DISSERTATION

FUNCTIONAL NANOSTRUCTURED IONIC LIQUID-BASED BLOCK COPOLYMER SYSTEMS FOR ENERGY APPLICATIONS

Submitted by

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ABSTRACT

FUNCTIONAL NANOSTRUCTURED IONIC LIQUID-BASED BLOCK COPOLYMER SYSTEMS FOR ENERGY APPLICATIONS

Room-temperature ionic liquids (RTILs) are pure molten salts that have zero vapor pressure, a wide range of thermal stability, negligible flammability, and high ionic conductivity. These qualities make them desirable as electrolyte replacements for the more common lithium salt-doped carbonate solvents which are ubiquitous in current battery technology despite being exceptionally flammable. Use of liquid electrolytes, even non-flammable ones, has its drawbacks and challenges, like preventing leakage of the electrolyte and maintaining good contact with electrode surfaces, particularly when the battery electrodes or container become physically warped. With the emergence of flexible electronics technologies like foldable phones, bendable displays, and "wearables," interest has grown in developing solid electrolytes that are mechanically robust and sufficiently good ionic conductors, as they greatly expand the design possibilities for batteries. Block copolymers (BCPs) are an ideal platform from which to develop solid electrolyte materials as the variety of polymerizable blocks and physical properties that can be derived from them are nearly limitless. In this dissertation, we explore two methods for incorporating ionic liquid components into solid BCP materials, and thoroughly delve into their interesting chemical, physical, and mechanical properties to demonstrate their potential as functional materials.

The first method is the direct, sequential polymerization of both ionic liquid-based and traditional monomers to create poly(ionic liquid) (PIL) BCPs that can microphase separate to form ordered nanostructures. We report on the synthesis of both cobalt-containing and imidazolium-based PIL BCPs and provide a comprehensive examination of their melt-state phase behavior, including the observation of all four equilibrium morphologies available to diblock copolymers:

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lamellae (Lam), bicontinuous gyroid (Gyr), hexagonally packed cylinders (Hex), and spheres (S). From the morphological phase behavior, we were able to build two phase diagrams and extract critical information about the materials, such as block density of the methyl-imidazolium PIL block. This is an essential parameter for BCP design that enables researchers to target specific morphologies when creating similar materials in the future. The morphology of solid-state conductive materials like PIL BCPs has direct implications on their transport properties, as only certain morphologies (Gyr, S) can have fully continuous domains in which ions can flow, so fully understanding the spectrum of phase behavior in a BCP material is incredibly important for creating truly functional materials from them.

The second method is the integration of RTIL into amphiphilic, non-ionic BCPs as a selective swelling solvent to create ion gels, or gel polymer electrolytes (GPEs). We have designed these BCPs, based on melt-state phase separating blends of polystyrene-bpoly(ethylene oxide) (SO) and polystyrene-b-poly(ethylene oxide)-polystyrene (SOS) in which the hydrophilic O block is the majority component, to form hydrophobic spherical domains of S that form a tethered, physically crosslinked networked that acts like an elastic solid when swollen. We demonstrate that SOS BCPs swollen in the RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, or [EMIM][TFSI], have exceptional ionic conductivity, elasticity, distensibility, recovery rates, bulk toughness, and fracture toughness. This rare combination of multiple excellent mechanical properties and high ionic conductivity makes SOS GPEs auspicious candidates as solid electrolytes in energy transport and storage applications.

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The contents of this dissertation were written by Alyssa Winter May, however, each chapter in this dissertation was highly collaborative. The contents of chapter 2 were adapted from the following manuscript: Z. Shi, A. W. May, Y. Kohno, T. S. Bailey and D. L. Gin, *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 2961–2965, DOI:10.1002/pola.28623. My contribution to this work was the SAXS and DSC characterization and morphological analysis of the block copolymers included in this study. Chapter 3 was adapted from the following manuscript: A. W. May, Z. Shi, D. B. Wijayasekara, D. L. Gin and T. S. Bailey, *Polym. Chem.*, 2019, **10**, 751–765, DOI:10.1039/c8py01414k. My contribution to this work was once again the SAXS, DSC, and also GPC characterization, and morphological analysis of the block copolymers included in this study. Many thanks go out to Zhangxing Shi and Professor Doug Gin at University of Colorado, Boulder who were the primary driving force behind these experiments and performed the synthesis and molecular characterization of all materials included in both of these studies.

Chapter 4 was the product of a full Bailey group team effort. Justin Gangwish, Allee Klug, and Zack Umstead all spent countless hours independently and by my side in the lab to help perform many of the syntheses that created the materials investigated in this chapter. They also provided vital insight into the investigative synthetic process that ultimately helped me solve our materials engineering woes. I performed the mechanical testing and materials characterization for this study.

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The conductivity measurements for chapter 5 were performed by Yuxin Yang and Professor Sergio Granados-Focil at Clark University. Yinan Lu and Professor Rong Long at University of Colorado, Boulder, performed the "pure shear" crack propagation measurements. Both groups provided their invaluable expertise in the analysis of the data they provided. I performed the material synthesis, sample preparation, and all other material characterization and mechanical experiments.

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DEDICATION



For Blocko the Polymer, may he inspire joy, wonder, and many squiggles in all future generations of BRG students.

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LIST OF COMMON ABBREVIATIONS, SYMBOLS, AND CHEMICAL STRUCTURES

REFERENCED IN THE DISSERTATION

Abbreviation	Full Name	Chemical Structure/Cartoon (where applicable)
ATRP	atom-transfer radical polymerization	
BCP	block copolymer	
χ (chi)	flory-like interaction parameter	
χN	effective degree of segregation	
Ð	dispersity, polydispersity, or polydispersity index, quantified by M _w /M _n	
DBX	α,α'-dibromo-p-xylene	Br
DP	degree of polymerization	
DSC	differential scanning calorimetry	
EIS	electrochemical impedance spectroscopy	
ЕМІМ	1-ethyl-3-methylimidazolium	
EO	ethylene oxide monomer	0
ε	conformational asymmetry	
f	BCP block volume fraction	
G'	storage (elastic) modulus	
G"	loss (viscous) modulus	
Γ	electrostatic cohesion	
GPC	gel permeation (also known as size exclusion) chromatography	
GPE	gel polymer electrolyte	
Gyr	bicontinuous gyroid	
Hex	hexagonally packed cylinders	
Hex (weakly ordered)	liquid-like packing of cylinders	
HMC	high molecular weight polymer contaminant	

IL	ionic liquid			
KNAP	potassium napthalenide	Γ΄ Κ ⁺		
Lam	lamellae			
MCIL	metal-containing ionic liquid			
Mn	number-average molecular weight			
MW	molecular weight			
N	degree of polymerization			
NMR	nuclear magnetic resonance			
	order to disorder transition			
001	order to order transition			
PBMA	poly(butyl methacrylate)			
PDI	dispersity, polydispersity, or polydispersity index, guantified by M _w /M _n			
PEO	poly(ethylene oxide)			
PIL	poly(ionic liquid)			
PS	polystyrene			
Q	swelling ratio, g liquid / g polymer	-		
q*	primary scattering wave vector			
RAFT	reversible addition-fragmentation chain-transfer			
RTIL	room temperature ionic liquid			
SAXS	small angle x-ray scattering			
S _{BCC}	body-centered cubic spheres			
S _{LLP}	liquid-like packing of spheres			
S-OH	PS-OH w-hydroxy-polystyrene			

SO-H	PS-PEO-H ω -hydroxy-polystyrene-b-poly(ethylene oxide)		
	PS-PEO-PS		
SOS	+ + + + + + + + + + + + + + + + + + +	H H H	
SPE	solid (or solvent-free) polymer electrolyte		
Tg	glass transition temperature		
THF	tetrahydrofuran		
TFSI	bis(trifluoromethylsulfonyl)imide $F_{3}C \sim V_{0} \sim V_{0}$		

BRIEF INTRODUCTION TO SOFT MATERIAL MECHANICAL PROPERTIES

Term	Description				
	when a material fractures with little to no plastic deformation when				
brittle fracture	subjected to stress				
	typical behavior in polymer gels				
	• the measure of a material's ability to absorb energy and deform without				
bulk toughness	fracture				
	• the area under a stress/strain curve (typically J m ⁻³)				
compressive	• the ability of a material to resist being compressed (pushed together)				
strength	typically measured in Pa				
distensible	capable of being stretched				
	ability of a material to resist permanent deformation (i.e. return to its				
elasticity	original shape and size) when stressed				
	opposite of plasticity				
fatique	the initiation and propagation of cracks, tears, or flaws in a material during				
	cyclical loading, resulting in diminished mechanical properties or failure				
	a measure of how well an intentionally flawed material resists crack				
fracture	propagation when stressed, as compared to the unflawed control				
tougnness	critical energy required to fracture a material per unit area of crack				
	growth' (In J m ²)				
G' (storage	• the elastic contribution to dynamic modulus (G [*]) during oscillatory shear				
modulus	• If $G' > G''$ then the material is more solid-like than liquid and is more				
,	likely to resist deformation under stress				
0" (1	 the viscous contribution to dynamic modulus (G*) during oscillatory 				
G [°] (IOSS					
modulus)	• if G' < G" then the material is more liquid-like than solid and is more				
	likely to permanently deform under stress				
hystorasia	energy dissipated as neat in a loading/unioading cycle the difference between energy abasehed and energy released (file dimension)				
nysteresis	• the difference between energy absorbed and energy released (lioading -				
	junioaung)				
isotropic	uniformity in all directions				
	applies to swelling and deformation benavior				
	measure of now difficult a material is to deform				
	• quantified by the slope of the stress/strain curve				
modulus	• stiffer materials will have higher modulus				
	a stress/strain curve may have multiple moduli at different points along				
plasticity	• used to describe materials that permanently deform when stressed				
	opposite of elasticity				
	• a type of tensile test where the length of the sample mounted (length is				
	parallel to grips) is very long compared to its height (distance between				
pure snear test	grips) in order to minimize contraction of the sample in the length				
	used for fracture toughness testing				

recovery	 the ability of a material to return to its initial mechanical properties after some number of loading and unloading cycles or rest periods between cycles often quantified in terms of time to recover or % recovery of initial properties 			
rheology	for polymers, the study of the viscoelasticity of the material			
strain	 deformation of a material relative to its starting position 100% tensile strain is the same as a stretch of double (λ = 2) the original material length 			
strength	the ability of a material to withstand mechanical loading without fracture or plastic deformation			
stress	the force per unit area (Pa = N m^{-2} = J m^{-3}) required to deform a material, typically reported at a particular strain			
tensile	the ability of a material to resist being pulled apart or stretched			
strength	typically measured in Pa			
yield point	 plastic deformation that occurs beyond a particular strain elastomers do not typically exhibit yield points 			
Young's	the initial elastic modulus of a material, quantified by the slope of the linear			
modulus	regression of the initial linear portion of stress/strain data			

CHAPTER 1: INTRODUCTION AND PERSPECTIVE OF DISSERTATION

1.1 Overview of the dissertation

The goal of this chapter is to provide context for the body of work that became the chapters and appendices of this dissertation. Functional soft materials made from phase separating block copolymers (BCPs) and particularly those with an ionic liquid component, are the main topic of discussion throughout this work which can be divided into two distinct sub-topics: a) the phase behavior of poly(ionic liquid)-containing block copolymers and b) the synthesis and mechanical behavior of thermoplastic elastomer SOS hydro- and ion-gels. Part (a) is discussed in chapters 2 and 3, which are both adapted from publications that resulted from collaborative efforts between the Travis Bailey research group at CSU and the Douglas L. Gin research group at the University of Colorado Boulder (see the acknowledgements section in the preliminaries above).^{1,2} Part (b) is covered in chapters 4 and 5. At the time of acceptance of this dissertation, chapter 5 is currently being prepared for submission as a manuscript in collaboration with Rong Long's group at CU Boulder and Sergio Granados-Focil's group at Clark University. While an in-depth literature background will be discussed in the introduction of each chapter, the following discussion will offer some additional perspective, motivation, and history behind the work of each chapter.

1.2 Phase behavior of poly(ionic liquid) block copolymers

At the turn of the century, Frank Bates described block copolymers as "designer soft materials" in the sense that the clever combination of just a few common polymers with well-known and established properties could be joined covalently to create a seemingly limitless array of new and customizable polymer species.^{3,4} Of these, the combinations that could microphase separate to form ordered nanostructures had the potential to have physical and mechanical properties that were completely inaccessible to the individual homopolymers or even physical mixtures of the homopolymers. In the two decades since, the field of block copolymer research has expanded exponentially, with new block chemistries,^{5–12} polymerization techniques,^{13,14} morphologies,^{15–17} architectures,^{18–20} mathematical models,^{21–23} and applications (such as drug delivery,^{24–26} selective ion or particle transport,^{27,28} energy conversion and storage,^{29–32} semi-conductor manufacturing,^{33–35} carbon sequestration,^{36–40} to name a few, the field is far too large for this list to be comprehensive) emerging constantly. Application-driven interest in BCPs relies on thorough understanding of the morphological phase behavior of the BCP being studied, as its chemical, physical, mechanical, and transport properties can vary widely depending on the adopted morphology.^{38,41–43} It is imperative, then, that when any novel BCPs are synthesized, the phase separation behavior is exhaustively studied and understood in order for the materials to be useful for their targeted applications in any appreciable way. There is a massive subset of block copolymer research dedicated almost exclusively to better understanding the phase behavior of both new and well established BCP systems.^{14,15,17,41,42,44–50}

For over a decade, the Gin group at CU Boulder has worked on developing new and functional polymeric materials that incorporate room temperature ionic liquids (RTILs) into the polymer backbone with the intent of accessing the desirable properties of ionic liquids through solid polymer platforms. RTILs are known for their chemical stability, non-flammability, non-volatility, unusual gas solubility and catalytic properties, and high ionic conductivity.^{51,52} Some polymerized ionic liquids (PILs) tend to still be very liquid-like in character, so more recently, the Gin group turned to nanostructured BCP architectures with both an RTIL block and a higher T_g non-ionic block to imbue their PIL materials with solid polymer characteristics. Their realm of expertise lies in the molecular design and synthetic strategies needed to create these interesting and unique polymers, whereas the Bailey group at CSU has deep roots in the world of BCP phase behavior dating back to Travis Bailey's graduate work in the Bates group at University of Minnesota, thus a collaboration between the two groups was established to study the phase behavior of these new RTIL based BCPs and better understand their structure-property

relationships. This started with synthetic work done in the early 2010's by Erin Wiesenauer in the Gin group, and morphological analysis performed by Vincent Scalfani from the Bailey group.^{9,46} We continued this collaboration through chapters 2 and 3 of this dissertation and the two publications mentioned above.

In chapter 2, Zhangxing Shi from the Gin group synthesized a series of cobalt-containing poly(butyl methacrylate)-b-PIL diblock BCPs via reversible addition-fragmentation chain-transfer (RAFT) polymerization that, to our knowledge, were the first example of metal-containing, phase separating BCPs in the literature, particularly one that was synthesized via the direct polymerization of an MCIL monomer, as opposed to post-polymerization functionalization of a non-ionic block. I used small angle x-ray scattering (SAXS) to analyze the melt-state microphase separation behavior and confirm the BCP architecture of these materials. In just six samples, we were able to observe all four classic diblock morphologies (Lam, Hex, Gyr, S), which was both unexpected and very exciting in that 1) the system was capable of phase separation at all, 2) the system was generally capable of forming highly ordered and predictable nanostructures, and 3) the presence of a highly charged MCIL block still allowed for the formation of the desirable gyroid morphology, which is notable for having a bicontinuous structure of both the minority and majority component blocks. That uninterrupted structure makes it excellent for transport (gases, ions, liquids, etc) related applications, however, the gyroid phase is also notorious for having a very narrow phase window and being challenging to "access."⁴⁷ As an added bonus, these BCPs also changed color in the presence of small protic molecules like water and MeOH, much like the color indicating Drierite dessicant that is common in most synthetic laboratories.

Chapter 3 continues our collaborative efforts with the phase behavior investigation of a significantly larger pool of imidazolium/polystyrene-based PIL diblock BCPs that were synthesized by Zhangxing Shi using atom-transfer radical polymerization (ATRP). This project continued an initial study by Shi, et al.¹⁴ that found these BCPs to capable of microphase separation into ordered structures at small degrees of polymerization of just 50 total repeat units,

and once again I used SAXS to analyze the melt state phase behavior of these PS-PILs. Because of the wide variety of samples provided by the Gin group, we were able to construct two phase diagrams for these samples, one for the set of methyl functionalized PS-PILs, and one for the n-butyl functionalized set of polymers. We were able to glean some very interesting information from the phase behavior of these polymers, including an estimation of the density of the methyl-PIL block, which was previously unknown but is an incredibly important parameter that is used to predict BCP morphology of new samples that utilize that same monomer in their synthesis. Its use could be expanded to help predict phase behavior project evolved quite rapidly in the context of my graduate career; what started as a small "data collection" side project transformed into more than a year of nearly full-time research work for me, two publications, the topic of my research seminar, and now two chapters of my dissertation. Ultimately, I hope that this work serves the greater BCP community and perhaps helps another confused graduate student to better understand diblock copolymer phase behavior in the same way that I learned an incredible amount from Vin Scalfani's 2012 work.

1.3 Thermoplastic elastomer SOS gels

Polymer gelators, that is, cross-linked polymer systems that can hold significant amounts of liquid while maintaining solid-like properties, are ubiquitous in our everyday life (i.e., gelatin, contact lenses, personal care products, wound care, etc) and play an important and significant role in soft material research. Gels that exhibit robust mechanical properties while maintaining high liquid content are particularly sought after for their ability to exhibit liquid-like character in a solid platform that can withstand repeated and significant mechanical deformation or loading. In the hydrogel (gels that are swollen in water) realm this has implications in biomimetic tissue replacements or scaffolds,^{53–56} drug delivery,^{26,57,58} 3D printing,⁵⁹ and more. Ion gels, also known as gel polymer electrolytes (GPEs), are polymer networks that can be swollen in organic electrolyte solutions or

RTILs, and those that are both highly conductive and mechanically tough are highly sought after for, but not limited to, flexible electronics,^{20,60,61} batteries,^{62,63} and sensors.^{64,65}

Achieving high swelling, good mechanical properties, and good transport properties (in the case of membranes or applications that require high conductivity), is exceptionally challenging and more often than not, advances in gel design are able to achieve certain properties to a high degree, but with significant trade-offs. A well-cited example of this is Gong et. al's double-network (DN) hydrogels in which early iterations had high water content and modulus, and were exceedingly tough on the first compression cycle, but that toughness was derived from the fracture of a pre-strained secondary network that interpenetrated the first, and any further mechanical load showed significant hysteresis in the material. The DN gel also had limited tensile stretchability, breaking at an extension of only 75%.⁶⁶ Since then, they have developed high modulus, highly stretchable and tough physical hydrogels based on "healable" ionic interactions between networks that can withstand multiple loads but require exceedingly long (timescale on the 10's of minutes) recovery times.^{67,68} Sun and coworkers reported similarly behaving materials based on an alginate/polyacrylamide DN with enormous stretchabilities (and consequently high toughness), but the gels have low moduli and strength, and take hours, if not days to recover their properties after loading.⁶⁹ The Ito group is notable for making "crack propagation resistant" slidering gels that can also be stretched to impressive lengths but also suffer from low moduli and strength, with no demonstration of elasticity.^{70–72} Kim and Moon recently reported on "ionoskin" materials with impressive mechanical properties (high modulus, strength, good stretchability, tensile cyclability at low strains) but only some of the gels displayed robust mechanical properties, and all of the gels showed more significant hysteresis and poor recoverability at high strains. Additionally, these gels are limited in their ionic liquid loading (< 50% by weight), and as a result, their ionic conductivity suffers.⁶⁴ The Lodge group has reported several examples of highly conductive BCP ion gels but their mechanical performance was lackluster, save for one example which demonstrated high toughness during tensile testing. This material was able to be stretched

to over 300%, with high modulus, but the polymer had to be irreversibly chemically cross-linked to achieve this.^{11,73,74}

Since 2010, the Bailey group has developed mechanically high-performing gels with high liquid content (80% to more than 95% by weight) based on melt-state phase separating, physically crosslinked blends of the thermoplastic BCP poly(styrene-b-ethylene-oxide)/poly(styrene-b-ethylene oxide), or SOS/SO. These blends are high molecular weight (typically 80 to 100 kDa for the SO, double that for the SOS) with low f_{PS} such that they form a spherical, micelle-like morphology (either S_{BCC} or S_{LLP}) where the PS spheres are hydrophobic and vitrified at room temperature and the PEO coronas are hydrophilic, amorphous, and stretchable when swollen in a selective solvent like water or ionic liquid. Swollen in water, these gels have shown to have a high modulus for swollen polymers (approaching 0.9 MPa), be highly elastic over many cycles, distensible to 99% compressive strains without damage to the network or 200% to 400% strain under tension before failure (depending on the ratio of SOS to SO), strong, tough, and fatigue resistant to 500,000 rapid (1s) cycles with over 90% recovery.^{54,75,76} Swollen in ionic liquid, they have shown excellent transport and separation properties for light gases like CO₂ and N₂, and promising, though preliminary, evidence of good mechanical properties.⁴⁰

Many different people in our group have made these same SOS materials in many different batches of various size and purpose over the past decade. Our synthetic methods have evolved since the original publication by Guo and Bailey⁷⁶ and along the way we started to make SOS blend materials with a mysterious "high molecular weight contaminant" (HMC) that was absent in the original materials made by Chen Guo. Materials that contained appreciable amounts of this contaminant appeared to have greater fatigue and diminished mechanical properties, so the work detailed in chapter 4 of this dissertation was dedicated to the systematic synthetic discovery of why we were generating such a contaminant in our polymerizations and how to prevent it. To fully assess its impact on the mechanical properties of our gels, I conducted a thorough investigation of the mechanical performance under compressive stress of a large series

of gels that contained varying amounts of the high molecular weight contaminant, from none to nearly 50% by weight. This chapter is also the first study within our group to compare the mechanical and physical properties of our SOS gels across many different batches of polymer. While this chapter is not likely to be published as a journal article, the findings within it are absolutely critical for the development and success of our group in the future, should we continue to make gels based off of the SOS/SO blend platform, and without it I would not have been able to have high quality gels for the experiments performed in chapter 5.

Chapter 5 continues and greatly expands upon efforts by Dilanji Wijayasekara⁴⁰ to study the mechanical and transport properties of our SOS gels when swollen in ionic liquid, specifically [EMIM][TFSI], which we have found to be an excellent selective solvent for the PEO component in SOS. We hypothesized that these gels would be highly conductive due to the free-flowing ions suspended in the PEO matrix, and thus established a collaboration with Sergio Granados-Focil and his research group at Clark University to study the ionic conductivity of our SOS ion gels at various swelling ratios. We found that these gels, regardless of triblock content and swelling ratio, were all exceptionally conductive, performing slightly above the ionic conductivity of the neat ionic liquid.

Through the course of this study, we were able to obtain quite a bit of mechanical data about SOS ion gels that has not been collected previously within our group, such as tensile strainto-break of high triblock content gels and cyclical tensile testing (thanks to recent access to an Instron 4442 mechanical tester, all of our previous tensile data had been collected on our TA Ares Rheometer, which required much smaller samples because of the limited Z-axis range) and rheological dynamic temperature ramps from 0 to 100 °C (the wider temperature range of the liquid phase of RTIL and its non-volatility make this possible, unlike gels swollen in water). Recently, our group has been interested in measuring toughness and tear resistance of our gels, as we believe the inherent nanostructure design creates fracture resistant mechanisms under strain, and past and present projects have explored toughening mechanisms in our network

structure,^{75,77} however, those studies measured toughness though bulk tensile testing only. Fracture testing, which involves measuring the crack propagation in an intentionally flawed sample, has become popular among soft material and hydrogel mechanics researchers as a more accurate representation of the toughness and fracture resistance of a material in addition to being more flaw insensitive than bulk tensile testing.^{76–82} A collaboration with Rong Long's fracture mechanics lab at CU Boulder enabled us to measure, for the first time, the fracture toughness of a series of SOS ion gels, which at greater than 10³ J m⁻² for the softest gels studied in this chapter puts our materials well within the range of other popular "tough" materials.^{69,81,83} What sets these ion gels apart, however, is their exceedingly low hysteresis, incredibly fast recovery rates, exceptional elasticity, and an observed mechanical toughening phenomenon known as "crack branching," which is atypical for isotropic, homogenous materials like ours and most gels. We are very excited to publish this chapter soon; these new and very interesting mechanical results coupled with the conductivity measurements mentioned previously allow us to explore new potential applications for these materials in soft and flexible electronics, batteries, and beyond.

1.4 Final remarks and where to find supporting information

Chapters 2 through 5 have supporting information available in the form of Appendices of this dissertation (Appendix A through D, respectively). As all chapters were highly collaborative, a more detailed acknowledgement of contributions is at the beginning of this dissertation. Chapter 6 is a summary of our conclusions from chapters 2 through 5, and also includes a discussion on our impacts to the scientific community and potential experiments that could be performed by us and our collaborators to push each project forward.

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CHAPTER 2: METAL-CONTAINING IONIC LIQUID-BASED, UNCHARGED-CHARGED DIBLOCK COPOLYMERS THAT FORM ORDERED, PHASE-SEPARATED MICROSTRUCTURES AND REVERSIBLY COORDINATE SMALL PROTIC MOLECULES¹

2.1 Chapter summary

In this chapter we present a series of six phase-separating, metal-containing poly(ionic liquid) block copolymers (MCIL BCPs) synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization of Co(II) bis(salicylate) complex containing monomers which, to our knowledge, are the first of their kind. We performed an in-depth morphological analysis of this series of polymers using small angle x-ray scattering (SAXS) and were able to observe all four equilibrium diblock copolymer morphologies (Lam, Hex, Gyr, and S). The highly asymmetric nature of the IL block, relative to the PBMA block, in these MCIL BCPs is apparent as the samples with the lowest ratios of charged to uncharged blocks (10/60 and 15/55) produced the most symmetrical nanostructures (Lam). This is the first example of a phase separating PIL BCP forming the bicontinuous gyroid phase, Gyr, which, as a solid polymer with a continuous ionic component, has potential uses in functional conductive materials. Additionally, we demonstrate the ability of these MCIL BCPs to coordinate with protic small molecules such as water or alcohols, easily detectable by a visible color change.

2.2 Introduction

Polymerized ionic liquids $(poly(IL)s)^{1-3}$ are macromolecules with charged repeat units prepared by polymerization of ionic liquid (IL) monomers (i.e., monomers that are molten salts at ≤ 100 °C),^{1,2} or that contain IL-like moieties if prepared by other methods.³ Since poly(IL)s have the

¹ This chapter is adapted from the following publication: Z. Shi, A. W. May, Y. Kohno, T. S. Bailey and D. L. Gin, *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 2961–2965, DOI:10.1002/pola.28623

properties of polymers and many of the desired features of ILs (e.g., negligible vapor pressure, ion conductivity, high solubility for certain gases), poly(IL)s have been shown to be useful for many applications (e.g., as gas separation membranes, solid-state ion conductors, etc.).^{1–3}

IL-based block copolymers (BCPs) are a distinct and relatively new class of BCPs that contain at least one poly(IL) segment.^{4,5} By combining the unique properties of poly(IL)s with the ability of BCPs to phase-separate into ordered microstructures, IL-based BCPs have shown promise as new functional materials.^{4,5} Over the past few years, a variety of IL-based BCPs have been prepared by either sequential controlled/living polymerization of an IL monomer and an uncharged co-monomer; or by post-polymerization functionalization of uncharged BCPs containing reactive units to generate charged moieties on the polymer.^{4,5} Although many IL-based BCPs have been studied as functional materials,^{4,5} only a small subset of them has been reported to phase-separate into periodic, nanostructured morphologies in the neat melt state.⁶⁻¹⁴ Solid phase separated polymer materials with a continuous conductive phase are particularly desirable due to their potential in functional electronics applications such as solid polymer electrolytes in batteries.¹⁵⁻¹⁷

One recent method for introducing new functional properties into ILs has been to incorporate a metal complex in the IL. These metal-containing ILs (MCILs) are a relatively new class of functional ILs with metal-based magnetic,^{18,19} optical,^{18–20} catalytic,^{18,19,21–23} or molecular binding properties.^{18,19,24} Consequently, MCIL-based BCPs with such properties and the structural advantages that can stem from the ability to form ordered microstructures are attractive as new functional materials. Whereas <u>uncharged</u> metal-containing polymers are fairly well known in the literature, MCIL-based poly(IL) homopolymers are rare,^{25,26} and MCIL-based BCPs are unprecedented to our knowledge. The closest reported materials with charged blocks are metallocene-based BCPs that are not true IL-based BCPs.^{27,28} These charged metallocene-based BCPs were made by copolymerizing uncharged monomers with charged monomers that are not molten salts and do not have typical IL structures.^{27,28}

Herein, we present the first example of a MCIL-based, uncharged-charged BCP platform (1) that exhibits ordered, phase-separated microstructures in the neat state and can reversibly coordinate protic small molecules with an accompanying color change.

2.3 Results and discussion

This MCIL-based BCP system was made by reversible addition-fragmentation chain-transfer (RAFT) polymerization of first butyl methacrylate to form uncharged poly(butyl methacrylate) (PBMA) macro-chain-transfer agents (macroCTAs) of controlled length (**2**), and then copolymerization of a styrenic phosphonium IL monomer with a cobalt(II) bis(salicylate) anion (**3**) (figure 2.1). Short BCPs of this system (**1a–f**) ranging from 35-*b*-35 to 60-*b*-10 (uncharged-*b*charged block ratios) show a range of ordered nanostructures (including lamellae (Lam), hexagonally packed cylinders (Hex), and gyroid (Gyr) by small-angle X-ray scattering (SAXS)) after annealing in their neat states. These MCIL-based BCPs were also found to reversibly coordinate to H₂O and small alcohols in their vapor form with a noticeable color change. This combination of properties makes this new BCP platform unique and potentially useful for applications development.

As shown in figure 2.1, MCIL-based BCPs **1a–f** were synthesized via sequential RAFT polymerization of butyl methacrylate and MCIL monomer **3** using 2-cyano-2-propyl benzodithioate (CPBD) as the chain-transfer agent, azobis(isobutyronitrile) (AIBN) as the radical initiator, and chlorobenzene as the polymerization solvent (see Appendix A, the Supporting Information, for details). MCIL monomer **3** is a new compound that was synthesized using a procedure based on one previously reported by the Gin group.²⁴ In our sequential RAFT copolymerization, reactive PBMA blocks **2** with controlled lengths and low PDI values were first synthesized and then used as RAFT macroCTAs to attach the subsequent poly(MCIL) block via addition of the appropriate amount of monomer **3**. This polymerization sequence was chosen because BCPs made via RAFT are typically synthesized by polymerizing the monomer with the better propagating radical leaving



Figure 2.1: Synthesis and structures of the MCIL-based BCPs in this study.

group first.²⁹ RAFT polymerizations of methacrylates and styrenic monomers are well established in literature,³⁰ but RAFT polymerization of monomers containing a Co(II) bis(salicylate) complex is unprecedented. Consequently, kinetics studies of the copolymerization of butyl methacrylate and **3** were performed to confirm controlled polymerization (see Appendix A).

The absolute lengths and block composition ratios of BCPs **1a–f** were confirmed by ¹H NMR analysis and the block lengths of the PBMA macroCTAs **2a–f** were determined by ¹H NMR end-group analysis using the aromatic protons on the CPBD as an integration reference.³¹ The PBMA:poly(**3**) block ratios for each BCP were determined by integrating and comparing distinct ¹H NMR signals indicative of each block. The poly(MCIL) block lengths were then calculated based on the PBMA block lengths and the block composition ratios.³¹ These results were further confirmed by monitoring the degree of conversion and monomer-to-initiator ratios. Then, the

absolute M_n values for **1a–f** were calculated by multiplying the absolute block lengths (from ¹H NMR spectroscopy) by the molecular weights of the repeat units (see Appendix A).

Unfortunately, GPC³² and other conventional polymer MW determination techniques could not be used to confirm the MW, PDI, or block structure of **1a–f** because of the unusual solubility and other physical properties of these uncharged-charged MCIL-based BCPs.¹³ Instead, a combination of alternative methods (i.e., surfactant behavior and solubility analysis, diffusionordered NMR spectroscopy, SAXS studies) was used to verify the block architectures of **1a–f** and differentiate their behavior from that of a physical blend of PBMA and poly(**3**) homopolymers, as described previously for characterizing IL-based BCPs¹³ (see Appendix A).

SAXS was particularly effective in demonstrating the block connectivity, as well as the MW and composition control afforded by the CPBD chain-transfer agent. As depicted in figure 2.2 and summarized in table 2.1, careful control of the relative sizes of each block in **1a–f** permitted synthesis of a series of macromolecules collectively displaying characteristics representative of each of the classic BCP phases (Lam, Gyr, Hex, and a weakly-ordered, liquid-like packing of spheres phase, S_{LLP}). Notably, sample **1d** may be the very first example of an IL-based BCP exhibiting the Gyr phase. In previous investigations of imidazolium-based IL-BCPs based on styrenic^{11,12} and norbornene^{13,14} monomer derivatives, the Gyr phase was noticeably absent, with systems preferring to produce (presumably metastable but persistent) regions of Lam/Hex

BCP	n	m	d* (nm) / {hkl}*	Morphology	Observed q*/q100
1a	35	35	14.8 / {110}	SLLP	weakly-ordered spheres
1b	40	30	14.8 / {100}	Hex	√1, (√3), √4, √7
1c	45	25	14.2 / {100}	Hex	√1, √3, √4, √7
1d	50	20	14.4 / {211}	Gyr (Hex)	√6, √8, √14, √16, (√20), √22, √24, (√26)
1e	55	15	13.5 / {100}	Lam	√1, √4, √9
1f	60	10	12.8 / {100}	Lam	√1, √4, (√9)

Table 2.1: Morphological characteristics of MCIL-based BCPs 1a-f.


Figure 2.2: SAXS patterns at 175 °C for MCIL-based BCPs **1a–f** after annealing at that temperature in vacuo for 2 h. Inverted triangles designate the expected reflection locations for the indicated morphologies (for sample **1d**, open triangles are Hex, filled are Gyr) based on the position of q*.

coexistence. MCIL-BCP **1d** exhibited behavior prototypical of many non-ionic BCPs, quickly transitioning from a metastable Hex phase to a persistent Gyr phase with minimal thermal annealing.^{33–35} SAXS data for **1a–f** as a function of temperature during heating, annealing, and cooling are provided in Appendix A.

The sequence of morphologies and their compositional distribution with respect to volume fraction in IL-BCPs has proven to mimic that of traditional uncharged BCP systems.^{6–14} However, one unique trait exhibited by these charged MCIL-based BCPs and shared with the previously

studied styrenic-^{11,12} and norbornene^{13,14}-based IL-BCP systems is a clear disparity in repeat unit volumes and its role in determining the selection of morphology. The data in table 2.1 reveal that even at uncharged-to-charged repeat unit ratios as high as 60:10 (**1f**), the relative volumes occupied by each block are likely similar, promoting the adoption of a nearly symmetric Lam phase. As this ratio decreases toward unity (**1a**), the charged block continues to occupy greater fractions of the overall BCP volume, and the adopted phases follow the prototypical path toward morphologies with increasing average mean curvature.³⁶ Under that observation, we suspect that **1a**, for which no higher order reflections are evident, is likely adopting a weakly-ordered sphere or micelle-like phase. Such phases tend to persist at the edges of the phase diagram, with the evolution of a more ordered lattice often constrained kinetically.^{14,37} Finally, it is notable that these MCIL-based BCPs are able to adopt ordered morphologies at such small numbers of repeat units. Clearly, the Flory-like interaction parameter, *χ*, for this combination of blocks is significant; however, direct *χ* measurement was beyond the scope of this initial work.



Figure 2.3: Reversible color change of 1d upon coordination with H₂O vapor.

MCIL-based BCPs **1a–f** were also found to selectively and reversibly coordinative to small protic molecules (e.g., H₂O, small alcohols such as MeOH, EtOH, etc.) with a distinct color change. After exposure to the vapor of these small protic molecules, **1a–f** undergo a color change from dark blue to light purple. The original dark blue color can be restored by mild heating or in vacuo treatment of the coordinated BCPs (see figure 2.3 for an example). This reversible colorimetric coordination behavior has been observed previously with MCILs containing the same Co(II) bis(salicylate) anion upon exposure to H₂O or alcohols.²⁴ The proposed mechanism for this behavior is described in a previous report.²⁴ However, the vapor of aprotic small molecules (e.g., Et₂O, acetone, ethyl acetate) will not trigger the reversible color change described above,

indicating no coordination between **1a–f** and these aprotic molecules (see Appendix A). Interestingly, preliminary SAXS of **1d** suggests that water vapor coordination does not appear to affect its Gyr morphology but may slightly increase domain spacing (see Appendix A).

2.4 Conclusions

In summary, we synthesized new MCIL-based BCPs **1a–f** that are capable of forming ordered nanostructures (including the Gyr phase) in their neat states and can also reversibly coordinate with H₂O and small alcohols with an associated color change. We are currently investigating the morphological behavior and phase stability of this MCIL-BCP system as a function of the extent of H₂O and small alcohol coordination. Future work will be focused on exploring on whether phase changes can be induced upon reversible water or alcohol coordination to allow these MCIL-based BCPs to be used in responsive applications.

2.5 Experimental

2.5.1 Synthesis of bis[tributyl(4-vinylbenzyl)phosphonium] [cobalt(II) bis(salicylate)] (3)

Tributyl(4-vinylbenzyl)phosphonium chloride (see the ESI) (1.000 g, 2.82 mmol) was dissolved in H₂O (5 mL). Subsequently, individual aq. aliquots (2.5 mL) of lithium salicylate (0.812 g, 5.64 mmol) and cobalt(II) chloride hexahydrate (0.335 g, 1.41 mmol) were prepared and then added dropwise. A deep purple liquid formed immediately and was extracted using CH₂Cl₂. The CH₂Cl₂ layer was then repeatedly washed with water until no halides were detected by the silver nitrate test. This solution was then dried over anhydrous Na₂SO₄, filtered, and then concentrated. The resulting liquid was dissolved in MeOH, stirred at R.T. for 24 h, filtered, and finally concentrated in vacuo to give 3 as a dark blue liquid (yield: 1.24 g, 91%). ¹H NMR (300 MHz, CD₃OD): δ 8.04 (s, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.33–7.17 (m, 4H), 7.10 (s, 1H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (dt, J = 17.6, 0.9 Hz, 1H), 5.23 (dt, J = 10.9, 1.0 Hz, 1H), 3.65 (d, J = 14.8 Hz, 2H), 2.17–

1.98 (m, 6H), 1.51–1.33 (m, 12H), 1.00–0.82 (m, 9H). ¹³C NMR (75 MHz, CD₃OD): δ 138.00 (d, J = 3.9 Hz), 135.64 (d, J = 2.2 Hz), 133.06, 129.80 (d, J = 5.1 Hz), 127.59 (d, J = 8.9 Hz), 126.84 (d, J = 3.3 Hz), 120.78, 118.86, 113.95 (d, J = 1.8 Hz), 25.41 (d, J = 45.4 Hz), 23.45 (d, J = 15.7 Hz), 22.77 (d, J = 4.7 Hz), 17.56 (d, J = 47.3 Hz), 12.15 (d, J = 0.9 Hz). The ¹³C signals of the phosphonium cation were split into doublets by the ³¹P nucleus. The number of ¹³C signals for the cobalt anion is less than expected due to the interference of the paramagnetic Co(II) center.²⁴ Anal. calcd. for $C_{56}H_{80}CoO_6P_2$: C 69.33, H 8.31, N 0; found: C 69.34, H 8.02, N 0. The full ¹H and ¹³C NMR spectra for isolated 3 are provided in Appendix A to help confirm its purity.

2.5.2 Example: synthesis of PBMA macroCTA 2d:

Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (46.7 mg, 0.211 mmol), chlorobenzene (1.2 mL) and AIBN (3.50 mg, 0.0213 mmol) were added to a flame-dried Schlenk flask and degassed by 3 freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask were cooled to R.T., diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA 2d as a pink solid (yield: 1.24 g, 80%). DP = 50; PDI = 1.04; $M_n = 7331$ g/mol (calculated using ¹H NMR polymer end-group analysis. See Appendix A for details on how the DP and absolute M_n were determined using ¹H NMR analysis). The synthesis and characterization details for the rest of the PBMA macroCTAs used are provided in Appendix A.

2.5.3 Example: synthesis of MCIL-based BCP 1d:

Monomer 3 (274 mg, 0.565 mmol), 2d (207 mg, 0.0282 mmol), chlorobenzene (1.5 mL) and AIBN (0.930 mg, 0.00566 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-

filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to R.T., diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1d as a dark blue solid (yield: 300 mg, 62%). Block repeat units molar ratio = 2.5:1 (butyl methacrylate:3); block length composition = 50-b-20 (PBMA-b-poly(3)); $M_n = 17,032$ g/mol (calculated based on ¹H NMR analysis. See Appendix A for details on how the copolymer block composition, block lengths, and M_n were determined).

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CHAPTER 3: SELF-ASSEMBLY OF HIGHLY ASYMMETRIC, POLY(IONIC LIQUID)-RICH DIBLOCK COPOLYMERS AND THE EFFECTS OF SIMPLE STRUCTURAL MODIFICATION ON PHASE BEHAVIOUR²

3.1 Chapter summary

A series of thermally processable, phase separating diblock copolymers made via sequential ATRP of styrene and styrenic ionic liquid (IL) monomers with various alkyl imidazolium substituents were synthesized to cover a wide range of volume fractions, most notably those on the IL-rich side of the phase diagram. Small-angle X-ray scattering (SAXS) analysis was used to confirm melt-state (and glassy state) phase behavior in which all four classic equilibrium diblock copolymer morphologies – body-centered cubic spheres (S_{BCC}), hexagonally packed cylinders (Hex), lamellae (Lam), and notably, bicontinuous gyroid (Gyr) – were observed. These PS-PIL diblock copolymers were found to have a high degree of conformational asymmetry and/or electrostatic cohesion within the PIL block, highlighted by the shift of the Lam phase window with boundaries falling between $f_{PIL} = 0.31$ and 0.55. Variation of the alkyl group appeared to influence the strength of the Flory-like interaction parameter of the system, $\chi_{PS/PIL}$, such that simple substitution of methyl by *n*-butyl on the imidazolium IL substituent resulted in the emergence of the (notoriously segregation-sensitive) Gyr phase, superseding the persistent coexistence of Lam and Hex in the methyl-substituted imidazolium diblock copolymer phase diagram.

3.2 Introduction

Ionic liquids (ILs) have been a major focal point in many areas of chemistry and engineering due to their favourable properties and emerging capabilities. ILs are popular as solvents for green

² This chapter is adapted from the following publication: A. W. May, Z. Shi, D. B. Wijayasekara, D. L. Gin and T. S. Bailey, *Polym. Chem.*, 2019, **10**, 751–765, DOI:10.1039/c8py01414k

chemistry due to their near-zero vapor pressure and negligible flammability. Their high ionic conductivity, stability, and sorption selectivity for certain light gases also make them attractive for use in energy applications¹ (i.e., as electrolytes in batteries² and post-combustion gas separation membranes³). In circumstances where the mechanical properties of a polymer are more desirable, researchers have turned to polymerized ionic liquids (PILs), or polymers that incorporate the (typically) cationic portion of the IL as part of each polymeric repeat unit.^{4,5} The counter-anion remains separate and weakly coordinated to the polymer backbone, which allows the material to maintain good ionic conductivity.

Due to the liquid-like nature of many PIL homopolymers of interest, the ability to tune the mechanical and other properties of PILs can be limited. One strategy to mitigate this problem has been to generate block copolymers (BCPs) containing a PIL block (PIL-BCPs). Taking advantage of the tunability of BCP morphologies and their associated long-range nanostructures gives PIL-BCPs the advantage of having one block dedicated to providing mechanical integrity while allowing the PIL block to retain many of the desirable qualities of the IL on which it is based.^{1,6} To produce PILs, incorporating IL functional units into a polymer backbone has been a commonly used strategy in recent years.^{1,4–6} Most often, these BCPs – which are frequently styrene-, acrylate-, vinyl-, or norbornene-based – contain a modified imidazolium-based IL component (typically with an alkyl substituent), but quaternized ammonium⁷ and phosphonium salts have been reported as well.^{1,4–6} Diblock copolymer (AB) architectures are typically the most widely synthesized; however, Matyjaszewski and co-workers recently reported several interesting BCP architectures including ABA or BCB triblock copolymers in which B is the charged PIL block.⁸

Generally, there have been three strategies employed to synthesize PIL-BCPs.^{1,6} These include (1) the post-polymerization modification of reactive groups on an uncharged BCP with an IL moiety, (2) the growth of PIL blocks on an uncharged macroinitiator, and (3) the sequential copolymerization of non-ionic and IL monomers. A multitude of polymerization techniques^{1,6} have been used to achieve this, including the earliest examples of PIL-BCPs synthesized via nitroxide-

mediated polymerization (NMP),^{7,9,10} reversible addition-fragmentation chain-transfer (RAFT) polymerization,^{11,12} atom-transfer radical polymerization (ATRP),^{8,13,14} ring-opening metathesis polymerization (ROMP),¹⁵ and anionic polymerization,¹ among others.¹⁶

While the synthetic development of novel PIL-BCPs continues to be a major research focus, it is also crucial that the self-assembly thermodynamics of this relatively new class of materials are fully understood and characterized. For example, Mahanthappa and co-workers showed that the conductivity of various styrene/imidazolium-functionalized styrenic BCPs varied widely depending on morphology, long-range order, and preparation of the polymer film.⁹ Additionally, for polymers intended as gas separation membranes, Drzal et al. and Nguyen et al. both showed that BCP morphology had a direct impact on the gas transport properties of the material.17,18 Therefore, we have spent some time focusing on applying polymerization techniques to IL monomers that allow for precise control over block ratios and molecular weight, as a means to probe the comprehensive phase separation behaviour of various PIL-BCP systems. We previously published work elucidating the phase behaviour of a series of alkylimidazolium norbornene block copolymers synthesized via ROMP.^{15,19} In fact, this was one of the earliest studies to show that imidazolium-based PIL-BCPs are capable of forming ordered nanostructures by phase separation in the neat melt. Some significant drawbacks to this norbornene system (i.e., the need for expensive ROMP catalysts, lengthy monomer synthesis, and poor mechanical properties due to the liquid-like¹⁹ nature of this BCP) led to exploration of more convenient polymerization techniques and monomers.

More recently, our groups performed a preliminary study¹⁴ investigating the morphology of several styrene/styrenic alkyl-imidazolium BCPs similar to those synthesized by He et al. and Weber et al.^{8,9} This class of materials has several advantages over the norbornene/ROMP system including (1) lower cost, (2) flexibility and ease of synthesis, (3) reduced metal contamination, (4) easier room-temperature handling and storage (solid powders vs. viscous liquids), and (5) thermal processability. While Mahanthappa and coworkers prepared a similar product by post-

polymerization modification of a styrene/4-vinylbenzyl chloride-based BCP, our groups and the Matyjaszewski group showed that imidazolium-based PIL-BCPs can be made by direct ATRP of IL monomers and uncharged monomers in scalable quantities with excellent control and purity. Since then, we have set out to further explore the self-assembly behavior and expand the known phase diagram for the linear diblock copolymer architecture of this class of materials. We believe a detailed understanding of how the densely charged PIL block influences BCP phase behavior even in these simple systems will add to the foundation from which more complex phase behavior of PIL-BCPs can be investigated, such as higher-order, linear BCPs (ABA, ABC, ABAC, etc.),^{20–23} small molecule-doped BCPs,²⁴ pom-pom BCPs,²⁵ or BCPs incorporated into unusual matrices.²⁶ Thus, in contrast to the ROMP/norbornene monomer system studied initially where the focus was on PIL-BCPs with a majority volume fraction in the non-ionic block, we expand the phase diagram to the PIL-rich region ($f_{PIL} > 0.5$). Herein, we present the melt-state phase behavior of these alkyl-imidazolium-containing styrenic diblock BCPs made by sequential ATRP as function of (a) PIL block volume fraction and (b) different alkyl groups on the imidazolium of the PIL block.

3.3 Results and discussion

3.3.1 Synthesis and characterization of PS-PIL BCPs

PS-PIL BCPs (1) were synthesized via the sequential ATRP procedures as described in our previous report; this is briefly outlined in figure 3.1.¹⁴ In this two-step sequential copolymerization, polystyrene (3) of controlled molecular weight and low Đ (dispersity) was first synthesized as a macroinitiator for the second PIL block. The imidazolium-based PIL block was then formed upon addition of the appropriate amount and type of IL monomer (2). The BCPs synthesized were targeted to contain approximately 50 total repeat units while varying the relative volume fraction



Figure 3.1: Synthesis and structures of the PS-PIL BCPs made via sequential ATRP in this study. of the PIL block. The block composition ratio and molecular weight of each PS-PIL BCP (**1**) were confirmed by ¹H NMR analysis (see the Supporting Information in Appendix B).¹⁴ The average degree of polymerization of the PS blocks were determined by end-group analysis using the TMS fragment of the initiator. The PS-PIL ratios for each BCP were calculated by integrating and comparing distinct ¹H NMR signals indicative of unique protons associated with the respective PS and PIL repeat units. The degree of polymerization of the each PIL block was then determined based on the calculated block composition ratios and PS degree of polymerization. Consequently, the number-average molecular weight (*M*_n) values for BCPs **1** could be calculated by multiplying the degree of polymerization of each block by the molecular weights (MWs) of the respective repeat units (see table 3.1 and the Supporting Information in Appendix B).

3.3.2 Overview of phase behavior

In a prior publication,¹⁴ we reported the synthesis of several styrenic-imidazolium PS-PIL BCPs with varying R-group functionality (methyl, *n*-butyl, *n*-decyl) on the imidazolium block, and we included a preliminary assessment of the role of the R group on the ability of these BCPs to phase

BCP	n	m	f_{PIL}^{a}	<i>М</i> _n ь	d ₁₀₀ *	Morphology	Observed q^*/q_{100}^{c}
				(g mol ^{−1})	(nm)		
R = methyl							
1a ^d	15	35	0.89	18600	16.6 ^e	S _{LLP}	form scattering
1b ^d	20	30	0.85	16700	16.5 ^e	S _{BCC}	√2, √4, √6, √8, √10, √12, √14, (√16)
1c ^d	25	25	0.79	14900	12.7	Hex (weakly ordered)	√1, (√3), √4, √7, (√9), (√12), (√13)
1d	30	18	0.70	12000	14.8	Hex (weakly ordered)	√1, √3, √4, √7, (√9), (√12), (√13)
1e	34	15	0.64	11000	16.7	Hex	√1, √3, √4, √7, (√9), √12, √13
1f	36	14	0.61	10800	16.7	Hex	√1, √3, √4, √7, (√9), √12, √13
1g	37	13	0.58	10400	15.5	Hex (weakly ordered)	√1, √3, √4, √7, (√9), (√12), (√13)
1h	40	12	0.55	10200	14.2	Lam (weakly ordered)	√1, √4, √9
					15.7	Hex (weakly ordered)	√1, √3, √4, (√7), (√9), (√12), (√13)
1i	34	10	0.54	8600	13.8	Lam	√1, √4, √9
					15.7	Hex	√1, √3, √4, (√7), (√9), √12, (√13)
1j	40	10	0.50	9200	13.0	Lam	√1, √4, √9
1k	40	9	0.48	8700	12.5	Lam	√1, √4, √9
11	40	8	0.45	8300	12.3	Lam	√1, √4, √9
1m	45	5	0.31	7400	11.7	Lam	√1, √4, √9
					11.0	Hex	√1, √3, √4, (√7), (√9)
R = <i>n</i> -butyl							
1n ^d	15	35	0.90	20100	16.3 ^e	S _{LLP}	form scattering
10 ^d	20	30	0.86	18000	15.6 ^e	S _{BCC}	√2, √4, √6, (√8)
1p ^d	25	25	0.80	15900	11.3	Hex (weakly ordered)	√1, (√3), (√4), (√7), (√9),
1q	30	18	0.71	12800	14.5	Hex	√1, (√3), √4, √7, (√9),
1r	34	14	0.63	11100	15.0	Hex	√1, √3, √4, √7, √9, √12, √13
					15.3	Gyr	√6, √8, (√14), (√16), √20, √22, √24, √26,
					(d ₂₁₁)		(√30), (√32), (√38), (√40), √42, √46,
1e	40	٩	0 / 9	9100	12.0	lam	$(\sqrt{48}), (\sqrt{50})$
15	40	5	0.49	7600	12.0	Lam	
$\mathbf{R} = \mathbf{r}_{\text{approx}} \mathbf{r}_{\text{b}} \mathbf{r}$							
1	35	15	0.65	11500	15.4	Hey	$\sqrt{1}$ ($\sqrt{3}$) $\sqrt{4}$ $\sqrt{7}$ ($\sqrt{9}$) ($\sqrt{12}$) $\sqrt{13}$
1v	40	10	0.52	9500	13.2	lam	<u>ν</u> 1 ν/4 ν/9
	-0	10	0.02	0000	14.0	Hex	$\sqrt{1}$ $\sqrt{3}$ $\sqrt{4}$ $\sqrt{7}$ $(\sqrt{9})$ $(\sqrt{12})$ $(\sqrt{13})$
B = n-hexvl							
1w	20	30	0.86	18800	13.9	none	none observed
1x	25	25	0.80	16600	10.6	none	none observed

Table 3.1: Morphological characteristics of PS-PIL BCPs 1a-t at room temperature after thermal annealing

^a f_{PIL} determined by $f_{\text{PIL}} = (M_{n,\text{PIL}} \circ \rho_{\text{PIL}}^{-1})/([M_{n,\text{PIL}} \circ \rho_{\text{PIL}}^{-1}] + [M_{n,\text{PS}} \circ \rho_{\text{PS}}^{-1}])$ where ρ_{PS} (0.969 g cm⁻³) and ρ_{PIL} (1.06 g cm⁻³, calculated from SAXS data of sample **1j**) are taken as nominal densities at 140 °C.²⁷ ^b Calculated based on n and m values obtained from ¹H NMR analysis and rounded down to nearest hundred g mol⁻¹.¹⁴ ^c Permitted reflections for the specified morphology; those not observed are listed in parentheses. ^d Data integrated from previous work.¹⁴

separate. Depending on the R-group, molar ratios of the IL block between 50–70% were observed to form spherical or cylindrical morphologies (methyl and *n*-butyl), or failed to phase separate (*n*-decyl). This revealed several intriguing characteristics about this polymer system. Specifically, R-

group length significantly affected the ability of the PS-PIL BCPs to phase separate, and a much wider compositional range of samples would need to be produced to understand the phase behavior of these polymers. Due to the lack of observable phase separation with the series of *n*-decyl-substituted BCPs previously studied,¹⁴ the focus of our phase behavior investigation was narrowed to BCPs with R-groups containing up to six carbons, with an emphasis on those with terminal methyl and *n*-butyl groups.

Gel permeation chromatography (GPC) data of the PS macroinitiators (see table B1 in Appendix B) in this study show fairly narrow Đ (1.08 to 1.15), with no observable correlation between macroinitiator Đ and ability to phase separate. Modification to our GPC system according to previously reported methods²⁸ proved unsuccessful and Đ of polymers **1a–1x** could not be calculated due to significant column interactions (see Supporting Information, Appendix B, section B.6). Even though the Đ of our final BCPs were unable to be measured, one of the many reasons ATRP was chosen as the synthetic method for this study is its ability to produce relatively narrow Đ in polymers, PILs included.^{8,13,14,28,29}

Small-angle X-ray scattering (SAXS) was used as the primary characterization method to describe the phase behaviour of various alkyl-substituted BCPs, polystyrene-b-poly(1-(4vinylbenzyl)-3-alkyl (methyl, *n*-propyl, *n*-butyl, *n*-hexyl) imidazolium bis(trifluoromethanesulfonyl)imide) (PS-MePIL, PS-PrPIL, PS-BuPIL, PS-HxPIL). All samples were thermally annealed in the bulk under vacuum in the sample chamber of the SAXS instrument, with data collection typically taken every 50 °C, starting at room temperature. All samples were stepped to 175 °C, subjected to an annealing period between 30 min and 2 h, and then stepped back down to room temperature (see the full temperature-dependent SAXS data presented in Appendix B). A maximum temperature of 175 °C was chosen as a compromise between providing the polymer chains sufficient mobility to achieve at/near equilibrium phase behavior in a short amount of time (~15 min for most samples) and limiting the potential for thermal degradation (see figure B4 – B6 in Appendix B). This temperature is also well above the observed

 T_g 's of the material (see figure B7 in the Appendix B) at ~80 °C for the PS block and ~32 °C for the MePIL block. Just under half of the samples showed ordered phases emerging at lower temperatures such as 100 °C or 125 °C, but all samples were annealed at 175 °C for consistency and efficiency.

Polymer phase behavior is best described by three fundamental parameters: (1) the volume fraction of one of the blocks (f), (2) the effective degree of segregation (χN), and (3) the conformational asymmetry (ϵ). Conformational asymmetry, while not shown explicitly in the phase diagram, accounts for the space-filling differences in the blocks of a BCP and routinely manifests itself as a shift in the phase boundaries of the phase diagram (such that symmetry around f = 0.5is lost).^{30,31} More recently, the parameter Γ was introduced to describe the strength of electrostatic cohesion between charged groups in a PIL block, and can also cause shifts (both horizontally and vertically) in the phase diagram.³² In general, a BCP phase diagram maps out the specific equilibrium morphology at each composition and segregation strength for which the overall free energy of the BCP is minimized.³³ Generally, f would be calculated using bulk homopolymer densities to determine the relative ratio of block volumes, however, in this study the bulk homopolymer density of the largely unstudied alkyl-PIL blocks were unknown. However, it was possible to estimate the PIL block densities using characteristics of the SAXS diffraction data (see Lamellae section below for further explanation), allowing block compositions to be determined. χ N is the product of χ , a Flory-like interaction parameter and N, the degree of polymerization. χ represents the free energy penalty (i.e. energy increase) associated with the interaction energy produced upon mixing of dissimilar repeat units.³³ While a typical phase diagram will present phase behavior data as χN versus composition (f), several factors that we, and others, have encountered with other PIL BCPs (e.g., an inability to disorder even low molecular weight PS-PIL BCPs at experimentally feasible temperatures) precluded simple determination of the value of $\chi_{PS/PIL}$ for these systems of study.^{9,15} Despite being unknown, the value of χ is largely considered to be independent of f for any A/B BCP pair. Additionally, as x is inversely related to temperature,

and all samples have a similar value of N (~50 repeat units) by synthetic design, reporting phase behaviour as a function of temperature (*T*) vs. composition (*f*) achieves a similar (although inverted) outcome as using a traditional χ N vs. *f* plot.

In figure 3.2, we report a summary of our study of phase behaviour results of the methylfunctionalized series of PS-MePIL BCPs, in which we were able to observe three out of the four classical diblock copolymer morphologies: Lam (data represented as square symbols in figure 3.2), Hex (hexagon symbols), and S_{BCC} (circle symbols) organized on a body-centered cubic lattice. Samples that never achieved any high degree of order (or adopted a liquid-like packing rather than an organized lattice) are represented as open circle symbols; and samples that were initially weakly ordered but became well-ordered upon thermal annealing (and remained ordered during cooling) are represented as half-filled symbols. In the two areas on either side of the



Figure 3.2: Phase diagram for methyl-substituted PS-PIL BCPs **1a–m** as a function of volume fraction of the PIL component. Open data points represent weakly ordered samples, filled data points represent highly ordered samples, and half-filled data points represent samples that ordered upon reaching an appropriate annealing temperature and remained ordered in that phase upon cooling.

experimental phase diagram where the Gyr morphology would traditionally appear for a diblock copolymer, a persistent coexistence of Lam and Hex (diamonds in figure 3.2) was observed instead.^{30,34–36} More compositionally asymmetric samples adopting a liquid-like packing of either cylinders or spheres provided the general location for the order-to-order (Hex to S_{BCC}) and order-to-disorder (S_{BCC} to S_{LLP}) phase boundaries on the high f_{PIL} side of the phase diagram. However, we were unable to observe any of the samples in this series in a completely disordered state.

Figure 3.3 shows the effect of modifying the R-group functionality of the dangling imidazolium unit (from methyl to *n*-butyl) on phase behaviour, and consequently, on decreasing the segregation strength between blocks. In a prior study, we were able to observe the Gyr morphology in coexistence with Hex in a series of metal-containing PIL-BCPs,¹¹ leading us to believe that indeed, the Gyr morphology should be observable in these imidazolium IL-containing



Figure 3.3: Phase Diagram of phase separating, n-butyl-substituted PS-PIL BCPs **1n–t** with respect to volume fraction of the PIL component. Open data points represent weakly ordered samples, filled data points represent highly ordered samples, and half-filled data points represent samples that ordered upon reaching an appropriate annealing temperature and remained as such upon cooling. Data for samples with f_{BuPIL} greater than 0.8 are integrated from previous work.¹⁴

BCPs, as well. However, its absence in the methyl-functionalized series was likely symptomatic of the high degree of segregation intrinsic to the system, notorious for thwarting Gyr formation.³⁷ However, by substitution of the methyl substituent with an *n*-butyl group, we found strong evidence for the emergence of a Gyr phase (in coexistence with Hex) in PS-PIL BCP **1r**. The full phase behaviour of the *n*-butyl series is discussed in detail below.

It is also of note that for all samples that formed ordered morphologies upon thermal annealing, no ordered-phase to ordered-phase transitions (OOTs) within any single sample were observed throughout the experimentally accessible range of temperatures examined (from room temperature to as high as 240 °C). That is, only one morphology (or persistent coexistence of morphologies) was observed for each individual sample. All morphologies developed through annealing at high temperature remained unchanged once cooled, even when annealed at lower temperatures just above the T_g of the PS block. In addition, the inability of these BCPs to disorder prior to thermal decomposition made it difficult to definitively classify any observed morphologies as true equilibrium phases, or directly determine the value of $\chi_{PS/PIL}$ from SAXS alone.^{15,38–40} However, given the extremely large temperature window in which they persisted once ordered, it is likely that most of the morphologies observed are in their equilibrium state; and for those that are in a persistent metastable state, the kinetics of any OOT's are too prohibitively slow for the timescale of this study.

While analysing our earlier norbornene PIL-BCP system, we surmised that the inability to disorder most of these polymer samples without inducing decomposition provided strong evidence for an extremely high segregation strength (χ N) between the blocks, despite the low degrees of polymerization (where N, or n+m ≤ 50). It is possible that χ is even higher in this study, as none of the BCPs studied showed any evidence of disordering, while two samples in the norbornene system either approached or even achieved disorder.

Below, we present a more detailed analysis of each morphology identified using SAXS data as a function of temperature for every PIL-BCP sample in this study. Each morphology-

specific discussion refers to the methyl-substituted PIL-BCPs only, with a discussion of the *n*-butyl, *n*-propyl, and *n*-hexyl PIL-BCPs, respectively, following.

3.3.3 Lamellae

SAXS analysis of BCP samples **1j–I**, from 45 to 50% by volume of PIL, exhibited evidence of the Lam morphology, as shown in figure 3.4. Upon thermal annealing, all of these samples showed higher-ordered SAXS diffraction reflections at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{9}$ (where q^* is the position of the primary scattering wave vector, q_{100}), consistent with the calculated allowed reflections⁴¹ for this classic diblock copolymer morphology (solid inverted triangle symbols in figure 3.4). These three samples, with approximate M_n values ranging from 8300 g mol⁻¹ (**1I**) to 9300 g mol⁻¹ (**1j**) were found to have small but steadily increasing domain spacings (d_{100} increasing from 12.3 to 13.0 nm, respectively) as is anticipated with a MW increase and the shift to higher PIL block copolymers like polystyrene-*b*-poly(vinylpyridine), degrees of polymerization of nearly double (N $\sim 95 - 105$) are required to achieve similar domain spacing values.⁴² This behaviour underscores the very extended nature of the ionic PIL block in the melt and its strong predilection for adopting a stretched chain conformation during self-assembly.

The near extinction of the even-order reflection $q/q^* = \sqrt{4}$ in sample **1j** suggests nearly symmetrical block volumes, a phenomenon observed previously with our norbornene-based PIL-BCPs and with the *n*-hexyl-functionalized styrene-imidazolium BCPs studied by Mahanthappa and coworkers.^{9,15} Using the bulk homopolymer density of polystyrene of 0.969 g cm⁻³ (at 140 °C)²⁷ and setting the relative volumes of the two blocks to 0.50, we were able to calculate an approximate density for the MePIL block of 1.06 g cm⁻³. This value was then used in conjunction with experimentally determined M_n values of each block (calculated from ¹H NMR data) to estimate the volume fraction of PIL for each PIL-BCP in this series. Interestingly, the difference between samples **1j** and **1k**, in which the $q/q^* = \sqrt{4}$ peak is suppressed, and clearly present,



Figure 3.4: Room temperature (25 °C) SAXS data collected post-annealing for lamellae-forming (Lam) PS-MePIL BCPs **1j–I**. Each sample was subjected to a two-hour annealing (*in vacuo*) at 175 °C. Solid inverted triangles represent the calculated values of allowed SAXS reflections (based on q*) for a Lam morphology, found at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{9}$ (where q^* , the primary scattering wave vector, is q_{100}). Volume fractions were calculated from sample **1j**, where nearly complete suppression of the even-order reflection at $q/q^* = \sqrt{4}$ indicates equal volumes of either block ($f_{PIL} \approx 0.5$)^{9,15} and allowed for estimation of the bulk homopolymer density of MePIL.

respectively, is only a single (on average) added MePIL repeat unit. Thus, even though suppression of the $q/q^* = \sqrt{4}$ is not absolute in **1j**, our estimation of the PIL block density is believed to be reasonably accurate given the apparent sensitivity of the $q/q^* = \sqrt{4}$ peak extinction to very small changes in BCP composition.

3.3.4 Hexagonally packed cylinders

In the region spanning $f_{\text{PlL}} = 0.58$ to 0.79, SAXS data of samples **1c-g** with M_{n} values ranging from 10400 to 14900 g mol⁻¹ showed evidence of the hexagonally-packed cylinder (Hex) morphology with all samples exhibiting multiple higher order SAXS reflections at allowed q/q* ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, and $\sqrt{13}$ (shown as hollow inverted triangle symbols in figure 3.5). This transition in phase behaviour in the PIL-rich region from a Lam to Hex phase just beyond $f_{\text{PIL}} = 0.5$ leads to the construction of a highly asymmetrical phase diagram. In the PS-rich region, however, we do not observe a Hex phase emerging until $f_{PIL} = 0.31$ (see next section for discussion of these coexistence regions). One way to quantify the asymmetry is with the conformational symmetry ratio, ϵ , which describes the inequality in space-filling characteristics of each block, where an $\epsilon \neq 1$ indicates a conformationally asymmetric polymer. A significant shift in the phase boundaries here suggests that the ϵ value of this BCP is significant; however, we are unable to calculate its value without the statistical segment length (b) of each block, which to our knowledge, has not been determined for any styrenic imidazolium-based PIL.^{30,35,39,43} We assume the shift in phase boundary occurs due to a much larger statistical segment length in the MePIL block, itself a product of an extended conformation of the main chain associated with both steric and electrostatic repulsion among the bulkier cationic imidazolium side groups.³⁹ When the PIL block occupies the majority of the volume, it encourages the interface between the PS and MePIL blocks to curve towards the PS domain, initiating a shift towards the PS cylinder phase at lower volume fractions of PIL than would otherwise be predicted for a conformationally symmetric polymer of $f_{PIL} > 0.5$.^{30,35} This effect is reminiscent of phase diagrams of other highly asymmetric block copolymers with an $\epsilon > 2$, such as poly(ethylene oxide)-b-polyisoprene (PEO-PI)⁴³ and the "brush-like" diblock copolymer poly(1,2-octylene oxide)-b-poly(ethylene oxide) (POO-PEO).34

Alternatively or concurrently, electrostatic cohesion or Coulomb interaction strength (Γ) between charged repeat units on the PIL block could be contributing to the asymmetry of this



Figure 3.5: Room temperature SAXS profiles (25 °C) collected post-anneal for hexagonally packed cylinder (Hex) forming PS-MePIL BCPs **1c–g**. Samples **1d–g** were subject to a two-hour annealing (*in vacuo*) at 175 °C, while sample **1c** was annealed for 30 min. Open inverted triangle symbols represent the calculated values of allowed SAXS reflections for a Hex morphology, at q/q^* ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, and $\sqrt{13}$ (where $q^* = q_{100}$). Samples **1e** and **1f** exhibit a high degree of order (left cartoon above), while the rest, **1c**, **1d**, and **1g** more closely match a liquid-like packing of cylinders (right cartoon above).

phase diagram. Theoretical work by Olvera de la Cruz and coworkers³² indicates that charged groups embedded into one block of a BCP can shift phase boundaries towards lower volume fractions of that charged block in the same way as conformational asymmetry. Higher values of Γ encourage nanostructure formation in a charged BCP with values of χ N and f_{PIL} that are low enough to cause disorder in an uncharged polymer. These phase diagrams are the most skewed

at values of $\chi N \leq 20~30$. At higher values of χN , the order of the phase boundaries more closely resemble those of an uncharged BCP system, albeit still shifted towards lower f_{PIL} , much like the phase diagram we have presented here. Whether the observed shifts in phase boundaries in our system are due to large values of ϵ , Γ , or some combination thereof, there is still little doubt that the χN parameter of our PS-PIL system is very high.

In this region of the phase diagram, we observed samples (**1c**, **1d**, **1g**) that experienced some difficulty in forming a highly ordered hexagonal packing, instead exhibiting more of a liquid-like packing of cylinders, even after two full hours of annealing at 175 °C (figure 3.6). In the norbornene-imidazolium system previously studied, this weakly ordered morphology was easily transformed into a Hex phase through thermal annealing.¹⁵ Because there is nothing thermodynamically favourable about weakly ordered cylinders, we expect that the observed lack



Figure 3.6: Temperature-dependent SAXS profiles for cylinder-forming samples **1d** and **1f** illustrating the difference in scattering profiles for a sample that formed highly-ordered, periodic hexagonal nanostructure very rapidly (**1f**), and a sample that phase separated rapidly but remained weakly ordered even after extended thermal annealing (**1d**).

of periodicity in samples **1c**, **1d**, and **1g** partially stems from extremely slow ordering kinetics as a result restricted chain mobility. This occurs when minority component chains experience difficulty diffusing through the majority matrix due to presumably high values of χ .^{44,45} Additionally, their location in regions of f_{PIL} close to the Hex/S or Hex/Lam phase boundaries, may also be influencing their driving force to exhibit a strong degree of order.⁴⁴

3.3.5 Coexistence of lamellae and cylinders

Three samples, **1h**, **1i**, and **1m**, with compositions of 0.55, 0.54, and 0.31 f_{PIL} (and M_n values of 10300, 8700 and 7400 g mol⁻¹) respectively, exhibited coexistence of Lam and Hex phases that persisted throughout the annealing process. In addition to two distinct q^* values (where q^* , the primary scattering wave vector, is q_{100} for both Lam and Hex phases), all samples showed at least one uniquely identifiable higher-order SAXS reflection for each morphology. Specifically, scattering peaks at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{9}$ for the Lam phases, and $\sqrt{1}$, $\sqrt{3}$, and $\sqrt{4}$ for the Hex phase (figure 3.7) could be typically identified.

Another interesting effect of the conformational asymmetry of these PIL-BCPs appears to manifest itself in the relative positions of q_{HEX}^* and q_{LAM}^* in the two coexistence regions on either side of the Lam phase window. That is, while q_{HEX}^* is less than q_{LAM}^* for coexistence samples in the majority PIL region of the phase diagram, q_{HEX}^* is greater than q_{LAM}^* in the majority (non-ionic) PS region. The latter is consistent with the positioning of q_{HEX}^* and q_{LAM}^* in our previous study of norbornene based PIL BCPs, where the focus was limited to the investigation of BCPs with the non-ionic block comprising the majority component. It is not clear whether or not the inversion in q^* position between the two coexistence regions that span opposite sides of the lamellar window constitutes a general phenomenon in strongly segregated, conformationally asymmetric, and highly charged systems showing coexistent phases.



Figure 3.7: Post-annealing SAXS data collected at room temperature (25 °C) for PS-MePIL BCPs 1h, 1i and 1m showing a persistent coexistence of the Lam and Hex phases. Samples 1g and 1j are included in this plot as BCPs that exhibit purely Hex and Lam morphologies, respectively, near the phase border. Samples 1h and 1i were subject to a 2-h annealing period (*in vacuo*) at 175 °C, while sample 1m was annealed for 8 h. Solid inverted triangle symbols represent the calculated positions of allowed SAXS reflections for a Lam morphology, at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{9}$, and open inverted triangles represent the calculated positions of allowed SAXS reflections for a Hex morphology, at q/q^* ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, and $\sqrt{13}$ (where $q^* = q_{100}$).

For all diblock copolymer morphologies except for Lam (which has both uniform domain thickness and constant mean curvature), there is a struggle between the need to have constant mean curvature to minimize interfacial tension between the blocks, and uniform domain thickness to maximize the entropic nature of chain stretching. This is known as packing frustration, because it is impossible to satisfy both requirements completely when there is enough asymmetry to cause interfacial curvature.^{46–48} Here, the bulky, space filling, and highly charged nature of the PIL block forces interfacial curvature towards the PS domains almost immediately after the PIL block

becomes the majority component by volume ($f_{PIL} > 0.5$). Early adoption of curvature appears to be in response to a need to relieve packing frustration felt particularly by the relatively short and bulky PIL blocks. Even though the stretching entropy is slightly reduced when the PS domains are forced to stretch to fill to the centre of the relatively large cylindrical domains, gains are made in the relaxation of the PIL chains through their larger interfacial area per chain. The opposite is true when PS is the majority component; PS does not experience space constraints the way the PIL block does, so we observe the Lam phase over a wider range of *f* and smaller spacing between PIL cylinders on this side of the phase diagram.⁴⁹

None of these three samples' SAXS patterns fit to any of the complex morphologies such as Gyr or the metastable hexagonally perforated lamellae. Given the apparent stability and small window of this coexistence between the Lam and Hex phases, it is probable that a complex morphology does not experimentally exist for this system. If this is the case, the most reasonable explanation is the ostensibly large χ N values, even at high temperature. Polymers with low χ N can adopt a Gyr morphology because the penalty for non-constant mean curvature is still more favourable relative to the entropic advantage of having a minority component with nearly uniform domain thickness.^{47,48,50} For a diblock copolymer with larger χ N values, morphologies in which the mean curvature must deviate significantly from a single constant value (characteristic of the Gyr phase) experience an increase in packing frustration that challenges the ability of these phases to remain experimentally stable.⁴⁹

While conformational asymmetry has been shown to affect the locations of phase boundaries, conformationally asymmetric BCPs have been observed to adopt the Gyr morphology, even in the strongly segregated regime around $\chi N \approx 50$, so conformational asymmetry alone cannot account for the absence of this phase.^{30,34,43} In fact, Cochran et al. showed that conformational asymmetry actually increased the width of the theoretical Gyr phase window at high segregations ($\chi N = 40, 80$), albeit the phase window was still extremely narrow.⁵¹ Davidock et al. produced several examples of highly segregated polymers that formed the Gyr

phase with xN values up to 120; however, these polymers were synthesized with anionic polymerization and therefore had very narrow Đ values.³⁷ Polydispersity has been shown to have significant effects on the location within the phase diagram of BCP morphologies⁵² but also does not inherently discourage the formation of complex morphologies. Self-consistent field theory (SCFT) predicts the existence of a Gyr phase window for AB diblock copolymers (with D of the A block between 1.0 and 2.0, and a monodisperse B block). But as polydispersity increases, that phase window narrows significantly. Above $\chi N \approx 20$, the Gyr phase window is virtually nonexistent on the more asymmetrical side of the predicted phase diagram for the most polydisperse model.⁴⁶ In 2005, Lynd and Hillmyer concluded that introducing polydispersity into a diblock copolymer melt causes it to relieve packing frustration much in the same way that conformational asymmetry does. That is, increased polydispersity in the minority component will encourage transitions to higher mean curvature (Lam \rightarrow Hex), while increased polydispersity in the majority component will push the system to adopt decreased overall curvature (Hex \rightarrow Lam). Indeed, they were able to observe the Gyr morphology in PEP-PLA (poly(ethylene-alt-propylene)-bpolylactide) BCPs in the weakly segregated regime ($\chi N \approx 10$ to 20) with \oplus of the respective blocks as large as 1.36 and 1.67 for one polymer.⁵³ Conversely, Bendejacg et al. studied a series of highly segregated ($\chi N > 50$) block copolymers and BCP/homopolymer blends with high D that exhibited persistent coexistence of Lam and Hex phase in lieu of a Gyr phase.⁵⁴ Another consideration is the presence of charged groups along the polymer backbone. Balsara and coworkers studied a series of poly(styrenesulfonate-b-methylbutylene) (PSS-PMB) BCPs with nearly symmetric compositions but with varied N and sulfonation levels.⁴⁰ Interestingly, even with nearly 50% charged groups on the PSS block, they were able to observe the formation of the Gyr morphology and easily accessible disorder regions for polymers with N = 54 and χ N values in the 10–20 range. For the polymers in this study with significantly larger N (and therefore larger χN), persistent coexistence regions without accessible disorder points were observed. Generally, increasing xN and the fraction of charged groups within the PSS domains of similar length PSS-

PMB BCPs caused morphologies with increased curvature towards the non-charged block and increased the chance of observing coexistent phases instead of Gyr.

Although we suspect that the polydispersity of this series of PIL-BCPs is not as significant as those mentioned previously, the compounded effect of some polydispersity, high charge density and electrostatic cohesion, and substantial conformational asymmetry is playing a major role in the observed morphology in the region of extremely high χ N that our methyl-functionalized PIL-BCPs appear to populate.

Even with a small amount of polydispersity within a polymer sample, self-fractionation during phase separation allows us to explain how a persistent coexistence of two very different morphologies lowers the free energy of the system enough to be preferable to the formation of Lam, Hex, Gyr phases or any metastable complex morphology alone. During the annealing process, more compositionally symmetric chains separate from more compositionally asymmetric chains to form Lam or Hex domains, respectively. SCFT models that allow distinct population distributions for each morphology have accounted for such behavior.⁴⁶ This phenomenon is only advantageous for a highly segregated sample; fractionation into discrete domains causes a significant reduction in system entropy, but this effect is negated by the overwhelming relief of packing frustration achieved through Lam and Hex phase coexistence.⁴⁶ This is a plausible explanation for the difference in primary scattering peak (q^*) resolution between samples **1h** and 1i, which have nearly identical volume fractions. Sample 1h, which is about 20% longer than 1i, appears to have a compositional makeup (e.g., compositional polydispersity) or reduced mobility⁴⁴ that produces a diminished desire or ability to fractionate. This would lead to a smaller difference in domain spacing, less distinction between coexisting domains, and more weakly defined scattering patterns of both morphologies. Additionally, fractionation accounts for the structure factor extinction of the $\sqrt{4}$ Lam peak seen in sample **1i**, particularly in figure 3.8, after extended annealing. The average volume fraction of PIL for 1i is 0.54, but if the more symmetrical chains

that separate to form the Lam domain were much closer to 0.50 then the $\sqrt{4}$ peak would disappear accordingly, as seen with sample **1***j*.

Sample **1i** was subject to extended thermal annealing between 125 °C and 175 °C in a vacuum-sealed ampule and placed in an oil bath for a total of 1 month, as a means to investigate the stability and equilibrium nature of this phase coexistence (figure 3.8). Within the first several hours of annealing, a shift in the prevalence for the Hex phase is apparent by the increase in intensity of q^*_{HEX} and the peaks at $q/q^*_{\text{HEX}} = \sqrt{3}$ and $\sqrt{4}$, coupled with a slight decrease in the $q/q^*_{\text{LAM}} = \sqrt{4}$ and $\sqrt{9}$ peaks shown by comparing figures 3.8a and 3.8b. Beyond 6 h of annealing, the differences from 6 h to 1 month (figures 3.8b and 3.8c) are very subtle, if not negligible,



Figure 3.8: Room-temperature SAXS data for sample **1i** showing persistent coexistence of Lam (solid inverted triangle symbols) and Hex (open inverted triangle symbols) after extended thermal annealing. Initially, the Lam phase dominates; but after 6 h of annealing at 175 °C, the Hex phase become more prevalent. After 1 month of thermal annealing under vacuum between 125 °C and 160 °C, a further shift toward the Hex phase is minimal, indicating that coexistence in this sample is persistent.

suggesting that at- or near-equilibrium phase behaviour is achieved within the first day of annealing, and that indeed, the coexistence phase is persistent.

3.3.6 Spheres

In the most compositionally asymmetric region of the phase diagram ($f_{PIL} \ge 0.85$), two samples¹⁴ showed SAXS patterns indicative of a sphere-based morphology. Upon thermal annealing, sample **1b** developed multiple higher-order SAXS reflections at q/q^* ratios (indicated as inverted triangle symbols with a strikethrough in figure 3.9) of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, etc., where q^* is the primary scattering wave vector, q_{100} , that are consistent with spheres arranged on a body-centred cubic lattice (S_{BCC}).¹⁵ As is expected with S_{BCC}, q_{100} is absent due to the reflection conditions of the *Im3m* space group. The lattice constant ($a = d_{100}$) for samples **1a** and **1b** can be easily calculated from the first observed q value (q_{110}) giving values of 16.6 and 16.5 nm, respectively. The broad,



Figure 3.9: Post-annealing SAXS data at room temperature (25 °C) for sphere forming PS-MePIL BCPs **1a** and **1b**. Samples **1a** and **1b** were subject to a 30-min annealing period (in vacuo) at 175 °C. Open inverted triangles with a strikethrough represent the calculated allowed SAXS reflections for a sphere morphology arranged on a BCC lattice, at q/q^* ratios of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$ and $\sqrt{16}$ (where q^* , the primary scattering wave vector, is q_{100}). Sample **1a** exhibits a more liquid-like packing of spheres (S_{LLP}), as opposed to the BCC lattice observed for **1b**.

form-factor scattering seen with sample **1a** (and with **1b** prior to annealing at 175 °C) is routinely observed for spherical micelles that persist with a liquid-like disordered packing (LLP), or S_{LLP} . The inability of spherical domains to order on a BCC lattice is typically due to compositional fluctuations near the ODT, sphere polydispersity, and limited chain mobility. The latter often a consequence of chain entanglements and slow chain diffusion kinetics.¹⁵ As a result, S_{LLP} is often observed in samples with volume fractions that theoretically fall in the BCC range.^{55,56} The persistence of liquid-like spherical domains in sample **1a** across the full experimental temperature range might imply that an *f* value of 0.89 PIL approaches the ODT but we are unable to pinpoint an actual disorder transition for this system.

3.3.7 R-group modification

In a preliminary study, we indirectly determined that R-group modification had a sizable impact on the interaction parameter χ between the PS and PIL blocks based on two observations; samples with *n*-butyl functionality but comparable block ratios had smaller *d*-spacings than their methyl counterparts, and the *n*-decyl-substituted blocks appeared to be miscible enough with the PS blocks to prevent phase separation altogether.¹⁴ To investigate this effect further, we have prepared four additional *n*-butyl-functionalized BCPs (PS-BuPIL). The post-annealing roomtemperature SAXS data for all seven samples are summarized in figure 3.10. In this series we observe all four classic diblock copolymer morphologies; S_{BCC} (**10**), Hex (**1q** and **1r**), Gyr (**1r**, in coexistence with Hex, represented as stars in figure 3.3), and Lam (**1s** and **1t**), as well as two samples (**1n** and **1p**) that showed no higher order SAXS reflections but we suspect have adopted a liquid-packing of spheres and cylinders, respectively, based on their relative positions in the phase diagram (figure 3.3).

We were unable to observe any structure factor extinction of the even-ordered reflections – such as the elimination of the $q/q^* = \sqrt{4}$ peak in sample **1j** – for the series of *n*-butyl-functionalized PIL BCPs, and therefore unable to estimate the density of the BuPIL block based



Figure 3.10: Post-annealing, room temperature SAXS profiles for *n*-butyl-substituted PS-PIL BCPs **1n–t**. The allowed reflections for each morphology shown are represented as inverted triangles, including the possible emergence of the Gyr morphology (with expected peak locations denoted by half-filled triangle symbols above **1r** at q/q^* ratios of $\sqrt{6}$, $\sqrt{8}$, $\sqrt{14}$, $\sqrt{16}$, $\sqrt{20}$, etc. where q^* , the primary scattering wave vector, is q_{100}). The possible emergence of the Gyr morphology suggests a lower χ value n the *n*-butyl-substituted PS-PIL BCPs than that associated with the methyl-substituted PS-PIL BCPs.

purely on SAXS evidence. To build a phase diagram using the volume fraction of the BuPIL block then, it was necessary to estimate the PIL block density using some known density values of similar block architectures, namely our density value of 1.06 g cm⁻³ for the MePIL block and Mahanthappa and coworkers' value of 1.096 g cm⁻³ for the HxPIL block.⁹ It is reasonable to assume that our PIL block with *n*-butyl functionality would have a density falling between that of the methyl- and *n*-hexyl-functionalized polymers; and therefore, we estimate the block density of the BuPIL at 1.08 g cm⁻³. This value was used to calculate the f_{PIL} values (listed in table 3.1) for figure 3.2.

Even though we were unable determine a quantitative value for χ , we believe we observe a significant enough shift with *n*-butyl R-group modification such that the Gyr morphology is able to emerge in coexistence with Hex in sample **1r** after extended thermal annealing (see the Supporting Information, Appendix B). This also affirms that χ (and consequently position within the phase diagram) is indeed tunable using the precisely controlled synthetic methods and selection of R-group previously reported.¹⁴ In this case, by adding a less polar group (i.e., *n*-butyl) to the end of the PIL repeat unit, we have achieved greater miscibility between the PS and PIL block. This effectively lowers the mixing penalty of the two blocks, relieving packing frustration within the system, and allowing the complex bicontinuous Gyr morphology to begin to form.⁵³

Additionally, we prepared two *n*-propyl-functionalized samples, **1u** and **1v** (which exhibited phase behaviour similar to the PS-MePIL series) and two *n*-hexyl-functionalized samples, **1w** and **1x** (see table 3.1 above and figure B3 of Appendix B for SAXS data) that showed phase separation but no higher-order SAXS reflections. Mahanthappa and co-workers investigated *n*-hexyl-functionalized polymers with identical structure that formed ordered nanostructures; however, they had significantly higher MW, and therefore much higher χ N values.⁹ Those samples were also on the PIL-lean side of the phase diagram (in contrast to the PIL-rich region on which we have focused). These differences make it difficult to glean any morphological insight about samples **1w** and **1x** from their work; but coupled with the observed shift in χ N from the methyl to the *n*-butyl series discussed earlier, it is reasonable to infer that χ N is lowered sufficiently in our *n*-hexyl series of polymers that these systems remain only weakly segregated and have difficulty establishing long-range periodic order.

3.4 Conclusions

We used SAXS data to show that a series of 13 methyl-, 2 *n*-propyl-, 7 *n*-butyl-, and 2 *n*-hexyl-functionalized PIL-BCPs synthesized via direct, sequential ATRP of styrene and styrenic imidazolium/TFSI IL monomers can form ordered, phase separated nanostructures that encompass the entirety of the classic diblock copolymer phase diagram. These ordered nanostructures, once formed through moderate annealing, were shown to remain well-ordered even upon cooling to room temperature. The ability of these PIL-BCPs to remain ordered at ambient temperature, coupled with their easy handling, thermally processable nature, and intrinsic ionic conductivity,⁹ suggests a potential future in solid-state polymer electrolyte membrane technologies.^{1,57}

We were able to observe well-ordered samples forming sphere, cylinder, and Lam morphologies, and notably, one example of a Gyr phase in coexistence with the Hex phase. A Lam-forming sample exhibiting near structure factor extinction of the even-ordered SAXS reflection at a q/q^* ratio of $\sqrt{4}$ provided the means to estimate MePIL block density and consequently volume fraction (*f*) of the MePIL block. The compilation of these data was used to build two phase diagrams – one for the methyl and one for the *n*-butyl series – detailing their phase behaviour with respect to f_{PIL} and temperature. Temperature was used as a proxy for χ N, due to a limited means of quantifying χ in this study. Regardless, we believe the χ N values for the methyl series of PIL BCPs to be substantial based on an observed persistent coexistence of Lam and Hex phases in two separate samples where the Gyr morphology was anticipated. It was also noted that both phase diagrams showed a horizontal shift in phase behaviour due to some combination of electrostatic cohesion (Γ) within the highly charged PIL block and conformational asymmetry (ϵ) between the charged and uncharged blocks.

We also demonstrated the apparent ability to tune χ through modification of pendant alkyl groups on the imidazolium block by showing that the *n*-butyl-functionalized PIL-BCPs are capable

of forming complex morphologies that are not present in the more highly segregated methylfunctionalized system. The bicontinuous network present in the Gyr morphology holds significant potential in many research areas – including conductive thin films,⁵⁸ transport applications,⁵⁹ solidstate batteries,⁵⁷ and organic photovoltaics⁶⁰ – where an ability to achieve charge transport in systems with domain continuity on the nanometer length scale has become so desirable.

3.5 Experimental

3.5.1 Instrumentation

¹H and ¹³C NMR spectra were obtained using a Bruker 300 UltrashieldTM (300 MHz for ¹H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. HRMS (ES) analysis was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado Boulder. Gel permeation chromatography (GPC) was performed using a Viscotek GPC-Max chromatography system outfitted with three 7.5 x 340 mm PolyporeTM (Polymer Laboratories) columns in series, a Viscotek differential refractive index (RI) detector, and an Alltech column oven (mobile phase: THF, 40 °C, 1 mL min⁻¹ flow rate). Molecular weight data obtained on this GPC system were referenced to polystyrene molecular weight standards. SAXS data were collected using a Rigaku SMax3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_a), a Confocal Max-Flux Optic, a Gabriel-type multi-wire area detector (1024 x 1024 pixel resolution), and a Linkam thermal stage. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC 2500 with an RCS90 cooling system.

3.5.2 Small-Angle X-ray Scattering (SAXS) measurements

Copolymer samples were sandwiched between Kapton windows (0.06 mm thick × 10 mm diameter). Before collection of temperature-dependent SAXS data, the sample stage temperature
was equilibrated for 5 min under vacuum, unless otherwise stated. Data were collected under vacuum (~100 mtorr) with exposure times ranging from 60 to 3600 s for all samples. SAXS data were azimuthally integrated from the 2D detector patterns and plotted as logarithmic intensity vs. the scattering wave vector, q, defined as $q = (4\pi/\lambda) \sin(2\theta_B/2)$, where $2\theta_B$ is the angle between the incident and scattered waves.

3.5.3 Materials and methods

1-Bromopropane, 1-bromohexane, sodium hydride, imidazole, 1-methylimidazole, 1butylimidazole, 4-vinylbenzyl chloride, 2-(trimethylsilyl)ethanol, α-bromoisobutyryl bromide, triethylamine, copper(I) bromide, butyronitrile, Dowex 50Wx4 ion-exchange resin, benzoyl peroxide, and *N*,*N*,*N'*,*N''*-pentamethyldiethylenetriamine (PMDETA) were all purchased from the Sigma-Aldrich Co. and used as received. Styrene was purchased from the Sigma-Aldrich Co. and purified by passage through a column of neutral alumina to remove the added radical inhibitor. Lithium bis(trifluoromethylsulfonyl)amide (LiTFSI) was purchased as Fluorad[™] Lithium Trifluoromethane Sulfonimide from the 3M Company. All solvents were purchased from Sigma-Aldrich or Mallinckrodt, Inc. and purified/dehydrated via N₂-pressurized activated alumina columns, and de-gassed. The H₂O used for synthesis was purified and deionized, with resistivity greater than 12 MΩ/cm. All polymerizations were carried out in a dry Ar atmosphere using standard Schlenk line techniques.

Synthesis of 1-propylimidazole

Synthesized as previously reported.⁶¹ Characterization data matched those reported.⁶¹

Synthesis of 1-hexylimidazole

Synthesized as previously reported.⁶¹ Characterization data matched those reported.⁶¹

Synthesis of 1-(4-vinylbenzyl)-3-alkylimidazolium bis(trifluoromethylsulfonyl)amide monomers (2)

These compounds were synthesized using the procedures previously reported.¹⁴ The characterization data of monomers **2** matched those reported.^{14,62,63}

Synthesis of 2-(trimethylsilyl)ethyl 2-bromo-2-methylpropanoate (TMS-EBMP)

Synthesized as previously reported.²⁸ Characterization data matched those reported.²⁸

Synthesis of polystyrene macro-initiators (3)

These compounds were synthesized using the procedures previously reported.¹⁴ In a typical procedure, the desired amount of purified styrene and PMDETA were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was warmed to room temperature and back-filled with Ar, the desired amount of CuBr was then added. The resulting mixture was stirred at room temperature for 30 min, and TMS-EBMP was then injected. The flask was then stirred at 90 °C for 22 h. The contents of the flask were cooled to room temperature, dissolved in acetone, stirred with Dowex 50Wx4 ion-exchange resin for 30 min, and filtered through a short plug of neutral alumina. The resulting solution was then concentrated, diluted with Et₂O, precipitated by adding into MeOH, and filtered to give the desired PS macro-initiator **3** as a white solid. The *DP* and M_n values of BCPs **3** were calculated based on the ¹H NMR end-group analysis (see the Supporting Information, Appendix B).

Synthesis of PS-PIL BCPs 1

These compounds were synthesized using the procedures previously reported.¹⁴ In a typical procedure, the appropriate amount of the desired imidazolium monomer **2**, PMDETA, and butyronitrile were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was warmed to room temperature and back-filled with Ar, the appropriate amount of CuBr was then added. The resulting mixture was then stirred at room temperature for 30 min, and the appropriate amount of the desired PS macro-initiator **3** was added. The flask was then stirred at 90 °C for 24 h. The contents of the flask were cooled to room temperature, diluted with acetone, stirred with Dowex 50Wx4 ion-exchange resin for 15 min, and then filtered through a short plug of neutral alumina. The resulting solution was then concentrated, diluted with

acetone, precipitated by adding into a MeOH/H₂O (3/1 (v/v)) mixture, and filtered. The resulting precipitate was then dissolved in acetone, re-precipitated by adding into hexanes, and filtered to give the desired BCP **1** as a white solid. The synthesis of **1j** is shown below as a representative example. The block compositions and M_n values of PS-PIL BCPs **1** were calculated based on the ¹H NMR analysis (see the Supporting Information, Appendix B).

Example: synthesis of PS-PIL BCP 1j

1-(4-Vinylbenzyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (303 mg, 0.632 mmol), PMDETA (31.3 mg, 0.181 mmol), and butyronitrile (1.70 mL) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was warmed to room temperature and back-filled with Ar, CuBr (25.9 mg, 0.181 mmol) was added. The resulting mixture was stirred at room temperature for 30 min, and macroinitiator **3** (n = 40, 200 mg, 0.0451 mmol) was added. The flask was then stirred at 90 °C for 24 h. The resulting reaction mixture was purified as described in the general procedure above to give **1j** as a white solid (yield: 0.342 g, 82%). Block repeat unit molar ratio = 4:1 (PS:PIL); block length composition = 40-*b*-10 (PS-*b*-PIL); $M_n = 9,227 \cong 9200$ g/mol (calculated based on ¹H NMR analysis; see Appendix B, the Supporting Information for details).

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CHAPTER 4: IMPACT OF HIGH MOLECULAR WEIGHT CONTAMINANT ON SOS HYDROGEL MECHANICAL PERFORMANCE AND SYNTHETIC STRATEGIES FOR ITS ELIMINATION

4.1 Chapter summary

The Bailey group has developed mechanically high-performing hydro- and ion-gels based on melt-state phase separating blends of poly(styrene-b-ethylene oxide-b-styrene)/poly(styrene-bethylene oxide) (SOS/SO-H) that are elastic, distensible, tough, and fatigue resistant¹⁻⁴ when the molecular weight distribution of the blend is both narrowly dispersed and bimodal. Recently, we found some samples to contain a high molecular weight polymer contaminant (HMC) that appeared to consist of very high MW PEO chains and have deleterious effects on the predictability of swelling behavior and mechanical performance of our gels. The purpose of this study was threefold; 1) to elucidate the cause of the HMC, 2) to develop anionic polymerization strategies that eliminate its presence, and 3) evaluate the effect of HMC on the mechanical properties of SOS hydrogels compared to HMC-free SOS hydrogels. We found that the HMC will only show up in the coupled (SOS) products of diblock (SO-H) polymerizations that have been run at high concentrations (less than 30 mL of solvent per gram of polymer, depending on the overall molecular weight of the final product), and to eliminate its presence one simply has to run the reaction at lower concentrations. We confirmed that polymer samples with high concentrations of HMC had generally diminished mechanical properties compared to blends that were free of HMC, and that presence of HMC in a gel makes the compressive modulus and swelling ratio significantly harder to predict due to the addition of untethered PEO chains of various molecular weight. Because of the tradeoff between HMC and SOS triblock content within each blend synthesized, gels with high HMC content tended to be softer. Finally, we were able to develop a reliable method for creating high SOS triblock content polymer in a single "one-pot" reaction.

4.2 Introduction

Over the course of the last decade, the Bailey group has employed a thermoplastic elastomer hydro- and ion-gel platform first developed by Guo and Bailey¹ to push the boundaries of application-driven polymer science such as greenhouse gas separation membranes,⁴ potential fibrocartilage replacement materials,³ and highly tunable photocurable membranes.^{5,6} The hydrogels detailed in Guo's original work and utilized in all the research that followed are based on microphase-separating, sphere-forming blends of poly(styrene-b-ethylene oxide) diblock (PS-PEO-H, or just SO-H) and poly(styrene-b-ethylene oxide-b-styrene) triblock (PS-PEO-PS, or just SOS) copolymers which have highly tunable and predictable mechanical properties simply by varying the relative amounts of SO-H and SOS.

The elastic, distensible, and fatigue-resistant nature of these high liquid content gels stems from clever design on the molecular level to create a highly regular and mechanically robust nanostructure (figure 4.1). The anchor points that hold the gel together are a physically crosslinked network of glassy, hydrophobic PS spheres with high aggregation numbers (over 200 PS chains per sphere). Each PS chain is covalently bonded to a chain made of hydrophilic PEO which, when coupled with another SO-H chain at the single hydroxyl terminus of the PEO block, creates the tethers that connect the spherical domains to one another. Several factors are at play that dictate whether or not an SO-H/SOS block copolymer blend will form a hydrogel, however. First, the parent SO-H must have a sufficiently high effective degree of segregation (χ N) in order for the PS and PEO domains to microphase separate from one another when given mobility (typically achieved via melt processing at temperatures > 125 °C). While χ represents a thermodynamic interaction parameter between the two blocks (put simply, the enthalpic penalty for mixing, where higher values indicate that two blocks are more likely to phase separate), and has a fixed value at a given temperature, N is the degree of polymerization and can be easily adjusted during the synthetic process. In this case, the minimum N necessary to induce phase



Figure 4.1: Melt state self-assembly of SOS block copolymer blends and gel formation. When (a) blends of SO and SOS are (b) heated in a melt press, PS phase separates from PEO to form spherical aggregate domains comprised of several hundred PS chains per sphere. At room temperature, the PS spheres are vitrified and form a dense, physically crosslinked network. c) When placed in water or ionic liquid (RTIL), the melt pressed polymer absorbs a finite amount of liquid and forms a solid gel that is held together by SOS tethers.

separation is far lower than the N actually employed due to the fact that the glass transition temperature of PS – while approximately 100 °C at high molecular weights – drops off sharply below 10kDa.^{7–9} Additionally, PS will only form spheres in a PS-PEO diblock copolymer when it amounts to approximately 8-13% of the overall volume of the polymer, which means that PEO molecular weights need to be about 10x that of PS. Therefore, typical PS molecular weights are in the 8 – 10 kDa range ($T_g \ge 80$ °C), to ensure that PS remains vitrified at all working temperatures of the gels (and – in particular – above the crystallization temperature of PEO, which is ~65 °C) while still also being small enough to make PEO molecular weights manageable to synthesize. Additionally, kinetic limitations can prevent ultra-high molecular weight diblock copolymers from forming ordered phases altogether.^{10–12} Other ordered diblock copolymer phases such as hexagonally packed cylinders or lamellae will not form gels because the PEO matrix phase is not continuous enough to freely swell.¹³

The SO-H diblock copolymer from which these gels are made is synthesized via the anionic polymerization of ethylene oxide (EO) using a polystyrene macroinitiator (PS-OH) which

is also synthesized anionically. This polymerization method produces polymers characterized by very low dispersity values (D ~ 1.05 near 100 kDa) and easily predictable molecular weights due to quantitative consumption of monomer and the simultaneous initiation of all growing chains. The triblock copolymer SOS is formed by coupling two SO-H chains together via a difunctional halogenated p-xylene (α , α '-dibromo-p-xylene, or DBX). This method keeps dispersity low because all triblock is exactly two chains of diblock, as opposed to the variability that can be introduced when polymerizing three blocks through successive monomer additions in a living polymerization (additionally, the oxyanion/potassium pair cannot initiate a carbanion, so it is impossible to polymerize an additional S block on an active diblock SO⁻K⁺ chain using our anionic polymerization methods). The downside to this method is that the highest coupling efficiencies achievable are typically 70 to 80%. The narrow dispersity of the block copolymer chain is critical to the mechanical performance of the gel because it provides the spherical network with a high degree of homogeneity, which, while under strain, prevents formation of stress concentrations within the gel that would ultimately lead to failure of the network.¹⁴ There is always some batch to batch variability in molecular weight and dispersity, however, and the polymer samples studied in Guo's work all originated from a single reaction. Since that time, many new batches of sphereforming SO-H and SOS have been produced in our lab with varying degrees of success in reproducing gels with similar mechanical integrity to those first reported.

In his doctoral dissertation, Jackson Lewis was the first to document the presence of a high molecular weight "contaminant" (HMC) that appeared in the gel permeation chromatograms (GPC) of certain DBX coupled SOS samples.¹⁵ Figure 4.2 shows some example GPC curves from this study to illustrate the difference in overall dispersity of the triblock and modality of the data when this contaminant is present. Lewis observed that the HMC had a deleterious effect on the mechanical performance of SOS gels. In figure 2.6 and table 2.2 (pages 47 to 48) of Lewis' dissertation, he shows GPC data for a sample that had 46 mol% SOS (probably about 10% of which was HMC) that had significantly higher stiffness and fatigue resistance than an "80 mol%"



Figure 4.2: Gel permeation chromatograms (GPC) of SOS triblock samples with varying amounts (% w/w from integration of GPC peaks) of high molecular weight contaminant (HMC). The middle and right-most chromatograms show presence of HMC as a lower retention time "shoulder" (starting around 15-16 min) on the SOS triblock peak (starting at 18-19 min).

SOS sample where about 40% of the "80 mol%" SOS was actually HMC. In this case, lack of resolution of the GPC curves made it difficult to distinguish the SOS triblock from the HMC. however the GPC was run under different conditions than those used in this study. If both samples had no HMC, we would expect the sample with greater SOS content to be much stiffer and have similar fatigue resistance. In order to characterize this HMC, Lewis employed a fractionation technique that allowed him to separate out higher molecular weight species within the same sample without destroying the integrity of the remaining polymer. Proton NMR showed no species other than the expected protons in PS and PEO present, and end-group analysis showed that polymer fractions that had increased amounts of HMC had significantly higher amounts of PEO repeat units relative to PS than an SOS sample with no HMC (note that the integration of PEO relative to PS is the same for both diblock and triblock because triblock is twice the molecular weight but also has double the end groups). This finding implies that the HMC is potentially comprised of a) PEO chains that initiated from something other than PS chains, b) PEO chains that initiated from a PS chain and then were cleaved from that PS chain, or some combination of both. The most perplexing thing about the presence of the HMC is that it only becomes evident once a polymer sample has been coupled, as GPC curves of affected SO-H diblock samples still adhere to Poisson distributions with low dispersity. It is likely, then, that the additional PEO chains

in the HMC fraction are similar in length to the PEO chains in diblock SO-H but are difunctional and couple to one another in series when DBX is introduced into the reactor. Figure 4.3 illustrates the potential configurations of HMC in an SOS hydrogel.



Figure 4.3: Theoretical configurations of a PEO-based high molecular weight contaminant in SOS hydrogels. a) Ideal SOS hydrogels contain a melt-phase-separated blend of just SOS triblock and SO diblock in which the SOS triblock chains are exactly twice the molecular weight of the SO diblock chains. The majority matrix is comprised of water-soluble PEO chains anchored together by glassy PS spheres. In addition to SOS and SO, gels with HMC may contain any combination of b) SOS triblock chains with longer PEO mid-blocks due to additional difunctional PEO chains coupling between the diblock chains, c) SO with a longer PEO block, or d) difunctional PEO chains that are coupled in series but not anchored in PS spheres.

Once the nature of the HMC was discovered, Lewis performed a series of coupling reactions and SO-H polymerizations with the goal of eliminating the HMC through the synthetic process. While it is possible to remove HMC via fractionation, that process is excessively solvent and time intensive and results in huge losses of polymer product. Ultimately, Lewis, in collaboration with Nabila Hug, was able to produce a single batch of SOS via a "one-pot" style

reaction (where DBX is introduced directly into the reactor post EO polymerization and the entire reaction is coupled) that was free of HMC.^{6,15} As a result, he incorrectly concluded that the elimination of the ethylene oxide purification step (which, in prior reactions had mistakenly utilized purification flasks with rubber septa) was the cause of the successful removal of the contaminant. Later polymerizations performed following this recommendation proved to not only produce SOS with the contaminant, but those batches of SOS had more HMC than any preceding batches of SO-H and SOS. Because of the HMC's overwhelming detriment to the mechanical properties of our gels, it became necessary to fully investigate the nature of and eliminate its cause in our synthetic methods. The purpose of this chapter is to detail the thought processes, discoveries, and methods involved in such an investigation and more thoroughly probe and compare the mechanical properties of both HMC containing and HMC free SOS gels.

4.3 Experimental

4.3.1 Materials and methods

All reagents were purchased from Sigma-Aldrich and all solvents were purchased from Fisher Chemical unless otherwise stated. Styrene monomer (99%, 50 ppm p-tert- butylcatechol inhibitor) was purified at 40 °C by distillations under static vacuum (15–30 mTorr) from di-nbutylmagnesium (1.0 M in heptane). Ethylene oxide (99.5+%, compressed gas) was purified by successive distillations from di-n-butylmagnesium (1.0 M in heptane) at 0–5 °C. Tetrahydrofuran (THF) was sparged with argon (10 psi) for 45 min and then purified over two neutral alumina molecular sieve columns (Glass Contour, Inc.). Cyclohexane (CHX) was degassed with argon and purified through a neutral alumina column followed by a Q5 copper(II) oxide catalyst column (Glass Contour, Inc.). Hydrogels were swollen in DI water of 18.2 M Ω resistivity (Evoqua/ U.S. Filter Service Deionization). Other common chemicals and solvents were used as received unless otherwise stated. Ultra-high purity argon (Ar, 99.998%, Airgas) was passed through a column of 5 Å molecular sieves with Drierite (Agilent) and oxygen-absorbing purifier column (Matheson Trigas). Potassium naphthalenide (KNAP) solution was prepared by mixing solid potassium metal (98% chunks in mineral oil, rinsed in cyclohexane prior to use) and a slight excess of recrystallized naphthalene under Ar in an air-free schlenk graduated cylinder in dry THF.

Synthesis of polystyrene-OH (S-OH) macroinitiator

Synthesized as previously reported.^{1,4} ¹H NMR characterization data is provided in the Supporting Information, Appendix C.

Example polymerization of polystyrene-b-poly(ethylene oxide)-H, (12-SO, see section 4.4.1 for explanation of nomenclature)

This procedure is a modification of synthetic methods originally published in 2010 by Guo and Bailey.¹ A 2 L air-free reaction vessel fitted with glass stir bar, pressure gauge, transfer arm, and 1 L solvent bulb filled with dry, unstabilized tetrahydrofuran (THF), was evacuated and backfilled with Ar gas five times. Under positive Ar pressure (1 psig), 1.729 g (0.216 mmol) of S-OH macroinitiator was added to the reactor. The reactor was evacuated and backfilled five more times and then evacuated overnight to ensure dryness of the S-OH. After backfilling with Ar (~3.5 psig), the THF was added to the reactor to dissolve the S-OH. The reactor was heated to 45 °C and then titrated (via 5 mL airtight glass Hamilton syringe) with concentrated KNAP until a light green color persisted in the reactor for approximately 20 minutes. After reducing the reactor pressure to ~3.5 psig, 17.15g (0.389 mol) of purified ethylene oxide monomer (EO, kept at 0 °C) was added via air-free glass buret. The reaction was stirred for 24 hrs. The reaction was then allowed to cool to room temp, vented for 20 min, and terminated with ~2 mL of 0.1 N HCI. The reaction was reduced to ~ 0.6 L via rotary evaporator, precipitated into 4 L of pentane, and recovered using vacuum filtration. Finally, the product was fully dried under vacuum at ambient temperature for two days. Yield (12-SO) = 16.83g, 89.1% ¹H NMR characterization data is provided in the Supporting Information, Appendix C.

Example synthesis of a "one-pot" polymerization of polystyrene-b-poly(ethylene oxide)-bpolystyrene (11-SOS, see section 4.4.1 for explanation of nomenclature)

This synthesis proceeded similarly to the procedure for **12-SO** above, with the following changes: 1.41 g of S-OH macroinitiator was placed in the reactor and reacted with 14.1 g of purified ethylene oxide monomer. After stirring the reaction for 24 hours, the reactor was cooled for 1 hour prior to venting reactor with a needle and positive Ar pressure in order to remove unreacted EO without exposing reactor to air. The reactor was sealed again and re-titrated with a fresh solution of concentrated KNAP using a glass syringe. 0.547 g (2.07 mmol) recrystallized α, α' -dibromo-p-xylene (DBX, Tokyo Chemical Industry Co., Ltd.) was dried in a 100 mL purification flask for 20 min. Dry THF was added to the purification flask via cannula and the solution was weighed so the concentration was known. The total amount of DBX (0.5 equivalents per K) to add to the reaction. 5.684 mL of DBX solution (0.226 mmol DBX, 0.55 equivalents) were added to the reactor via syringe pump over 10 hours. The reaction was reduced to 500 mL with rotary evaporation, precipitated into 3.5 L of pentane, and recovered using vacuum filtration. Finally, the product was fully dried under vacuum at ambient temperature for two days. Yield (**11-SOS**) = 14.444 g, 93.0%. ¹H NMR characterization data is provided in the Supporting Information, Appendix C.

Example synthesis of polystyrene-b-poly(ethylene oxide)-b-polystyrene via standalone coupling reaction (12-SOS, see section 4.4.1 for explanation of nomenclature)

1 g of SO-H (**12-SO**) and a glass stir bar were placed in an air-free 500 mL round bottom schlenk purification flask (with 24/40 septa opening). The polymer was dried under vacuum overnight. 100 mL of dry THF was then added to the flask via cannula to dissolve the polymer. Concentrated KNAP (1.41 mg K mL⁻¹) was added via air-free syringe slowly to titrate the reaction until a light green color persisted in solution (3.0 mL, 0.1 mmol total). Based on the amount of KNAP needed to titrate, a 0.55 equivalence of air free DBX solution (6.059 mL, 0.06 mmol) was added to the reaction over 8 hours using a syringe pump. The product was then precipitated into 1 L of pentane,

vacuum filtered, and dried under vacuum at ambient temperature for two days. Yield (**12-SOS**) ~0.9 g, 90%.

Gel fabrication: thermal processing and swelling.

Polymer samples were thermally processed using a Carver Model CH manual hydraulic press and stainless steel circular molds (5.55 mm dia x 1.05 mm thick). Samples were well packed (overfilled to 50% more mass than final disc) into the mold that was placed on a sheet of FEP coated Kapton FN (Dupont, 500FN131) on top of a pre-heated aluminum plate. The mold was then covered by a second piece of Kapton FN and topped with a second pre-heated aluminum plate. The mold was placed in the Carver press set to 125 °C and allowed to melt with slight pressure for 13 minutes. Pressure (5000 lbs) was then applied to the sample for two minutes. Samples were removed and allowed to cool to room temperature before removing from molds.

Melt processed discs were weighed and placed individually in an excess of water (sparged with UHP Argon for 10 min) and allowed to swell for 12-48 hrs to achieve equilibrium swelling. Immediately prior to mechanical testing, the gels were patted dry with kimwipes, measured, and weighed again.

4.3.2 Characterization

Instrumentation for molecular characterization

¹H NMR spectra were collected in CDCl₃ using a Bruker NEO Avance 400 MHz Spectrometer equipped with Prodigy BBFO cryo-Probe (ns = 256, 10 s delay). Gel permeation chromatography was performed on a Viscotek RIMax system fitted with three 7.5 x 300 mm PolyPore (Agilent) columns in series, an Alltech external column oven set to 40 °C, and a Viscotek differential refractive index (RI) detector with sample concentrations of 2 mg mL⁻¹. Stabilized THF running at 1.0 mL min⁻¹ was used as the eluent and run time was 45 minutes for all samples. Synchotron small angle x-ray scattering (SAXS) experiments were run at the 12-ID-B beamline at the Advanced Photon Source (Argonne, IL). All SAXS measurements utilized a beam energy of 13.30

keV (0.9322 Å) and were recorded by a Pilatus 2M detector (1475 x 1679 pixel resolution) at a sample-to-detector distance of 3.6 m. The scattering wave vector, q, was calibrated using a silver behenate standard (d = 58.38 Å). Samples were thermally processed for 15 minutes prior to SAXS measurements to initiate phase separation and minimize air bubbles. Dry polymer discs were sandwiched between Kapton tape and mounted to a multi-sample DSC pan holder made for the multi-sample heated stage. The samples remained at ambient pressure and were ramped between 100 °C and 200 °C, with exposure times of 1 s for all data collected.

Mechanical characterization

Unconfined compression testing was performed on a TA Instruments Ares rheometer fitted with an 8 mm upper and 25 mm lower parallel plate. Swollen gel samples (all larger than 8mm diameter and approximately 2 mm thick) were sandwiched between parallel plates with an initial stress of 10 to 15 g force (lower for extremely soft samples) to ensure full contact with the parallel plates. Stress was applied at a strain rate of 10% s⁻¹ up to 50% strain for 10 successive compression/decompression cycles.

Overall compressive modulus of each gel was determined by averaging compressive stress between 0 and 50% strain across all 10 cycles, and then calculating the slope of the averaged data. The three replicates were then averaged to determine mean compressive modulus per polymer sample.

4.4 Results and discussion

4.4.1 Synthetic approach and eliminating high weight contaminants in SOS BCPs

A total of 13 anionic poly(ethylene oxide) polymerizations and 26 coupling reactions (tables 4.1 and 4.2) were performed before and throughout this study in order to systematically discover the origins of and remove the HMC from our SO-H and SOS polymers. In table 4.1, Each polymerization/reaction is referred to by the order in which it was synthesized and whether it is

polymerization	concentration	monomer purification ^a	actual Mn ^b	predicted Mn	volume PS°	termination method	
	ml g⁻¹		kDa	kDa	%		
1-SOS ^d	16	no	79.4	77.8	8.8	coupled with DBX	
2-SO	8	no	117.3	104.2	8.6	0.1 M HCI	
3-SO	8	no	112.3	99.6	8.9	0.1 M HCl in MeOH	
4-SO	27	yes	26.3	27.6	37.3	excess MeOH	
5-SO	11	yes	114.3	105.0	8.8	excess MeOH	
6-SO	11	yes	130.3	121.1	7.7	stirred open to air for 1 hr	
7A-SO ^e	45	no	72.2	89.1	12.3	0.1 M HCl in MeOH	
7B-SO ^e	45	no	72.2	89.1	12.3	excess MeOH	
7C-SO ^e	45	no	72.2	89.1	12.3	excess water	
7D-SOS ^{d,e}	45	no	72.2	89.1	12.3	coupled with DBX	
8-SO	10	no	131.3	116.2	7.8	0.1 M HCI in MeOH	
9-SO	30	no	109.2	103.5	8.2	0.1 M HCI in MeOH	
10-SOS ^d	27	no	87.2	84.3	10.2	coupled with DBX	
11-SOS ^d	58	yes	88.2	89.1	10.1	coupled with DBX	
12-SO	48	yes	88.2	89.5	10.1	0.1 M HCI	
13-SOS ^d	53	no	66.2	88.6	13.4	coupled with DBX	

Table 4.1: List of polymerizations performed for this study.

^apurification of ethylene oxide monomer via vacuum distillation over n-dibutyl magnesium ^bMn of SO diblock chains, calculated using ¹H NMR end group analysis ^ccalculated using ¹H NMR and the nominal densities of each block at 140 °C ($\rho_{PS} = 0.969$ g cm⁻³ and $\rho_{PEO} = 1.064$ g cm⁻³)²¹ ^dperformed as "one-pot" sequential anionic polymerization and coupling reactions, no "parent diblock" SO-H diblock exists for these reactions, Mn reported is for a single SO diblock chain ^eproducts 7A-D are fractions split from a single polymerization reaction

diblock or triblock (for example, 1-SOS was the first reaction performed and was also a "one pot" polymerization and coupling reaction) In table 4.2, each SOS triblock is referred to by the number of its parent reaction, then SOS, and then a letter denoting the order in which it was synthesized (for example, 2-SOS-a and 2-SOS-b were both synthesized from the diblock 2-SO). Note that in this chapter, all polymer blends of SO-H/SOS/HMC will be described by their relative species fractions in terms of mass %, not mol % as seen in Lewis' study and prior Bailey group publications.^{1–6,15} This is because we cannot confidently assign accurate molecular weights to the HMC fraction due to high dispersity and uncertainty of end groups, and therefore calculating mole fractions of each component is not feasible.

Polymer groups **1** and **2** were synthesized prior to this study but the clear abundance of HMC in SOS **2-SOS-a** through **2-SOS-d** and their poor mechanical performance as a result was

sample	SO diblock	SOS triblock	НМС	average Q ^a	Q	average modulus ^{a,b}	modulus
	% (w/w)	% (w/w)	% (w/w)	g H ₂ O / g poly	Std Dev	kPa	Std Dev
1-SOS*	52.3	44.5	3.3	10.1	0.22	176.5	1.60
2-SOS-a*	13.2	70.4	16.4	5.82	0.23	649.7	43.0
2-SOS-b*	22.8	64.4	12.8	11.4	1.6	137.7	36.8
2-SOS-c	30.1	59.8	10.1	6.60	0.054	480.6	10.6
2-SOS-d*	18.1	66.9	15.0	6.41	0.097	493.2	23.2
3-SOS-a*	9.4	51.7	38.9	6.60	0.030	482.6	15.5
3-SOS-b	23.7	50.7	25.7	8.71	0.041	250.1	2.75
4-SOS ^c	8.7	91.3	0.0	С	С	С	С
5-SOS-a	6.6	48.4	45.0	8.85	0.36	252.6	9.75
5-SOS-b	12.4	50.2	37.4	9.11	0.16	231.6	11.8
5-SOS-c	12.5	49.0	38.5	8.45	0.054	268.1	3.40
6-SOS-a	8.1	51.6	40.3	7.36	0.10	419.7	10.0
6-SOS-b	20.9	51.1	28.0	9.21	0.74	208.2	2.79
7A-SOS-a	14.4	84.6	1.0	5.58	0.028	643.2	2.28
7A-SOS-b	19.3	78.9	1.8	5.61	0.10	644.1	1.07
7B-SOS-a	16.6	81.8	1.6	5.42	0.045	677.6	7.97
7B-SOS-b	35.8	62.3	1.9	7.08	0.38	343.1	3.65
7C-SOS	13.4	85.0	1.6	5.80	0.024	573.4	9.80
7D-SOS	73.4	26.6	0.0	15.2	0.040	44.56	1.87
8-SOS-a*	8.3	59.4	32.3	6.23	0.17	519.0	27.3
8-SOS-b	74.0	23.5	2.5	24.0	0.088	12.91	0.30
9-SOS	10.4	80.2	9.4	6.46	0.12	552.1	24.7
10-SOS*	62.7	36.1	1.2	13.6	0.16	69.87	2.14
11-SOS	17.0	82.4	0.6	5.37	0.048	795.1	46.8
12-SOS	15.6	84.1	0.3	7.06	0.23	448.2	4.88
13-SOS	32.0	65.9	2.1	5.80	0.073	511.7	7.22

Table 4.2: List of coupling reaction products, gel swelling ratios (Q), and moduli.

^amean of three gels ^bmodulus for each gel was calculated by taking the average of 10 compression cycles (from 0 to 50% strain) and then the slope over that full range °4-SOS does not form gels due to the high volume fraction of PS relative to PEO (and consequential lamellar morphology) and therefore there is no mechanical data for this sample *indicates polymer samples that formed gels with significant flaws in the form of cracks, bubbles, bumps, or roughness, regardless of processing technique

a big motivating factor in the work that followed (table 4.2, also see Appendix C, the Supporting Information for all chromatograms). Diblock batch **3-SO** was also synthesized previously and was used in our initial troubleshooting steps. Guo's original DBX based coupling reactions were run just overnight, but all four **2-SOS-x** reactions were run between 18-36 hours of slow and slight excess DBX addition so the first theory tested was that prolonged exposure to DBX in solution was creating radical species that could degrade and then further couple the polymer. The coupling reaction that produced **3-SOS-a** was run for a strict 8 hours followed by immediate precipitation

and resulted in a polymer with 38.9% w/w HMC. Neither polymerization for **2-SO** or **3-SO** involved an ethylene oxide purification step so at this point we were confident that Lewis' aforementioned theory regarding that was incorrect.

NMR end group analysis of polymers loses accuracy and GPC loses resolution with higher molecular weights, so we synthesized **4-SO** with a relatively short chain of PEO (17 kDa) to help us better characterize the polymer with both methods. We also noticed that in Guo's original methods, the EO polymerization was terminated with just methanol. **2-SO**, **3-SO**, and some prior SO-H diblocks had been terminated with one molar equivalent of HCl added to the methanol to cap chains with a proton and neutralize the strong base (potassium napthalenide, KNAP) that had been added, so **4-SO** was terminated with only methanol to be consistent with Guo's procedures. The coupling reaction for this relatively short chain diblock, **4-SOS**, produced a polymer with no discernable HMC. Given these promising results, the next reaction, **5-SO** was performed in similar conditions (EO purified, MeOH to terminate, same PS macroinitiator) to **4-SO** except with a high MW target once again. The coupling reaction that immediately followed, **5-SOS-a** resulted in the highest amount of HMC observed yet (45%). Since termination with MeOH appeared to be unsuccessful, the next reaction was performed under the same conditions as **5-SO** except we allowed the reaction to terminate open to the ambient moisture in the room. The coupling reaction (**6-SOS-a**) for this polymerization (**6-SO**) also contained significant amounts of HMC.

Several years prior to this study, Huq and Lewis performed a diblock polymerization and coupling via a "one-pot" reaction that resulted in a SOS blend with virtually no detectable HMC.^{6,15} For this reaction, two fractions were separated and collected from the reactor via cannula in order to perform end-group chemistry separately before DBX was added to the main reactor to couple the remaining active SO chains. For our next experiment we decided to use this method to compare all termination methods within the same reaction to conclusively rule out that termination method was a factor in this issue. To do this, polymerization **7** was split into four fractions after the polymerization step, 3 of which were removed from the reactor and terminated by HCI,

methanol, or water for A, B and C, respectively (**7A-SO**, **7B-SO**, **7C-SO**). **7D-SOS** was the fourth fraction that remained in the reactor and was coupled directly without precipitation. In addition to **7D-SOS**, all initial coupling reactions that were performed on **7A-C** resulted in negligible amounts of HMC (**7A-SOS-a**, **7B-SOS-a**, **7C-SOS**, <2% HMC content).

To cover our bases at this point, we set out to make sure that our titration method (KNAP) for activating polymer chains in a coupling reaction was not a factor. We had been following Lewis' method that utilizes slow and careful titration with a syringe in order to achieve very high coupling ratios¹⁵ with the bare minimum of KNAP added to the reaction, so we decided to take polymer samples **7A-SO** and **7B-SO** and titrate them with excessive amounts of KNAP before coupling. The resulting polymers, **7A-SOS-b** and **7B-SOS-b**, had HMC content consistent with earlier coupling reactions performed with these diblocks (<2%) and careful titration methods. We also used the exact same KNAP solution to couple another batch of both **5-SO** and **6-SO** with careful titration to make **5-SOS-c** and **6-SOS-b**, both of which had high amounts of HMC.

Taking into account all the minor nuanced changes and discoveries we had made, but without any real conclusions as to the root cause of the issue, we set out again to make a bigger batch of polymer so large-scale mechanical experiments could be performed without any batch to batch variability. The next reaction, **8-SO**, once again had high amounts of HMC when coupled (**8-SOS-a, 8-SOS-b**). It was clear by now that there were many factors that were irrelevant to the issue at hand: EO purification (or lack thereof), KNAP titration method, DBX manufacturer, termination method, etc. When we finally compared the method details of all the reactions that had resulted in polymer with little to no HMC, one common thread appeared between them: reaction concentration. All of the problematic polymer samples were synthesized in large batches (typically 30 g or more in one reaction) with typical reaction concentrations of 10 mL g⁻¹ or less (for the purposes of this discussion, reaction concentration will be presented as volume per gram of polymer) and the successful batches had at least 30 mL g⁻¹ of solvent, Guo's original polymer included. It then became clear why the "one-pot" method had produced successful results for

Lewis and Huq and polymerization **7**; in order to cannula out fractions of the reactions without clogging the thin metal tubing, the reactions needed to have sufficiently low viscosity and therefore both reactions were coincidentally performed fairly dilute. To illustrate the effect concentration had on each reaction, figure 4.4 shows HMC content as a function of polymerization concentration with respect to molecular weight.



Figure 4.4: High molecular weight contaminant (HMC) content as a function of polymerization concentration with respect to overall molecular weight of the SO diblock. With only one exception, polymerizations performed at more dilute concentrations (> 30 mL g^{-1}) have little to no HMC present after coupling.

The next polymerization, **9-SO**, was performed at 30 mL g⁻¹ to match the concentration of Guo's original SO-H polymerization. The coupled product, **9-SOS**, contained 9.4% by weight HMC, which was a significant improvement over some of the SOS samples that contained upwards of 45% HMC, but it was still not good enough considering the fact that it was possible to make SOS with no HMC. Aside from procedures that had already been determined to be insignificant, like EO purification, the only difference between Guo's polymer and **9-SO** was the volume fraction of PS, and therefore molecular weight of PEO. Both polymers had been synthesized from PS-OH macroinitiators of very similar weight, but Guo's polymer contained 10% by volume PS (83 kDa PEO) whereas the PS block in **9-SO** was only 8.3% by volume (101 kDa

PEO). We theorized that this 18 kDa difference in molecular weight must have made a significant impact on how the polymer chains entangle and interact with one another in solution, otherwise there should have been no difference in HMC content.

For the next polymerization, we targeted a volume fraction (f_{PS}) of 0.1 and a similar reaction concentration (27 mL g⁻¹) to better replicate Guo's SO-H. In light of the success of polymerization **7**, we decided to revisit the one-pot polymerization method for polymerization **10**, but instead of separating the reaction into fractions and terminating them, the entire reaction was coupled in the original reactor after 48 hrs - the amount of time Guo ran her reaction for. While the product of this reaction, **10-SOS** contained low, if negligible, amounts of HMC (~1%), the reaction also unfortunately had a very low coupling efficiency (which will be discussed further in section 4.4.4) and evidence of some triblock chain degradation, most likely due to running the coupling reaction at the same temperature as the polymerization (historically, coupling reactions with DBX were run at room temperature but in this case the reactor was maintained at 40 °C for duration of the experiment).

After considering our issues with reaction **9** and molecular weight, we decided to re-try the one-pot method for **11-SOS** but with a much higher dilution (58 mL g⁻¹) than reaction **10** (27 mL g⁻¹), since coupling the polymer in the reactor effectively doubles the molecular weight of a significant fraction of the polymer chains. In addition to diluting the reaction two-fold from **10**, we also purified the EO monomer and ran the polymerization for only 24 hrs – but at 45 °C instead of 40 °C. Prior to coupling, we cooled the reactor to room temperature, re-pressurized with Ar, and re-titrated with KNAP to re-activate any chains. Essentially, this procedure eliminated the termination, precipitation, drying, and re-dissolution steps involved in producing an SO-H diblock and SOS triblock in two separate reactions. Using this method, not only were we able to produce a nearly 15 g batch of high SOS material (82.4% w/w triblock) but it also contained negligible amounts (0.6% w/w) of HMC. These positive results from **11-SOS** made it abundantly clear that

reaction concentration and molecular weight were the two most important factors in eliminating the presence of HMC in SOS block copolymers.

12-SO, 12-SOS, and 13-SOS were created to verify these conclusions. We ran polymerization 12 separately from its coupling reaction to confirm that the one-pot method was not required to generate SOS polymer that was free of HMC, and reaction 13 was run using the one-pot method to demonstrate reproducibility. Reaction 12 produced SOS with essentially undetectable amounts of HMC and exceptionally high coupling. Reaction 13 was also free of HMC but coupling was not quite as successful as the prior one-pot reaction, 11-SOS. Yield and overall Mn of reaction 13 were also somewhat lower than expected, so we suspect that the polymerization step had some contamination or other unrelated issue that negatively impacted the outcome. Despite this, we are confident that the lack of HMC in reactions 11 through 13 demonstrates that careful consideration of polymerization scale, concentration, and molecular weight are crucial in producing a linear SOS triblock copolymer that has low dispersity and is predictably bimodal.

4.4.2 Morphological phase behavior of SO-H and SOS block copolymers

All but three block copolymer samples displayed small angle x-ray form factor scattering (SAXS) indicative of a liquid-like packing of PS spheres within the PEO matrix that is typical of high molecular weight SO diblock copolymers with volume fractions of PS (f_{PS}) at or less than 0.1 (figure 4.5). **4-SO**, at $f_{PS} = 0.373$, forms a well-ordered lamellar phase, which prevents the PEO blocks from swelling due to lack of a continuous water-soluble matrix. Because of this, triblock **4-SOS** was precluded from mechanical investigations.

Both **3-SO** and **7A-SO** show emergence of a BCC lattice of spheres, which is expected¹⁶ for sphere forming SO diblocks with f_{PS} around 0.13 such as **7A-SO** ($f_{PS} = 0.123$), but is not expected for an SO polymer sample with an f_{PS} as low as 0.089 and a molecular weight over 100 kDa, as is the case for **3-SO**. One possible explanation is that the molecular weight of **3-SO** as calculated by NMR end group analysis is greatly overestimated due to the presence of HMC



Figure 4.5 Small angle x-ray scattering data for each polymerization in this study, measured at 120 °C after 4 hours of thermal annealing at that temperature. Open inverted triangles with a strikethrough represent the calculated allowed SAXS reflections (based on q*, the primary scattering wave vector) for a sphere morphology arranged on a body-centered cubic lattice, at q/q* ratios of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, and $\sqrt{8}$ (where q* is q₁₀₀). Solid inverted triangles represent the calculated values of allowed SAXS reflections for a lamellar morphology, found at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{9}$ (where q* is q₁₀₀).

precursors (PEO chains that are capable of coupling in series and are unlikely to be connected to a PS macroinitiator and are, essentially, homopolymer) in the diblock. The overall M_n of PEO in the diblock is calculated by integration relative to an end group on the PS macroinitiator, therefore any PEO chain that is not connected to a PS chain will artificially drive the molecular weight of the PEO block higher. However, even if the effective M_n of PEO in each diblock chain is actually lower than observed, presence of these "free" PEO chains in lieu of diblock would not alter the overall volume fraction of PS in the polymer sample and does not directly explain how a diblock of this nature would be able to form a BCC lattice. Instead, we must consider the massive kinetic limitations that a very high molecular weight sphere forming diblock experiences while undergoing phase separation. Once in the melt, SO diblock phase separates immediately (< 5 minutes) but it can take much longer to reach a state of lowest energy conformation (for sphereforming diblocks this is theoretically the BCC lattice, which minimizes packing frustration¹⁷). When we consider a large diblock with a PS volume fraction of ~0.08-0.1 where all or most of the PEO chains are attached to PS spheres (for example, 9-SO and 12-SO), rearrangement into a BCC lattice requires overcoming prohibitively high energy barriers within a reasonable timeframe due to high numbers of entanglements per chain and the anchoring effect of the PS spheres. This effect is magnified significantly when the phase behavior of SOS triblock is observed, as in the case of 13-SOS, where the volume fraction of PS falls comfortably in the BCC region, however, this polymer was coupled in the reactor and therefore the vast majority of it is effectively double the molecular weight (132.4 kDa for the triblock vs 66.2 kDa of the remaining diblock). For triblock species, chain movement is particularly restricted by being anchored into spheres on both ends and the topological entanglements that result during the formation of this physically crosslinked network.

If we then compare **3-SO**, in which the volume fraction of PS is more comparable to **9-SO** and **12-SO**, but upwards of ~40% of its mass is "free" PEO, then a significant portion of those kinetic limitations are reduced during the phase separation process. Not only are the diblock chains lower in molecular weight than calculated and therefore less kinetically restricted than initially assumed, but the free PEO chains in the matrix serve to "lubricate" the movement and rearrangement of polymer chains, allowing formation of a BCC lattice at lower PS volume fractions than initially thought possible for such a high degree of polymerization.

4.4.3 The role of HMC in the swelling behavior and mechanical performance of SOS hydrogels

We investigated 25 separate SOS polymer samples from 12 unique SO polymerizations to assess the impact of the presence of HMC on the physical and mechanical properties of our hydrogels. In his dissertation, Lewis observed that samples with higher relative amounts of HMC were softer and less fatigue-resistant than samples with less HMC, however his study was limited to only three samples, all of which contained some HMC.¹⁵ He also could not distinguish between HMC and SOS triblock quantitatively due to poor resolution of the SOS and HMC peaks in the GPC chromatograms and therefore considered those peaks as one "triblock" peak which, in this chapter, we will refer to as SOS + HMC (the sum of the integrals of the two separate GPC peaks, in %w/w).

In 2010, Guo noted that increasing SOS concentration in hydrogel samples caused an exponential increase in stiffness (compressive modulus) due to each additional SOS strand contributing more than one effective cross-linked strand through topological entanglements.¹ In Lewis' study, if all HMC were considered the same as SOS triblock and contributing to the mechanical behavior of each gel equally, then this apparent relationship between SOS concentration and modulus breaks down rapidly when we consider that he found an "80 mol% SOS" sample to be much softer than a sample with "46 mol% SOS." This in mind, we set out to study the mechanical behavior of the gels in this study with the following questions: 1) What parameter is the best predictor of modulus and 2) What role does HMC play in the mechanical properties of SOS hydrogels?

Lewis employed unconfined compression testing to assess the compressive modulus of each of the three gels over the course of 10k cycles in order to determine their stiffness and fatigue resistance. Each of the 25 samples (3 gels per polymer sample) in this study were also subject to unconfined compression testing to measure stiffness (compressive modulus, in kPa)

but due to current limitations in instrumentation, the mechanical study of each gel was limited to 10 cycles and therefore long-term fatigue-resistance will not be a consideration in this discussion. It is of note, however, that these gels are fatigue-resistant enough to have no detectable decay in mechanical properties over the course of 10 compressive cycles. Qualitatively, most gels that contained considerable amounts of HMC (>5% w/w HMC) were visually indistinguishable from those that that did not (<5% w/w HMC); they were able to form clear, evenly swollen, and smooth gels with little to no noticeable flaws or cracks (with a few exceptions, noted in table 4.2). Figure 4.6 compares the mechanical performance of three different gels with varying amounts of HMC. All three samples, regardless of HMC content, show excellent and rapid elastic recovery between compressive cycles and no evidence of mechanical fatigue after 10 compressive cycles. The hysteresis present in each decompression cycle is a function of redistribution of water within the



Figure 4.6: Example mechanical behavior of the first and tenth cycles of SOS triblock gels during unconfined compression and decompression with varying amounts of HMC (0.6% orange curves are 11-SOS, 9.4% blue curves are 9-SOS, 40.3% pink curves are 6-SOS-a). Presence of HMC does not affect the elasticity or short-term fatigue resistance (over 10 cycles) of these gels, however gels with high amounts of HMC are generally softer than gels with high amounts of SOS triblock.

gel during compression, so instant recovery of modulus is slightly hindered by entanglements within the polymer network that slow down mass transfer but is not indicative of permanent deformation of the material. It is important to note that all the gels (except for 2-SOS-b) tested in this study, independent of swelling ratio, HMC content, or SOS triblock content, exhibited similar behavior (see section C.4 of Appendix C for more detailed results).

Figure 4.7 is the compilation of average compressive modulus for each of the 25 polymer samples with respect to four different measurable parameters. We used a linear least-squares regression to assess the degree of correlation of compressive modulus to each parameter by



Figure 4.7: Average compressive modulus of 25 SOS triblock gels with respect to a) swelling ratio (inset is the data represented on a linear scale), b) SOS triblock content, c) SOS triblock content and HMC content added together, and d) just HMC content. There is a very high correlation between modulus and swelling ratio of the gel, regardless of HMC content. SOS triblock has a moderately strong positive correlation to gel stiffness, particularly in gels with low HMC (<5%). HMC content has no discernable relationship to gel stiffness.

comparing their r² values. Section a of figure 4.7 shows a very strong correlation ($r^2 = 0.982$) between the swelling ratio of a gel and its measured modulus, regardless of composition. Considering only those gels with low HMC (<5%), the correlation improves, but only slightly ($r^2 =$ 0.991). Part b of figure 4.7 shows the relationship between compressive modulus and SOS triblock content. While there is a fairly strong positive correlation between SOS triblock content and modulus for gels with low HMC ($r^2 = 0.887$), that relationship weakens considerably when considering all gels ($r^2 = 0.742$). This is partly due to some of the high HMC gels being stiffer than predicted based on their SOS triblock content alone. That suggests that in certain samples, the HMC is actually contributing to (and also sometimes detracting from) the modulus in some small and unpredictable way. However, when we compare modulus to the amount of SOS combined with HMC in figure 4.6c, it becomes clear that the HMC is not contributing to the modulus equally to SOS. If this were the case, then every sample with an SOS + HMC value greater than 70% would have a modulus of at least 400 kPa and there would likely be a positive correlation between HMC and modulus in figure 4.6d. Instead, part d shows us that as HMC content increases, the upper limit of gel stiffness decreases significantly and there is no definable relationship between the two values given that gels with virtually no HMC can display a very wide range of modulus values.

Because of the high correlation between gel swelling ratio and gel stiffness, we can use the linear regression of the log-log plot in figure 4.7a to estimate a relationship between Q and compressive modulus that will allow us to predict the stiffness of any gel in the future. Since the relationship is exponential, we know that modulus (E) is proportional to Q raised to some power (k):

$E \sim aQ^k$

Taking the log of this function gives us the linear form of this relationship in the log-log plot,

$$\log(E) \sim k \cdot \log(Q) + \log(a)$$

where k is the slope of the linear regression and log(a) is the "intercept" (the value of E when log(Q) = 0, or on a linear plot, when Q = 1). Substituting in the slope and intercept values from the linear regression of the "all data" set of the Q vs modulus plot gives us:

$$\log(E) \cong -2.60 \cdot \log(Q) + 4.80$$

For convenience, we can now convert back to the exponential form of the equation:

$$E \cong \frac{6.3 \times 10^4}{Q^{2.6}}$$

That gel stiffness is largely determined by swelling ratio is no surprise, however, this is the first study within our group that demonstrates this trend amongst such a large and diverse set of SOS block copolymer gels. When an SOS sample is placed in water, the extremely high solubility of PEO in water creates sufficient osmotic pressure to cause the material to swell rapidly until an equilibrium has been reached. That equilibrium is ultimately determined when the network of PEO chains reaches a point where the osmotic forces caused by the chemical potential of PEO in water can no longer overcome the tensile forces created by stretching highly entangled polymer chains to accommodate water uptake. In other words, the system reaches a free energy minimum when further reduction in enthalpy by increased water absorption becomes unfeasible due to the decrease in entropy of uncoiled polymer chains in a crosslinked network. The minimization of the entropy term (T Δ S) is the reason why the swelling ratios of SOS gels increase quite dramatically at reduced temperatures.¹

The next question, then, is what determines the point at which the entropic restoring forces of the polymer coils prevent further swelling, i.e. what governs the density of entanglements, and ultimately, the value of Q in an SOS gel? Generally, this is a function of the amount of SOS triblock chains in the sample and the molecular weight of those chains.¹⁸ These act as anchors between spheres and contribute significant topological entanglements that define the effective strand length of chains in lieu of a traditionally chemically cross-linked homopolymer system. Without the triblock tethers, thermally processed SO diblock will micellize and "swell" infinitely in water. Given

this, it would be logical for Q to scale predictably with SOS triblock content (and does when various weight % SOS blends of a single batch of polymer are compared, as in Guo's study¹), but even for samples with low HMC (<5%), there is noticeable "noise" in the data in the high SOS triblock regime that reduces the correlations between SOS triblock and both Q and modulus. We believe that the variability in molecular weights¹⁸ between polymer samples and slow kinetics during melt-state processing play a much larger role in network formation and organization when the polymer is in a highly tethered entangled state (than say, a pure SO diblock which has ONLY dynamic entanglements between micelles) and therefore makes it more likely for gels with high (but similar) amounts of SOS triblock to have a relatively wide range of working swelling ratios (and consequently, moduli).

As mentioned previously, samples with significant HMC content are generally softer and more swollen than those with low HMC content but high amounts of coupling (samples with >60% SOS + HMC part c of both figure 4.7 and figure 4.8), mostly due to the fact that the amount of HMC limits the overall amount of SOS triblock that a polymer sample can have. However, some deviations from the trend between Q, modulus, and SOS triblock content for samples with >5% HMC tend towards being stiffer and having lower water content than what we would expect for gels with comparable amounts of SOS triblock but no additional HMC (part b of both figure 4.7 and 4.8). If we consider the different possible configurations of HMC illustrated in figure 4.3, it would be possible for a gel with HMC to have a lower Q than expected based on SOS triblock content alone if some of the HMC was providing additional topological entanglements to the network by being anchored in two different PS spheres such as in part b of figure 4.3. The rest of the HMC, illustrated in part c and d of figure 4.3, behaves more like SO diblock and increases swelling due to the increased proportion of untethered hydrophilic PEO chains. In several cases, this leads to samples with higher-than average Qs and lower moduli. These samples, in particular, may have larger proportions of "loose" HMC chains (figure 4.3.d) that consist of difunctional PEO chains coupled in series and effectively dilute the SOS triblock concentration more than SO



Figure 4.8: Average swelling ratio (Q) with respect to a) both SOS triblock and HMC content, b) SOS triblock content, c) SOS triblock and HMC content added together, and d) HMC content alone. There is a strong negative correlation between SOS triblock content and swelling ratio, and no relationship between HMC content and swelling ratio. For samples at or greater than 50% (w/w) SOS triblock content, presence of HMC generally leads to a softer, more highly swollen gel.

diblock can. The variety and high dispersity of the HMC populations lead to a wide range of unpredictable swelling ratios, especially when we consider SOS and HMC content together, as in part c of figure 4.8. Despite the small boost in stiffness from the fraction of tethered HMC chains, the overall detriment to the mechanical properties of these gels that comes from having other fractions of HMC present in lieu of more SOS triblock is evident, and there has been no reason to believe that there is any advantage to a gel system that contains HMC over one without.

4.4.4 Maximizing coupling efficiency in a "one-pot" polymerization

When Huq and Lewis originally developed the one-pot methodology, their product contained 50% w/w SOS triblock copolymer species, which was not high enough in SOS triblock content for the experiments that this reaction was intended for.⁶ Through fractionation¹⁸ they were able to obtain a polymer sample with a much higher ratio of SOS triblock to SO diblock, however this was an extremely inefficient way to achieve that product due to the time consuming nature and significant loss of polymer associated with the fractionation process. Ultimately, Huq needed high-fraction SOS polymer in order to blend it with a SO diblock species with end-group modifications, so limiting the amount of leftover "dead" SO chains (i.e. the *other* 50%) from the one-pot coupling reaction was more of a priority than having a large amount of polymer material.

Knowing that fractionation after every one-pot was not a feasible solution for the long term, the clear solution was either to find a way to achieve high coupling within the one-pot method or scrap the one-pot method entirely. Both reaction **1** and **7D** were one-pot reactions that resulted in even lower coupling ratios than Huq and Lewis' product, so when we performed polymerization **10** we monitored the coupling reaction with GPC by pulling a small sample from the reactor after all of the DBX had been added, but before the precipitation step. That sample showed very low coupling (<36% SOS w/w) so we decided to add a second aliquot of DBX solution (1.6x the original amount added) in hopes that the amount of DBX we had originally added was just simply not enough. After this second addition of DBX, the reaction was precipitated and the final product was observed with GPC; no more SOS triblock had formed upon adding more DBX (figure 4.9).

Lewis had spent some time exploring the subject of maximizing coupling efficiency when working with SO-H diblock (that had been previously synthesized), and his method was fairly simple: use a syringe (instead of a cannula¹) to titrate the dissolved SO-H diblock with KNAP and then calculate the amount of DBX to add based on the number of "titratable groups" in a 2:1 (K:DBX) ratio.¹⁵ In following his methods, we were able to consistently achieve high coupling



Figure 4.9: Gel permeation chromatogram (GPC) of the "one-pot" reaction 10-SOS. The solid black line shows the coupled product drawn from the reactor before a second aliquot of DBX was added. The dotted grey line is the final reaction product which shows minimal additional coupling from the extra DBX, indicating that most of the "live" chain ends from the polymerization step had prematurely deactivated.

efficiencies greater than 80% w/w for the vast majority of SOS samples explored in this study, however, the titration for a one-pot reaction occurs during the initiation step of the S-OH macroinitiator – prior to addition of EO – and at least 24 hours before any DBX is added. In order for Lewis' method to achieve near 100% coupling efficiency, it assumes that *all* of the "titratable groups" being coupled are still initiated when DBX is added, and this was clearly not the case for reaction **10**, otherwise more chains would have coupled when the second syringe of DBX was added. In ideal conditions, a living anionic polymerization is defined by its resistance to spontaneous chain termination and presence of persistently active anionic chain-end species that allow for quantitative chain-end functionalization or addition of additional monomer(s), but in practice, the amount of active terminal anions will decline over time.¹⁹ 48 hours after polymerization **10** was initiated with KNAP, barely more than a third of the chain ends in the reactor were still active.

To counteract this problem for reaction **11**, we made a second batch of KNAP on the same day we initiated the polymerization, and re-titrated to a persistent light green color (with a syringe again) immediately prior to addition of DBX. The second titration required nearly as much KNAP as the first titration did, confirming the need to re-activate most of the polymer chains in the
reactor. Ultimately, this reaction produced a batch of SOS polymer that contained more than 80% w/w triblock, which was as good or better than many of the coupling reactions we had performed independently of their respective polymerizations, and proved the viability of the one-pot method as a useful means for generating large batches of high-triblock SOS block copolymer without the need for fractionation.

4.5 Conclusions

In brief, we were able to effectively identify the cause and eliminate the presence of a high molecular weight contaminant (HMC) in our SOS triblock copolymer blends through a systematic investigation of our polymerization techniques. We recommend that anyone seeking to synthesize sphere-forming SOS triblock copolymer in the future thoroughly investigate recommendations for the anionic polymerization of ethylene oxide in the literature²⁰ and adhere to the following guidelines to avoid generating HMC in their product:

- Ethylene Oxide monomer should be purified with di-n-butylmagnesium via vacuum distillation prior to polymerization (one flask minimum, two preferred).
- SO-H polymerizations should be run at ≥30 mL g⁻¹ (less concentrated is particularly recommended for any molecular weight target of ≥ 90 kDa).
- "One-pot" sequential polymerization and coupling reactions should be run at ~60 mL g⁻¹.
- A second titration with KNAP immediately prior to addition of DBX is necessary for "onepot" reactions to achieve a high coupling ratio.
- Coupling reactions with DBX should always be run at room temperature.
- Avoid rotary evaporation, if possible. A reaction run at ~30 mL g⁻¹ should precipitate easily as a fine (but sticky) powder without any additional rotary evaporation. Less concentrated reactions may need evaporation but use caution to avoid over-concentration of the reaction.

This study was also the first of its kind to quantitatively compare the physical and mechanical properties of a wide variety of SOS hydrogels made from many different polymerizations and coupling reactions. We observed that the swelling ratio, Q, of a gel is highly correlated to its compressive modulus, regardless of reaction conditions, polymer composition, processing conditions, or molecular weight. SOS triblock content has a slightly weaker correlation to compressive modulus; the relationship is much more sensitive to changes in molecular weight, presence of HMC, and/or kinetic limitations during thermal processing. Importantly, we established that presence of HMC does not provide any reliable mechanical advantages to the material, and only serves to muddle the relationship between SOS triblock content and compressive modulus.

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CHAPTER 5: HIGHLY CONDUCTIVE AND MECHANICALLY TOUGH GEL POLYMER ELECTROLYTE ELASTOMERS

5.1 Chapter summary

Electrolytes with high ionic conductivity and the mechanical integrity of solid materials are highly sought-after for battery and flexible electronics applications. Ideally, gel polymer electrolytes (GPEs) combine the high ionic conductivity associated with highly mobile ions in liquid electrolytes and the mechanical robustness of solid polymers, but in practice often suffer a tradeoff of one or the other. Here, we present a unique block copolymer (BCP) platform based on sphere forming, melt phase-separated blends of narrowly dispersed and high molecular weight poly(styrene-bethylene oxide-b-styrene) (SOS) and poly(styrene-b-ethylene oxide) (SO) triblock and diblock copolymers. We were able to selectively swell the PEO component in room-temperature ionic liquid (RTIL) to form ion gels that excelled as both ionic conductors and tough elastomeric solids. The ionic conductivities of these elastomeric SOS gels were not only very high (4 to 13 mS cm⁻¹) over a wide range of operating temperatures, but measurably higher than the conductivity of the neat RTIL, suggesting a synergistic effect between the RTIL and the RTIL-soluble PEO matrix. Mechanically, these gels were exceptionally distensible, tough, and elastic, capable of extensions up to 7.5x, bulk toughness up to 2 MJ m⁻³, tunable moduli in the kPa range, rapid recovery, and no permanent hysteresis upon cyclical loading. We also found that these SOS ion gels had significant fracture resistance with fracture toughness values between 1000 and 5000 J m⁻², two to three orders of magnitude higher than what would be expected for homogenous single network gel materials. During pure shear fracture testing we observed an unexpected and unique crack branching phenomenon (among ion gels) that we believe is contributing significantly to the superior toughness of these gels by hindering the continuous path of the crack propagation and preventing rapid and catastrophic failure of the material.

5.2 Introduction

Room temperature ionic liquids (RTILs) are desirable electrolytes in electrochemical applications due to their chemical and thermal stability, non-volatility, and non-flammability.¹ As liquid electrolytes, however, incorporation into devices – particularly flexible electronics – poses many design challenges and limitations, including containment of the electrolyte, maintained contact with electrode surfaces, and potential leakage under deformation.² The future of flexible electronics,^{3,4} including batteries,^{2,5} bendable displays,⁶⁻⁸ artificial muscle actuators,^{9,10} and sensors,^{11,12} relies on the development of deformable electrolyte systems with high ionic conductivity (> 0.1 mS cm^{-1})² and desirable mechanical properties (such as high modulus, elasticity, extensibility, toughness, and fatigue resistance) while avoiding the traditional design restrictions of a liquid electrolyte system. Solid, or solvent-free polymer electrolytes (SPEs), typically comprised of salt-doped polymer matrices, have the advantage of mechanical robustness from crystalline or cross-linked domains within the polymer network, but often suffer from reduced ionic conductivities.¹³ Gel polymer electrolytes (GPEs) are a class of materials with the potential to combine the excellent transport properties of liquid electrolytes with the increased mechanical integrity of solid materials, and GPEs that utilize RTILs as plasticizers in lieu of the more common organic carbonate solvents also benefit from the enhanced stability of RTILs.

Among the various preparation methods for creating GPEs, phase-separated block copolymers (BCPs) that exploit chemical incompatibility and solubility differences between the various blocks are particularly promising. In this class of materials, an RTIL insoluble block like polystyrene vitrifies to form physical crosslinks while an RTIL soluble block like poly(ethylene oxide) or poly(methyl methacrylate) swells in the ionic liquid and provides a highly porous matrix in which ions can flow.^{6,14–18} The RTIL soluble block gives the network flexibility once swollen. Physically crosslinked ion gels are simple to prepare, usually by some means of solution blending polymer with RTIL and a cosolvent, and then drying to form a gel. This strategy allows for tunability

of both mechanical properties and conductivity of the gel by modifying the ratio of polymer to RTIL, where greater polymer loading increases modulus and higher RTIL loading increases conductivity, but inevitably leads to a trade-off between the the two properties. Chemical crosslinking of physical gels in-situ can increase their mechanical strength but reduces the recyclability of the material and often requires additional (and expensive) reagents.^{14,19} Producing a physically crosslinked block copolymer GPE with both exceptional conductivity and superior mechanical properties, then, relies on clever design of the polymer itself to support high RTIL loading while also being able to withstand mechanical stress.

In the last decade we have developed highly distensible thermoplastic elastomer hydroand ion gels based on sphere-forming blends of linear AB/ABA block copolymers that phase separate in the (solvent-free) melt state, where the hydrophobic A block is polystyrene (PS or S) and the hydrophilic B block is poly(ethylene oxide) (PEO or O), as illustrated in figure 5.1.¹⁹⁻²⁶ These SO/SOS blend materials are characterized by low dispersity and high molecular weight polymer chains with high aggregation numbers within the spherical domains when phase separated. Generally, for the SO diblock copolymer, D is around 1.05 or less, molecular weights are between 80 and 100 kDa, the volume fraction of PS (f_{PS}) is ~ 0.1, and the spherical domains contain several hundred PS chains per sphere. To reinforce the physically crosslinked network and generate elasticity (when swollen) at and near room temperature, we employ PS chains of sufficiently high molecular weight (> 8 kDa) such that the PS spheres remain vitrified up to ca. 60 °C and chain pullout from the spheres under strain is minimized.²⁷ Forming the network structure in the melt instead of in solution maximizes the density of topologically fixed entanglements among both bridging and looping SOS chains. The density of these entanglements promotes the retention of a tightly bound mesh even after the introduction of a swelling medium. Thus, we have found that increasing the amount of SOS triblock copolymer in the blend improves gel modulus, because of the increased coronal overlap and entanglement density of PEO chains between neighboring spheres.^{20,21} By blending SOS with diblock SO, we can tune the overall physical and



Figure 5.1: Melt state self-assembly of SOS block copolymer blends and ion gel formation. When (a) blends of SO and SOS are (b) heated in a melt press, PS phase separates from PEO to form spherical aggregate domains comprised of several hundred PS chains per sphere. At room temperature, the PS spheres are vitrified and form a dense, physically crosslinked network. c) When placed in RTIL, the melt pressed polymer absorbs a finite amount of liquid and forms a solid gel that is held together by SOS tethers.

mechanical characteristics of the gel without the need for any chemical modifications to the polymer.

When swollen in water, these SOS gels are particularly strong, tough, elastic, and fatigue resistant.^{19,20,22} Such favorable properties, combined with the non-volatility and gas transport RTIL properties²⁸ of the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]), motivated us to investigate SOS blends swollen in RTIL (instead of water) as CO2 separation membranes.²⁶ This study of our SOS materials as ion gel membranes included some preliminary but promising mechanical property data, including compressive and tensile moduli in the $10^4 - 10^5$ Pa range, and the ability of membranes formed from these gels to withstand feed pressures of several hundred kPa during permeability testing without fracture. Given that the gas permeability of these membranes was on par with that of the neat RTIL, we were inspired to examine the potential to apply these ion gels in other transport-related applications. Herein, we present the synthesis, fabrication, ionic conductivity, and comprehensive mechanical evaluation of our SOS blend ion gels as durable, exceptionally conductive gel polymer electrolytes. The

results suggest that these materials have great potential for use as GPEs in flexible electronics, sensors, batteries or other such physically demanding environments where a traditional liquid electrolyte is incompatible, and a solid polymer electrolyte has insufficient conductivity or flexibility.

5.3 Experimental

5.3.1 Materials and synthetic methods

All reagents were purchased from Millipore-Sigma and all solvents were purchased from Fisher Chemical unless otherwise stated. Styrene monomer (99%, 50 ppm p-tert- butylcatechol inhibitor) was purified at 40 °C by distillations under static vacuum (15–30 mTorr) from di-nbutylmagnesium (1.0 M in heptane). Ethylene oxide (99.5+%, compressed gas) was purified by successive distillations from di-n-butylmagnesium (1.0 M in heptane) at 0–5 °C. Tetrahydrofuran (THF) was sparged with argon (10 psi) for 45 min and then purified over two neutral alumina molecular sieve columns (Glass Contour, Inc.). Cyclohexane (CHX) was degassed with argon and purified through a neutral alumina column followed by a Q5 copper(II) oxide catalyst column (Glass Contour, Inc.). Other common chemicals and solvents were used as received unless otherwise stated. Ultra-high purity argon (99.998%, Airgas) was passed through a column of 5 Å molecular sieves and oxygen-absorbing purifier column (Matheson Trigas). Potassium naphthalenide (KNAP) solution was prepared by mixing solid potassium metal (98% chunks in mineral oil, rinsed in cyclohexane prior to use) and a slight excess of recrystallized naphthalene under Ar in an air-free schlenk graduated cylinder in dry THF.

Synthesis of polystyrene-OH (S-OH) macroinitiator

Synthesized as previously reported.^{20,26} ¹H NMR characterization data is provided in the Supporting Information, Appendix D.

Synthesis of polystyrene-b-poly(ethylene oxide)-H, (SO-H)

This procedure is a modification of synthetic methods originally published in 2010 by Guo and Bailey.²⁰ A 2 L air-free reaction vessel fitted with glass stir bar, pressure gauge, transfer arm, and 1 L solvent bulb filled with dry, unstabilized tetrahydrofuran (THF), was evacuated and backfilled with Ar gas five times. Under positive Ar pressure (1 psig), 1.729 g (0.216 mmol) of S-OH macroinitiator was added to the reactor. The reactor was evacuated and backfilled five more times and then evacuated overnight to ensure dryness of the S-OH. After backfilling with Ar (~3.5 psig), the THF was added to the reactor to dissolve the S-OH. The reactor was heated to 45 °C and then titrated (via 5 mL airtight glass Hamilton syringe) with concentrated KNAP until a light green color persisted in the reactor for approximately 20 minutes. After reducing the reactor pressure to ~3.5 psig, 17.15g (0.389 mol) of purified ethylene oxide monomer (EO, kept at 0 °C) was added via air-free glass buret. The reaction was stirred for 24 hrs. The reaction was then allowed to cool to room temp, vented for 20 min, and terminated with ~2 mL of 0.1 N HCl. The reaction was reduced to ~ 0.6 L via rotary evaporator, precipitated into 4 L of pentane, and recovered using vacuum filtration. Finally, the product was fully dried under vacuum at ambient temperature for two days. Yield (SO-H) = 16.83g, 89.1%, see Appendix D for ¹H NMR spectra.

Synthesis of a "one-pot" polymerization of polystyrene-b-poly(ethylene oxide)-b-polystyrene (SOS83)

This synthesis proceeded similarly to the procedure for SO-H above, with the following changes: 1.41 g of S-OH macroinitiator was placed in the reactor and reacted with 14.1 g of purified ethylene oxide monomer. After stirring the reaction for 24 hours, the reactor was cooled for 1 hour prior to venting reactor with a needle and positive Ar pressure in order to remove unreacted EO without exposing reactor to air. The reactor was sealed again and re-titrated with a fresh solution of concentrated KNAP using a glass syringe. 0.547 g (2.07 mmol) recrystallized α , α '-dibromo-pxylene (DBX, Tokyo Chemical Industry Co., Ltd.) was dried in a 100 mL purification flask for 20 min. Dry THF was added to the purification flask via cannula and the solution was weighed so the concentration was known. The total amount of KNAP required to titrate the reaction (titration #1 and #2) was used to calculate the amount of DBX (0.5 equivalents per K) to add to the reaction. 5.684 mL of DBX solution (0.226 mmol DBX, 0.55 equivalents) were added to the reactor via syringe pump over 10 hours. The reaction was reduced to 500 mL with rotary evaporation, precipitated into 3.5 L of pentane, and recovered using vacuum filtration. Finally, the product (83 wt% SOS triblock, 17 wt% SO diblock) was fully dried under vacuum at ambient temperature for two days. Yield (SOS83) = 14.444 g, 93.0%. See Appendix D for ¹H NMR spectra.

Synthesis of 1-ethyl-3-methylimidazolium bromide, [EMIM][Br]²⁸

100 mL each of 1-methylimidazole (1.26 mol, Alfa Aesar) and bromoethane (1.34 mol, Tokyo Chemical Industry Co., Ltd.) were added to a 1 L round bottom flask with PTFE stir bar, condenser, and argon bubbler. 200 mL of acetonitrile was then added to the flask. The mixture was stirred and heated to reflux at 40 °C, slowly ramped to 75 °C over the course of two hours, then left to stir overnight. The acetonitrile was removed via rotary evaporation and the product, [EMIM][Br] was precipitated into 600 mL of diethyl ether (Millipore). Twice the ether was decanted from the product and replaced with 500 mL of fresh ether and stirred. Finally, the ether was decanted from the product, and the product was vacuum dried overnight. Yield = 218.8 g (91.2%) See Appendix D for ¹H NMR spectra.

Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][TFSI]²⁸

115 g (0.60 mol) of [EMIM][Br] were dissolved in 150 mL of DI water in a 500 mL round bottom flask with PTFE stir bar, at room temperature. 190 g of lithium bis(trifluoromethylsulfonyl)imide (0.66 mol, Tokyo Chemical Industry Co., Ltd.) were added to the flask and stirred for 3 hours. The reaction separated into distinct layers and the top water layer was decanted off. To wash out the remaining LiBr salt from the reaction, the remaining reaction mixture was poured into a 1 L separatory funnel, along with 200 mL each of methylene chloride and DI water. After shaking, the water layer was removed and replaced with fresh water. This process was repeated twice. The

methylene chloride layer containing ionic liquid was dried on a rotary evaporator and then further dried overnight on a Schlenk line with stirring at ambient temperature. Yield = 227.124g, 96.4% See Appendix D for ¹H NMR spectra.

5.3.2 Preparation of SOS blends and gel fabrication

Preparation of SOS blends via precipitation

SOS blends were prepared by weighing and combining 0.540 g SOS83 with 0.559 g SO-H for SOS40 (40 wt% SOS triblock and 60 wt% SO diblock in the final blend) and 0.770 g SOS83 with 0.330 g SO-H for SOS57 (57 wt% SOS triblock and 43 wt% SO diblock). Each polymer mixture was then dissolved in 25 mL of chloroform and precipitated into 250 mL of pentane for a yield of approximately 1g of each blend. The blends were vacuum dried overnight.

Preparation of SOS40 blend via freeze-drying

2.400 g of SOS83 was combined with 2.484 g SO-H and 24.4 mg BHT (0.5 wt%) in ~150 mL of benzene with stir bar in a flat-bottomed vacuum flask and sealed under ambient pressure. The mixture was stirred and very briefly heated until dissolved, then frozen on LN_2 until solid (about 20 - 30 min). Once frozen, the flask was evacuated to ~100 mTorr, at which point the LN_2 flask was removed. The benzene was removed by vacuum over approximately 12 hours, during which the pressure in the flask slowly increased to ~1 Torr and then gradually decreased back to baseline.

Gel fabrication: thermal processing and swelling.

Polymer samples were thermally processed using a Carver Model CH manual hydraulic press and various stainless-steel circular and rectangular molds (see table D2 in Appendix D). Samples were well packed (overfilled to at least 50% more mass than final disc) into the mold that was placed on a sheet of FEP coated Kapton FN (Dupont, 500FN131) on top of a pre-heated aluminum plate. The mold was then covered by a second piece of Kapton FN and topped with a second pre-heated aluminum plate. The mold was placed in the Carver press set to 150 °C and allowed to melt with slight pressure for 10 minutes. Pressure (~5000 to 7000 lbs) was then applied to the sample for 5 minutes. Samples were removed and allowed to cool to room temperature before removing from molds.

The day prior to swelling, [EMIM][TFSI] ionic liquid was stirred and vacuum dried on a Schlenk line overnight at ambient temperature. Melt processed discs were weighed and placed individually in an excess of dry [EMIM][TFSI] and allowed to swell for 12-48 hrs to achieve equilibrium swelling, depending on the thickness of the disc. Immediately before testing, the gels were removed from the ionic liquid, patted dry with kimwipes, and weighed again.

Removal of ionic liquid from swollen gels for GPC analysis

A small piece of each gel (~100 mg) was trimmed off, placed in 7 mL of ethylene glycol, and stirred overnight to leech the ionic liquid from the gel. The resulting "dry" piece of polymer was removed from the ethylene glycol, rinsed briefly with acetone to remove excess ethylene glycol, and then dried in a vacuum oven.

5.3.3 Molecular and material characterization

NMR, GPC, thermal analysis, and SAXS

¹H NMR spectra were collected in CDCl₃ (unless otherwise stated) using a Bruker Avance NEO 400 MHz Spectrometer equipped with Prodigy BBFO cryo-probe (ns = 256, 10 s delay for polymer samples). Gel permeation chromatography (GPC) was performed on a Viscotek RIMax system fitted with three 7.5 x 300 mm PolyPore (Agilent) columns in series, an Alltech external column oven set to 40 °C, and a Viscotek differential refractive index (RI) detector with sample concentrations of 2 mg mL⁻¹. Stabilized THF running at 1.0 mL min⁻¹ was used as the eluent and run time was 45 minutes for all samples. Thermal analysis was performed on a TA Instruments TGA Q500 and Discovery DSC 2500.

Synchotron small angle x-ray scattering (SAXS) experiments were run at the 12-ID-B beamline at the Advanced Photon Source (Argonne, IL) for all neat polymer samples. All SAXS

measurements utilized a beam energy of 13.30 keV (0.9322 Å) and were recorded by a Pilatus 2M detector (1475 x 1679 pixel resolution) at a sample-to-detector distance of 3.6 m. The scattering wave vector, q, was calibrated using a silver behenate standard (d = 58.38 Å). Samples were thermally processed for 15 minutes prior to SAXS measurements to initiate phase separation and minimize air bubbles. Dry polymer discs were sandwiched between Kapton tape and mounted to a multi-sample DSC pan holder made for the multi-sample heated stage. The samples remained at ambient pressure and were ramped between 100 °C and 200 °C, with exposure times of 1 s for all data collected. SAXS of ion gel samples were collected using an inhouse Rigaku SMax3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_a), a Confocal Max-Flux Optic, a Gabriel-type multi-wire area detector (1024 x 1024 pixel resolution), and a Linkam thermal stage.

Electrochemical impedance spectroscopy (EIS)

Impedance spectroscopy measurements were done using a 1287 Potentiostat/1260 FRA combination from Solartron in the 0.1Hz-200kHz range applying a 100mV sinusoidal voltage. The samples, swollen gel discs, were heated under vacuum to 50 °C prior to the first cycle of EIS measurements and their impedance was measured periodically as the vacuum oven cooled to RT. The samples were heated to 80 °C under vacuum for the second cycle of measurements. The EIS measurements for all swollen gels were done using a reusable quick assembly split coin cell (20mm I.D.) from MTI corporation. All EIS measurements for the RTIL were done using standard CR2032 SS316 coin cells using Viton gaskets and stainless-steel spacers and springs.

5.3.4 Mechanical characterization

Unconfined compression testing

Unconfined compression testing was performed at room temperature on a rheometer (Ares, TA Instruments) fitted with an 8 mm upper and 25 mm lower parallel plate. Swollen gel samples (all larger than 8mm diameter and approximately 2 mm thick) were sandwiched between the parallel

plates with an initial compressive force of 0.10 to 0.15 N force (~ 2 to 3 kPa of initial compressive stress) to ensure full contact with the parallel plates. Compression was applied at a strain rate of 10% s⁻¹ up to 50% strain for 10 successive compression/decompression cycles.

Overall compressive modulus of each gel was determined by averaging compressive stress between 0 and 50% strain across all 10 cycles, and then calculating the slope of the averaged data. The three replicates were then averaged to determine mean compressive modulus per polymer sample.

Uniaxial tensile testing (strain-to-break and cyclical testing)

Tensile testing was performed at room temperature on a tensile tester (Instron Model 4442 electromechanical universal testing system) fitted with pneumatic tensile grips (pressurized to 15 – 20 psig depending on the stiffness of the gel). Gels were swollen to approximately 10 mm x 35 mm x 1 mm rectangles, punched into a dog-bone shape (where the cross section of the narrow section was 3 mm x ~1 mm), and then mounted in the grips with an initial gauge length of ~20 mm between grips (measured once mounted). A pre-stress of approximately 3 to 5 kPa was applied prior to initiation of the test to ensure that the sample was properly straightened. Gels were stretched at a strain rate of 2% s⁻¹ until failure for strain-to-break testing, and at a rate of 10% s⁻¹ from 0% to 200% strain for cyclic tensile testing.

Young's modulus was determined for each sample/extension cycle by taking the slope of the linear regression of the initial 10 to 20% strain on the stress vs strain (kPa vs λ -1) curve.

Rheology

Frequency sweeps and dynamic temperature ramps were performed on a TA Instruments Ares rheometer fitted with 25 mm upper and lower parallel plates. Swollen gel samples (all approximately 25mm in diameter and approximately 1 mm thick) were sandwiched between the parallel plates with an initial z-axis strain of 10% (~200 to 600 g normal force, depending on the stiffness of the gel) to ensure full contact with the parallel plates. Oscillatory strain was set

between 0.3 and 0.6%, depending on the maximum strain of the linear viscoelastic regime of the gel, determined by strain sweeps performed at 1 Hz.

Fracture toughness testing

"Pure shear" fracture testing^{29,30} was adopted to characterize the fracture toughness of three SOS40 gels. Specifically, samples with dimensions of 49 mm × 49 mm × 1 mm (width × height × thickness) were prepared by swelling polymer discs that were melt pressed in a 20 mm × 20 mm × 0.4 mm square stainless steel mold. Each sample was clamped by two sets of wide rigid plates (100 mm × 25 mm) on an mechanical testing machine (Instron 5965), leaving a long strip area for fracture testing with the following dimensions: width $L_0 = 49$ mm, height $H_0 = 20$ mm and thickness $T_0= 1.0$ mm. An initial crack with length $c_0 = 10$ mm was introduced at the middle of the left edge of each sample by a razor blade. The top boundary of each sample was subjected to a vertical displacement Δ at a fixed velocity of $\dot{\Delta} = 0.2$ mm/s, while the bottom boundary of the sample was fixed. The applied loading is quantified by the stretch ratio $\lambda = 1 + \Delta/H_0$ with an effective strain rate of $\dot{\Delta}/H_0 = 0.01$ s⁻¹. During the experiment, a digital camera (Canon XF10) was used to image the crack propagation process. In addition to the fracture tests, an unnotched control sample with the same dimensions was stretched under the loading conditions until failure.

5.4 Results and discussion

5.4.1 Synthesis and material characterization

For this study, we employed a "one-pot" anionic polymerization technique that allowed us to grow narrowly dispersed, high molecular weight SO polymer (table 5.1, figure 5.2a) and achieve high triblock coupling (83 wt% SOS) in a single, large reaction. The product, SOS83, could then be used to make gels directly, or solution blended with a similar molecular weight SO-H diblock to reduce the amount of SOS triblock. We have previously reported strategies for generating SOS triblock in a "one-pot" reaction,^{22,24} but the final triblock coupling was only ~50% by mass, and

Table 5.1: List of block copolymers used in this study

polymer	M _n (kDa)	PDI	f PS
S-OH	8.2	1.03	1.00
SOS83 "one-pot"	88.2 (diblock) 176.4 (triblock)	1.04	0.101
SO-H	88.2	1.05	0.101



Figure 5.2: Molecular characterization of SOS/SO BCPs. a) GPC curves for the S-OH macroinitiator (dotted line), and the products from the two polymerizations performed for this study, SO-H (dashed line) and SOS83 (solid line). b) Comparison of relative SOS triblock amounts in SOS83, SOS57, and SOS40 using GPC. c) SAXS data for both SO-H and SOS83 in the unswollen melt state at 120 °C after 4 hrs of thermal annealing and SOS83 in the swollen state at room temperature. Open inverted triangles with a strikethrough represent the calculated allowed SAXS reflections for a sphere morphology arranged on a BCC lattice, at q/q^* ratios of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$ and $\sqrt{16}$ (where q^* , the implied primary scattering wave vector, is q_{100}). Both samples exhibit broad, form-factor scattering that is typical for sphere forming BCPs that adopt a liquid-like packing when forming a BCC lattice is kinetically hindered. When swollen, the downward shift in q* indicates an expansion of the domain spacing between spheres.

required time- and solvent-intensive fractionation to increase the amount of SOS triblock in the product in both cases. We have since found that the simple addition of a second KNAP titration step, performed after the initial polymerization of ethylene oxide but before the addition of the coupling agent (DBX), we were able to greatly increase the yield of SOS triblock chains in the final product, such that fractionation was unnecessary. We speculate that the second titration reactivates a reversibly dormant fraction of ethylene oxide chain ends produced during the extended reaction times required for the anionic polymerization of ethylene oxide. To demonstrate the full potential of these materials as polymer gel electrolyte elastomers we chose to study three different triblock copolymer blend concentrations: high (83 wt% SOS), medium (57 wt% SOS) and

low (40 wt% SOS) (figure 5.2b). Because the amount of SOS triblock has been shown to directly affect swelling ratio and modulus in our SOS hydrogels,^{19,20,22} this range of concentrations was selected to allow us to evaluate the impact of SOS triblock content on swelling ratio, ionic conductivity, and mechanical behavior when swollen in RTIL.

We observed form factor scattering in the melt state SAXS analysis (figure 5.2c) of both SOS83 and SO-H, indicative of a liquid-like packing of spherical domains that is typical for these materials at such high molecular weights and low f_{PS} .^{19–22,26} When swollen, the morphology remained unchanged, however, the primary scattering wave vector (q*) of SOS83 was nearly halved (from 0.02012 Å⁻¹ to 0.01148 Å⁻¹), which translates to an almost two-fold increase in the domain spacing between spheres. This is consistent with our observations that the swollen dimensions of SOS83 gels are nearly double that of the thermally processed neat polymer discs (see Appendix D, the Supporting Information for a table of swelling dimensions).

5.4.2 lonic conductivity

The ionic conductivities (shown in table 5.2, figure 5.3, and Appendix D section D.2) of our SOS ion gels (SOS83, SOS57, and SOS40), the neat ionic liquid, [EMIM][TFSI], and unswollen SOS83 discs were measured using electrochemical impedance spectroscopy (EIS) while under vacuum. Figure 5.3 shows the ionic conductivity of all samples as a function of temperature, measured between room temperature and 50 °C. Ionic conductivity values for the neat ionic liquid, **Table 5.2:** Summary of swelling behavior and ionic conductivity of SOS ion gels and unswollen polymer

	Amount of Triblock	Q range	RTIL loading	conductivity (σ) 1 st cycle	σ 2 nd cycle
	wt% in the neat blend	g RTIL g SOS	wt% in the gel	mS/cm at 50 °C – 30 °C	mS/cm at 80 °C – 30 °C
SOS83 gels		8.7 – 10.7	89.7 – 91.4	7.73 – 4.75 (gel 1)	11.6 – 4.21 (gel 1)
	83			8.70 – 5.27 (gel 2)	12.7 – 4.77 (gel 2)
SOS83 neat		n/a	n/a	2.65x10 ⁻³ – 7.25 x10 ⁻⁴	0.583 – 0.0167
SOS57 gel	57	12.5 – 16.2	92.6 - 94.2	8.28 - 5.43	9.98 – 5.29
SOS40 gel	40	14.5 – 21.1	93.5 – 95.5	7.89 – 5.87	9.78 – 5.06
[EMIM][TFSI]	n/a	n/a	n/a	4.85 - 3.47	6.34 - 3.47



Figure 5.3: Temperature dependence of the ionic conductivity (σ) of SOS gels, the neat RTIL, [EMIM][TFSI], and an unswollen sample of SOS83 from 50 to 30 °C. All gels exhibit high conductivity (> 4 mS cm⁻¹ across this temperature range, regardless of swelling ratio. Interestingly, σ for the tested gels is higher than the neat RTIL at all temperatures.

[EMIM][TFSI], are consistent with literature values (ca. 10⁻² S cm⁻¹).^{14,17,31–34} Surprisingly, all SOS gels tested presented slightly higher ionic conductivity values than the neat RTIL at all temperatures, suggesting that the suspension of RTIL in the PEO matrix of the SOS gels seems to enhance its conductivity. We initially suspected that this enhanced conductivity was, in part, due to some residual salt contamination in the SOS polymer associated with the anionic polymerization process, as the neat SOS83 polymer had a significantly higher conductivity (ca. 10⁻⁶ to 10⁻³ S cm⁻¹) than would be expected for pure PEO (10⁻⁹ to 10⁻⁷ S cm⁻¹).³⁵ This was found to be particularly true when the polymer was heated beyond the melting point of crystalline PEO domains (> 55 °C, see figure D6 in Appendix D), granting mobility to both the polymer chains and the ions trapped within them. Interestingly, however, results of a recent conductivity study of salt-

doped ionic liquids suggested that salt concentration had only a minor effect on the ionic conductivity of ionic liquid, and actually served to suppress the ionic conductivity of the neat RTIL slightly.³¹ Additionally, GPE materials in the literature show ionic conductivities that are comparable to or lower than the neat electrolyte.^{11,12,14,16–18,36,37} These studies together suggest that there may be factors related to the molecular interactions between RTIL and PEO that are enhancing the conductivity of our gels over the neat ionic liquid, an effect that warrants further investigation. Certainly, the high RTIL loading (90 to 96 wt% RTIL) was a major contributor to the excellent conductivity of these SOS gels, and interestingly, the variation in RTIL loading among the three blends did not appear to have a substantial effect on conductivity performance. Mechanical softening of the gels (see figure 5.6) under extended (up to 80 °C) thermal annealing during a second cycle of testing did not affect the ionic conductivity significantly (see figure D7 and D8 in the Supporting Information, Appendix D); conductivity values of the gels at 30 °C after the second cycle were only marginally lower than the initial cycle but were still above that of the neat RTIL.

5.4.3 Mechanical performance

The range of mechanical performance of GPE materials is broad and exceedingly varied, however, when investigating potential GPEs prepared from physically crosslinked block copolymer systems that scope narrows considerably. Often, the mechanical performance is described by one advantageous mechanical property that the material has exhibited, such as high ultimate tensile strength or stretchability, while the tradeoffs in ionic conductivity or other aspects of mechanical performance (or both) as a direct result of achieving that favorable property are largely de-emphasized when (if) evaluated.^{6,11,12,14,17,18,38} Consequently, our goal for this study was to perform a comprehensive mechanical investigation that could showcase the full potential of our SOS ion gel materials, and perhaps physically crosslinked BCP materials in general. To probe the mechanical behavior of these gels, we performed uniaxial tensile and compression

testing, as well as rheology, to glean information on mechanical strength, stiffness, stretchability, elasticity, toughness, cyclability, hysteresis, and viscoelastic response.

In recent years, with the advent of tougher, more mechanically advanced soft materials, particularly highly swollen hydrogels, investigation of fracture mechanics has become essential for adequately evaluating the suitability (i.e. fracture resistance, toughness, and failure mechanisms) of these materials in mechanically demanding environments.²⁹ In this chapter, we have included a preliminary fracture toughness study of our SOS ion gels, which is, to the best of our knowledge, the first report of fracture toughness of physically crosslinked BCP GPEs.

Bulk mechanical properties

Figure 5.4 shows the results of uniaxial tensile testing, unconfined compression testing, and dynamic frequency sweeps for SOS GPE elastomers and table 5.3 provides a summary of these results. In figure 5.4a, the SOS83 gels exhibited excellent ultimate tensile strength (UTS) and stretchability, with one sample reaching nearly 0.9 MPa at 500% strain. This is remarkably high UTS for a homogenous, single network material that is comprised of only 10% polymer by weight and is physically crosslinked. SOS57 blends reached UTS values upwards of 500 kPa at ~500% strain, and even the softest SOS40 blends were able to reach ~250 kPa with exceptional extensibilities up to nearly 8x without yielding, with most of the specimens reaching 400 to 600% strains. While some of our tensile specimens failed at lower elongations, none failed below 100% strain, and all but one above 200%. We believe those were likely a product of microscopic defects

	Young's Modulus	Elongation at Break	Ultimate Tensile	Bulk Toughness	Compressive Modulus	Fracture Toughness	
	(tensile)	ut Brouk	Strength	louginicoo	modulus	Γc	Γ in
	kPa	λ-1	kPa	kJ/m ³	kPa	J/m	2
SOS83	391	4.9	863	2026	436		
	(maximum) 362 ± 22 (mean)	2.8 ± 1.3	482 ± 229	817 ± 706	432 ± 5		
SOS57	134	5.1	511	1079	194		
	129 ± 6	3.8 ± 1.3	331 ± 171	627 ± 427	184 ± 9		
SOS40	91	6.5	294	883	109	5233	208
	66 ± 13	4.5 ± 1.0	200. ± 56	411 ± 182	106 ± 4	2772±1785	191±15

Table 5.3: Summar	y of mechanical	properties of SOS ion gels
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Figure 5.4: Bulk mechanical properties of three blends of SOS GPE elastomers while under a) tensile strain until failure, b) cyclical compressive strain from 0 to 50% strain, and c) oscillatory shear at varying frequencies with shear strains between 0.3 and 0.6%, depending on the linear viscoelastic regime of each gel (determined by dynamic strain sweeps). Part d) is a comparison of modulus extracted from parts a, b, and c.

in the material due to imperfect laboratory processing techniques and equipment, to which uniaxial tensile testing can be very sensitive. The vast majority of these SOS gels were stretched to failure well past 300% strain, with even the "worst" samples being stretchable far beyond other reported GPE materials,^{6,12,14} though tensile data is often just precluded from the literature.^{15,16,18,36,38}

We would like to note here that the tensile strain-to-break data of SOS40 originates from two different blends, one prepared by precipitation and the other by freeze drying. The amount of SOS triblock and mechanical results for both blends were virtually indistinguishable and therefore have been pooled into results for just "SOS40." All further mechanical results reported were performed on the freeze-dried SOS40 blend only because of the limited amounts of the precipitated blend. We feel confident that the mechanical performance of the material is irrespective of the method in which the blend is prepared because the phase separated network structure is formed during subsequent thermal processing of those blends.

These tensile strain-to-break results translate to achievable bulk toughness values of over 2 MJ m⁻³ for SOS83, 1 MJ m⁻³ for SOS57, and nearly 900 kJ m⁻³ for SOS40, exceeding any tensile extension behavior observed in SOS gel materials to date^{14,19,22,26} and without the need for irreversible chemical crosslinking¹⁴ or a sacrificial secondary network to strengthen them as is the case for highly stretchable double network gels.^{39,40} Figure 5.5 illustrates the mechanical advantage of our SOS gels over a traditional covalently crosslinked system. While the vitrified PS cores provide mechanical integrity as fixed network junction points, the solubilized PEO chains forming topologically fixed and dynamic entanglements contribute to the modulus of the gel in a manner similar to additional chemical crosslinks, but with the ability to redistribute stress concentrations by sliding past one another when extended or compressed. The absence of "fixed" strand lengths between the topological entanglements greatly increases the maximal extension and toughness of the gel and is reminiscent of the slide-ring systems developed by Ito and coworkers.⁴¹

By simply modifying the amount of SOS triblock in the blend, we can control the number of chains that can form those topological "crosslinks," which in turn directly affects the swelling ratio, modulus, and strength of the material while only impacting potential extensibility to a minor degree. We have demonstrated excellent control of modulus – particularly compressive modulus – with typical standard deviations within each blend and test type of less than 5%. The cyclical



Figure 5.5: a) A typical covalently crosslinked network with irregular strand lengths develops stress concentrations when pulled, leading to permanent weakening or failure of the network. b) Our tethered, physically crosslinked network can re-distribute stress concentrations when pulled or compressed to prevent premature failure or degradation of the network by sliding past one another. Regularly spaced, glassy PS spheres (blue spheres) anchor the PEO chains (black and red) to prevent plastic deformation of the network. This is further illustrated in part c) to show the flexibility of topological entanglements that form between bridging and looping SOS chains.

unconfined compression results (figure 5.4b) show the outstanding compressibility, elasticity, and negligible hysteresis of these materials at all levels of SOS triblock content. A small amount of single-cycle hysteresis is expected, even in an ideal swollen elastomer system, due to forced redistribution of liquid within the gel as it is compressed. This is particularly pronounced at the fast strain rates (10% s⁻¹) used in this study and in chapter 4. Upon decompression, mass transfer limitations within the highly entangled PEO matrix cause a very slight delay in the gel's return to its original conformation, however, the deformation is not permanent, and the gels fully elastically recover before the next compression cycle begins. Additionally, the modulus and compressive strength remained constant over all 10 cycles for each gel, which suggests that not only is the recovery of this material exceptionally rapid (<1s) but that the network does not sustain any permanent damage from repeated compressive loading. Interestingly, the compressive hysteresis in the SOS83 ion gels studied in this chapter was appreciably smaller than the hysteresis

observed in SOS83 (11-SOS) in chapter 4, likely due to the increased viscosity, molecular weight, and ionic interactions, which may prevent the RTIL from redistributing throughout the gel as quickly as water does upon decompression.

Rheological frequency (ω) sweeps further confirmed the elastic nature of gels formed from all three blends. In Figure 5.4c, the storage modulus (G') exhibits plateau behavior typical of elastomeric materials and significantly exceeds the loss modulus (G'') for each gel at all frequencies – by an order of magnitude or more for most values of ω – indicating a stable, solidlike polymer network structure. The upward trend of the loss modulus at higher frequencies, however, suggests that while the polymer network remained solid and elastic at higher strain rates, the viscous contributions to the gels' complex modulus and are not completely frequency independent.

With increasing temperature, we observed a decrease in storage modulus during dynamic temperature ramps for all three blends (figure 5.6). Between 0 and 60 °C, the [EMIM][TFSI] experiences an order of magnitude drop in viscosity,¹ from ~100 mPa·s to ~10 mPa·s and could be a contributor to the observed change modulus over the temperature range tested. At some point beyond 50 °C the vitrified PS cores and consequently, the gels, softened irreversibly, however, the storage modulus remained higher than the loss modulus over the full temperature range and the gels retained their shape when removed from the rheometer at room temperature (see figure 5.6b and c). At equilibrium swelling, the PEO chains in the gels are already under stress such that once the PS domains soften above their T_g, it is likely that this stress leads to PS chain rearrangement, producing a reduced modulus without disruption of the network. The solubility of PS in [EMIM][TFSI] is extremely poor up to and well past 100 °C, so it is unlikely that plasticization of the PS spheres by the RTIL at elevated temperatures is responsible for softening the gels.⁴²



Figure 5.6: a) Dynamic temperature ramps from 0 to 100 °C at a rate of 1 °C min⁻¹ of SOS ion gels. A gel is pictured at room temperature before (b) and after (c) heating to 100 °C.

Cyclability under tensile strain

Lewis et al. previously demonstrated the excellent compressive fatigue resistance of SOS hydrogels in which the gels were subject to fast, low strain (1 Hz cycles, 12% strain s⁻¹) but extraordinarily high cycle (up to 500k continuous) measurements to mimic the repeated loading experienced by tissue in a biomechanical environment, such as the knee meniscus. They observed nearly complete recovery of the modulus after short rest periods.²² While it was unfeasible to repeat these extended compressive fatigue experiments for the ion gels explored in this study, based on the 10-cycle compression experiments and the similar chemical and morphological structure, we have reason to believe that swapping out water for RTIL as the liquid component of the gel should not significantly impact the compressive fatigue resistance of the network.

For applications in soft, flexible, and foldable electronics, we felt it crucial to observe the cyclability of our SOS ion gels under repeated tensile strain, however true high-cycle "fatigue"

testing was not within the scope of the study due to instrumentation limitations. Therefore, we chose to test a sample at a high strain amplitude and rapid strain rate to demonstrate cyclability of the material under relatively extreme loading conditions over the course of a few hundred cycles, instead of many thousands. An SOS40 ion gel was pulled repeatedly to 200% strain (at 10% s⁻¹) until failure, and this data is shown in figure 5.7a. 200% strain was chosen as the highest strain that was still comfortably below the failure strength range for SOS40 gels, based on the tensile strain-to-break data (figure 5.4a). This gel was able to be stretched to 3x its initial length over the course of 161 cycles before failure at cycle 162, likely due to a defect in the material that caused a propagating crack. Importantly, over the course of those cycles, the initial (Young's) modulus of the material remained largely constant (shown in figure 5.7b), implying that the elastic network was not being progressively damaged simply due to the repeated loading. The elastic modulus at strains approaching 200% did decay slightly during the last 10 cycles or so, presumably when the crack initiated and began to propagate in the gel. The gel also showed



Figure 5.7: An SOS40 gel under cyclical tensile loading at 10% strain s⁻¹. The gel exhibits no hysteresis, excellent elasticity, rapid recovery, and virtually no decay in modulus when repeatedly loaded. We believe the failure at cycle 162 is likely due to initiation and propagation of a crack in the material due to a flaw from the melt processing step. The relatively high amplitude (200% strain) used in this test demonstrates the excellent flexibility and durability of the material under extreme loading conditions.

excellent elasticity throughout the experiment, with no detectable hysteresis during each unloading cycle, even when the gel was close to failure.

Fracture mechanics of SOS GPE elastomers

In "pure shear" fracture testing,^{29,30} the fracture toughness Γ_c , defined as the energy required to advance the crack by a unit area, can be evaluated using $\Gamma_c = W(\lambda_c)H_0$, where λ_c is the critical stretch ratio for maintaining crack propagation in the notched samples, $W(\lambda_c)$ is the work per unit volume to bring the unnotched control sample to the stretch ratio λ_c , and H_0 is the initial gauge height of the precut samples (figure 5.8a). The function $W(\lambda)$ is evaluated by integrating the forcedisplacement curve of the unnotched sample for a given stretch ratio λ (= 1 + Δ/H_0) and dividing it by the initial volume $L_0H_0T_0$, while λ_c is determined using the precut samples. For isotropic elastic gels, the crack is expected to propagate horizontally (i.e., perpendicular to the applied tension) in an unstable manner.²⁹ The onset of unstable crack propagation should correspond to the peak force experienced by precut samples, based on which we determine the critical stretch ratio λ_c .

Using the approach above, we found a large range for Γ_c , i.e., 1053 to 5233 J m⁻² among three SOS40 gels tested (see Appendix D, the Supplementary Information, for the complete set of data). In particular, the largest Γ_c (5233 J m⁻²) was for a notched sample of which the critical stretch λ_c (5.86) exceeded that of the unnotched sample ($\lambda_c = 4.74$) (see figure 5.8b). This is surprising since intuitively the initial crack in the notched sample should reduce the critical stretch λ_c . As a result, we had to fit the force-displacement curve of the unnotched sample and extrapolate it beyond the critical stretch of failure. To resolve this apparent paradox, we examined images of the crack propagation process and discovered a crack branching behavior in all three notched gels tested; after the initial crack started to propagate, secondary sideways cracks emerged around the blunted tip of the primary crack (figure 5.8c).



Figure 5.8: a) Geometry of the "pure shear" fracture test. b) Force versus stretch data for the SOS40 control (black line) and the second SOS40 notched sample tested. It is highly unusual for a sample with an introduced crack to stretch beyond the failure point of the control, but we believe that the crack branching behavior, seen here as jagged "teeth" in the force-displacement plot, acts as a toughening mechanism. c) Images and illustrated traces of notched sample 2 as it was stretched and the crack propagated perpendicular to the initial crack. d) An unswollen disc of SOS40 after thermal processing. e) An SOS40 disc after swelling in RTIL to more than twice its initial size in all dimensions. f) Notched sample 2 after pure shear fracture testing. Note the tortuous crack path that is evidence of crack branching.

Formation of the sideways cracks caused local unloading as evidenced by the teeth-like profile in figure 5.8b, where we observed slight force drops as the propagating crack branched. This crack branching behavior – which was also observed in the two other notched samples – can arrest the primary crack or deflect its propagation direction, which eventually results in a tortuous crack path (figure 5.8f).

The physical mechanism behind crack branching is not known for these particular materials. Crack branching or deflection often occurs near filler/matrix interfaces in composite materials. For example, crack branching was observed in elastomeric composites with stiff and soft domains⁴³ and was exploited as a strategy to enhance fracture toughness and fatigue resistance.^{44,45} However, our ion gels have an amorphous network structure and are macroscopically homogeneous. In a recent work, crack branching was also found in a homogenous silicone elastomer,⁴⁶ which was attributed to the structural rearrangement of polymer chains near the crack tip due to high stretch. Whether this is true for our ion gels needs to be investigated by molecular characterizations such as in-situ X-ray scattering during loading, which will be pursued in future work.

Regardless of the physical origin, crack branching serves as a mechanism to enhance the fracture toughness in our SOS ion gels without requiring sacrificial bonds.⁴⁷ To illustrate this point, we identified the stretch ratio, λ_{in} , at the onset of crack propagation (see figure D9 and table D1 in Appendix D) and calculated the corresponding fracture toughness, Γ_{in} , for initiating crack propagation. We found that Γ_{in} fell into a much narrower range (172-208 J m⁻²), similar to the Γ_c values exhibited by physically crosslinked block copolymer and traditional hydrogels in the literature, which are typically very low (< 100 J m⁻²)⁴⁸⁻⁵⁰. For a typical homogenous gel material for which the onset of crack propagation is in the same direction as the initial crack and for which crack branching is not observed, Γ_{in} and Γ_c are similar, if not the same. In contrast, the Γ_c of our gels is orders of magnitude higher (1000 to 5000 J m⁻²) and its variation from sample to sample

is much larger. This significant difference in effective toughness is most certainly due to the crack branching effect, which causes stable crack propagation and delays ultimate failure. We can attribute the large variation in Γ_c to the stochastic nature of crack branching, but despite that, all three gels performed well into the range of "tough" materials like DN gels, composites, or liquidfree elastomers.^{39,43,47}

5.5 Conclusions

In this work we have shown that physically cross-linked ion gels that are formed by swelling cleverly designed SOS BCPs in RTIL after their melt-state self-assembly can bypass the classic mechanical/conductivity trade-off and be both highly conductive and mechanically tough. We believe these materials show great promise as ionic conductors in flexible electronics applications that require electrolytes with the excellent mechanical properties of elastomers. All of the gels measured, regardless of SOS triblock or RTIL content, showed exceptional ionic conductivities (4 to 13 mS cm⁻¹), outperforming the neat RTIL at all temperatures. Mechanically, we demonstrated that these ion gels have tunable elastic moduli over a span of several hundred kPa, high stretchability (up to $\lambda \sim 7.5$), and bulk toughness values up to 2 MJ m⁻³. All of our gels are highly elastic and showed nearly instantaneous recovery from deformation upon cyclic loading. Under repeated tensile loading, an SOS40 gel displayed no hysteresis at fast loading rates (10% s⁻¹) and high amplitude (200%) strain, surpassing 150 cycles before failure.

Despite being macroscopically homogenous and isotropic, we identified an unusual crack branching phenomenon in the fracture behavior of our SOS40 gels during pure shear fracture toughness testing. This behavior, marked by the propagation of cracks perpendicular to the path of the induced crack has been observed and targeted in composite and intentionally anisotropic materials, but is very rare in homogenous polymers. We believe this is the first example of crack branching behavior in a swollen elastomer. Crack branching serves to toughen the gels by creating a tortuous fracture pattern that delays the ultimate failure of the material, and as a result

we were able to observe high fracture toughness values $(1000 - 5000 \text{ Jm}^{-2})$ that were well beyond what we would expect for a homogenous, physically cross-linked, single network polymer gel with such high liquid content (> 90 wt%). The uniqueness of these results certainly warrants further investigations into the crack branching and propagation mechanisms observed here.

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CHAPTER 6: FINAL REMARKS

6.1 Final remarks for chapters 2 and 3, the synthesis and phase behavior of PIL BCPs

6.1.1 Summary

Chapter 2 details the synthesis, melt-state phase behavior, and some unique physical properties of a series of MCIL BCPs derived from the sequential RAFT polymerization of PBMA and Co(II) bis(salicylate) complex containing monomers, which at the time of publication in 2017 were the first true metal containing IL-based BCPs in the literature. Using SAXS, we were able to identify all four classic equilibrium diblock copolymer morphologies (Lam, Hex, Gyr, and S) that formed in the melt state but remained upon cooling. Additionally, we demonstrated a fully reversible color change when coordinated to small protic molecules like water and methanol.

Chapter 3 continues the work by Shi et al.,¹ in which they reported on the first direct, sequential synthesis of imidazolium based PIL BCPs using styrene and styrenic-imidazolium based IL monomers with varying R-group functionality using ATRP. This chapter focuses largely on the melt-state behavior analysis using SAXS of a larger library of these PIL BCPs which allowed us to construct phase diagrams of both the methyl- and butyl-functionalized series of PIL BCPs. Among the methyl-functionalized PIL BCPs, we identified the Lam, Hex, and S morphologies, and a persistent coexistence of the Lam and Hex phases in the region where we would typically expect a Gyr phase in a system with lower segregation. In the butyl-functionalized series of PIL BCPs we were also able to identify the Gyr phase, which allowed us to conclude that simple modification of the dangling imidazolium R-group allows additional control of BCP phase behavior by changing the segregation strength (χ) within the system regardless of degree of polymerization (N), which in this case was held constant. We were also able to estimate the
previously unknown block density of both the Me-PIL and Bu-PIL blocks, which enabled us to construct phase diagrams based on volume fraction (f) of the PIL block. Block density and synthetic technique allow for fine control of f and χN , which, coupled with knowledge of preestablished phase behavior are critically important when targeting specific morphologies in synthesis, therefore we believe this work will be useful to anyone synthesizing chemically similar materials in the future.

6.1.2 Broader impacts to the scientific community

- Synthetic strategies for the direct, sequential, well controlled synthesis of both cobalt- and imidazolium-based PIL BCPs using IL containing monomers via RAFT or ATRP
- First example of a true metal containing IL-based BCP
- Contribution of a wealth of melt-state phase behavior information from a large catalog of phase separating PIL BCPs
- Estimation of density of the imidazolium based Me-PIL block to enable better morphological control in future syntheses
- Demonstration of the highly sought-after bicontinuous gyroid phase in both highly segregated and asymmetric PIL BCP systems
- Potential as solid-phase conducting materials; easily melt processible and nanostructure remains upon cooling to room temperature

6.1.3 Future directions

lonic polymers like these PIL and MCIL BCPs have significant potential as functional materials such as solid polymer electrolytes, but their ionic conductivity must be explored. SPEs with conductivity at or near liquid or gel electrolytes are highly sought after in the battery research community but in order for any highly conductive SPE to be useful, it also needs to be mechanically robust.² The Gyr phase is an ideal morphology to achieve both high conductivity

and high modulus, as the dually continuous morphology could achieve high conductivity through the continuous matrix of the PIL block, and mechanical integrity through the continuous PS or PBMA block, in the case of the materials studied in this chapter. It would be worthwhile, then, to explore the ionic conductivity and mechanical properties of these polymers as a function of both morphology and molecular weight, with a particular focus initially on finding the right combination of parameters to synthesize PIL BCPs that can form a pure Gyr phase. These experiments would also warrant an investigation into the best methods for melt processing or solution processing to produce polymer discs or films that could be used for conductivity and mechanical testing. It is likely that the molecular weights of these PIL BCPs will need to be increased to exceed the entanglement molecular weight of the polymer and promote mechanical robustness in the material, as most of the materials studied in chapters 2 and 3 were brittle (the exception being the polymers that had significant hexyl-PIL content, which were ultra-viscous, sticky liquids and could not phase separate), even after thermal annealing.

6.2 Final remarks for chapter 4, the impact of high molecular weight contaminant on SOS hydrogel mechanical performance and synthetic strategies for its elimination

6.2.1 Summary

For over a decade, the Bailey group has been making highly distensible, tough, and fatigue resistant hydro- and ion gels based on amphiphilic, melt-state phase separating blends of SOS/SO block copolymers. Recently, we discovered the presence of a high molecular weight contaminant in certain batches of our SOS polymers that appeared to increase the dispersity of our polymers and negatively impact the mechanical performance of the gels. This "contaminant" appeared to be comprised largely of PEO homopolymer, which led us to theorize that it was being generated at some point in our synthetic process, as opposed to a contaminant that would have

been introduced to our polymer mixtures accidentally from an outside source. Chapter 4 documents our efforts to determine the procedural cause of the HMC, how to eliminate it from our polymers, and how its presence, or lack thereof, directly impacts the mechanical properties of our SOS materials when swollen in water.

After many different polymerizations and triblock coupling reactions, we found that the largest, and perhaps only, contributor to the presence of HMC was the concentration of the anionic polymerization reaction to create SO diblock; reactions that contained less than 30 mL of solvent per gram of final polymer product were much more likely to contain HMC (and particularly those that had less than 10 mL g^{-1}), and we had the greatest success with high molecular weight (> 90 kDa) products when the reaction concentration was upwards of 60 mL g⁻¹. Polymer samples with high HMC content were able to form elastic gels similar in look and feel to samples with no HMC, however their swelling ratios and mechanical properties were highly unpredictable. We also found there to be a trade-off between HMC content and SOS triblock content in any given blend, which meant that there was an upper limit to the modulus in blends with high HMC content since mechanical properties in a gel are largely determined by the swelling ratio, and swelling ratio is directly related to the amount of triblock in the blend. Based on the mechanical performance of the high HMC content gels in this study, we can conclude that presence of HMC in a gel does not contribute to the modulus of the material in any meaningful way, therefore, for anyone making SOS materials via anionic polymerization in the future, it would be best to use good synthetic practices that avoid generating HMC.

6.2.2 Broader impacts to the Bailey group and the scientific community

- A reproducible method for synthesizing narrowly dispersed, bimodal, high triblock SOS/SO blend polymer
- The first study in our group to compare physical and mechanical properties of hydrogels across a wide variety of polymer batches

- Established a relationship between Q and compressive modulus for our hydrogels, regardless of batch or HMC content, that can be used to predict the mechanical properties of new materials based on their swelling ratio.
- This study, while not explicitly contributing to the scientific literature, has allowed us to move forward with our research on tough and distensible gels, and made the work in chapter 5 and beyond possible

6.2.3 Future directions

This chapter mostly resolved the largest roadblock to the success of SOS hydro- and ion gels as reproducible and commercially viable materials, but we did not attempt to fully understand what the HMC is, why HMC forms at high concentration, or elucidate any mechanisms behind its formation. Mechanistic studies would be difficult but incredibly valuable to our group, however, in lieu of or possibly even in conjunction with such experiments, it would be worthwhile to reproduce this study in a far more controlled manner. Likely, this would involve varying the targeted SO molecular weight across a range of concentrations, to create a "matrix" of successful and unsuccessful polymerizations that would enable us to estimate the concentration at which HMC will form at any targeted molecular weight. Alternatively, a simple test could be performed to narrow down the potential mechanisms of HMC formation; take a "good" diblock (that was synthesized at low concentration and can be coupled without HMC forming) and stir it in dry, air free solvent for ~24 hrs at various concentrations. That would likely narrow down whether the HMC forms because of high-concentration solvent and entanglement effects in solution, or if it happens through side reactions in the anionic polymerization process at high concentrations.

A more rigorous investigation into what the HMC is comprised of would be crucial prior to any mechanistic studies. After fractionation or chromatography to isolate HMC from the polymer samples that contain high amounts of it, various molecular characterization techniques (NMR,

GPC, SAXS) could be useful to analyze molecular weight, dispersity, morphology, and end groups. High resolution MALDI-TOF/TOF spectrometry could be particularly useful to accurately determine the various molecular weight distributions in the HMC isolate and would allow us to deconvolute the different populations of chains. This could help us determine if there are PS macroinitiator "end groups" on those various populations of what we believe to be long PEO chains.

6.3 Final remarks for chapter 5, highly conductive and mechanically tough gel polymer electrolyte elastomers

6.3.1 Summary

In the world of soft and flexible electronics and battery innovations, highly conductive, non-volatile electrolytes that are also mechanically robust are extremely desirable for improving battery design and safety and many other applications. In chapter 5, we explored the potential of our SOS gels swollen in the ionic liquid [EMIM][TFSI] as gel polymer electrolytes, polymer materials that are swollen in conductive solvent but behave like solids in response to mechanical stimuli. Ideal GPEs should be the amalgamation of the best properties of SPEs and liquid electrolytes; both mechanically tough (and flexible) and highly conductive.

We explored the ionic conductivity of our SOS ion gels using electrochemical impedance spectroscopy and found our gels to be exceptionally conductive (> 4 mS cm⁻¹ at 30 °C) regardless of swelling ratio and triblock content. Additionally, suspension in the PEO matrix appeared to enhance conductivity of the ionic liquid, as all gels tested had ionic conductivities that exceeded the neat [EMIM][TFSI] at all temperatures.

Mechanically, SOS ion gels were shown to be exceptionally distensible, elastic, and tough via uniaxial tensile and compression testing. The elastic modulus was easily reproducible, both under tension and compression, despite our suboptimal bench-scale processing equipment.

Modulus was also tunable by several hundred kPa just by modifying the amount of SOS triblock in the polymer blend prior to swelling. Elasticity of the SOS ion gels was not affected by triblock content, but the lowest triblock gels (SOS40) were the most distensible, on average. Cyclical compression and tensile testing highlighted the elasticity, minimal hysteresis, and extremely rapid recovery rates (seconds or less) of SOS ion gels. Under rapid, high amplitude (200% strain) cyclical tension, an SOS40 gel exhibited virtually no hysteresis or decay of modulus until the material began to fatigue just prior to failure at around 155 cycles. Recently, fracture toughness has become an incredibly important parameter by which the fracture resistance of hydrogels and ion gels is quantified, and we believe that we are the first to report the fracture toughness of a set of physically crosslinked SOS BCP gels. With fracture toughness values in the range of 1000 to 5000 J m², our SOS ion gels fall well within the range of other "tough" gels. We also observed a crack branching toughening phenomenon in the fracture behavior of these gels, which is highly unusual for homogenous materials and certainly warrants further investigation.

6.3.2 Broader impacts to the scientific community

- Demonstration of the potential for mechanical toughness in well-designed physically crosslinked gels, which are typically perceived of as weak materials
- Very high conductivity and impressive mechanical properties make SOS BCP gels excellent candidates as GPE materials for batteries and soft electronics
- Discovery of a crack branching toughening phenomenon in a homogenous, isotropic swollen material which is highly unusual
- Demonstration of recoverability of the polymer from non-volatile RTIL

6.3.3 Future directions

This chapter was able to demonstrate excellent mechanical properties in our SOS gels, but some of the experiments, especially the pure shear fracture testing, were limited by material constraints.

To continue this project, fracture toughness should be measured on a larger sample set and for different amounts of SOS triblock to gauge how tuning the stiffness of the material affects fracture toughness. We have shown significant fatigue resistance in our hydrogels under compressive loading, and we believe that our gels are likely to be fatigue resistant under tensile loading as well, however, measuring fatigue threshold under low amplitude and high frequency conditions in our SOS ion gels was beyond the scope of this study. For flexible electronics applications where these materials would undergo repeated loading for many years, measuring the fatigue threshold at various amounts of SOS triblock and swelling ratios is imperative.

The crack branching phenomenon that we observed in this study suggests that the nanostructure of the material has inherent toughening mechanisms that prevent catastrophic crack propagation within the material, and we believe that crack propagation testing that utilizes particle tracking on the surface of the gel would allow us to explore the fracture mechanisms more thoroughly in these materials. Additionally, we could employ SAXS and a micro-tensile tester to observe if there are any morphological changes, structure alignment, or in-situ crystallization of PEO domains while the gels are being stretched.

I believe it would also be worth investigating the recyclability of this polymer system. The non-volatility of ionic liquid poses significant difficulties for those looking to recover materials swollen in RTIL, however, we were able to demonstrate that RTIL can be leeched out of SOS gels remarkably easily by soaking in ethylene glycol for a day. As thermoplastic materials, SOS BCPs can theoretically be thermally reprocessed infinitely but we have never investigated the effect of reprocessing on mechanical properties, dispersity, and swelling behavior. We do believe that the xylene linkage between PEO blocks is susceptible to cleavage under extended thermal annealing when not under vacuum, so experimenting with different coupling agents or air-free melt processing techniques may be critical to the success of this project.

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APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 2, METAL-CONTAINING IONIC LIQUID-BASED, UNCHARGED-CHARGED DIBLOCK COPOLYMERS THAT FORM ORDERED, PHASE-SEPARATED MICROSTRUCTURES AND REVERSIBLY COORDINATE SMALL PROTIC MOLECULES

Contents of the supporting information

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A.13 Reversible coordination experiments of the MCIL-based BCPs **1a-f** upon exposure to small alcohols and aprotic molecule vapors.

A.14 Thermal stability of MCIL-based BCPs 1a-f

A.1 Materials

Tributylphosphine, 4-vinylbenzyl chloride, cobalt(II) chloride hexahydrate, lithium salicylate, 2cyano-2-propyl benzodithioate (CPBD), and chlorobenzene were all purchased from Sigma-Aldrich and used as received. Butyl methacrylate was purchased from Sigma-Aldrich and purified by passage over a column of basic alumina to remove the added radical inhibitor. Azobis(isobutyronitrile) (AIBN) was purchased from the Sigma-Aldrich Co. and recrystallized from methanol. All solvents were purchased from Sigma-Aldrich or Mallinckrodt, Inc., and purified/dehydrated via N₂-pressurized activated alumina columns, and de-gassed. The H₂O used for synthesis was purified and de-ionized, with a resistivity value greater than 12 MΩ/cm. All polymerizations were carried out in a dry Ar atmosphere using standard Schlenk line techniques.

A.2 Instrumentation

¹H and ¹³C NMR spectra were obtained using a Bruker 300 Ultrashield[™] (300 MHz for ¹H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. Gel permeation chromatography (GPC) was performed using a Viscotek GPC-Max chromatography system outfitted with three 7.5 x 340 mm Polypore[™] (Polymer Laboratories) columns in series, a Viscotek differential refractive index (RI) detector, and an Alltech column oven (mobile phase THF, 40 °C, 1 mL min⁻¹ flow rate). Molecular weight data obtained on this GPC system were referenced to polystyrene molecular weight standards. Elemental analysis was performed with a Vario EL III (Elementar) instrument at the Tokyo University of Agriculture and Technology. Small-angle X-ray scattering (SAXS) data were collected using a Rigaku SMax3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_α), a Confocal

Max-Flux Optic, a Gabriel-type multi-wire area detector, and a Linkam thermal stage. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC2500 instrument. UV-visible spectroscopy was performed using a UV-2450 instrument (SHIMADZU). Thermogravimetric analysis (TGA) was performed with an EXSTAR TG/DTA 7200 system (Seiko Instruments, Inc.) at a heating rate of 10 °C min⁻¹.

A.3 Synthetic methods

A.3.1 Synthesis of tributyl(4-vinylbenzyl)phosphonium chloride¹

Synthesized as previously reported.¹ Characterization data matched those reported.¹

A.3.2 Synthesis of PBMA macro-chain-transfer agents (macroCTAs) 2a-f²

The DP, M_n , and PDI values of **2a–f** are shown in Table A1 below.

PBMA MacroCTA	DP	<i>M</i> _n (g/mol)	PDI	
2a	35	5,198	1.08	
2b	40	5,909	1.06	
2c	45	6,620	1.10	
2d	50	7,331	1.04	
2e	55	8,042	1.07	
2f	60	8,753	1.10	

Table A1: The DP, *M*_n, and PDI values for PBMA macroCTAs 2a–f.

Procedure for the RAFT polymerization of butyl methacrylate to form PBMA macroCTA 2a.

Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (66.7 mg, 0.301 mmol), chlorobenzene (1.2 mL) and AIBN (5.00 mg, 0.0304 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of the butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask

were cooled to room temperature, diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA **2a** as a pink solid (yield: 1.32 g, 84%). DP = 35; PDI = 1.08; M_n = 5198 g/mol (calculated using ¹H NMR polymer end-group analysis. See the following sections for details on how the DP and absolute M_n were determined using ¹H NMR analysis).

Procedure for the RAFT polymerization of butyl methacrylate to form PBMA macroCTA 2b.

Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (58.4 mg, 0.264 mmol), chlorobenzene (1.2 mL) and AIBN (4.30 mg, 0.0264 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of the butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA **2b** as a pink solid (yield: 1.27 g, 82%). DP = 40; PDI = 1.06; M_n = 5909 g/mol (calculated using ¹H NMR polymer end-group analysis. See the following sections for details on how the DP and absolute M_n were determined using ¹H NMR analysis).

Procedure for the RAFT polymerization of butyl methacrylate to form PBMA macroCTA 2c.

Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (51.9 mg, 0.234 mmol), chlorobenzene (1.2 mL) and AIBN (3.80 mg, 0.0231 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of the butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA **2c** as a pink solid (yield: 1.15 g, 74%). DP = 45; PDI = 1.10; $M_n = 6620$ g/mol (calculated using ¹H NMR polymer end-group

analysis. See the following sections for details on how the DP and absolute M_n were determined using ¹H NMR analysis).

Procedure for the RAFT polymerization of butyl methacrylate to form PBMA macroCTA 2e. Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (42.5 mg, 0.192 mmol), chlorobenzene (1.2 mL) and AIBN (3.2 mg, 0.0194 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of the butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA **2e** as a pink solid (yield: 1.18 g, 76%). DP = 55; PDI = 1.07; M_n = 8042 g/mol (calculated using ¹H NMR polymer end-group analysis. See the following sections for details on how the DP and absolute M_n were determined using ¹H NMR analysis).

Procedure for the RAFT polymerization of butyl methacrylate to form PBMA macroCTA 2f. Butyl methacrylate (1.50 g, 10.5 mmol), CPBD (38.9 mg, 0.176 mmol), chlorobenzene (1.2 mL) and AIBN (2.9 mg, 0.0176 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 70 °C for 24 h. Upon complete consumption of the butyl methacrylate (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with THF, precipitated by adding into MeOH, and the precipitate recovered by filtration to give the desired PBMA macroCTA **2f** as a pink solid (yield: 1.21 g, 79%). DP = 60; PDI = 1.10; M_n = 8753 g/mol (calculated using ¹H NMR polymer end-group analysis. See the following sections for details on how the DP and absolute M_n were determined using ¹H NMR analysis).

A.3.3 Synthesis of MCIL-based BCPs 1a-f

The calculated block compositions and M_n values of MCIL-based BCPs **1a-f** are shown in table

A2 below:

Table A2: The calculated block compositions and M_n values of MCIL-based BCPs **1a-f** from ¹H NMR analysis.

BCP	notebook reference	n	m	<i>M</i> _n (g/mol)
1a	zs-2082	35	35	22,175
1b	zs-3068	40	30	20,461
1c	zs-3004	45	25	18,747
1d	zs-2135	50	20	17,033
1e	zs-3069	55	15	15,318
1f	zs-3005	60	10	13,604

Synthesis of MCIL-based BCP 1a

Monomer 3 (235 mg, 0.484 mmol), 2a (72.0 mg, 0.0139 mmol), chlorobenzene (1.00 mL) and AIBN (0.500 mg, 0.00304 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of monomer 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1a as a dark blue solid (yield: 220 mg, 72%). Block repeat units molar ratio = 1:1 (butyl methacrylate:monomer 3); block length composition = 35-*b*-35 (PBMA-*b*-poly(3)); M_n = 22,175 g/mol (calculated based on ¹H NMR analysis. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

Synthesis of MCIL-based BCP 1b

Monomer 3 (246 mg, 0.507 mmol), 2b (99.9 mg, 0.0169 mmol), chlorobenzene (1.20 mL) and AIBN (0.600 mg, 0.00365 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and

back-filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of monomer 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1b as a dark blue solid (yield: 286 mg, 83%). Block repeat units molar ratio = 1.33:1 (butyl methacrylate:monomer 3); block length composition = 40-*b*-30 (PBMA-*b*-poly(3)); M_n = 20,461 g/mol (calculated based on ¹H NMR analysis. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

Synthesis of MCIL-based BCP 1c

Monomer 3 (266 mg, 0.548 mmol), 2c (145 mg, 0.0219 mmol), chlorobenzene (1.20 mL) and AIBN (0.700 mg, 0.00426 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of monomer 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1c as a dark blue solid (yield: 322 mg, 78%). Block repeat units molar ratio = 1.8:1 (butyl methacrylate: monomer 3); block length composition = 45-*b*-25 (PBMA-*b*-poly(3)); M_n = 18,747 g/mol (calculated based on ¹H NMR analysis. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

Synthesis of MCIL-based BCP 1e

Monomer 3 (214 mg, 0.441 mmol), 2e (236 mg, 0.0294 mmol), chlorobenzene (2.40 mL) and AIBN (1.00 mg, 0.00609 mmol) were added to a flame-dried Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of monomer 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to room

temperature, diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1e as a dark blue solid (yield: 338 mg, 75%). Block repeat units molar ratio = 3.67:1 (butyl methacrylate:monomer 3); block length composition = 55-*b*-15 (PBMA-*b*-poly(3)); M_n = 15,318 g/mol (calculated based on ¹H NMR analysis. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

Synthesis of MCIL-based BCP 1f

Monomer 3 (256 mg, 0.528 mmol), 2f (462 mg, 0.0528 mmol), chlorobenzene (3.00 mL) and AIBN (1.70 mg, 0.0104 mmol) were added to a flame-dried Schlenk flask and degassed by three freezepump-thaw cycles. The flask was then allowed to warm to room temperature and back-filled with Ar. The resulting mixture was then stirred at 90 °C for 48 h. Upon complete consumption of monomer 3 (as verified by ¹H NMR analysis), the contents of the flask were cooled to room temperature, diluted with ethyl acetate, precipitated by adding into hexane/ethyl acetate (4/1 (v/v)) mixture. The resulting precipitate was recovered by filtration to give the MCIL-based BCP 1f as a dark blue solid (yield: 512 mg, 71%). Block repeat units molar ratio = 6:1 (butyl methacrylate:monomer 3); block length composition = 60-b-10 (PBMA-*b*-poly(3)); *M*_n = 13,604 g/mol (calculated based on ¹H NMR analysis. See following sections for details on how the copolymer block composition, block lengths, and *M*_n were determined).

A.4 ¹H NMR and ¹³C NMR spectra of monomer 3

When monomer **3** is dissolved in common non- or weakly coordinating NMR solvents (i.e., CDCl₃, CD_2Cl_2 , $(CD_3)_2CO$), its ¹H and ¹³C signals are broad peaks due to the paramagnetism of the Co(II) ion present in the anion. However, the ¹H and ¹³C signals of the phosphonium cation of **3** are sharp peaks when **3** is dissolved in CD₃OD because of the combined effects of coordination of CD_3OD to the Co(II) anion and good solvent separation of the phosphonium cation from the paramagnetic Co(II) anion.



Figure A1: ¹H NMR spectrum and peak assignments for 3



Figure A2: ¹³C NMR spectrum and peak assignments for **3**. As mentioned before, the carbon signals of Co(II) anion is hard to interpret due to the paramagnetic effect of Co(II).

A.5 Determination of the DP and *M*_n values of PBMA macroCTAs 2a-f³

The RAFT of butyl methacrylate to make macroCTAs has been established in the literature to have controlled polymerization character.² The DP and M_n values of synthesized PBMA macroCTAs **2a–f** were calculated based on the ¹H NMR peak integral of aromatic protons (<u>A</u>) on the CPBD end-group relative to that of the protons (<u>B</u>) on the ester group for these polymers (Equations 1 and 2).³ See figure A3 below for example data used to calculate these values for **2d**.

$$DP = \frac{B_{1H \text{ NMR Integration}}}{A_{1H \text{ NMR Integration}}}$$
(Eq. 1)

(Eq. 2)

$$M_{\rm n} = ({\rm DP} \times M_{\rm monomer}) + M_{\rm CPBD}$$



Figure A3: Example ¹H NMR spectrum of **2d** in CD₃OD, and the ¹H NMR peak assignments used for calculating the DP and M_n value. Calculated DP = 50.3 (\cong 50), M_n = 7,331 g/mol.

A.6 Determination of BCP compositions and molecular weights.

The block composition ratios, overall lengths, and M_n values of MCIL-based BCPs **1a–f** were determined via ¹H NMR analysis. For example, see figure A4 for ¹H NMR peak assignments and

an example spectrum used for these calculations: The signals of protons \underline{D} on the butyl ester of **1d** overlap to create a broad peak between 3.89–4.09 ppm (signal \underline{D}). The signals of the benzylic protons (protons \underline{E}) on phosphonium overlap to create a broad peak between 3.54–3.88 ppm (signal \underline{E}). So, the PBMA:poly(**3**) ratio can be calculated by Eq. 3. The length of the poly(**3**) block can be calculated by Eq. 4 and confirmed by conversion (Eq. 5). The M_n of BCPs can be calculated by Eq. 6.

$$PBMA:poly(3) ratio = \frac{D_{1H NMR Integration}}{E_{1H NMR Integration}}$$
(Eq. 3)

Poly(3) block length, m =
$$\frac{\Pi}{PBMA:poly(3) ratio}$$
 (Eq. 4)

Poly(3) block length, m = (monomer: macroCTA ratio) × conversion (Eq. 5)

$$M_{n} = (n \times M_{BMA}) + (m \times M_{monomer 3}) + M_{CPBD}$$
(Eq. 6)



Figure A4: Example: The ¹H NMR spectrum of MCIL-based BCP 1d in CD₃OD, and the ¹H NMR peak assignments used for calculating the block composition ratio, overall length, and M_n value. The calculated PBMA:poly(**3**) ratio is 2.47, m = 20.24 (\cong 20), and M_n = 17,033 g/mol.

A.7 Polymerization kinetics experiments

To confirm the controlled RAFT polymerization of monomer **3** from the PBMA macroCTAs, the kinetics plots of the RAFT reaction of **3** from PBMA macroCTA **2d** are shown in figure A5 below, as representative example data. The degree of conversion was calculated based on the ¹H NMR peaks integrals of proton (\underline{A}) on the styrene unit double bond relative to the peak of the benzylic protons (\underline{B}) next to the phosphonium group on monomer **3** (Eqs. 7 and 8). See figure A6 below for ¹H NMR assignments and example data used to calculate the degree of monomer conversion for the RAFT of monomer **3** to generate MCIL-based BCP **1d**. The DP and M_n of each block copolymer were determined as mentioned in the prior sections.



Figure A5: System used for monitoring the kinetics of the RAFT polymerization of **3** from PBMA macroCTA **2d** to form MCIL-based BCP **1d**: (a) Plot of the calculated $ln([M]_0/[M])$ vs. reaction time (R² = 0.9933). (b) Plot of the calculated M_n vs. calculated degree of monomer conversion (R² = 0.9915).

$$ln \frac{[M]_{0}}{[M]} = ln \left[\frac{B_{1H \text{ NMR Integration}}}{A_{1H \text{ NMR Integration} \times 2}} \right]$$
(Eq. 7)
Conversion =
$$\frac{B_{1H \text{ NMR Integration}} - A_{1H \text{ NMR Integration} \times 2}}{B_{1H \text{ NMR Integration}}}$$
(Eq. 8)



Figure A6: An example ¹H NMR spectrum of the reaction mixture for the RAFT of monomer 3 from PBMA macroCTA **2d** in CD₃OD, and the ¹H NMR peak assignments used for calculating the degree of monomer conversion. The calculated conversion is 47.8%.

A.8 Verification of the block copolymer architecture for MCIL-based BCPs 1a-f.

The block architectures of MCIL-based BCPs **1a–f** were verified by a combination of surfactant behavior and solubility analysis, diffusion-ordered spectroscopy (DOSY) and small-angle X-ray scattering (SAXS) studies, as described previously in an earlier publication on IL-based BCPs prepared by ROMP from our research groups.⁴

A.8.1 Surfactant behavior and solubility analysis⁴

MCIL-based BCPs **1a–f** all showed surfactant behavior (i.e., extensive foaming when agitated) when mixed in CH₂Cl₂, THF, acetone, and EtOAc, as would be expected from amphiphilic BCPs. Control experiments with physical blends of PBMA and poly(**3**) of the same length as blocks in the BCPs did not show this behavior. MCIL-based BCPs **1a–f** also showed very different solubility behavior compared to physical blends of the two homopolymers, PBMA and poly(**3**). For example, when mixed with EtOAc (10 mg/mL) **1d** forms a clear solution, whereas the physical blend yields

a dark blue solid within a clear solution on top (i.e., PBMA is soluble in EtOAc while poly(3) is insoluble, figure A7).



Figure A7: Picture showing different solubilities of BCP 1d in EtAcO (vial labelled: **Poly EA**) and a physical blend of PBMA + poly(**3**) in in EtOAc (vial labelled: **PB EA**) at room temperature.

A.8.2 NMR DOSY studies⁴

In the room-temperature NMR DOSY spectrum of BCP **1d** in CD₃OD (10 mg/mL) (figure A8), all peaks corresponding to both the PBMA and poly(**3**) blocks exhibited the same diffusion constant $(1.50 \times 10^{-6} \text{ m}^2 \text{ s}^{-1})$. This result indicates that **1d** consists of only one macromolecular species (as expected for a BCP) and is different with a physical blend of two distinct homopolymer species (figure A9). Collectively, the results of these comparative studies are consistent with a covalently linked BCP architecture for **1a–f**, instead of a physical blend of the two homopolymers⁴ (i.e., PBMA + poly(**3**)).



Figure A8: An example NMR DOSY spectrum of BCP **1d** in CD₃OD at room temperature showing only one diffusion constant: $D = 1.50 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The total gradient time (δ) used was 2.5 ms, and the diffusion delay (Δ) was 170 ms.



Figure A9: An example NMR DOSY spectrum of a physical blend of PBMA and poly(**3**) in CD₃OD at room temperature showing two diffusion constants: $D_1 = 4.47 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $D_2 = 2.10 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The peaks do not perfectly correspond to the two components due to the overlap of the broad peaks. The total gradient time (δ) used was 2.5 ms, and the diffusion delay (Δ) was 80 ms.

A.8.3 SAXS analysis⁴

SAXS data of MCIL-based BCPs **1a–f** were collected (see ESI Section 13 for procedural details), together with data collected for the physical blends of the two homopolymers (i.e., PBMA + poly(**3**)) with the same lengths as the BCP blocks for comparison. For example, MCIL-based BCP **1d** forms the gyroid (GYR) phase after annealing, whereas the physical blend yields a disordered phase under the same conditions (FIGURE S10). Similar results were observed when comparing the other BCPs to their analogous physical blends.



Figure A10: SAXS profiles of physical blends of the two homopolymers (PBMA + poly(3)) at different temperatures during annealing.

A.9 Differential Scanning Calorimetry (DSC).

The DSC studies on MCIL-based BCPs **1a–f** (see figure A11 for representative DSC profiles) only revealed evidence of a single glass transition falling consistently between 20 and 40 °C, typical of PBMA homopolymer. During the DSC studies on MCIL-based homopolymer poly(**3**), a typical glass transition peak was observed at 55 °C (figure A11). However, this transition was not detected in any of the DSC profiles of the MCIL-based BCPs **1a–f**. Given the clear evidence of phase separation established by the SAXS data, it appears the limited domain sizes for these small overall molecular weights strongly inhibits the ability of the MCIL-based block to undergo the same thermal transitions as the bulk homopolymer poly(**3**).



Figure A11: DSC profiles of poly(3) and a representative MCIL-based BCP 1f at heating and cooling rates of 5 °C min⁻¹.

A.10 Ultraviolet–visible (UV-vis) spectroscopy analysis of the prepared polymers.

UV-vis studies were performed to help confirm that the Co(II) bis(salicylate) anion was unchanged during the RAFT polymerization process. The UV-vis spectrum of monomer **3** and MCIL-based BCP **1d** show the same absorption bands (figures A12 and A13). This result indicates that the Co(II) anion remains unchanged after the polymerization.



Figure A12: UV-visible spectrum of monomer 3 in dichloromethane (10 mM). Two distinct bands at 533 and 573 nm were observed.



Figure A13: UV-visible spectrum of 1d in dichloromethane (10 mM). Two distinct bands at 533 and 573 nm were observed.

A.11 SAXS characterization of MCIL-based BCPs 1a-f

1D Azimuthally integrated temperature-dependent SAXS data (heating and cooling) for MCILbased BCPs **1a–f** (figure A14): Inverted triangles represent the locations of allowed reflections (listed in table 2.1 in the manuscript) for the morphology depicted. Each sample was sandwiched neat between thin circular Kapton film (10 mm diameter x 0.05 mm thick) and mounted on a Linkam thermal stage. The thermal stage was then placed into the SAXS sample chamber, and the entire system evacuated to 5–10 mtorr. Once vacuum was established, samples were heated to 175 °C at a rate of 10 °C min⁻¹, annealed at 175 °C for 2 h, and then allowed to cool to ambient temperature. For each temperature point, samples were allowed to equilibrate for 5 min. Data were then collected for the sample, with exposure times ranging from 600 to 3600 s.







Figure A14: SAXS characterization of MCIL-based BCPs 1a-f

A.12 SAXS characterization of hydrated and non-hydrated MCIL-based BCP 1d

1D Azimuthally integrated SAXS data at ambient temperature for **1d** before and after treatment with hydrated argon gas (figure A15): The annealed SAXS sample was treated with the hydrated gas, ground into a fine powder, and sealed under air in a 1.0 mm diameter quartz capillary. SAXS data of both sample **1d** and the background were then collected for 4500 s. Final data shown reflect sample data with background subtracted.



Figure A15: SAXS characterization of hydrated and non-hydrated MCIL-based BCP 1d

A.13 Reversible coordination experiments of the MCIL-based BCPs 1a-f upon exposure to small alcohols and aprotic molecule vapors.

MCIL-based BCPs **1a-f** undergo a color change from dark blue to light purple upon exposure to the vapor of small alcohols (e.g., methanol, ethanol, etc.). The original dark blue color can be restored by mild heating or in vacuo treatment of the coordinated BCPs (see figure A16 for an example). However, upon exposure to aprotic molecule vapors (e.g., Et₂O, acetone, ethyl acetate), no color change was observed for these MCIL-based BCPs (see figure A17 for an example).



Figure A16: Reversible color change of 1d upon coordination with CH₃OH vapor.



Figure A17: No color change of 1d upon exposure to Et₂O vapor.

A.14 Thermal stability of MCIL-based BCPs 1a-f

The thermal stabilities of MCIL-based BCPs **1a–f** were determined by TGA measurements using a temperature ramp rate of 10 °C min^{-1,} with the samples under a dry N₂ atmosphere. Interpretation of the obtained TGA curves revealed that BCPs **1a–f** have fairly good thermal stability ($T_{decomp,} = 231$ °C, see figure A18 for an example).



Figure A18. Example TGA profile of **1d** under a dry N₂ atmosphere with a temperature ramp rate of 10 °C min⁻¹. The thermal decomposition temperature (T_{decomp}) was determined as the temperature at which 10% mass loss of the sample occurred.

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APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 3, SELF-ASSEMBLY OF HIGHLY ASYMMETRIC, POLY(IONIC LIQUID)-RICH DIBLOCK COPOLYMERS AND THE EFFECTS OF SIMPLE STRUCTURAL MODIFICATION ON PHASE BEHAVIOUR

Contents of the supporting information

- B.1 Determination of the DP and M_n values of the series of PS macro-initiators 3
- B.2 Determination of the block composition ratio and Mn values of the series of PS-PIL BCPs 1
- B.3 Temperature-dependent SAXS profiles for PS-PIL BCPs 1a-t
- B.4 Thermal Gravimetric Analysis (TGA)
- B.5 Differential Scanning Calorimetry (DSC)
- B.6 Gel Permeation Chromatography (GPC)

B.1 Determination of the DP and *M*_n values of the series of PS macro-initiators 3

Table B1: DP, M_n , and PDI values of the PS macro-initiators **3**. The M_n values are rounded down to nearest hundred g/mol.

PS	DP	<i>M</i> _n (g/mol)	PDI	
3a	15	1,800	1.15	
3b	20	2,400	1.10	
3c	25	2,900	1.12	
3d	30	3,400	1.08	
3e	34	3,800	1.12	
3f	36	4,000	1.13	
3g	37	4,100	1.13	
3h	40	4,400	1.11	
3i	45	5,000	1.13	

The PS macro-initiators **3a–i** were synthesized using the procedures previously reported.¹ The DP and M_n values of the synthesized PS macro-initiators **3a–i** were calculated based on the ¹H NMR peak integral of protons (<u>*D*</u>) on the TMS end-group relative to that of the protons (<u>*E*</u>) on the

benzene ring for these polymers (Eqs. 1 and 2).¹ See figure B1 below for example data used to calculate these values for **3h**.

DP =	$\frac{E_{1H \text{ NMR Integration}} \times 9}{D_{1H \text{ NMR Integration}} \times 5}$	(Eq. 1)
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(Eq. 2)

 $M_{\rm n} = ({\rm DP} \times M_{\rm monomer}) + M_{\rm TMS-EBMP}$



Figure B1. Example ¹H NMR spectrum of **3h**, and the ¹H NMR peak assignments used for calculating the DP and M_n value. Calculated DP = 39.8 \cong 40, M_n = 4,433 \cong 4,400 g/mol.

B.2 Determination of the block composition ratio and *M*_n values of the series of

PS-PIL BCPs 1

Table B2: Block composition ratios and M_n values of PS-PIL BCPs **1**. The M_n values are rounded down to nearest hundred g/mol.

BCP	notebook reference	n	m	<i>M</i> n (g/mol)
1a	zs-1128	15	35	18,600
1b	zs-1117	20	30	16,700
1c	zs-1116	25	25	14,900

1d	zs-2009	30	18	12,000
1e	zs-3062	34	15	11,000
1f	zs-3010	36	14	10,800
	zs-3044			
1g	zs-3007	37	13	10,400
1h	zs-3006	40	12	10,200
1i	zs-2010	34	10	8,600
1j	zs-2134	40	10	9,200
1k	zs-2129	40	9	8,700
	zs-3046			
11	zs-2133	40	8	8,300
1m	zs-2130	45	5	7,400
1n	zs-1123	15	35	20,100
10	zs-1121	20	30	18,000
1р	zs-1120	25	25	15,900
1q	zs-2012	30	18	12,800
1r	zs-2013	34	14	11,100
1s	zs-2131	40	9	9,100
1t	zs-2132	45	5	7,600
1u	zs-3009	35	15	11,500
1v	zs-3008	40	10	9,500
1w	zs-2019	20	30	18,800
1x	zs-2005	25	25	16,600

The block composition ratios and M_n values of PS-PIL BCPs **1a–t** were determined via ¹H NMR analysis.¹ See figure B2 for an example spectrum and ¹H NMR peaks assignments used for these calculations. The PS:PIL ratio can be calculated by Eq. 3. The length of PIL block can be calculated by Eq. 4 and confirmed by end-group analysis (Eq. 5). The M_n of PS-PIL BCPs can be calculated by Eq. 6.

$$PS:PIL ratio = \frac{[F_{1H NMR Integration} - (6 \times B_{1H NMR Integration})]}{B_{1H NMR Integration} \times 5}$$
(Eq. 3)

PS block length m =
$$\frac{n}{\text{Styrene:imidazolium-styrene ratio}}$$
 (Eq. 4)

$$PIL \text{ length } m = \frac{B_{1H \text{ NMR Integration}} \times 9}{D_{1H \text{ NMR Integration}}}$$
(Eq. 5)

$$M_{\rm n} = (n \times M_{\rm styrene}) + (m \times M_{\rm monomer\,2}) + M_{\rm TMS-EBMP}$$
(Eq. 6)



Figure B2: Example ¹H NMR spectrum of PS-PIL BCP **1j**, and the ¹H NMR peak assignments used for calculating the block composition ratio and M_n value. The calculated PS:PIL is 4.02, m = 9.93 \cong 10, M_n = 9,227 \cong 9,200 g/mol.
B.3 Temperature-dependent SAXS profiles for PS-PIL BCPs 1a-t

For a complete description of the SAXS analysis procedures, see the Experimental Section in the main publication.































Figure B3: Temperature dependent SAXS profiles for PS-PIL BCPs 1a-t

B.4 Thermal Gravimetric Analysis (TGA)

TGA was run on three PS-PIL BCPs, **1j**, **1r**, and **1t**. All measurements were performed under nitrogen atmosphere with a temperature ramp rate of 10 °C/min from room temperature to 400

°C. No degradation of any sample was observed until 180 °C or higher, with onset degradation temperatures (at 10% weight loss) around 360 °C for all three samples.



Figure B4: TGA curve for sample 1j



Figure B5: TGA curve for sample 1r



Figure B6: TGA curve for sample 1t.

B.5 Differential Scanning Calorimetry (DSC)

DSC was run on three PS-PIL BCPs, **1d**, **1g**, and **1k**, using a heat-cool-heat-cool method at 10 $^{\circ}$ C min⁻¹ from -40 $^{\circ}$ C to 180 $^{\circ}$ C. Weak transitions around 32 $^{\circ}$ C and 80 $^{\circ}$ C were observed for these three BCP samples. The transition at approximately 80 $^{\circ}$ C is likely the T_g of the PS block, and any transitions at lower temperatures can be attributed to the MePIL block, which is more liquid-like in character due to the IL moiety. It is also possible that no transition is observed for the MePIL block.



Figure B7: Differential scanning calorimetry data for samples 1d, 1g, and 1k

B.6 Gel Permeation Chromatography (GPC)

The following samples were run on a Viscotek GPC-Max chromatography system fitted with three 7.5 x 300 mm PolyPore (Agilent) columns in series, an Alltech external column oven set to 40 °C, and a Viscotek differential refractive index (RI) detector. 10mM LiTf₂N in THF was used as the eluent,² and flow rate was 1.0 ml min⁻¹. PS-MePIL samples **1g**, **1d**, and **1i** are plotted below, as compared to an ~8700 Da PS sample with a D < 1.10. Sample **1i** has a molecular weight comparable to that of the PS sample. The PS-MePIL samples all show significant peak widths (all greater than 6 minutes) and variable peak shape. Additionally, sample **1d** is 3400 Da larger than sample **1i**, and should elute earlier than the smaller **1i**, which suggests that column interactions are complicating the elution of these polymers. Based on this evidence, we believe that definitive analysis of these materials with this GPC method is unfeasible.



Figure B8: Gel permeation chromatography (GPC) results for selected PS-MePIL BCPs, 1g, 1d, and 1i, compared to an uncharged PS homopolymer with low dispersity and a comparable molecular weight.

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APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 4, IMPACT OF HIGH MOLECULAR WEIGHT CONTAMINANT ON SOS HYDROGEL MECHANICAL PERFORMANCE AND SYNTHETIC STRATEGIES FOR ITS ELIMINATION

Contents of the supporting information

- C.1 Gel permeation chromatograms
- C.2 ¹H NMR characterization
 - C.2.1 Calculating MW of the S-OH macroinitiator
 - C.2.2 Calculating MW of SO-H
- C.3 Additional synthetic information and sample identification history
- C.4 Stress-strain data for all SOS gels



C.1 Gel permeation chromatograms of all S-OH, SO-H, and SOS polymer samples.













Figure C1: Gel permeation chromatograms of all S-OH, SO-H, and SOS polymer samples.

C.2 ¹H NMR characterization

C.2.1 Example for Calculating the MW of the S-OH macroinitiator, S-OH: B

We use end-group analysis of our polymers to determine *approximate* molecular weight of the S-OH macroinitiator. We normalize the spectrum to the sec-butyl initiator fragment, integral A in figure C2 below, which contains 6 protons. From there, we calculate the average molecular weight of the polymer using the integral (B) of the 5 protons on the PS phenyl group as follows:



Figure C2: ¹H spectrum of S-OH: B. The molecular weight of this macro-initiator is 8.2 kDa according to end group analysis

C.2.2 Example for Calculating the MW of SO based BCPs: 12-SO

The accuracy of the integral of the initiator fragment is reduced at high molecular weights, even with the significant transients (ns = 256) acquired for this spectrum. Therefore, to calculate the molecular weight of PEO (integral C in figure C3 below) we normalize the integral of the PS phenyl protons to the same value as the S-OH spectrum shown in C2, since that is the S-OH macroinitiator that was used to grow this polymer, 12-SO.



Figure C3: ¹H spectrum of 12-SO. The molecular weight of diblock copolymer is 88.2 kDa according to end group analysis









Figure C4: ¹H spectrum of S-OH: A through 13-SOS. All S-OH spectra are normalized to the sec-butyl initiator fragment, and all SO-H and SOS spectra are normalized to the aromatic protons on the PS phenyl group according to the NMR of the corresponding S-OH macroinitiator.

C.3 Additional synthetic information and sample identification history.

Table C1: Additional synthetic information and sample identification history. Green rows represent "one-pot" sequential polymerization with coupling.

 Red rows represent diblock polymerizations. Blue rows represent coupling reactions. Amount of solvent is estimated.

Sample	Notebook	_	PS	Mass	Mass	Theo.			amt of	PS-OH Mn by	PEO Mn by
Name	Reference	Parent DB	Macroinitiator	PS	EO	yield	yield	yield	solvent	NMR	NMR
unit				g	g	g	g	%	mL	kDa	kDa
SO-H: A	asw-1110									9.3	
SO-H: B	dbw-1142									8.2	
SO-H: C	cjs-2057									6.4	
1-SOS	asw-1095	one pot	cjs-2057	4.616	51.479	55.116			900	6.4	73
2-SO	asw-1117	n/a	asw-1110	4.869	50.3	55.169	52.53	0.9522	450	9.3	108
2-SOS-a	asw-1190	asw-1117	asw-1110			2.016			200		
2-SOS-b	asw-1193	asw-1117	asw-1110			4.003			200		
2-SOS-c	asw-1194	asw-1117	asw-1110			3.999			200		
2-SOS-d	asw-1199	asw-1117	asw-1110			5.125			200		
3-SO	ask-1147	n/a	asw-1110	5.04	49.5	54.54			450	9.3	103
3-SOS-a	asw-1213	ask-1147	asw-1110								
3-SOS-b	asw-1223	ask-1147	asw-1110			1.618			100		
4-SO	asw-1218	n/a	asw-1110	5.507	11	16.507	12.859	0.779	450	9.3	17
4-SOS	asw-1221	asw-1218	asw-1110			0.988			100		
5-SO	asw-1227	n/a	asw-1110	6.6	68.7	75.3	72.232	0.9593	800	9.3	105
5-SOS-a	asw-1232	asw-1227	asw-1110			5			200		
5-SOS-b	zcu-1008	asw-1227	asw-1110			1.042			100		
5-SOS-c	asw-2020	asw-1227	asw-1110			1.025			100		
6-SO	asw-2006	n/a	asw-1110	3.002	36.5	39.502	37.897	0.9594	450	9.3	121
6-SOS-a	asw-2008	asw-2006	asw-1110			4.96			200		
6-SOS-b	asw-2019	asw-2006	asw-1110			1.003			100		

7A-SO	asw-2012A	n/a	dbw-1142	1.56	15.4	16.96			760	8.2	64
7A-SOS-a	asw-2017A	asw-2012A	dbw-1142			1			90		
7A-SOS-b	asw-2017A2-OT	asw-2012A	dbw-1142			1			90		
7B-SO	asw-2012B	n/a	dbw-1142	1.56	15.4	16.96			760	8.2	64
7B-SOS-a	asw-2017B	asw-2012B	dbw-1142			1			90		
7B-SOS-b	asw-2021	asw-2012B	dbw-1142			1.073			100		
7C-SO	asw-2012C	n/a	dbw-1142	1.56	15.4	16.96			760	8.2	64
7C-SOS	asw-2017C	asw-2012C	dbw-1142			1			90		
7D-SOS	asw-2012D	one pot	dbw-1142	1.56	15.4	16.96			760	8.2	64
8-SO	asw-2024	n/a	asw-1110	3.603	41.9	45.503			450	9.3	122
8-SOS-a	jpg-1121	asw-2024	asw-1110			5.024					
8-SOS-b	jpg-1123	asw-2024	asw-1110			7.528					
9-SO	asw-2027	n/a	dbw-1142	1.204	14	15.204	13.848	0.9108	450	8.2	101
9-SOS	asw-2029	asw-2027	dbw-1142			5.05			200		
10-SOS	asw-2032	one pot	dbw-1142	1.627	15.1	16.727			450	8.2	79
11-SOS	asw-2038	one pot	dbw-1142	1.43	14.1	15.51	14.444	0.9313	900	8.2	80
12-SO	asw-2049	n/a	dbw-1142	1.729	17.15	18.879	16.83	0.8915	900	8.2	80
12-SOS	asw-2053	asw-2049	dbw-1142			1.003			100		
13-SOS	asw-2066	one pot	dbw-1142	1.56	15.3	16.86			900	8.2	58

C.4 Stress-strain data for all SOS gels










Figure C5: Stress-strain curves for the 1st and 10th cycle of each SOS hydrogel measured in this study.

APPENDIX D: SUPPORTING INFORMATION FOR CHAPTER 5, HIGHLY CONDUCTIVE AND MECHANICALLY TOUGH GEL POLYMER ELECTROLYTE ELASTOMERS

Contents of the supporting information

- D.1 ¹H NMR characterization
 - D.1.1 Calculating the MW of S-OH macroinitiator
 - D.1.2 Calculating the MW of SO-H
 - D.1.3 Calculating the MW of SOS83
 - D.1.4 NMR spectra of RTIL and its precursors
- D.2 Additional ionic conductivity data
- D.3 Pure shear fracture testing data
- D.4 Mold and sample dimensions for mechanical characterization
- D.5 Material identification history
- D.6 Thermal analysis

D.1 ¹H NMR characterization

D.1.1 Calculating the MW of S-OH macroinitiator

We use end-group analysis of our polymers to determine *approximate* molecular weight of the S-OH macroinitiator. We normalize the spectrum to the sec-butyl initiator fragment, integral A in figure D1 below, which contains 6 protons. From there, we calculate the average molecular weight of the polymer using the integral (B) of the 5 protons on the PS phenyl group as follows:



Figure D1: ¹H spectrum of S-OH. The molecular weight of this macro-initiator is 8.2 kDa according to end group analysis

D.1.2 Calculating the MW of SO-H

The accuracy of the integral of the initiator fragment is reduced at high molecular weights, even with the significant transients (ns = 256) acquired for this spectrum. Therefore, to calculate the molecular weight of PEO (integral C in figure D2 below) we normalize the integral of the PS phenyl protons to the same value as the S-OH spectrum shown in D1, since that is the S-OH macroinitiator that was used to grow this polymer.



Figure D2: ¹H spectrum of SO-H. The molecular weight of this diblock copolymer is 88.2 kDa according to end group analysis

D.1.3 Calculating the MW of SOS83

MW for SOS83 is calculated using the same method as SO-H, as each chain of SOS is exactly two SO-H chains with a xylene linkage between them, as shown in figure D3 below.



Figure D3: ¹H spectrum of SOS83. The molecular weight of the diblock portion (SO) of this copolymer is 88.2 kDa according to end group analysis, the full triblock copolymer is double that at 176.4 kDa.

D.1.4 NMR spectra of RTIL and its precursors



Figure D4: ¹H spectrum of [EMIM][Br] and its precursors.



Figure D5: ¹H spectrum of the RTIL [EMIM][TFSI]. [EMIM][Br] and [EMIM][TFSI] have the same protons and the chemical shifts are very similar, however, [EMIM][Br] is an off-white, water soluble solid at room temperature, and [EMIM][TFSI] is a hydrophobic, slightly yellow liquid at room temperature.

D.2 Additional ionic conductivity data



Figure D6: Ionic conductivity of the pure components, [EMIM][TFSI] ionic liquid, and a melt processed disc of SOS83. The ionic conductivity of SOS83 is much higher than would be expected for pure polymer, particularly during the second cycle in which the polymer was heated beyond the T_g of PS and T_m of crystalline PEO. Likely, this polymer has residual salt contamination from the anionic polymerization process.



Figure D7: Ionic conductivity of SOS gels, unswollen SOS, and RTIL as a function of temperature during a second thermal cycling starting at 80 °C



Figure D8: Zoomed-in comparison of the ionic conductivity of the SOS gels and RTIL during the first and second heating cycles. Thermal annealing at higher temperatures does not significantly impact ionic conductivity of the gels.

D.3 Pure shear fracture testing data



Figure D9: Pure shear fracture testing data for an unnotched sample (a) and three notched samples (b-d) of SOS40. Evidence of the crack branching phenomenon can be seen as "dips" in the force-strain curve, where the crack propagated perpendicular to the path of the crack.

Table D1: Summary of the fracture toughness of SOS40 gels at the initiation of crack propagation (Γ_{in}) and at the point of failure (Γ_c)

	Fracture toughness Γ_{in} (J/m ²)	Ultimate toughness $\Gamma_c(J/m^2)$
Notched Sample 1	207.80	1052.59
Notched Sample 2	171.97	5232.5*
Notched Sample 3	193.94	2031.46

*Calculated by extrapolating the force-displacement curve of the unnotched sample

D.4 Mold and sample dimensions for mechanical characterization

	mold dimensions (mm)			average swollen dimensions (mm)		
rectangular	width	length	thickness	width	length	thickness
tensile (SOS40)	5	15	0.4	11.7	35.2	1.0
tensile (SOS57)	5	16	0.5	10.7	34.1	1.2
tensile (SOS83)	6	17	0.5	11.4	32.5	1.0
fracture (SOS40)	20	20	0.4	49	49	1.0
circular	diameter	area (mm ²)	thickness	diameter	area (mm ²)	thickness
compression (SOS40)		24	1	12.4	121	2.0
compression (SOS57)	5.6			11.9	111	1.9
compression (SOS83)				11.1	97	1.8
rheology (SOS40)	12	113	0.5	29	661	1.2
rheology (SOS57)				27	573	1.1
rheology (SOS83)]			24	452	1.0

 Table D2:
 Summary of the dimensions of unswollen samples (size of the mold used) and the average dimensions of the samples post-swelling.

D.5 Material identification history

Table D3: Notebook references for all RTIL and polymer samples used in this study

Material	M _n (g mol ⁻¹)	Notebook Reference
[EMIM][Br]		asw-2059
[EMIM][TFSI]		asw-2060, also pages 2105-6
S-OH	8200	dbw-1142 (jar 2)
SO-H	88200	asw-2049
SOS83	88200/176400	asw-2038
SOS40 blends	88200/176400	asw-2057A, pages 2057, 2067 (precipitated)
		asw-2090A (freeze-dried)
SOS57 blends	88200/176400	asw-2057B, pages 2057, 2067 (precipitated)

D.6 Thermal analysis



Figure D10: TGA data for a swollen SOS83 gel. The first drop in weight at around 300 °C corresponds to the onset degradation temperature of SOS, and the second drop starting around 400 °C corresponds to the onset of degradation of [EMIM][TFSI].



Figure D11: DSC data for unswollen SOS40 polymer. The large endothermic peak at ~ 60 °C represents the T_m of crystalline PEO. The T_g of PS is also likely in this range, but we are unable to observe it because the melting of crystalline domains of PEO dominates.



Figure D12: DSC data for neat RTIL, [EMIM][TFSI]. The endothermic peak at ~ -15 °C represents the T_m of the RTIL.



Figure D13: DSC data for a swollen SOS40 gel. The endothermic peak at ~ -15 °C represents the T_m of the RTIL. The large endothermic peak at ~ 60 °C is absent, indicating that there is no detectable remaining PEO crystallinity in the gel once swollen.