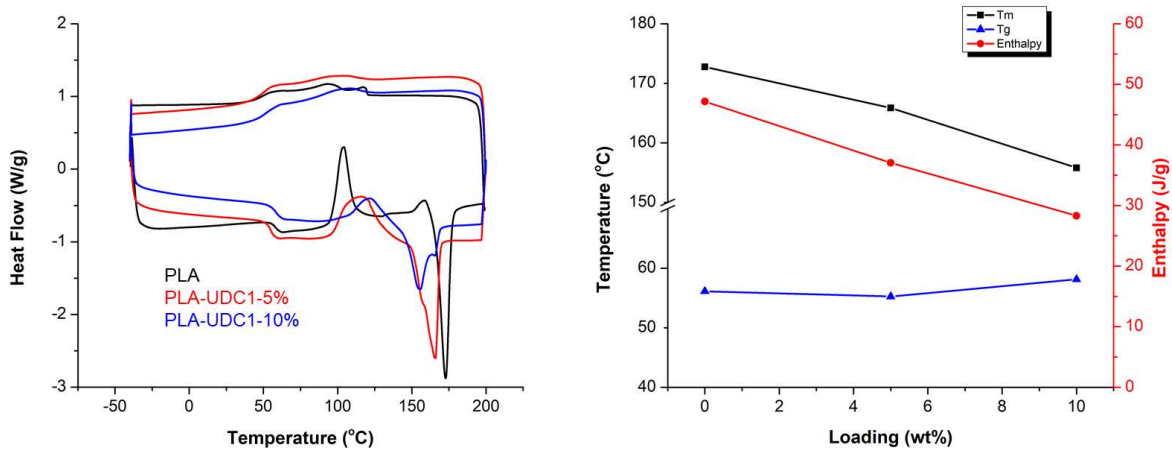
The specified polyester (50 mg) was mixed with chloroform (15 mL) in a 20 mL glass scintillation vial and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Upon full or near-full solubility, a solution of selected UDC (2.5 mg) dissolved in chloroform (1 mL) was added quantitatively to the stirring mixture. The UDC was briefly mixed into the polymer solution before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (50 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbenes. Crosslinked polymers appeared light yellow, a visual signal of successful installment.



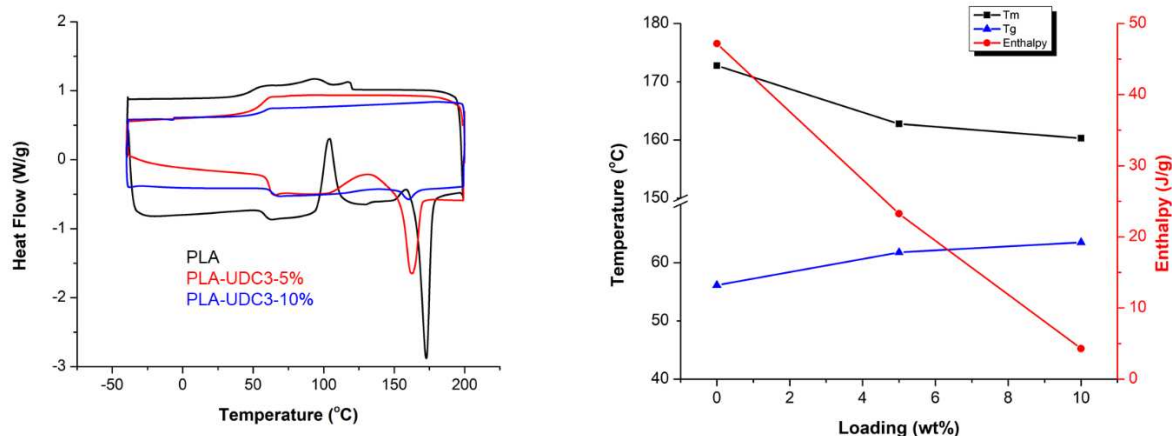
**Figure D19.** Thermal behavior and trends for P3HB at 0, 5, and 10 wt.% loading of UDC1.



**Figure D20.** Thermal behavior and trends for P3HB at 0, 5, and 10 wt.% loading of UDC3.



**Figure D21.** Thermal behavior and trends for PLA at 0, 5, and 10 wt.% loading of UDC1.



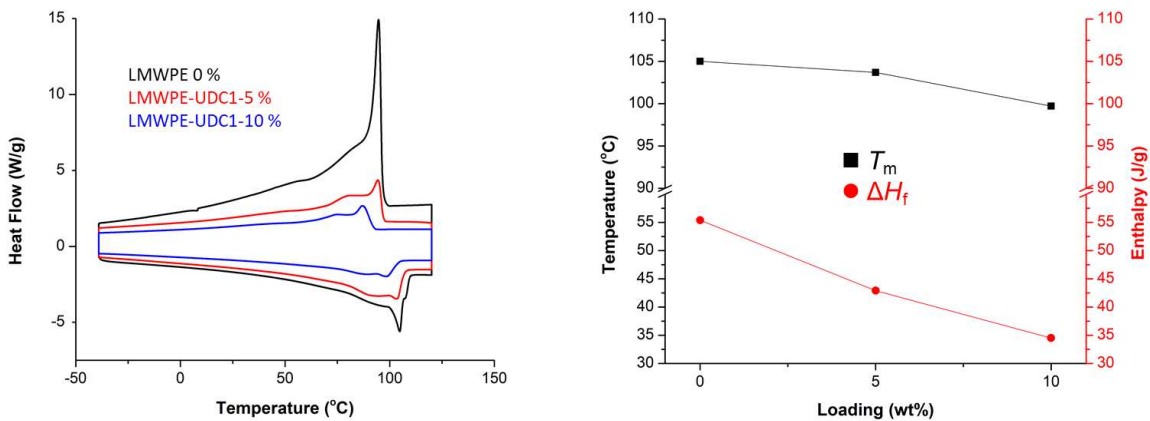
**Figure D22.** Thermal behavior and trends for PLA at 0, 5, and 10 wt.% loading of UDC3.

### Applicable Polyolefins:

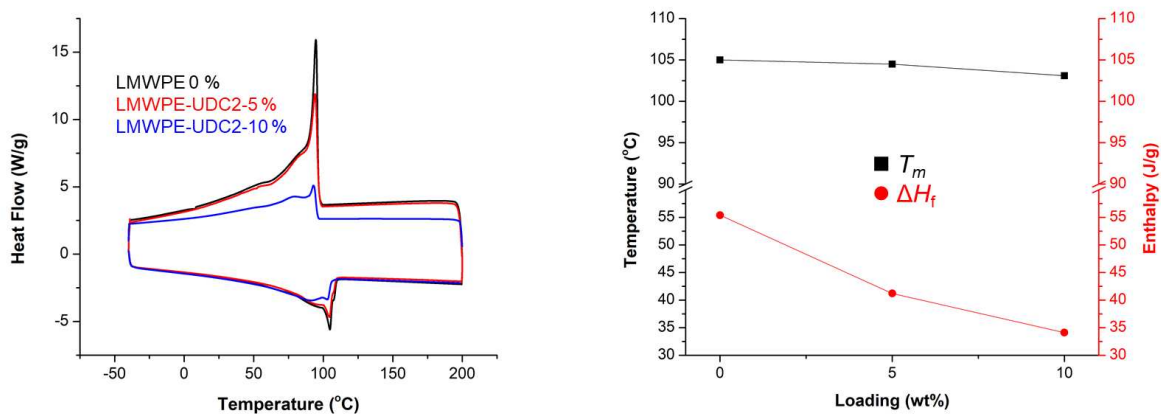
LMWPE, LDPE, HDPE, UHMWPE, *it*-PP

The specified polymer (50 mg) was mixed with toluene (15 mL) in a 20 mL glass scintillation vial and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Upon full solubility, a solution of selected UDC (2.5 mg) dissolved in toluene (1 mL) was added quantitatively to the stirring mixture. The UDC is briefly mixed into the polymer solution before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (60 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbenes. Crosslinked polymers appeared light yellow, a visual sign of successful installment.

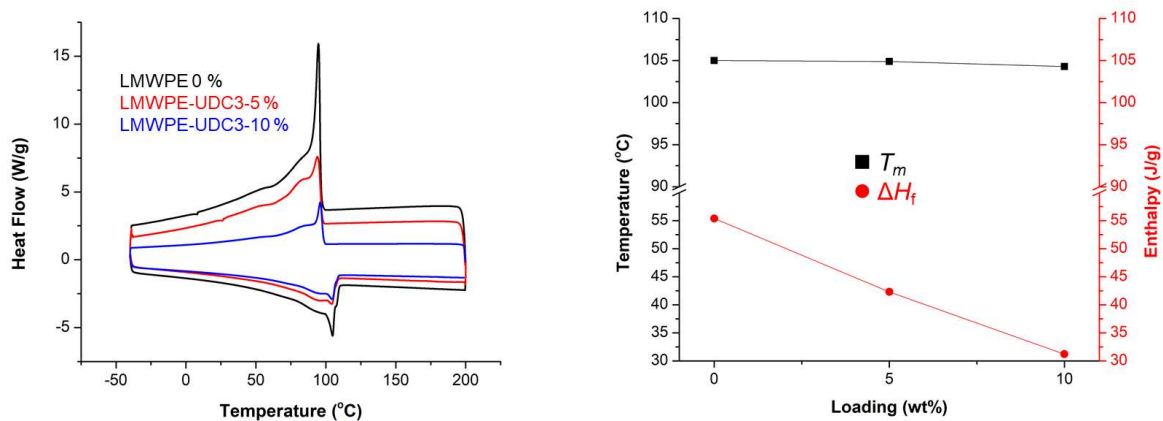




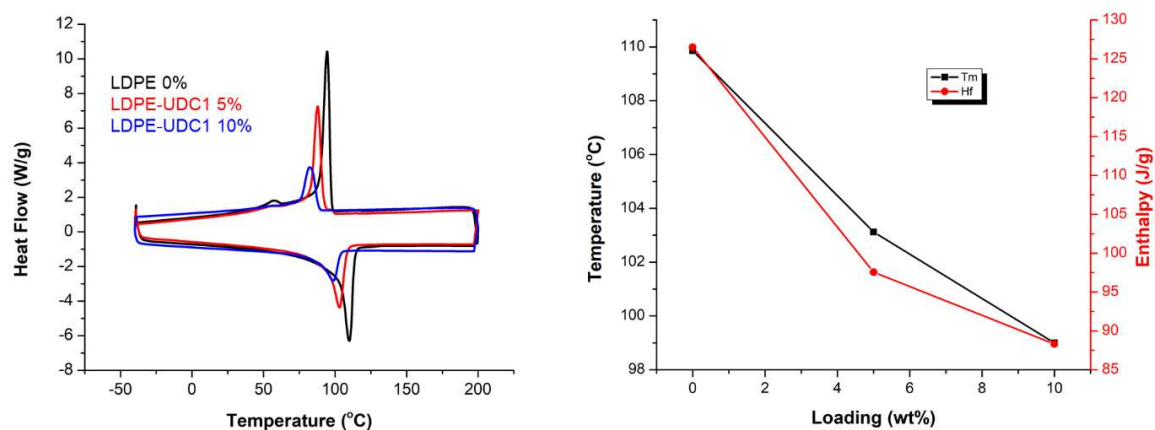
**Figure D23.** Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC1.



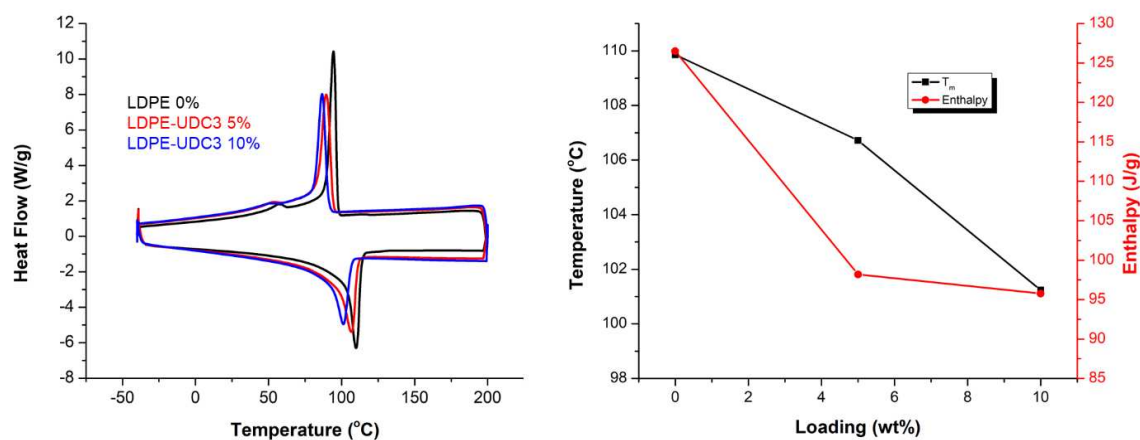
**Figure D24.** Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC2.



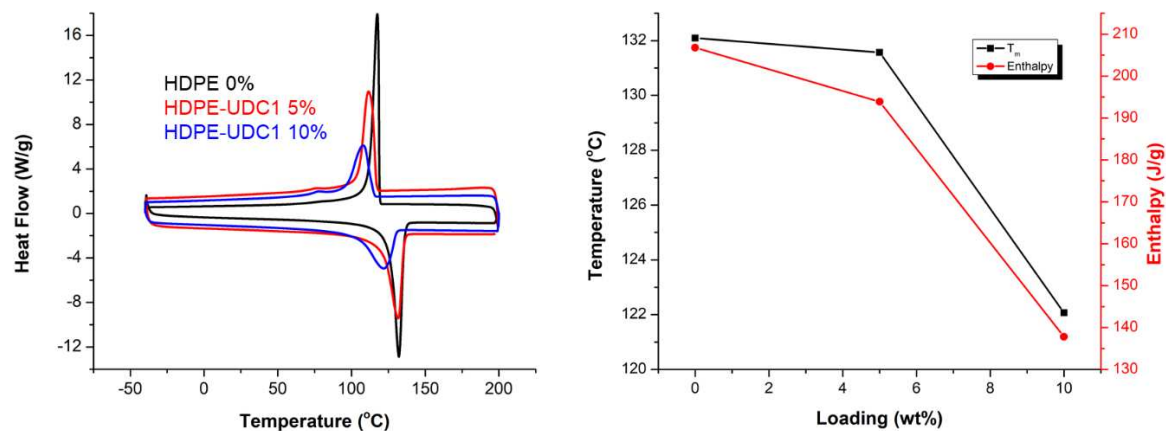
**Figure D25.** Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC3.



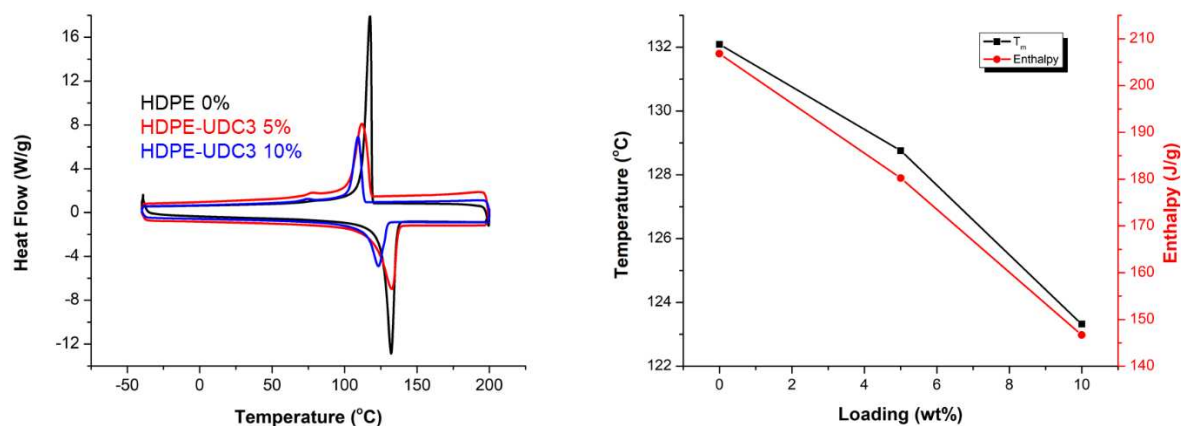
**Figure D26.** Thermal behavior and trends for LDPE at 0, 5, and 10 wt.% loading of UDC1.



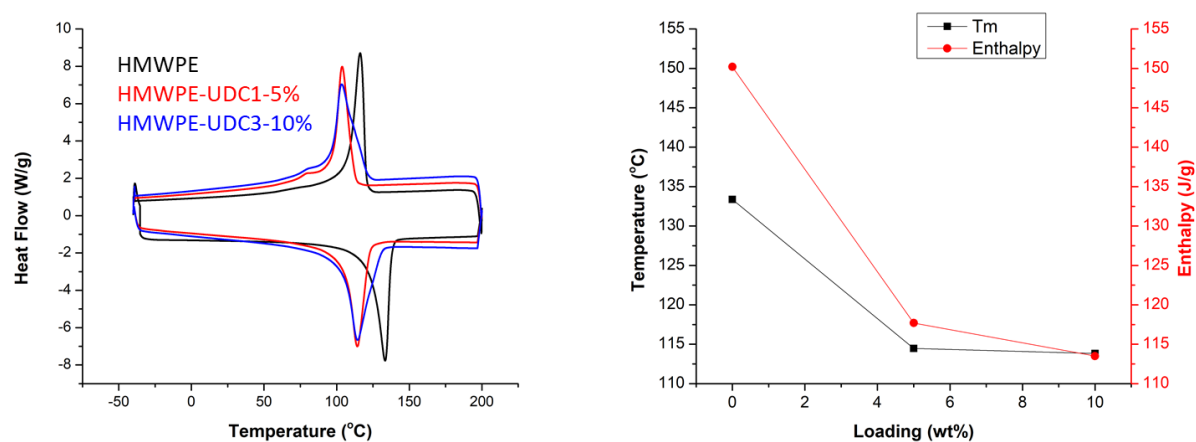
**Figure D27.** Thermal behavior and trends for LDPE at 0, 5, and 10 wt.% loading of UDC3.



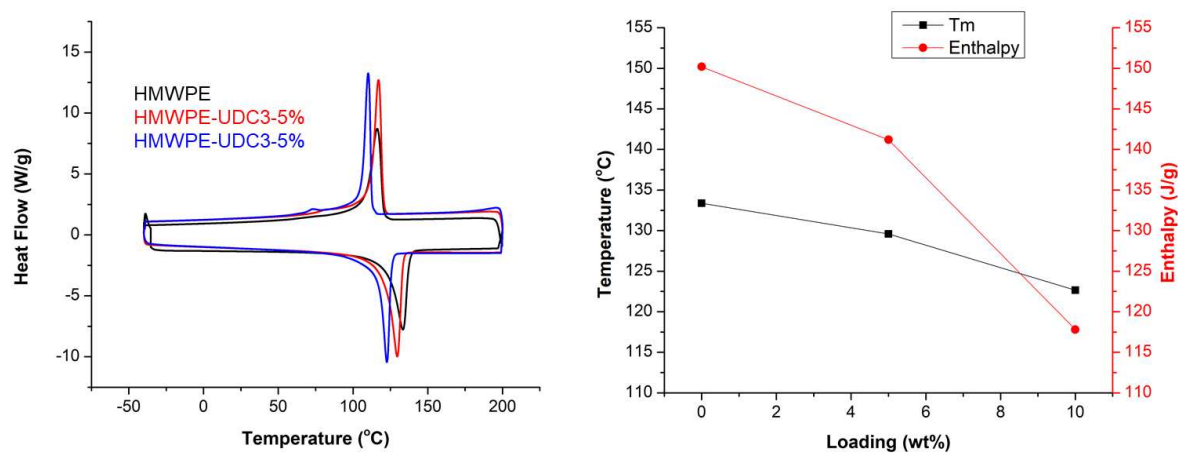
**Figure D28.** Thermal behavior and trends for HDPE at 0, 5, and 10 wt. % loading of UDC1.



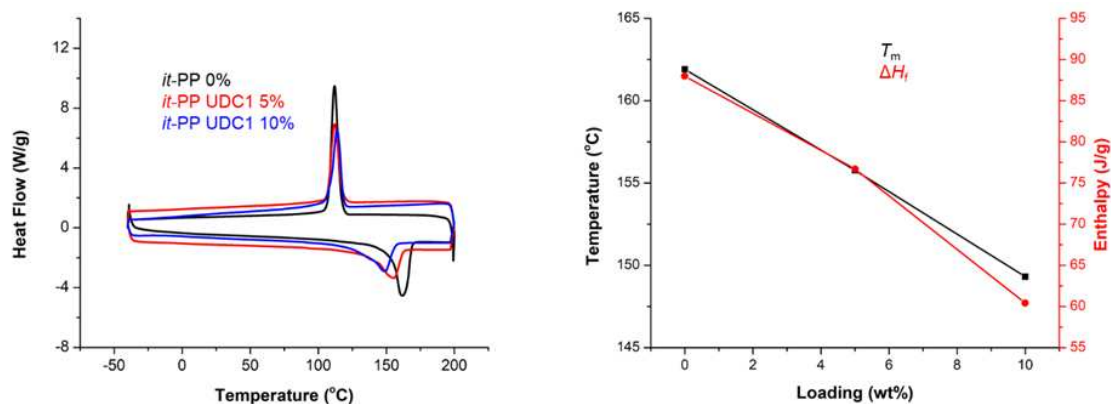
**Figure D29.** Thermal behavior and trends for HDPE at 0, 5, and 10 wt.% loading of UDC3.



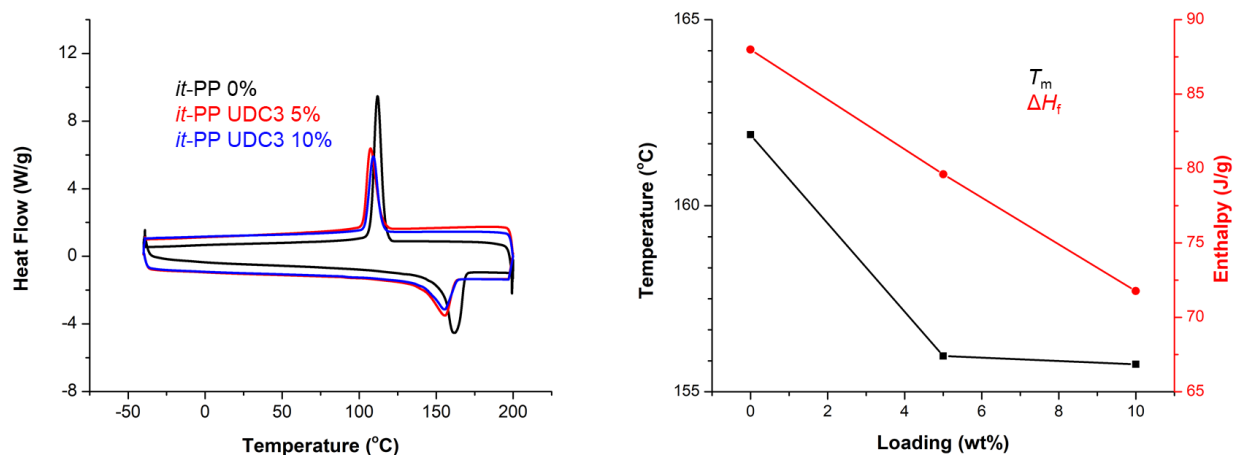
**Figure D30.** Thermal behavior and trends for UHMWPE at 0, 5, and 10 wt.% loading of UDC1.



**Figure D31.** Thermal behavior and trends for UHMWPE at 0, 5, and 10 wt.% loading of UDC3.



**Figure D32.** Thermal behavior and trends for *it*-PP at 0, 5, and 10 wt.% loading of UDC1.



**Figure D33.** Thermal behavior and trends for *it*-PP at 0, 5, and 10 wt.% loading of UDC3.

### Example Homopolymer Crosslinking Procedure (5 wt.% UDC)

#### Applicable Polymers:

HDPE, LDPE, LMWPE

A 500 mL round bottom flask was charged with toluene (100 mL), specified polymer powder or pellets (5.0 g), and a stir bar. The mixture was heated to 85 °C and allowed to stir until partial or full solubility was observed, at which point selected UDC (0.25 g, 5.0 wt.%) in a separate toluene solution (5 mL) was added into the solution. (*Note: PMMA and others may not require heating to achieve solubility*). The mixture was stirred briefly before cooling over an ice bath (0 °C), which yielded a gelatinous white precipitate. Toluene was then removed under vacuum at 60 °C and the precipitated UDC-imbedded-polymer was dried under vacuum at 60 °C overnight or until a constant mass was achieved. The resulting white powder was then placed in a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbenes. Crosslinked polymers appeared light yellow, a visual sign of successful installment.

### Example 50/50 wt.% Polyolefin/Polyester Blend Small-Scale Crosslinking Procedure

**Applicable Polymers:**

LMWPE, PLA, and P3HB

In a 20 mL glass scintillation vial polyethylene (25 mg) was mixed with toluene (10 mL) and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Separately, a 20 mL scintillation vial was charged with the specified polyester (25 mg, 50 wt.%), 10 mL of chloroform, and a stir bar and mixed until full solubility was observed. The polyester solution was added to the heated toluene mixture, and allowed to mix for 30 minutes, at which time a solution of selected UDC (2.5 mg) dissolved in toluene (1 mL) was added quantitatively to the stirring mixture. The solution blend of all three components was briefly mixed before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (60 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbenes. Crosslinked blends appeared light yellow, a visual sign of successful installment.

**Example 50/50 wt.% Polyolefin/Polyester Blend Crosslinking Procedure****Applicable Polymers:**

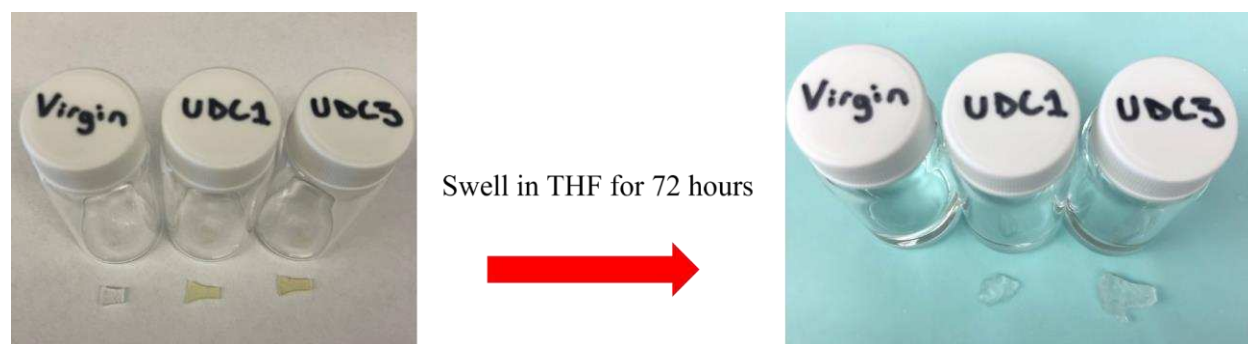
LMWPE, PLA, and P3HB

In a 250 mL round bottom flask polyethylene (2.5 g) was vigorously stirred in toluene (100 mL) at 85 °C until full solubility was observed. In a separate 250 mL round bottom flask, specified polylactic acid or poly-3-hydroxybutyrate pellets (2.5 g, 50 wt.%) were vigorously stirred in chloroform (50 mL) until full solubility was observed. The polyester solution was then quickly added to the polyethylene solution. Additional stirring at 85 °C was carried out for 30 min, which achieved stable solution-blended polymers. Selected UDC (0.25 g) was then dissolved in toluene

(5 mL) and added quantitatively to the stirring mixture. The UDC-blend was stirred briefly before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed under vacuum at 60 °C and the received UDC-blend was dried under vacuum at 60 °C overnight or until a constant mass was achieved. The white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbenes. Crosslinked blends appeared light yellow, a visual sign of successful installment.

Virgin (0 %) blends of LMWPE and PLA/P3HB were prepared by the above procedures, without the steps of UDC addition.

### General Crosslinked Polymer Characterizations



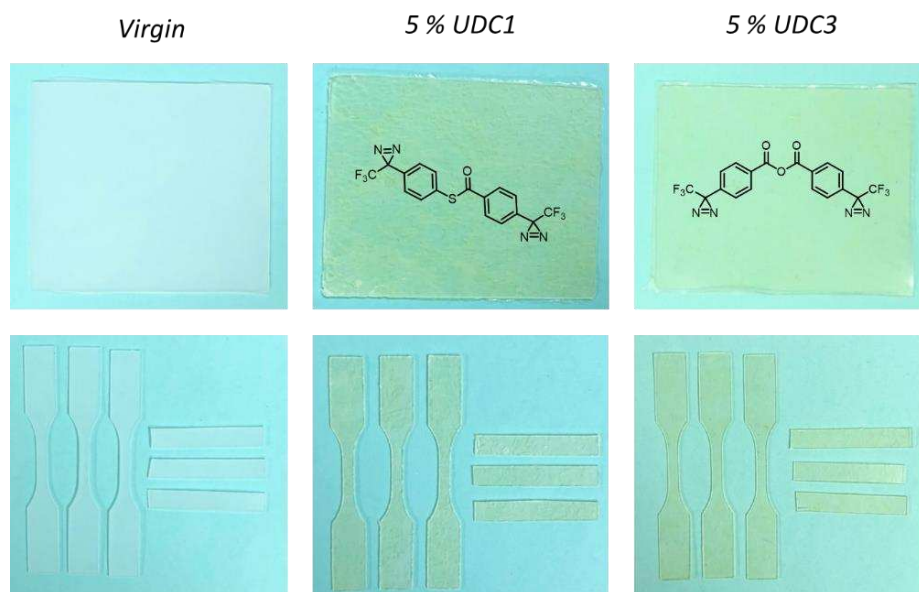
**Figure D34.** Solubility test on amorphous PMMA-UDC1 and -UDC3 at 5 wt.% loading (THF, 72 h, 50 °C).

### Tensile Testing, Photos, and FTIR: Reprocessing Studies

Reprocessability experiments were carried out on LMWPE and LDPE:

1. Melt compression reprocessed film homogeneity. Film processing conditions are reported in materials & methods.

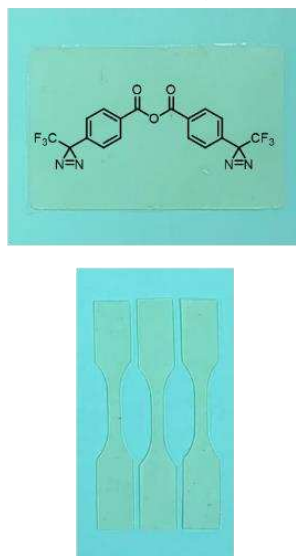
2. Tensile pulling experiments (stress/strain, ~23 °C, 5 mm/min) on both virgin materials and re-compression molded films to study performance enhancements and retention following use. Tensile curves are an average of 3-4 individual ASTM D638 samples with error margins reported in the supplemental tables (~23 °C, 5 mm/min until fail).
3. FTIR spectral analysis for signs of decomposition or structural differences following reprocessing, and anticipated bond exchange events, at high temperature. No noticeable changes were observed in any of the samples, supporting clean network reprocessing.



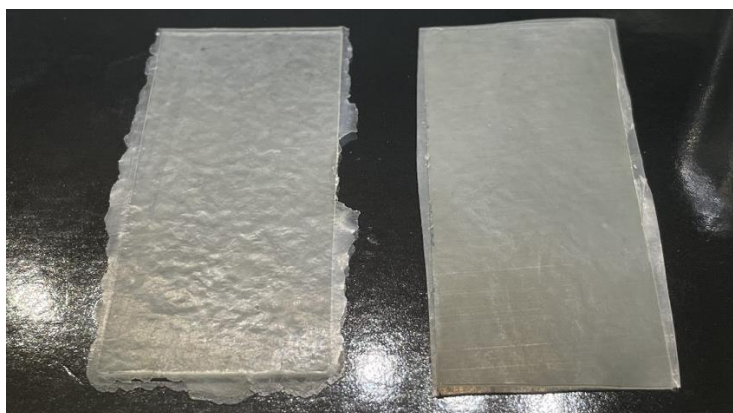
**Figure D35.** Photos of USC and UDC1-3 treated (labeled, 5 wt.%) LDPE films and corresponding tensometer/DMA samples.



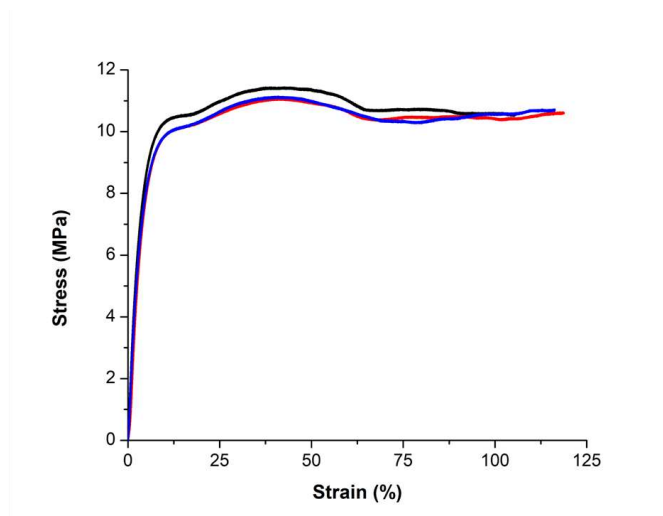
*LDPE-UDC3 5% Reprocessed*



**Figure D36.** Photos of USC and UDC3-treated (labeled, 5 wt.%) LDPE film and corresponding tensometer/DMA samples following one melt-reprocessing step.

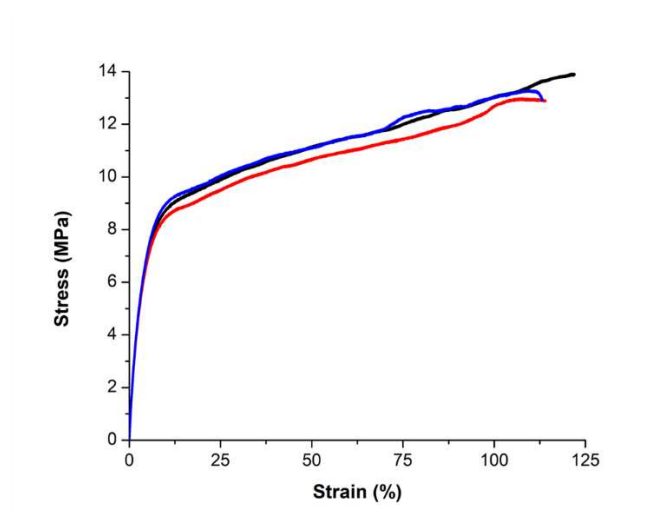


**Figure D37.** Photos of USC (left) and UDC3 (right) crosslinked films of LDPE at an angle highlighting the distinctions in surface homogeneity, a pre-text for subsequent mechanical performance, upon reprocessing.



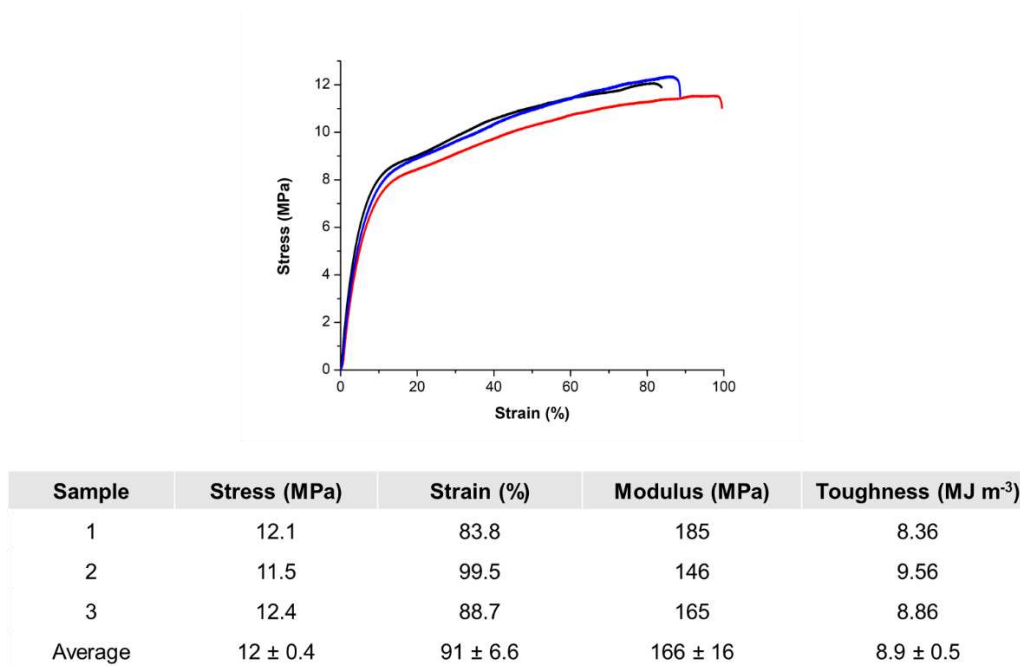
| Sample  | Stress (MPa) | Strain (%) | Modulus (MPa) | Toughness (MJ m <sup>-3</sup> ) |
|---------|--------------|------------|---------------|---------------------------------|
| 1       | 10.4         | 105.4      | 354           | 11.4                            |
| 2       | 10.5         | 118.7      | 333           | 12.9                            |
| 3       | 10.6         | 116.2      | 330           | 13.0                            |
| Average | 10.5 ± 0.1   | 113 ± 5.8  | 345 ± 14      | 12.4 ± 0.7                      |

**Figure D38.** Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE (MFI = 26).

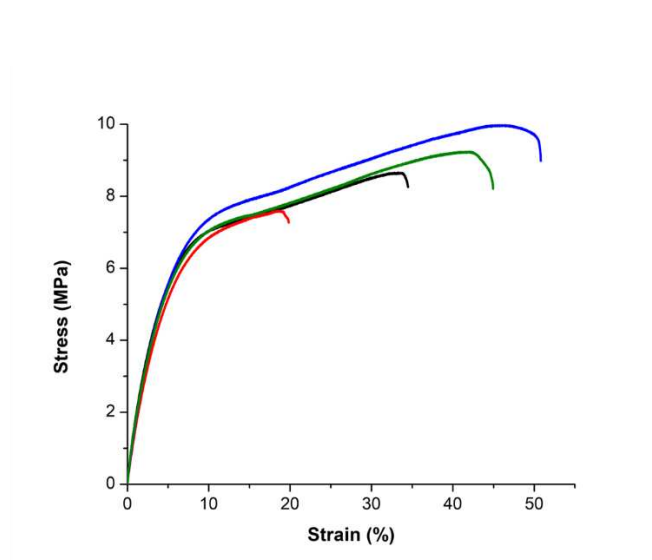


| Sample  | Stress (MPa) | Strain (%) | Modulus (MPa) | Toughness (MJ m <sup>-3</sup> ) |
|---------|--------------|------------|---------------|---------------------------------|
| 1       | 13.9         | 122.0      | 244           | 13.6                            |
| 2       | 13.0         | 114.0      | 243           | 12.1                            |
| 3       | 13.3         | 113.1      | 248           | 12.5                            |
| Average | 13 ± 0.4     | 116 ± 4.0  | 245 ± 3.0     | 12.7 ± 0.6                      |

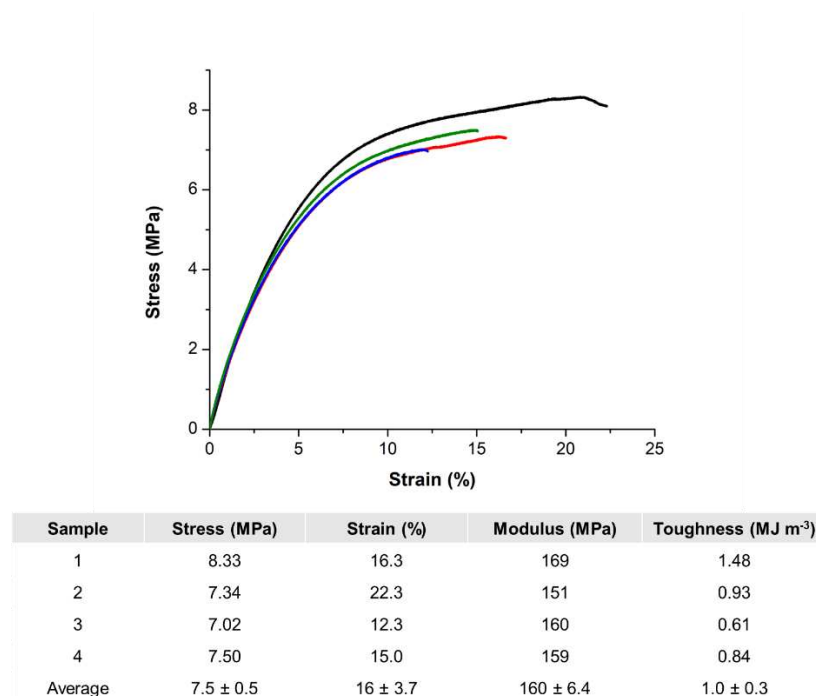
**Figure D39.** Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for LDPE-UDC3.



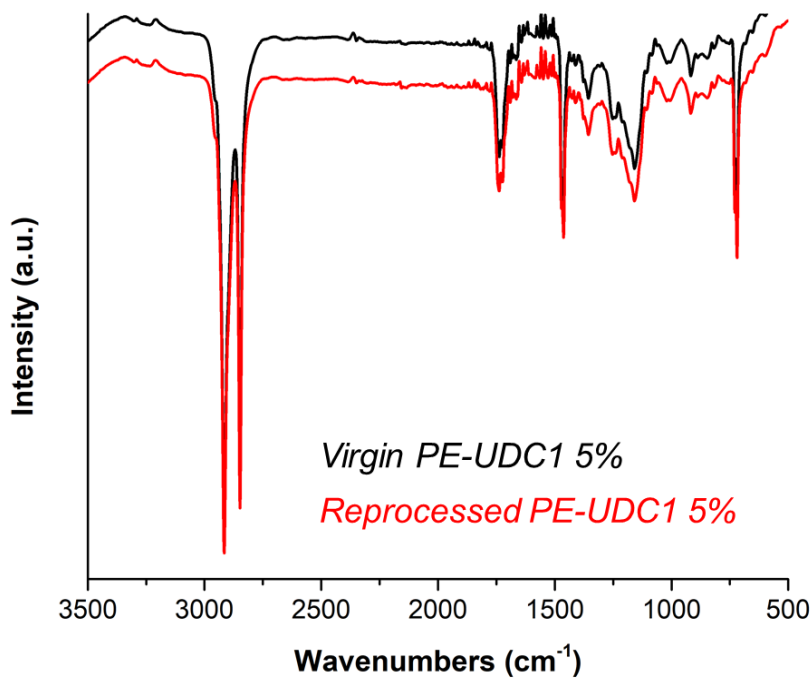
**Figure D40.** Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-UDC3 after reprocessing.



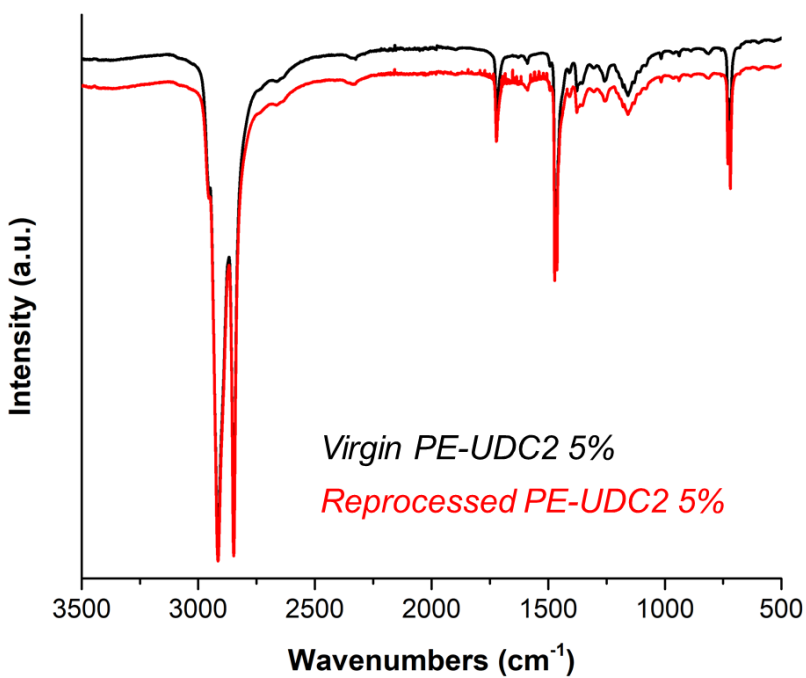
**Figure D41.** Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-USC.



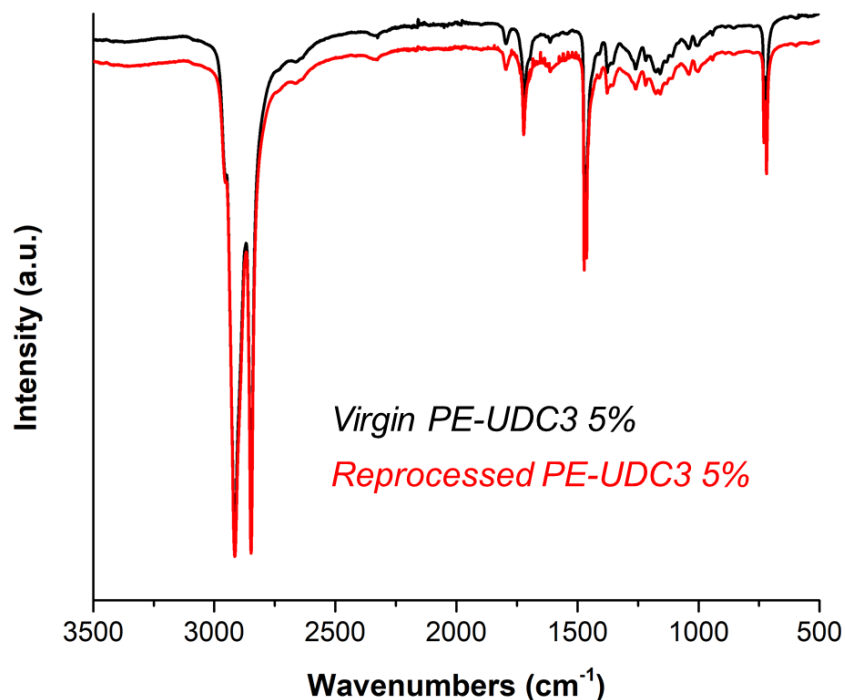
**Figure D42.** Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-USC after reprocessing.



**Figure D43.** Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC1 (5 wt.%)



**Figure D44.** Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC2 (5 wt.%)



**Figure D45.** Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC3 (5 wt.%)

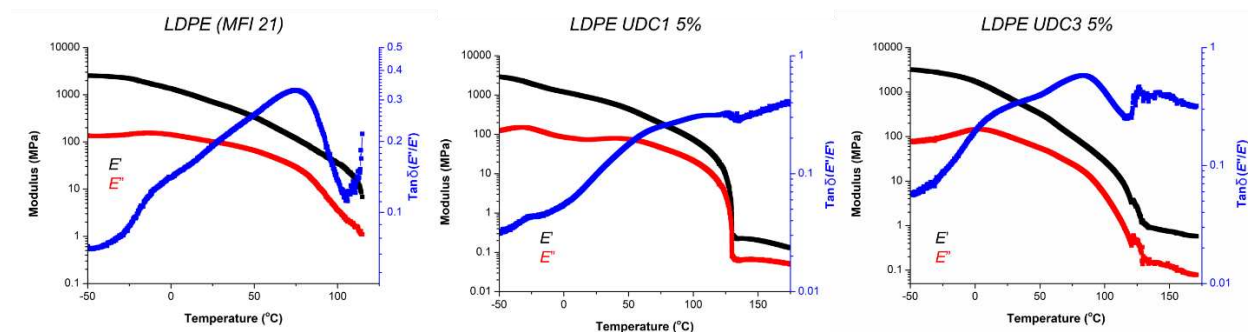
### Dynamic Mechanical Analysis

Tension-film mode experiments were performed on the above-referenced DMA on LMWPE, LDPE, and HDPE dynamic thermosets.

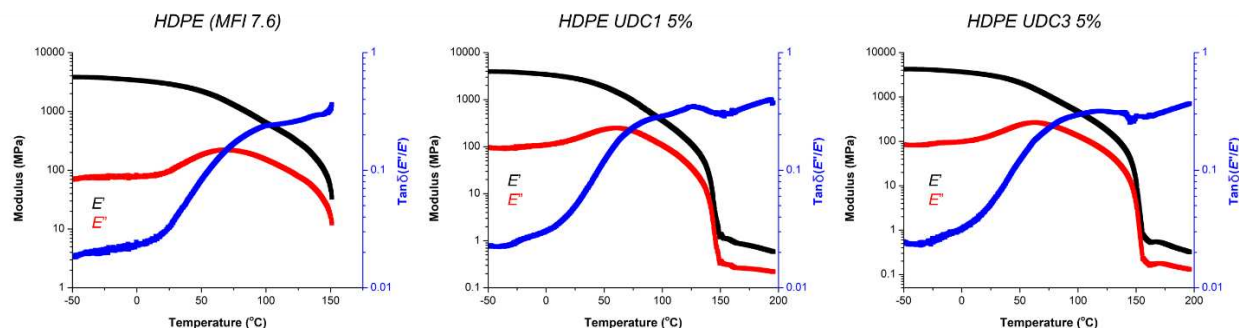
Thermomechanical frequency sweeps were performed between -50 – 200 °C at a heating rate of 5 °C/min, 0.3 % strain, and an oscillation frequency of 1 Hz. Creep-recovery experiments were performed at a constant stress of 2 MPa for HDPE and LDPE samples, and 5 MPa for UHMWPE. Prolonged creep-recovery experiments on HDPE samples were run for 240 minutes (4 h) with constant load at 40 °C followed by 30 minutes of recovery time. Elevated temperature (80 – 110

°C) creep-recovery tests for LDPE and HDPE were run under similar 2 MPa stress loading for 600 sec (10 min), with 300 sec (5 min) allotted for strain recovery.

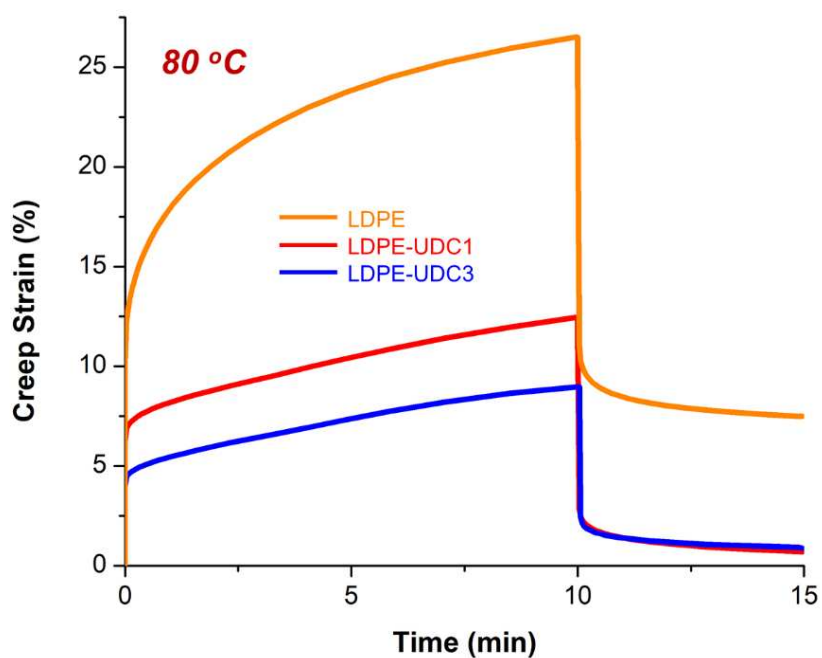
1. Frequency sweeps were performed between -50 – 200 °C at consistent 5 °C/min heat ramp rate, 0.1 – 0.3 % strain, and an oscillation frequency of 1 Hz. DMA curves are a reported average of 2-3 samples and further reported in the supplementary tables.
2. Low-Temperature Creep-Recovery experiments were performed below the melt transition temperature to exhibit working behavior upon addition of dynamic crosslinks. A 2 MPa stress was applied for 600 s (10 min) at specified temperatures, following which the recovered strain (non-permanent deformation) was tracked for 300 s (5 min). In the case of HDPE at 40 °C, performed to mimic possible prolonged working conditions, operated on 240 min (4 h) of creep, and 30 min (0.5 h) of recovery. Strain loss was converted to creep recovery (%) by inverse-normalizing and reversing the strain values immediately upon entering the recovery phase in the main text, for clarification, though the original plots are reported herein below.



**Figure D46.** Representative DMA temperature-ramp frequency-sweeps for LDPE (MFI 21) samples treated with 5 wt.% UDC1 and 3 as specified (-50 to 175 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

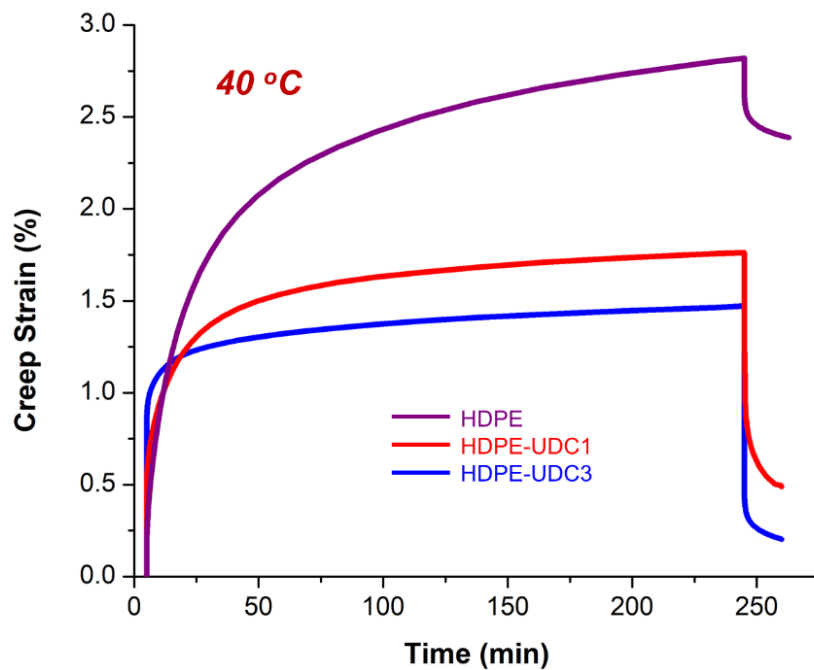


**Figure D47.** Representative DMA temperature-ramp frequency-sweeps for HDPE (MFI 7.6) samples treated with 5 wt.% UDC1 and 3 as specified (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

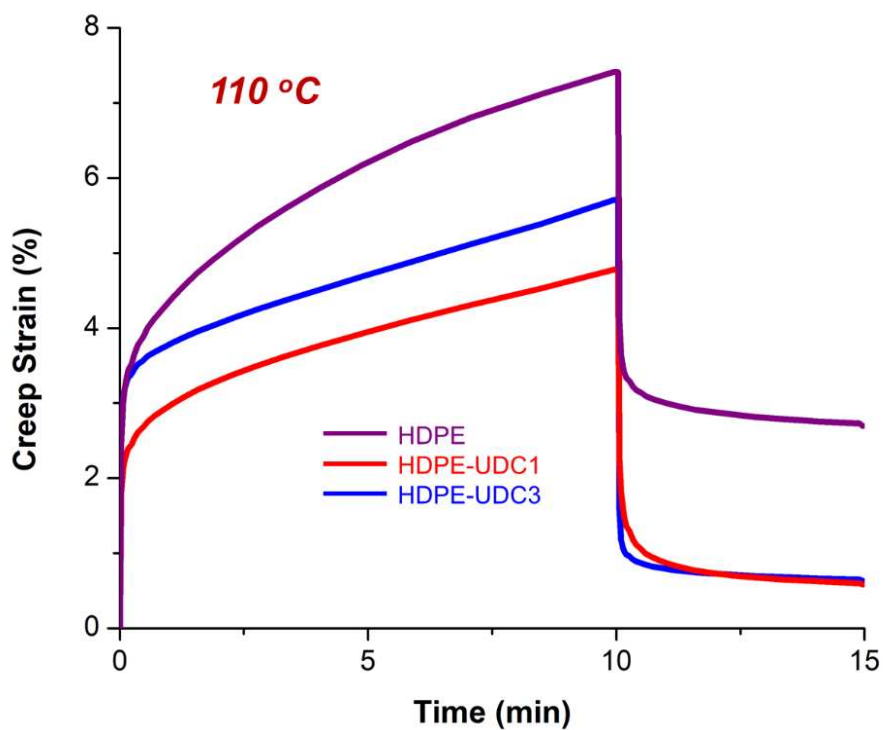


**Figure D48.** Prolonged creep-recovery plots for virgin LDPE (orange), and LDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 80 °C, 600 s creep, 300 s recovery).





**Figure D49.** Near-ambient-condition creep-recovery plots for virgin HDPE (purple), and HDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 40 °C, 240 min creep, 30 min recovery).

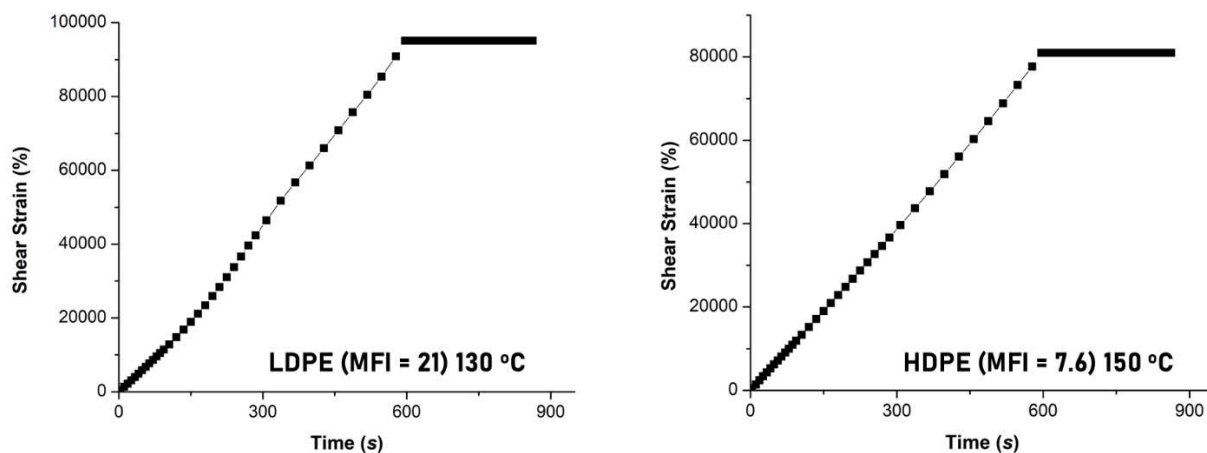


**Figure D50.** High-temperature creep-recovery plots for virgin HDPE (purple), and HDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 110 °C, 240 min creep, 30 min recovery).

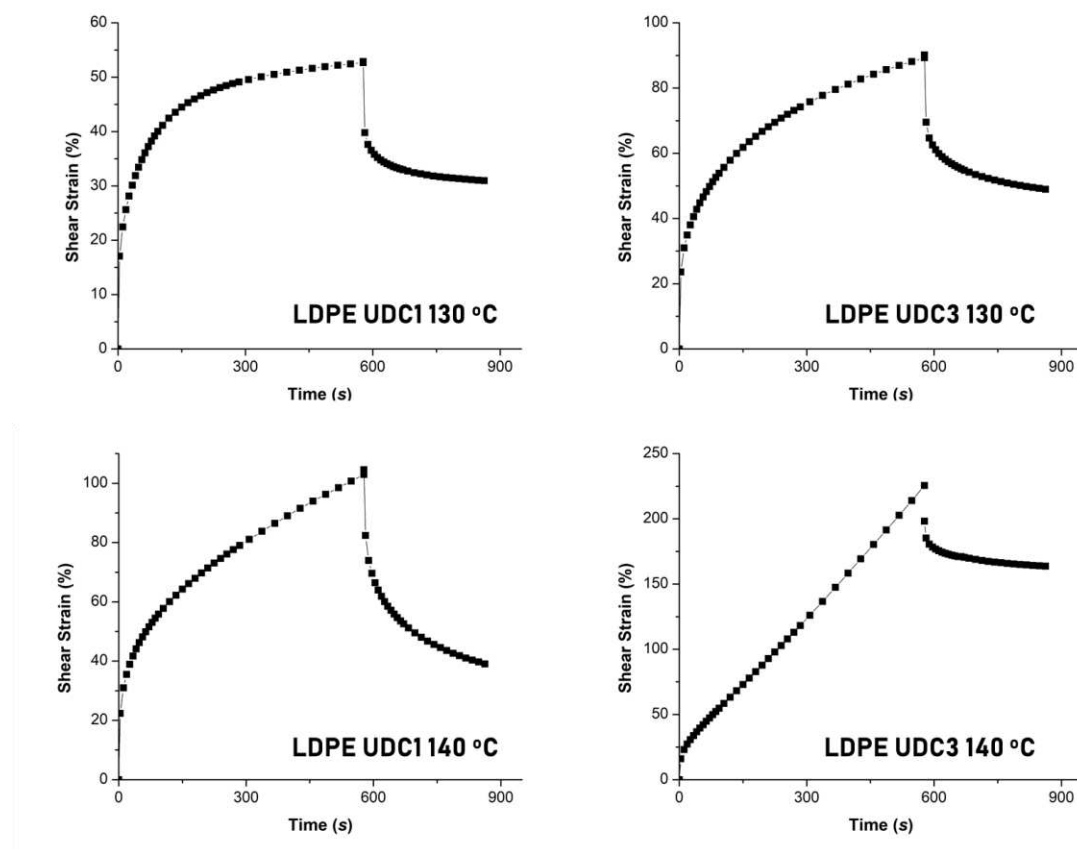
### Bulk-Shearing Oscillation Rheology

As our dynamic thermosets retained the capacity for flow behavior, we were able to further observe chain behavior under rheological testing conditions. Similarly, nuances between exchange mechanisms in various UDCs highlighted material performance tunability.

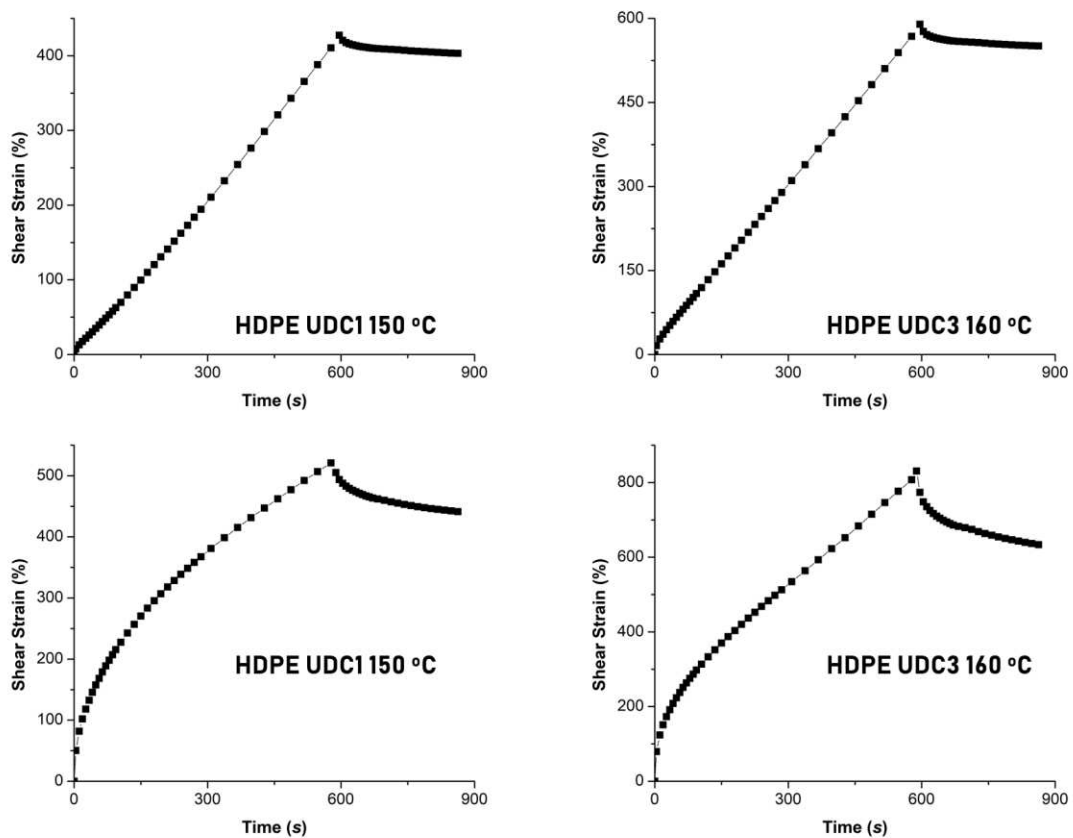
1. Creep-recovery was carried out for 600 s under 2.5 kPa shear stress (creep) and additionally 300 s with removed shear stress (recovery). Strain was applied with a 1 s rise time. Temperature listed above.
2. High-temperature frequency sweeps and crosslink density were carried out in the rubbery plateau and above the melt temperature of LDPE. The sample was oscillated to 0.1 % shear strain at angular frequencies between 0.5 to 100 rad/s. Values for the average storage moduli ( $G'$ , Pa) at each temperature are averaged from the plateau at frequencies 0.5 – 5.0 rad/s.



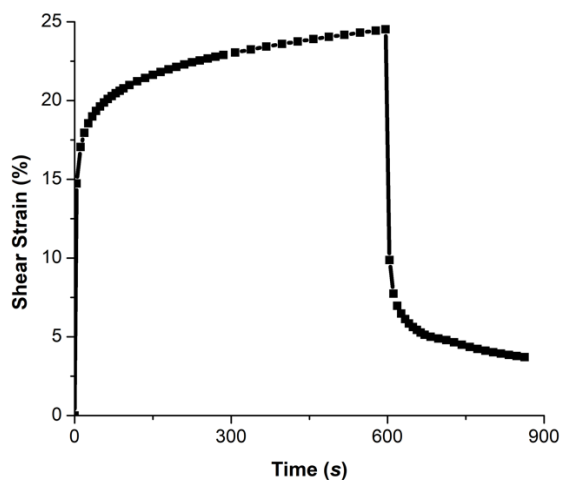
**Figure D51.** Rheological creep-recovery for virgin thermoplastics LDPE (left, 130 °C) and HDPE (right, 150 °C) (2.5 kPa shear stress, 600 s creep, 300 s recovery).



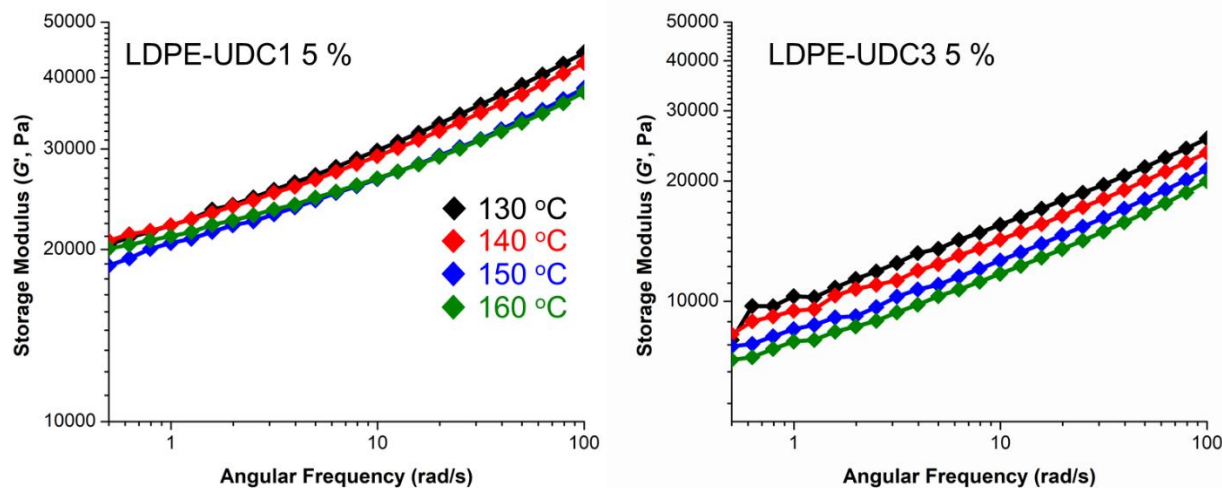
**Figure D52.** Rheological creep-recovery plots from LDPE with 5 wt.% UDC1 (left) and UDC3 (right) at 130 °C (top) and 140 °C (bottom) (2.5 kPa shear stress, 600 s creep, 300 s recovery).



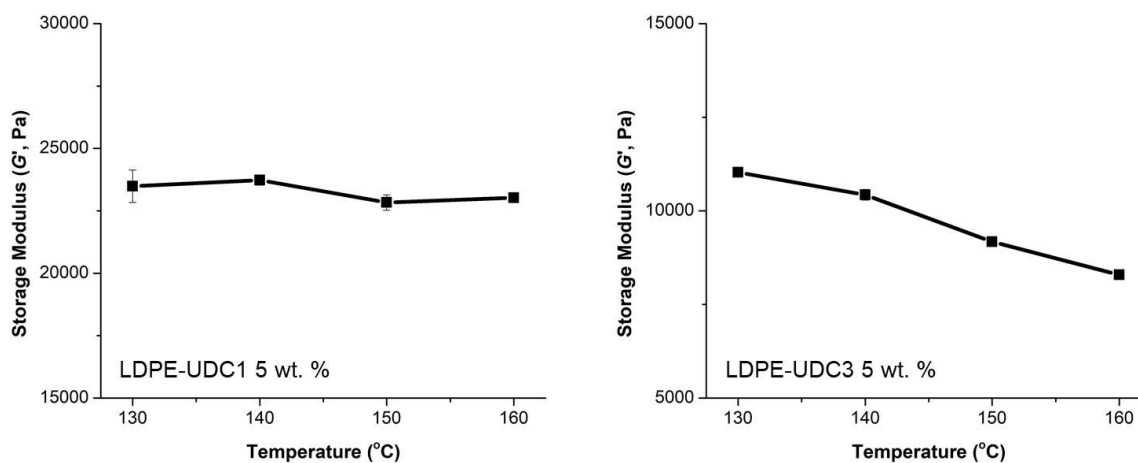
**Figure D53.** Rheological creep-recovery for HDPE with 5 wt.% UDC1 (red) and UDC3 (blue) at 130 °C (solid) and 140 °C (dashed) (5 kPa shear stress, 600 s creep, 300 s recovery).



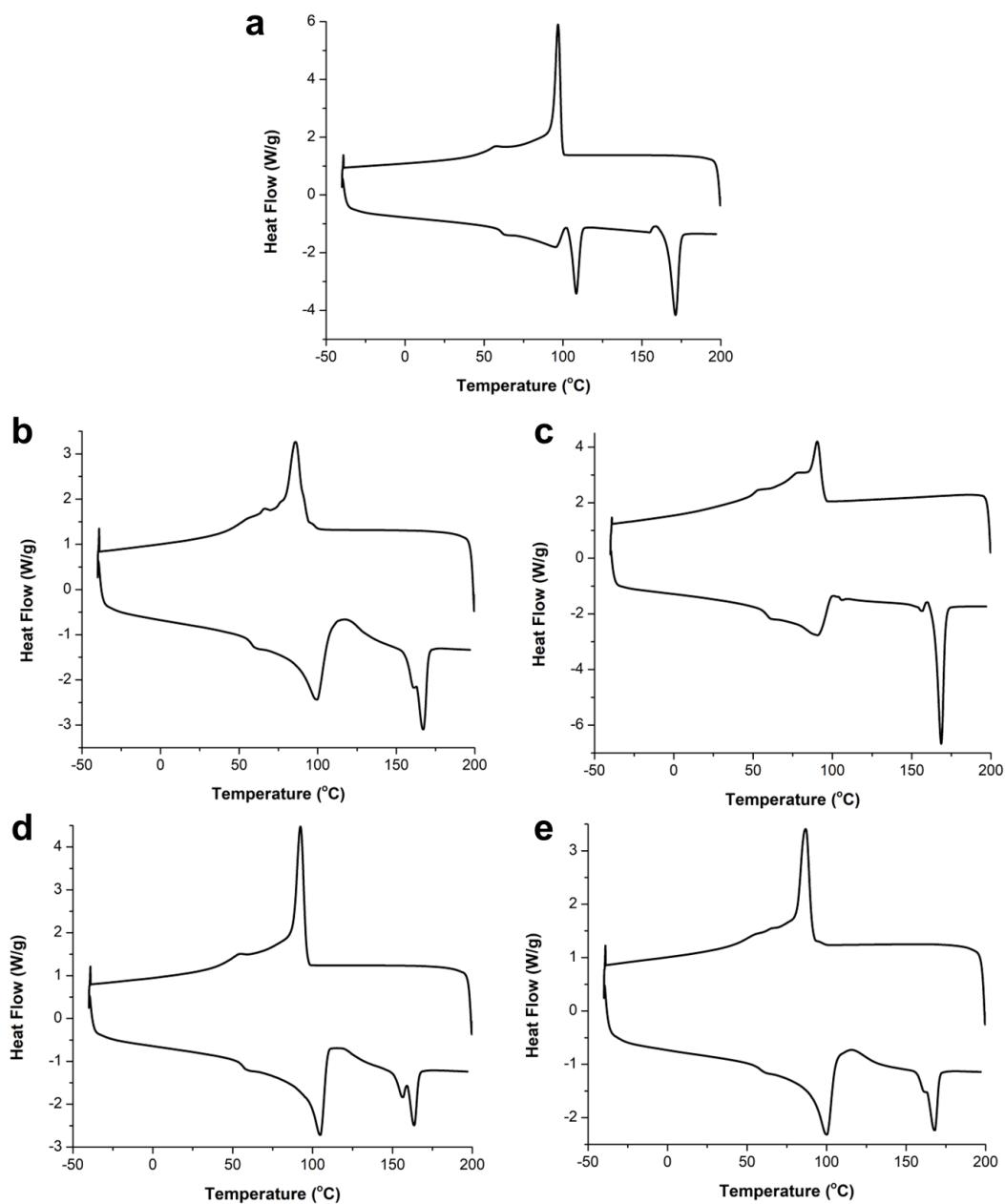
**Figure D54.** Rheological creep-recovery for LDPE with 5 wt.% USC at 130 °C highlighting the most flow/creep suppression (2.5 kPa shear stress, 600 s creep, 300 s recovery).



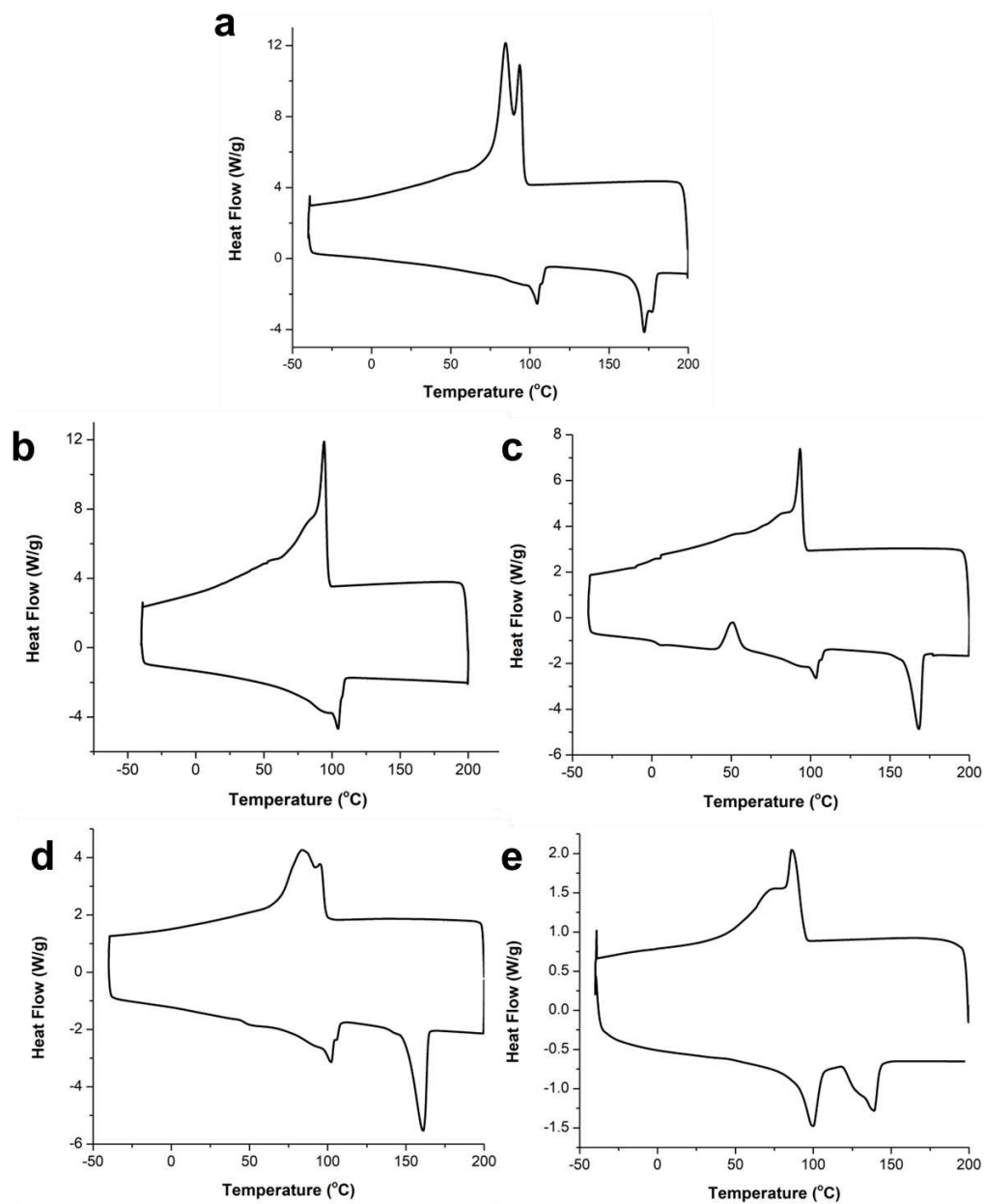
**Figure D55.** High temperature frequency sweeps for LDPE with 5 wt.% UDC1 and UDC3 (130 – 160 °C, 0.1 % shear strain, 0.5 – 100 rad/s).



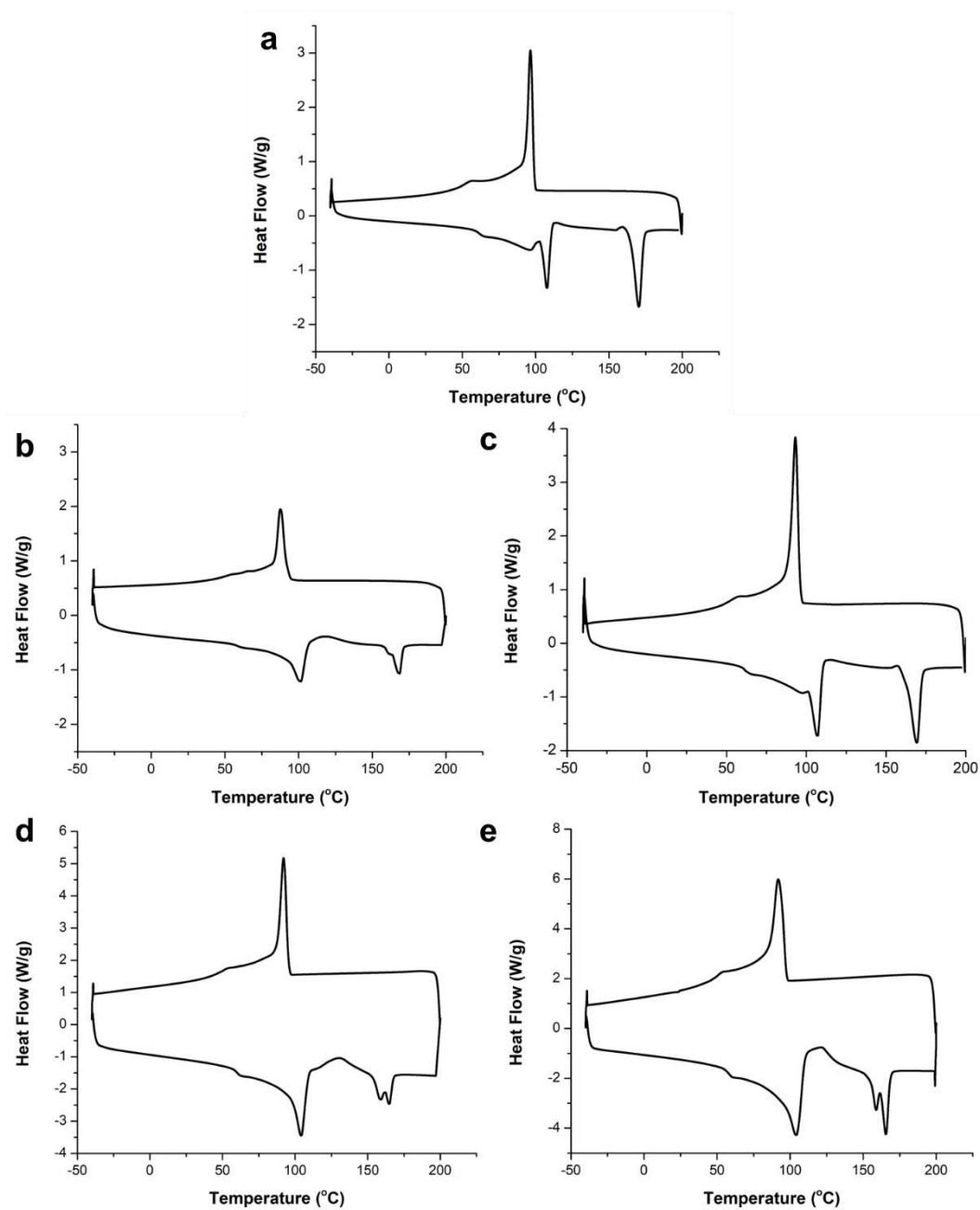
**Figure D56.** Frequency sweep values tracing the rubbery plateau storage modulus with varied temperature ( $G'$ , Pa).



**Figure D57.** DSC trials for blends of LMWPE-PLA with **a)** no crosslinks, **b)** 5 wt. % UDC1, **c)** 5 wt. % UDC2, **d)** 5 wt. % UDC3, and **e)** 5 wt. % USC (10 °C/min heating and cooling, second heating scan).

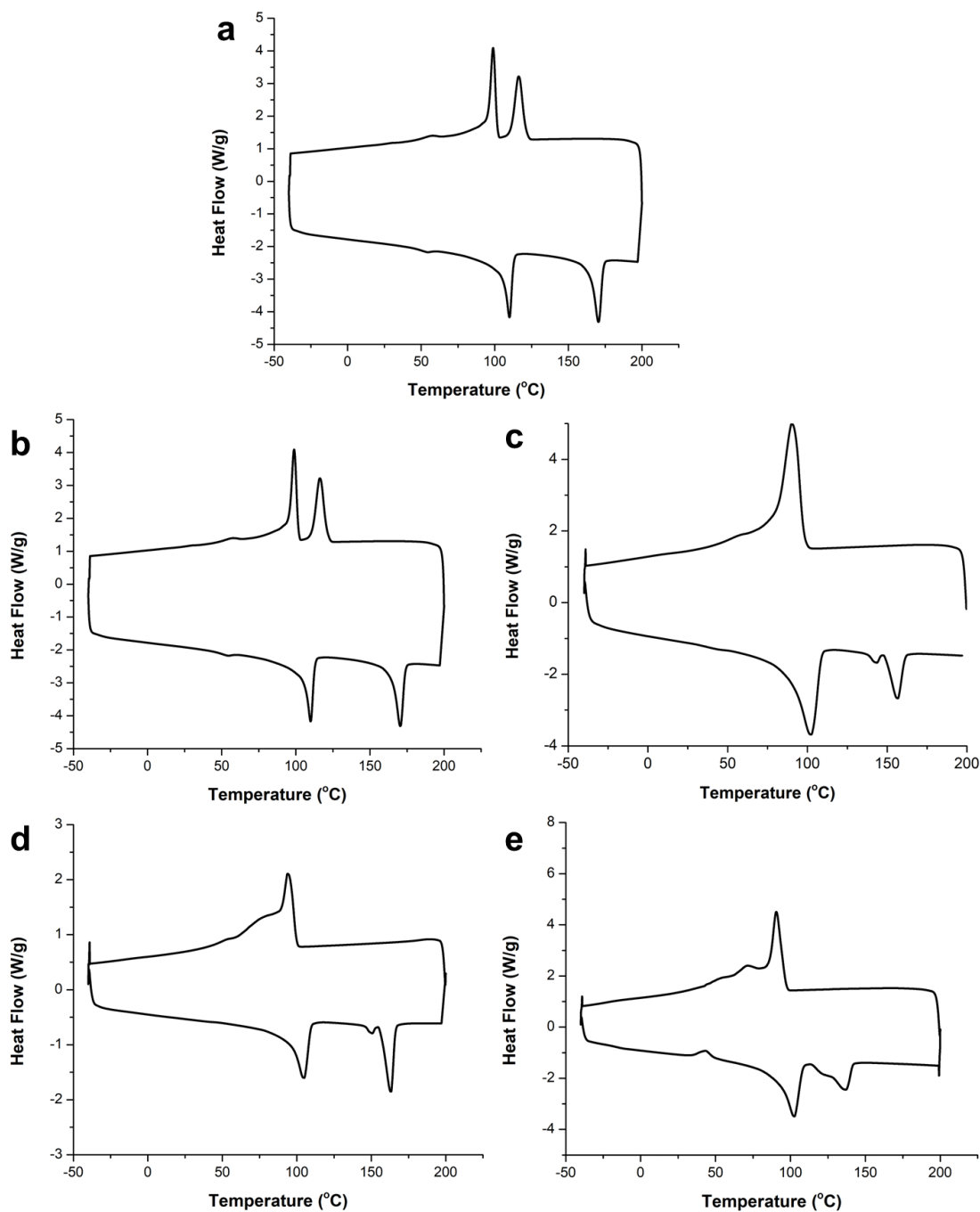


**Figure D58.** DSC trials for blends of LMWPE-P3HB with **a)** no crosslinks, **b)** 5 wt. % UDC1, **c)** 5 wt. % UDC2, **d)** 5 wt. % UDC3, and **e)** 5 wt. % USC (10 °C/min heating and cooling, second heating scan).



**Figure D59.** DSC trials for blends of LDPE-PLA with **a)** no crosslinks, **b)** 5 wt. % UDC1, **c)** 5 wt. % UDC2, **d)** 5 wt. % UDC3, and **e)** 5 wt. % USC (10 °C/min heating and cooling, second heating scan).

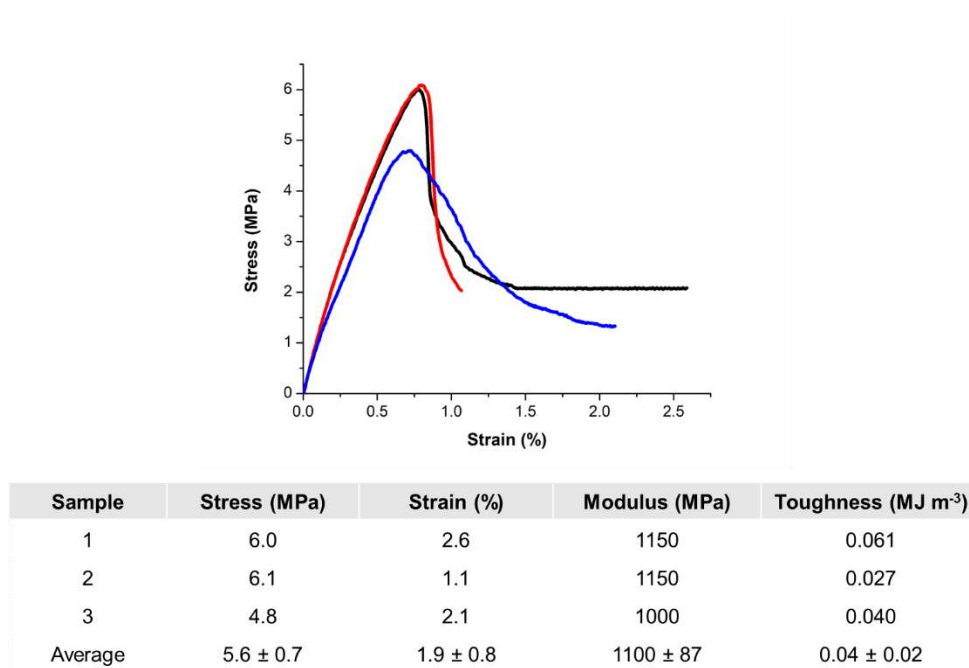




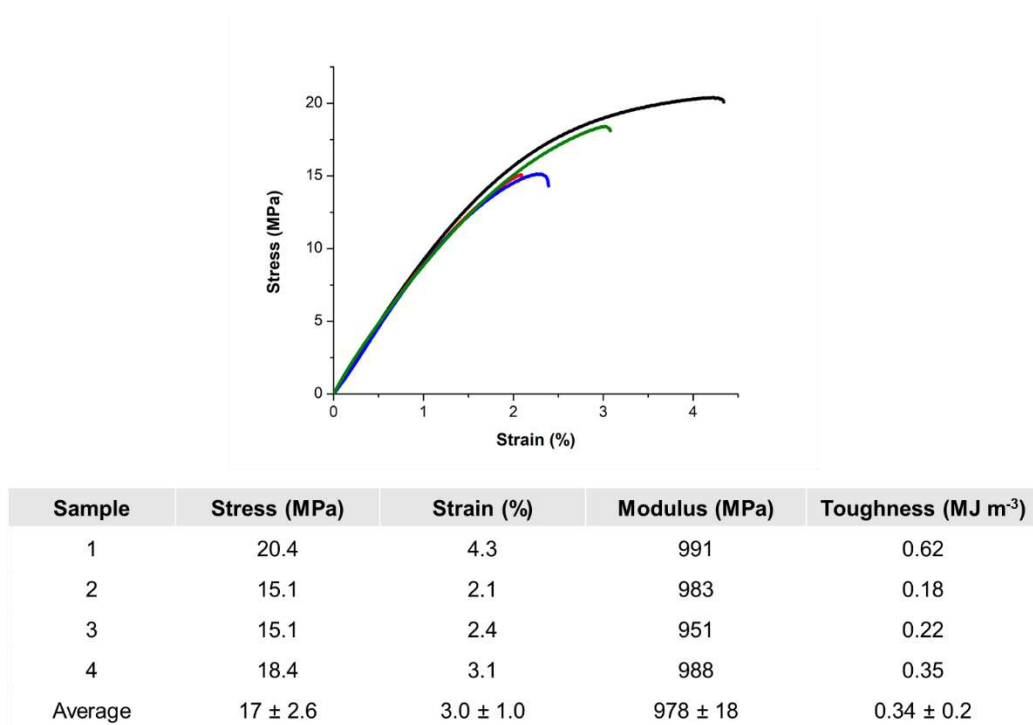
**Figure D60.** DSC trials for blends of LDPE-P3HB with **a)** no crosslinks, **b)** 5 wt. % UDC1, **c)** 5 wt. % UDC2, **d)** 5 wt. % UDC3, and **e)** 5 wt. % USC (10 °C/min heating and cooling, second heating scan).



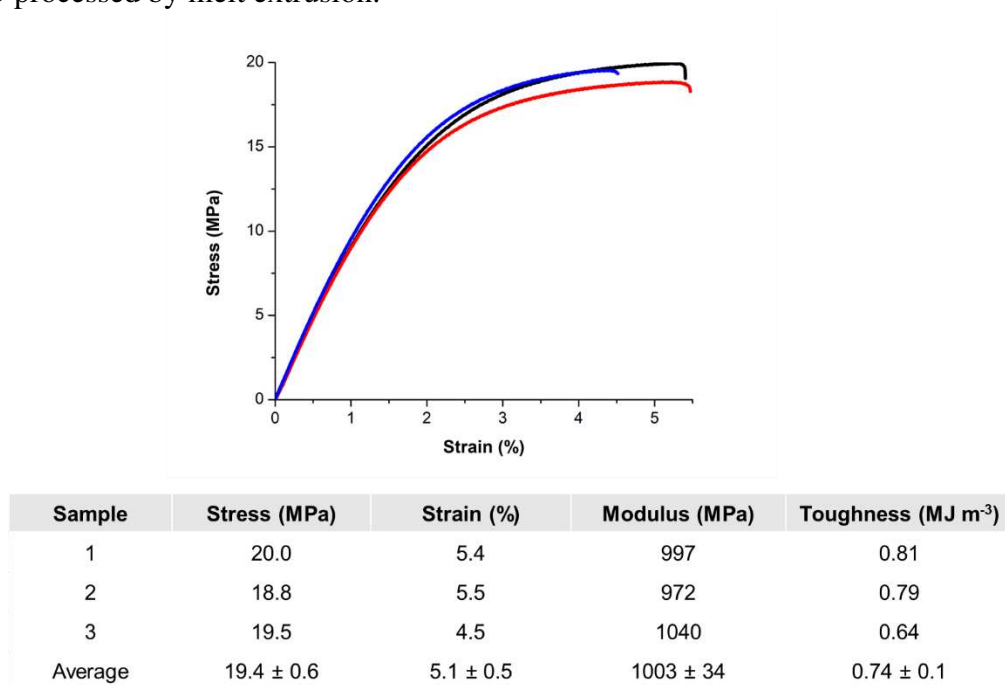
**Figure D61.** Digital images of LDPE-PLLA (50/50 wt%) + UDC3 (5wt%) blend extrudate flakes (left) and dogbone tensile specimens generated from reprocessing post-tensile test specimens (right). The original blend of LDPE-PLLA (50/50 wt%) + UDC3 (5wt%) was first compounded via melt-extrusion, and the blend extrudate was reprocessed via compression molding into dogbone specimens for initial tensile tests. After these tensile tests, the broken pieces were mixed with 50wt% virgin LDPE and melt-extruded, and the resulting blend extrudate (now 75/25 wt% LDPE-PLLA + 2.5wt% UDC3) was once again compression-molded to the reprocessed/recycled dogbone specimens (right image) for additional tensile tests. The results were reported in Figure S65.



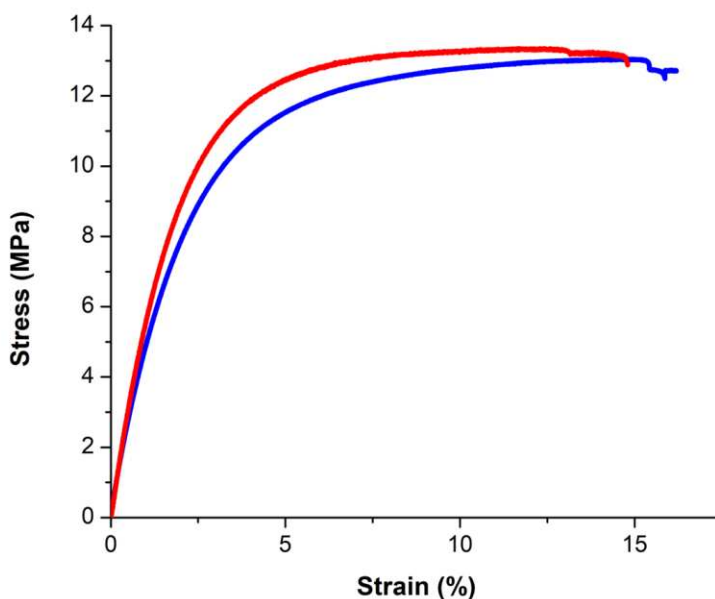
**Figure D62.** Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for virgin LDPE-PLA.



**Figure D63.** Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for LDPE-PLA 5 % UDC3 processed by melt extrusion.

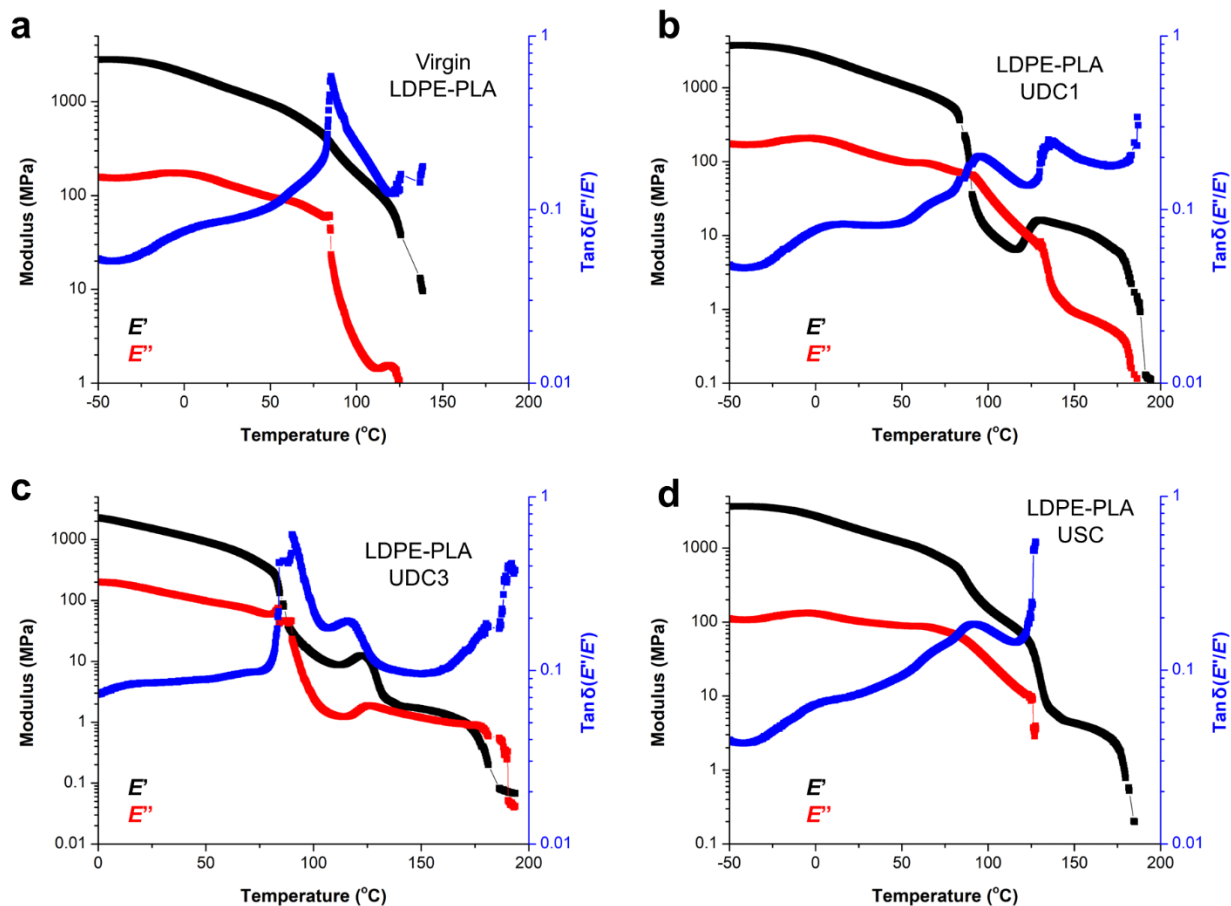


**Figure D64.** Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for reprocessed LDPE-PLA 5 % UDC3 specimens reprocessed by melt extrusion.

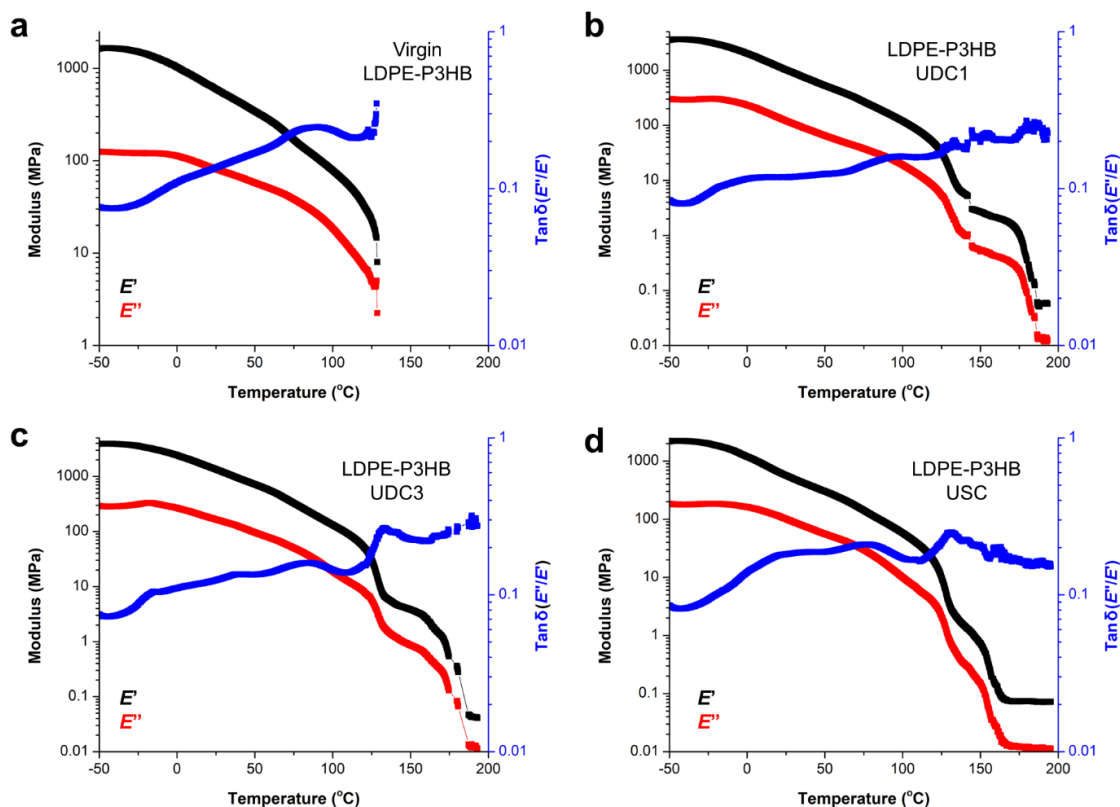


| Extruded LDPE-PLA-UDC3 75:25 Blend Seeded with 50 wt. % Virgin LDPE |              |            |               |                                 |
|---------------------------------------------------------------------|--------------|------------|---------------|---------------------------------|
| Sample                                                              | Stress (MPa) | Strain (%) | Modulus (MPa) | Toughness (MJ m <sup>-3</sup> ) |
| 1                                                                   | 12.7         | 17.7       | 508           | 1.95                            |
| 2                                                                   | 12.8         | 15.9       | 567           | 1.75                            |
| 3                                                                   | 13.6         | 15.4       | 589           | 1.79                            |
| Average                                                             | 13.0 ± 0.5   | 16.3 ± 1.2 | 555 ± 42      | 1.83 ± 0.1                      |
| Reprocessed Average                                                 | 13.4 ± 0.07  | 14.0 ± 1.2 | 642 ± 15      | 1.62 ± 0.15                     |

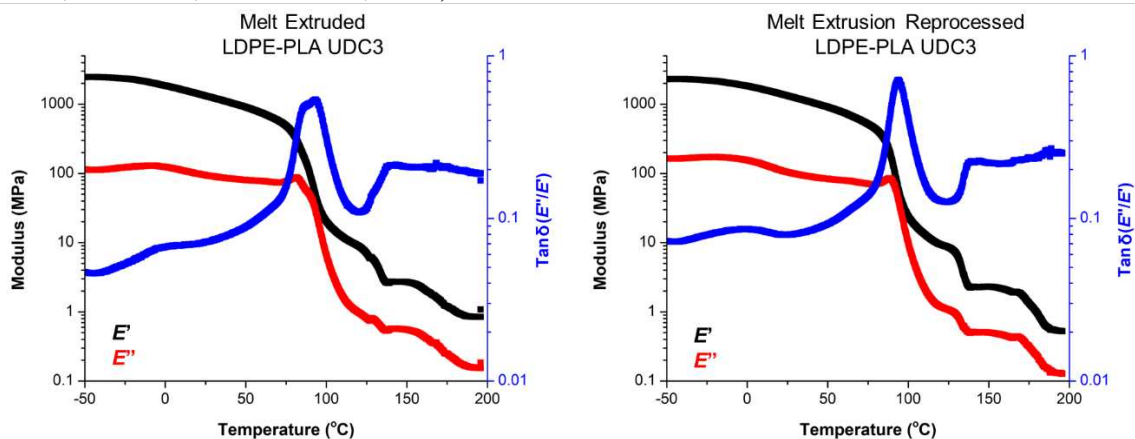
**Figure D65.** Tensile overlay (5 mm/min, ~23 °C) and tabulated data for UDC3 (2.5wt%) compatibilized LDPE-PLA (75:25) blend, prepared by melt-extrusion of added 50wt% LDPE to 50wt% LDPE-PLA (50:50) compatibilized by UDC3 (5wt%) (red) and melt-extrusion reprocessed resulting LDPE-PLA-UDC3 blend (blue). More details were provided in Figure S61.



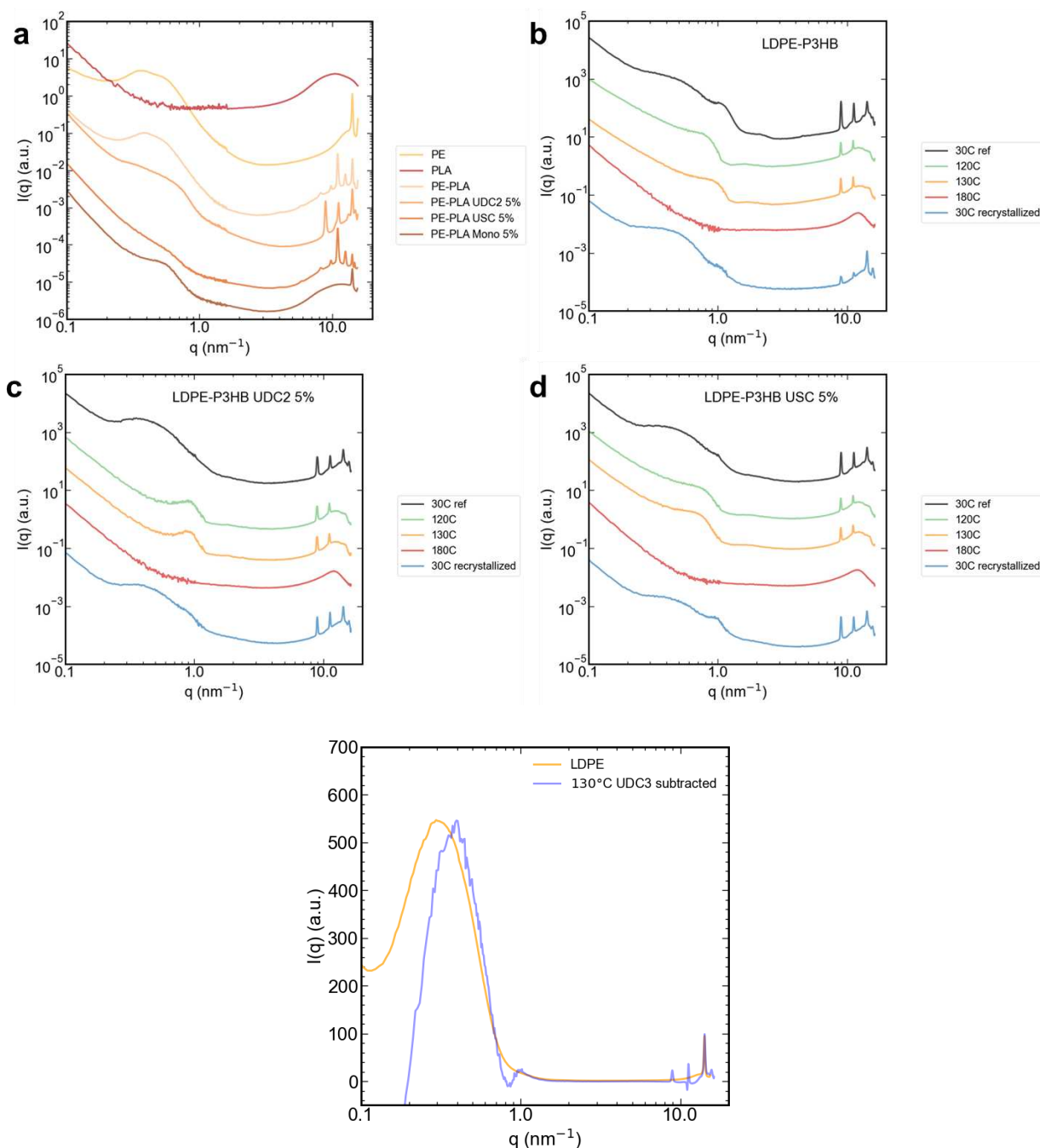
**Figure D66.** Representative DMA temperature-ramp frequency-sweeps for blends of LDPE-PLA **a**, virgin, **b**, with 5 % UDC1, **c**, with 5% UDC3, and **d**, with 5 % USC (-50 to 200  $^{\circ}\text{C}$  or failure, 5  $^{\circ}\text{C}/\text{min}$ , 0.3 % strain, 1 Hz).



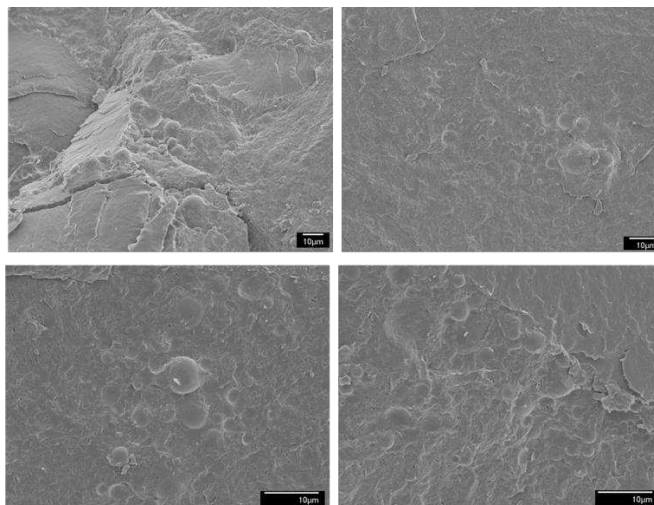
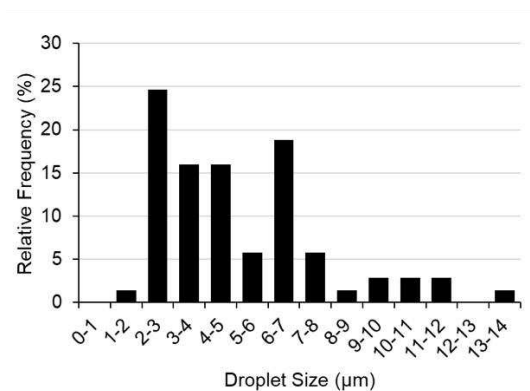
**Figure D67.** Representative DMA temperature-ramp frequency-sweeps for blends of LDPE-P3HB **a**, virgin, **b**, with 5 % UDC1, **c**, with 5 % UDC3, and **d**, with 5 % USC (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).



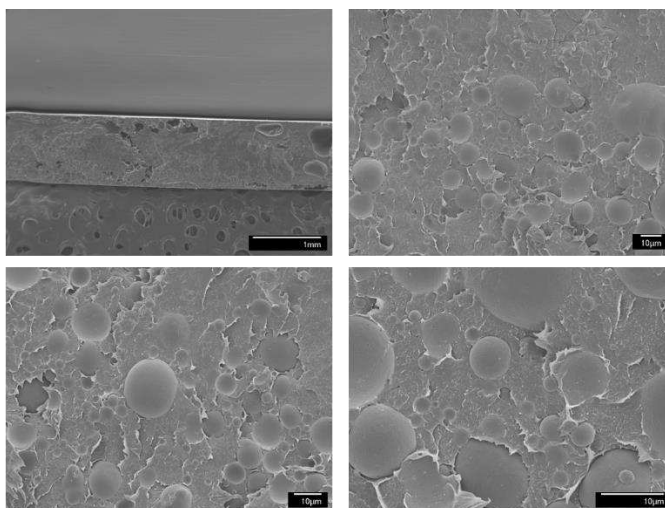
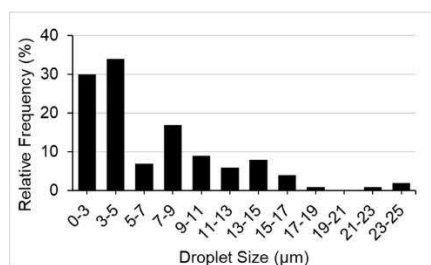
**Figure D68.** Representative DMA temperature-ramp frequency-sweep for blends of LDPE-PLA with 5 % UDC3 prepared by reactive melt extrusion (left) and the reprocessed cycle by melt extrusion (right) (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).



**Figure D69.** Additional SAXS/WAXS Curves. **a**, SAXS/WAXS comparison curves for cross-linked PE-PLA blends relative to virgin blend and reference homopolymers. **b**, Effect of temperatures above the component  $T_m$ s on domain-averaged combination SAXS/WAXS curves for non-cross-linked LDPE-P3HB blend. **c**, Effect of temperatures above the component  $T_m$ s on domain-averaged combination SAXS/WAXS curves for UDC2 compatibilized LDPE-P3HB blend. **d**, Effect of temperatures above the component  $T_m$ s on domain-averaged combination SAXS/WAXS curves for USC compatibilized LDPE-P3HB blend. **e**, SAXS/WAXS pattern of P3HB subtracted from LDPE-P3HB compatibilized UDC3 blend heated to 130 °C; determination of structure of the melted component (i.e., LDPE). LDPE at 30 °C given as reference.

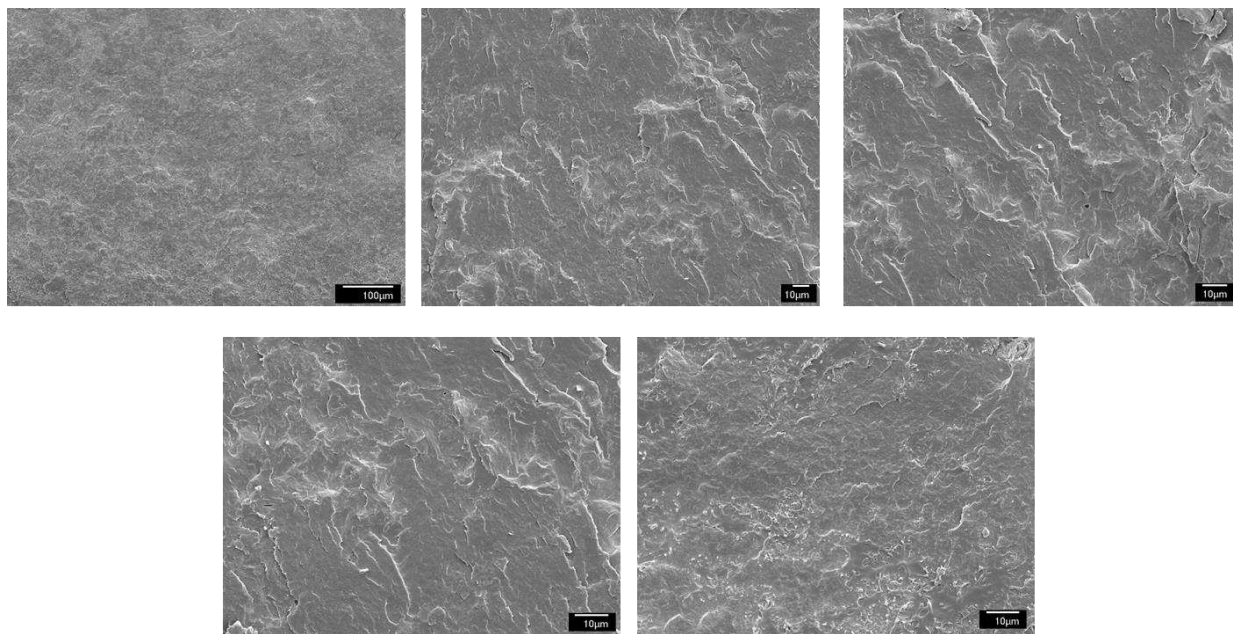


**Figure D70.** Cross section images of the virgin 50/50 wt% LDPE-P3HB blend and cross-section droplet diameter size analysis.

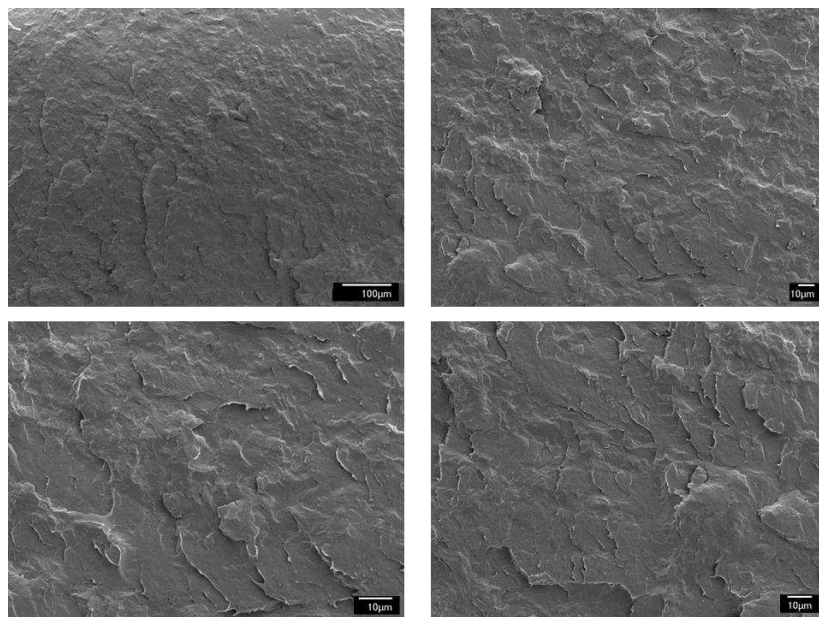


**Figure D71.** Cross section images of the virgin 50/50 wt% LDPE-PLA blend and cross-section droplet diameter size analysis.

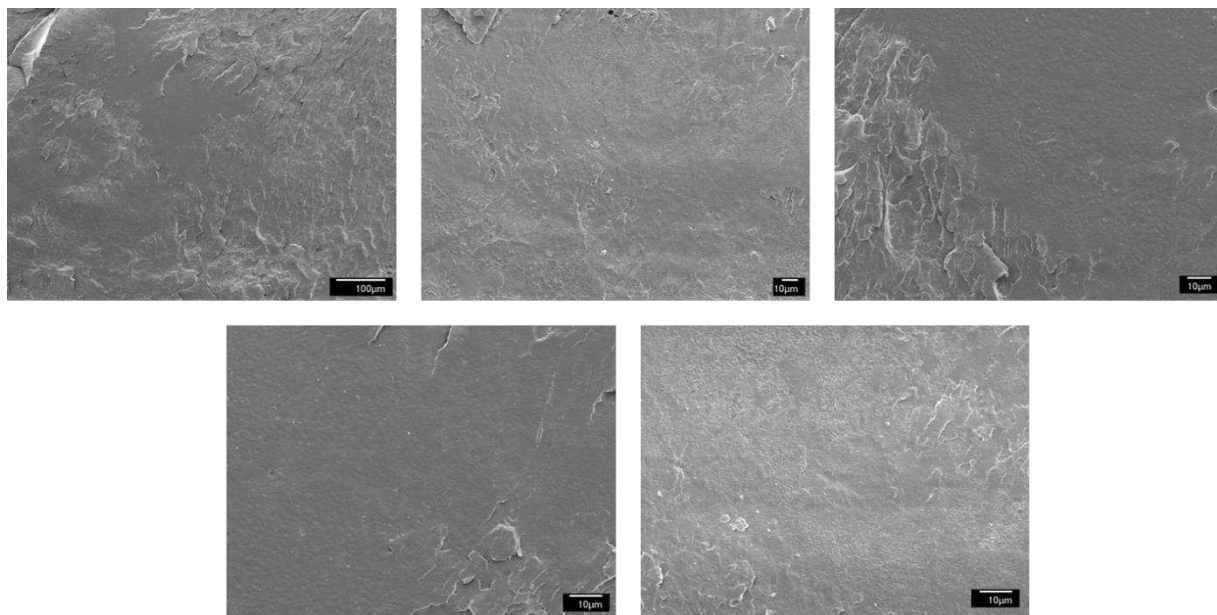




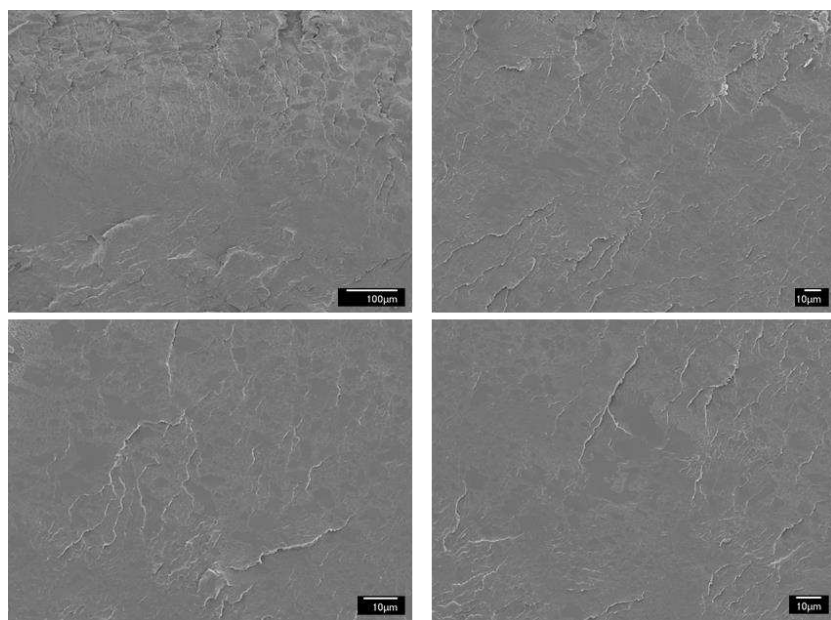
**Figure D72.** Cross section images of the 50/50 wt% LDPE-P3HB blend crosslinked with 5 wt. % UDC1.



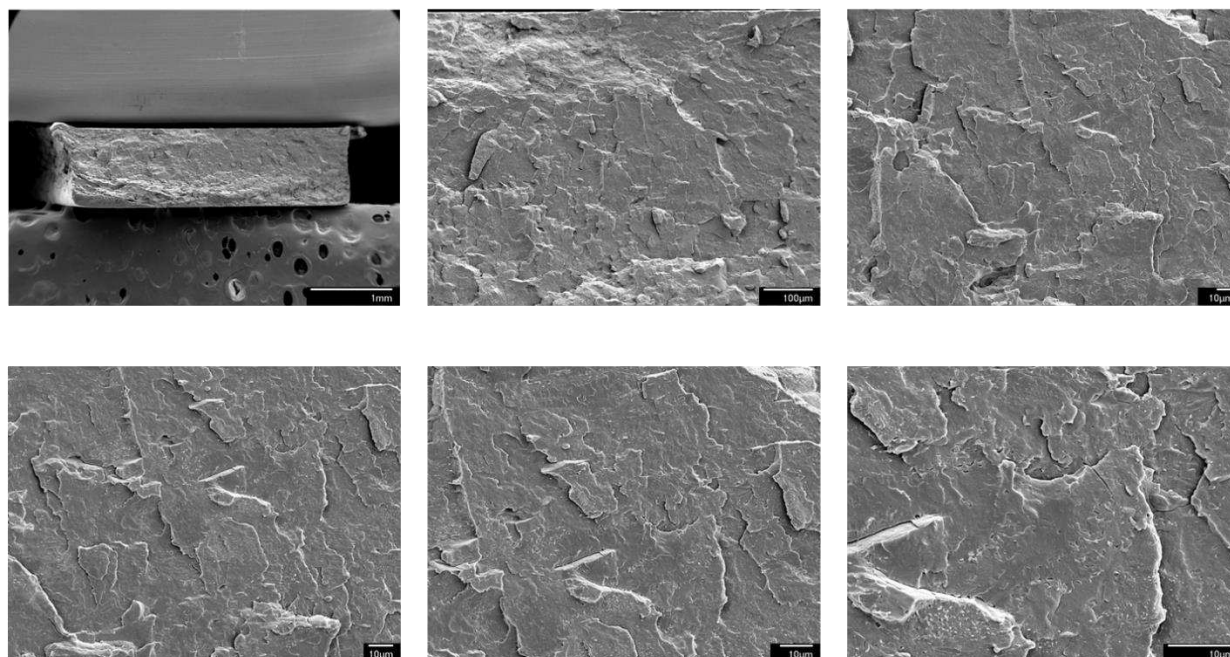
**Figure D73.** Cross section images of the 50/50 wt% LDPE-P3HB blend crosslinked with 5 wt. % UDC3.



**Figure D74.** Cross section images of the 50/50 wt% LDPE-PLA blend crosslinked with 5 wt. % UDC1.



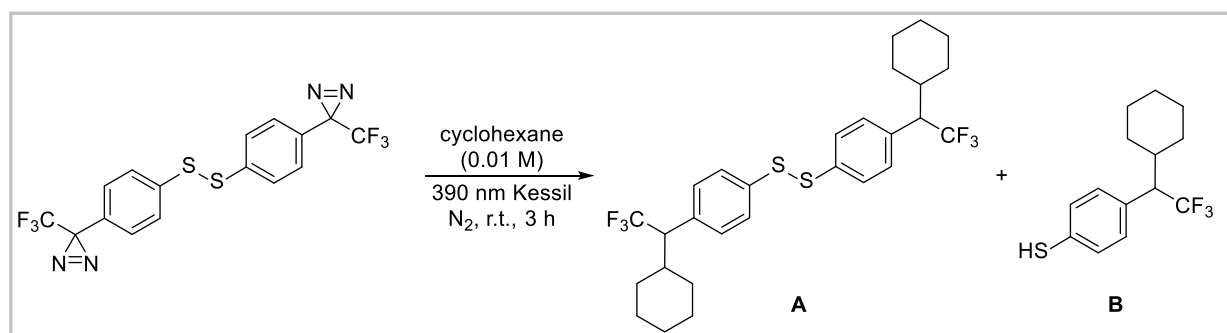
**Figure D75.** Cross section images of the 50/50 wt% LDPE-PLA blend crosslinked with 5 wt. % UDC3.



**Figure D76.** Cross section images of the 50/50 wt% LDPE-PLA blend crosslinked with 5 wt. % UDC3 processed by melt-extrusion.

## Supplementary Tables

**Table D1.** Tabulated cyclohexane insertion screening under varied conditions for UDC2.

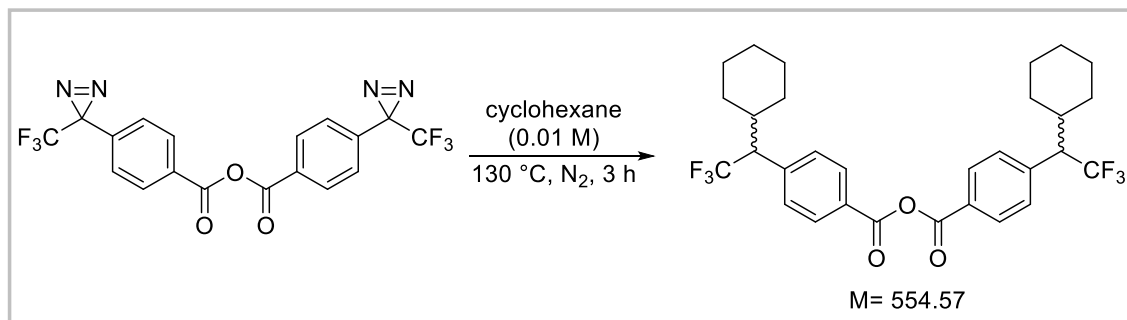


| Entry | Deviation from standard conditions | Yield A <sup>a</sup> | Yield B <sup>a</sup> |
|-------|------------------------------------|----------------------|----------------------|
| 1     | none                               | 15%                  | 3%                   |
| 2     | 370 nm Kessil lamp                 | 12%                  | 2%                   |

|   |                                                    |        |        |
|---|----------------------------------------------------|--------|--------|
| 3 | air                                                | 11%    | traces |
| 4 | H <sub>2</sub> O (2.0 equiv)                       | 15%    | 4%     |
| 5 | O <sub>2</sub> atmosphere                          | traces | n.d.   |
| 6 | 130 °C in the dark                                 | 39%    | traces |
| 7 | 130 °C in the dark + air                           | 33%    | n.d.   |
| 8 | 130 °C in the dark + H <sub>2</sub> O (15.0 equiv) | 38%    | n.d.   |
| 9 | 130 °C in the dark, O <sub>2</sub> atmosphere      | 14%    | n.d.   |

Reactions run on 0.04 mmol scale. n.d. = not detected. (a) Yields were determined by <sup>1</sup>H-NMR spectroscopy of crude reaction mixtures using 1,4-dinitrobenzene as an internal standard.

**Table D2.** Tabulated cyclohexane insertion screening under varied conditions for UDC3.



| Entry | Deviation from standard conditions | Yield <sup>a</sup> |
|-------|------------------------------------|--------------------|
| 1     | none                               | 53%                |
| 2     | air                                | 51%                |
| 3     | H <sub>2</sub> O (5.0 equiv)       | 49%                |
| 4     | 390 nm Kessil lamp                 | 29%                |

Reactions run on 0.02 mmol scale. (a) Yields were determined by <sup>1</sup>H-NMR spectroscopy of crude reaction mixtures using 1,4-dinitrobenzene as an internal standard.

**Table D3.** Evolution of thermal transitions in LMWPE with varied UDC loading.

| Polymer        | $T_m$ (°C) | $\Delta H_f$ (J/g) |
|----------------|------------|--------------------|
| LMWPE 0%       | 105        | 103                |
| LMWPE 5% UDC1  | 104        | 88.9               |
| LMWPE 10% UDC1 | 98.6       | 62.6               |
| LMWPE 5% UDC2  | 104        | 85.8               |
| LMWPE 10% UDC2 | 91.5       | 74.4               |
| LMWPE 5% UDC3  | 105        | 92.1               |
| LMWPE 10% UDC3 | 104        | 84.1               |

**Table D4.** Evolution of thermal transitions in LDPE with varied UDC loading.

| Polymer       | $T_m$ (°C) | $\Delta H_f$ (J/g) |
|---------------|------------|--------------------|
| LDPE 0%       | 110        | 127                |
| LDPE-UDC1 5%  | 103        | 97.6               |
| LDPE-UDC1 10% | 99.0       | 88.3               |
| LDPE-UDC3 5%  | 107        | 98.2               |
| LDPE-UDC3 10% | 101        | 95.8               |

**Table D5.** Evolution of thermal transitions in HDPE with varied UDC loading.

| Polymer       | $T_m$ (°C) | $\Delta H_f$ (J/g) |
|---------------|------------|--------------------|
| HDPE 0%       | 132        | 127                |
| HDPE-UDC1 5%  | 132        | 194                |
| HDPE-UDC1 10% | 122        | 138                |
| HDPE-UDC3 5%  | 129        | 187                |
| HDPE-UDC3 10% | 123        | 147                |

**Table D6.** Evolution of thermal transitions in UHMWPE with varied UDC loading.

| Polymer        | $T_m$ (°C) | $\Delta H_f$ (J/g) |
|----------------|------------|--------------------|
| HMWPE 0%       | 133        | 150                |
| HMWPE-UDC1 5%  | 114        | 118                |
| HMWPE-UDC1 10% | 114        | 114                |
| HMWPE-UDC3 5%  | 130        | 141                |
| HMWPE-UDC3 10% | 123        | 118                |

**Table D7.** Evolution of thermal transitions in *it*-PP with varied UDC loading.

| Polymer               | $T_m$ (°C) | $\Delta H_f$ (J/g) |
|-----------------------|------------|--------------------|
| <i>it</i> -PP 0%      | 162        | 88.0               |
| <i>it</i> -PPUDC1 5%  | 156        | 76.7               |
| <i>it</i> -PPUDC1 10% | 149        | 60.4               |
| <i>it</i> -PPUDC3 5%  | 156        | 79.6               |
| <i>it</i> -PPUDC3 10% | 156        | 71.8               |

**Table D8.** Evolution of thermal transitions in PLA with varied UDC loading.

| Polymer      | $T_m$ (°C) | $\Delta H_f$ (J/g) | $T_g$ (°C) |
|--------------|------------|--------------------|------------|
| PLA 0%       | 173        | 47.2               | 56.1       |
| PLA-UDC1 5%  | 166        | 37.1               | 55.2       |
| PLA-UDC1 10% | 156        | 28.3               | 58.1       |
| PLA-UDC3 5%  | 163        | 23.3               | 61.8       |
| PLA-UDC3 10% | 160        | 4.3                | 63.5       |

**Table D9.** Evolution of thermal transitions in P3HB with varied UDC loading.

| Polymer       | $T_m$ (°C) | $\Delta H_f$ (J/g) | $T_g$ (°C) |
|---------------|------------|--------------------|------------|
| P3HB 0%       | 171        | 89.0               | 5.9        |
| P3HB-UDC1 5%  | 166        | 87.2               | 0.4        |
| P3HB-UDC1 10% | 161        | 72.6               | 1.1        |
| P3HB-UDC3 5%  | 165        | 79.8               | 4.3        |
| P3HB-UDC3 10% | 159        | 72.4               | 4.2        |

**Table D10.** Temperature-ramp frequency sweep results for virgin and UDC-treated LDPE/HDPE samples (0.3 % strain, 1 Hz, -50 to 200 °C, 5 °C/min).

| Polymer       | $E'_{RT}$ (MPa) | $E'_{max}$ (MPa) |
|---------------|-----------------|------------------|
| LDPE 0 %      | 784 ± 149       | 2531 ± 208       |
| LDPE 5 % UDC1 | 730 ± 92        | 3055 ± 157       |
| LDPE 5 % UDC3 | 977 ± 110       | 3198 ± 12        |
| HDPE 0 %      | 2990 ± 74       | 3818 ± 138       |
| HDPE 5 % UDC1 | 2840 ± 105      | 3941 ± 72        |
| HDPE 5 % UDC3 | 3127 ± 158      | 4224 ± 188       |

**Table D11.** Tensile stress/strain data for each reported LDPE-UDC and LDPE-USC sample, along with reprocessing trial data.

| Polymer          | Stress (MPa) | Strain (%) | Modulus (MPa) | Toughness (MJ m <sup>-3</sup> ) |
|------------------|--------------|------------|---------------|---------------------------------|
| LDPE             | 10.5 ± 0.1   | 113 ± 5.8  | 345 ± 14      | 12.4 ± 0.7                      |
| LDPE 5 % UDC3    | 13 ± 0.4     | 116 ± 4.0  | 245 ± 3.0     | 12.7 ± 0.6                      |
| LDPE 5 % UDC3 R1 | 12 ± 0.4     | 91 ± 6.6   | 166 ± 16      | 8.9 ± 0.5                       |
| LDPE 5 % USC     | 8.9 ± 1.0    | 38 ± 12    | 166 ± 10      | 2.8 ± 1.1                       |
| LDPE 5 % USC R1  | 7.5 ± 0.5    | 16 ± 3.7   | 160 ± 6.4     | 1.0 ± 0.3                       |

**Table D12.** Creep-recovery data for virgin and UDC-treated LDPE and HDPE by DMA, in tension film mode, below the melt thermal transition (40 – 110 °C, 2 MPa, 5 °C/min 600 s or 4 h as specified creep duration, 300 s or 0.5 h as specified recovery time).

| Sample         | Temperature (°C) | Creep/Recovery (min) | Creep (%) | Recovered (%) |
|----------------|------------------|----------------------|-----------|---------------|
| LDPE (MFI 21)  | 80               | 10/5                 | 26.5      | 19.1          |
| HDPE (MFI 7.6) | 110              | 10/5                 | 7.4       | 4.7           |
| HDPE (MFI 7.6) | 40               | 240/30               | 2.8       | 0.4           |
| LDPE UDC1 5%   | 80               | 10/5                 | 12.4      | 11.7          |
| LDPE UDC3 5%   | 80               | 10/5                 | 9.0       | 8.1           |
| HDPE UDC1 5%   | 110              | 10/5                 | 4.8       | 4.2           |
| HDPE UDC3 5%   | 110              | 10/5                 | 5.7       | 5.1           |
| HDPE UDC1 5%   | 40               | 240/30               | 1.8       | 1.3           |
| HDPE UDC3 5%   | 40               | 240/30               | 1.5       | 1.3           |

**Table D13.** Creep-recovery data for virgin, USC-, and UDC-treated LDPE and HDPE by bulk shear rheology in the flow-state (130 – 160 °C, 10 min creep, 5 min recovery, 2.5 kPa).

| Sample         | Temperature (°C) | Creep (%) | Recovered (%) |
|----------------|------------------|-----------|---------------|
| LDPE (MFI 21)  | 130              | 90877     | 112           |
| HDPE (MFI 7.6) | 150              | 77681     | 28            |
| LDPE UDC1 5%   | 130              | 53 ± 8.0  | 22 ± 1.1      |
| LDPE UDC1 5%   | 140              | 103 ± 7.5 | 66 ± 0.6      |
| LDPE UDC3 5%   | 130              | 89 ± 34   | 41 ± 1.2      |
| LDPE UDC3 5%   | 140              | 190 ± 33  | 40 ± 1.6      |
| HDPE UDC1 5%   | 150              | 411 ± 16  | 25 ± 0.3      |
| HDPE UDC1 5%   | 160              | 610 ± 20  | 31 ± 1.4      |
| HDPE UDC3 5%   | 150              | 521 ± 25  | 73 ± 14       |
| HDPE UDC3 5%   | 160              | 808 ± 19  | 207 ± 7.5     |
| LDPE USC 5%    | 130              | 24 ± 1.6  | 21 ± 1.1      |

**Table D14.** Rheological high-temperature frequency sweeps: rubbery plateau storage moduli ( $G'$ ) and crosslinking density ( $C_x$ ) (130-160 °C, 0.1 % shear strain, 0.5 to 5 rad/s).

| Sample       | Temperature (°C) | $G'$ (Pa)   |
|--------------|------------------|-------------|
| LDPE UDC1 5% | 130              | 23185 ± 646 |
| LDPE UDC1 5% | 140              | 23377 ± 208 |
| LDPE UDC1 5% | 150              | 23226 ± 307 |
| LDPE UDC1 5% | 160              | 23381 ± 32  |
| LDPE UDC3 5% | 130              | 11027 ± 61  |
| LDPE UDC3 5% | 140              | 10433 ± 144 |
| LDPE UDC3 5% | 150              | 9173 ± 42   |
| LDPE UDC3 5% | 160              | 8293 ± 61   |

**Table D15.** Baseline thermal transition and crystallinity data for homopolymers advanced to dynamic blending (-50 to 200 °C, 10 °C/min heat/cool ramp).

| Polymer | $T_m$ °C | $\Delta H_f$ (J/g) | $T_g$ (°C) | % $X_c$ |
|---------|----------|--------------------|------------|---------|
| LMWPE   | 105      | 55.4               | -          | 18.9    |
| LDPE    | 110      | 127                | -          | 43.2    |
| P3HB    | 171      | 89.0               | 5.9        | 61.4    |
| PLA     | 173      | 47.2               | 58.0       | 50.6    |

**Table D16.** LMWPE-PLA blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

| Sample            | $T_m$ LMWPE (°C) | $\Delta H_f$ LMWPE (J/g) | $X_c$ (%) | $T_m$ PLA (°C) | $\Delta H_f$ PLA (J/g) | $X_c$ (%) | $T_g$ PLA (°C) |
|-------------------|------------------|--------------------------|-----------|----------------|------------------------|-----------|----------------|
| LMWPE-PLA 0%      | 108              | 20.2                     | 6.6       | 171            | 28.8                   | 29.3      | 59.0           |
| LMWPE-PLA 5% UDC1 | 99.9             | 18.5                     | 6.0       | 167            | 20.8                   | 21.1      | 58.0           |
| LMWPE-PLA 5% UDC2 | 91.4             | 8.8                      | 2.9       | 169            | 27.1                   | 27.5      | 59.2           |
| LMWPE-PLA 5% UDC3 | 105              | 25.8                     | 8.4       | 164            | 15.3                   | 15.5      | 56.3           |
| LMWPE-PLA 5% USC  | 100              | 31.0                     | 10.1      | 168            | 17.9                   | 18.2      | 58.0           |



**Table D17.** LMWPE-P3HB blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

| Sample             | $T_m$ LMWPE (°C) | $\Delta H_f$ LMWPE (J/g) | $X_c$ (%) | $T_m$ P3HB (°C) | $\Delta H_f$ P3HB (J/g) | $X_c$ (%) | $T_g$ P3HB (°C) |
|--------------------|------------------|--------------------------|-----------|-----------------|-------------------------|-----------|-----------------|
| LMWPE-P3HB 0%      | 105              | 25.2                     | 8.2       | 175             | 35.9                    | 23.6      | -               |
| LMWPE-P3HB 5% UDC1 | 101              | 15.8                     | 5.1       | 161             | 32.2                    | 21.1      | 1.6             |
| LMWPE-P3HB 5% UDC2 | 104              | 16.3                     | 5.3       | 168             | 31.9                    | 20.9      | 3.4             |
| LMWPE-P3HB 5% UDC3 | 103              | 19.1                     | 6.2       | 161             | 36.7                    | 24.0      | 3.0             |
| LMWPE-P3HB 5% USC  | 100              | 12.2                     | 4.0       | 139             | 19.9                    | 13.1      | -               |

**Table D18.** LDPE-PLA blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

| Sample           | $T_m$ LDPE (°C) | $\Delta H_f$ LDPE (J/g) | $X_c$ (%) | $T_m$ PLA (°C) | $\Delta H_f$ PLA (J/g) | $X_c$ (%) | $T_g$ PLA (°C) |
|------------------|-----------------|-------------------------|-----------|----------------|------------------------|-----------|----------------|
| LDPE-PLA 0%      | 108             | 15.3                    | 4.9       | 170            | 27.3                   | 27.7      | 59.3           |
| LDPE-PLA 5% UDC1 | 102             | 16.8                    | 5.4       | 168            | 13.9                   | 14.2      | 58.7           |
| LDPE-PLA 5% UDC2 | 107             | 13.5                    | 4.4       | 169            | 22.4                   | 22.7      | 60.9           |
| LDPE-PLA 5% UDC3 | 105             | 14.0                    | 4.6       | 165            | 12.8                   | 13.0      | 59.3           |
| LDPE-PLA 5% USC  | 105             | 19.3                    | 6.3       | 165            | 18.6                   | 18.9      | 60.0           |

**Table D19.** LDPE-P3HB blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

| Sample            | $T_m$ LDPE (°C) | $\Delta H_f$ LDPE (J/g) | $X_c$ (%) | $T_m$ P3HB (°C) | $\Delta H_f$ P3HB (J/g) | $X_c$ (%) |
|-------------------|-----------------|-------------------------|-----------|-----------------|-------------------------|-----------|
| LDPE-P3HB 0%      | 110             | 24.0                    | 7.8       | 170             | 33.7                    | 22.1      |
| LDPE-P3HB 5% UDC1 | 103             | 17.0                    | 5.4       | 166             | 26.5                    | 17.4      |
| LDPE-P3HB 5% UDC2 | 103             | 30.0                    | 9.7       | 157             | 15.5                    | 10.2      |
| LDPE-P3HB 5% UDC3 | 105             | 24.8                    | 8.1       | 163             | 30.1                    | 19.8      |
| LDPE-P3HB 5% USC  | 103             | 31.6                    | 10.3      | 137             | 20.7                    | 13.6      |

**Table D20.** Tabulated maximum storage modulus values (-50 °C) for LDPE-PLA/P3HB blends at virgin and with UDC or USC incorporation (0.3 % strain, 1 Hz, -50 – 200 °C, 5 °C/min).

| LDPE-P3HB Blend                   | $E'_{max}$ (-50 °C, MPa) |
|-----------------------------------|--------------------------|
| 0%                                | 1635 ± 14                |
| 5% UDC1                           | 3535 ± 45                |
| 5% UDC3                           | 2883.9 ± 11.2            |
| 5% USC                            | 2179 ± 856               |
| LDPE-PLA Blend                    | $E'_{max}$ (-50 °C, MPa) |
| 0%                                | 2795 ± 91                |
| 5% UDC1                           | 3714 ± 148               |
| 5% UDC3                           | 3008 ± 79                |
| 5% USC                            | 3634 ± 187               |
| Extruded LDPE-PLA Blend           | $E'_{max}$ (-50 °C, MPa) |
| 1 <sup>st</sup> Cycle             | 2458 ± 229               |
| Reprocessed 2 <sup>nd</sup> Cycle | 2312 ± 68                |

**Table D21.** Tabulated maximum storage modulus values (-50 °C) for blends of LDPE-PLA/P3HB at virgin and with UDC or USC incorporation (0.3 % strain, 1 Hz, -50 – 200 °C, 5 °C/min).

| Polymer              | Stress (MPa) | Strain (%) | Modulus (MPa) | Toughness (MJ m <sup>-3</sup> ) |
|----------------------|--------------|------------|---------------|---------------------------------|
| LDPE-PLA             | 5.6 ± 0.7    | 1.9 ± 0.8  | 1100 ± 87     | 0.04 ± 0.2                      |
| LDPE-PLA 5 % UDC3    | 17 ± 2.6     | 3.0 ± 1.0  | 978 ± 18      | 0.34 ± 0.2                      |
| LDPE-PLA 5 % UDC3 R1 | 19.4 ± 0.6   | 5.1 ± 0.5  | 1003 ± 34     | 0.74 ± 0.1                      |

**Table D22.** Average diameter (micrometers) and median diameter (micrometers) for droplets imaged within the cross-sections of LMWPE-PLA/P3HB binary blends both of virgin quality and once crosslinked with UDCs 1-3, USC, or functionalized with MDC as described (10 micrometers gold, 3 kV).

| Blend Sample   | Average Diameter (μm) | Median Diameter (μm) | Notes                                |
|----------------|-----------------------|----------------------|--------------------------------------|
| Virgin PE-PLA  | 29 ± 11               | 29                   | Minority smaller droplets also found |
| PE-PLA UDC2    | -                     | -                    | No droplets found                    |
| PE-PLA USC     | 2.1 ± 0.9             | 2.0                  | Minority larger droplets also found  |
| PE-PLA MDC     | 45 ± 23               | 43                   | Minority smaller droplets also found |
| Virgin PE-P3HB | 32 ± 13               | 25                   | Minority smaller droplets also found |
| PE-P3HB UDC1   | 2.8 ± 1.4             | 2.7                  | Low droplet population               |
| PE-P3HB UDC2   | -                     | -                    | No droplets found                    |
| PE-P3HB UDC3   | -                     | -                    | No droplets found                    |
| PE-P3HB USC    | 1.6 ± 0.7             | 1.8                  | Minority smaller droplets also found |
| PE-P3HB MDC    | 48 ± 17               | 47                   | Minority larger droplets also found  |

**Table D23.** Average diameter (micrometers) and median diameter (micrometers) for droplets imaged within the cross-sections of LDPE-PLA/P3HB binary blends both of virgin quality and once crosslinked with UDCs 1-3 as described (10 micrometers gold, 3 kV).

| Blend Sample | Average Diameter (μm) | Median Diameter (μm) | Notes             |
|--------------|-----------------------|----------------------|-------------------|
| LDPE-PLA     | 6.6 ± 4.8             | 4.7                  | -                 |
| PE-PLA UDC1  | -                     | -                    | No droplets found |
| PE-PLA UDC2  | -                     | -                    | No droplets found |
| PE-PLA UDC3  | -                     | -                    | No droplets found |
| LDPE-P3HB    | 5.1 ± 2.6             | 4.5                  | -                 |
| PE-P3HB UDC1 | -                     | -                    | No droplets found |
| PE-P3HB UDC2 | -                     | -                    | No droplets found |
| PE-P3HB UDC3 | -                     | -                    | No droplets found |

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