DISSERTATION

ADVANCEMENTS IN THE CHEMICAL RECYCLABILITY OF ACRYLIC POLYMERS THROUGH INVESTIGATION OF MONOMER DESIGN

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Spring 2024

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ABSTRACT

ADVANCEMENTS IN THE CHEMICAL RECYCLABILITY OF ACRYLIC POLYMERS THROUGH INVESTIGATION OF MONOMER DESIGN

Depolymerization is a key avenue of state-of-the-art recycling of polymeric materials. Although many polymers have been investigated for their ability to depolymerize, a subset of polymers has been widely left out of the conversation, polyolefins, or polymers containing C-C bonds in the polymer main-chain. Acrylic polymers are an important class of polyolefins used throughout the world in a variety of applications. One of the key drawbacks of the polymer, however, is their unfavorable depolymerization conditions, requiring high temperatures in expensive reactors. Although much work has been performed on the depolymerization of the most widely used acrylic polymer, poly(methyl methacrylate) (PMMA), there have been few reports on trying to improve upon the recycling methods, such as decreasing depolymerization temperature or gaining control over the depolymerization mechanism.

In this work, key mechanistic steps of acrylic polymer depolymerization are investigated to gain fundamental understanding on the limitations faced during depolymerization and try to improve upon them. When poly(α-methylene-γ-butyrolactone) (PMBL) and poly(α-methylene-γ-methyl-γ-butyrolactone) (PMMBL) were investigated, the suppression of side reactions that occurred with PMMA depolymerization were identified and attributed to the pendant lactone tethering radical species together. Employing this tethering effect, the design of new polymers with pendant lactones and lower equilibrium polymerization temperatures (ceiling temperature or T_C), was carried out, overall decreasing depolymerization temperatures and improving

polymer recyclability. Finally, these new polymers were incorporated into the design of copolymers with PMMA and PMMBL in order to exploit the new polymers' depolymerizability without hindering thermomechanical properties. Overall, this work has shed light onto the importance of polyolefin design in, not just thermomechanical properties, but also polymerization and depolymerization behavior which will benefit the continued development of recyclable-by-design polymers.

ACKNOWLEDGEMENTS

I would first like to thank my graduate committee: Professor Eugene Chen, Professor Garret Miyake, Professor Matthew Shores, and Professor Margarita Herrera-Alonso. They have been supportive and insightful in their help and guidance throughout my graduate studies. I would also like to thank some of the other Colorado State University professors for their help and guidance: Professor Jeff Bandar, Professor Joe Zadrozny, Professor Amy Prieto, Professor Melissa Reynolds, and Professor Justin Sambur.

Through my graduate studies and undergraduate studies, I have been lucky enough to encounter some amazing people that helped me in innumerable ways. I would like to thank all the undergraduate students, graduate students, postdoctoral researchers, and visiting scholars in both the Chen Group and Miyake Group. You have made such a dramatic impact on my life, and I would not be here without you all. I would like to call out a few particular people, however: Dr. Ryan Clarke, your constant guidance, support, encouragement, and entertainment was extremely welcoming. Watching your transformation from your first year to now has been amazing and you make me strive to be better. Dr. Andrea Westlie, your insight and expertise in every aspect of chemistry have been indispensable. Your drive to know more and be the best you can is infectious, and I will be forever grateful for having been able to work with you. Dr. Eswara Chokkapu, your striving for perfection and undying happiness has pushed me past a lot of big hurdles. You have helped me in so many ways I cannot describe. Dr. Ravikumar Gowda, your guidance and support have allowed me to get here, I would have been lost without your support. Dr. Ryan Pearson, you showed me what it would take to get here, you are my first mentor in chemistry, and I cannot thank you enough. Matthew Nicki, you supported me both in and out of lab, helping me through the challenges computational chemistry and the world beyond graduate school. Also, everyone from the BOTTLE consortium, I am grateful to have been able to contribute to the wonderful work you all have done, and I can't wait to read whatever comes next for you all.

I would also like to thank my advisor Professor Eugene Chen. You taught me more than just science, you taught me about life. You allowed me to grow as both a person and a scientist. I am thankful for everything you have done for me and, even though we have had ups and downs, I will be forever grateful for the time I was able to spend around you and for your guidance throughout my graduate studies.

I would like to thank my undergraduate advisor, Professor Garret Miyake. You inspired my passion for polymer chemistry and showed me how to learn outside of a classroom. The group you have built since I left has become something truly special. I am excited whenever I get to delve back into the amazing research your group does. I always look back at the late nights at CU Boulder in the Cristol Chemistry building with Ryan, Matt, and Blaine doing "bucket chemistry" with fondness.

I would like to thank my parents: Barbara, Daniel, Dave, and Tracey. You have all made it possible for me to get to where I am. Without your support and help throughout my life I can say that I would not have even made it to this point. The sacrifices and pitfalls you all faced in the light of my success will always mean so much to me. I am thankful for you all every day.

Finally, I would like to thank my partner, Kimberly Barosh. You have been my guiding light through everything. You have supported me through my highs and lows, brought be back from the edge, and allowed me to meet every goal I have set. I love you.

Chapter 2: This dissertation chapter contains the manuscript of an article [Gilsdorf, R.A.; Chokkapu, E. R.; Chen, E. Y.-X. Integration of Biobased Building Blocks in Circular Polymer Strategies: The Case of Vinyl Polymers. *In preparation*].

Chapter 3: This dissertation chapter contains the manuscript of an article [Gilsdorf, R. A.; Nicki, M. A.; Chen, E. Y.-X. High Chemical Recyclability of Vinyl Lactone Acrylic Bioplastics. *Polym. Chem.* **2020**, *11* (30), 4942–4950.]. Eugene Chen conceived of the idea, provided funding, directed the project, wrote the manuscript, and edited the final report. Matt Nicki performed density functional theory (DFT) experiments used in this work under the guidance of Reid Gilsdorf and edited the final report. Reid Gilsdorf performed the experiments, analyzed and interpreted results, wrote the manuscript, and edited the final report.

The writing of this chapter was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office (AMO) and Bioenergy Technologies Office (BETO). This work was performed as part of the BOTTLE™ Consortium and funded under contract no. DE-AC36-08GO28308 with the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy.

Chapter 4: This dissertation chapter contains the partial manuscript of an article [Gilsdorf, R. A.; Chokkapu, E. R.; Athaley, A.; Uekert, T.; Gowda, R. R.; Singh, A.; DesVeaux, J.; Beckham, G. T.; Chen, E. Y.-X. Bio-based Recyclable Lactone-acrylic Plastics with Performance-advantaged Properties. *Cell Reports Physical Science*, **2024**, *Accepted*]. Eugene Chen and Gregg Beckham conceived of the idea, provided funding, directed the project, wrote the manuscript, and edited the final report, Jason DesVeaux performed technoeconomic analysis, interpreted the results, and edited the final report. Avantika Singh directed the technoeconomic analysis. Ravikumar Gowda performed gel permeation chromatography analysis, directed the project, and edited the final report. Taylor Uekert performed the life cycle assessment, interpreted the results, wrote the manuscript, and edited the final report. Abhay Athaley performed the technoeconomic analysis, interpreted results, wrote the manuscript, and edited the final report. Eswara Chokkapu performed the experiments, analyzed and interpreted results, wrote the manuscript, and edited the final report. Reid Gilsdorf performed the experiments, analyzed and interpreted results, wrote the manuscript, and edited the final report.

The work described in this chapter was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Materials and Manufacturing Technologies Office (AMMTO) and Bioenergy Technologies Office (BETO). This work was performed as part of the Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE) Consortium and was supported by AMMTO and BETO under Contract DE-AC36-08GO28308 with the National Renewable Energy Laboratory (NREL), operated by Alliance for Sustainable Energy, LLC. The BOTTLE Consortium includes members from Colorado State University.

Chapter 5: This dissertation chapter contains the manuscript of an article [Gilsdorf, R. A.; Chokkapu, E. R..; Gowda, R. R.; Chen, E. Y.-X.. Depolymerization of PMMA Copolymers Under Mild, Catalyst-free Conditions. *In preparation*]. Eugene Chen conceived of the idea, provided funding, directed the project, wrote the manuscript, and edited the final report. Eswara Chokkapu conceived of the idea, performed the experiments, analyzed and interpreted results, wrote the manuscript, and edited the final report. Reid Gilsdorf conceived of the idea, performed the experiments, analyzed and interpreted results, wrote the manuscript, and edited the final report.

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DEDICATION

This dissertation is dedicated to my partner Kimberly Barosh.

I would truly be lost without you.

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CHAPTER 1.

INTRODUCTION

Thesis Structure

This dissertation describes the work done to address the growing plastics crisis by studying bio-based recyclable-by-design acrylic polymers as alternatives for petroleum-based commodity acrylic polymers. The first development was originally intended to be a pursuit toward catalytic recycling of the most widely used acrylic polymer, PMMA, however, it quickly became clear that polymers previously developed by members of the Chen group were poised to be just as insightful in addressing similar problems, warranting more extensive investigations. This lead to developing a thorough understanding of the depolymerization mechanism of acrylic polymers containing pendant lactones. This mechanism is described and utilized for the development of polymers with improved recyclability. Finally, the new monomers were used to produce copolymers with MMA that showed improved recyclability.

The overall structure of this dissertation follows a journal-format style. Select publications from the author's graduate studies have been utilized for the body of the work, with each chapter being modeled from one manuscript. The first chapter includes a mini-review on the development of bio-based vinyl polymers, The rest of this dissertation includes research articles by the author including one published in *Polymer Chemistry* and two others yet to be submitted articles. The topics covered in this thesis are submitted in four chapter with the following titles:

1. Integration of Biobased Building Blocks in Circular Polymer Strategies: The Case of

Vinyl Polymers

2. High Chemical Recyclability of Vinyl Lactone Acrylic Bioplastics

3. Bio-based Recyclable Lactone-acrylic Plastics with Performance-advantaged Properties

4. Depolymerization PMMA Copolymers Under Mild, Catalyst-free Conditions

In addition to these topics, the author published an additional article not included in the scope of this dissertation: Song, Y.; He, J.; Zhang, Y.; Gilsdorf, R. A.; Chen, E. Y.-X. Recyclable Cyclic Bio-Based Acrylic Polymer via Pairwise Monomer Enchainment by a Trifunctional Lewis Pair. *Nat. Chem.* **2023**, *11*, 366–376. Reid Gilsdorf performed thermogravometric analysis coupled mass spectroscopy experiments, interpreted the results, and edited the final report.

Motivations

At the beginning of this work in 2017, the depolymerization of polymers was an extremely active area of research. Acrylic polymers, however, were not well investigated, with the first modern publication on catalytic depolymerization being published in 2019.[1] This initial report kickstarted the development of catalytic depolymerization of acrylic polymers with functionalized chain-end groups.[2–8] Instead of attempting to dive into this burgeoning area of interest, other researchers were focused on recyclable-by design materials, or polymers developed from the ground up with the intention of being able to be depolymerized back to monomer.[9] These materials allowed for iterative tuning to develop polymers with desirable properties while still allowing for recycling. The initial focus, however, was on polymers containing heteroatoms in their backbones (i.e. C-X in the polymer main chain).[10–12] Therefore, a wide space was left empty for the development of vinyl polymers with a similar focus of first designing for recyclability. Previously, our group, in particular, had been developing methods for the polymerization of lactone acrylate monomers, mainly α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL) as bio-based alternatives to PMMA.

Over the course of this work, these monomers were utilized as the template for recyclable-by-design acrylic monomers, as the initial investigation into their recyclability showed the potential of the privileged lactone in the mechanism of depolymerization (Chapter 3). The design principles developed from this mechanistic understanding enabled the selection of a previously utilized bio-based monomer, α-methylene-δ-valerolactone (MVL), and the design of a new monomer, α-methylene-δ-decalactone (MDL). These two monomers enabled the enhanced recyclability of the scaffold monomer, MMBL, at much lower temperatures and in higher yield (Chapter 4). This work was then adapted to address the recyclability of PMMA in copolymers with nearly identical properties to PMMA homopolymer (Chapter 5).

Overall, this work has provided a foundational understanding for the design of recyclable acrylic monomers. In a global context, the insights gained from this work will be helpful in the development of future materials constructed to address the looming issues of recyclability at scale. Additionally, this works illustrates that the understanding that has been cultivated from the design of heteroatom containing polymers can be directly applied to acrylic polymers, allowing for new avenues of discovery to be opened within the field of acrylic materials - a field that has generally been resigned to simple ester substitutions for a means of tuning material properties.

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CHAPTER 2.

INTEGRATION OF BIOBASED BUILDING BLOCKS IN CIRCULAR POLYMER STRATEGIES: THE CASE OF VINYL POLYMERS

Overview

Vinyl polymers are an important class of polymers with unique properties that are not easily replicated by other polymer classes. Despite this, vinyl polymers have seen little attention in their recycling to enable a circular polymer economy. As recycling technologies and design advance for polymers with C-X linkages within the polymer backbone it is necessary to turn attention to vinyl polymers and address the challenges these materials possess. The clever design of monomers can readily enable depolymerizability and provide vinyl polymers access to circularity while maintaining the desirable properties of this robust class of polymers.

Introduction

In recent years, there has been a focus on polymers with C-X (heteroatom) linkages within the polymer backbone (polyesters, polyamides [nylons], polycarbonates, polyurethanes, etc.) for circular polymer strategies,[1–6] however, the properties and performance advantages of vinyl polymers is important to the materials economy and these properties may not be replicated by C-X containing polymer mimics. Carbon-carbon bonds in the polymer backbone allow for the high solvent resistance, glass transition temperature (T_g), degradation temperature (T_d), and strength which are desirable for a variety of products.[7,8] These C-C bonds, however, prove to be the reason for the low depolymerizability of these materials.[9–13] Due to this challenge, there have been relatively few advances in recycling vinyl polymers that enable a circular economy.

Although these technologies are advancing, vinyl polymer design has stagnated in terms of circular polymers. Many bio-building blocks are well suited for use as vinyl monomers with little to no derivation needed to make them suitable as monomers in current polymerization strategies. The main issues with these monomers, however, is the lack of importance in depolymerization strategies, preventing these biobased polymers from being truly circular. Designing vinyl polymers to be intrinsically circular polymers (iCPs) is relatively difficult and, generally, it consists of selecting a monomer with a low ceiling temperature (T_C) or the equilibrium temperature of polymerization. This low T_C allows for a polymer to depolymerize readily to monomer upon being reactivated to an active species. Although this may seem straightforward, designing a monomer with a low T_C and is readily polymerizable at reasonable temperatures still proves to be challenging.[14] In this article the design of monomers with this ideal T_C are examined through four separate reports. These examples provide ample evidence that monomer design is critical in addressing the challenges of vinyl polymers and their place within the circular materials economy.

Addressing Poly(methyl methacrylate)

Biobased alternatives for poly(methyl methacrylate) (PMMA) have been a focus of the polymer community due to its ubiquity in polymer methodology research.[15–17] Although PMMA can be depolymerized back to monomer (MMA) in high yield, the processes are energy intensive and result in monomer that must be purified to make virgin quality polymer due to side reactions that occur during depropagation in the radically initiated depolymerization.[11,18–24] The elimination of the ester functional group from the backbone is a key design flaw with MMA. Therefore, a widely investigated pair of monomers was investigated in which this flaw was eliminated. α-methylene-γ-butyrolactone (MBL) and α-methylene-γ-methyl-γ-butyrolactone (MMBL) are biobased alternatives to MMA,[25–28] however, the depolymerization of their polymers (PMBL and PMMBL) had not been explored until 2020.[29] The key differences between MMA and M(M)BL are the fusing of the methyl groups on the ester and the olefin into a lactone and the T_C of the polymers. The lactone functionality allows for facile depolymerization of polymer to monomer while suppressing the fragmentation of the pendant group. Comparing monomer purity in exaggerated conditions, the lactone monomers exhibited near pristine purity as compared to the parent monomer, MMA. As the T_Cs of PMBL and PMMBL were estimated to be higher than that of PMMA, these results were surprising, but as PMMA has been shown to be depolymerizable, most monomers with similar moieties are expected to exhibit similar behaviors.

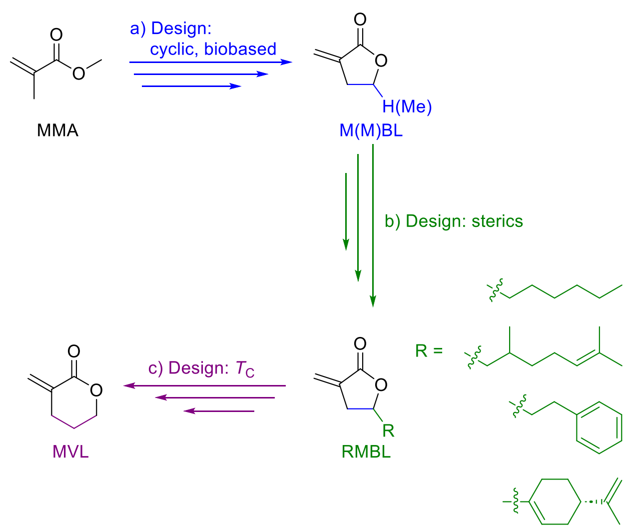

Figure 2.1. *Iteration on MMA with bio-based monomers. a) applying cyclization to MMA and establishing M(M)BL. b) Enhancing upon M(M)BL by altering the γ-substituent to sterically bulky groups. c) Expanding the MBL ring to reduce the TC and potentially enable enhanced circularity.*

Improving upon Poly(α-methylene-γ-butyrolactones)

Building upon this work, derivatives of MMBL were developed by employing a variety of biorenewable aldehydes in a facile zinc catalyzed one-step synthesis.[30] MMBL requires harsh conditions in order to be synthesized from levulinic acid, its bio building block.[26] With the zinc catalyzed allylation-lactonization reaction to MMBL derivatives, yield was improved to >90%. The bulky γ-substituents provided an excellent hand for tunability of T_g, T_d, and, seemingly, T_C. Poly(γ-hexyl-α-methylene-γ-butyrolactone) (PHMBL) exhibited the lowest depolymerization temperature, at 310 °C, yielding 17.4% of pure monomer and exhibited a quantitative isolated monomer yield at 370 °C. These steps in monomer design enabled the development of a subset of polymers with tunable properties while maintaining circularity. It shows that slight iteration can lead to dramatic improvements, not only in polymer properties, but also in depolymerizability.

Expanding the Ring: The Potential of α-methylene-δ-valerolactone

As the previous example showed, substitution on the lactone ring in the MBL family of monomers proved to be fruitful in increasing circularity. This concept has been applied to polyesters as well, enabling the ring-opening polymerization of MBL.[31] There may be more potential in examples from polyester circularity that can be borrowed in designing iCPs from vinyl monomers. The ring-opening polymerization of δ-valerolactone (DVL) is well understood,[32–34] but the T_C is too high to enable facile depolymerization of PVL.[35] In order to stabilize the 6-membered ring and enable depolymerization, researchers looked to α-methylene-δ-valerolactone (MVL).[36] The polyester of MVL was shown to be completely thermochemically recyclable back to monomer, in addition to allowing for post-functionalization, enabling the ability to tune mechanical and thermal properties. Interestingly, MVL was first investigated for use in vinyl-addition polymerization (VAP) , and its T_C was determined to be just 83 °C ([M] = 1 mol/L).[37] In comparison, MBL and MMBL are estimated to possess T_Cs over 300 °C ([M] = 1 mol/L).[29] Polyester chemistry has shown that decreasing T_C enables more facile depolymerizability, as is the case with going from DVL to γ-butyrolactone (GBL).[38]

Hybrid Design in the Vinyl Polymer Family

Another trend in polyester chemistry is that of 'hybridization.'[2–4,39,40] These poly(thio)esters exhibit unique properties and circularity. Essentially, combining two low T_C monomers into a single moderate T_C monomer, allows for facile polymerization and depolymerization under reasonable conditions. Applying this concept to a classically 'non-polymerizable' monomer in cyclohexene and a low T_C monomer in GBL produced a novel monomer in 6-oxabicyclo[3.2.1]oct-3-en-7-one ($BiL^{=}$). $BiL^{=}$ proved to be extremely versatile in that it could undergo two separate ROP pathways to give either $P(BiL^{=})_{ROP}$ or $P(BiL^{=})_{ROMP}$ based on the catalyst, either a yttrium-catalyst or Grubbs-second (G2) or third (G3) generation catalyst respectively. Amazingly, both the polyester *and* poly(cyclic olefin) showed intrinsic recyclability under mild conditions (~40 °C with either $ZnCl_2$ [$P(BiL^{=})_{ROP}$] or G2 [$P(BiL^{=})_{ROMP}$]). Additionally, quantitative depolymerization of a copolymer, $P(BiL^{=})_{ROMP}$-*co*-$P(BiL^{=})_{ROP}$, which was made from, first, producing $P(BiL^{=})_{ROP}$ from a norbornane-diol and then reacting the initiating group with $BiL^{=}$ in the presence of G2, was established with a stepwise method. This stride in polymer circularity was achieved by applying well-established techniques in the polyesters space to the vinyl polymers. It shows that expanding and attempting to exploit chemistries that are highly established to other subsets of polymers may prove effective for enabling the development of iCPs in every polymer family.

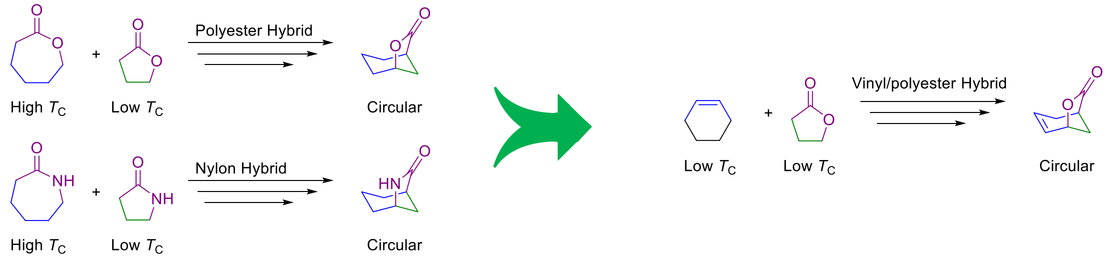

Figure 2.2. *Applying hybrid design from polyesters and nylons to vinyl polymers in order to enable circularity.*

Conclusions and future directions

These examples are just a few in which iterative design and unique approaches enabled circularity. It is important to note that T_C, ring structures, and substitution provide critical avenues to establishing enhanced recyclability in an intrinsic sense. There are recent reports of enabling recyclability of vinyl polymer via end-group enabled mechanisms on polymers produced by reversible controlled radical polymerization.[41–44] These methods prove to be useful with polymers whose method of synthesis is known, and high chain-end fidelity is established. Although these methods can be used to establish circularity with well-known petroleum based polymethacrylates, for end-of-life vinyl polymers, these methods may prove to be challenging as the materials break down and chain-end fidelity is lost.

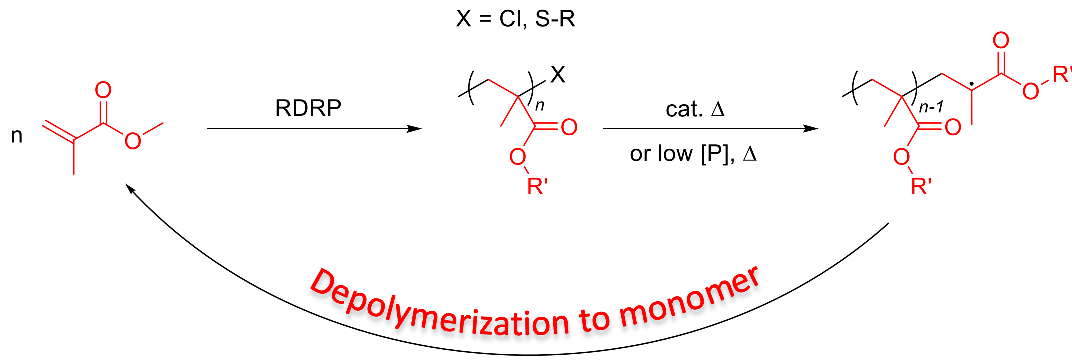

Figure 2.3. *The chemical depolymerization strategy for RDRP produced polymers.*

Vinyl polymers contain some of the oldest and most widely used synthetic polymers on the planet.[1,7,8,45–47] Due to this dependency, alternatives and advancements in monomer design have been slow and is only now catching up with other classes of polymers. There are many avenues to exploit for establishing a circular plastics economy for vinyl polymers - from designing for depolymerization to catalyst enabled-depolymerization of commodity materials. Design is still in its infancy, with promise being seen in biobased MMA alternatives. Catalysis for depolymerization is still focused on a specific subset of polymers produced from very specific mechanisms. The future holds large potential in this space as catalysts are discovered for C-H activation and new bio-based monomers are designed for depolymerization of their polymers under mild conditions.

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CHAPTER 3.

HIGH CHEMICAL RECYLABILITY OF VINYL LACTONE ACRYLIC BIOPLASTICS

Overview

Without specialized reactor setups that can reduce polymer resonance time at high temperatures, the depolymerization selectivity of the most important member of the petroleum-based acrylic plastic family, poly(methyl methacrylate) (PMMA), is inherently limited by the polymer repeat unit structure, leaving much (~47%) of PMMA to fragment and carbonize to char rather than produce pure monomer. Here we show that renewable, high-performance alternatives to PMMA (cyclic ester or lactone analogs) with vinyl lactone repeat units, poly(α-methylene-γ-butyrolactone) (PMBL) and poly(γ-methyl-α-methylene-γ-butyrolactone) (PγMMBL), depolymerize much more selectively and recover monomers with considerably higher yield and purity than PMMA (76% isolated monomer with quantitative purity in the case of PγMMBL) and are also devoid of char formation, leaving the residue (24%) as only the oligomers that can be reused. To uncover the origin of the unexpected high chemical recyclability of P(M)MBL, this study has ascertained their ceiling temperature (T_c) by density functional theory, trapped and analyzed both primary and tertiary macroradicals generated during the depolymerization, and probed the stability of macroradicals using Lewis acid additives and mixed plastic feeds. The evidence obtained through this study suggests that the much-enhanced recyclability of P(M)MBL bioplastics relative to PMMA is not due to their differences in T_c values, but rather the linear ester and cyclic ester-imparted difference in stability and monomer-production roles of primary and tertiary macroradicals generated in the random chain scission processes.

Introduction

Synthetic polymers have become indispensable in our daily life and the global economy. From cling wraps used to prevent food from spoiling to aircraft and automobile parts for transportation, polymers are ubiquitous and vital. Most synthetic polymers, especially commodity vinyl-addition polymers such as polyethylene (PE), polystyrene (PS), and polymethyl methacrylate (PMMA), come with the cost of high chemical stability in terms of chemical recycling.[1–10] Though the high stability may be a desired property for certain practical applications at first glance, it makes such thermally and chemically robust synthetic polymers a burden to dispose of, in particular through chemical recycling to obtain their monomers for repolymerization to virgin-quality plastics, contributing to massive environmental pollution and infrastructural strain.[11–15]

The high stability of these polymers stems from the highly exergonic nature of their vinyl-addition polymerizations. The chain-growth polymerization of ethylene releases 22 kcal/mol chemical energy, giving rise to a thermodynamically highly stable PE with an extremely high bulk ceiling temperature (T_c) reaching 610 °C.[16] Note that T_c is defined as the temperature at which the polymerization and depolymerization reactions reach an equilibrium, thus serving as a measure of de/polymerizability, depending on whether the polymer or monomer is referred to. At a working temperature (T) below T_c, the monomer can be polymerized into the corresponding polymer as the thermodynamically more stable state, but at T above T_c the polymer is thermodynamically unstable and can revert back to its monomer (when the kinetic barrier is overcome). Thus, many challenges exist while developing methods to recycle these high T_c polymers, such as PE, for chemical recycling, including high energy inputs and multiple competing decomposition pathways of organic matter under such high T conditions. Hence, recent advances in recycling PE have, therefore, been focused on increasing depolymerization selectivity to oligomers that can be transformed into other useful products, rather than complete depolymerization of the polymer to the monomer.[17,18]

Medium range T_c polymers, such as PMMA with a T_c of 205 °C in 1.0 M or 296 °C in 9.35 M (bulk), still possess high stability (ΔH_p = -13.4 kcal/mol, ΔS_p = -28.0 cal/mol K),[16] but complete depolymerization can be achieved through exploitation of depolymerization mechanisms and setups. PMMA can undergo thermally induced depolymerization through two separate mechanisms, chain-end scission and random chain scission.[19–21] Chain-end scission is favored at lower temperatures, where a tertiary radical is generated at the end of the polymer chain and depolymerization proceeds from there. Random chain scission, on the other hand, is favored at higher temperatures, where two macroradicals, a tertiary and a primary radical, are generated at a random bond in the polymer backbone and both species can proceed to depolymerize, with the tertiary radical leading to more monomer production (Figure 3.1).

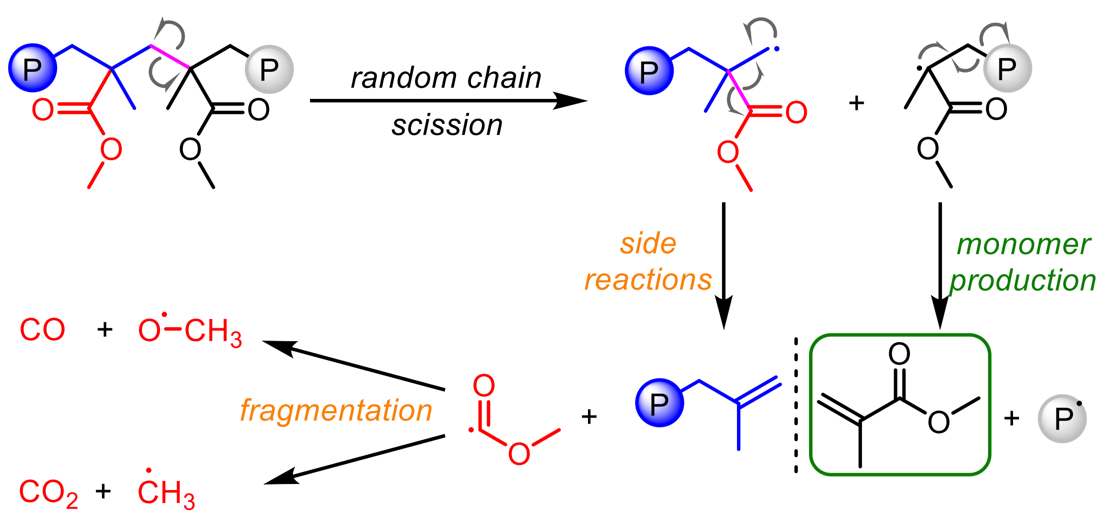

Figure 3.1. *Random chain scission mechanism of PMMA depolymerization.*

Utilizing fixed and fluid bed reactors to drive the reaction at temperatures exceeding 400 °C (typically at around 450 °C) that favors the random chain scission mechanism has been reported to depolymerize PMMA to methyl methacrylate (MMA) with high to quantitative conversions.[22–29] These more complex reactors were employed in order to reduce the PMMA's resonance time within the reactor and prevent the primary radical species from undergoing unproductive side reactions that would lower overall yield and purity of the recovered MMA. Recently, strides have even been made in controlled depolymerization of chloride-capped PMMA (PMMA-Cl) at low temperature (100 °C) catalyzed by a ruthenium(II) complex.[30] After reaching equilibrium monomer concentration at this temperature, ~5% MMA was released, but applying three evaporation cycles (thus four depolymerization processes) generated collectively ~15% MMA after 40 h. Performing this depolymerization at higher temperature (120 °C) began to experience side reactions.

There has been significant interest in developing renewable acrylic alternatives to the petroleum-based MMA.[31–33] These alternatives include biomass-derived, cyclic MMA analogs, such as α-methylene-γ-butyrolactone (MBL), γ-methyl-α-methylene-γ-butyrolactone (γMMBL), and γ-methyl-α-methylene-γ-butyrolactone (γMMBL).[34–37] Although we have studied the polymerization of such biorenewable vinyl lactone monomers for almost a decade,[38–45] the depolymerizability of the resulting polymers, P(M)MBL, has not been investigated. This inactivity has been in part because of the current assumption that (M)MBL is more reactive than MMA, exhibits higher polymerizability, and leads to more thermodynamically stable P(M)MBL polymers with superior properties (e.g., solvent and heat resistance) to PMMA; thus, P(M)MBL is considered to be less depolymerizable and thus chemically recyclable. Here we report that the vinyl lactone repeat units in P(M)MBL prove to be critical in mitigating the side reactions encountered with the primary radical species produced by random chain scission processes. The understating of this beneficial feature is based on our working hypothesis that the five-membered lactone units tethered to the P(M)MBL backbone with two carbon-carbon linkages keep any alkoxycarbonyl radicals formed by β-scission in close proximity, which allows for facile, reversible primary radical "fragmentation" and reformation, overall suppressing side reactions and therefore increasing depolymerization yield and selectivity (Figure 3.2). The combined experimental and density functional theory (DFT) studies described below present evidence to support this hypothesis.

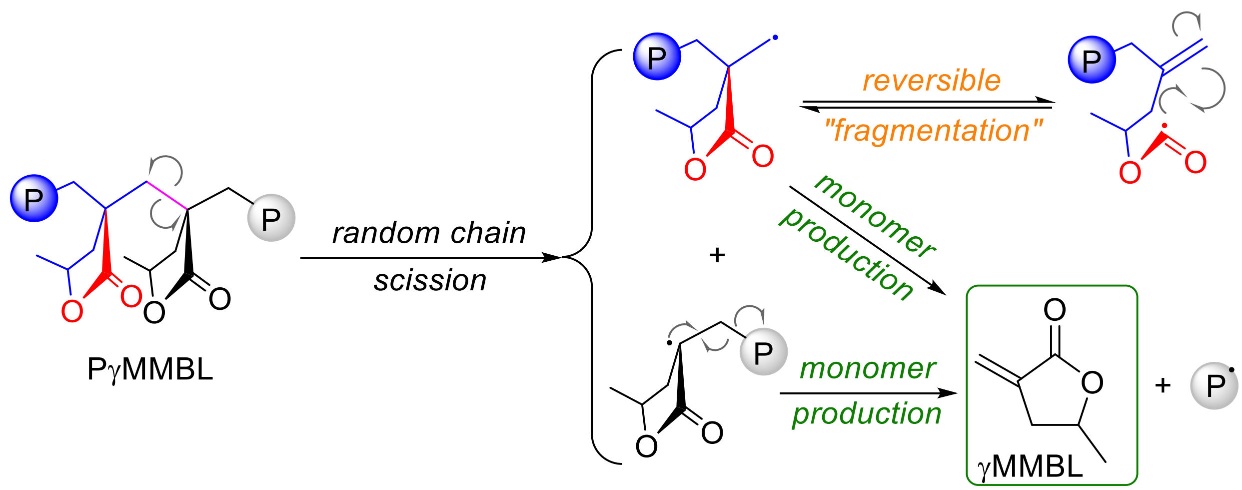

Figure 3.2. *Proposed tethering effect of the lactone units within PγMMBL on enhancing depolymerization selectivity by suppressing fragmentation side reactions.*

Results and Discussion

Thermally induced depolymerization of PMMA and P(M)MBL

As mentioned earlier, the bulk T_c of PMMA was reported to be ~300 °C, but that value does not mean one can readily depolymerize PMMA at this temperature. It is important to note that Tc values of polymers only indicate their thermodynamic stability relative to their monomer states in an equilibrium situation under given conditions (temperature, concentration, state). Once the polymer is out of the polymer–monomer equilibrium (i.e., the quenched, dead polymer chains), it will need to be reactivated and brought back to the equilibrium before depolymerization can take place at T ≥ T_c. This activation could be a chain scission reaction to generate reactive intermediates or active species (e.g., a radical, cation, anion, coordination complex, etc.) by which de/polymerization can proceed, which could be achieved by thermolysis at T (much) greater than T_c or catalysis under milder conditions to overcome the kinetic (activation) barrier.

In this context, previous studies showed that MMA yield from the thermally induced depolymerization of PMMA were maximal at 450 °C in fixed or fluidized bed reactors or in molten metal (Pb or Sn) baths.[23,26] These specialized setups are generally not accessible in laboratory settings and, in the case of using molten metal baths, can lead to toxic organometallic impurities in the recovered monomer that requires further purification. For the current comparative chemical recyclability study, we employed a more traditional glassware distillation apparatus that enabled the depolymerization experiments to be performed at relatively small laboratory scale under identical conditions. Therefore, typical synthetic glassware was employed as the depolymerization apparatus with a hemispherical heating mantle equipped with a thermocouple for heating. In contrast with flowing gas, vacuum was used and volatile products were distilled off of the reaction as they were produced. Under the current long-residence time and high-temperature depolymerization conditions (400 °C, 50 mTorr, 3 h), however, the recovered MMA yield was only modest (53%, run 1, Table 3.1), leaving a substantial amount of char residue. In the glassware distillation apparatus, the polymer was in contact with the hot glass for extended periods of time, leading to the residue carbonizing and side reactions to proceed. Carbon monoxide, carbon dioxide, and highly reactive methyl and methoxy radicals could also be eliminated from the primary macroradical chain end (Figure 3.1). These elimination products can lead to the production of a variety of undesirable products,[25] overall lowering the yield and also the purity of the recovered monomer in the distillate (Figure 3.3). This decrease in purity necessitates the need for further purification in order to obtain MMA suitable for repolymerization, which has been the case with the more specialized reactor setups as well.[25]

The lack of high selectivity for MMA reformation in PMMA depolymerization under the current long-residence-time conditions can be attributed to the structure of the repeat units within the polymer. As the primary macroradical chain end is well understood to have limited ability to produce monomer and instead eliminate radicals that inhibit the tertiary macroradical from producing monomer,[25] we hypothesized that structural alteration of the pendant group to a cyclic ester (lactone) rather than a linear ester present in PMMA would enable the primary macroradical to produce monomer by blocking elimination side reactions (Figure 3.2). Indeed, under identical depolymerization conditions, PMBL depolymerization achieved notably increased monomer recovery by 12% relative to PMMA, while carbonizing of the residual polymer was completely avoided and instead sublimation of oligomeric residue (with complete mass balance) was observed (run 2, Table 3.1). Accompanying the greater yield of monomer recovery was also the increased purity of the recovered monomer, although it’s still not spectroscopically pure by nuclear magnetic resonance (NMR) spectra (Figure 3.4A). Apparently, the lactone pendant groups within the polymer repeat units decrease the proliferation of side reactions, effectively preventing carbonization. Excitingly, depolymerization of PγMMBL exhibited not only a further increase in monomer recovery yield by 23% relative to PMMA (76%, run 3, Table 3,1), but also a drastic increase in monomer purity to recover spectroscopically pure monomer γMMBL (Figure 3.4B). The remaining balanced mass was for the recovered, not yet fully depolymerized oligomers. This further enhanced depolymerization selectivity towards monomer formation relative to PMBL could be attributed to the methyl group on the γ-position of the lactone ring that imparts more stability due to hyperconjugation, which further stabilizes the primary macroradicals and allows for more productive monomer formation and suppression of side reactions. Worth noting here is that, as the recovered residue was the incompletely depolymerize oligomeric residue in the depolymerization of P(M)MBL, not the intractable carbonized char in the case of PMMA, it presents a possibility to design a more effective depolymerization setup to achieve quantitative monomer recovery in the chemical recycling of P(M)MBL.

Table 3.1. *Results of thermal depolymerization of selected three acrylic polymers.*[a]

Run	Polymer (M_n,, kDa)[b]	T_d (°C)[c]	Monomer recovery (%)[d]	Residue identity (%)[e]	Residue M_n (kDa)[b]
1	PMMA (44.8)	340	53 ± 4	char (n.d.)	n.d.
2	PMBL (11.7)	344	65 ± 4	oligomer (~35)	1.50
3	PγMMBL (120)	356	76 ± 1	oligomer (~24)	1.60

[a] Conditions: 500 mg polymer sample, 400 °C, 50 mTorr, 3 h; n.d. = not determined. [b] number-average molecular weight (M_n) data were obtained by gel-permeation chromatography (GPC) in DMF against PMMA standards. [c] T_d is the decomposition temperature at 5% mass loss obtained from thermal gravimetric analysis (TGA) experiments. [d] Percent recovery was determined from the mass of the collected over two runs. [e] Residue was isolated by dissolution in chloroform before filtration and characterization by ^{1}H NMR and GPC analysis.

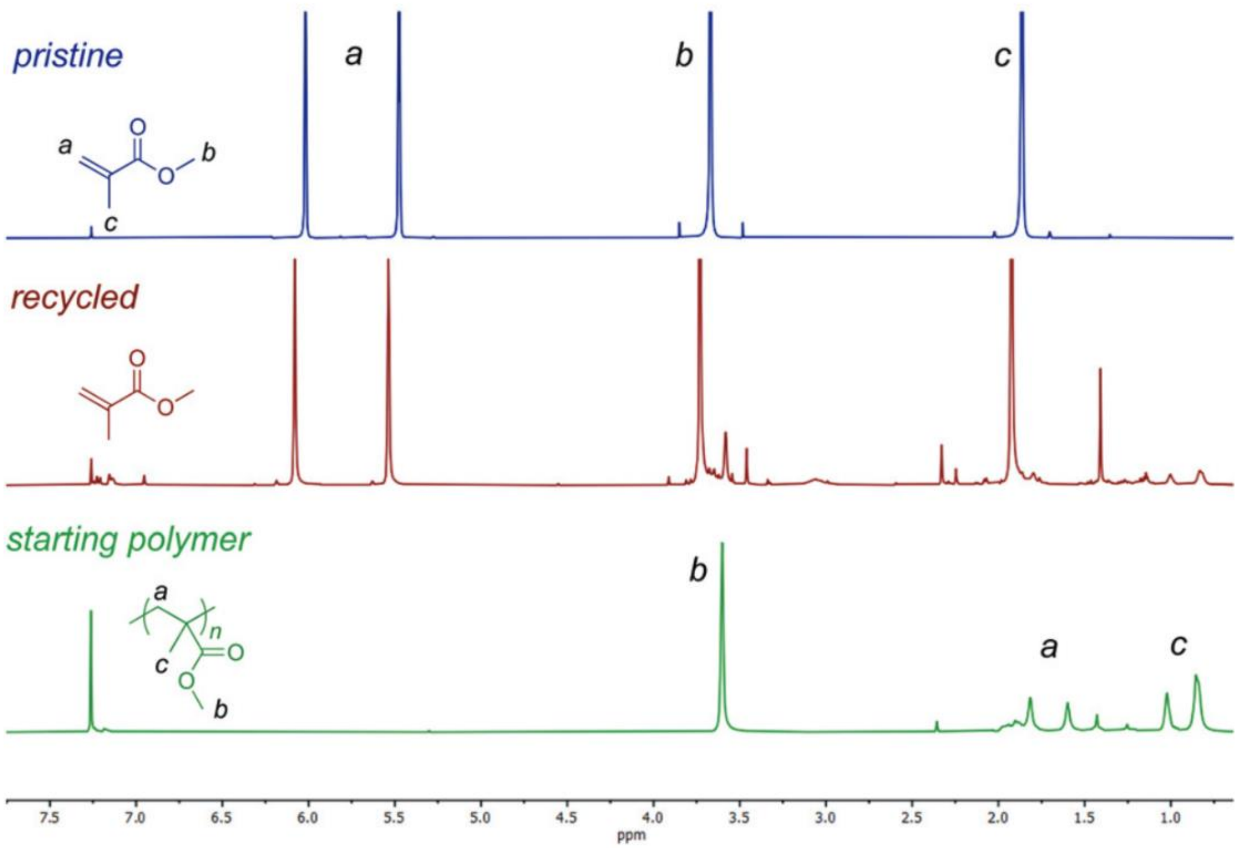

Figure 3.3. *Stacked NMR spectra comparing pristine MMA with recycled MMA and starting PMMA used for polymerization.*

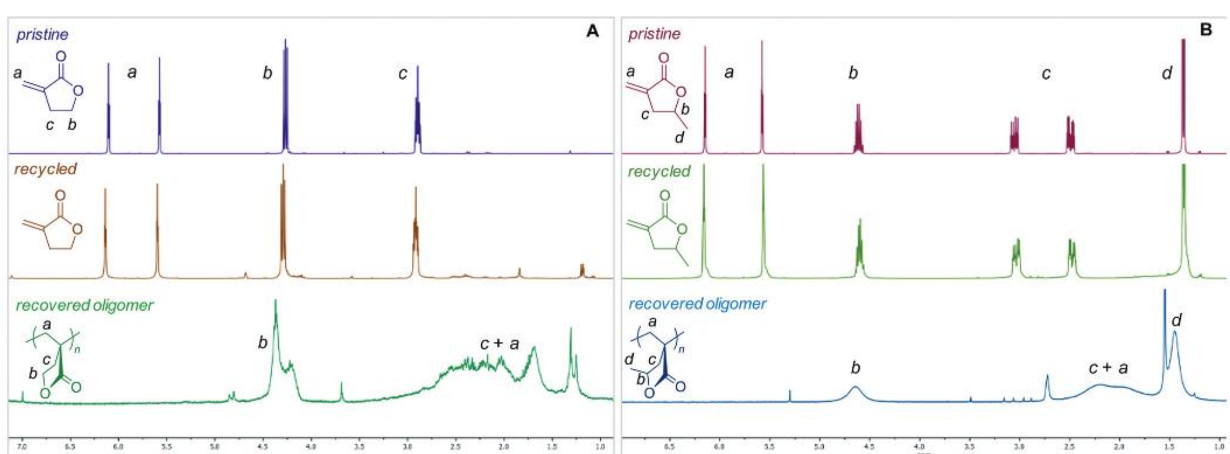

Figure 3.4. *Stacked NMR ($CDCl_3$) spectra of (A) PMBL recycled to form MBL and oligomeric residue and (B) PγMMBL recycling to form pure γMMBL and oligomeric residue. In both cases the total mass balance was achieved for the recovered monomer and oligomers.*

DFT calculations to estimate T_C values of PMBL and PγMMBL

An alternative hypothesis for the much-enhanced chemical recyclability of bio-based P(M)MBL vs. PMMA is due to reduced T_c values for P(M)MBL, which would render monomer production more favorable. To provide evidence to either support or dispute this alternative hypothesis, we performed DFT calculations to estimate T_c values for PMBL and PγMMBL as their experimental values are currently not available and difficult to measure experimentally. Included also in this DFT study are PMMA to establish an empirical relationship between the computed ΔH_p and ΔS_p values and literature values, and a new vinyl lactone polymer poly(α-ethylidene-γ-butyrolactone) (PEBL) designed with a low T_c for more energy-efficient chemical recycling, thus establishing a broader data set for comparisons amongst high to lower T_c acrylic polymers.

These relatively inexpensive DFT calculations were carried out at the BP86/SVPD[46–48] level to calculate enthalpy and entropy changes of polymerization, ΔH_p and ΔS_p, for each polymer with the ultimate goal of establishing a method for estimating/predicting acrylic polymers' T_c values. This estimation was done by averaging the ΔH_p and ΔS_p values between each successive oligomer up to the tetramer (Table 3.5), where the beginnings of chain-entanglement and favorable intra-chain interactions were observed. The raw averages overestimate the stability of these structures for a well-studied polymer, PMMA, by -9.01 kcal/mol and -29.4 cal/mol K for ΔH_p and ΔS_p, respectively, which was subsequently used to adjust the averages for the polymer series as reported in Table 3.2. Specifically, for ΔH_p corrections a subtraction of 9.01 from the raw averages was applied, whereas for ΔS_p corrections, a division of the raw averages by 2.05 was applied. This hybrid correction method was shown to work the best on the basis of fitting the DFT calculations results against the full set of

Table 3.2. Results of DFT calculations performed on lactone acrylic polymer systems.

Entry	Polymer	Estimated[a] ΔH_p (kcal/mol)	Estimated[a] ΔS_p (cal/mol K)	Estimated T_c (°C)[b] at 1.0 M	Estimated T_c (°C)[b] in Bulk [M]
1	PγMMBL	-17.3	-30.0	305	405 (9.36 M)
2	PMBL	-15.9	-25.3	354	502 (11.4 M)
3	PEBL	-8.6	-29.2	23	80 (10.7 M)

[a] ΔH_p and ΔS_p are the averages of BP86/SVPD calculations on oligomer series adjusted using PMMA correction factors described in the main text. [b] T_c values were calculated using the equation: $T_c = \Delta H_p/(\Delta S_p + R\ \mathrm{Ln}\{[M]\})$, where ΔH_p and ΔS_p are enthalpy and entropy changes of polymerization, R is the idea gas constant, and [M] is monomer concentration.

experimental data at various [M] concentrations (Fig. S3.1) for our previously studied ring-opening polymerization of MBL.[49] While the accuracy of these estimations could be improved in the future by modeling and incorporating more vinyl polymers with known ΔH_p and ΔS_p values and experimenting with more expensive basis sets and functionals, the computationally estimated bulk T_c values of P(M)MBL (~400 °C for PγMMBL and ~500 °C for PMBL) are considerably higher than that PMMA (~300 °C), thus ruling out the alternative hypothesis that the much enhanced depolymerization selectivity of P(M)MBL relative to PMMA is due to their more favorable (lower) T_c values than PMMA. Note that the order of estimated T_c values of MBL > γMMBL > MMA is consistent with the observed reactivity and polymerizability trend following the same order.

Trapping macroradicals during PγMMBL depolymerization

To further shed light on the surperior depolymerization seletivity of PγMMBL, radical trapping studies were performed. The experiment was conducted such that the depolymerization of the PγMMBL prepared by the Lewis-acid catalyzed group-transfer polymerization (GTP) with known end groups (Figure 3.5) was initiated before being quenched with a potent radical trap, galvinoxyl, which traps the macroradicals and allows for analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 3.5). The presence of trapped tertiary macroradical was apparent from Figure 3, in addition to the undepolymerized PγMMBL chains, indicating that the depolymerization of PγMMBL followed a similar mechanism proposed for the PMMA depolymerization (Figures 3.1 and 3.2).

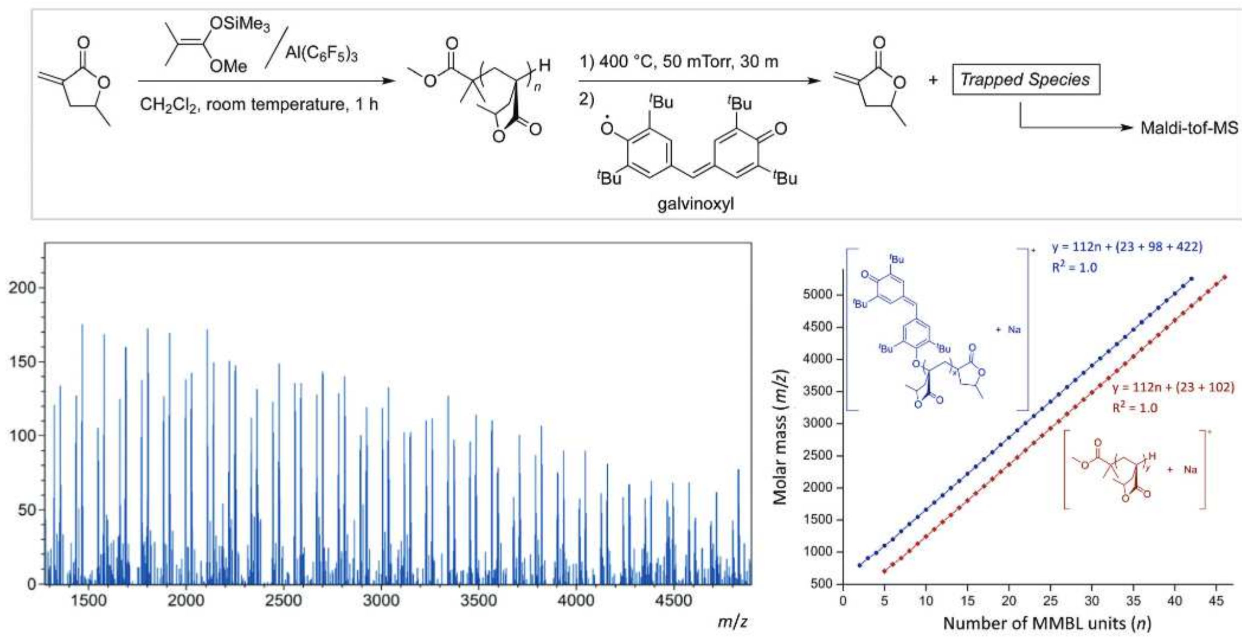

Figure 3.5. *MALDI-TOF MS spectrum and chain-end analysis of polymer residues from depolymerization of PγMMBL synthesized by GTP.*

The results of this radical trapping experiment also suggest that the tertiary macroradical species formed in the depolymerization are more stable, as it is persistent enough to be quenched, whereas the primary macroradical species were too transient or the concentration is too low to be trapped for detection. This interesting result could be attributed to the stabilization of the highly reactive primary macroradical leading to more facile depolymerization, rendering the tertiary macroradical less productive, a scenario that is in stark contrast to that of PMMA depolymerization.

To detect primary macroradicals during the PγMMBL depolymerization through radical trapping experiments, we performed another study on the PγMMBL sample prepared by atom-transfer radical polymerization (ATRP). The quenched polymer carries bromide chain ends that were utilized to increase radical concentration in situ during the depolymerization to enable the persistence of the macroradicals. Trapping these radicals with galvinoxyl allowed for analysis of the trapped species with MALDI-TOF MS to reveal the identity of the species.

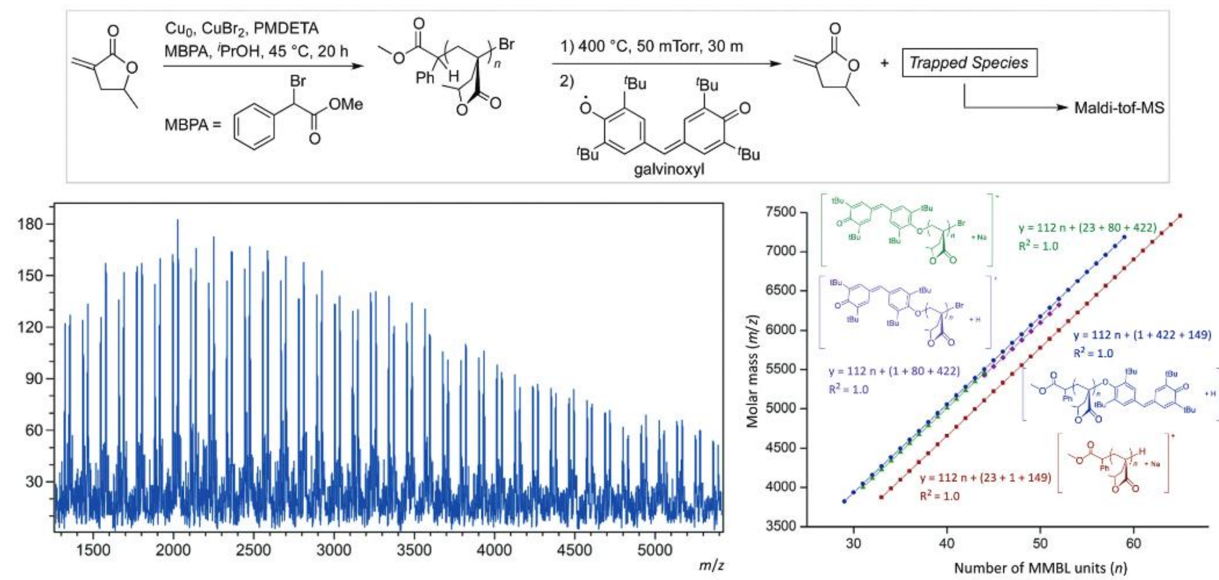

Figure 3.6. *MALDI-TOF MS spectrum and chain-end analysis of polymer residues from depolymerization of PγMMBL synthesized by ATRP.*

The results depicted in Figure 3.6 indeed confirmed the presence of both primary and tertiary macroradicals, thus allowing for a more complete picture of the mechanism of depolymerization as shown in Figure 3.2.

Probing the stability of macroradicals in PγMMBL depolymerization

As both the tertiary and primary macroradicals generated in the depolymerization were successfully trapped and then observed in the MALDI-TOF spectra, we hypothesized that their stability could be modulated through addition of additives. First, destabilization of the primary macroradical via addition of Lewis acids would render the depolymerization to behave similarly to that of PMMA. As a result, the destabilization of the primary macroradical would allow for proliferation of side reactions, handing the monomer production roll back to the tertiary macroradical, overall decreasing monomer yield and purity while increasing carbonization. Lewis acids have recently been employed to facilitate the depolymerization of various renewable polyesters.[49,50] They catalyze the reaction by coordinating to the carboxyl groups and enable attack from more electron rich carboxyl groups. Therefore, we hypothesized that a Lewis acid would coordinate to the most electron rich carboxyl group in the lactone pendant groups of the PγMMBL, namely, the lactones closest to the primary macroradical chain end, which would enable the destabilization of the primary macroradical. Under the current standard conditions (400 °C, 50 mTorr, 3 h), the depolymerization of PγMMBL (M_n = 22.8 kDa) in the presence of Lewis acids such as $FeCl_3$ (0.05 – 0.1 mol% loading) and $ZnCl_2$ (1 – 5 mol% loading) noticeably lowered the monomer recovery yield to 20 – 37% for $FeCl_3$ and 10 – 46% for $ZnCl_2$. The purity of the recovered monomer was also negatively impacted. This finding appears to support the above hypothesis that primary macroradicals are the majority monomer producing units in the depolymerization.

To further probe the stability of the primary macroradicals derived from the PγMMBL depolymerization, we conducted mixed feed depolymerization experiments (Table 3.3).

Table 3.3. *Chemical recycling of PγMMBL from mixed plastic feeds.*

Entry number	Polymer additive [a]	γMMBL yield (%)	Additive monomer yield (%)
1	PMMA	74	67
2	PMBL	52	52
3	PS	74	-
4	PET	49	-
5	PE	44	-

[a] Conditions: 1/1 weight mixed feed, 500 mg PγMMBL and 500 mg polymer additive, 400 °C, 50 mTorr, 3 h.

We hypothesized that if either of the primary and tertiary macroradical species were in contact with other synthetic polymers, carbonization and side reactions would proliferate due to the macroradicals reacting with the other polymers. This, however, was not the case and carbonization was only observed in mixtures with PMMA (entry 1, Table 3.3) and PMBL (entry 2, Table 3.3), where the PMMA residue carbonized and the PγMMBL residue sublimed. This observation was attributed to the difference in T_c between the two polymers, where PMMA began to depolymerize first and PγMMBL after, leading to no inhibition in monomer production and rather, an increase in monomer production from PMMA due to the PγMMBL acting as mechanically fluidized reactor bed. When mixed with PS, PET [poly(ethylene terephthalate)], and PE, monomer production was either completely unhindered (entry 3, Table 3.3) or monomer was trapped in the viscous polymer melt (entries 4 and 5, Table 3.3), and no carbonization was observed. Interestingly, with mixtures of PMBL and PγMMBL, both polymers showed decreases in monomer production (entry 2, Table 3.3). This finding could be attributed to the similar reactivity of each polymer's macroradicals causing the quenching of PγMMBL macroradicals with PMBL macroradicals which lead to carbonization.

Conclusion

In summary, the results obtained from this comparative chemical recyclability study demonstrated that, under the current depolymerization conditions (400 °C, 50 mTorr, 3 h) without using specialized reactor setups, the depolymerization of PMMA recovered ~53% of the impure MMA, leaving ~47% of PMMA to carbonize into intractable char. In sharp contrast, the depolymerization of vinyl lactone acrylic bioplastics, especially PγMMBL, led to recovery of the pure monomer γMMBL in 76% isolated yield. Importantly, the depolymerization is devoid of carbonization, and the residue is that of incompletely depolymerized oligomers with a total mass balance. Hence, it is conceivable that, with a more effective depolymerization setup or recycling of the oligomers, achieving quantitative monomer recovery with high monomer purity in the chemical recycling of P(M)MBL is feasible.

Multiple experiments and DFT calculations were designed to help understand the origin of their sharp chemical recyclability differences between these two types of acrylic plastics, namely PMMA with open, linear ester pendant groups, and P(M)MBL with closed, cyclic ester (lactone) pendant groups. DFT calculations estimated that both PMBL and PγMMBL actually have considerably higher T_c values than PMMA (by 200 and 100 °C, respectively), thus ruling out the hypothesis that the enhanced recyclability of P(M)MBL is due to their more favorable T_c features. Next, the evidence accumulated through trapping and analysis of macroradicals generated during the depolymerization, as well as probing the stability of macroradicals using Lewis acid additives and mixed feed plastics, suggests that the difference in selectivity for monomer production between PMMA and P(M)MBL is due to the linear ester and cyclic lactone-imparted difference in stability and monomer-production roles of primary and tertiary macroradicals generated in the random chain scission process. In the case of PMMA depolymerization, tertiary macroradicals lead to more monomer production, while the unstable, highly reactive primary macroradicals undergo unproductive side reactions, lowering the overall yield and purity of the recovered MMA. In contrast, the stabilization of the highly reactive primary macroradicals provided by the lactone moiety in the case of P(M)MBL renders both primary and tertiary macroradicals to be productive in monomer reformation, thus suppressing the side reactions for reforming the pure monomer. As vinyl-addition polymers, the bulk T_c's of PMMA (~300 °C) and PγMMBL (~400 °C) are still high, requiring high energy input for their chemical recycling. It is known that substituting the α-methyl group in PMMA with the ethyl group led to low T_c acrylic polymer, poly(methyl ethacrylate) (PMEA),[51,52] with a reported bulk T_c of only 82 °C, thus drastically lowering the T_c of the acrylic polymer by more than 200 °C relative to PMMA. For the lactone-bearing acrylic polymer, introducing of the methyl group to the exocyclic methylene moiety predicted a novel low T_c (80 °C) vinyl lactone acrylic bioplastic, PEBL (Figure 3.7). Coupled with the macroradical stabilizing lactone function, the low T_c PEBL could be readily recyclable under relatively mild conditions to recover monomer in high selectivity and purity. Experimentation to materialize this potential is underway.

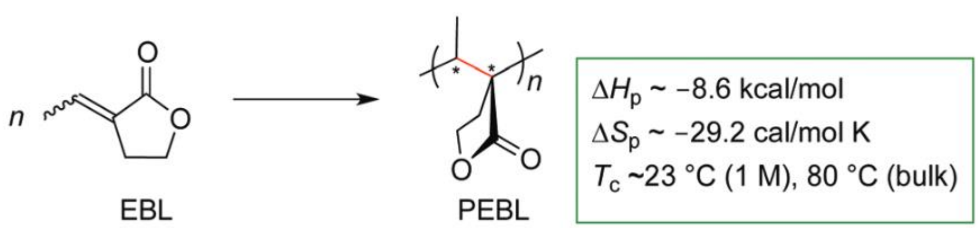

Figure 3.7. *Predicted low T_c vinyl lactone acrylic polymer PEBL that could be depolymerized under mild conditions.*

Experimental

Materials and Methods

The synthesis of air and moisture sensitive materials were carried out in flame-dried Schlenk glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N_2) glovebox. Organic solvents were dried with CaH_2 or sodium/potassium alloy (for hexanes) between 24 and 48 h before being distilled and stored under nitrogen atmosphere. NMR solvents ($CDCl_3$, dimethyl sulfoxide-d_6, and benzene-d_6) were used as received. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances.

Triethyl aluminum, methyl trimethylsilyl dimethylketene acetal (^{me}SKA), *n*-butyllithium, methyl α-bromophenylacetate (MBPA), *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMEDTA), and galvinoxyl were purchased from Sigma-Aldrich Chemical Co. Copper(II) bromide and zinc(II) chloride were purchased from Alfa-Aesar. Iron(III) chloride was purchased from Spectrum Chemical Mfg. Corp. Polyethylene (M_w = 35 kDa), poly(methyl methacrylate) (M_w = 15 kDa), poly(ethylene terephthalate) (granular), isotactic polypropylene (M_w = 12 kDa), and Merrifield peptide resin (PS) were purchased from Sigma-Aldrich Chemical Co. The above commercial reagents were used as received. *α*-Methylene-*γ*-butyrolactone (MBL) and *γ*-methyl-*α*-methylene-*γ*-butyrolactone (*γ*MMBL) were purchased from TCI America, dried over CaH_2 overnight, vacuum distillated, and stored over activated Davison 4 Å molecular sieves in a brown bottle inside a freezer of the glovebox for further use.

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and was further purified by sublimation (twice). Tris(pentafluorophenyl)alane,

$Al(C_6F_5)_3$ (unsolvated form) was prepared by the ligand exchange reaction between $B(C_6F_5)_3$ and either $AlMe_3$ or $AlEt_3$ in dry hexanes, following literature procedures.[45,53] *As the unsolvated alane is thermal and shock sensitive, extreme caution should be exercised while handling this material!*

Polymer Samples Prepared by Group Transfer Polymerization (GTP)[38,39]

All GTP reactions were carried out in an inert gas (Ar or N_2) glovebox at room temperature in 500 mL oven-dried glass reactors. In a typical polymerization, monomer was premixed with $Al(C_6F_5)_3$ (2 equiv. relative to initiator) in CH_2Cl_2. ^{me}SKA was dissolved in CH_2Cl_2 before being added to the vigorously stirring monomer solution to start the polymerization (1.0 M). Polymerizations were quenched with 100 mL of 5% HCl in methanol. The polymers were precipitated into 500 mL of methanol and collected by filtration before being washed with excess methanol to remove catalyst residue and unreacted monomer. The polymers were then dried overnight in a vacuum oven at 50 °C to consistent weights before NMR and GPC analyses were performed. Polymer characterization data are summarized in Table 3.4.

Polymer Samples Prepared by Atom Transfer Radical Polymerization (ATRP)[54]

All ATRP reactions were performed in septum sealed, argon filled, oven-dried, 20 mL scintillation vials at 45 °C in a silicon oil bath. In a typical polymerization, the vial was brought into an inert gas (Ar or N_2) filled glovebox, and a magnetic stir bar was wrapped with around 2 cm of concentrated HCl washed copper wire before being loaded into the vial. Then monomer, MBPA (1 equiv.), and copper(II) bromide (0.05 equiv.) were loaded into the vial before it was covered with a rubber septum and sealed with electrical tape. The vial was removed from the glovebox and a solution of PMEDTA (0.36 equiv.) in isopropanol (equal volume solvent to monomer) was added to the vial before it was heated to 45 °C and polymerization was left to proceed. Polymerizations were quenched by dissolving any solid that had precipitated in $CHCl_3$ and passed the resulting solution through a column of neutral alumina. The quenched solution was concentrated and then precipitated into methanol before polymers were collected by filtration and washed with excess methanol to remove impurities. The polymers were then dried overnight in a vacuum oven at 50 °C to consistent weights before NMR and GPC analyses were performed. Polymer characterization data are summarized in Table 3.4.

Table 3.4. *Summary of polymerization methods and data.*

Entry	Polymer	Method	[monomer]:[initiator]:[catalyst]	M_n (kDa)	$Đ$
1	PMMA	GTP	500:1:1	44.8	1.18
2	PMBL	GTP	200:1:1	11.7	1.40
3	PγMMBL	GTP	800:1:1	120	3.43
4	PγMMBL	ATRP	50:1:0.05	9.73	1.10

Polymer and Pyrolysis Residue Characterization

Polymer number-average molecular weights (M_n), weight-average molecular weights (M_w), and dispersities ($Đ = M_w/M_n$) were obtained from gel permeation chromatography (GPC) analyses carried out at 40 °C with a flow rate of 1.0 mL/min, with DMF as the eluent, on a Waters University 1500 GPC equipped with four PL gel 5 μm mixed-C columns (Polymer Laboratories). Chromatograms were processed with Waters Empower software (version 2002). Chromatogram files were processed with Origin for presentation. Ten molecular weight PMMA standards were acquired from Polymer Laboratories. To obtain a calibration curve, three different molecular weight sample sets were dissolved in DMF to known concentration.

Matrix-assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS)

MALDI-TOF MS was performed on a Ultraflex MALDI-TOF mass spectrometer (Bruker Daltonics) operated in positive ion reflector mode using a Nd:TAG laser at 355 nm and 25 kV accelerating voltage. Samples were prepared on a 96-well plate by first depositing a layer of NaI solution (1%), followed by 0.5 μL of a solution of polymer or pyrolysis sample and dithranol matrix in $CHCl_3$ on top of the NaI crystals. Calibrants were prepared by depositing a layer of NaI solution (1%) on the plate before 0.5 μL of a solution of peptide calibration mixture and α-cyano-4-hydroxycinnamic acid (HCCA) matrix was deposited on top of the NaI crystals. Obtained spectra were processed using mMass processing software.

Typical Procedure for Acrylic Plastic Chemical Recycling

Depolymerization experiments were performed in 25 to 50 mL oven-dried round-bottom flasks fixed with Teflon-coated magnetic stir bars. Additives (if used) were loaded into the flask inside an inert gas (Ar or N_2) filled glovebox before the vessel was sealed, brought outside the glovebox, loaded with polymer sample, and fixed with a microdistillation apparatus (short path, no Vigreux) with a collection flask and thermometer. The reaction flask was wrapped in aluminum foil before the reaction apparatus was slowly evacuated to between 50 and 100 mTorr. The collection flask was submerged in dry ice while a heating mantle (100 mL, 115 V, Glas-Col, hemispheric) in circuit with a thermocouple was heated to a predetermined temperature and held there. The reaction flask was introduced to the heating mantle before being wrapped in glass wool. After the reaction was complete, the residues in the condenser and reaction flask were isolated and analyzed with NMR and GPC (Figure S2 to S3). The distillate in the collection flask was weighed and analyzed by NMR spectroscopy.

Radical Trapping of Depolymerization Residues with galvinoxyl for MALDI-TOF Analysis

A typical procedure for chemical recycling of acrylic polymers was followed (500 mg polymer). Upon depolymerization for 30 min, the vacuum was released and galvinoxyl (50 mg for all experiments) was added to the reaction flask and heat was removed. The apparatus was allowed to cool to room temperature before the reaction flask was exacted with chloroform and the solution was analyzed via MALDI-TOF MS.

Thermal Analysis

Thermal gravimetric analysis (TGA) was performed on a Q50 TGA Analyzer (TA Instruments) to obtain decomposition temperatures (T_d, defined by the temperature of 5 % weight loss) and maximum rate decomposition temperatures (T_{max}) of the polymers. Between 5 and 10 mg of polymer sample was heated from 30 °C to 700 °C at 10 °C/min while the mass of the sample was continuously measured. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots by selecting the peak values, while T_d values were obtained from wt % vs. temperature (°C) plots by selecting the point of the weight percent versus temperature (°C) plots indicating 95 weight percent of sample remaining (Figures S2-S4). Differential scanning calorimetry (DSC) was performed on an Auto Q20 (TA Instruments) to obtain the glass transition temperature (T_g) and melting temperature (T_m). Between 3 and 10 mg of polymer sample was weighed into an aluminum pan and sealed with an aluminum lid. Samples were then heated at 10-20 °C/min from room temperature to 250 °C and cooled to -40 °C to remove thermal history before being reheated to 250 °C. During this time, the thermal response was measured relative to a reference pan.

Computational Details

All the density functional theory (DFT) calculations were performed using ORCA 4.2.[55] Geometry optimizations were performed using the BP86 functional with the def2-SVPD basis set.[46–48] The dispersion correction scheme of D3BJ was employed. Geometry minima were confirmed with frequency calculations and all energies are BP86/SVPD electronic energies calculated at 298 K using the BP86/SVPD method. All structures modeled a charge of zero and were capped with a proton for simplicity of calculation. Computational details are summarized in Table 3.5.

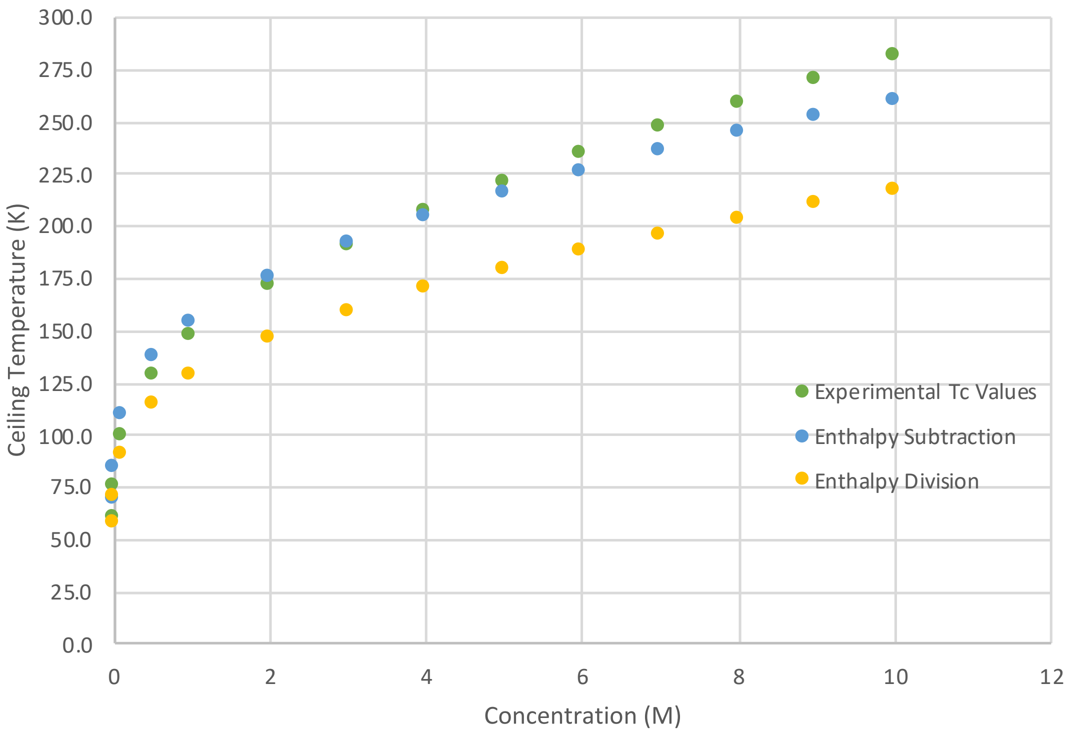

Figure S1. *Test of fitting the DFT calculated T_c values as a function of monomer centration [M] for the ring-opening polymerization of MBL against the full set of experimental data at various [M] concentrations. The best fitting correction made to the computed T_c values was found with ΔH_p correction by subtraction and ΔS_p correction by division.*

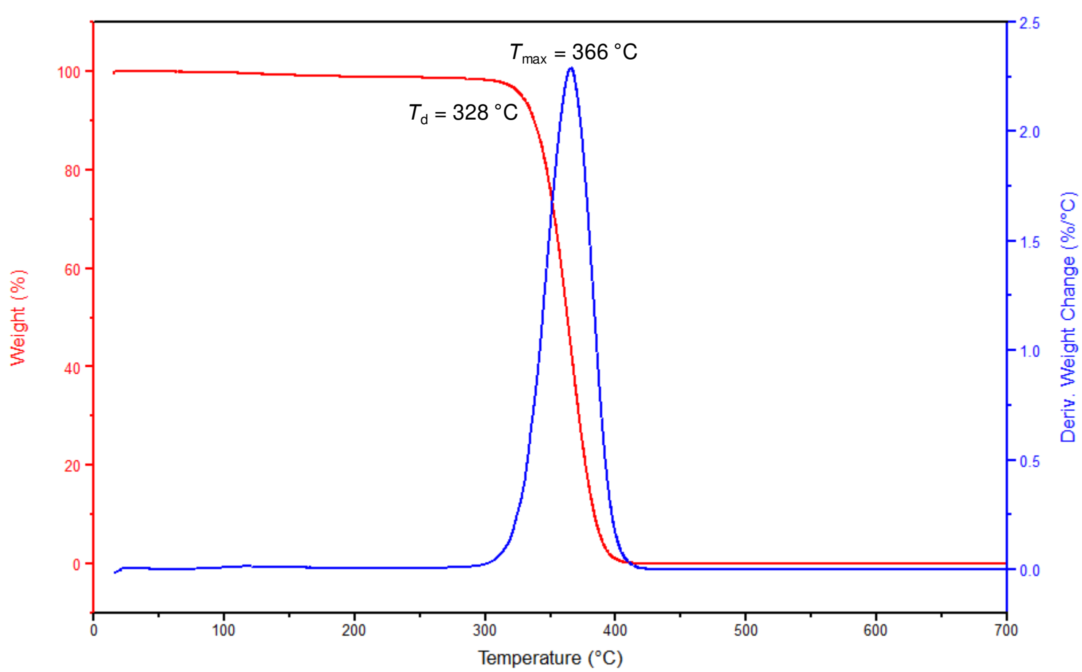

Figure S2. *TGA thermograph for PMMA used in this study.*

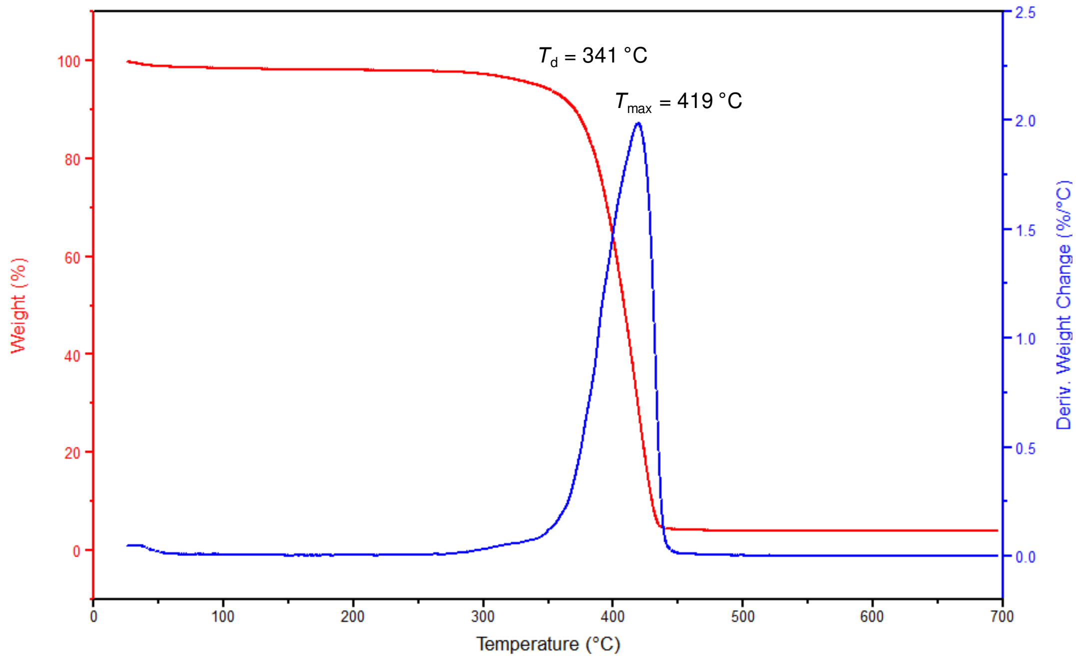

Figure S3. *TGA Thermograph for PMBL used in this study.*

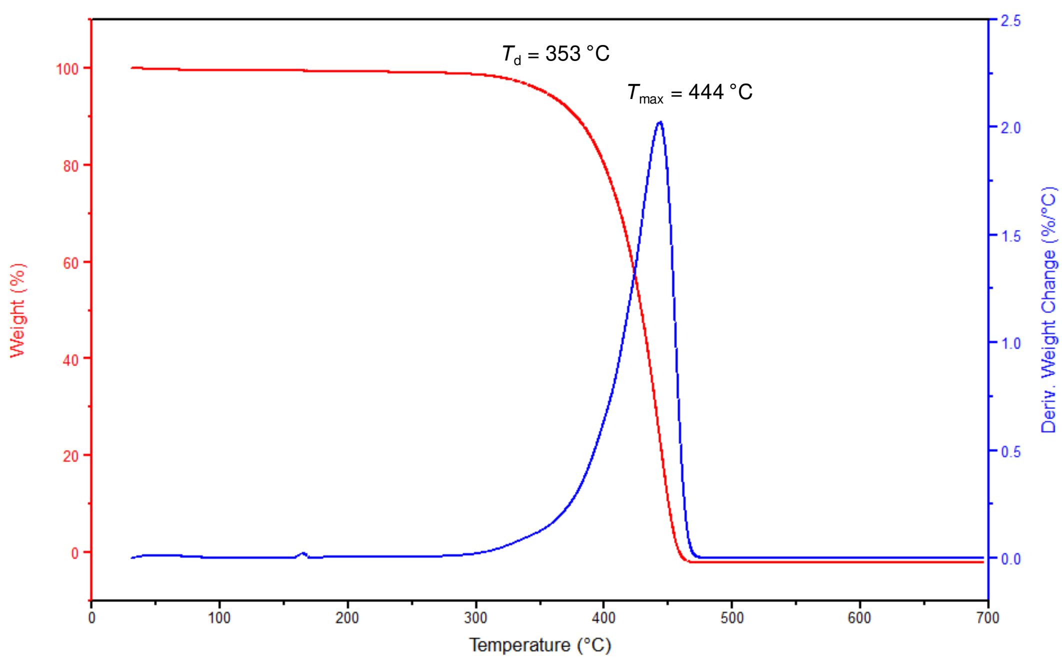

Figure S4 *TGA Thermograph for PγMMBL.*

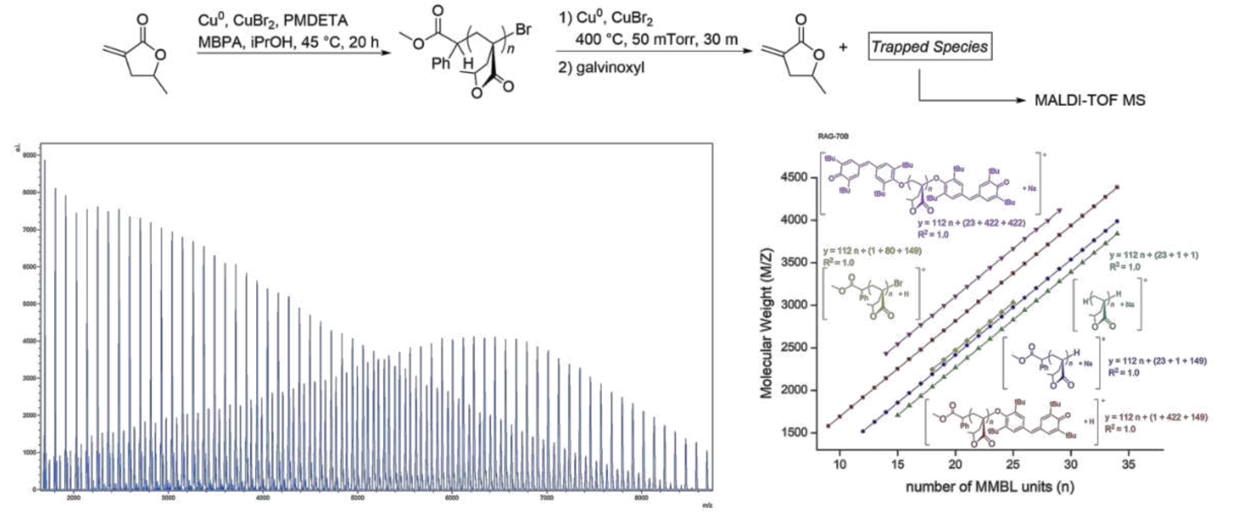

Figure S5 *MALDI-TOF MS spectrum and chain-end analysis of polymer residues from catalyzed depolymerization of PγMMBL synthesized by ATRP.*

Table 3.5. *Cartesian coordinates of species reported in the manuscript and in reference to Table 3.2.*

MBL

C	-0.35134	-0.03306	0.21783
C	-0.43551	-0.51821	1.46941
C	-0.07211	1.36916	-0.26205
C	-0.54506	-0.91325	-0.98155
C	-0.11859	1.23679	-1.80601
O	-0.40402	-0.14792	-2.11290
O	-0.78659	-2.10026	-1.02623
H	-0.29566	0.11840	2.35388
H	-0.65105	-1.58577	1.61955
H	0.91482	1.73012	0.08690
H	-0.83096	2.08491	0.10900
H	0.84385	1.49078	-2.28843
H	-0.91679	1.84890	-2.26592

PMBL Monomer

C	0.46550	-1.68414	0.30963
C	-0.43700	-2.46265	1.28230
C	1.87513	-2.15888	0.70120
C	0.40276	-3.71138	1.59356
O	1.78488	-3.30305	1.44639
O	2.93694	-1.65005	0.42190
C	0.38654	-0.15470	0.31404
C	-0.59440	1.99864	-0.41412
O	-0.47813	2.69481	-1.40727
O	-0.51613	2.49613	0.84765
C	-0.26372	3.90995	0.94623
C	-0.84041	0.48019	-0.40269
C	-0.94746	-0.00141	-1.85794
C	-2.16540	0.21206	0.34884
H	0.31672	-2.06208	-0.72575
H	-1.42274	-2.72700	0.86268
H	-0.60413	-1.86445	2.19874
H	0.27832	-4.09698	2.62020
H	0.20931	-4.53416	0.87539
H	1.31120	0.21707	-0.17036
H	0.41676	0.20258	1.36134
H	-0.22277	4.13191	2.02474
H	0.69521	4.16323	0.45789
H	-1.07567	4.48064	0.45927

H	-1.72506	0.56387	-2.40040
H	-1.22051	-1.07216	-1.89151
H	0.00558	0.13861	-2.39917
H	-2.08670	0.48157	1.41646
H	-2.98979	0.80003	-0.09618
H	-2.44480	-0.85405	0.27317

PMBL Dimer

C	0.03786	-1.46603	1.22764
C	-1.02959	-2.13599	2.12439
C	1.34141	-1.84404	1.98787
C	-0.26469	-3.30676	2.75625
O	1.10674	-2.85405	2.86364
O	2.43116	-1.32514	1.86584
C	0.00008	0.07758	1.18797
C	0.06339	-2.15162	-0.16669
C	-1.10015	2.25638	1.00247
O	-1.95139	2.74493	1.72496
O	0.02938	2.91622	0.64140
C	0.18249	4.23976	1.18746
C	-1.13081	0.83254	0.41601
C	1.36140	-1.97047	-0.97345
C	-0.86262	0.93422	-1.10388
C	-2.53140	0.25171	0.66494
C	2.18269	-3.26461	-1.01453
C	1.25933	-1.60507	-2.46242
O	2.87899	-3.32458	-2.19029
C	2.58054	-2.16500	-3.00966
O	2.22562	-4.14490	-0.18432
H	-1.91937	-2.47647	1.56707
H	-1.36743	-1.43427	2.90874
H	-0.60586	-3.57081	3.77145
H	-0.27155	-4.21573	2.12355
H	0.97539	0.43470	0.80954
H	-0.03202	0.40718	2.24623
H	-0.09664	-3.23609	-0.01873
H	-0.80357	-1.78646	-0.74417
H	1.14031	4.61606	0.79399
H	-0.65481	4.88654	0.86759
H	0.20191	4.19857	2.29204
H	2.01812	-1.23321	-0.46254
H	-1.54696	1.67080	-1.56496
H	-1.03945	-0.03184	-1.60512
H	0.17203	1.25844	-1.30736
H	-2.76556	0.19742	1.74157
H	-3.29990	0.88926	0.19356
H	-2.61398	-0.75900	0.22860
H	1.15888	-0.52192	-2.64485
H	0.39485	-2.11907	-2.92751
H	3.41290	-1.44044	-2.89983
H	2.53417	-2.50577	-4.05829

PMBL Trimer

C	-0.55573	-0.07840	0.90755
C	-1.80724	-0.88565	1.32172
C	-0.13661	0.48658	2.30556
C	-1.51195	-1.31941	2.75981
O	-0.68783	-0.26851	3.30707
O	0.59450	1.41981	2.53727
C	-0.81409	1.18078	0.02008
C	0.69518	-0.97903	0.60807
C	-2.11118	2.76973	-1.29067
O	-3.20825	3.25627	-1.07179
O	-1.02196	3.51382	-1.59477
C	-1.21995	4.93885	-1.61918
C	-1.76857	1.26380	-1.23495
C	0.95740	-1.73130	-0.71929
C	-1.12333	0.90474	-2.59148
C	-3.10309	0.51175	-1.10041
C	1.74583	-0.82699	-1.70207
C	2.03108	-2.83132	-0.52315
O	2.59806	-1.59913	-2.44677
C	2.63539	-2.95008	-1.92529
O	1.71552	0.37548	-1.81716
C	-0.66051	-3.77258	-1.20517
C	-1.01227	-4.21555	0.22818
C	-1.92061	-4.10363	-2.01775
C	-2.54765	-4.38681	0.20757
O	-2.93778	-4.46887	-1.18085
O	-2.05352	-4.04879	-3.21859
C	-0.30265	-2.29140	-1.45484
H	-2.03815	-1.73434	0.66339
H	-2.68566	-0.22063	1.32234
H	-2.41262	-1.40300	3.39192
H	-0.94866	-2.27325	2.82539
H	0.16688	1.58548	-0.27762

H	-1.22640	1.91998	0.73461
H	1.58091	-0.33785	0.77475
H	0.73342	-1.73517	1.41791
H	-0.23935	5.37086	-1.87525
H	-1.97809	5.20875	-2.37694
H	-1.55885	5.29539	-0.62899
H	-1.80717	1.19876	-3.41015
H	-0.96173	-0.17902	-2.68702
H	-0.16015	1.41395	-2.73312
H	-3.65726	0.79825	-0.19079
H	-3.75130	0.75443	-1.96037
H	-2.94650	-0.58088	-1.10460
H	1.63642	-3.78403	-0.13201
H	2.80024	-2.47032	0.18656
H	2.04577	-3.60614	-2.59646
H	3.68846	-3.27954	-1.93906
H	0.14329	-4.40327	-1.62602
H	-0.69086	-3.49340	0.99711
H	-0.52481	-5.17857	0.46249
H	-2.89164	-5.31079	0.70425
H	-3.08425	-3.52925	0.65838
H	-1.16434	-1.65130	-1.20729
H	-0.17729	-2.19685	-2.54914

PMBL Tetramer

C	0.95925	1.29544	-1.12331
C	-0.08015	1.72992	-2.18913
C	1.77181	2.58514	-0.94891
C	0.68228	2.79330	-2.98612
O	1.60358	3.39494	-2.03669
O	2.45785	2.92424	-0.00723
C	1.80251	0.13959	-1.75760
C	0.30467	0.76694	0.17147
C	3.55353	-1.59619	-1.83018
O	4.41863	-1.87295	-2.64068
O	2.72423	-2.54380	-1.29908
C	2.94822	-3.88921	-1.75508
C	3.24697	-0.19561	-1.26889
C	-0.22798	1.72185	1.25883
C	4.26644	0.79191	-1.86419
C	3.41349	-0.26053	0.26711
C	0.91864	2.10651	2.23111
C	-0.76560	3.10291	0.82536
O	0.79654	3.40221	2.61512
C	-0.33956	4.03095	1.97727
O	1.74858	1.35522	2.69480
C	-2.39580	0.11090	1.66801
C	-3.48731	0.04404	2.76428
C	-3.13725	0.89352	0.56530
C	-4.28502	1.33089	2.52982
O	-4.16230	1.60804	1.10545
O	-2.88602	0.92883	-0.62293
C	-1.23135	0.99654	2.22098
C	-0.73371	-1.94239	1.73043
C	-0.12830	-3.08576	0.90226
C	-0.97178	-2.59350	3.09275
C	0.56824	-3.92177	1.98369
O	-0.21839	-3.72905	3.19069
O	-1.69436	-2.21446	3.99057
C	-1.96994	-1.27641	1.11784
H	-0.98529	2.14541	-1.71692
H	-0.40820	0.88196	-2.81567
H	1.28058	2.36507	-3.81415
H	0.04975	3.60337	-3.38671
H	1.87904	0.32179	-2.84703
H	1.16631	-0.75834	-1.64552
H	-0.52320	0.14229	-0.18741
H	1.01819	0.10368	0.68363
H	2.20417	-4.51116	-1.23124
H	2.81066	-3.95535	-2.84999
H	3.97441	-4.21449	-1.50413
H	5.29626	0.46576	-1.63692
H	4.12903	1.79780	-1.43594
H	4.17383	0.84876	-2.96379
H	3.20948	0.71946	0.72784
H	2.75012	-1.01383	0.72525
H	4.45487	-0.53962	0.51225
H	-1.85674	3.12132	0.66798
H	-0.29700	3.44550	-0.10929
H	-0.01766	5.03033	1.63905
H	-1.13032	4.15213	2.74436
H	-4.12993	-0.84066	2.60361
H	-3.06724	-0.03864	3.78015
H	-3.87970	2.20231	3.08031
H	-5.36142	1.24097	2.75278
H	-0.66129	0.36373	2.92381

H	-1.68308	1.78148	2.85585
H	0.06113	-1.19007	1.90921
H	0.57417	-2.73243	0.12642
H	-0.93108	-3.66942	0.41073
H	0.59595	-5.00581	1.78024
H	1.59792	-3.56357	2.18452
H	-1.80463	-1.17929	0.02909
H	-2.82973	-1.96559	1.22272

MMA

C	-0.57253	0.65236	0.73023
C	0.74786	0.15852	0.21076
C	-0.53225	1.43039	1.83409
C	-1.86447	0.27236	0.03666
O	0.60252	-0.61581	-0.90100
O	1.83984	0.40184	0.70218
C	1.82411	-1.13397	-1.45369
H	-1.45282	1.83182	2.28059
H	0.42954	1.67439	2.30450
H	-1.68087	-0.30730	-0.88099
H	-2.50245	-0.33821	0.70611
H	-2.44167	1.17703	-0.23550
H	1.52697	-1.72345	-2.33602
H	2.49722	-0.30557	-1.74350
H	2.34269	-1.76930	-0.71132

PMMA Dimer

C	-5.03952	-1.77722	0.10990
C	-4.83940	-2.88640	1.15276
O	-3.92409	-3.80479	0.73820
O	-5.42952	-2.98032	2.21439
C	-3.69558	-4.90288	1.63937
C	-5.86921	-0.64818	0.74194
C	-3.66773	-1.27954	-0.41477
C	-2.66687	-0.77969	0.64381
C	-3.05088	0.54250	1.29328
C	-1.25809	-0.63926	0.02904
O	-3.39711	1.47649	0.36767
O	-3.01268	0.77592	2.48946
C	-3.76425	2.76459	0.89229
C	-5.81484	-2.39568	-1.07879
H	-2.94071	-5.53958	1.14966
H	-3.32280	-4.53089	2.61122
H	-4.63263	-5.46447	1.80882
H	-5.97636	0.18396	0.02233
H	-6.87563	-1.01062	1.01305
H	-5.40743	-0.26612	1.66828
H	-3.84958	-0.47253	-1.15057
H	-3.18541	-2.10858	-0.96517
H	-2.61142	-1.50086	1.48207
H	-0.53171	-0.25422	0.76833
H	-0.90504	-1.62652	-0.32165
H	-1.27689	0.04915	-0.83703
H	-4.65358	2.67081	1.54348
H	-2.93334	3.19411	1.48147
H	-3.98813	3.39233	0.01488
H	-6.80652	-2.76251	-0.75557
H	-5.97166	-1.62589	-1.85879
H	-5.25526	-3.23763	-1.52464

PMMA Trimer

C	-6.84160	7.58871	-1.64300
C	-6.18219	8.84133	-1.04694
O	-6.39399	8.92891	0.29321
O	-5.56448	9.69012	-1.66866
C	-5.88362	10.10976	0.93651
C	-6.82214	7.72038	-3.17401
C	-6.15587	6.28924	-1.10634
C	-4.88317	5.72184	-1.79560
C	-5.21009	5.21484	-3.21702
C	-4.49023	4.43445	-1.01828
O	-6.37451	4.51076	-3.23906
O	-4.50874	5.34017	-4.20523
C	-6.73127	3.94183	-4.51005
C	-8.31212	7.55124	-1.15606
C	-3.69822	6.71945	-1.91081
C	-1.82843	5.68516	-0.46658
C	-2.73403	6.88922	-0.71150
C	-3.36378	7.37329	0.59628
O	-1.27102	5.23954	-1.62307
O	-1.58024	5.18932	0.62017
C	-0.37771	4.12096	-1.49549
H	-6.47237	10.99164	0.62334
H	-5.99265	9.93518	2.01922
H	-4.82499	10.27895	0.66817
H	-7.33231	6.85821	-3.63544

H	-7.35163	8.63987	-3.48029
H	-5.80069	7.78831	-3.58173
H	-6.91921	5.49075	-1.14308
H	-5.92908	6.43983	-0.03690
H	-3.61222	3.94818	-1.47852
H	-4.24629	4.66925	0.03129
H	-5.32568	3.71264	-1.01978
H	-6.84883	4.73749	-5.26948
H	-5.94976	3.23865	-4.85093
H	-7.68600	3.41703	-4.34508
H	-8.37233	7.38508	-0.06628
H	-8.84036	8.49426	-1.39200
H	-8.84011	6.72444	-1.66626
H	-3.09507	6.41459	-2.78174
H	-4.09318	7.71947	-2.16269
H	-2.02640	7.67751	-1.05036
H	-2.58593	7.56673	1.35499
H	-4.05912	6.63096	1.02606
H	-3.91524	8.30945	0.41424
H	-0.08129	3.85650	-2.52269
H	0.50537	4.39952	-0.89127
H	-0.89013	3.27271	-1.00432

PMMA Tetramer

C	-3.13212	-4.92667	4.97094
C	-1.98984	-3.92037	4.77868
O	-2.17459	-2.79807	5.52976
O	-1.00043	-4.08842	4.08822
C	-1.14838	-1.79912	5.40986
C	-2.95595	-5.51359	6.39641
C	-4.52040	-4.23144	4.94117
C	-5.05257	-3.68444	3.59232
C	-5.47811	-4.82742	2.65023
C	-4.01954	-2.82888	2.83576
O	-6.17121	-5.79409	3.30318
O	-5.29110	-4.85118	1.44540
C	-6.68723	-6.85397	2.48029
C	-2.98774	-6.05024	3.93378
C	-6.39916	-2.91202	3.81900
C	-6.63445	-2.55631	6.28970
C	-6.52130	-1.84002	4.93978
C	-5.37378	-0.81212	4.91640
O	-5.86440	-1.98246	7.24828
O	-7.34599	-3.52794	6.48767
C	-5.86883	-2.57956	8.55532
C	-7.83810	-1.01925	4.70251
C	-9.62588	-1.88576	6.37301
C	-9.24022	-1.63347	4.91781
C	-9.62376	-2.84287	4.05177
O	-8.96796	-1.05365	7.23018
O	-10.47747	-2.67183	6.74305
C	-9.32004	-1.20864	8.61495
H	-0.17088	-2.20921	5.72090
H	-1.07138	-1.45345	4.36222
H	-1.45513	-0.97288	6.07107
H	-3.07644	-4.73121	7.16737
H	-3.72340	-6.29037	6.56935
H	-1.95904	-5.97726	6.51558
H	-4.46209	-3.39725	5.65938
H	-5.26176	-4.94142	5.34679
H	-3.61658	-2.02624	3.46868
H	-3.17748	-3.44429	2.47586
H	-4.47965	-2.37446	1.94191
H	-7.22908	-7.52598	3.16533
H	-7.36766	-6.44754	1.70967
H	-5.85879	-7.38770	1.97936
H	-3.78746	-6.79709	4.08069
H	-3.04310	-5.67117	2.89930
H	-2.01020	-6.55088	4.04233
H	-6.65560	-2.42085	2.86051
H	-7.17915	-3.66089	4.01543
H	-4.40541	-1.25696	5.19335
H	-5.57250	0.00892	5.62622
H	-5.28806	-0.37601	3.90444
H	-6.43405	-3.52692	8.54117
H	-4.81626	-2.75439	8.83797
H	-6.33109	-1.86820	9.26262
H	-7.77652	-0.11157	5.32873
H	-7.78801	-0.67108	3.65203
H	-9.92700	-0.80315	4.63290
H	-9.16780	-3.76937	4.44035
H	-9.29875	-2.69186	3.00647
H	-10.71734	-2.98693	4.06326
H	-9.11468	-2.24321	8.94557
H	-8.69567	-0.48746	9.16644

H	-10.39322	-0.99181	8.76711

PMMA Pentamer

C	14.48110	-23.61024	-8.13672
C	13.00694	-23.74223	-7.72804
O	12.81788	-24.69313	-6.77189
O	12.09511	-23.10759	-8.22766
C	11.46899	-24.94350	-6.33937
C	14.49902	-23.68863	-9.68018
C	15.15612	-22.30220	-7.59488
C	14.67151	-20.84500	-7.88089
C	14.40630	-20.65185	-9.39196
C	15.88724	-19.91872	-7.56846
O	15.53068	-20.89242	-10.12720
O	13.36245	-20.29849	-9.90515
C	15.37620	-20.75316	-11.54713
C	15.32795	-24.76947	-7.56909
C	13.37402	-20.35952	-7.16827
C	11.90815	-19.54941	-5.36838
C	13.14014	-20.44820	-5.62670
C	12.75718	-21.87943	-5.19199
O	11.43146	-19.70772	-4.09744
O	11.37271	-18.80847	-6.16749
C	10.31678	-18.86717	-3.75615
C	14.38432	-19.92574	-4.84924
C	13.60602	-18.23113	-3.16823
C	14.38298	-19.53844	-3.34472
C	13.89406	-20.64968	-2.39832
O	13.25004	-18.02400	-1.87037
O	13.37594	-17.42375	-4.04932
C	12.63474	-16.75104	-1.60167
C	15.88958	-19.22706	-3.03470
C	16.25395	-18.72260	-1.63075
C	15.99596	-17.23232	-1.46048
C	17.74995	-18.97738	-1.33536
O	15.82093	-16.91779	-0.14899
O	16.01131	-16.39720	-2.34798
C	15.72330	-15.51326	0.14772
H	11.32190	-26.03730	-6.35273
H	11.35497	-24.56577	-5.30743
H	10.75142	-24.44036	-7.01038
H	14.19774	-24.70060	-10.00771
H	13.79198	-22.97313	-10.13081
H	15.51511	-23.48590	-10.05999
H	16.19431	-22.36383	-7.97386
H	15.24620	-22.40218	-6.49654
H	16.26755	-20.08157	-6.54763
H	16.71063	-20.12311	-8.27135
H	15.60308	-18.85490	-7.66858
H	14.61209	-21.45924	-11.92347
H	15.06318	-19.72466	-11.80231
H	16.36313	-20.98136	-11.98127
H	16.36426	-24.68644	-7.94551
H	15.35878	-24.74907	-6.46499
H	14.92530	-25.74898	-7.88006
H	13.26419	-19.29578	-7.43982

H	12.52107	-20.85723	-7.65571
H	13.59931	-22.57354	-5.34690
H	11.89732	-22.23404	-5.78324
H	12.47964	-21.91973	-4.13047
H	10.54031	-17.81753	-4.01852
H	9.41381	-19.18967	-4.30571
H	10.17100	-18.98970	-2.67037
H	15.16447	-20.70278	-4.96187
H	14.74520	-19.03148	-5.38171
H	14.13204	-20.41881	-1.34671
H	14.39328	-21.60246	-2.65694
H	12.80536	-20.78875	-2.46845
H	12.54891	-16.68890	-0.50501
H	11.63626	-16.70234	-2.07080
H	13.25971	-15.93584	-2.00714
H	16.43390	-20.17645	-3.20522
H	16.26738	-18.49911	-3.77835
H	15.65942	-19.24228	-0.85667
H	18.38623	-18.49271	-2.09957
H	17.95650	-20.06341	-1.35193
H	18.03545	-18.58615	-0.34281
H	14.86777	-15.06013	-0.38524
H	16.64791	-14.99014	-0.16011
H	15.58227	-15.44751	1.23861

EBL

O	1.54013	-0.97186	1.77725
C	0.98352	-1.85803	0.77967
C	0.22083	-0.98259	-0.24846
C	0.41955	0.41625	0.27831
C	1.23754	0.34642	1.52463
O	1.61516	1.24444	2.24844
C	-0.01950	1.59515	-0.21163
C	-0.84075	1.78502	-1.44535
H	1.82361	-2.41703	0.32629
H	0.32488	-2.57578	1.30388
H	-0.85150	-1.25655	-0.29862
H	0.63416	-1.10209	-1.26937
H	0.26248	2.49294	0.36384
H	-1.07453	0.83251	-1.95449
H	-1.79642	2.29601	-1.20404
H	-0.31596	2.44642	-2.16629

PEBL Monomer

O	-0.44051	-2.44276	3.13052
C	-1.24434	-3.04244	2.09000
C	-1.46159	-1.94269	1.04019
C	-0.30980	-0.92957	1.27382
C	0.13062	-1.26986	2.71642
O	0.88128	-0.65240	3.43883
C	0.89186	-1.17265	0.32513
C	1.49064	-2.58222	0.36380
C	-0.88177	0.51851	1.17212
C	0.02419	1.74970	0.89155
C	0.64090	1.70069	-0.51384
C	1.13481	1.97165	1.92818
C	-0.90917	2.99314	0.89364
O	1.78655	1.99881	-0.80048
O	-0.27603	1.33820	-1.45618
C	0.20554	1.31448	-2.81042
H	-2.17873	-3.39720	2.55971
H	-0.69300	-3.91678	1.69501
H	-1.46972	-2.33992	0.00872
H	-2.43546	-1.44751	1.21177
H	1.68493	-0.44509	0.57362
H	0.55342	-0.94224	-0.70329
H	2.37461	-2.63767	-0.29698
H	0.77457	-3.35009	0.01547
H	1.82351	-2.85737	1.38269
H	-1.64097	0.50031	0.36870
H	-1.43305	0.73001	2.10953
H	1.67228	2.91093	1.70936
H	1.86978	1.15231	1.94547

H	0.69513	2.03442	2.93859
H	-0.34174	3.90651	0.63647
H	-1.74024	2.88017	0.17431
H	-1.33398	3.12979	1.90599
H	-0.64617	0.98359	-3.42631
H	0.54410	2.32060	-3.11867
H	1.05445	0.61161	-2.90593

PEBL Dimer

O	-1.05176	-0.68820	3.64630
C	-2.19842	-1.08958	2.87223
C	-2.05823	-0.35038	1.54202
C	-0.51935	-0.18628	1.35223
C	-0.08084	-0.13718	2.84732
O	0.94464	0.28198	3.33116
C	0.09718	-1.53369	0.80269
C	1.63314	-1.59755	0.87058
C	-0.29555	1.20133	0.65444
C	1.03720	1.83880	0.12214
C	0.64566	3.31480	-0.13392
C	2.19239	1.85139	1.13203
C	1.52103	1.28952	-1.24113
O	1.14535	4.28975	0.39654
O	-0.35243	3.41871	-1.05621
C	-0.77538	4.75863	-1.36454
C	-0.52390	-2.10450	-0.55496
C	0.58492	-2.90959	-1.27588
C	-1.53403	-3.23351	-0.23015
C	-1.04596	-1.04630	-1.55060
O	0.48297	-4.23764	-0.96689
C	-0.63376	-4.46586	-0.07407
O	1.43980	-2.48706	-2.02150
H	-3.10287	-0.81467	3.44230
H	-2.17608	-2.19336	2.76119
H	-2.55966	-0.87831	0.71661
H	-2.52351	0.64970	1.62277
H	-0.22903	-2.27501	1.56027
H	1.97414	-2.64483	0.78622
H	1.99251	-1.21346	1.83814
H	2.12596	-1.03624	0.06428
H	-1.01223	1.25467	-0.18102
H	-0.68435	1.92144	1.40309
H	3.02620	2.45502	0.73236
H	2.55605	0.83332	1.32914
H	1.88563	2.29098	2.09372
H	1.80296	0.22548	-1.18840
H	0.75136	1.40792	-2.02256
H	2.41740	1.85035	-1.56515
H	-1.58195	4.65454	-2.10837
H	-1.14429	5.26600	-0.45404
H	0.06691	5.34188	-1.77978
H	-2.23721	-3.38731	-1.06757
H	-2.12848	-3.04392	0.67973
H	-1.84100	-0.44723	-1.07623
H	-0.21391	-0.35883	-1.76116
C	-1.57083	-1.59916	-2.88053
H	-0.23675	-4.57874	0.95479
H	-1.11097	-5.41319	-0.37706
H	-1.84100	-0.76352	-3.55162
H	-0.80638	-2.20526	-3.39960
H	-2.47812	-2.21937	-2.75569

PEBL Trimer

O	-0.10212	-2.77450	3.06992
C	-1.12203	-1.77019	2.85307
C	-0.54251	-0.84557	1.78107
C	0.31696	-1.80231	0.91561
C	0.79006	-2.77888	2.03066
O	1.77966	-3.47466	2.04784
C	-0.57946	-2.68518	-0.06823
C	0.04608	-4.07506	-0.31229
C	1.55112	-1.19003	0.22579
C	2.33105	-0.05892	0.94067
C	1.48584	1.21877	0.93371
C	2.83933	-0.44041	2.34208
C	3.55292	0.27422	0.03974
O	0.74057	1.55984	0.02527
O	1.68846	1.99405	2.02758
C	0.97181	3.24159	2.04749
C	-1.07855	-2.08602	-1.46888
C	0.01244	-2.40194	-2.52820
C	-2.27825	-2.95726	-1.95490
C	-1.46013	-0.56540	-1.34332
O	-0.47294	-3.21507	-3.50119
C	-1.88108	-3.49914	-3.33532
O	1.17765	-2.06084	-2.54093

C	-1.56434	0.38460	-2.60079
C	-2.77196	-0.44190	-0.53019
C	-1.59951	1.85733	-2.10033
C	-2.78230	2.50399	-2.84046
O	-3.56541	1.42301	-3.40663
C	-2.90893	0.23427	-3.33308
C	-0.45615	0.19862	-3.66615
O	-3.37329	-0.77301	-3.83159
C	-0.49601	1.20594	-4.82149
H	-1.30615	-1.27210	3.82055
H	-2.05434	-2.27808	2.53450
H	0.10569	-0.10556	2.27944
H	-1.31471	-0.28936	1.24013
H	-1.52118	-2.85963	0.48721
H	0.06153	-4.67994	0.60819
H	-0.52834	-4.64736	-1.06116
H	1.08471	-3.99406	-0.67490
H	1.27656	-0.82223	-0.76996
H	2.26357	-2.01397	0.04397
H	2.02334	-0.59116	3.07066
H	3.49965	0.34469	2.74835
H	3.40768	-1.38427	2.27919
H	4.22019	-0.60573	-0.00670
H	3.22990	0.52139	-0.98720
H	4.12979	1.12396	0.44945
H	1.23848	3.85386	1.16715
H	1.27262	3.74436	2.98006
H	-0.11862	3.05702	2.03726
H	-2.47607	-3.78217	-1.24936
H	-3.20435	-2.37234	-2.04253
H	-0.64101	-0.09801	-0.77156
H	-2.00432	-4.59239	-3.43470
H	-2.42519	-2.98681	-4.14724
H	-2.86615	-1.22453	0.24038
H	-3.66256	-0.53635	-1.17594
H	-2.84891	0.53366	-0.01979
H	-0.64763	2.37288	-2.30476
H	-1.74111	1.90809	-1.01028
H	-3.45646	3.08079	-2.18262
H	-2.46466	3.15266	-3.67808
H	0.52241	0.24016	-3.15562
H	-0.55090	-0.81022	-4.10139
H	0.29014	0.96008	-5.55764
H	-1.46407	1.18228	-5.35806
H	-0.31216	2.24350	-4.48562

PEBL Tetramer

O	1.54506	-0.17999	5.46692
C	1.50163	1.07385	4.74715
C	1.62255	0.68060	3.27454
C	0.90005	-0.68912	3.20898
C	1.28590	-1.22568	4.62083
O	1.34865	-2.37366	4.99503
C	-0.69094	-0.55316	3.25160
C	-1.35409	-1.82744	3.81672
C	1.36028	-1.68660	2.13226
C	2.86841	-1.84423	1.74937
C	2.87622	-3.10520	0.86162
C	3.42502	-0.68339	0.88437
C	3.78438	-2.10828	2.95239
O	3.40000	-4.17088	1.13162
O	2.19151	-2.88835	-0.29114
C	2.04651	-4.02094	-1.16284
C	-1.54297	-0.07061	1.96911
C	-1.89869	-1.32790	1.13242
C	-2.94014	0.37318	2.51264
C	-0.83059	1.09010	1.16993
O	-3.22163	-1.59818	1.18741
C	-3.95459	-0.66565	2.00855
O	-1.14891	-2.06564	0.52200
C	-1.26767	1.49402	-0.32139
C	-0.86296	2.34933	2.07024
C	-0.50539	2.77895	-0.74220
C	-1.50354	3.93179	-0.53219
O	-2.80434	3.32303	-0.31421
C	-2.72557	1.96539	-0.27601
C	-1.07441	0.33788	-1.35194
O	-3.72340	1.27705	-0.18547
C	0.37114	-0.17721	-1.31284
C	-1.50057	0.54049	-2.86646
C	-0.32719	1.01234	-3.75553
C	-1.81184	-0.87072	-3.44243
C	-1.06501	-0.94020	-4.78398
O	-0.09942	0.13892	-4.77142
O	0.32561	2.03389	-3.65579
H	2.33671	1.69597	5.11231

H	0.54858	1.58606	4.99058
H	1.24597	1.45515	2.59789
H	2.68752	0.53571	3.04165
H	-0.88136	0.24772	3.99136
H	-2.44948	-1.71609	3.87332
H	-1.00483	-2.05190	4.83499
H	-1.13663	-2.71150	3.19298
H	1.01057	-2.67775	2.47821
H	0.79817	-1.50213	1.20816
H	3.69132	0.19390	1.49742
H	4.35081	-1.00310	0.37061
H	2.70500	-0.36660	0.11305
H	3.43490	-2.96840	3.54513
H	4.81261	-2.32302	2.61107
H	3.83010	-1.22696	3.61740
H	1.46599	-3.65860	-2.02630
H	1.50431	-4.83315	-0.64541
H	3.03707	-4.39293	-1.48267
H	-3.22305	1.36962	2.14951
H	-2.94138	0.42652	3.61436
H	0.21956	0.77973	1.04348
H	-4.42171	-1.25039	2.82276
H	-4.73894	-0.21842	1.37699
H	-0.75030	2.08970	3.13371
H	-1.81745	2.89547	1.98507
H	-0.05407	3.05647	1.82461
H	0.42498	2.92711	-0.16971
H	-0.21130	2.71263	-1.80184
H	-1.28279	4.56358	0.34700
H	-1.59851	4.58538	-1.41771
H	-1.74498	-0.46836	-1.01886
H	0.56698	-0.73798	-0.39357
H	1.09548	0.65039	-1.41409
H	0.57216	-0.88675	-2.13437
C	-2.67522	1.51697	-3.12246
H	-2.89760	-1.02812	-3.56524
H	-1.44801	-1.65611	-2.75779
H	-0.50232	-1.87895	-4.92924
H	-1.72416	-0.78262	-5.65776
H	-3.54278	1.17073	-2.53489
H	-2.39932	2.51632	-2.74095
C	-3.08112	1.66633	-4.59353
H	-3.89251	2.41017	-4.68597
H	-2.24130	2.01422	-5.22452
H	-3.46246	0.71881	-5.01733

MMBL

C	1.08890	-0.44020	0.68930
C	1.44510	-0.86370	1.90860
H	1.47580	-0.15570	2.75080
H	1.71600	-1.90890	2.11890
C	0.69720	0.95790	0.31210
C	1.00490	-1.20700	-0.42420
C	0.47420	0.82830	-1.20140
O	0.63090	-0.52450	-1.54220
O	1.23770	-2.39870	-0.45220
C	-0.89950	1.32130	-1.64930
H	1.50750	1.68110	0.55940
H	-0.23370	1.24320	0.85310
H	1.26240	1.40080	-1.75040
H	-1.02470	1.20900	-2.75080
H	-1.03480	2.39870	-1.40020
H	-1.71600	0.74760	-1.15430

PMMBL Monomer

C	0.36860	0.11140	-1.24630
C	-0.09000	-0.51160	0.08340
C	0.25550	0.22260	1.40180
C	-0.11050	-0.75890	2.53060
O	0.98710	-1.40200	3.01850
C	0.77270	-2.37130	4.01670
O	-1.24320	-0.94910	2.91550
C	1.74230	0.62830	1.45240
C	-0.60300	1.48630	1.61910
C	-0.30270	1.42950	-1.63240
C	0.05480	-0.76410	-2.45200
C	-0.27190	1.38020	-3.15470
O	-0.28290	0.02850	-3.50300
O	0.10540	-1.97380	-2.48610
C	-1.44060	2.11020	-3.80850
H	1.47900	0.22680	-1.26390
H	0.38500	-1.52150	0.14490
H	-1.19000	-0.69060	0.03350
H	1.76090	-2.80240	4.29280
H	0.32350	-1.89940	4.91920
H	0.12350	-3.18640	3.62550

H	2.01760	1.03860	2.45060
H	1.97220	1.42580	0.71110
H	2.41770	-0.22820	1.22870
H	-1.68650	1.29430	1.45020
H	-0.48480	1.87380	2.65690
H	-0.30780	2.31740	0.94450
H	0.22370	2.32690	-1.23750
H	-1.35840	1.43410	-1.27430
H	0.69050	1.81180	-3.52630
H	-1.37420	2.05360	-4.91920
H	-1.44410	3.18640	-3.52040
H	-2.41770	1.67000	-3.50490

PMMBL Dimer

C	0.31630	0.30790	-0.16470
C	-0.55980	-0.15090	1.02800
C	-2.08330	-0.42500	0.87470
C	-2.88160	0.88790	0.85380
O	-3.80830	0.90860	-0.14480
O	-2.70780	1.79480	1.63700
C	-2.40850	-1.34160	-0.32040
C	-2.57060	-1.14880	2.15520
C	-0.29420	1.48420	-0.94720
C	1.55320	1.04540	0.37190
C	0.07620	2.70040	-0.11160
O	1.30280	2.37870	0.46460
O	2.61270	0.53400	0.65620
C	0.18370	3.98550	-0.92620
C	1.19240	-2.20860	-0.59700
C	0.78960	-0.81280	-1.12380
C	1.82800	-3.04520	-1.71730
C	2.27890	-2.30090	0.46540
C	3.31140	-2.76240	-1.51030
O	3.47110	-2.55410	-0.13850
O	2.11340	-2.20000	1.66160
C	4.21390	-3.89590	-1.98700
C	-4.59390	2.07020	-0.26790
H	-0.10310	-1.07890	1.43170
H	-0.43190	0.58240	1.85840
H	-3.48360	-1.63000	-0.34430
H	-1.84080	-2.29510	-0.26460
H	-2.17860	-0.86240	-1.29610
H	-2.33430	-0.57000	3.07700
H	-3.67280	-1.31010	2.13790
H	-2.09490	-2.14990	2.26440
H	0.20020	1.56980	-1.94380
H	-1.38110	1.39990	-1.14400
H	-0.65540	2.85560	0.71540
H	0.46440	4.84610	-0.27660
H	-0.79070	4.22560	-1.41020
H	0.95360	3.90090	-1.72660
H	0.29450	-2.73840	-0.20270
H	-0.02420	-0.98300	-1.86730
H	1.63790	-0.41110	-1.72730
H	1.62000	-4.12780	-1.54190
H	1.47200	-2.78950	-2.73970
H	3.60010	-1.81690	-2.03180
H	5.28680	-3.64840	-1.81650
H	4.07420	-4.07890	-3.07700
H	3.99590	-4.84610	-1.44850
H	-5.28680	1.92490	-1.12650
H	-5.19540	2.22590	0.65560
H	-3.94460	2.95000	-0.47750

PMMBL Trimer

C	1.43910	0.32210	1.30650
C	-0.03430	0.59050	1.72950
C	-0.82260	-0.18340	2.82400
C	-2.01750	0.73460	3.17090
O	-3.10420	0.46490	2.39290
O	-1.97830	1.61770	3.99920
C	-1.36120	-1.55860	2.37300
C	-0.03230	-0.39530	4.12880
C	1.85600	1.34800	0.23580
C	2.38880	0.79750	2.42230
C	2.25380	2.58750	1.02410
O	2.71610	2.10510	2.24510
O	2.81210	0.11960	3.33310
C	3.33010	3.42330	0.33710
C	1.51320	-1.81120	-0.43810
C	1.81290	-1.13350	0.93320
C	2.68860	-1.72840	-1.42630
C	1.56540	-3.32020	-0.12830
C	3.60390	-2.88120	-1.04200
O	2.77550	-3.83820	-0.46140
O	0.66160	-3.95660	0.36950

C	4.36310	-3.47900	-2.22290
C	-4.23670	1.28350	2.56260
C	0.03540	-0.45470	-2.17850
C	-1.22640	0.41030	-2.08230
C	-0.09810	-0.98870	-3.60030
C	-1.40040	0.87850	-3.52060
O	-0.88770	-0.14610	-4.31840
O	0.42050	-1.99070	-4.04050
C	-2.85030	1.17210	-3.89080
C	0.13350	-1.52370	-1.07580
H	-0.05620	1.65920	2.05150
H	-0.66510	0.57570	0.81350
H	-2.03540	-1.99410	3.14550
H	-0.55510	-2.30490	2.22230
H	-1.93970	-1.50920	1.42500
H	0.45540	0.54070	4.48150
H	-0.69680	-0.75200	4.94880
H	0.74820	-1.17720	4.00830
H	2.74880	0.98160	-0.31700
H	1.06070	1.58460	-0.50110
H	1.36590	3.23570	1.22290
H	3.59250	4.31570	0.95040
H	2.97500	3.78300	-0.65580
H	4.26400	2.83810	0.17620
H	2.91740	-1.22590	1.06690
H	1.40360	-1.76360	1.75210
H	2.33180	-1.91010	-2.46250
H	3.21970	-0.75420	-1.43260
H	4.33770	-2.55170	-0.26600
H	5.01980	-4.31570	-1.89110
H	5.00750	-2.71000	-2.70730
H	3.66830	-3.88140	-2.99510
H	-5.01980	0.93500	1.85270
H	-4.62670	1.18820	3.60080
H	-3.98360	2.34100	2.32450
H	0.93860	0.19650	-2.19000
H	-1.13830	1.25700	-1.36660
H	-2.09640	-0.22010	-1.78240
H	-0.77690	1.78920	-3.70020
H	-2.92970	1.51230	-4.94880
H	-3.26810	1.97460	-3.24080
H	-3.49180	0.26880	-3.77650
H	-0.56900	-1.28370	-0.25390
H	-0.28820	-2.45690	-1.51760

PMMBL Tetramer

C	0.88170	-2.69290	1.83310
C	-0.25400	-1.70690	2.21770
C	-1.56290	-2.09500	2.95150
C	-2.39640	-0.79290	2.95650
O	-3.12760	-0.66610	1.81220
O	-2.36880	0.03240	3.84270
C	-2.36000	-3.21630	2.25860
C	-1.32880	-2.48200	4.42760
C	2.25320	-2.00050	1.93690
C	1.08820	-3.73590	2.93510
C	2.58060	-2.09230	3.42150
O	1.99000	-3.28060	3.84500
O	0.54310	-4.81590	3.00380
C	4.07840	-2.10560	3.71220
C	0.94100	-2.77030	-0.92200
C	0.63940	-3.40990	0.47530
C	2.35590	-3.13250	-1.39870
C	0.07760	-3.60420	-1.88180
C	2.18490	-4.44250	-2.15620
O	0.84380	-4.51930	-2.52860
O	-1.12400	-3.49670	-2.01170
C	3.08300	-4.55610	-3.38500
C	-3.80830	0.55010	1.61610
C	0.96590	-0.33950	-2.22250
C	2.33210	0.32810	-1.98620
C	1.22070	-1.09300	-3.52760
C	3.09450	0.20510	-3.29860
O	2.41290	-0.73480	-4.06700
O	0.46770	-1.89100	-4.03790
C	3.21960	1.50760	-4.08560
C	0.56630	-1.27080	-1.03910
C	-0.43150	1.95740	-1.74790
C	-0.16630	0.67480	-2.56980
C	0.26040	3.20700	-2.30530
C	-0.10770	2.01000	-0.26840
C	0.47450	4.07220	-1.07180
O	0.44790	3.21360	0.02760
O	-0.31640	1.14060	0.54480
C	1.78470	4.85350	-1.09960
H	0.18740	-0.86490	2.80040

H	-0.58780	-1.24650	1.26690
H	-3.36010	-3.34420	2.73210
H	-1.84830	-4.19880	2.33800
H	-2.52210	-3.01850	1.17550
H	-0.64090	-1.77410	4.94280
H	-2.28800	-2.50010	4.99380
H	-0.89700	-3.49740	4.54220
H	3.01850	-2.58430	1.38020
H	2.28260	-0.95290	1.56740
H	2.10790	-1.25390	3.98840
H	4.27010	-2.18050	4.80720
H	4.55870	-1.17030	3.34380
H	4.58440	-2.96770	3.22120
H	1.19890	-4.37560	0.49880
H	-0.43020	-3.71670	0.49530
H	2.76280	-2.36740	-2.08750
H	3.10600	-3.22590	-0.58720
H	2.39030	-5.30420	-1.47380
H	2.93310	-5.53330	-3.89870
H	4.15680	-4.48200	-3.09800
H	2.86880	-3.75100	-4.12410
H	-4.30680	0.50620	0.62200
H	-4.58440	0.68660	2.40210
H	-3.08580	1.39690	1.61390
H	2.26120	1.36910	-1.61290
H	2.90470	-0.21910	-1.20100
H	4.12530	-0.18600	-3.11120
H	3.84880	1.36310	-4.99380
H	3.69540	2.30530	-3.47080
H	2.22800	1.87380	-4.43230
H	-0.53900	-1.21710	-0.91220
H	1.00380	-0.78200	-0.14490
H	-1.53290	2.16600	-1.77510
H	-1.12070	0.09590	-2.61590
H	-0.02400	1.02230	-3.62170
H	-0.33240	3.71940	-3.09670
H	1.24570	2.94970	-2.74620
H	-0.38150	4.78260	-0.95850
H	1.89650	5.47650	-0.18260
H	1.82080	5.53330	-1.98140
H	2.66420	4.17180	-1.15450

Methyl 2-ethacrylate

O	-0.53119	1.81396	0.64941
C	-0.91330	1.06369	-0.24055
O	-2.17801	1.06881	-0.72080
C	-3.08461	2.02467	-0.13408
H	-3.18747	1.84193	0.95088
H	-4.04910	1.88008	-0.64507
H	-2.71503	3.05338	-0.29862
C	-0.06527	0.04239	-0.93964
C	0.81632	-0.65315	-0.19046
H	0.91130	-0.48138	0.88964
H	1.45511	-1.42107	-0.64900
C	-0.27297	-0.17199	-2.42190
C	-0.32615	1.12809	-3.23572
H	-1.20509	-0.75183	-2.59600
H	0.56566	-0.80429	-2.77118
H	-1.23321	1.71933	-3.01555
H	-0.34328	0.89017	-4.31678
H	0.56892	1.75194	-3.04059

PMEA Monomer

C	-4.26880	-0.41947	-0.42191
C	-2.97756	0.21529	0.14726
C	-5.44441	0.48250	-0.01186
O	-5.35033	1.55069	0.58117
O	-6.63138	-0.02855	-0.40124
C	-7.80555	0.75066	-0.08454
H	-7.89197	0.88110	1.00929
H	-8.65791	0.17272	-0.47468
H	-7.74878	1.74031	-0.57277
C	-4.50760	-1.84308	0.12977
H	-4.49660	-1.85200	1.23529
H	-3.72175	-2.52801	-0.23718
H	-5.47852	-2.23812	-0.21393
C	-4.22677	-0.45527	-1.96877
H	-4.09342	0.56021	-2.38696
H	-5.15706	-0.88578	-2.37867
H	-3.38267	-1.08260	-2.30992
C	-1.67657	-0.57632	-0.08628
C	-1.52299	-1.71102	0.91289
O	-1.19835	-2.87766	0.31370
O	-1.63347	-1.59596	2.12808
C	-0.99728	-4.01220	1.18691
H	-0.16621	-3.81165	1.88680

H	-0.75307	-4.85620	0.52365
H	-1.92074	-4.21816	1.75780
H	-3.09767	0.38009	1.23454
H	-2.85486	1.21700	-0.30551
C	-0.44751	0.35995	0.04497
H	-1.65995	-1.02056	-1.09962
C	0.90055	-0.34115	-0.13982
H	-0.48984	0.85709	1.03526
H	-0.56692	1.15718	-0.71469
H	1.08208	-1.09399	0.65206
H	1.72977	0.38945	-0.09843
H	0.94963	-0.85982	-1.11710

PMEA Dimer

C	-3.65808	-0.38263	-0.83461
C	-2.59373	0.30787	0.07609
C	-4.98827	0.27205	-0.42108
O	-5.15212	1.47690	-0.31357
O	-5.98681	-0.62281	-0.22148
C	-7.26394	-0.05708	0.13021
H	-7.18908	0.49501	1.08486
H	-7.95193	-0.91240	0.22661
H	-7.60696	0.63730	-0.65851
C	-3.69058	-1.91023	-0.66427
H	-3.86224	-2.19851	0.38761
H	-2.73380	-2.34988	-0.99480
H	-4.49342	-2.35684	-1.27495
C	-3.50904	-0.01887	-2.33713
H	-3.38316	1.07082	-2.46558
H	-4.41096	-0.32979	-2.89789
H	-2.64665	-0.53260	-2.79343
C	-1.14402	-0.25385	0.21987
C	-1.21247	-1.53362	1.06320
O	-0.65506	-2.59969	0.44322
O	-1.69759	-1.59575	2.18117
C	-0.65300	-3.84069	1.16983
H	-0.19395	-3.70017	2.16449
H	-0.05795	-4.53602	0.55749
H	-1.68904	-4.20438	1.29995
H	-3.00055	0.33011	1.10455
H	-2.51607	1.36446	-0.23974
C	-0.40341	0.82360	1.08311
C	0.95165	0.46986	1.70778
H	-1.09306	1.09676	1.90382
H	-0.30603	1.72741	0.44869
H	0.91250	-0.49349	2.25074
H	1.22995	1.24584	2.44469
H	1.77041	0.41889	0.96961
C	-0.49149	-0.46375	-1.16234
C	0.97239	-0.98505	-1.20242
H	-0.54168	0.50972	-1.68669
H	-1.11899	-1.14848	-1.74928
C	1.91503	0.03589	-1.87929
C	3.38829	-0.37615	-1.88223
H	1.79477	0.99493	-1.33510
H	1.55749	0.22156	-2.91208
H	3.75480	-0.54357	-0.85075
H	4.01671	0.40724	-2.34534
H	3.54969	-1.31650	-2.44264
C	1.09099	-2.33794	-1.88248
H	1.34305	-1.17704	-0.18388
O	1.72073	-3.29375	-1.46006
O	0.44029	-2.36115	-3.07963
C	0.52846	-3.59481	-3.81213
H	1.58348	-3.83819	-4.03483
H	-0.03964	-3.43346	-4.74256
H	0.08902	-4.42299	-3.22588

PMEA Trimer

C	-0.86460	0.33510	-0.62281
C	-1.46189	1.74925	-0.41835
O	-2.67455	1.86851	-0.99596
C	-3.33411	3.14577	-0.85585
H	-2.72207	3.94199	-1.31637
H	-3.49683	3.37420	0.21287
H	-4.29553	3.04086	-1.38224
O	-0.93429	2.66980	0.19371
C	-0.82702	0.06431	-2.14411
H	-1.83429	0.17582	-2.57890
H	-0.49229	-0.96471	-2.35193
H	-0.13929	0.75885	-2.65873
C	-1.83822	-0.65448	0.06340
H	-2.86814	-0.48954	-0.29561
H	-1.82666	-0.53420	1.16227
H	-1.57565	-1.69821	-0.17807
C	0.54535	0.39915	0.02622

C	1.57098	-0.79838	0.07983
H	0.40464	0.70696	1.07875
H	1.07445	1.23512	-0.46481
C	1.08042	-1.84253	1.11811
C	1.83550	-3.16740	1.29666
H	0.02055	-2.06730	0.93334
H	1.06249	-1.30465	2.08608
H	2.10350	-3.64185	0.33988
H	1.19989	-3.87798	1.85563
H	2.76511	-3.05352	1.87737
C	1.83165	-1.23315	-1.39017
O	2.40359	-0.46809	-2.15669
O	1.47403	-2.43101	-1.92548
C	0.40335	-3.30975	-1.53688
H	-0.31433	-3.33809	-2.37590
H	-0.11299	-2.97940	-0.62758
H	0.82358	-4.31710	-1.38275
C	2.87774	-0.05478	0.56331
C	4.10569	-0.70436	1.27202
H	2.53601	0.71421	1.28078
H	3.23291	0.50062	-0.31837
C	3.81774	-0.80936	2.80381
C	4.85728	-1.46521	3.71690
H	2.84506	-1.30641	2.95592
H	3.66248	0.23819	3.13124
H	4.92020	-2.55381	3.55094
H	4.57252	-1.29290	4.77212
H	5.87002	-1.04644	3.57145
C	4.60985	-2.01293	0.66638
O	4.09843	-2.23754	-0.55740
C	4.55000	-3.41883	-1.24901
H	3.98773	-3.43466	-2.19407
H	4.32737	-4.31721	-0.64634
H	5.63450	-3.34757	-1.43643
O	5.44743	-2.75101	1.17178
C	5.27878	0.31946	1.10231
C	5.87025	0.46484	-0.31443
H	6.09051	0.06842	1.80562
H	4.87600	1.30155	1.41671
C	6.48337	1.87638	-0.49866
C	7.12964	2.10651	-1.86637
H	7.21938	2.05314	0.31119
H	5.66099	2.60207	-0.34191
H	8.00364	1.44488	-2.02236
H	7.48071	3.15088	-1.96201
H	6.40877	1.91002	-2.68375
C	6.91356	-0.59316	-0.64066
H	5.08030	0.33028	-1.07763
O	7.85577	-0.69302	0.31864
C	8.88211	-1.68578	0.11036
H	9.52788	-1.63574	1.00080
H	9.45803	-1.45456	-0.80349
H	8.42176	-2.68567	0.01804
O	6.94271	-1.25555	-1.67243

PMEA Tetramer

O	1.52396	1.99692	0.04194
C	1.74091	1.47624	-1.19391
C	1.43653	3.43105	0.10953
H	2.37460	3.89105	-0.25261
H	1.26838	3.67033	1.17191
H	0.59778	3.79480	-0.51200
O	1.84487	2.17127	-2.19023
C	1.85793	-0.06185	-1.15274
C	1.82744	-0.55911	-2.61108
H	0.95926	-0.12646	-3.13840
H	1.72609	-1.65547	-2.64524
H	2.73408	-0.25597	-3.16246
C	0.63983	-0.62943	-0.39040
H	-0.29402	-0.29856	-0.88241
H	0.61307	-0.28344	0.65629
H	0.65873	-1.73284	-0.40969
C	3.24261	-0.29680	-0.45981
C	3.76869	-1.71961	-0.00232
C	3.07026	-2.06392	1.34065
C	3.17860	-3.48311	1.89963
H	2.00031	-1.83428	1.23012
H	3.46735	-1.34579	2.08166
H	2.76424	-4.22526	1.19644
H	2.59843	-3.54307	2.83891
H	4.20879	-3.77549	2.15096
C	3.40281	-2.70922	-1.10105
O	2.42888	-3.44663	-1.09988
O	4.26223	-2.64854	-2.15542
C	3.96277	-3.52523	-3.25251
H	3.95626	-4.57693	-2.91127

H	4.76092	-3.35956	-3.99341
H	2.97454	-3.28409	-3.68461
H	3.26817	0.31195	0.46306
H	3.99753	0.13387	-1.14517
C	5.30865	-1.45510	0.10824
C	6.43890	-2.36973	0.71994
H	5.37844	-0.51387	0.67913
H	5.65028	-1.22987	-0.91671
C	6.63966	-3.69375	-0.06109
C	5.56461	-4.78384	-0.03671
H	7.59343	-4.15131	0.24726
H	6.79410	-3.38878	-1.11387
H	5.33621	-5.14999	0.97645
H	5.91296	-5.64870	-0.63124
H	4.60759	-4.46067	-0.46608
C	6.21635	-2.42801	2.25436
O	5.79217	-1.44440	2.83724
O	6.44754	-3.52781	3.02811
C	7.28394	-4.66873	2.76591
H	7.50461	-5.08763	3.76166
H	8.23444	-4.39696	2.27859
H	6.75331	-5.43127	2.17111
C	7.69310	-1.43967	0.45632
C	9.13773	-1.69528	0.98971
H	7.42343	-0.43386	0.82672
H	7.76958	-1.36143	-0.64330
C	9.16555	-1.67304	2.53655
C	10.53403	-1.60957	3.22230
H	8.63986	-2.55851	2.92075
H	8.55732	-0.80346	2.85186
H	11.17177	-2.46410	2.93435
H	10.39632	-1.65002	4.31826
H	11.07486	-0.67156	3.00046
C	9.67967	-3.01295	0.44096
O	9.70467	-3.00931	-0.91480
O	10.04533	-3.97253	1.10284
C	9.98838	-0.51211	0.41722
C	11.51365	-0.73867	0.27988
H	9.81660	0.34866	1.09200
H	9.59231	-0.21058	-0.56779
C	12.28362	0.57726	0.55201
C	13.80340	0.45156	0.43017
H	12.01286	0.90402	1.57623
H	11.90150	1.35739	-0.13645
H	14.19100	-0.34535	1.09374
H	14.30007	1.39997	0.70659
H	14.11216	0.19945	-0.60228
C	11.92530	-1.29018	-1.07755
H	11.86555	-1.49765	1.00017
O	12.66037	-2.24855	-1.25517
O	11.43375	-0.54026	-2.09724
C	11.79189	-0.97339	-3.41945
H	11.30264	-0.26723	-4.10923
H	11.43150	-2.00347	-3.59585
H	12.88933	-0.95314	-3.54952
C	10.19554	-4.21386	-1.53393
H	9.63441	-5.08887	-1.15975
H	11.27061	-4.33386	-1.31507
H	10.03174	-4.07935	-2.61437

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CHAPTER 4.

BIO-BASED, RECYCLABLE LACTONE-ACRYLIC PLASTICS WITH PERFORMANCE-ADVANTAGED PROPERTIES

Overview

As the plastics industry evolves, there is a drive to use bio-based feedstocks in polymers and to engineer these new materials for circularity. Here we aimed to study bio-based alternatives to petroleum-based poly(methyl methacrylate) with lower ceiling temperatures to achieve enhanced recycling and performance properties. We show that poly(α-methylene-δ-valerolactone) and poly(α-methylene-δ-decalactone), derived from their corresponding bio-based monomers α-methylene-δ-valerolactone and α-methylene-δ-decalactone, exhibit five advantages compared to poly(methyl methacrylate), including: exceptionally high polymerization rates under green conditions; quantitative bulk depolymerization of poly(α-methylene-δ-valerolactone) to recover the pure monomer under mild conditions; enhanced solvent-resistance and glass-transition temperatures; reversible upcycling of poly(α-methylene-δ-valerolactone) to advanced materials; and reduction of the temperature needed for recycling high-ceiling-temperature polyacrylates by forming copolymers doped with α-methylene-δ-decalactone. Lastly, techno-economic analysis and life cycle assessment for producing poly(α-methylene-δ-valerolactone) show that the production could be economically and environmentally competitive with poly(methyl methacrylate) under ambitious recycling scenarios that leverage the inherent recyclability of poly(α-methylene-δ-valerolactone).

Introduction

Poly(methyl methacrylate) (PMMA), a transparent thermoplastic, is the most important member of the large a,b-conjugated polar vinyl polymer or acrylic family, a technologically important class of polymers in today's materials economy.[1] PMMA is found in a variety of applications, from automotive parts to electronic displays, optical fibers, and construction industries, valued at about \$1.2 billion in the US market (~\$4 billion globally) in 2022, and is expected to grow at a compound annual growth rate of 5.4% from 2023 to 2030.[2,3] With this broad use comes a US annual supply chain energy cost of 110 PJ/year and US annual green-house gas emissions of 3.8 million metric tons/year (based on production volumes from 2017-2019).[4] This broad relevancy and use calls for more sustainable production, use, and recycling of acrylic plastics, much like other commodity plastics produced globally that have an overall less than 10% recycling rate.[5–8] In terms of depolymerizability, PMMA exhibits a ceiling temperature (T_c) of 205 °C at a 1.0 M concentration or 296 °C in bulk,[9] which still requires a relatively high temperature to thermally shift the polymerization/ depolymerization equilibrium to the monomer. Pyrolysis of PMMA has been studied extensively using different reactor configurations and molten metal (*e.g.*, Pb, Sn) bath processes at temperatures above 400 °C, demonstrating that bulk PMMA depolymerizes (by radical unzipping starting at 350 °C) to methyl methacrylate (MMA) (>90 wt%) at 450 °C.[10–13] Given the high temperature required for PMMA thermal depolymerization, there has been a drive[14,15] to develop catalytic strategies to reduce the energy input and increase the selectivity and bio-based alternatives that could exhibit similar or even superior properties to PMMA and more facile and selective depolymerization schemes back to monomer.

There are three general strategies that have been developed to enhance the chemical recyclability of PMMA, its analogs, or bio-based alternatives, aiming to lower the depolymerization temperature (*i.e.*, decreasing energy input) and enhance the selectivity toward pure monomer recovery (*i.e.*, suppressing side reactions during thermolysis to eliminate the need for additional purification). The first is to install a specific lower-energy end-group (i.e., a weaker C–X bond) on the terminal end of the polymer chain so that the chain-end radical that triggers subsequent chain zipping or scissions can be initiated at lower temperatures. These methods rely on precision synthesis of polymers so that the end-group has high fidelity, allowing for catalytic depolymerization,[16] typically coupled with use of dilute polymerization solutions to maximize monomer recovery (by lowering the T_c using concentration effects to shift the equilibrium to monomer).[17–23] These requirements render polymers made by alternative polymerization methods with not well-defined chain-end groups essentially inert and also hinder the scalability of the depolymerization when polymerization solutions are needed. The second strategy is to use analogous MMA structures that exhibit a low ceiling temperature (LCT), which renders intrinsic chemical recyclability into the polymer.[24] For example, bulk depolymerization of poly(ethyl cyanoacrylate), derived from LCT, highly reactive, super-glue monomer ethyl cyanoacrylate that requires special handling, can be performed at 210 °C to achieve a monomer recovery yield of 92%.[25] However, side reactions were reported to still persist, akin to PMMA depolymerization, leading to carbonaceous material remaining in the reaction flask.

The third strategy, employed within this study, is to utilize the lactone ring (the cyclic form of the ester moiety) possessed in bio-based vinyl lactone polymers, such as α-methylene-γ-methyl-γ-butyrolactone (MMBL) (Figure 4.1), which have been shown to enhance the bulk depolymerization selectivity to yield pure monomer in high to quantitative yields, by suppressing the small-molecule-forming side-reactions (*i.e.*, irreversible radical fragmentation) with the cyclic pendent group.[26–28] Although this unique feature is advantageous, these monomers exhibit a higher ceiling temperature (HCT), thus requiring a high temperature of 400 °C for efficient depolymerization.[26] Nonetheless, this approach is promising as it adheres to the principles of the bio-based economy for developing bio-based polymers with performance-advantaged properties that harness the inherent chemical functionalities of the starting bio-feedstocks.[29]

The above overview of the current three strategies highlights the advantages and limitations of each approach. We posit that, ideally, new acrylic plastics should be bio-based and exhibit advantages over the incumbent PMMA in both performance and end-of-life options, especially in chemical recyclability. In addition, the depolymerization should be performed with bulk polymer and achieve high selectivity and yield for pure monomer recovery, while the closed-loop de/polymerization should be performed under energy-efficient conditions. Centering on this objective, we reasoned that the beneficial effects of selectivity- and property-enhancing lactone rings and LCT monomer structures of low energy input and higher monomer recovery yield could be synergistically coupled, rendering a bio-based acrylic plastic system possessing the above-stated desirable properties (Figure 4.1). The lactone in the acyclic monomer structure is critical for enhancing both polymerization activity and performance over the linear analogues, and employing hybrid monomer design we hypothesized that a LCT lactone acrylic monomer would render both high polymerization rate and bulk depolymerization selectivity.[24,30,31] As shown in this work, α-methylene-δ-valerolactone (MVL)[32] and α-methylene-δ-decalactone (MDL), two bio-based six-membered lactone-containing acrylic monomers (Figure 4.1), meet the above stringent criteria and exhibit advantages in both enhancing the polymerization rate and bulk depolymerization selectivity to recover monomer in essentially quantitative yield under mild conditions. In addition, they exhibit advantages in enhancing physical properties or recyclability of HCT polymers and establishing atom-efficient reversible post-functionalization to advanced materials. Techno-economic analysis (TEA) and life cycle assessment (LCA) are used to assess MVL scalability and sustainability in industrial context to highlight the advantages in the chemically recyclable polymers and to identify areas of improvements needed as consumer polymers.

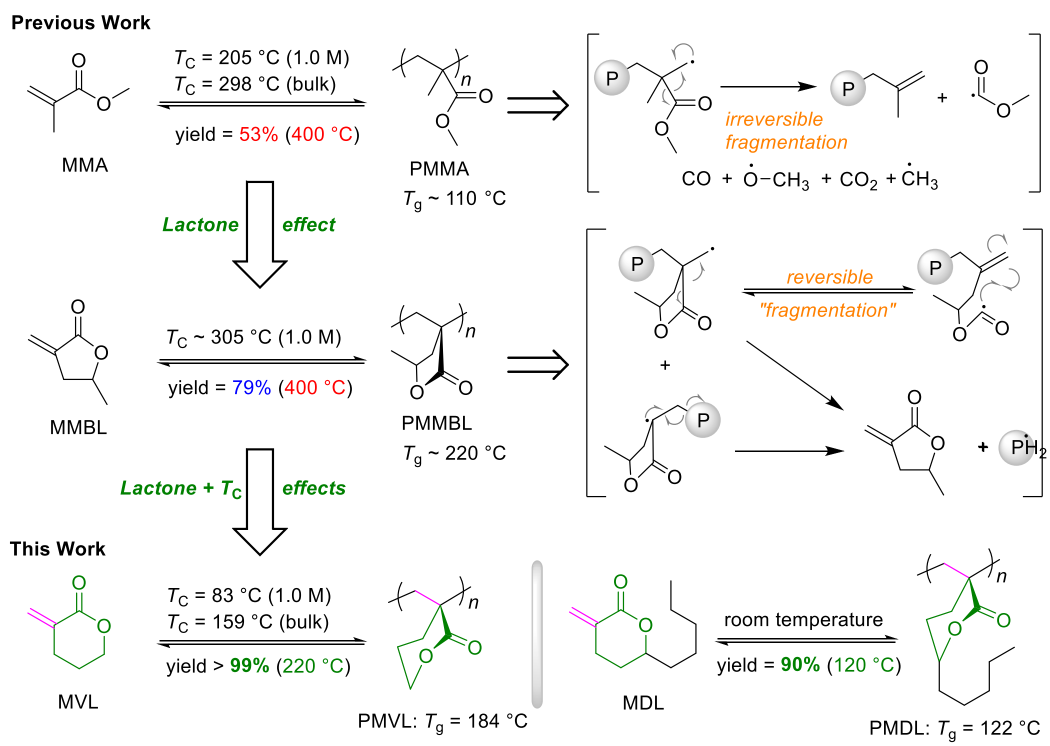


Figure 4.1. *Outlined effects of the lactone incorporation that suppresses side reactionsduring thermolysis and the LCT-enabling six-membered lactone, δ-valerolactone (DVL, the ring highlighted in green), that lowers the depolymerization temperature and enhances selectivity to achieve quantitative monomer recovery with combined lactone and LCT effects. Note that the incorporation of the DVL in acrylic plastics increases Tg (vs. PMMA) and recyclability to pure monomer recovery under even milder conditions (vs. PMMA and PMMBL), and the depolymerization can be performed with bulk polymer without specific end-group requirements.*

Results and Discussion

Advantages in exceptionally rapid organopolymerization

Prior to investigations into MVL and MDL, we examined its LCT linear analogue, methyl ethacrylate (MEA) which exhibits a T_c of 20 °C at 1.0 M or 82 °C in bulk.[33–35] Bulk depolymerization of the corresponding polymer poly(methyl ethacrylate) (PMEA) was indeed facile, recovering monomer in > 95% yield at 265 °C and 50 mTorr in 1 h (Figures 4.8-11 and the Experimental section). However, PMEA (Figures 4.26-27) exhibits a relatively low glass-transition temperature (T_g) of 65 °C (*i.e.*, inferior to 110 °C of PMMA), and the polymerization was quite burdensome, requiring either extremely high pressures (for free radical polymerization) or exceptionally low temperatures and long reaction times (for anionic polymerization).

Turning to lactone-acrylic monomers, developing their efficient and cost-effective synthesis starting with a bio-based feedstock, such as δ-valerolactone (DVL) derived from bio-derived 1,5-pentanediol (PDO),[36–38] is essential for potential industrial implementation of their derived acrylic plastics. Monomer MVL was typically prepared by aldol condensation of DVL with diethyl oxalate or ethyl formate, followed by reacting the resulting aldol with formaldehyde,[32,39] and monomer MDL was synthesized from δ-decalactone (DDL), which can be derived from bio-based 6-amyl-α-pyrone,[40] using the same procedures (see Supplementary Information). Switching the base from sodium hydride to sodium ethoxide (NaOEt) reduced the pyrophoric hazards (Figure 4.2), and the synthesis was further optimized through concurrent process modelling efforts (*vide infra*), by employing sodium carbonate instead of potassium carbonate due to the cost and solubility of the reagent in the aqueous workup of MVL.

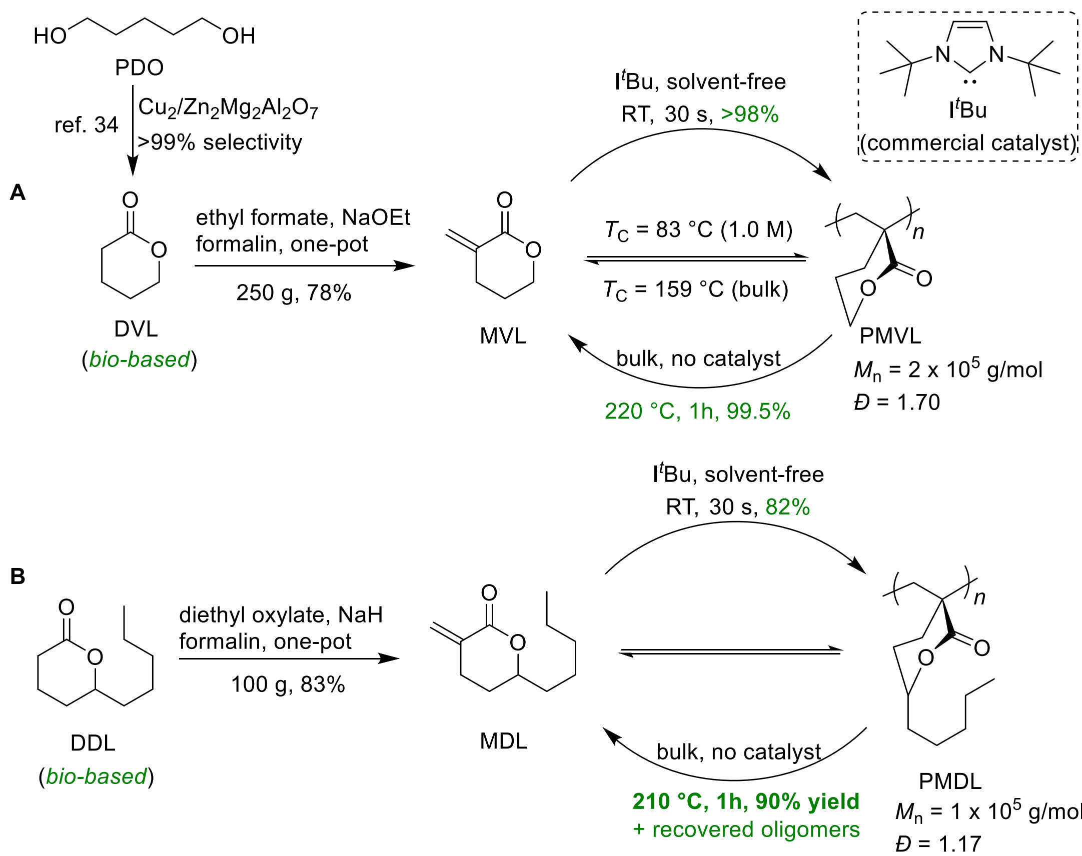


Figure 4.2. *Synthetic schemes to produce (A) MVL and conduct its rapid organopolymerization to PMVL, which can be depolymerized back to MVL in quantitative selectivity and yield to close the loop and (B) MDL with the same process.*

MVL can be polymerized rapidly via conjugate-addition polymerization initiated by a commercially available organic *N*-heterocyclic carbene (NHC), 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu).[39] This polymerization bears several hallmarks of a green process, namely it employs an organic catalyst at ambient conditions, and it is solvent-free, catalytic, rapid (in a few seconds), and essentially quantitative (Figure 4.2A). This organopolymerization of MVL can readily afford high-molar-mass PMVL with number-average molar mass (M_n) up to 2.0 ´ 10^5 g/mol and dispersity (*Đ*) of 1.70. In contrast, organopolymerization of MMA by an NHC is sluggish, achieving only 68% conversion, even after 1 h.[41]The substantially higher reactivity of MVL relative to MMA can be rationalized by its highly activated double bond (the methylene moiety highlighted in magenta in Figure 4.2) that is exo-cyclic and in the *s*-cis conformation (thus more sterically accessible), relative to the conjugated ester carbonyl of the lactone (further activation by the electron-withdrawing group). Conversely, the double bond in MMA is more sterically hindered and less activated due to its linear structure that adopts both *s*-trans and *s*-cis conformations.

To demonstrate that the high depolymerizability of PMVL (*vide infra*) is inherent to its lactone ring and LCT but independent of chain ends, we also prepared PMVL employing simple, conventional free radical polymerization initiated by azobisisobutyronitrile (AIBN), which we found requires a longer reaction time (1 h).[32] Worth noting here is that the polymerization by AIBN is carried out at 60 °C (the temperature required to generate the radical initiator from AIBN) in bulk to achieve high conversions and thus high-molar-mass PMVL. LCT monomers like MVL require high monomer concentrations, most desirably in bulk, to achieve high conversion to polymer. Thus, the previously reported radical polymerizations using MVL solutions[32] were not particularly effective, yielding only low-molar-mass PMVL that was isolated in low yields and appeared to be viscous. Our above-described bulk polymerization methods by I^{t}Bu and AIBN were effectively applied to MDL, achieving similar polymerization results (Figure 4.2B).

Advantages in physical properties and bulk depolymerization selectivity to recover pure monomer

Compared to PMMA, vinyl lactone polymers such as PMMBL are more solvent-resistant and exhibit a much higher T_g, due to the presence of the bulky lactone rings tethered to the polymer backbone.[42] In this context, while PMMA is readily soluble in common organic solvents including toluene and acetone, PMVL is only soluble in selective chlorinated, polar solvents such as CH_2Cl_2, $CHCl_3$, and *N*,*N*-dimethylformamide. As expected, the rigidified polymer backbone in PMVL due to the DVL rings enhanced its T_g to 184 °C, relative to the T_g of ~110 °C for (atactic) PMMA. Incorporation of the plasticizing alkyl group (C_5H_{11}) in PMDL-resulted in a lower T_g of 122 °C relative to PMVL, highlighting the tunability in thermal properties of the lactone acrylic polymers. Conversely, both onset (5% weight loss) decomposition temperature ($T_{d,5\%}$ = 304 °C) and maximum rate decomposition temperature (T_{max} = 345 °C) values of PMVL, determined by thermal gravimetric analysis (TGA), are about 20 °C lower than those of PMMA, but these values are sufficiently high and suitable for thermal processing. As compared to PMVL, PMDL bearing the pentyl group on the DVL ring exhibits a slightly higher $T_{d,5\%}$ of 312 °C and a similar T_{max} of 345 °C.

LCT lactone acrylics PMVL and PMDL also showed advantages in selective depolymerization to recover pure monomer under milder temperatures. In contrast to bulk depolymerization of PMMA, which required a high temperature of 400 °C and also suffered a low monomer recovery of 53% (due to competing thermal decomposition at high temperatures for HCT polymers),[26] PMVL and PMDL were depolymerized in bulk selectively at 220 °C and 210 °C, respectively, in a glass tube distillation reactor under vacuum for 1 h (Figure 4.25). Under these mild conditions, pure monomer was isolated in 99.5% yield and 90% yield for MVL and MDL, respectively (Figures 4.3-4). The recycled MVL (rMVL) can be repolymerized without further purification via free radical polymerization initiated by AIBN, yielding recycled PMVL (rPMVL) in 98% isolated yield with a M_n of 5.0 ´ 10^4 g/mol and a $Đ$ of 1.68, which exhibited thermal properties comparable to those of the virgin PMVL (Figures S23-S24). The use of different initiating systems to polymerize MVL to PMVL that can be depolymerized in similar selectivity and monomer recovery yield highlights the end-group tolerance of the platform, enabling different polymerization techniques to be utilized without compromising the polymer's ability to efficiently depolymerize in mild conditions.

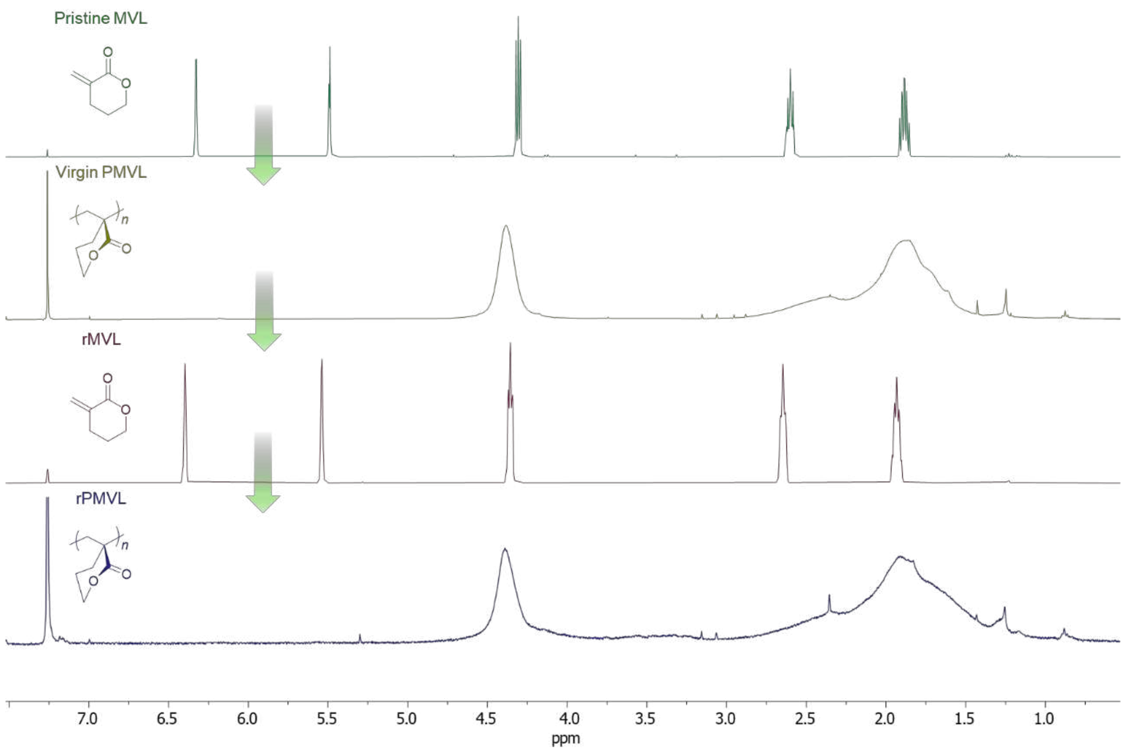


Figure 4.3. *NMR spectroscopic characterization of MVL species. Stacked ^1H NMR spectra ($CDCl_3$) comparing pristine MVL, high-molar-mass virgin PMVL obtained by organopolymerization with I^tBu, rMVL recovered from depolymerization, and rPMVL obtained by free radical polymerization with AIBN, demonstrating closed-loop chemical recycling of PMVL.*

The enhanced chemical recyclability PMVL and PMDL not only enabled lower depolymerization temperature (T_{dp}) relative to PMMA, but also resulted in a much higher selectivity and yield for the pure monomer recovery (Figure 4.5), which is attributed to both the LCT and the pendent lactone structure. The lower T_c allows for lower temperatures to be used for depolymerization, while the lactone pendent group further prevents or suppresses side-reactions (*e.g.*, irreversible radical fragmentation) from occurring by ensuring that no or negligible small molecule radical species can be eliminated. It is noteworthy that, although both T_c and T_d relate to the polymer thermal stability, they are different. Specifically, the T_c defines the relative thermodynamic stability of polymer vs. monomer: at a temperature below the T_c, the polymer is more stable than monomer, and vice versa. However, polymers can still be thermally stable, once kinetically trapped (the quenched polymer chain from the polymerization reaction), at a temperature far exceeding the T_c, as the "dead" chain must be reactivated or cleaved at a temperature that is a function of bond type, which defines T_d, before depolymerization can take place to revert to monomer. Hence, T_c is purely a thermodynamic parameter (*e.g.*, independent of catalyst), while T_d has to do with both thermodynamic (onset temperature or energy required to break a bond) and kinetic (rate, thus catalyst-dependent) parameters of the system.

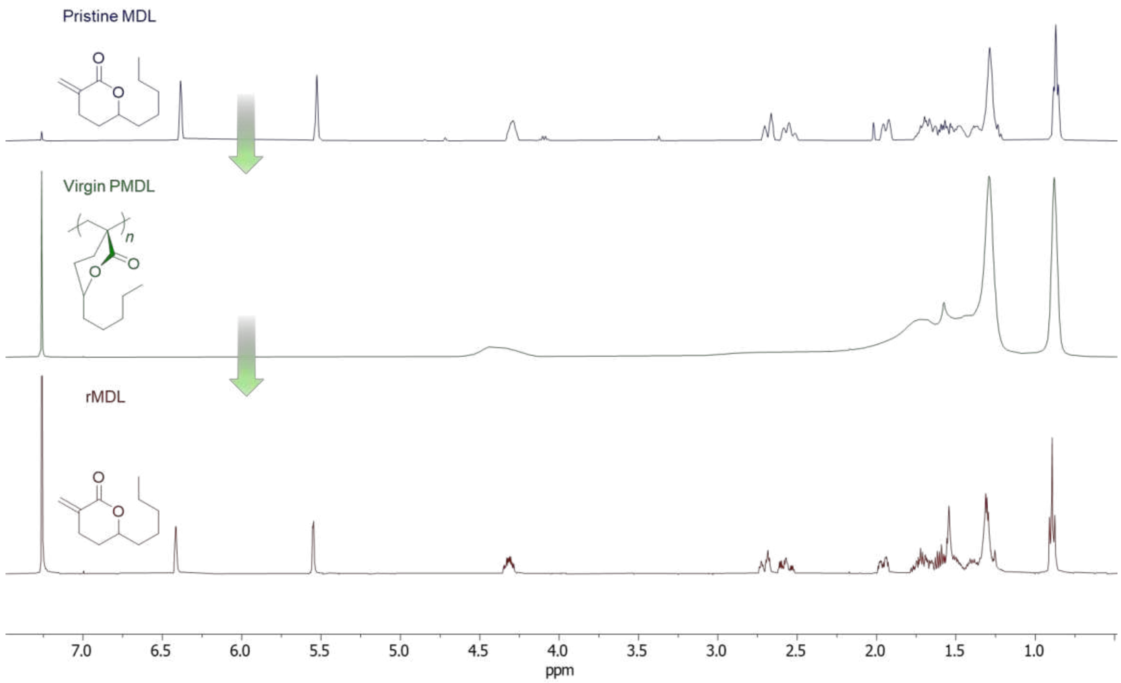


Figure 4.4. *NMR spectroscopic characterization of MDL species. Stacked [1] H NMR spectra ($CDCl_3$) comparing pristine MDL, virgin PMDL obtained by organopolymerization with I^{t}Bu, and rMDL recovered from depolymerization, demonstrating closed-loop chemical recycling of PMDL.*

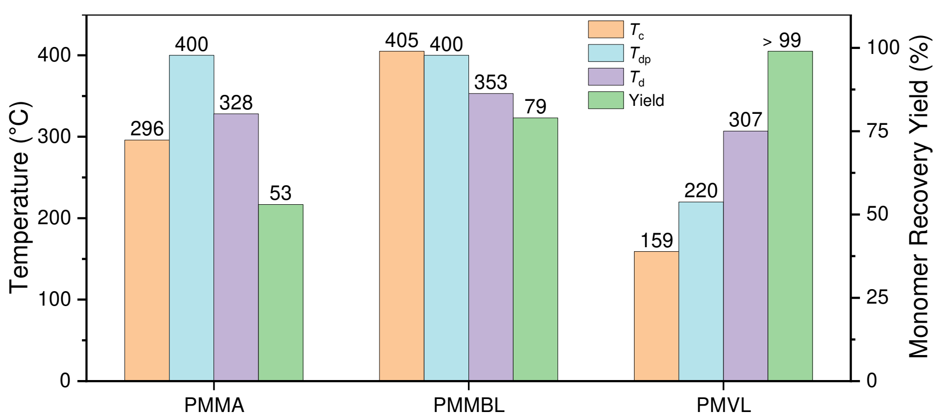


Figure 4.5. *Comparison of the thermal properties of commercial and bio-based acrylics. Comparisons of monomer recovery yield among three representative acrylic plastics with their T_c (orange), T_{dp} (blue), T_d (purple), and isolated monomer yield (green) values, highlighting the importance of coupling the LCT with the six-membered lactone ring in PMVL for achieving quantitative monomer recovery under mild conditions.*

It is worth noting here that the PMVL produced from NHC-initiated conjugate addition and free radical polymerization methods showed no difference in their depolymerization activity and selectivity. This important result indicates that the depolymerization of PMVL is not dependent on a specific polymerization method or the installation of specific end-groups. Previously, enhanced depolymerization of acrylic plastics was completely reliant on how polymer was synthesized, as the specific end-groups installed on the terminal end of the polymer chains are the key species required in the specific depolymerization mechanism.[18,19,21–23] These results further demonstrate advantages of redesigned, LCT acrylic plastics for establishing closed-loop chemical recycling in an energy-efficient and selective manner and for exhibiting broader applicability to various de/polymerization methods.

Advantages in exceptionally rapid organopolymerization

Considering the fact that the ester moiety in PMVL is covalently tethered to the backbone of the repeating unit, we further posited that a PMVL ionomer would have a distinct advantage over a PMMA ionomer in that the transformation does not involve any carbon loss (methoxy elimination occurs with PMMA upon treatment with a base) and the additional pendent hydroxyl group left from the ring-opening of the lactone (Figure 4.6). Because of this unique structural feature of PMVL, it should also render circularity (*i.e.*, virgin PMVL to the ionomer and back) of this post-functionalization via simple acid/base treatment. Hence, formation of the PMVL ionomer was explored by opening only a fraction of the lactone rings along the polymer chain. Indeed, a water-soluble ionomer can be readily produced upon treatment of PMVL with aqueous NaOH at 80 °C. As predicted, the resulting ionomer showed a two-step decomposition profile with two separate T_{max} values of 349 and 454 °C on the TGA thermogram (Figure 4.32), which corresponds to the fraction of the retained PMVL and ring-opened ionomer, respectively, highlighting thermal stability enhancement by 105 °C via ionomer formation. Based on the TGA characterization, the weight fraction of the ionomer in the resulting copolymer was calculated to be ~40%. Neutralization of the copolymer ionomer with HCl can partially revert it back to PMVL with about 26% remaining as the ionomer. The partial reversibility could be attributed to a reaction between the free hydroxyl groups with carbonyl groups on other monomer units.

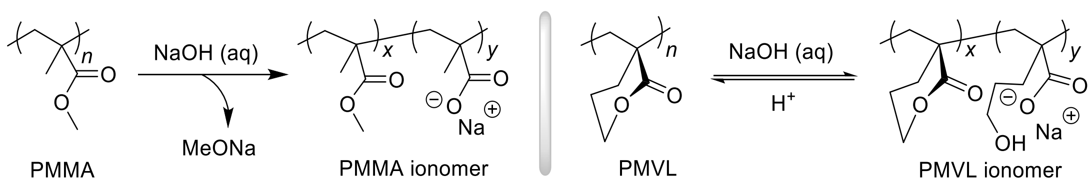


Figure 4.6. *Comparison between irreversible and reversible post-functionalization of PMMA and PMVL, respectively, in the case of ionomer formation.*

Additionally, we reasoned that DVL-containing LCT vinyl monomers such as MDL could enhance the depolymerizability of HCT monomers such as MMBL in the form of LCT/HCT copolymers via the doping effect. To this end, copolymerization of MMBL and MDL was performed to assess if the depolymerization of PMMBL could be improved by incorporating the LCT monomer units within the polymer chain. Random copolymers were readily prepared by conjugate-addition polymerization of mixed monomer solutions with different (molar) feed ratios (MMBL:MDL = 1:1, 20:1) and subsequently depolymerized. The copolymer P($MMBL_{0.5}$-*co*-$MDL_{0.5}$) from the 1:1 ratio was depolymerized in bulk at 210 °C with a collective monomer recovery yield of 95%, whereas copolymer P($MMBL_{0.95}$-*co*-$MDL_{0.05}$) from the 20:1 copolymer was depolymerized at 330 °C with a monomer recovery yield of 92% (Figure 4.7). These results showed that the presence of MDL decreases the activation energy of depolymerization, therefore allowing for lower temperatures to be used. More interestingly, even with MDL incorporation as low as 5%, PMMBL depolymerization temperature was lowered by 70 °C, while synergistically increasing monomer recovery yield by over 10%. These results indicate that the limiting factor in the HCT polymers depolymerization is the high-energy random-chain scission required of high temperature and the LCT polymer exhibits advantage in lowering the energy input (temperature) for depolymerization and increasing selectivity for monomer recovery (suppressing competing thermal decomposition).

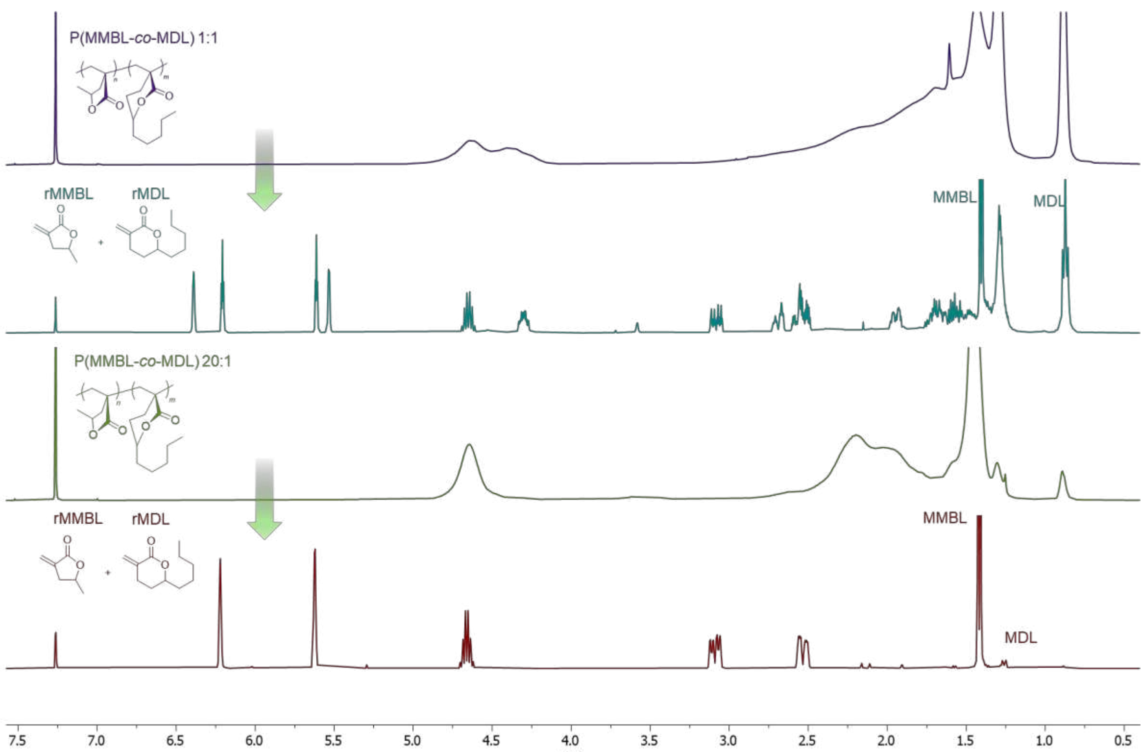


Figure 4.7. *NMR spectroscopic characterization of P(MMBL-co-MDL) species. Stacked ^1H NMR spectra ($CDCl_3$) comparing HCT/LCT copolymers P(MMBL-co-MDL) obtained by organopolymerization with I^tBu in two different molar ratios and the comonomers recovered from their depolymerizations.*

Conclusion

In this study, the bio-based acrylic PMVL polymer has been shown to exhibit the highlighted five advantages relative to the petroleum-based incumbent PMMA, all of which can be accredited to the presence of the bio-privileged six-membered DVL ring in the monomer MVL and corresponding polymer PMVL structures. First, the highly activated exocyclic double bond in MVL, as a result of the constrained *s*-cis conformation by the conjugated ester carbonyl of the lactone, renders its exceptional organopolymerization rate under desired solvent-free and ambient conditions, achieving quantitative monomer conversion in seconds to high-molar-mass PMVL. Second, the rigid lactone ring tethered to the polymer's all-carbon backbone provides PMVL with more solvent resistance and a much higher T_g. Third, the coupling of the selectivity-enhancing lactone and the LCT monomer structure, also due to the presence of the six-membered lactone that links the α-substituent and ester alkyl group, brings about the highly selective bulk depolymerization to recover monomer in essentially quantitative yield under mild (220 °C) conditions. Fourth, this high depolymerization selectivity is independent of polymerization mechanisms and thus chain-end groups, and this strategy can also be applied to enhance recyclability of HCT polymers via doping with the LCT lactone-acrylic comonomer. Fifth, taking advantage of reversibility of lactone's ring opening and closing under base and acid conditions, respectively, PMVL can undergo reversible post-functionalization to advanced materials such as ionomers for achieving atom-efficient reversible upcycling of PMVL. It should be possible to enable other types of atom-efficient upcycling via the ring-opening of the DVL ring in PMVL upon treatment a variety of nucleophiles such as alcohols and amines. These five characteristics of PMVL, particularly its selective polymerization and depolymerization, will be crucial for lowering the costs and environmental impacts associated with MVL synthesis from

PDO.

Experimental

Materials and Methods

The synthesis of air- and moisture-sensitive materials were carried out in flame-dried Schlenk glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N_2) glovebox. Organic solvents were dried with CaH_2 or sodium/potassium alloy (for hexanes) between 24 and 48 h before being distilled and stored under nitrogen atmosphere. NMR solvents ($CDCl_3$, D_2O) were used as received.

Dimethyl ethylmalonate, sodium hydroxide, formalin, diethylamine, azobisisobutyronitrile (AIBN), ethyl formate, sodium ethoxide, 1,1-diphenylethylene, and *sec*-butyl lithium (1.4 M solution in cyclohexane) were purchased from Sigma-Aldrich Chemical Co. Lactones δ-valerolactone and δ-decalactone were purchased from Beantown Chemical Co., and 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) was purchased from TCI America. All of the above commercial reagents were used as received. Synthesized monomers (*vide infra*) including methyl ethacrylate (MEA), α-methylene-δ-valerolactone (MVL), and α-methylene-δ-decalactone (MDL) were dried by stirring the liquid monomer with CaH_2 for 24 h before distilling by vacuum and storing in brown bottles under nitrogen atmosphere. Recycled MVL (rMVL) by depolymerization was not dried or purified after recovery, and it was instead polymerized directly after isolation from depolymerization.

Analytical Methods

NMR Spectroscopy. All NMR spectral characterizations were carried out by ^{1}H NMR experiments using a Bruker Advance NEO 400 MHz spectrometer or a Bruker AVIII 400 MHz spectrometer. Chemical shifts were referenced to internal solvent resonance corresponding to 7.26 ppm ($CDCl_3$) or 4.79 ppm (D_2O) and reported in ppm relative to $SiMe_4$.

Gel Permeation Chromatography (GPC). Measurements of polymer absolute weight-average molecular weight (M_w) and number-average molecular weight (M_n) were performed by GPC. Polymer concentrations ranged from 2 to 4 mg/mL. The GPC system was composed of an Agilent HPLC system equipped with one guard column and three PL gel 5 µm mixed-C gel permeation columns coupled with a Wyatt DAWN HELEOS II multi-angle (18) light scattering detector and a Wyatt Optilab TrEX dRI detector. The analyses were performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL/min. Data was analyzed using Wyatt ASTRA 7.1.2 software.

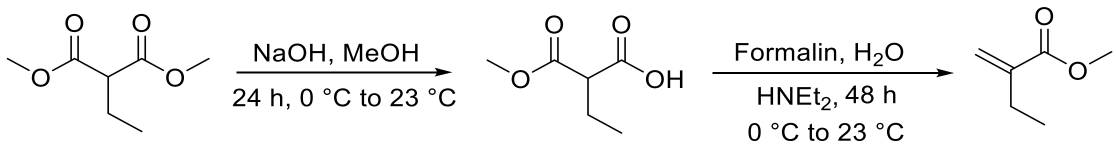
Thermal Characterizations

Thermogravimetric Analysis (TGA). TGA was performed on a Q50 TGA Analyzer (TA Instruments) to obtain decomposition temperatures (T_d, defined by the temperature of 5 % weight loss) and maximum rate decomposition temperatures (T_{max}) of the polymers. Between 5 and 10 mg of polymer sample was heated from 30 °C to 700 °C at 10 °C/min while the mass of the sample was continuously measured. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots by selecting the peak values, while T_d values were obtained from wt % vs. temperature (°C) plots by selecting the point of the weight percent versus temperature (°C) plots indicating 95 weight percent of sample remaining.

Differential Scanning Calorimetry (DSC). DSC was performed on an Auto Q20 (TA Instruments) to obtain the glass transition temperature (T_g) and melting temperature (T_m). Between 3 and 10 mg of polymer sample was weighed into an aluminum pan and sealed with an aluminum lid. Samples were then heated at 10-20 °C/min from room temperature to 250 °C and cooled to -40 °C to remove thermal history before being reheated to 250 °C. During this time, the thermal response was measured relative to a reference pan.

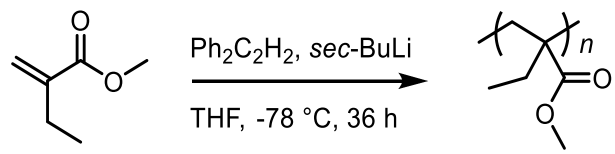
Thermogravimetric Analysis coupled Mass-Spectroscopy (TGA-MS). TGA-MS experiments were performed with a TGA-55 thermogravimetric analyser (TA Instruments) fitted with an evolved gas analysis furnace (TA Instruments). The analyser was coupled to a Cirrus 3 electron ionization mass spectrometer (MKS Instruments). The TGA data were processed using TRIOS software (TA Instruments, v5.1.1.46572), and the MS data were processed using both TRIOS and ProcessEye Professional software (MKS Instruments, v5.83.20111.1). In a standard TGA-MS experiment, polymer samples of between 3 and 5 mg were heated from 30 to 600 °C at 10 °C min^{-1} with nitrogen flow rates through the balance and furnace of 10- and 90-ml min^{-1}, respectively, while the sample mass was continuously measured, and MS data were collected. $T_{d,5\%}$ and T_{max} values were obtained from derivative (wt% °C^{-1}) versus temperature plots by selecting the point of the weight percentage versus temperature (°C) corresponding to 95 wt% of sample remaining (for $T_{d,5\%}$) and the maximum point (for T_{max}). The mass spectra were captured at the maximum signal of the decomposition products for all samples.

Experimental Details

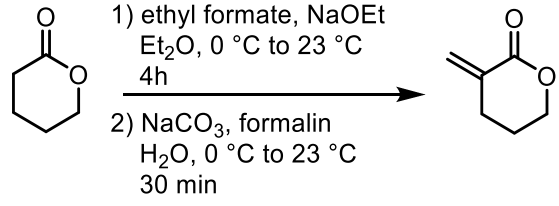


Synthesis of MEA. The synthesis of MEA was performed with literature procedures.[32,40,41] Dimethyl ethylmalonate (100 g, 1 eq, 624 mmol) was added to a 500 mL round-bottom flask with a stirbar and cooled to 0 °C while stirring. Sodium hydroxide (27 g, 1.1 eq, 687 mmol) was dissolved in methanol (250 mL) and slowly added to the solution over the course of 30 min via an addition funnel. After the addition the solution was allowed to stir for 4 h before the reaction was warmed to room temperature (~23 °C). The methanol was removed via rotary evaporation to give a while crystalline solid. This solid was redissolved in distilled water (250 mL) and a solution of 3N HCl was added until no more oily droplets separated from the solution. The resulting acidified solution was extracted with ether (3 x 300 mL) and dried over magnesium sulfate before being concentrated to yield a viscous colorless oil (87 g, 95% yield).

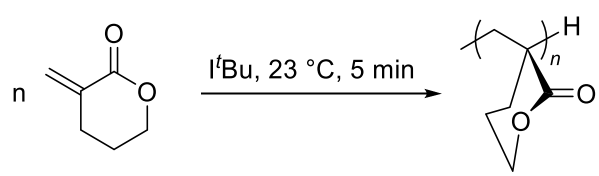
The colorless oil was added to a 500 mL round-bottom flask with a stir bar and cooled to 0 °C. Diethylamine (57.2 g, 81 mL, 1.25 eq., 782 mmol) was added to the solution dropwise with an addition funnel over the course of 30 minutes. The reaction was then allowed to stir for 48 h at room temperature before the addition of an aqueous potassium bicarbonate solution (13.0 g, 0.15 eq., 93.8 mmol in 25 mL H_2O). The organic phase was separated and washed with 4.25 M sulfuric acid (150 mL) and then water (100 mL) before being dried over magnesium sulfate, filtered, and concentrated via rotary evaporation. The remaining liquid was distilled (50 °C, 50 mTorr) to yield MEA (73 g, 84% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (t, 1H), 5.36 (d, 1H), 3.58 (s, 3H), 2.16 (qt, 2H), 0.91 (t, 3H).



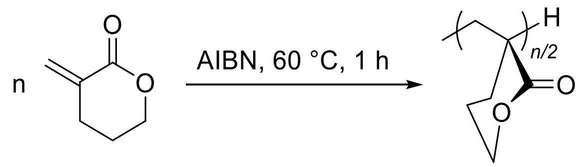
Polymerization of MEA. THF (75 mL) was added to a 100 mL flame-dried Schlenk flask with a stirbar, sealed with a rubber septum, and cooled to -78 °C with a dry ice/acetone bath. To this flask 1,1-diphenylethylene (395 mg, 387 µL, 10 eq., 2.19 mmol) was added before *sec*-butyl lithium (1.4 M solution in cyclohexane, 156 µL, 1 eq., 219 µmol) was added slowly until a red color was maintained for 5 min under stirring. The remaining *sec*-butyl litium was added and a deep red color was achieved. After the addition was complete, MEA (10.0 g, 10.5 mL, 400 eq., 87.6 mmol) was quickly added and the reaction was left to stir at -78 °C for 36 h. After the reaction reached completion ethanol (1 mL) was added to the solution and it was allowed to warm to room temperature before being exposed to air. The polymer was precipitated into vigorously stirring hexane (500 mL), filtered and dried to a consistent weight in a vacuum oven at 60 °C. PMEA: 50% yield, T_g = 65 °C, T_d = 281 °C, T_{max} = 329 °C.



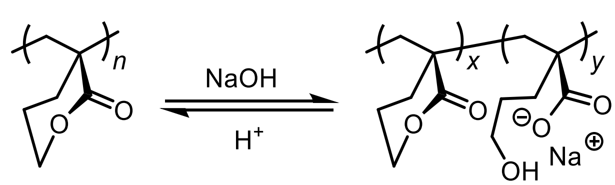
Synthesis of MVL. The synthesis of MEA was performed with literature procedures.[30] δ-valerolactone (250 g, 1 eq., 2.5 mol) and ethyl formate (185 g, 1 eq., 2.5 mol) were added to a 5 L round-bottom flask fixed with an overhead stirrer and cooled to 0 °C. To this solution a separate solution of sodium ethoxide (187 g, 1.1 eq., 2.75 mol) in diethyl ether (50 mL) was added dropwise over the course of 15 min while stirring. The reaction mixture was then allowed to warm to room temperature and stirred for another 4 h. The mixture was then cooled to 0 °C before the addition of sodium carbonate (1.04 kg, 3 eq., 7.49 mol) in water (1.4 L) and formaldehyde (375 g, 5 eq., 12.5 mol). The mixture was allowed to stir for 30 min before being washed with saturated aqueous sodium chloride solution (250 mL) and then a saturated aqueous sodium bicarbonate solution (250 mL) The organic and aqueous layers were separated before the aqueous layer was washed with diethyl ether (3 x 400 mL) and combined with the organic layer. The combined organic layers were washed with aqueous saturated sodium chloride solution (400 mL), dried over magnesium sulfate, filtered, and the ethyl ether was removed to yield a yellow oil. This oil was purified by distillation (100 °C, 50 mTorr) to yield MVL as a colorless oil (210 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.39 (s, 1H), 5.54 (s, 1H), 4.36 (t, 2H), 2.63-2.66 (t, 2H), 1.91-1.95 (m, 2H).



Synthesis of PMVL. Conjugate addition polymerizations initiated by the organic *N*-heterocyclic carbene I^{t}Bu was performed in a 500 mL oven-dried round-bottom flask inside of a glovebox in a nitrogen atmosphere. I^{t}Bu (603 mg, 3.34 mmol, 1 equiv.) was dissolved in dimethyl formamide (225 mL) in a separate flask before being added to the round-bottom flask filled with rapidly stirring MVL (75 g, 669 mmol). The reaction became too viscous to stir in less than 5 min but was allowed to stand for 60 min before proceeding. The reaction mixture was dissolved in chloroform (1000 mL) and quenched with methanol (500 mL) before being precipitated into hexanes (3 L). The precipitated solutions were stirred for 24 h, filtered, and washed with hexane and methanol before being dried in a vacuum oven at 50 °C to a constant weight. PMVL: 98% yield, T_g = 184 °C, T_d = 304 °C, T_{max} = 345 °C.

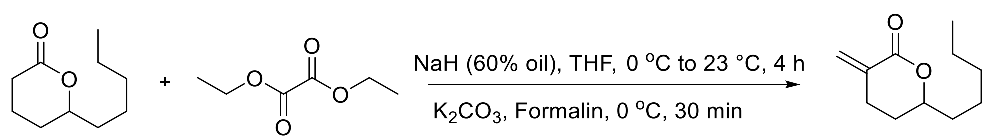


Free radical polymerization of MVL initiated by AIBN was performed in a 20 mL oven-dried round-bottom flask. MVL (5.0 g, 45 mmol, 400 equiv.) was added to the flask in a nitrogen filled glovebox and the flask was sealed with a rubber septum. The flask was then brought out of the glovebox and AIBN (18 mg, 0.11 mmol, 1 equiv.) was added (400:1 molar ratio). The solution was purged with nitrogen for 15 min before the flask was submerged into a 60 °C silicon oil bath to initiate polymerization. After 45 min the reaction became too viscous to stir but was allowed to stand for another 15 min. The polymerization was dissolved in chloroform (3 mL) and quenched with methanol (5 mL) before being precipitated into hexanes (500 mL). The precipitated solution was stirred for 1 h, filtered, and washed with hexanes and methanol before being dried in a vacuum oven at 50 °C overnight to a constant weight. PMVL: 96% yield, T_g = 197 °C, T_d = 285 °C, T_{max} = 342 °C.

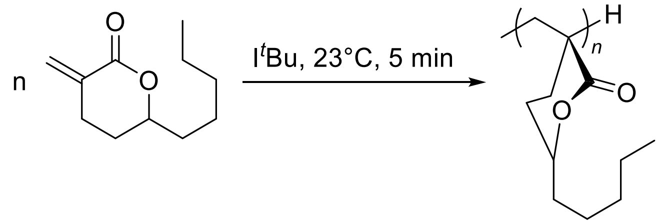


Synthesis of PMVL Ionomer. To a 20 mL reaction tube, PMVL (0.5 g) was added and suspended in an aqueous NaOH solution (10 wt%, 5 mL). The tube was then fixed with a stir bar, sealed, heated to 80 °C, and allowed to stir for 4 h. During this time the polymer dissolved into solution, leaving it slightly viscous and clear. The solution was concentrated via rotary evaporation. The collected polymer was then dried in a 50 °C vacuum oven overnight to a constant weight. PMVL ionomer: 99% yield, T_d = 302°C, T_{max1} = 349 °C, T_{max2} = 454 °C.

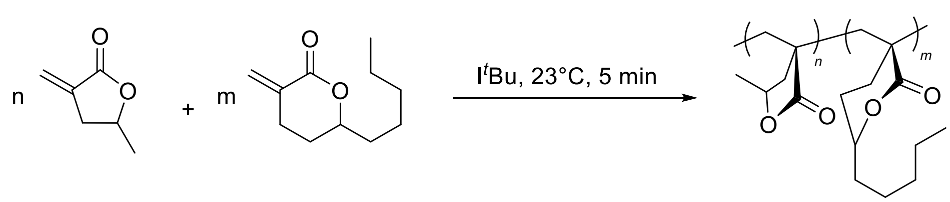
Recycling of PMVL Ionomer. To a PMVL ionomer aqueous solution prepared according to the above-described procedure, concentrated HCl was added until the pH reached 5 and the polymer precipitated. The polymer was collected, washed with methanol, and dried in a 50 °C vacuum oven overnight to a constant weight. PMVL recycled ionomer: 99% yield ($CHCl_3$ insoluble fraction = 26% by mass, soluble fraction = 74% by mass).



Synthesis of MDL. A suspension of sodium hydride (60 wt % dispersion in mineral oil, 24.0 g, 1.7 eq, 999 mmol) in THF (600 mL) was cooled to 0 °C, and a solution of *δ*-decalactone (100 g, 587 mmol) and diethyl oxalate (85.5 g, 1.0 eq, 587 mmol) in THF (50 mL) was added dropwise while stirring. After the addition was complete, ethanol (0.5 eq., 13.5 g) was added dropwise, and the reaction mixture was warmed to room temperature and stirred for 4 h. Then the mixture was cooled to 0 °C before the addition of K_2CO_3 (244 g, 1.76 mol, 3 eq) in water (341 mL) and formaldehyde (37 wt % aqueous solution, 654 g, 37.1 eq), and the reaction mixture was stirred for 30 min. The mixture was washed with saturated NaCl aqueous solution (200 mL) and saturated $NaHCO_3$ aqueous solution (200 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 300 mL). The combined organic layers were washed with saturated NaCl aqueous solution, dried over Na_2SO_4, filtered, and evaporated to yield a yellow oil. Purification by column chromatography (hexane/ethyl acetate 80:20) provided MδDL as a colorless oil (89 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.41 (d, 1H), 5.55 (d, 1H), 4.30-4.33 (m, 1H), 2.57-2.73 (m, 1H), 1.93-1.95 (m, 1H), 1.72-1.31 (m, 10H), 0.89 (t, 3H).



Synthesis of PMDL. Polymerization was performed in a 20 mL oven-dried glass vial inside a glovebox under inert atmosphere and ambient conditions (*ca.* 20 ºC). I^{t}Bu (0.005 mmol) was dissolved in 0.8 mL of dry DMF (3.0 M), and the polymerization was started by rapid addition of MDL (0.5 g, 2.77 mmol). For runs with a higher [MVL]/[I^{t}Bu] ratios, *i.e*., 1000:1, after the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4-mL vial containing 0.6 mL of undried $CDCl_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ^{1}H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched with 250 ppm of BHT-H containing chloroform (3 mL). The quenched mixture was precipitated into 100 mL of cold methanol, stirred for 1 h, filtered, washed cold methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. PMDL: 82% yield, T_g = 122 °C, T_d = 312 °C, T_{max} = 345 °C.



Synthesis of P(MMBL-co-MDL). Polymerization was performed in a 20 mL oven-dried glass vial inside the glovebox under inert atmosphere and ambient conditions (*ca.* 20 ºC). I^{t}Bu (0.005 mmol) was dissolved in 0.8 mL of dry DMF (3.0 M), and the copolymerization was started by the addition of MDL (0.5 g, 2.77 mmol) and MMBL (0.31 g, 2.77 mmol) within 5 min. For runs with higher [MMBL]/[MDL]/[I^{t}Bu] ratios (i.e. 1000:1000:1; 1000:500:1; 1000:50:1) after the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4-mL vial containing 0.6 mL of undried $CDCl_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were analyzed by ^{1}H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched with 250 ppm of BHT-H containing chloroform (3 mL). The quenched mixture was precipitated into 100 mL of cold methanol, stirred for 1 h, filtered, washed cold methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. PMMBL-*co*-MDL (1:1): 70% yield, T_g = 169 °C, T_d = 341 °C, T_{max} = 370 °C. PMMBL-*co*-MDL (20:1): 60% yield, T_g = 189 °C, T_d = 356 °C, T_{max} = 403 °C

General Depolymerization Procedure. Polymer (between 50 mg and 1.0 g) was loaded into a flame dried Schlenk-type storage tube with a 14/20 ground glass joint. To this a vacuum distillation head and a Schlenk flask were attached. The apparatus was brought under vacuum slowly (50 mTorr) and the receiving Schlenk flask was cooled with dry ice. The Schlenk-type storage tube was affixed with a thermocouple and wrapped with heat tape which was insulated with glass wool. The storage tube was heated for 1 h to a desired depolymerization temperature: T_{dp} = 220 °C for PMVL, 210 °C for PMDL, 265 °C for PMEA, 210 °C for PMMBL-*co*-MDL (1:1), 330 °C for PMMBL-*co*-MDL (20:1). After the depolymerization was complete the apparatus was placed under nitrogen gas and the collection flask was allowed to cool to room temperature. The collected liquid was weighed, recovery yield calculated, and analyzed by ^{1}H NMR spectroscopy.

Supporting Figures

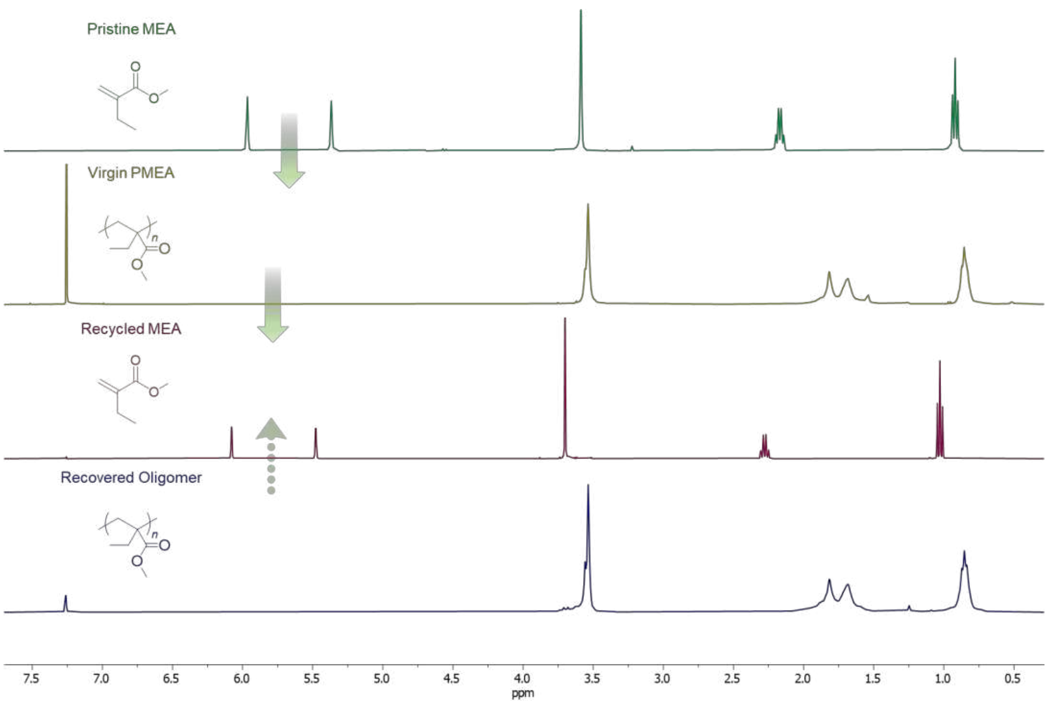


Figure 4.8. *Stacked ^{1}H NMR spectra ($CDCl_3$) comparing pristine MEA, virgin PMEA, recycled MEA, and recovered MEA oligomer from depolymerization.*

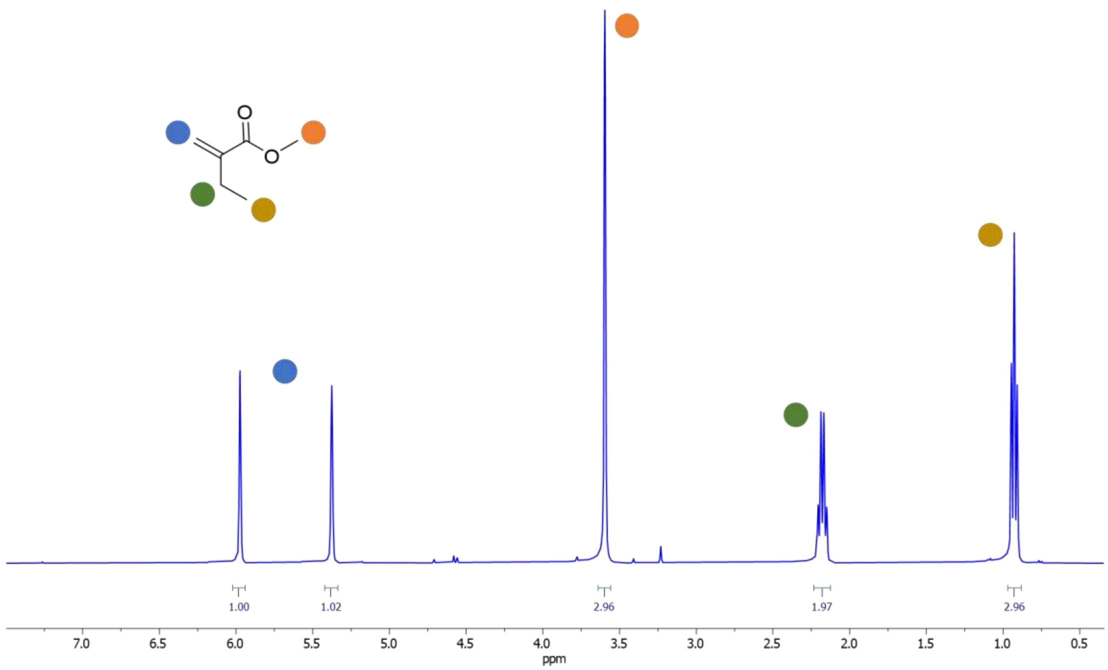


Figure 4.9. *[1]H NMR spectrum ($CDCl_3$) of MEA.*

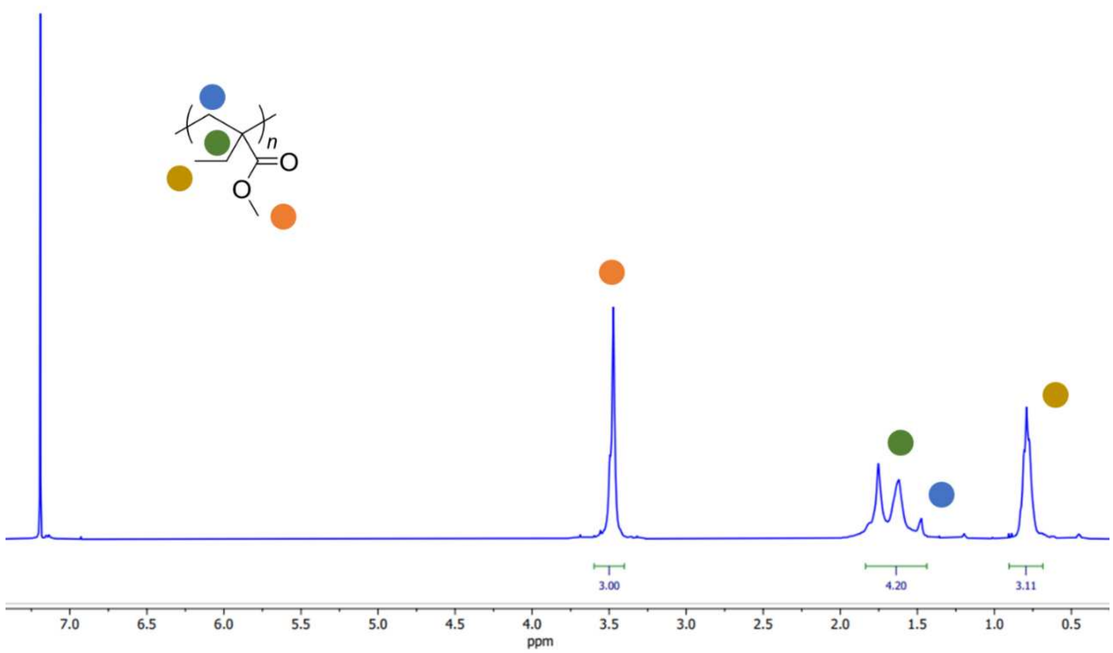


Figure 4.10. *[1]H NMR spectrum ($CDCl_3$) of PMEA.*

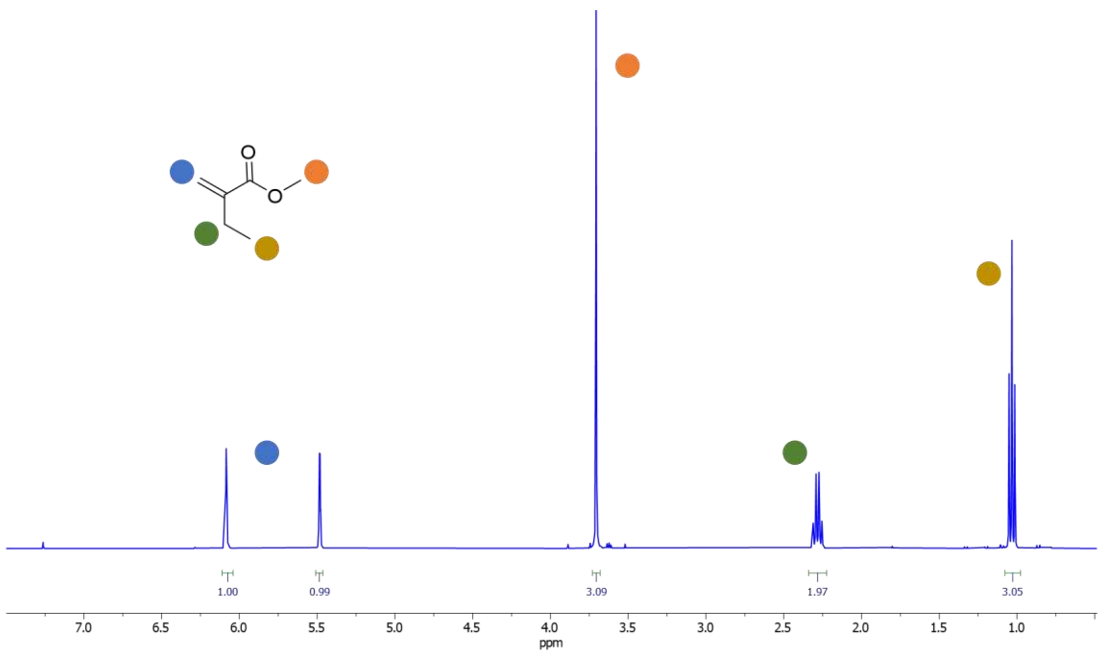


Figure 4.11. *[1]H NMR spectrum (CDCl3) of recycled MEA.*

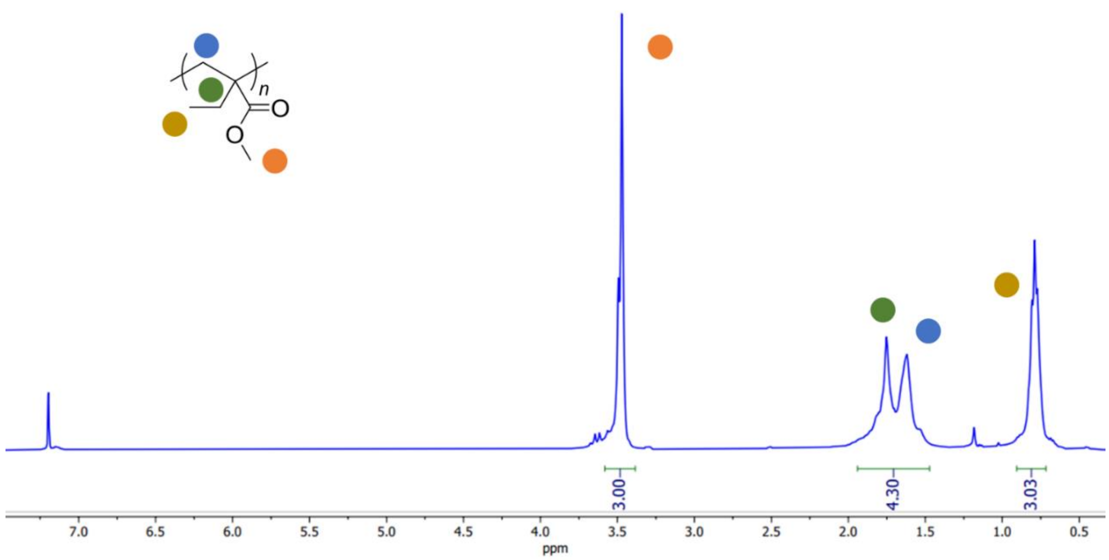


Figure 4.12. *[1]H NMR spectrum (CDCl3) of recovered PMEA oligomer.*

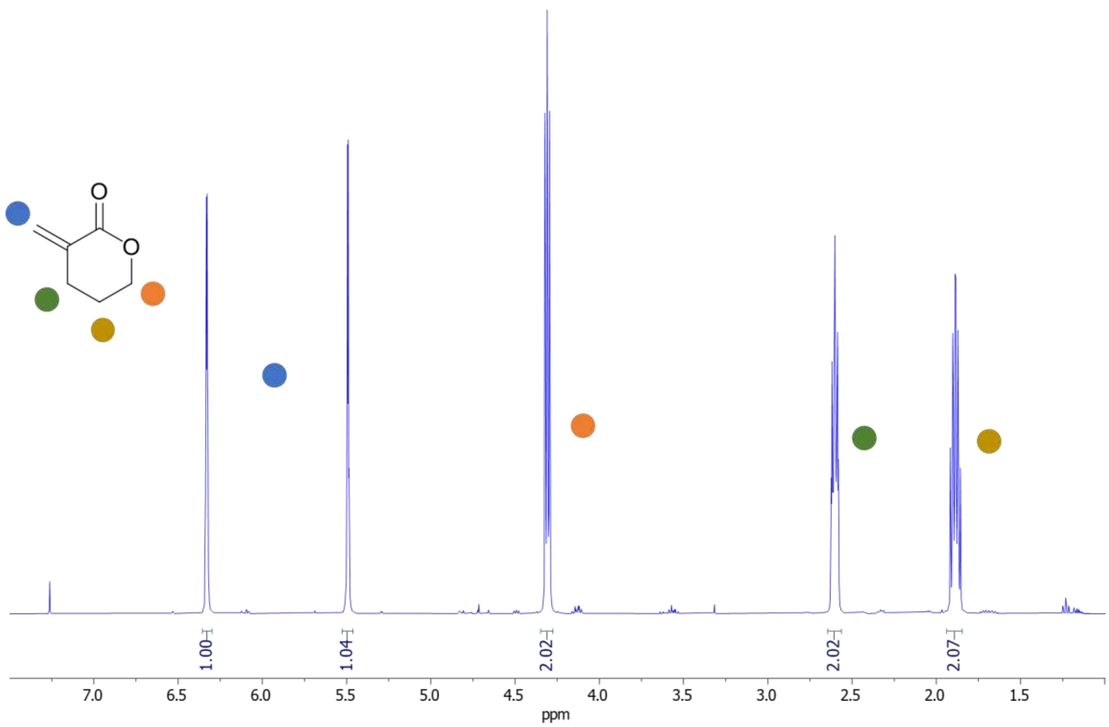


Figure 4.13. *[1]H NMR spectrum (CDCl₃) of MVL.*

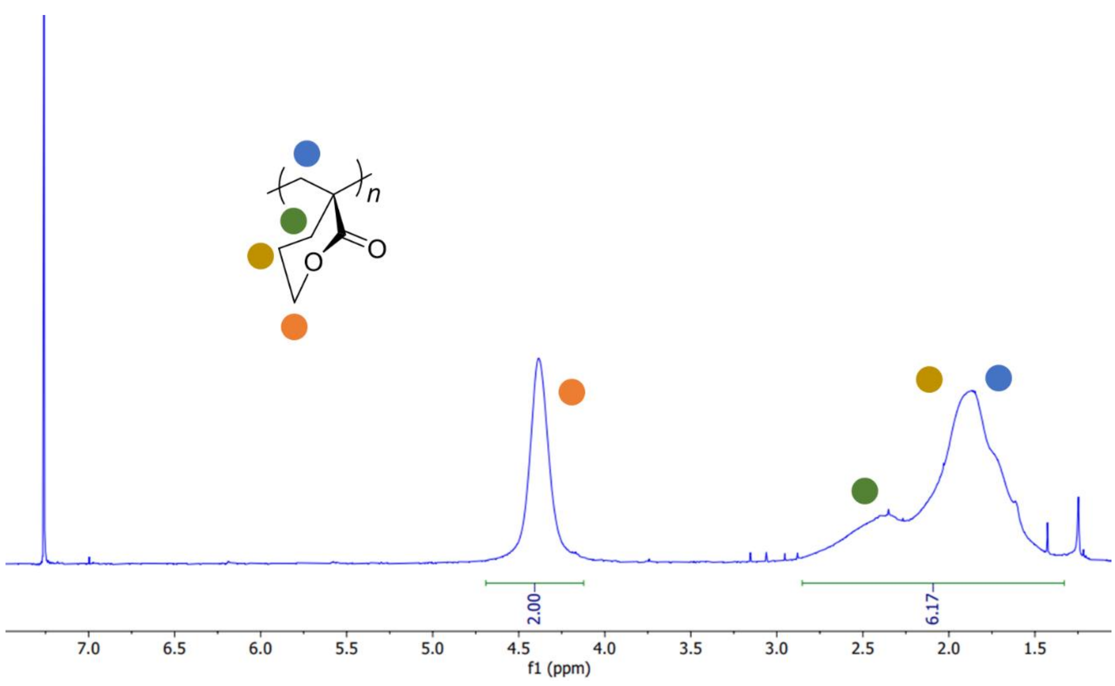


Figure 4.14. *[1]H NMR spectrum (CDCl₃) of PMVL.*

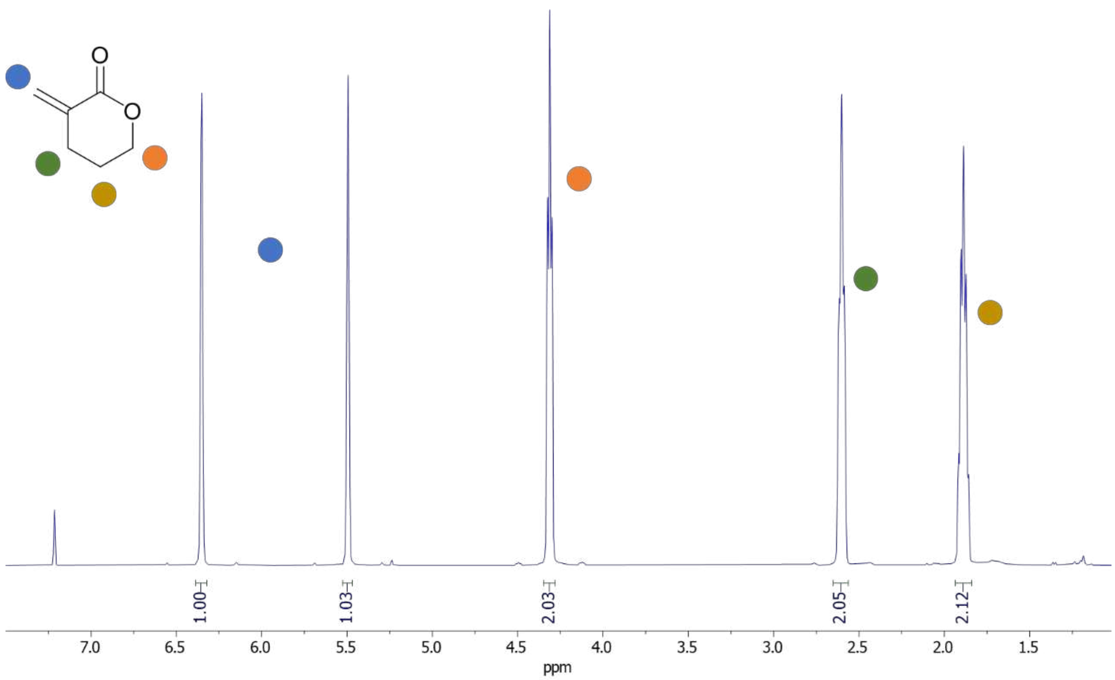


Figure 4.15. *[1]H NMR spectrum (CDCl$_3$) of rMVL.*

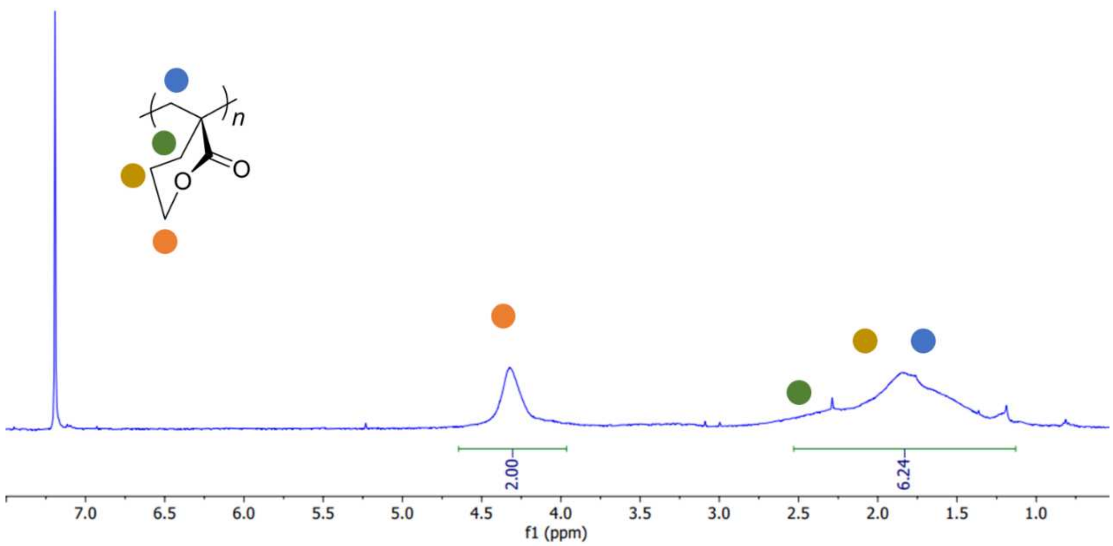


Figure 4.16. *[1]H NMR spectrum (CDCl$_3$) of rPMVL.*

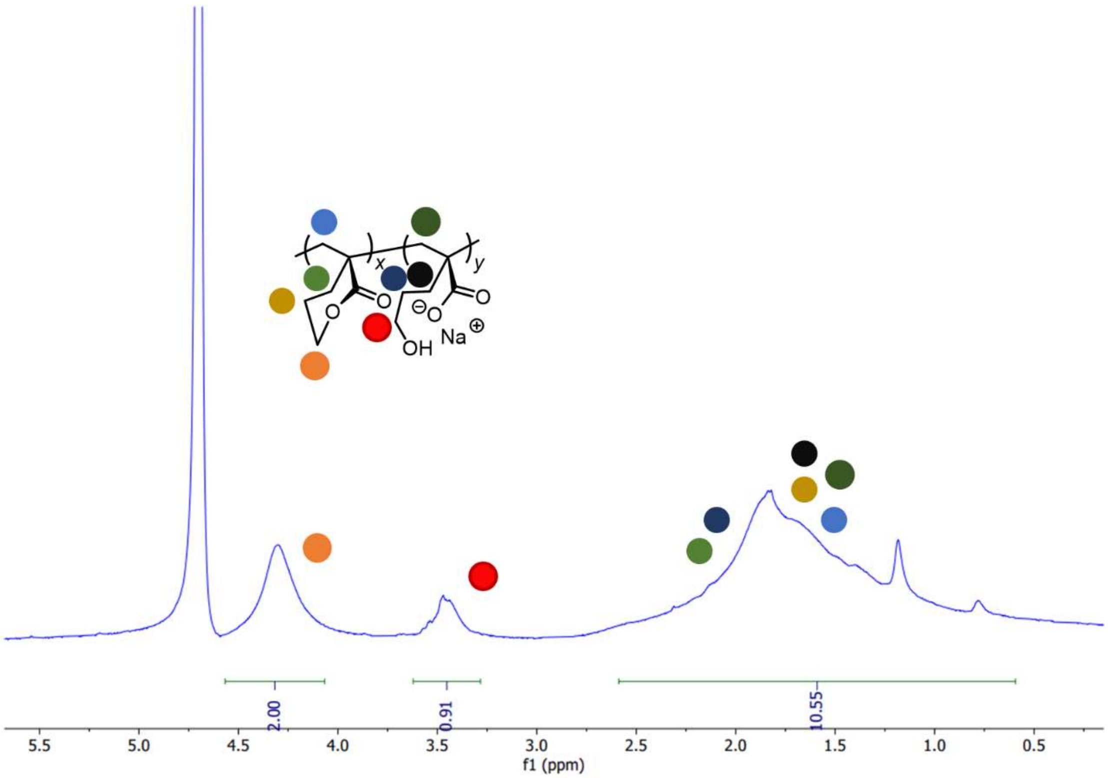


Figure 4.17. *[1]H NMR spectrum (D$_2$O) of PMVL ionomer.*

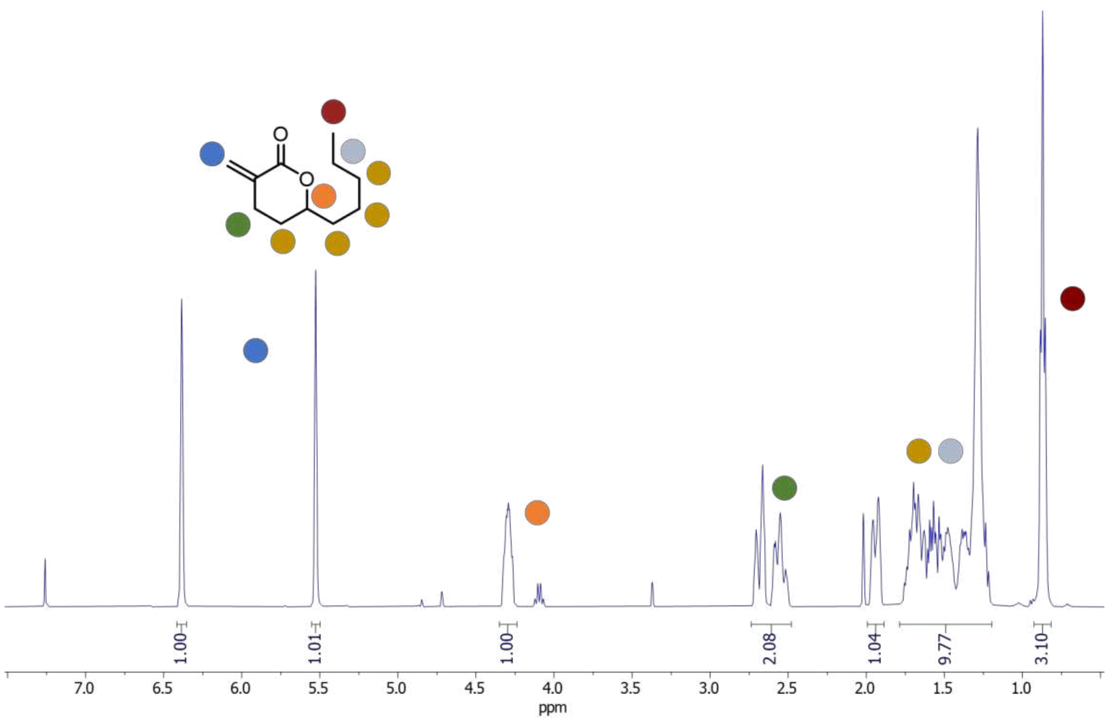


Figure 4.18. *[1]H NMR spectrum (CDCl$_3$) of MDL.*

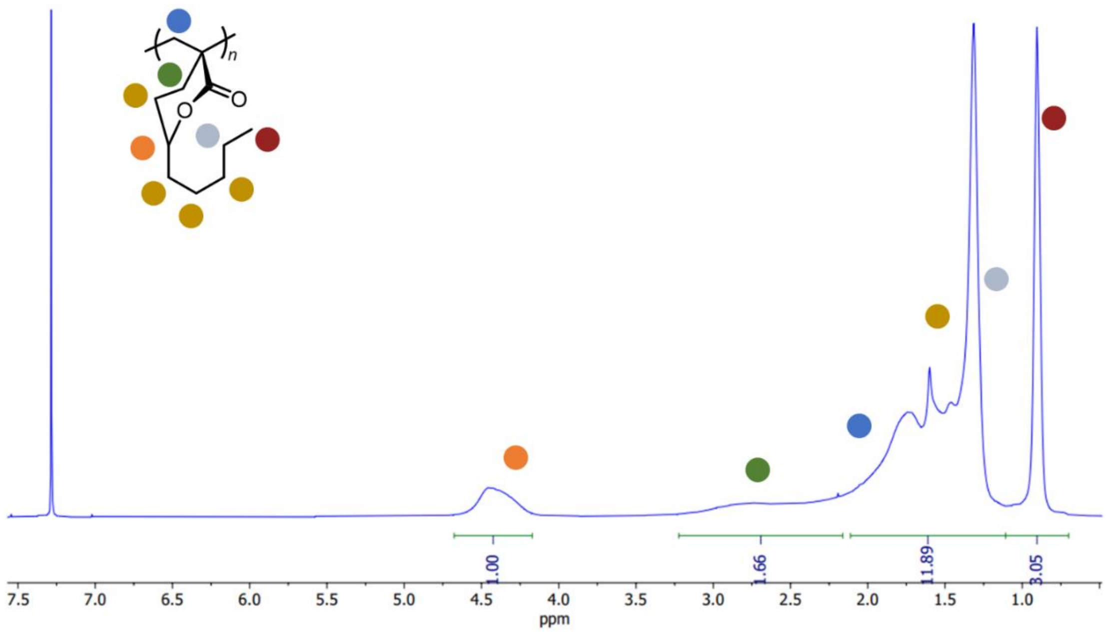


Figure 4.19. *[1]H NMR spectrum (CDCl$_3$) of PMDL.*

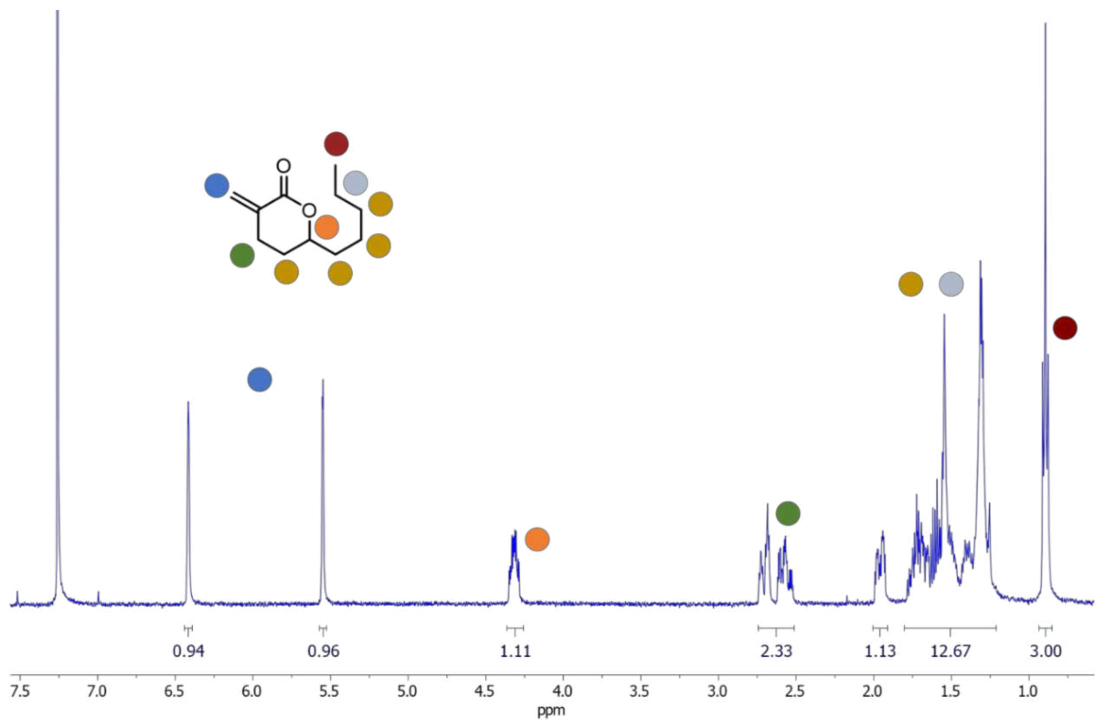


Figure 4.20. *[1]H NMR spectrum (CDCl$_3$) of recycled MDL.*

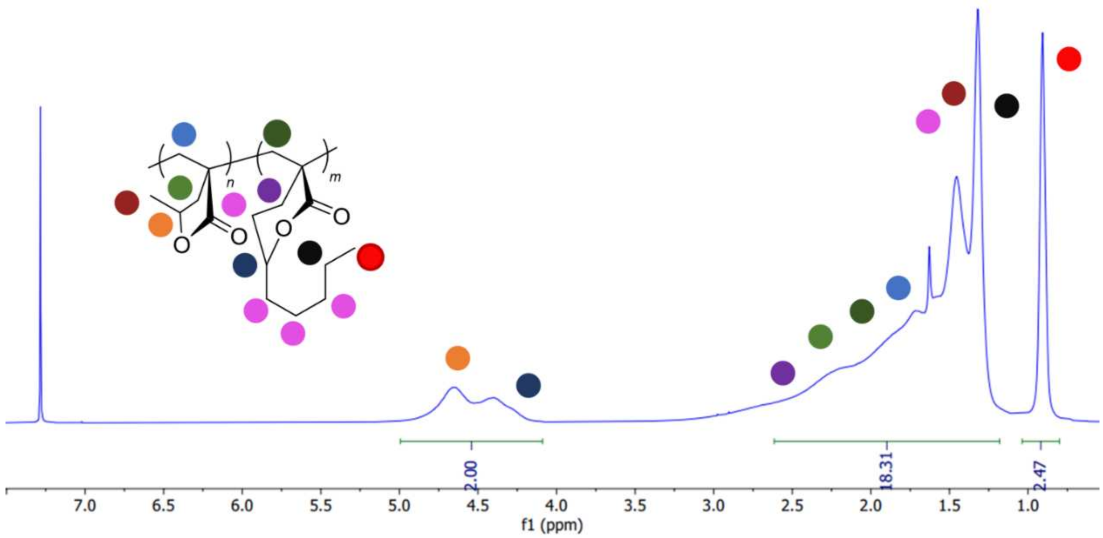


Figure 4.21. *[1]H NMR spectrum (CDCl3) of P(MMBL-co-MDL) (1:1).*

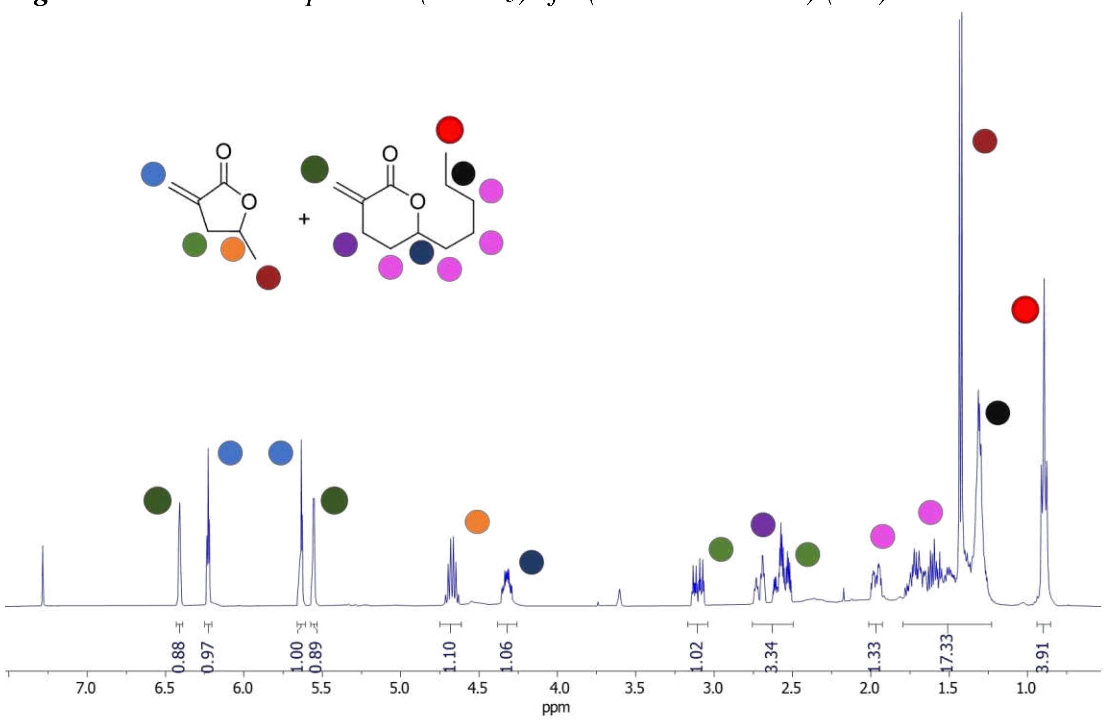


Figure 4.22. *[1]H NMR spectrum (CDCl3) of recycled MMBL and MDL from PMMBL-co-MDL (1:1).*

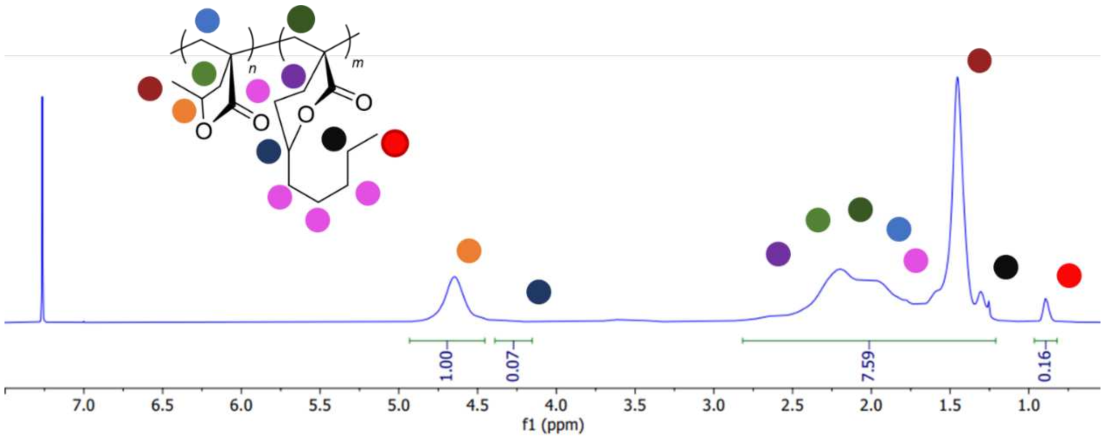


Figure 4.23. *[1]H NMR spectrum ($CDCl_3$) of P(MMBL-co-MDL) (20:1).*

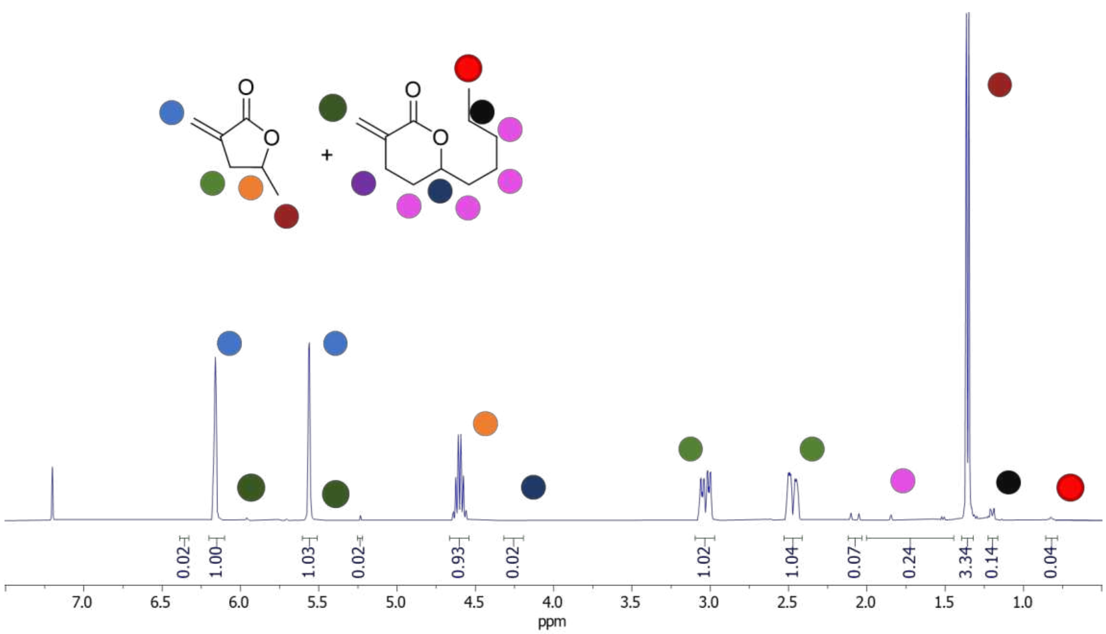


Figure 4.24. *[1]H NMR spectrum ($CDCl_3$) of recycled MMBL and MDL from PMMBL-co-MDL (20:1).*

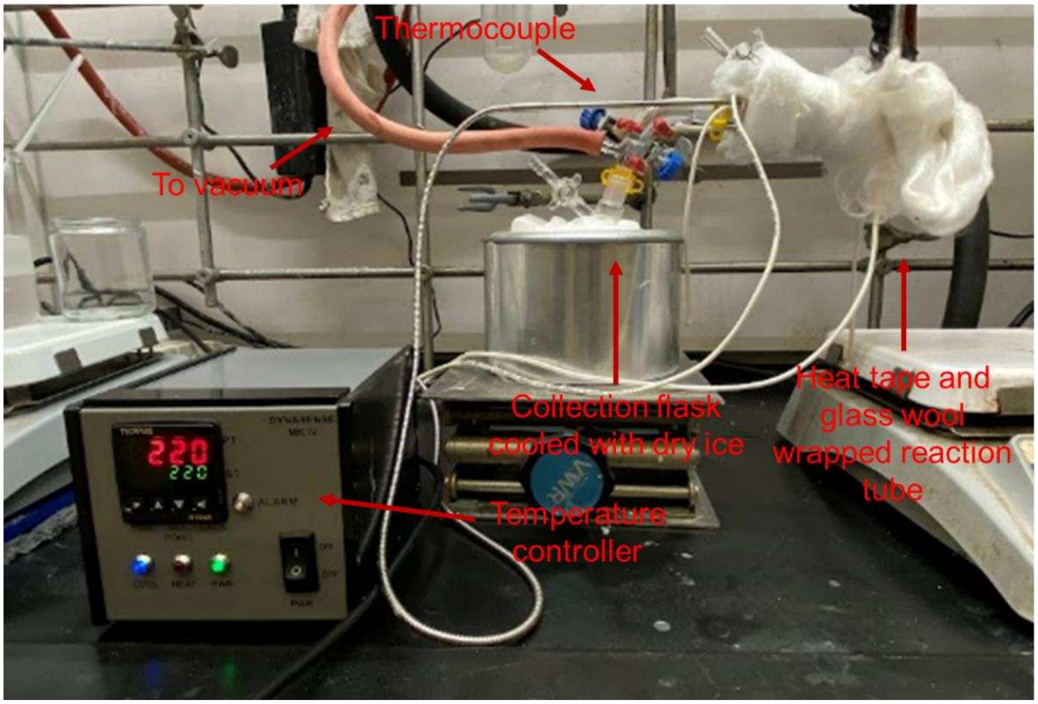


Figure 4.25. *Labelled photograph of the apparatus used for all depolymerization reactions.*

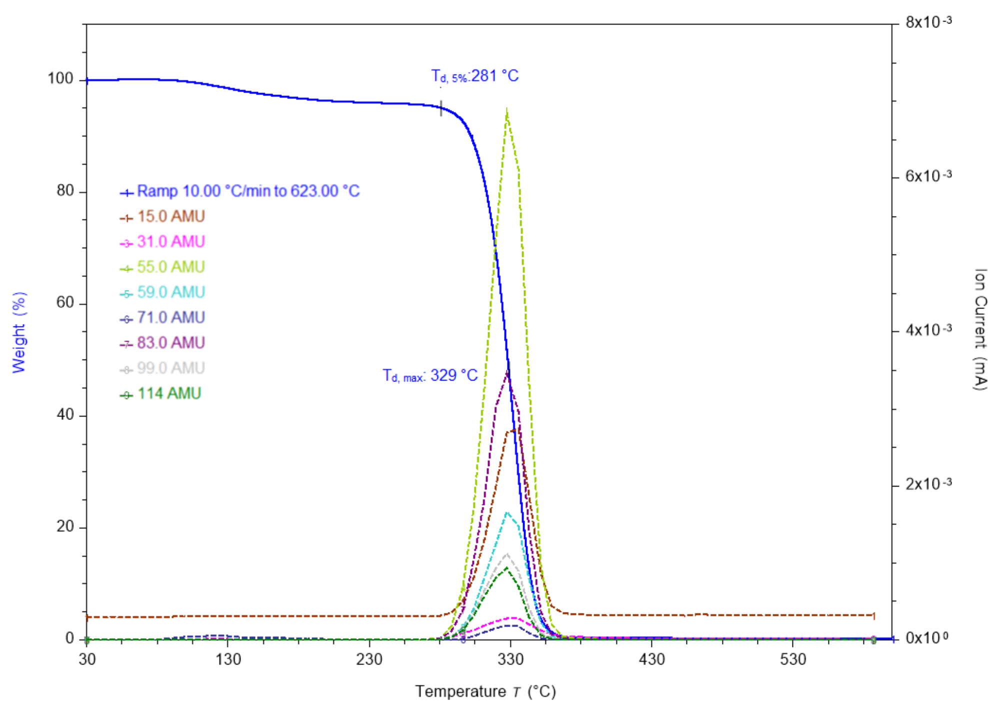


Figure 4.26. *TGA-MS overlay of PMEA (T_d = 281 °C, T_{max} = 329 °C).*

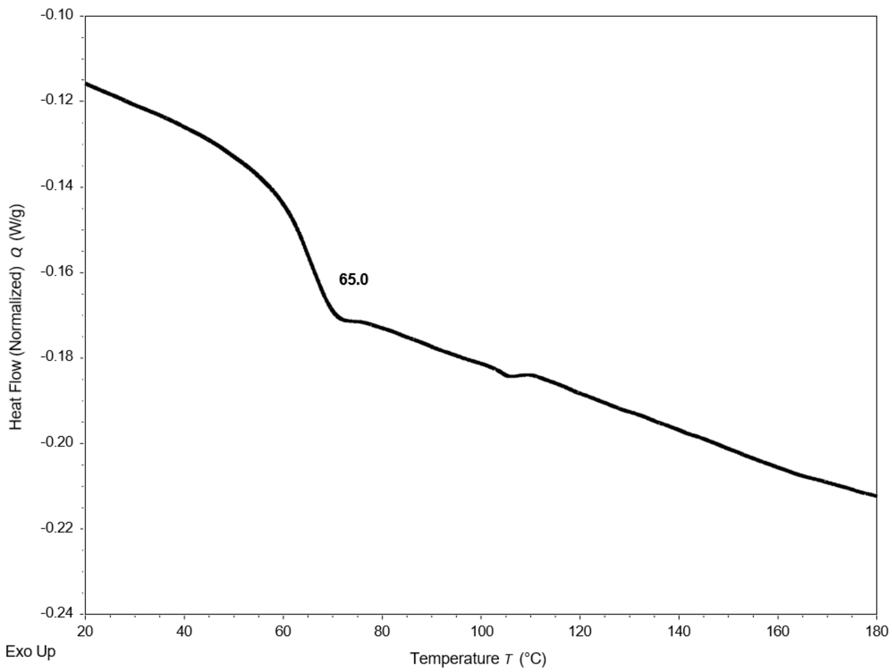


Figure 4.27. *DSC trace for PMEA (T_g = 65 ℃).*

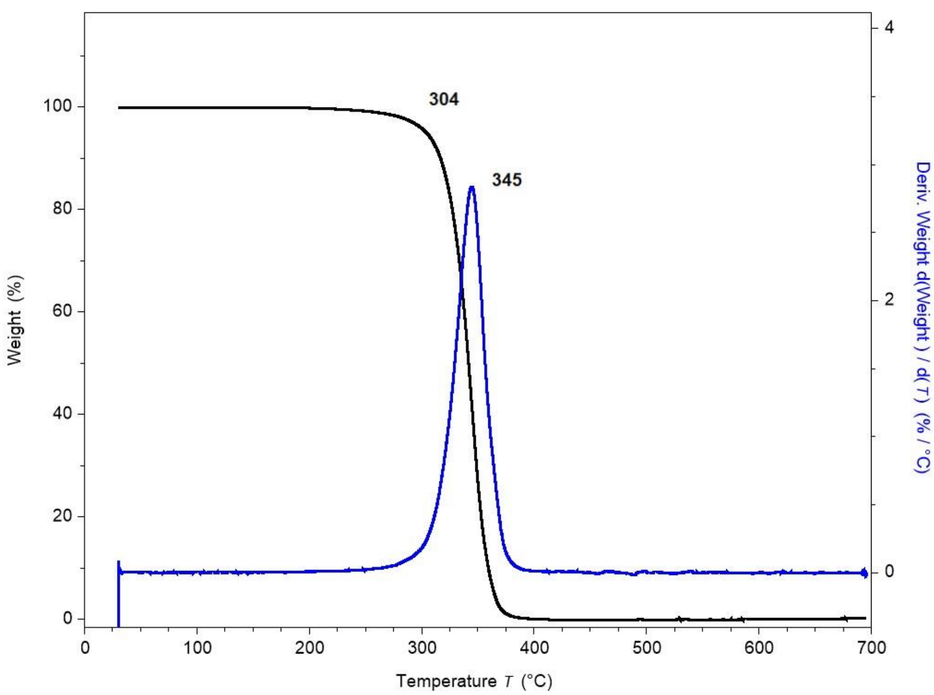


Figure 4.28. *TGA thermograph of PMVL (T_d = 304 ℃, T_{max} = 345 ℃).*

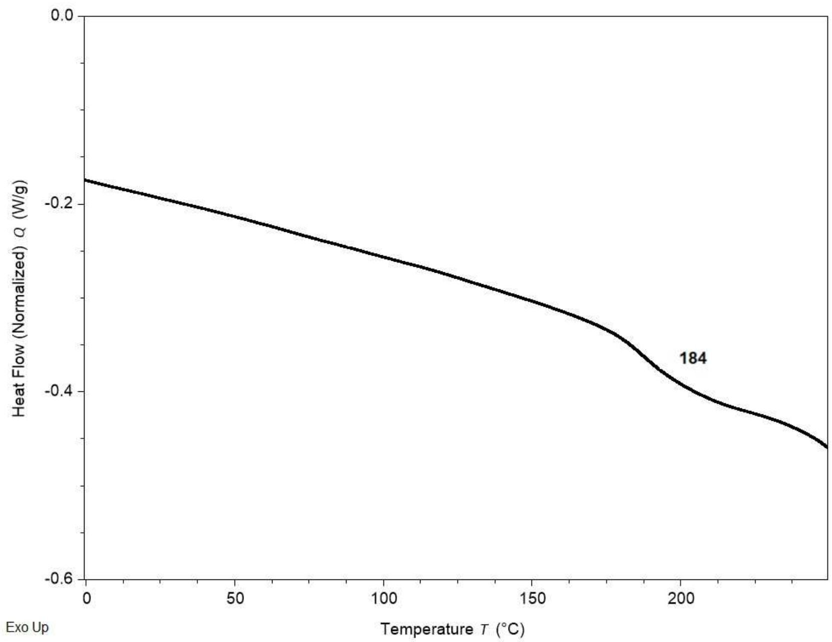


Figure 4.29. *DSC trace for PMVL (T_g = 184 °C).*

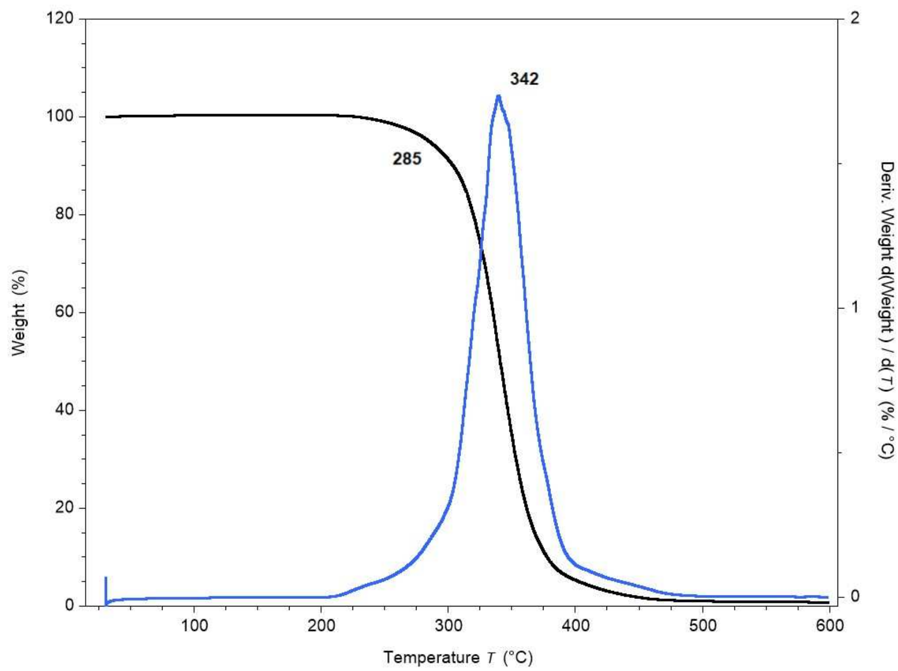


Figure 4.30. *TGA thermograph of rPMVL (T_d = 285 °C, T_{max} = 342 °C).*

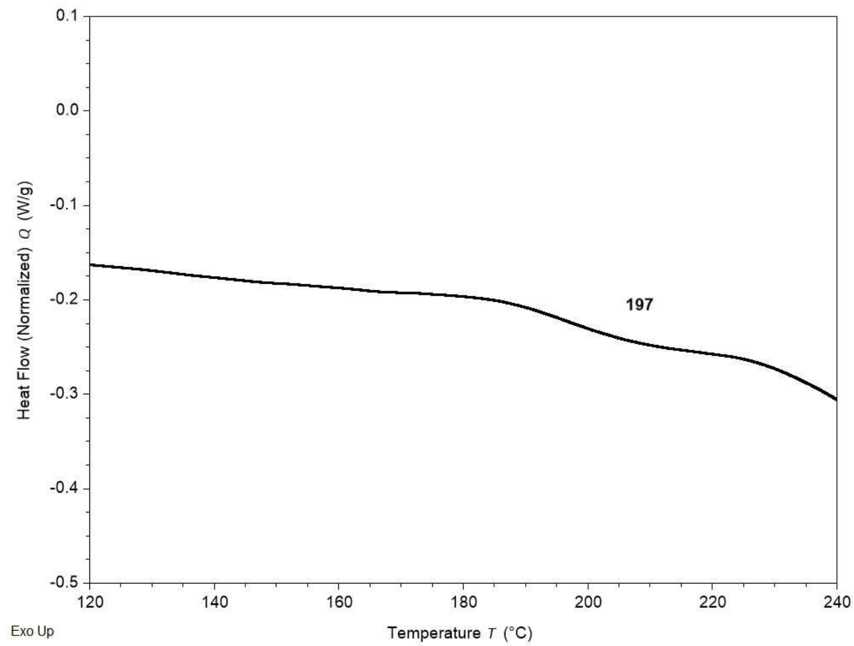


Figure 4.31. *DSC trace for rPMVL (T_g = 197 ℃).*

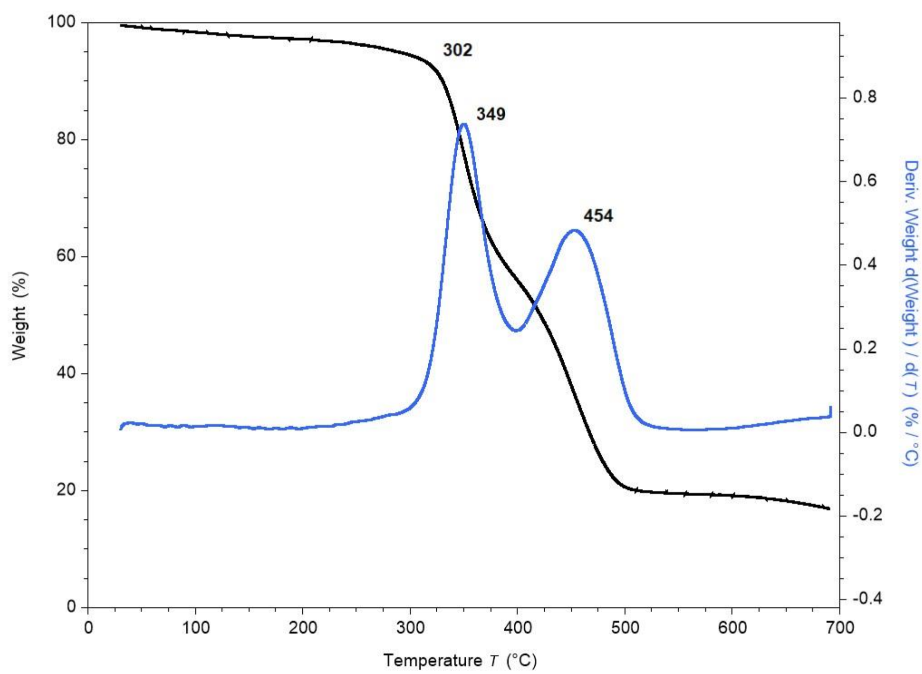


Figure 4.32. *TGA thermograph of PMVL ionomer (T_d = 302 ℃, T_{max1} = 349 ℃, T_{max2} = 454 ℃).*

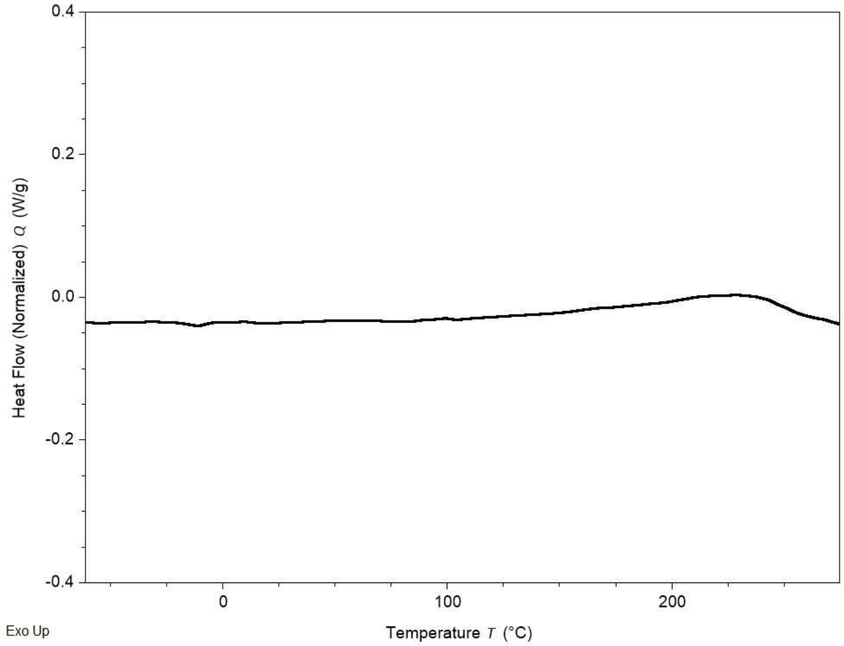


Figure 4.33. *DSC trace for PMVL ionomer.*

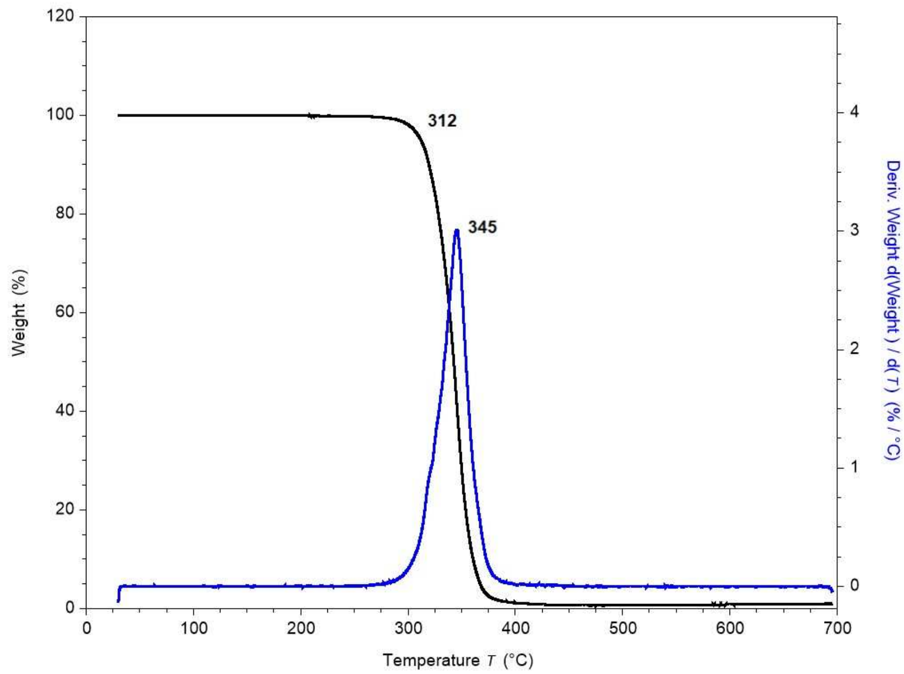


Figure 4.34. *TGA thermograph of PMDL (T_d = 312 ℃, T_{max} = 345 ℃).*

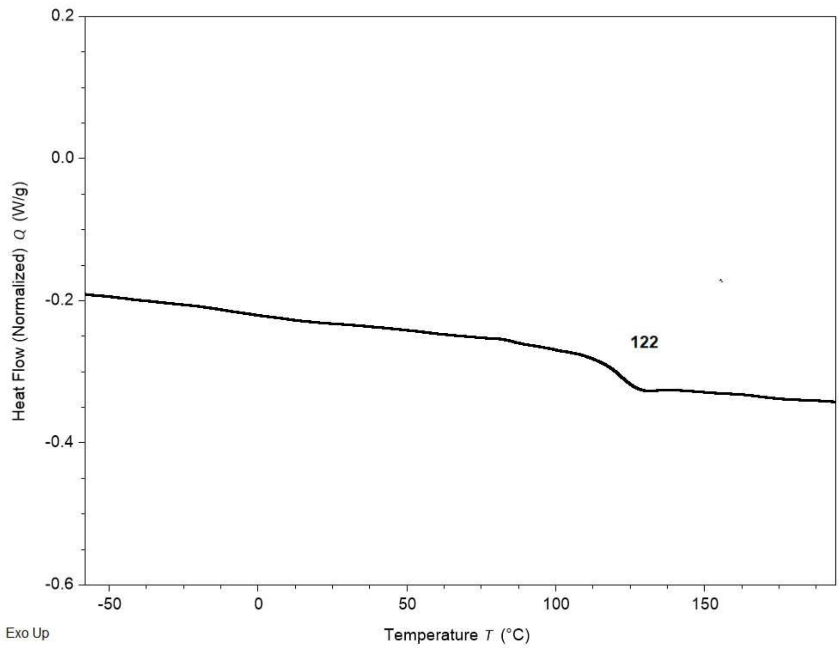


Figure 4.35. *DSC trace for PMDL (T_g = 122 ℃).*

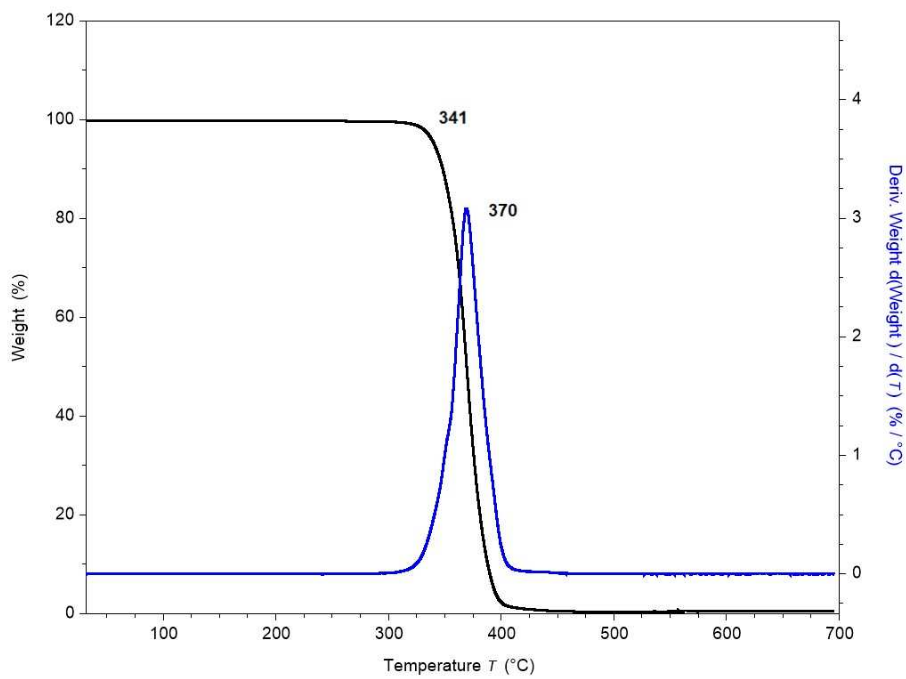


Figure 4.36. *TGA thermograph of PMMBL-co-MDL (1:1) (T_d = 341 ℃, T_{max} = 370 ℃).*

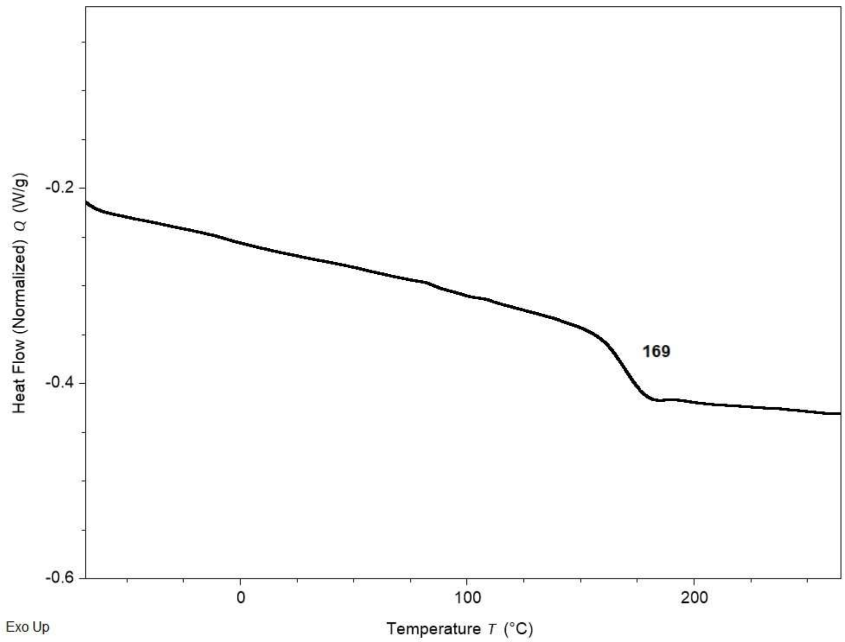


Figure 4.37. *DSC trace for PMMBL-co-MDL (1:1) (T_g = 169 ℃).*

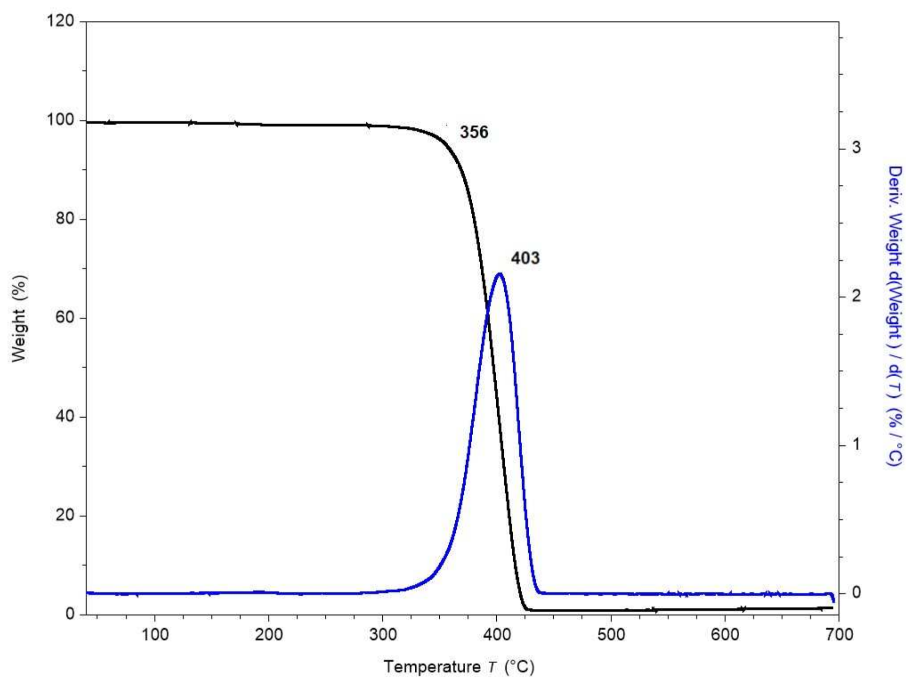


Figure 4.38. *TGA thermograph of PMMBL-co-MDL (20:1) (T_d = 356 ℃, T_{max} = 403 ℃).*

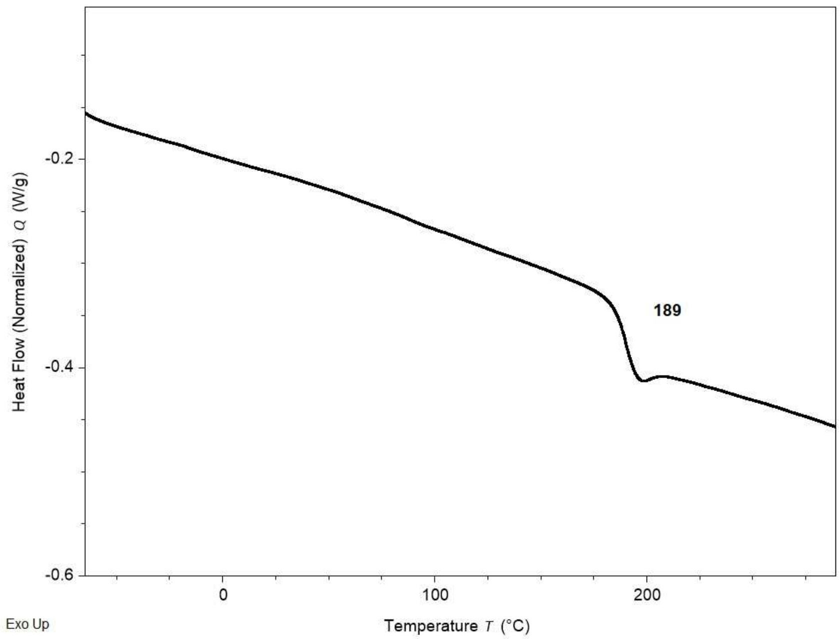


Figure 4.39. *DSC trace for PMMBL-co-MDL (20:1) (T_g = 189 °C).*

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CHAPTER 5.

DEPOLYMERIZATION OF PMMA COPOLYMERS UNDER MILD, CATALYST-FREE CONDITIONS

Overview

Poly(methyl methacrylate) (PMMA) homopolymer is an important plastic in our current materials economy. Current technologies for recycling the polymer are focused on either bulk depolymerization at high temperatures in specialized reactors (>400 °C, fluidized-bed reactors) or precision synthesis of the polymer with specific chain-end groups, allowing for low energy depolymerization. Here we report the bulk depolymerization of acrylic copolymers containing varying percentages of α-methylene-γ-decalactone with methyl methacrylate prepared by conjugate addition polymerization. The low percent incorporation copolymers show nearly identical thermal properties as poly(methyl methacrylate) homopolymer with only the depolymerizabilility being effected. Depolymerization reaction at 1.0 g scale gave pure monomer in yields as high as 85% within 1 hour at temperatures as low as 250 °C (75:25 MMA:MDL). This approach shows that depolymerization initiated via random-chain scission is competitive with chain-end scission approaches, leading toward alternative avenues to approach the issue of recycling methacrylate polymers.

Introduction

The current impetus in poly(methyl methacrylate) (PMMA) recycling utilizes chain-end functionalization to drive depolymerization via readily cleavable functional groups installed during polymerization (Figure 5.1A).[1–9] This approach, although extremely fruitful, has shown to be limited to reversible deactivation radical polymerization (RDRP) synthesis methods, leaving polymers produced with the more broadly implemented industrial polymerization methods (anionic and conventional free-radical polymerization) from taking advantage of these processes.[7] A few alternatives exist that utilize the alternative approach of monomer design to increase polymer depolymerizability. Recently, Christy and Philips explored the depolymerization of a PMMA analogue, poly(ethyl cyanoacrylate), which was found to recycle back to monomer in bulk polymer concentration at a yield greater than 90% (Figure 5.1B).[10] Additionally, since 2020 the Chen group has been investigating acrylic lactone polymers, such as poly(α-methylene-γ-methyl-γ-butyrolactone) (PMMBL) and poly(α-methylene-δ-valerolactone) (PMVL), showing that the lactone pendant groups on the polymer backbone allow for "reversible fragmentation" to prevent unproductive depolymerization[11] and lower ceiling temperatures (T_C) can decrease depolymerization temperatures (T_{dp}) dramatically while still achieving nearly quantitative monomer recovery.[12] Designing new polymers, however, does not directly address the current issues with PMMA recycling (Figure 5.1C).[13]

In a recent publication, the Chen group reported that the depolymerization of high T_C polymer can be modulated to decrease T_{dp} and allow for higher monomer recoveries to be achieved.[12] This modulation method takes advantage of a low T_C co-monomer which, in the copolymer, act as more readily cleavable units when exposed to depolymerization conditions. These low T_C monomers were incorporated into copolymers with the high T_C monomers at low percentages with no adverse effects to polymer properties, allowing for a robust material that could be recycled back to monomer quite easily.

These approaches have been the focus of current research because they take advantage of the depolymerization mechanism of PMMA and other methacrylate polymers. These polymers depolymerize through a controllable radical chain unzipping mechanism; essentially proceeding in the reverse direction of a radical propagation mechanism. There are, however, two different initiation steps that can occur: chain-end scission and random chain scission.

Herein we report the utilization of this method again to achieve low temperature recycling of PMMA copolymers with as low as 25% low T_C co-monomer incorporation. These incorporations do not impact the thermomechanical properties of PMMA and only act to allow for facile depolymerization back to monomer at much lower temperatures than conventional PMMA recycling.[14–17]

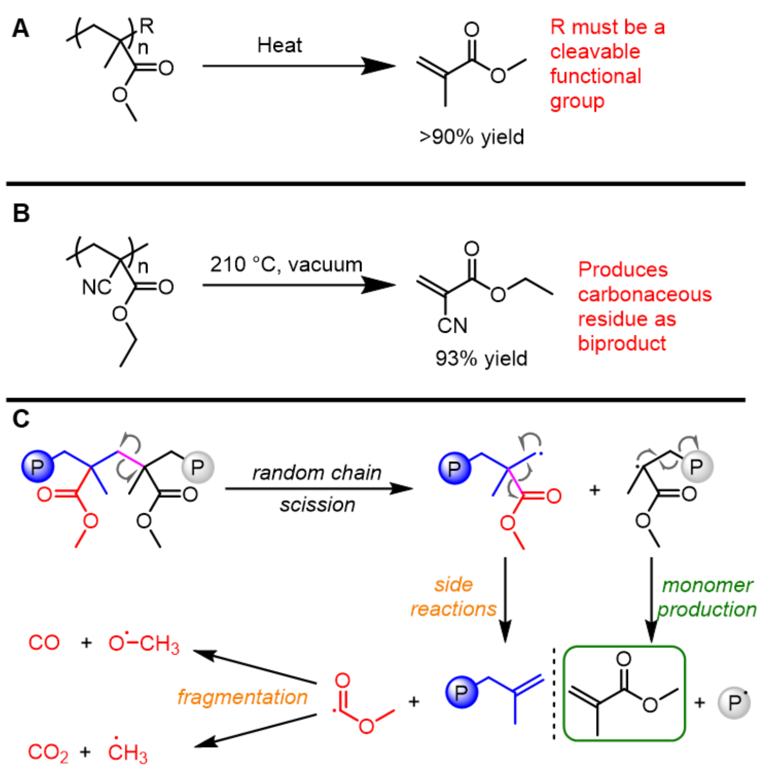


Figure 5.1. *Examination of the differences between (A) current reversed radical depolymerization, (B) poly(cyano ethacrylate), and (C) the challenges with unfunctionalized PMMA depolymerization*

Results and Discussion

Comparing PMMA with P(MMA-co-MDL)

MMA is typically polymerizable with a variety of systems, including radical, anionic, cationic, and coordination chemistries. These systems, however, remain relatively unexplored for the polymerization of MDL, therefore, copolymerizations were carried out with a system utilized for the synthesis of other bio-based lactone acrylate polymers, that of conjugate addition.[12] This method comes with the unfortunate drawback of lack of control, therefore, the resulting copolymers are produced with a random incorporation of each monomer, with MMA generally being higher incorporation due to the more favorable polymerization kinetics.[18,19] For example, a 1000:1000:1 ([MMA]:[MDL]:[I]) loading polymerization produced a poly(methyl methacrylate-*co*-α-methylene-δ-decalactone) [P(MMA-*co*-MDL)] copolymer with a ratio of 75:25 MMA:MDL incorporation a M_n of 43.9 kDa and a Đ of 1.63 (Figure 5.2). This copolymer possessed a T_g only 4 °C higher than that of PMMA homopolymer (typically ~120 °C) and a T_d only 5 °C higher (typically around 330 °C) (Figure 5.3).[20]

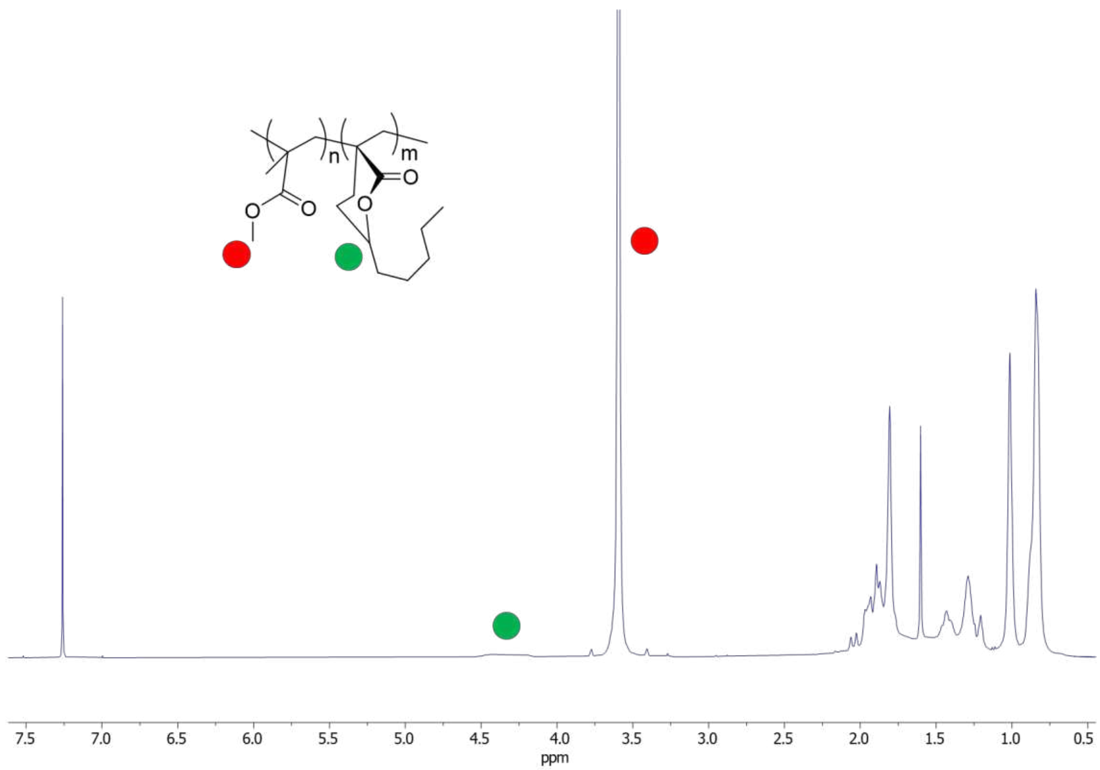


Figure 5.2. *^{1}H NMR ($CDCl_3$) spectrum of P(MMA-co-MDL) with the identifying alkoxy protons labeled for each repeat unit.*

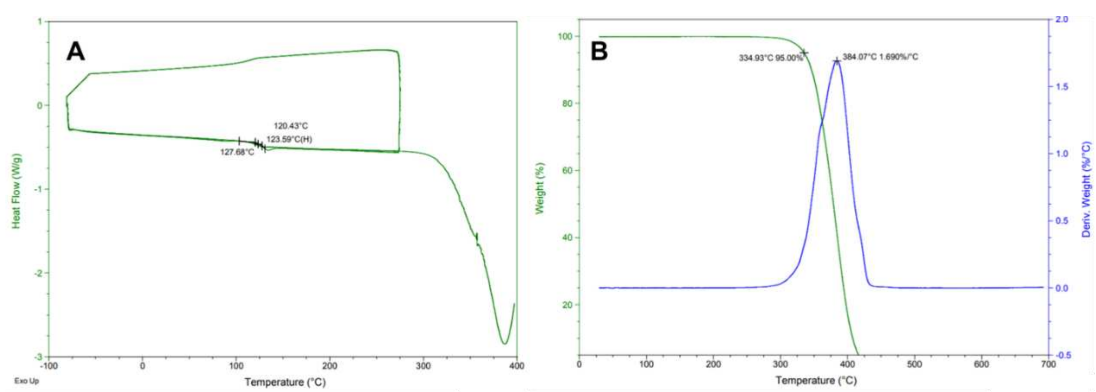


Figure 5.3. *(A) DSC and (B) TGA traces of P(MMA-co-MDL).*

Depolymerization of PMMA-co-PMDL

Typically, unfunctionalized PMMA homopolymers require high temperatures and expensive reactors to undergo facile depolymerization back to monomer in appreciable yields, with the isolated monomer requiring further purification in order to obtain MMA suitable for repolymerization. These unfavorable conditions are due to the high T_C of PMMA, thus leading to side reactions during depolymerization as the monomer is free to release other small molecule radicals. PMDL homopolymer, however, has been observed to depolymerize at just 220 °C to high yields with quantitatively pure MDL being isolated. It was hypothesized that by incorporating MDL into the PMMA main chain that 'weak points' would be introduced, allowing the PMMA to depolymerize at lower temperatures, thus allowing for the release of MMA. At these lower temperatures the thermally-induced side reactions that MMA undergoes can be suppressed, much like how the low temperatures utilized for the depolymerization of poly(methyl ethacrylate) (PMEA) prevent the fragmentation of the monomer.[12] Considering this, depolymerizations were carried out at 250 °C in 1 hour. This resulted in the isolation of a mixture of MMA and MDL monomers (Figure 5.4) at a combined yield of 85% with the remaining residue being isolated as soluble oligomer.

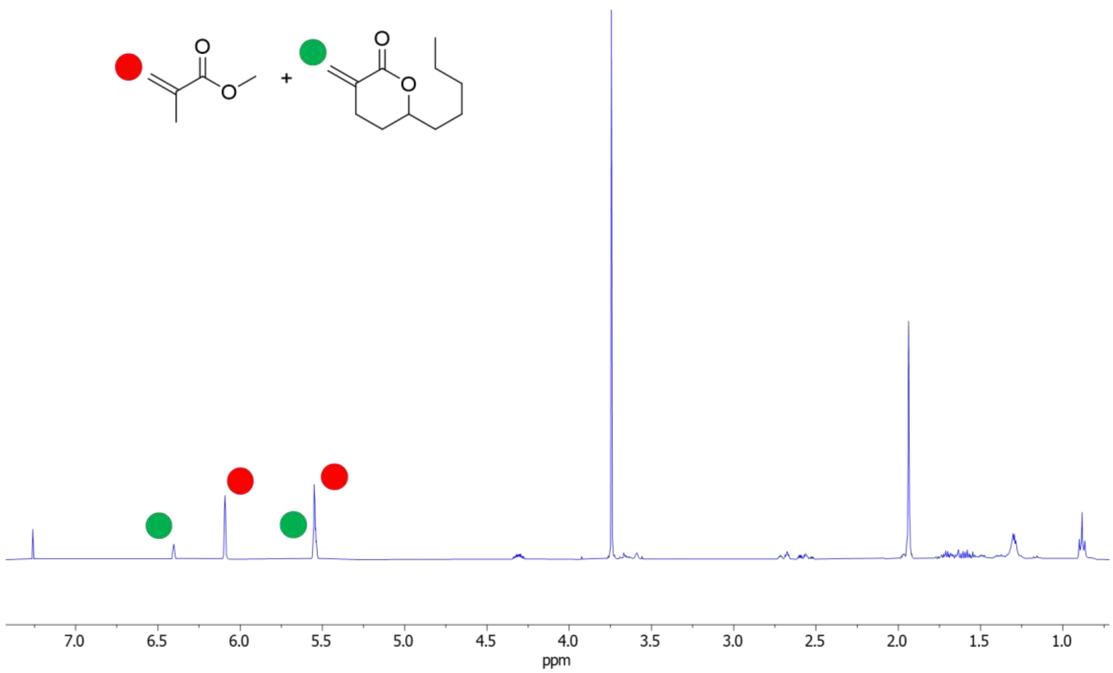


Figure 5.4. *[1]H NMR ($CDCl_3$) spectrum of recycled MMA and MDL with the methylene protons labeled for each monomer.*

Conclusion

In conclusion, the synthesis of copolymers containing MMA and MDL was carried out resulting in copolymers with 75:25 MMA:MDL incorporation. These copolymers were analyzed for their thermal properties and were found to be comparable to that of PMMA homopolymer, hinting at the ability for MDL to be easily incorporated into industrial systems as a 'drop-in' component. The copolymers were depolymerized to yield 85% monomer at just 250 °C in 1 hour with the remaining material being isolated as oligomer, enabling the reintroduction to repeat depolymerization cycles. With these advances, depolymerization can be tuned much like thermal properties, with the addition of MDL during the polymerization process, followed by other additives after polymerization. These discoveries with hopefully be utilized in the fabrication of commodity acrylic products that can be recovered and depolymerized under mild-catalyst free conditions.

Experimental

Materials and Methods

The synthesis of air- and moisture-sensitive materials were carried out in flame-dried Schlenk glassware on a dual-manifold Schlenk line or in an inert gas (Ar or N_2) glovebox. Organic solvents were dried with CaH_2 between 24 and 48 h before being distilled and stored under nitrogen atmosphere. NMR solvent ($CDCl_3$) was used as received.

Formalin, sodium hydride (60% in mineral oil), and diethyl oxalate were purchased from Sigma-Aldrich Chemical Co. *δ*-decalactone were purchased from Beantown Chemical Co., and 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) was purchased from TCI America. All of the above commercial reagents were used as received. α-methylene-δ-decalactone (MDL) was dried by stirring the liquid monomer with CaH_2 for 24 h before distilling by vacuum and storing in brown bottles under nitrogen atmosphere.

Analytical Methods

NMR Spectroscopy. All NMR spectral characterizations were carried out by ^1H NMR experiments using a Bruker Advance NEO 400 MHz spectrometer or a Bruker AVIII 400 MHz spectrometer. Chemical shifts were referenced to internal solvent resonance corresponding to 7.26 ppm ($CDCl_3$) and reported in ppm relative to $SiMe_4$.

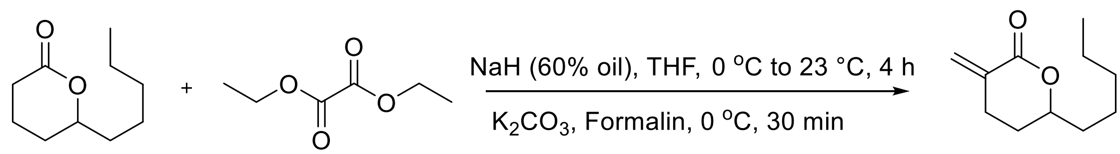
Gel Permeation Chromatography (GPC). Measurements of polymer absolute weight-average molecular weight (M_w) and number-average molecular weight (M_n) were performed by GPC. Polymer concentrations ranged from 2 to 4 mg/mL. The GPC system was composed of an Agilent HPLC system equipped with one guard column and three PL gel 5 μm mixed-C gel permeation columns coupled with a Wyatt DAWN HELEOS II multi-angle (18) light scattering detector and a Wyatt Optilab TrEX dRI detector. The analyses were performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL/min. Data was analyzed using Wyatt ASTRA 7.1.2 software.

Thermal Characterizations

Thermogravimetric Analysis (TGA). TGA was performed on a Q50 TGA Analyzer (TA Instruments) to obtain decomposition temperatures (T_d, defined by the temperature of 5 % weight loss) and maximum rate decomposition temperatures (T_{max}) of the polymers. Between 5 and 10 mg of polymer sample was heated from 30 °C to 700 °C at 10 °C/min while the mass of the sample was continuously measured. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots by selecting the peak values, while T_d values were obtained from wt % vs. temperature (°C) plots by selecting the point of the weight percent versus temperature (°C) plots indicating 95 weight percent of sample remaining.

Differential Scanning Calorimetry (DSC). DSC was performed on an Auto Q20 (TA Instruments) to obtain the glass transition temperature (T_g) and melting temperature (T_m). Between 3 and 10 mg of polymer sample was weighed into an aluminum pan and sealed with an aluminum lid. Samples were then heated at 10-20 °C/min from room temperature to 250 °C and cooled to -40 °C to remove thermal history before being reheated to 250 °C. During this time, the thermal response was measured relative to a reference pan.

Experimental Details



Synthesis of MDL.[12] A suspension of sodium hydride (60 wt % dispersion in mineral oil, 24.0 g, 1.7 eq, 999 mmol) in THF (600 mL) was cooled to 0 °C, and a solution of *δ*-decalactone (100 g, 587 mmol) and diethyl oxalate (85.5 g, 1.0 eq, 587 mmol) in THF (50 mL) was added dropwise while stirring. After the addition was complete, ethanol (0.5 eq., 13.5 g) was added dropwise, and the reaction mixture was warmed to room temperature and stirred for 4 h. Then the mixture was cooled to 0 °C before the addition of K_2CO_3 (244 g, 1.76 mol, 3 eq) in water (341 mL) and formaldehyde (37 wt % aqueous solution, 654 g, 37.1 eq), and the reaction mixture was stirred for 30 min. The mixture was washed with saturated NaCl aqueous solution (200 mL) and saturated $NaHCO_3$ aqueous solution (200 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 300 mL). The combined organic layers were washed with saturated NaCl aqueous solution, dried over Na_2SO_4, filtered, and evaporated to yield a yellow oil. Purification by column chromatography (hexane/ethyl acetate 80:20) provided M*δ*DL as a colorless oil (89 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ* 6.41 (d, 1H), 5.55 (d, 1H), 4.30-4.33 (m, 1H), 2.57-2.73 (m, 1H), 1.93-1.95 (m, 1H), 1.72-1.31 (m, 10H), 0.89 (t, 3H).

General Depolymerization Procedure. Polymer (between 50 mg and 1.0 g) was loaded into a flame dried Schlenk-type storage tube with a 14/20 ground glass joint. To this a vacuum distillation head and a Schlenk flask were attached. The apparatus was brought under vacuum slowly (50 mTorr) and the receiving Schlenk flask was cooled with dry ice. The Schlenk-type storage tube was affixed with a thermocouple and wrapped with heat tape which was insulated with glass wool. The storage tube was heated for 1 h to 250 °C. After the depolymerization was complete the apparatus was placed under nitrogen gas and the collection flask was allowed to cool to room temperature. The collected liquid was weighed, recovery yield calculated, and analyzed by ^{1}H NMR spectroscopy.

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CHAPTER 6.

SUMMARY

When the work described in this dissertation first began in 2017, there was a poor understanding about the depolymerization of acrylic polymers. Since then, the field has expanded dramatically, including polymers designed for degradation and new methods for depolymerization. In this dissertation, significant efforts to expand the understanding of acrylic monomer design were described (Figure 7.1). All this work focused on understanding the properties of pendant lactone containing acrylates. From this focused work, we know have empirical finding supporting the mechanistic advantages lactone containing acrylates possess over traditional linear acrylates.

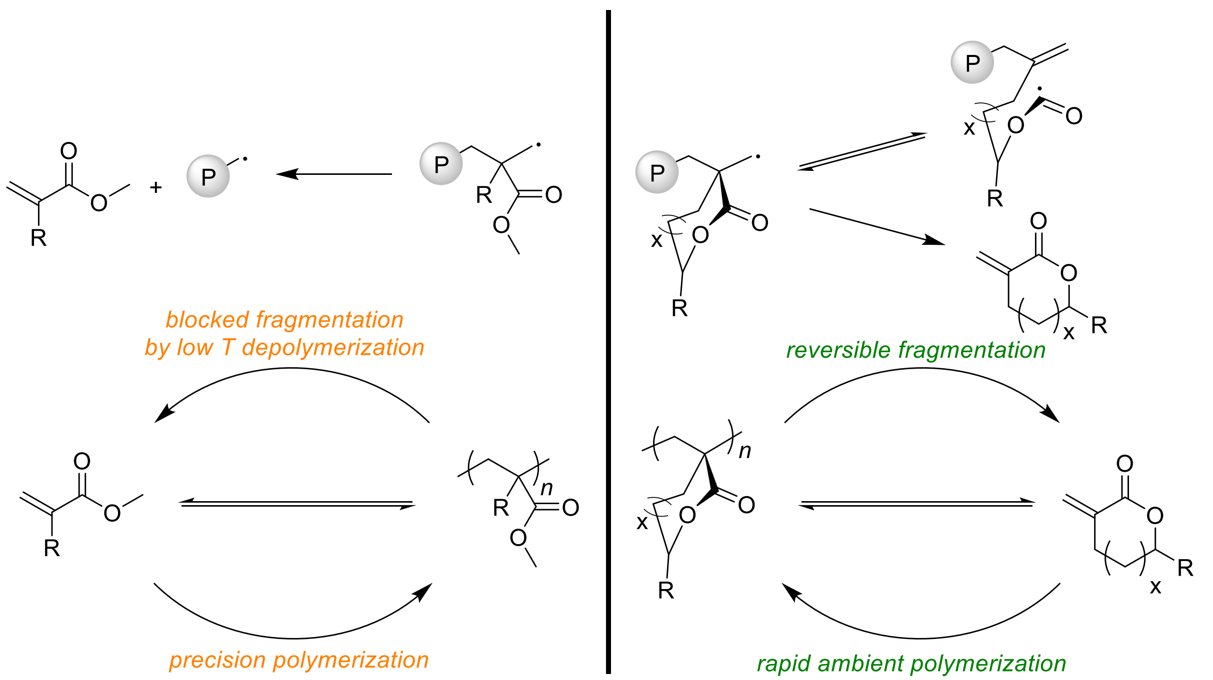

Figure 6.1. *Summary of work completed in this dissertation on the development of recyclable-by-design acrylic materials.*

These insights have led to the development of a handful of novel monomers that are not only recyclable, but bio-based, alternatives to traditional acrylics. These advances may allow for further development in bio-based alternatives to monomers typically sourced from petroleum feedstocks. Finally, the recyclability of PMMA itself was improved by utilizing these bio-based lactone acrylates in low percent incorporation copolymers with thermomechanical properties that are comparable to those of PMMA homopolymer. With these types of materials, the short-term issue with polymer recyclability may be addressed without widespread overhauls of current industrial infrastructure, providing a massive financial incentive to industry to adopt similar strategies.