

SYNTHESIS AND DEVELOPMENT OF ORDERED, PHASE-SEPARATED,
ROOM-TEMPERATURE IONIC LIQUID-BASED AB AND ABC BLOCK COPOLYMERS
FOR GAS SEPARATION APPLICATIONS

By

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ROOM-TEMPERATURE IONIC LIQUID-BASED AB AND ABC BLOCK COPOLYMERS
FOR GAS SEPARATION APPLICATIONS”

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The final copy of this thesis has been examined by the signatory, and we
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ABSTRACT

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Synthesis and Development of Ordered, Phase-Separated, Room-Temperature Ionic Liquid-based AB and ABC Block Copolymers for Gas Separations Applications

Thesis directed by Prof. Douglas L. Gin

CO₂ capture process development is an economically and environmentally important challenge, as concerns over greenhouse gas emissions continue to receive worldwide attention. Many applications require the separation of CO₂ from other light gases such as N₂, CH₄, and H₂ and a number of technologies have been developed to perform such separations. While current membrane technology offers an economical, easy to operate and scale-up solution, polymeric membranes cannot withstand high temperatures and aggressive chemical environments, and they often exhibit an unfavorable tradeoff between permeability and selectivity. Room-temperature ionic-liquids (RTILs) are very attractive as next-generation CO₂-selective separation media and their development into polymerized membranes combat these challenges. Furthermore, polymers that can self-assemble into nanostructured, phase-separated morphologies (e.g., block copolymers, BCPs) have a direct effect on gas transport as materials morphology can influence molecular diffusion and membrane transport performance.

In this thesis, nanophase-separated, RTIL-based AB and ABC di- and tri-BCPs were prepared via the sequential, living ring-opening metathesis polymerization (ROMP) of an IL-based monomer and one or more mutually immiscible co-monomers. This novel type of ion-containing BCP system forms various ordered nanostructures in the melt state via primary and

secondary structure control. Monomer design and control of block composition, sequence, and overall polymer lengths were found to directly affect the ordered polymer assembly. Supported, composite membranes of these new BCPs were successfully fabricated, and the effect of BCP composition and nanostructure on CO₂/light gas transport properties was studied. These nanostructured IL-based BCPs represent innovative polymer architectures and show great potential CO₂/light gas membrane separation applications.

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TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION.....	1
1.1 Gas Transport Through Dense Polymer-Based Membranes	1
1.2 Block Copolymers	4
1.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy	7
1.2.1.1 Block Copolymer Characterization via NMR Spectroscopy.....	7
1.2.2 Gel Permeation Chromatography (GPC)	8
1.2.3 Rheology	9
1.2.4 Small-Angle X-ray Scattering (SAXS)	10
1.2.5 Direct Nanostructure Imaging Techniques	12
1.2.6 Structural Factors that Determine Phase-separated BCP Morphologies.....	13
1.2.7 Effect of Nanostructured BCP Morphology on Transport Properties	14
1.2.8 BCPs Comprised of Neutral and Charged Blocks	16
1.3 Room-Temperature Ionic Liquids (RTILs)	19
1.4 References	22
 2. DISSERTATION RESEARCH GOALS	 27
2.1 Overview of Thesis Research	27
2.2 Specific Research Aims.....	28
2.3 References	31
 3. SYNTHESIS AND ORDERED PHASE SEPARATION OF IMIDAZOLIUM-BASED ALKYL-IONIC DIBLOCK COPOLYMERS MADE VIA ROMP	 32
3.1 Abstract	32
3.2 Introduction.....	33

3.3 Results and Discussion	35
3.4 Summary	42
3.5 Acknowledgments	43
3.6 Supporting Information	44
3.6.1 Materials and General Procedures	44
3.6.2 Instrumentation	44
3.6.3 Synthesis	45
3.6.3.1 Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (end:exo 80:20) (2)	45
3.6.3.2 1-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1 <i>H</i> -imidazole (end:exo 80:20) (4)	46
3.6.3.3 3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3 <i>H</i> -imidazolium bis(trifluoromethylsulfonyl)amide (end:exo 80:20) (3)	47
3.6.4 General Procedure for ROMP of Monomers 2 and 3 to Form Diblock Copolymers	48
3.6.4.1 Procedure for Sequential ROMP of Monomers 2 and 3 to Form Diblock Copolymer 1A	49
3.6.4.2 Procedure for Sequential ROMP of Monomers 2 and 3 to Form Diblock Copolymer 1B	50
3.6.4.3 Procedure for Sequential ROMP of Monomers 2 and 3 to Form Diblock Copolymer 1C	51
3.6.5 Determination of BCP Composition and Molecular Weights	53
3.6.5.1 Determination of BCP Alkyl:Imidazolium Block Composition Ratios via ¹ H NMR Analysis	53
3.6.5.2 Verification of Living Character with Molecular Weight Control	58
3.6.5.3 Calculating Block Length Composition	61
3.6.5.4 Calculating BCP Molecular Weight	62
3.6.6 Differential Scanning Calorimetry (DSC)	62
3.6.7 NMR DOSY Studies	63
3.6.8 Rheology	64
3.6.9 Preparation and Purification of Higher Length Homologues of BCPs 1A-C	64
3.7 References	65
 4. MORPHOLOGICAL PHASE BEHAVIOR OF POLY(RTIL)-CONTAINING DIBLOCK COPOLYMER MELTS	 68
 4.1 Abstract	 68
4.2 Introduction	69

4.3 Results and Discussion	73
4.3.1 Synthesis of Alkyl-Imidazolium DOD-IMD Diblock Copolymers	73
4.3.2 Overview of Melt State Phase Behavior	75
4.3.2.1 Lamellae	80
4.3.2.2 Hexagonally Packed Cylinders	85
4.3.2.3 Coexistence of Lamellae and Hexagonally Packed Cylinders	89
4.3.2.4 Spherical	100
4.4 Summary	104
4.5 Experimental Section	106
4.5.1 Materials and Methods	106
4.5.2 General Synthetic Procedures for the Synthesis of Imidazolium-Based Alkyl-Ionic BCPs	107
4.5.3 Representative Synthesis of Diblock Copolymer 1S	108
4.5.4 Physical Measurements	108
4.5.5 Sample Preparation for Morphological Analysis	109
4.5.6 Dynamic Mechanical Spectroscopy	109
4.5.7 Small-Angle X-Ray Scattering (SAXS)	110
4.5.8 Synchrotron SAXS Characterization	110
4.6 Acknowledgments	111
4.7 Supporting Information	111
4.7.1 Morphological Behavior	111
4.7.2 Thermogravimetric Analysis (TGA)	112
4.7.3 Temperature-Dependent SAXS and Rheology Data	113
4.8 References	145
 5. EFFECT OF COMPOSITION AND NANOSTRUCTURE ON CO₂/N₂ TRANSPORT PROPERTIES OF SUPPORTED ALKYL-IMIDAZOLIUM BLOCK COPOLYMER MEMBRANES	 153
5.1 Abstract	153
5.2 Introduction	154
5.3 Experimental Section	159
5.3.1 Materials and General Synthetic Procedures	159

5.3.1.1 Materials and Methods	159
5.3.2 General Synthesis and Polymerization of Alkyl-Imidazolium BCPs 1T–1W	160
5.3.3 Alkyl-Imidazolium Block Copolymer Membrane Fabrication.....	161
5.3.4 Supported Thin-Film BCP Membrane Characterization	162
5.3.4.1 Small Angle X-ray Scattering (SAXS).....	162
5.3.4.2 Scanning Electron Microscope (SEM) Imaging	163
5.3.5 Gas Transport Properties Measurements via the Time-Lag Method.....	163
5.4 Results and Discussion	165
5.4.1 Synthesis and SAXS Characterization of Alkyl-Imidazolium BCPs	165
5.4.1.1 BCP Structure and Synthesis.....	165
5.4.1.2 SAXS Characterization.....	166
5.4.2 Membrane Fabrication	169
5.4.3 CO ₂ /N ₂ Transport Studies	170
5.4.3.1 Permeabilities and Selectivity Measurement	170
5.4.3.2 CO ₂ Solubility Coefficient Determination	173
5.4.3.3 CO ₂ Diffusion Coefficient Measurement.....	174
5.5 Comparison with Other Polymers Tested for CO₂/light Gas Separation; Future Work.....	177
5.6 Conclusions.....	179
5.7 Acknowledgments	181
5.8 References	181
 6. IMIDAZOLIUM-CONTAINING, HYDROPHOBIC-IONIC-HYDROPHILIC ABC TRIBLOCK COPOLYMERS: SYNTHESIS, ORDERED PHASE-SEPARATION, AND SUPPORTED MEMBRANE FABRICATION	 185
 6.1 Abstract	 185
6.2 Introduction.....	186
6.3 Results and Discussion	188
6.3.1 Block Copolymer Synthesis	188
6.3.2 ¹ H NMR Analysis to Determine Block Composition Ratios	189
6.3.3 Block Copolymer Morphology Characterization	190

6.3.3.1 Solubility Testing.....	190
6.3.3.2 ¹ H NMR DOSY Analysis.....	191
6.3.3.3 Small Angle X-ray Scattering (SAXS) Analysis.....	191
6.3.4 Composite Membrane Fabrication and Analysis	193
6.3.5 Membrane Permeation Analysis.....	195
6.4 Conclusions.....	197
6.5 Acknowledgments	198
6.6 Supporting Information	198
6.6.1 Materials and General Procedures	198
6.6.2 Instrumentation	199
6.6.3 Synthesis	199
6.6.3.1 Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (end:exo 80:20) (2)	199
6.6.3.2 3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3 <i>H</i> -imidazolium bis(trifluoromethylsulfonyl)amide (end:exo 80:20) (3)	200
6.6.3.3 Triethylene glycol monomethyl ether tosylate (9)	200
6.6.3.4 2-(2-(2-Methoxyethoxy)ethoxy) ethyl bicycle[2.2.1]hept-5-ene-2-carboxylate (8)	200
6.6.4 General Procedure for ROMP of Monomers 2 , 3 , and 8 to Form Triblock Copolymers	201
6.6.5 Sample Procedure for Sequential ROMP of Monomers 2 , 3 , and 8 to Form Triblock Copolymer 7A	203
6.6.6 Determination of BCP Composition and Molecular Weights.....	205
6.6.6.1 Solubility Analysis	213
6.6.6.2 NMR DOSY Analysis	214
6.6.6.3 SAXS Analysis	214
6.6.7 Supported Membrane Fabrication	216
6.6.8 Scanning Electron Microscope (SEM) Imaging.....	216
6.6.9 Gas Transport Properties Measurements via the Time-Lag Method.....	217
6.7 References	217
 7. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK	 220
 7.1 Thesis Objectives	 220

7.2 Summary of Thesis Accomplishments	221
7.3 Recommendations for Future Work	223
7.3.1 (BCP + free RTIL) Composites.....	223
7.3.2 Cross-linkable RTIL-based Block Copolymer Architectures.....	224
7.3.3 Alternative Living Polymerization Platforms and Techniques	226
7.4 References	228
 BIBLIOGRAPHY	 231

LIST OF TABLES

3.S1	Relative M_n and M_w GPC Data (vs. Polystyrene Standards) and PDI Values for Confirming the Living ROMP of Monomer 2.	59
4.1	Summary of synthesized imidazolium-based alkyl-ionic BCPs and their corresponding phase behavior.....	75
4.S1	Summary of synthesized imidazolium-based alkyl-ionic BCPs and their corresponding morphological phase behavior.	112
4.S2	Summarized dynamic rheological data for BCPs 1D-1S at a chosen strain rate within the linear viscoelastic regime.	114
6.1	Gas permeabilities (in barrers) and selectivities of 7A (ABC) and 7B (CAB) triblock CP-based composite membranes. Experimental error was less than 1.5%. Thicknesses of the active layers were 12.4 mm and 12.6 mm for 7A and 7B.....	196

LIST OF FIGURES

1.1	Example of a log-log Robeson Plot showing measured CO ₂ /N ₂ gas selectivity data vs. CO ₂ permeability through a range of known dense polymers and the apparent selectivity-permeability performance trade-off represented by an observed "upper bound". Figure reproduced from ref. 14. (Copyright 2008 Elsevier).....	4
1.2	Common AB copolymer architectures.....	5
1.3	(a) Phase-separation of a physical blend of two homopolymers resulting in an un-ordered heterogeneous mixture with features on the micrometer scale, and (b) phase-separation of analogous, covalently tethered linear BCP architectures resulting in self-assembled ordered morphologies on the nanometer scale.....	6
1.4	Geometric relationship between the Bragg angle (θ_B) and scattering wave vector, q (top). Schematic of a hexagonally-packed cylindrical "poly-crystalline" BCP sample diffracting an X-ray source. Wide-angle detection is located centimeters from the sample source, similar to the proximity of a powder XRD detector utilized for small, crystalline molecules. Small-angle detection is located meters from the BCP sample source, as to acquire very small angle diffraction scattering as a result of large domain spacings. After data collection, the 2D scattering results are transformed into a 1D plot of q vs. intensity. Unique SAXS diffraction patterns are indexed similarly to powder XRD patterns. Figure and caption reproduced from ref. 35. (Copyright 2012 V. F. Scalfani).....	11
1.5	Theoretical AB di-BCP phase diagram, showing the geometries of the most commonly formed ordered phases (LAM, HEX, gyroid, and BCC). Adapted from ref. 20. (Copyright 2006 American Chemical Society)	14
1.6	Example configurations of (a) alkyl substituted-, (b) polar substituted-, and (c) polymerizable-RTILs, where the anionic species X could represent OTf, dca, BF ₄ , or Tf ₂ N.....	20
2.1	Research explored in Chapter 3: synthesis and sequential ring-opening metathesis polymerization of novel norbornene alkyl- and imidazolium ionic liquid- based monomers with Grubbs' 1 st -generation catalyst into BCPs 1A–C.	28
2.2	Research explored in Chapter 4: sketch of the thoroughly elucidated phase diagram from a synthesized library of alkyl, hydrophobic ("DOD")– <i>block</i> –imidazolium, ionic ("IMD") di-BCPs. Reproduced from ref. 1. (Copyright 2012 ACS Publications).	29
2.3	Research explored in Chapter 5: pictorial graphic representing the BCP chemical composition, solvent-free phase-separated morphologies, and experimentally tested	

	gas separation application of alkyl hydrophobic- <i>b</i> -imidazolium ionic di-BCP membranes.	30
2.4	Research explored in Chapter 6: novel hydrophobic-ionic-uncharged hydrophilic ABC triblock copolymers synthesized via ROMP phase-separate into unique morphologies based on block sequence order.	31
3.1	The synthesis and structures of alkyl-imidazolium diblock copolymers 1A–C made via ROMP that show ordered phase-separation in the melt-state. The values of <i>m</i> and <i>n</i> depicted in 1A–C are derived from the observed NMR block length ratios of the BCPs and the monomer-to-catalyst ratios as used in the living ROMP of 2 and 3.....	35
3.2	Different solubilities of copolymer 1A and a physical blend (PB) of poly(2) + poly(3) in hexanes at room temperature.	38
3.3	Representative SAXS data for imidazolium BCPs containing block ratios of 1: 0.90 (1A), 1:0.66 (1B), and 1:0.42 (1C), with the corresponding 2D detector images (inset). Inverted triangles represent the location of the allowed reflections for the lamellar morphology, calculated based on the position of the primary scattering wave vector q_{100} : (L) q/q^* at v_1 , v_4 , v_9 , v_{16} , v_{25} , v_{36} , etc. The physical blend (PB) of poly(2) and poly(3) shows no observable diffraction peaks, in contrast to the BCPs.	42
3.S1	An example ^1H NMR spectrum of BCP 1A, and the ^1H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in 1A.	55
3.S2	An example ^1H NMR spectrum of BCP 1B, and the ^1H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in 1B.	56
3.S3	An example ^1H NMR spectrum of BCP 1C, and the ^1H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in 1C.	57
3.S4	Linear relationship between monomer-to-catalyst molar ratio used and absolute M_n from ^1H NMR endgroup analysis for various poly(2) oligomers. Note: this NMR-based polymer molecular weight data does not provide PDI information.	59
3.S5	Linear relationship between monomer-to-catalyst molar ratio used and absolute M_n from ^1H NMR endgroup analysis for various and poly(3) oligomers.	60
3.S6	DSC profiles of BCP 1A and the respective homopolymers of 2 and 3, performed at heating and cooling rates of $5\text{ }^\circ\text{C min}^{-1}$	63
3.S7	Dynamic temperature ramp experiment data for 1C performed while heating at $1\text{ }^\circ\text{C min}^{-1}$ at an angular frequency of 1 rad s^{-1} and a strain of 1%.	64
4.1	Sequential ROMP of monomers 2 and 3 to yield imidazolium-based DOD-IMD BCPs 1D–S.....	74

- 4.2 Phase diagram of morphologies observed in the imidazolium-based alkyl-ionic copolymer melt system including lamellae (Lam), hexagonally packed cylinders (Hex), coexisting Lam and Hex, spheres on a body-centered cubic lattice (SBCC), and a liquid-like packing (LLP) of spheres. Solid symbols represent regions of well-defined ordered structures, observed by multiple resolved SAXS diffraction reflections, semi-filled and open circles represent regions of poorly ordered structures, evident by broad peaks in SAXS, and cross symbols depict the disordered region..... 79**
- 4.3 SAXS data at 125 °C (first heating cycle) for Lam forming BCPs 1M–1S. Inverted solid triangles represent the locations of allowed reflections for the Lam morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc. The near complete suppression of even-order reflections in samples 1R, 1Q, and 1P suggests an almost perfect symmetric volume fraction of 0.5 (left). Samples of 2D scattering patterns (center). Dynamic temperature ramps (first heating cycle) of BCPs 1M–1S at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} and with strain values of 2.5–8% (within the linear viscoelastic regime). Solid and open circles represent G' and G'' , respectively (right). 82**
- 4.4 SAXS data at 150 °C (upon cooling) for Hex forming BCPs 1G–1I. Inverted open triangles represent the locations of allowed reflections for the Hex morphology based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. Relative intensity differences are consistent with variations in composition, most notably the near complete suppression of the $\sqrt{4}$ reflection in sample 1I, which is suggestive of approaching a volume fraction of 0.726. Inset pictures are the 2D scattering patterns..... 87**
- 4.5 SAXS data of sample 1G along a complete heating (left) and cooling (center) thermal cycle. Morphologies observed during heating include a distorted poorly ordered LLP of cylindrical domains before obtaining the well-ordered Hex morphology. Upon cooling, the highly ordered Hex phase is preserved. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. Dynamic temperature ramp heating and cooling cycle of 1G (right) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} , and 8% strain (within the linear viscoelastic regime). The cooling cycle has been shifted vertically 2 orders of magnitude for clarity. The rheological behavior mimics that of the SAXS, where a subtle transition is observed upon obtaining the well-ordered Hex morphology during heating, while any transitions are notably absent upon cooling. Insets are 2D scattering patterns depicting the initial weakly ordered morphology and final highly ordered morphology after the melt-processing..... 88**

- 4.6 SAXS data at 150 °C (upon cooling) for coexisting (Lam + Hex)-forming BCPs 1J–1L, plotted with the samples 1M and 1I, that exhibit a fully developed pure Lam and Hex phase, respectively, for comparison. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}: q/q^{*,\text{hex}}$ at $v1, v3, v4, v7, v9, v12, v13$, etc., and inverted solid triangles represent the locations of allowed reflections for the Lam morphology, $q^* = q_{100}: q/q^{*,\text{lam}}$ at $v1, v4, v9, v16, v25, v36$, etc. Relative diffraction intensity differences are consistent with variations in composition (relative amounts of coexisting (Lam + Hex) domains), most notably the scattering profile of 1L most closely resembles that of 1M (pure Lam), while 1J most closely resembles sample 1I (pure Hex). Inset figure is the high-resolution synchrotron integrated and 2D SAXS data of sample 1J, donated with double asterisks, showing the primary peak could not be resolved..... 91
- 4.7 Dynamic temperature ramps (first heating cycle) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} , and with strain values of 6–8% (within the linear viscoelastic regime) for coexisting (Lam + Hex)-forming BCPs 1J–1L, plotted with samples 1M and 1I that exhibit a fully developed pure Lam and Hex phase, respectively, for comparison. Solid circles represent G' , and open circles represent G'' . Differences in rheological response is consistent with variations in composition (relative amounts of coexisting (Lam + Hex) domains), most notably the temperature ramp profile of 1L most closely resembles that of 1M (pure Lam), while 1J most closely resembles the profile of sample 1I (pure Hex). Double arrows mark the subtle rheological transition present in the pure Hex 1I sample arising from a delay in ordering kinetics. No such transitions were observed in rheology for samples in the coexistence region, despite the kinetic delay in ordering observed in SAXS data for samples 1K and 1J (see Supporting Information for temperature-dependent SAXS data)..... 94
- 4.8 SAXS data of sample 1J annealing at 150 °C for a total of 2 months, depicting the very slow ordering kinetics that suppresses the Lam phase and transitions toward a pure Hex phase, which is evident by the increased intensity of Hex reflections coupled with the substantial decrease in Lam reflection intensity with time. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}: q/q^{*,\text{hex}}$ at $v1, v3, v4, v7, v9, v12, v13$, etc. Inverted solid triangles represent the locations of allowed reflections for the Lam morphology, $q^* = q_{100}: q/q^{*,\text{lam}}$ at $v1, v4, v9, v16, v25, v36$, etc..... 97
- 4.9 Dynamic temperature ramp (first heating cycle) for samples 1D (left) and 1E (right) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} with 30 and 8% strain, respectively (within the linear viscoelastic regime). The rheological behavior of both samples is characteristic of enhanced liquid-

	like properties where G'' is greater than G' . No clear ODT is observed via rheology in either sample. SAXS data of sample 1D (left) and 1E (right) along a complete heating thermal cycle are both indicative of a LLP of spheres, evident by broadness of scattering and absence of higher order diffraction reflections. Sample 1D appears to clearly disorder upon heating marked by the drastic decrease in intensity and enhanced broadness of the scattering. In contrast, sample 1E retains a fairly intense primary scattering peak throughout the entire heating cycle.....	102
4.10	SAXS data of sample 1F along a complete heating (left) and cooling (center) thermal cycle. Morphologies observed during heating include a distorted poorly ordered LLP of spherical domains before obtaining the well-ordered SBCC morphology. Upon cooling, the highly ordered SBCC phase is preserved. Inverted triangles with a strikethrough represent the locations of allowed reflections for the SBCC morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$ (absent for SBCC): q/q^* at $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$, etc. Dynamic temperature ramp heating and cooling cycle of 1F (right) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} , and 8% strain (within the linear viscoelastic regime). The cooling cycle has been shifted vertically 2 orders of magnitude for clarity. The rheological behavior mimics that of the SAXS, where a subtle transition is observed upon obtaining the well-ordered SBCC morphology during heating, while any transitions are notably absent upon cooling. Insets are 2D scattering patterns depicting the initial weakly ordered morphology and final highly ordered morphology after the melt-processing.	104
4.S1	Example TGA analysis of BCP 1H under N_2 (temperature ramp rate: $20\text{ }^\circ\text{C/min}$	113
5.1	Sequential ROMP of monomers 2 and 3 to yield alkyl-imidazolium BCPs 1T–1W.	166
5.2	SAXS data at room temperature for 1U–1W bulk and membrane samples. Sample 1U bulk and membrane nanoscale structures are consistent with the lamellae phase. Inverted solid triangles represent the calculated locations of allowed reflections for the lamellae morphology based on the position of the primary scattering wave vector, $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. Samples 1V and 1W bulk morphologies exhibit a weakly-ordered liquid-like packing of the phase-separated domains. Membrane samples 1V and 1W show phase separation evident by the observed primary scattering reflection. Insets accentuate scattering observed in membrane samples by plotting intensity $\times q^2$ vs. q	167
5.3	(A) Physical blend of poly(2) + poly(3) macroscale phase-separating on the PAN membrane support. (B) An example of a thin, uniform coating made possible with our BCP materials on the PAN membrane support. (C) SEM cross-sectional image of BCP 1U showing a uniform, defect-free surface ($13.4\text{ }\mu\text{m}$).	170

5.4	CO ₂ /N ₂ selectivity vs. CO ₂ permeability (Robeson plot) of alkyl-imidazolium BCP membranes. Content of imidazolium block in the block copolymer active layer is indicated in wt% and the type of nanostructure is identified. Experimental error is within the data points and represents less than 4%.....	172
5.5	CO ₂ solubility coefficient vs. imidazolium block content in the block copolymer active layer.	174
5.6	CO ₂ diffusion coefficient vs. imidazolium block content in the block copolymer active layer.	176
5.7	Comparison of the performance at room temperature of block copolymer membranes and other materials for CO ₂ /light gas separation on a Robeson plot.	178
6.1	Example sequential ROMP of imidazolium-containing ABC triblock CP 7A.	189
6.2	SAXS data for imidazolium-containing triblock CPs 7A–C, with corresponding 2D detector images (inset). The inverted filled triangles represent the location of allowed reflections for the L morphology, calculated from the primary scattering wave vector q_{100} : (L) q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. The inverted open triangles represent the location of allowed reflections for the HCP phase, calculated from the primary scattering wave vector q_{100} : (L) q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. The PB sample of poly(2), poly(3), and poly(8) shows no observable SAXS peaks, in contrast to the triblock CPs.	193
6.3	(a) Picture (top view) of a thin, uniform coating of our triblock CP 7B on a porous PAN membrane support. (b) Cross-sectional SEM image of triblock CP 7B coated on a porous PAN support showing a uniform, defect-free coating.....	194
6.S1	An example ¹ H NMR spectrum of triblock copolymer 7A, and the ¹ H NMR peak assignments used to calculate the hydrophobic:ionic:non-charged hydrophilic block composition (i.e., repeat unit) ratio in 7A.	207
6.S2	An example ¹ H NMR spectrum of triblock copolymer 7B, and the ¹ H NMR peak assignments used to calculate the non-charged hydrophilic:hydrophobic:ionic block composition (i.e., repeat unit) ratio in 7B.	208
6.S3	An example ¹ H NMR spectrum of triblock copolymer 7C, and the ¹ H NMR peak assignments used to calculate the hydrophobic:non-charged hydrophilic:ionic block composition (i.e., repeat unit) ratio in 7C.	209
6.S4	Linear relationship between monomer-to-catalyst molar ratio used and M_n from GPC analysis for various poly(8) oligomers (10A–D). PDI values were consistent and ranged from 1.14–1.26, indicative of living polymerization with molecular weight control...	211

- 6.S5 Photographs showing the difference in solubility behavior at 10 wt% loading in MeOH between: (a) triblock copolymer 7A; (b) a (poly(A) + poly(B) + poly(C)) homopolymer physical blend; and (c) a (B-*b*-C diblock CP + poly(2)) physical blend.213
- 6.S6 Comparison of SAXS data (collected at 100 °C from heating). Inverted filled triangles represent the location of the allowed reflections for the lamellar morphology, calculated based on the position of the primary scattering wave vector q_{100} : $(L) q/q^*$ at $v1, v4, v9, v16, v25$, etc. Inset pictures are the 2D scattering patterns.215
- 6.S7 SAXS data (collected at 100 °C from heating) of triblock CP composite membranes samples show phase separation evident by the observed primary scattering reflections of (a) triblock CP composite membrane 7A and (b) triblock CP composite membrane 7B.....216
- 7.1 Chemical structures of an example (RTIL-based BCP + free RTIL) composite system consisting of a hydrophobic-*b*-imidazolium di-BCP and free EMIM Tf2N RTIL. Such a composite material could posses improved membrane gas transport properties.224
- 7.2 Potential design of a curable, post-polymerization BCP system that can incorporate high loadings of non-polymerizable “free” RTIL, phase-separate, and later cross-link to lock morphology into place. The blue * symbol denotes an orthogonal chain-addition polymerizable group that can be activated for chain-cross-linking after initial BCP synthesis and phase-separation with RTIL inclusion.224
- 7.3 Successful synthesis of a cinnamate ester-functionalized norbornene monomer that is compatible with ring-opening metathesis polymerization and shows molecular weight control and living character, with the potential to photochemically cross-link upon UV irradiation.225
- 7.4 [2+2] photochemically allowed coupling of the cinnamate ester alkene bond that is not ROMP active. This functional group and coupling chemistry can thus be used for ROMP-prepared BCP post-polymerization chain cross-linking.....226
- 7.5 Proposed imidazolium-based BCP system synthesized via NMP that could undergo post-polymerization chemical modification to afford photo-cross-linkable BCPs.228

LIST OF EQUATIONS

1.1	$n\lambda = 2d\sin\theta_B$	10
3.S1	$2m + 2n = C_{1H}$ NMR Integration	54
3.S2	$2m + 4n = D_{1H}$ NMR Integration	54
3.S3	$[(\text{Mon:Cat loading ratio})(m_{\text{block ratio}})] - b - [(\text{Mon:Cat loading ratio})(n_{\text{block ratio}})]$	61
5.1	$P_i = J_i \frac{l}{\Delta p} = \frac{V_p V_m}{ART} \left(\frac{dp_p}{dt} \right) \frac{l}{\Delta p}$	164
5.2	$D_i = \frac{l^2}{6\theta}$	164
5.3	$P_i = D_i \times S_i$	164
5.4	$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j}$	165
6.S1	$2x + 2y + 2z = B_{1H}$ NMR Integration	206
6.S2	$2x + 4y + 2z = C_{1H}$ NMR Integration	206
6.S3	$13 = D_{1H}$ NMR Integration	206
6.S4	$[(\text{Mon:Cat})(x_{\text{block ratio}})] - b - [(\text{Mon:Cat})(y_{\text{block ratio}})] - b - [(\text{Mon:Cat})(z_{\text{block ratio}})]$	212
6.S5	$[(\text{Mon:Cat})(z_{\text{block ratio}})] - b - [(\text{Mon:Cat})(x_{\text{block ratio}})] - b - [(\text{Mon:Cat})(y_{\text{block ratio}})]$	212
6.S6	$[(\text{Mon:Cat})(x_{\text{block ratio}})] - b - [(\text{Mon:Cat})(z_{\text{block ratio}})] - b - [(\text{Mon:Cat})(y_{\text{block ratio}})]$	212

CHAPTER 1

INTRODUCTION

1.1 Gas Transport Through Dense Polymer-Based Membranes

The production of clean energy is becoming increasingly important as concerns over greenhouse gas emissions and the need for more economic, efficient fuel sources continue to receive worldwide attention.¹⁻⁴ Carbon dioxide (CO_2) is a known greenhouse gas, and billions of tons of CO_2 are annually emitted as a direct result of fossil fuel combustion used to generate electricity.⁵ Tangentially, naturally mined gas (principally composed of methane, CH_4) contains around 10% CO_2 which, when combusted as-is, considerably decreases the value of the natural gas because CO_2 is not combustible.⁶ Selective gas separation is a principle challenge for yielding cleaner, more efficient means of energy from abundant sources such as coal and methane.

A number of technologies are currently being implemented for removal of CO_2 from other light gases such as N_2 (post-combustion reactions) and CH_4 (natural gas production). Gas-liquid absorption processes, such as aqueous amine scrubbing, involves contacting the post-combustion flue gas with a chemical solvent (e.g., typically an amine) in a large scrubbing column to reversibly chemically react with and remove the CO_2 . While highly efficient, this technology is highly energy-intensive. Gas-solid membrane-based processes, however, have gained considerable attention as an attractive alternative separation mechanism for CO_2 /light gas separation applications (e.g., CO_2/N_2 ,

CO₂/CH₄).⁷ In fact by 2002, membrane-based gas separations had grown into a \$150 million/year business and substantial growth in the near future is evident.⁸

Polymeric membrane-based processes offer a mechanically stable, less energy-intensive approach to CO₂/light gas separations and have been under the topic of several reviews.⁹⁻¹¹ A polymeric membrane is a semi-permeable material that specifically restricts the movement of one or more molecules across its barrier to selectively separate dissimilar gases.¹² Polymers are the most broadly used membrane material because they can be easily fabricated into various membrane configurations such as free-standing membranes, thin-film composites (TFCs), or hollow fibers.¹² In general, polymer membranes can be classified as being dense (i.e., nonporous) or porous materials, and the aforementioned configurations dictate the transport mechanism.

While porous membranes are created from materials that can phase-separate into ordered structures with discrete pores, dense membranes are typically fabricated from amorphous polymers with no porous structured morphology. Gas transport occurs through a solution-diffusion (S-D) mechanism.¹² In S-D, a partial pressure difference between the upstream (i.e., the feed) and downstream sources causes the driving force across the membrane. Through this mechanism, molecular transport occurs upon absorption of the solute on the membrane at the upstream surface, diffusion through the dense membrane, and finally desorption from the membrane at the downstream surface. Each solute has a distinct permeability (P), which is the product of both the unique gas solubility (S) and diffusivity (D) properties. The ratio of permeabilities between two solutes or gases is called the permselectivity (α) and separation can be achieved through differences in solubilities and/or diffusivities. Therefore, larger differences in solubilities

and diffusivities lead to larger differences in permeabilities, and thus, better solute separation.

Dense, homogenous polymer membranes are typically fabricated by one of three methods.¹² The first method is a simple melt extrusion process in which a polymer or polymeric blend is heated above the melting point, cast as a solvent-less liquid onto a substrate, and allowed to cool into a solid membrane. The second more commonly used method is called solution-casting, in which a polymer or polymeric blend is dissolved into a solvent, cast onto a substrate, and the solvent is removed via evaporation. This method tends to yield substantially thinner membranes. The third method is called interfacial polymerization and requires use of reactive species (i.e., monomers) in two solvent systems. In this process, one reactive solvent phase is impregnated within a porous substrate while the second reactive solvent phase is outside or above the substrate surface. The polymeric membrane forms at the interface between the two phases where the two monomer solutions contact and produce a thin film on the surface and not within the substrate pores.

When using dense, polymer membranes for gas separations, there tends to be a permeability-selectivity trade-off.¹³ Increases in gas permeability tends to be due to increases in interchain void volumes, allowing for higher gas throughput productivity; however, this means a more open polymer structure resulting in lower gas separation selectivity. This phenomenon is illustrated by the empirically observed selectivity-permeability “upper bound” or trade-off indicated on a log-log Robeson Plot for polymer gas separation membranes shown in Figure 1.1.¹⁴

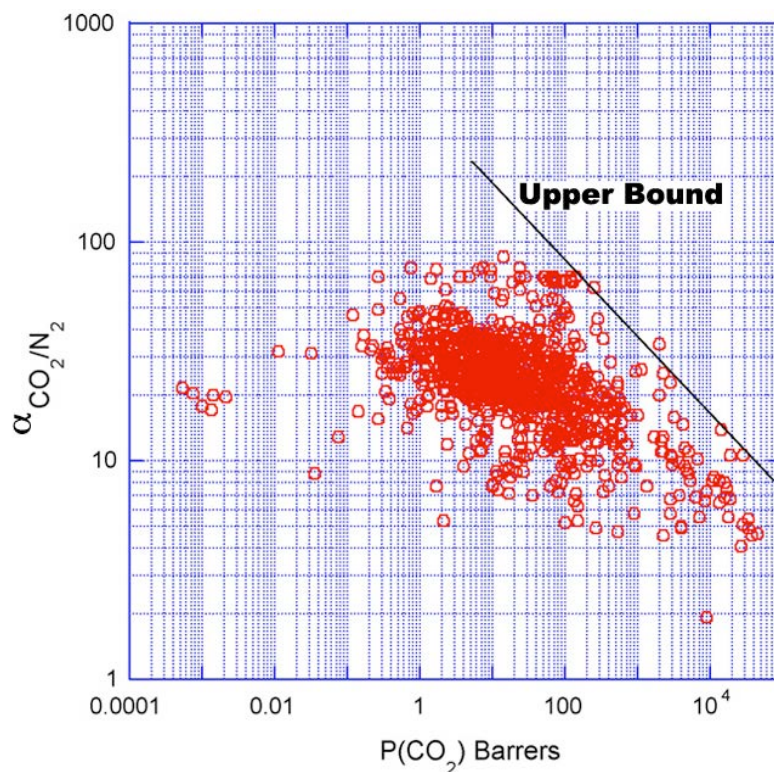


Figure 1.1. Example of a log-log Robeson Plot showing measured CO_2/N_2 gas selectivity data vs. CO_2 permeability through a range of known dense polymers (red dots) and the apparent selectivity-permeability performance trade-off represented by an observed "upper bound" (black line). Figure reproduced from ref. 14. (Copyright 2008 Elsevier).

Improving separation performances while maintaining high permeabilities with homogenous polymer membranes is largely difficult due to the upper bound trade-off but very recently, development with heterogeneous membranes have been demonstrated to exceed the upper bound.⁵ The outlook of research and development in the field of self-assembled block copolymers is exciting and has grave potential in the realm of gas separation membranes.

1.2 Block Copolymers

A polymer is a large macromolecule created by covalently bonding many smaller structural units (called monomers) together. When only one monomer species is used to do this, the resulting macromolecule is called a homopolymer or simply a polymer. When two different monomer species are used, the resulting polymer is known as a copolymer.¹⁵ In the simplest case of an AB copolymer with two different monomers (and consequently two different repeat units), its result can be of four general architectures in terms of the sequence or placement of the repeat units: alternating, random, block, and graft (Figure 1.2).¹⁵

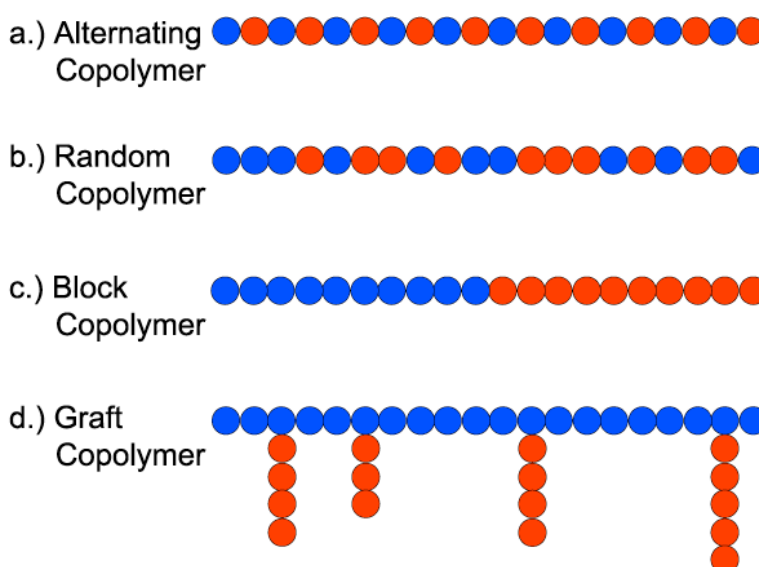


Figure 1.2. Common AB copolymer architectures.

Correspondingly more complex architectures based on similar sequencing ideas are possible with copolymers, and are fabricated with more than two different monomers (i.e., an ABC copolymer).¹⁵

Of the different copolymer configurations, block copolymers (BCPs) (see Figure 1.2c) represent an interesting copolymer architecture that has many applications in fields including thermoplastic elastomers¹⁶, nanotechnology,¹⁷ nanolithography¹⁸, and fuel cells¹⁹. Linear di- and tri-block copolymers are formed by the sequential polymerization of two or more monomers and have been of considerable scientific interest over the past several decades as a result of their inherent ability to self-assemble into unique morphologies on the nanometer length scale (10–100 nm).^{5,20,21} This self-assembly is unique to BCPs, as physical blends of analogous homopolymers cannot form said ordered nanostructures. Figure 1.3 shows a pictorial difference in phase-separation behavior for a physical blend of two homopolymers and that of an analogous AB diblock copolymer (di-BCP).

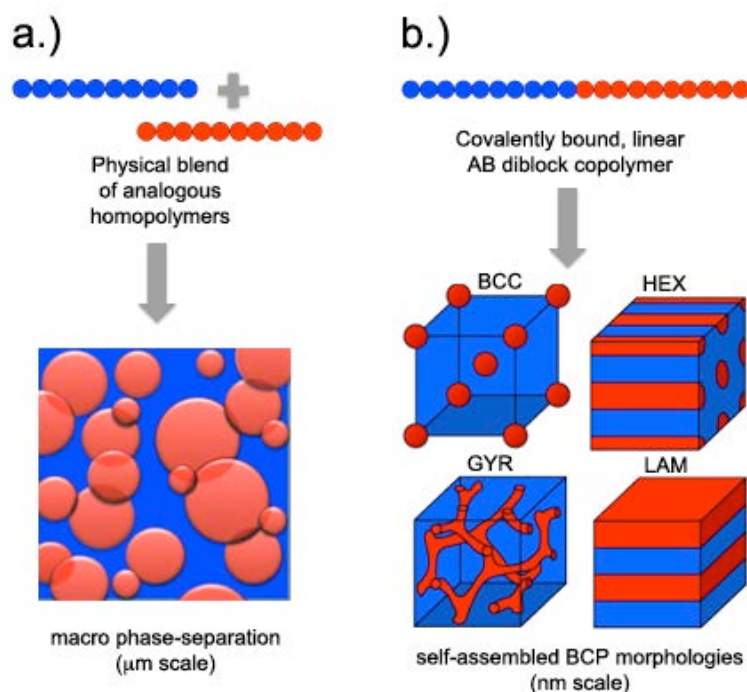


Figure 1.3. (a) Phase-separation of a physical blend of two homopolymers resulting in an un-ordered heterogeneous mixture with features on the micrometer scale, and (b) phase-

separation of analogous, covalently tethered linear BCP architectures resulting in self-assembled ordered morphologies on the nanometer scale.

Ordered, self-assembled morphologies can be precisely controlled by block length and composition of the chemically dissimilar, covalently tethered polymer blocks. A strong foundation has been laid by previous theoretical^{20,22–24} and experimental^{25,26} research exploring the self-assembled phase behavior of BCPs for several decades. BCP molecular weight, block composition, and ultimately nanostructured morphology can be determined by a number of characterization techniques, as summarized in the following sections.

1.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is one of the most versatile and informative characterization techniques employed in research labs to distinguish the chemical structures of molecules.^{27,28} While there are a number of different types of NMR experiments²⁷, this thesis primarily found proton (¹H) and diffusion-ordered spectroscopy (DOSY) NMR most relevant and helpful in the characterization of polymers. In contrast to the narrow, well-resolved spectral line widths associated with small molecules, ¹H NMR spectra of polymers tend to be much broader. This is a result of longer correlation times (i.e., slower molecular movement) and the presence of the same nuclei in slightly different environments (i.e., the repeat units of polymers with different molecular weights) that will absorb at slightly different frequencies as opposed to one single frequency.²⁸ Regardless, signal integrations on polymer samples are still relatively accurate and quite effective in calculating block composition ratios.

1.2.1.1 Block Copolymer Characterization via NMR Spectroscopy

^1H NMR is very helpful in quantifying relative block composition ratios (i.e., A:B molar ratio in an AB copolymer) by integrating and comparing fundamental chemical shifts unique to each block. If a known quantity of protons affiliated to particular chemical shift are integrated and compared to the integration of a different chemical shift, a ratio can be calculated to quantify the composition of one block in relation to another.¹⁵

Where ^1H NMR cannot easily verify covalent block connectivity or repeat unit sequence in BCP macromolecules, DOSY can; and it is an important NMR tool used to disentangle the overlapped NMR spectra of individual mixture components.²⁹ DOSY capitalizes on solution diffusion variations between macromolecules of differing hydrodynamic radii and molecular weights to separate overlaid NMR spectra.²⁹ In other words, DOSY is a powerful technique that can differentiate BCPs from a physical blend of analogous homopolymers.

1.2.2 Gel Permeation Chromatography (GPC)

Alternatively known by its more descriptive name, size-exclusion chromatography (or SEC), GPC is a liquid chromatography technique that provides rapid, efficient, and reliable means to characterizing traditional polymer samples of various sizes.¹⁵ The method depends on two phases: (1) a mobile phase (i.e., solvent) and (2) a non-ionic stationary phase (i.e., a column) commonly composed of cross-linked polystyrene that forms a distribution of different pore sizes, which effectively separate polymer samples based on their effective molecular size in solution (i.e., their

hydrodynamic volume).¹⁵ Mechanistically, larger polymers are excluded from the smaller pores and pass quickly through the larger channels resulting in a faster elution time from the column. As molecular size decreases, elution time increases since polymer chains are more likely to diffuse into the smaller pores, slowing their passage through the column. Once through the column and information about polymer size is detected and calibrated,¹⁵ GPC curves are presented as a function of elution time. Narrowly dispersed BCP samples will show one prominent peak (i.e., low polydispersity index or PDI) whereas analogous homopolymer blend samples with drastically varying molecular weights will show multiple broad (i.e., high PDI value), shallow peaks. It is important to highlight that while GPC is a quick and relatively inexpensive method for proving synthetic molecular weight increase and covalent connectivity, this technique is often limited to non-charged, traditional BCP materials.³⁰ GPC analysis of charged species is not generally possible as they can aggregate in solution and may foul the non-charged columns.

1.2.3 Rheology

Rheology, or the study of flow in liquids or soft solids in response to an applied force, is sometimes used as a means to characterize BCP phase-separation in conjuncture with other techniques (e.g., SAXS, TEM, etc.).^{15,31} The rheological characterization of BCP materials is commonly performed by applying a dynamic sinusoidal (oscillating) strain to the sample and observing the complex modulus response (ratio of stress to strain).³¹ Two modulus components are mathematically calculated, where the storage modulus (G') is a measure of the solid elastic properties of the material and the loss

modulus (G'') is a measure of the viscous liquid properties.³¹ BCPs typically possess considerable components of each and rheological responses vary wildly between ordered morphological structures (or lack thereof).^{25,26,32} In addition, there are also rheological trends associated with BCP structures that can be used to help assign morphologies.^{26,32} While rheological studies cannot directly be used to determine BCP morphologies, it becomes extremely powerful when combined with other direct nanostructure determination methods such as small-angle X-ray scattering (SAXS).

1.2.4 Small-Angle X-ray Scattering (SAXS)

SAXS is a powerful technique used to directly detect the highly periodic, mesomorphous, or even amorphous morphologies of macromolecules and BCPs.^{32,33} BCP melts (i.e., solvent-free) that exhibit periodic nanostructures can be characterized by their unique SAXS diffraction patterns, similarly to that in conventional X-ray diffraction of molecular powders or crystals.³² By nature, SAXS is used to investigate relatively large-scale structures, whereas wide-angle X-ray scattering (WAXS) is typically used for small, crystalline atomic structures. X-ray diffraction from BCP melts occurs at very small angles (θ_B), which can only be detected via SAXS, due to the large interplanar domain spacings (d) in BCP nanostructures (ca. 1–10 nm range) compared to the smaller interplanar spacings (ca. 0.1–1 nm range) and larger diffraction angles associated with small molecule.^{32,33} Even still, this relationship is consistent with the Bragg Equation, where the constructive Bragg angle (θ_B) is inversely related to interplanar distance d at constant radiation wavelength, λ (Equation 1.1):

$$n\lambda = 2d\sin\theta_B$$

Equation 1.1

A simplified SAXS schematic is shown Figure 1.4. An X-ray source, typically from copper or molybdenum,³³ will penetrate a BCP sample (often an ordered polydomain sample, as shown), and the resulting diffraction patterns will appear as a series of Debye-Scherrer rings which is a result of an infinite number of diffraction spots from the many orientations of the ordered polydomains. Once diffraction patterns are observed and recorded by the detector, they are transformed from polar coordinates to a Cartesian coordinate system and azimuthally integrated to create 2D or 1D plots of intensity vs. scattering wave (q) vs. scattering angle (Figure 1.4). Diffraction patterns can then be indexed to identify phase-separated morphologies.³² Past comprehensive theoretical^{21,34} and experimental research²⁶ has pioneered the indexing coordinates we use today to identify BCP nanostructures from their SAXS diffraction patterns.

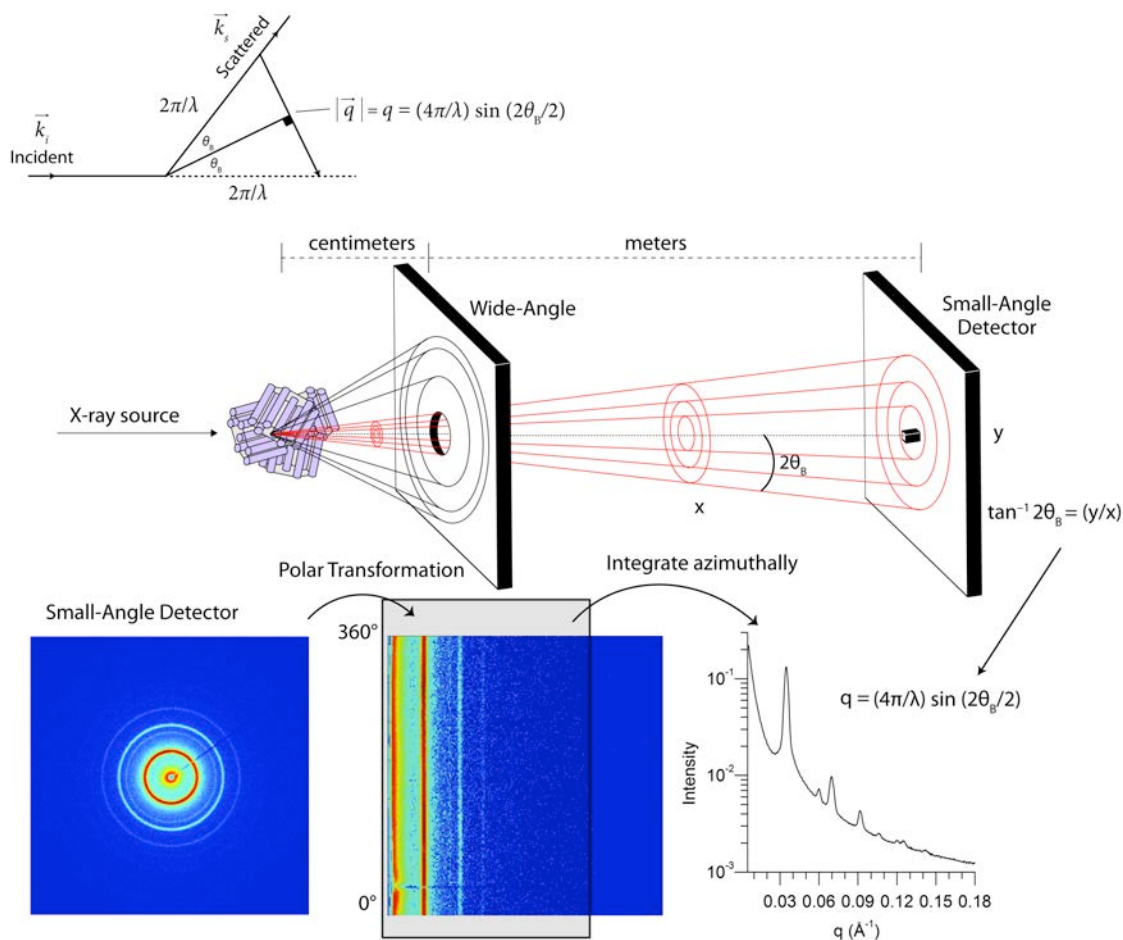


Figure 1.4. Geometric relationship between the Bragg angle (θ_B) and scattering wave vector, q (top). Schematic of a hexagonally-packed cylindrical “poly-crystalline” BCP sample diffracting an X-ray source. Wide-angle detection is located centimeters from the sample source, similar to the proximity of a powder XRD detector utilized for small, crystalline molecules. Small-angle detection is located meters from the BCP sample source, as to acquire very small angle diffraction scattering as a result of large domain spacings. After data collection, the 2D scattering results are transformed into a 1D plot of q vs. intensity. Unique SAXS diffraction patterns are indexed similarly to powder XRD patterns. Figure and caption reproduced from ref. 35. (Copyright 2012 V. F. Scalfani).

1.2.5 Direct Nanostructure Imaging Techniques

It is important to note that transmission electron microscopy (TEM) can also be used to characterize phase-separated BCP morphologies. SAXS data is often paired with TEM images to visualize and confirm a particular morphology.³² Magnifications of

400,000 times can be visualized for many materials and atoms can be imaged at 15 million times. In TEM, a focused beam of electrons is directed at a thin sample and the electrons that are transmitted through the sample determine the 2-dimensional topography.³⁵ Transmitted electrons are collected by a detector, which creates an image of dark and light regions. The darker images represent the areas of the sample through which fewer electrons are transmitted (e.g., thicker, more dense material), whereas the lighter areas represent those areas through which more electrons are transmitted (e.g., thinner, less dense material). A major drawback to TEM is that samples must be specifically prepared to thicknesses that allow for electron transmittance; therefore, correct sample preparation is often key to obtaining quality TEM images.³⁵ An additional drawback is that the instrument is costly and not often readily available. With block copolymer self-assembly on the nm-scale, many research groups^{16,25,26,30,36,37} have utilized TEM as a tool to visualize phase separated morphologies but only when these difficulties can be overcome.

1.2.6 Structural Factors that Determine Phase-Separated BCP Morphologies

There are three critical intrinsic molecular parameters that affect the nature of BCP phase-separated morphologies: f_A (volume fraction of A in the polymer), χ (Flory-Huggins interaction parameter), and N (the degree of polymerization).²⁰ The degree of segregation, χN , indicates whether the blocks will phase-separated into multiple domains or mix into a homogeneous domain based on how chemically immiscible they are. Higher χ equates to a higher chemical incompatibility between the two blocks. Interestingly, researchers have found that BCPs can exhibit a broad range of

nanostructures upon altering f_A or χN . This multiphase spectrum is presented in a BCP phase diagram (Figure 1.5).

In a typical A-*b*-B di-BCP phase diagram, f_A is plotted as a function of the product χN ; and a theoretical, symmetrical trend is observed around 0.5 volume fraction.³⁴ When each block component reserves 50% of the total volume, a lamellae phase is observed. If the volume fraction of one block decreases (and the other increases), a range of morphologies can be seen (Figure 1.5). Representations of the phase structures are shown, ranging from body-centered cubic (BCC), cylindrical hexagonal (HEX), gyroid, and lamellar (LAM) phases.³⁴

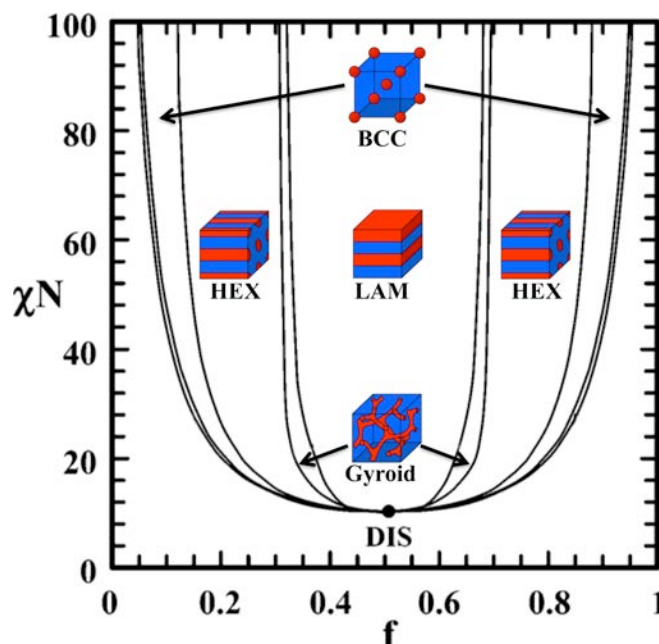


Figure 1.5. Theoretical AB di-BCP phase diagram, showing the geometries of the most commonly formed ordered phases (LAM, HEX, gyroid, and BCC). Adapted from ref. 20. (Copyright 2006 American Chemical Society).

1.2.7 Effect of Nanostructured BCP Morphology on Transport Properties

Though largely unexplored, there have been a few reports in the literature of the significant benefits of nanostructured morphology in BCP membrane materials on transport properties.³⁷⁻⁴³ In 1974 (and perhaps the first report on the permeation of gases through nanostructured BCPs), Odani et al.³⁸ investigated poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers (tri-BCPs) that formed both alternating lamellae domains and styrene rod-like domains dispersed in butadiene. Via desorption and time-lag methods, they found that gas permeation and diffusion were correlated with nanodomain structures. Ten years later, Knight and Lyman³⁹ published findings on the effect of chemical structure and fabrication variables on the gas permeability of various poly(ether-*b*-urethane) BCPs. BCPs with longer poly(propylene glycol) (PPG) segments yielded higher gas permeabilities for CO₂, N₂, and O₂ compared to larger poly(ethylene glycol) (PEG) segments, due to the proposed decrease in block packing. Additionally, Knight and Lyman found that changes in casting solvents had minor effects on gas permeabilities. The Cohen group^{40,41} reported several experimental and modeling studies on phase-separated poly(styrene-*b*-butadiene) BCPs and their affiliated gas permeabilities. They visualized BCP orientation with 2D-SAXS and TEM and found that the effective permeability of the semi-crystalline BCPs was highly dependent on nanodomain orientation.

The influence of BCP orientation on gas transport was again realized 11 years later in 2000 by Drzal et al.⁴² In this work, gas permeability coefficients were studied in microstructured poly(ethylene-*b*-ethylene-propylene-*b*-ethylene) tri-BCPs. When coupled with SAXS analysis, Drzal and co-workers found a direction correlation between changes in microstructure and observed changes in gas transport properties. They stated

that gas transport does not favor crystalline regions, and that randomly oriented polycrystalline domains yield lower gas permeabilities compared to BCP microstructures oriented parallel to the direction of gas permeation. Most recently, Xue et al.⁴³ fabricated poly(ethylene oxide-*b*-styrene) BCP-based free-standing CO₂-selective membranes that were observed to self-assemble into cylindrical domains (HEX phase). The microphase-separated structure was confirmed via TEM, and it was concluded to play an important role in the high performance of the membrane. It is clear that reports investigating and correlating the benefit of BCP self-assembled morphology with gas transport properties are few and far between.

Tangentially, Balsara et al.³⁷ studied the effect of BCP nanoscale morphology on ethanol/water transport through poly(styrene-*b*-butadiene-*b*-styrene) and poly(siloxane-*b*-octene-*b*-siloxane)-type tri-BCP membranes. They reported that ethanol selectivity and overall flux increase with domain spacing and can be optimized by altering the BCP domains.

To our knowledge, prior to the work described in this thesis, these are the only reports in the literature that discuss the correlation between BCP nanoscale morphology and membrane transport properties. It is important to reiterate that the above references explored hydrophobic-*b*-non-charged hydrophilic (i.e., *non-ionic*), phase-separated BCP membrane systems.

1.2.8 BCPs Comprised of Neutral and Charged Blocks

In the last decade, di- and tri-BCPs containing both neutral and charged blocks have gained considerable attention from the polymer membrane community as well as

from polymer physicists.³⁰ This attention is largely motivated by interest in charged BCP materials as proton-exchange membranes (PEM),¹⁹ catalytic materials,⁴⁴ polyelectrolytes in fuel cell and battery applications^{36,45,46}, and most limited, CO₂/light gas separation materials.⁴⁷

(Neutral-*b*-charged) BCPs can be synthesized by a variety of polymerization techniques, but they have predominately been made using “living” or “controlled” radical polymerization techniques such as atom-transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), and nitroxide-mediated polymerization (NMP).³⁰ Two major benefits to using these controlled polymerizations techniques are precisely-defined, narrowly dispersed BCPs (i.e., low PDI) and distinct molecular weight control. Researchers can polymerize, with relatively high control, exact block molecular weights and A:B block ratios. This is important since block length and volume fraction wholly dictate self-assembled morphologies, which in turn, can affect the transport properties of the resulting copolymer material. The introduction of charged blocks into well-defined BCPs has only emerged thanks to recent advances and monomer functionality tolerances in controlled radical polymerizations and initiators.³⁰

The preparation of ion-containing di-BCPs have focused on more traditional polyelectrolyte systems, such as those containing acrylic acid,^{48–51} sulfonated styrene,^{52,53} and protonated lysine residues.^{49,50} Most recently, imidazolium-containing di-BCPs have emerged as a multifaceted synthetic platform for amphiphilic BCP systems.^{36,47,54,55} Li et al.⁵⁴ prepared polystyrene (PS)-*b*-poly(imidazolium) di-BCPs via condensation polymerization combined with NMP. It is important to highlight that the imidazolium repeat units in these di-BCPs were synthesized as main-chain groups; in other words,

they were not pendant to the polymer chain. The (unordered) micelle formation of these amphiphilic BCPs in water was characterized by TEM and dynamic light scattering (DLS).⁵⁴ Stancik et al.⁵⁵ also studied the micelle formation of poly(imidazolium)-*b*-PS di-BCPs in water. These BCPs were synthesized via NMP followed by post-polymerization modification to yield pendent imidazolium groups. In this research, they found that the length of the imidazolium block governed the micelle dimensions and water sequestration. Weber et al.³⁶ studied the effect of nanoscale morphology on the conductivity of poly(imidazolium-*b*-styrene) di-BCPs, prepared by NMP in combination with post-polymerization modification.³⁶ Subsequent morphology evaluation was studied via SAXS and TEM. The effects of copolymer morphology on ionic conductivity were investigated and it was found that lamellae morphologies lent to the highest conductivity measurements over lamellae-cylindrical mixed-phase morphologies.

Besides ionic di-BCPs, charged tri-BCPs have also been explored but in much more limited scope, focusing almost entirely on ABA-type symmetrical structures with A or B consisting of traditional sulfonated polystyrene moieties.³⁰ Studies of sulfonated BCPs originated in the early 1990s by Weiss et al.⁵⁶ in which PS-*b*-poly(ethylene butylene)-*b*-PS modified with low sulfonation functionality (0–18 wt%) were used to fabricate physically cross-linked thermoplastic elastomers. Microstructured phase behavior was documented, with ionic domains 3–4 nm in size. Later studies of sulfonated ABA tri-BCPs showed that increasing the degree of sulfonation caused broadening of the SAXS peaks due to the ion-rich domains tethered to the PS moieties, which disturbed the microphase separation. In other words, it is hard to establish or

thermally induce phase equilibrium in highly sulfonated tri-BCPs because of strong anionic interactions.³⁰

More recently, cationic imidazolium monomers were successfully polymerized into ionic ABA-type tri-BCP systems.^{47,57–59} In particular, vinyl- or acrylate-containing imidazolium monomers were polymerized via RAFT^{47,57} and NMP^{58,59} techniques to fabricate systems potentially useful for ion conductivity^{57–59} and membrane gas transport.⁴⁷ Most notably, Lodge et al.⁴⁷ studied the gas separation performance of imidazolium-containing tri-BCPs synthesized via RAFT in combination with post-polymerization modification. While no self-assembly nor morphological effects were explored, it was shown that these tri-BCPs could gel (i.e., physically cross-link and incorporate) quite a large quantity of free room-temperature ionic liquid (RTIL) which yielded good CO₂ transport properties.⁴⁷ While Lodge et al. and other groups have demonstrated the novel use of imidazolium-based monomers for ABA-type tri-BCP synthesis, the ordered microphase-separation of these ionic BCPs has yet to be studied and utilized in gas separation applications.⁵

1.3 Room-Temperature Ionic Liquids (RTILs)

Room-temperature ionic liquids (RTILs) are highly tunable molten salts that are liquid below <100 °C.⁴ RTILs are deemed “green” solvents because of their minimal volatility and recyclability, and have been tailored for a variety of engineering applications including CO₂ separation from other light gases. Specifically, imidazolium-based RTILs are at the center of new membrane-based gas transport applications due to their commercial availability, modular nature, and high intrinsic CO₂ gas solubility.⁴

Whereas traditional polymers cannot withstand high testing temperatures and aggressive chemical environments, RTILs offer a thermally stable alternative to meeting industrial requirements and improving CO₂/light gas separation membrane materials.⁹

Imidazolium-based RTILs can be synthetically “tuned” for various CO₂ separations by tailoring the cation and/or anion structures (Figure 1.6). Functionalization can occur within the 5-membered ring as well as quaternizing either nitrogen atom. These R groups can range from hydrophobic alkyl chains to polar oligo(ethylene glycols), nitriles, or amines.^{4,7} Anion species can also affect selective transport and include triflate (OTf), dicyanamide (dca), tetrafluoroborate (BF₄), and bis(trifluoromethane)-sulfonimide (Tf₂N).⁴

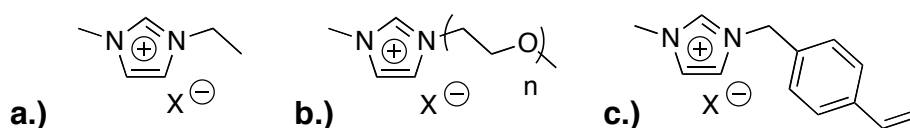


Figure 1.6. Example configurations of (a) alkyl substituted-, (b) polar substituted-, and (c) polymerizable-RTILs, where the anionic species X could represent OTf, dca, BF₄, or Tf₂N.

A straightforward approach to using RTILs for membrane-based gas separation applications has been to impregnate the RTIL into a porous polymer substrate or support. This platform, called supported ionic liquid membranes (SILMs), provides large gas permeabilities due to high gas diffusions through the dense liquid film.⁷ The negligible volatility of the RTIL “solvent” within the support inhibits evaporation that leads to degradation of membrane integrity or selectivity.

In the laboratory, SILMs show excellent performances as summarized in a review by Scovazzo:⁶⁰ CO₂ permeabilities range between 100 and 1700 barrers and CO₂/N₂

selectivities from 10 to as high as 61.^{4,60} The best combinations of RTIL properties are superior to polymeric membranes as SILMs can exceed the Robeson Plot “upper bound” (see Section 1.1). Unfortunately SILM thickness is limited to the support thickness itself (approximately 150 μm).⁶⁰ Thus, in practice, SILM thicknesses reported in literature are sometimes two orders of magnitude thicker than the selective layer thickness required for high-throughput membrane applications ($\leq 1 \mu\text{m}$).^{4,60} Additionally, SILMs are prone to RTIL leaching or “blow-out” through the pores of the support when the pressure differential across the membrane exceeds the capillary forces that stabilize the liquid within the polymer matrix.⁷

To combat these issues, imidazolium-based RTILs can be functionalized with polymerizable groups such as styrene or acrylate moieties to create RTIL-based monomers that can be polymerized into polymerized(RTILs) (i.e., poly(RTIL)s).^{7,61,62} Poly(RTIL)-based membranes drastically improve membrane mechanical stability under higher pressures while retaining intrinsic RTIL charged chemical nature.⁷ Bara et al. synthesized and studied the gas transport properties of various neat,⁷ gemini,⁶³ alkyl-⁶¹ and polar-substituted⁶² poly(RTIL) membranes. Therein, they reported poly(RTIL) membrane performances with CO_2/N_2 selectivity values that range from 30-40, accompanied by CO_2 permeability values that range from 4 to 30 barrers. This significant reduction in CO_2 permeability compared to analogous liquid-phase membranes (e.g., SILMs) is due to the large decrease in gas diffusivity after polymerization (i.e., gas diffusivity is lower in a dense solid compared to a dense liquid). As a way to achieve greater gas permeability while maintaining CO_2 selectivity and retaining material stability, poly(RTIL)-RTIL composite membranes have been explored.

The addition of non-polymerizable “free” RTIL to a poly(RTIL) matrix creates poly(RTIL)-RTIL composite materials. It has been shown that incorporating free RTIL leads to an enhancement of CO₂ permeability compared to neat poly(RTIL) membranes when RTIL-based cross-linkers are integrated into the membrane.^{64,65} Li et al.⁶⁴ were able to incorporate up to 60 wt% free RTIL in their poly(vinyl-RTIL) materials without compromising membrane mechanical integrity. Carlisle et al.⁶⁵ cross-linked poly(vinylimidazolium) membranes and were able to load up to 75 wt % free RTIL. While increasing loading levels of free RTIL dramatically increased CO₂ permeability performances, the addition had no effect on CO₂/N₂ selectivity.

Recently, amorphous poly(RTIL)-RTIL composite materials such as those listed above seem to dominate the literature in pursuit of highly permeable, highly CO₂-selective membranes. With modest work documenting the unique transport benefits that can arise from self-assembled non-ionic BCPs (see Section 1.2) and the inherently high CO₂ selectivity and permeability properties of RTILs (see Section 1.3), it is no wonder that the combination of the two warrants exploration with purposeful application. However, due to the unique, charged nature of IL-based polymers and copolymers, traditional polymer characterization techniques (e.g., GPC, TEM, mass spectrometry, etc.) are not often feasible, making composition, sequence, molecular weight characterization the largest challenges to overcome when studying such materials.

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CHAPTER 2

DISSERTATION RESEARCH GOALS

2.1 Overview of Thesis Research

The overall objective of this Ph.D. research was to design, develop, and explore ordered, phase-separated, room-temperature ionic liquid (RTIL)-based block copolymers (BCPs) as a new type of membrane material for CO₂/light gas separation applications. As described in more detail in the following thesis chapters, novel RTIL-based monomers were synthesized and block-copolymerized via living ring-opening metathesis polymerization (ROMP). The phase-separated nanostructures of the resulting BCPs were characterized prior to and following the fabrication of composite membranes for gas transport testing.

Two major RTIL-based BCP architectures were synthesized: (1) AB *diblock* copolymers (di-BCPs) and (2) ABC *triblock* copolymers (tri-BCPs). Phase diagrams mapping the morphological behavior of both systems were studied in correlation to monomer chemical disposition, block length ratios, and block sequence. The successful fabrication of BCPs into supported composite membranes was demonstrated, and their subsequent gas transport properties were tested and discussed. Finally, future directions exploring the addition of free RTIL into curable di-BCP networks to retain morphological order are designed and discussed.

2.2 Specific Dissertation Research Aims

Chapter 3 describes the synthesis and ordered phase separation of previously unprecedented imidazolium-based, alkyl-ionic di-BCPs (Figure 2.1). This first-generation, proof-of-concept project initiated and inspired the novel synthetic approach to polymerizing RTIL-based monomers with Grubbs' 1st-generation catalyst into innovative block copolymer architectures. Hydrophobic alkyl and RTIL-based norbornene monomers were synthesized and sequentially polymerized via living ROMP. Due to its ionic character, traditional and several non-traditional BCP characterization techniques were implemented to verify block connectivity and molecular weight.

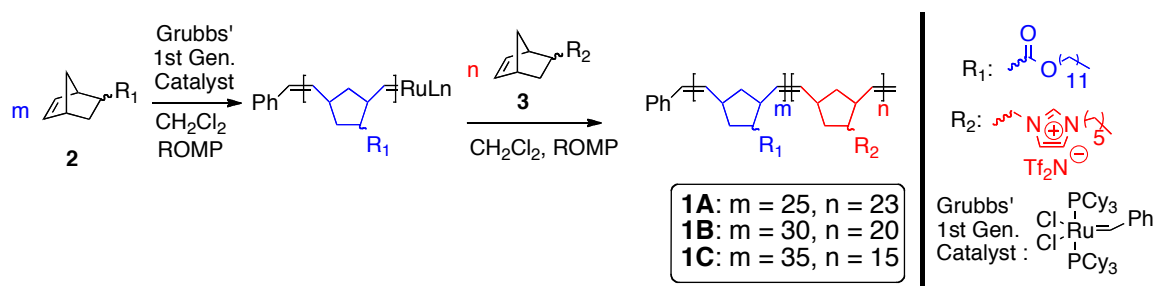


Figure 2.1. Research explored in Chapter 3: synthesis and sequential ring-opening metathesis polymerization of novel norbornene alkyl- and imidazolium ionic liquid-based monomers with Grubbs' 1st-generation catalyst into BCPs **1A–C**.

Chapter 4 describes the synthesis of a library of alkyl-ionic poly(RTIL)-containing di-BCPs and elucidation of a thorough phase diagram of the morphological behavior of these melt-state BCPs using SAXS and dynamic rheology. A series of 16 BCP samples were synthesized, varying both the relative block volume fractions of the monomer derivatives as well as the overall BCP number-average molecular weights (M_n values from 5000–20,100 g mol⁻¹). Largely thanks to the joint collaboration with Colorado State University and the help of Dr. Vincent Scalfani, clear compositional

phase boundaries for each of the classic BCP phases were identified, including lamellae, hexagonally packed cylinders, and spheres in a body-centered-cubic lattice (Figure 2.2). This morphological phase diagram work established the foundation for exploring the distinct phase morphologies of these RTIL-based BCPs for selective CO₂ gas transport.

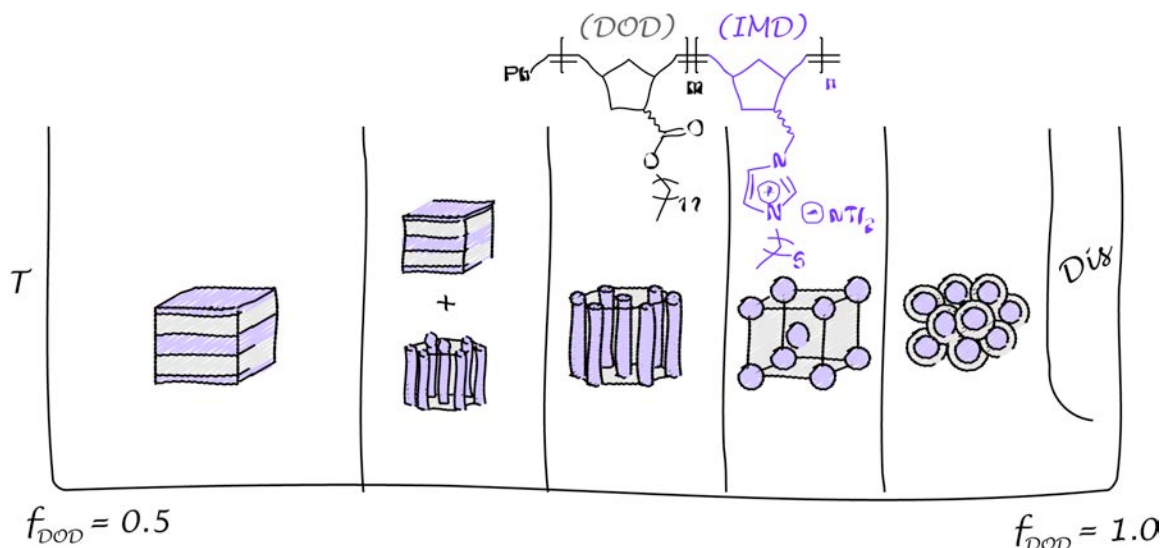


Figure 2.2. Research explored in Chapter 4: sketch of the thoroughly elucidated phase diagram from a synthesized library of alkyl, hydrophobic (“DOD”)–*block*–imidazolium, ionic (“IMD”) di-BCPs. Reproduced from ref. 1. (Copyright 2012 American Chemical Society).

Chapter 5 examines the effect of composition and phase-separated nanostructure in these alkyl-ionic poly(RTIL)-containing BCPs on their CO₂/N₂ transport properties in a supported membrane configuration (Figure 2.3). RTIL-based BCPs were synthesized with varying morphological nanostructures (confirmed by SAXS) and fabricated into defect-free, 3–20 μm-thick composite membranes on an asymmetric support. Productive and thorough membrane fabrication and testing was performed thanks in part to the guidance of Dr. Phuc Tien Nguyen in our group. These BCPs show distinct advantages over analogous physical blends of the parent homopolymers with respect to composite

membrane fabrication and CO₂/light gas transport properties. BCP nanostructure was found to have a significant effect on the CO₂ diffusion coefficient, and thus CO₂ permeability, to the effect of two orders of magnitude compared to amorphous BCP materials.

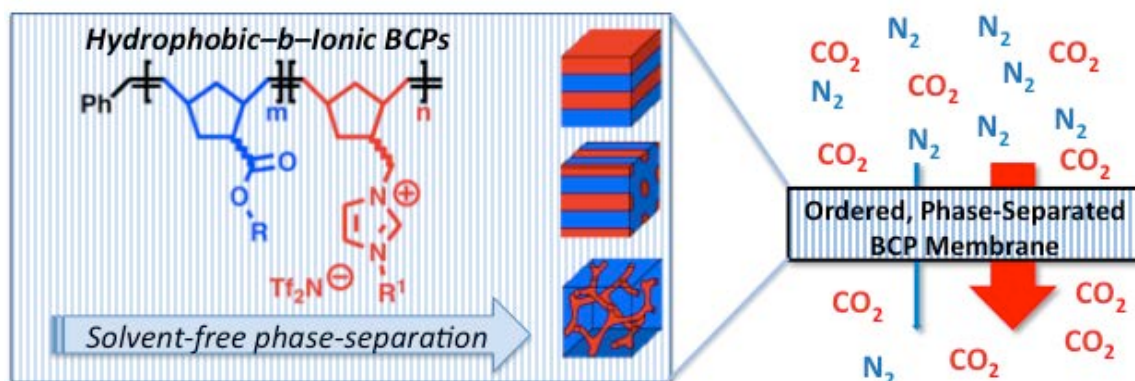


Figure 2.3. Research explored in Chapter 5: pictorial graphic representing the BCP chemical composition, solvent-free phase-separated morphologies, and experimentally tested gas separation application of alkyl hydrophobic-*b*-imidazolium ionic di-BCP membranes.

Chapter 6 explores unprecedented imidazolium-containing, hydrophobic-ionic-uncharged hydrophilic ABC triblock copolymer architectures synthesized via ROMP. The synthesis of three chemically immiscible norbornene monomers and their successful polymerization into varying-sequence tri-BCPs (e.g., ABC, CAB, ACB) was accomplished. SAXS nanostructure characterization revealed unique morphologies dependent on block sequence (Figure 2.4). Membrane fabrication and preliminary CO₂/light gas transport studies demonstrated the potential of this highly modular, new RTIL-based BCP system for CO₂/light gas separation applications.

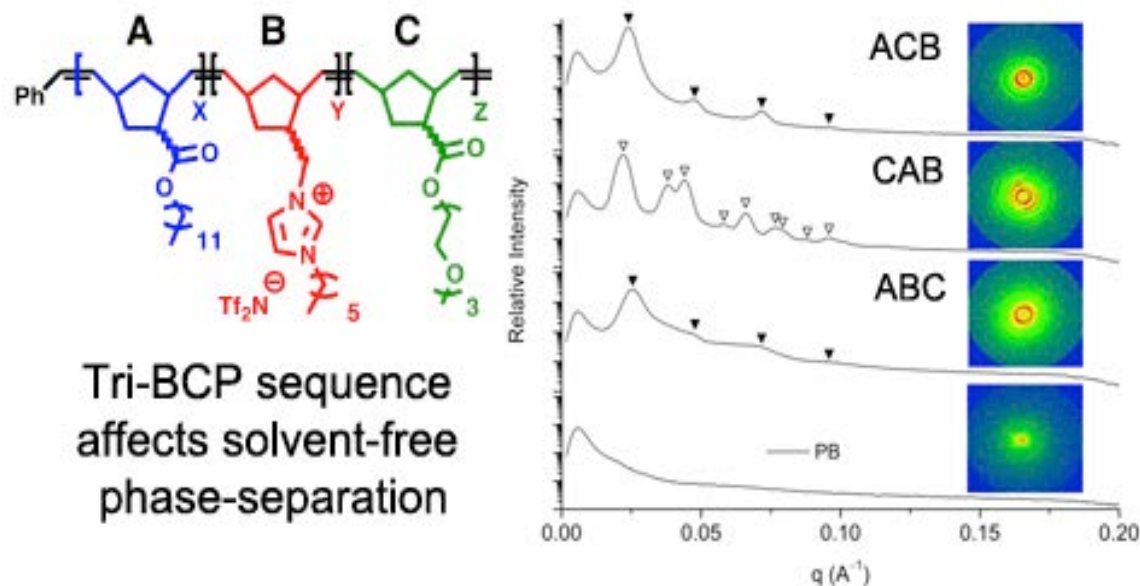


Figure 2.4. Research explored in Chapter 6: novel hydrophobic-ionic-uncharged hydrophilic ABC triblock copolymers synthesized via ROMP phase-separate into unique morphologies based on block sequence order.

Chapter 7 details possible future directions of the new RTIL-based BCP materials pioneered in this thesis work. The conclusion of this thesis project will hopefully catalyze the development of synthetically innovative and economical second-generation BCP materials that will continue to take advantage of BCP phase-separation for membrane transport applications. The improvement of CO₂/light gas selectivities through monomer design and non-polymerizable RTIL additives is outlined. Alternative polymerization techniques such as NMP are discussed as potential means of alleviating the use of expensive Grubbs polymerization catalysts and simplifying monomer synthesis.

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CHAPTER 3

Synthesis and Ordered Phase Separation of Imidazolium-based Alkyl-Ionic Diblock Copolymers Made via ROMP

(Manuscript published under the same title in *Macromolecules* **2011**, *44*, 5075–5078,

co-authored with Edwards, J. P.; Scalfani, V. F.; Bailey, T. S.; Gin, D. L.)

3.1 Abstract

A new type of imidazolium-based, alkyl-ionic block copolymer (BCP) has been synthesized that undergoes ordered phase separation in the melt state (25 °C) and exhibits surfactant behavior in several non-aqueous solvents. This new BCP platform is synthesized via the sequential, living ring-opening metathesis polymerization of a hydrophobic, non-charged alkylnorbornene monomer and a cationic imidazolium-norbornene ionic liquid (IL) monomer. This living polymerization behavior, which was experimentally confirmed for both monomers, provides convenient block molecular weight and length control. Small-angle X-ray scattering analysis on samples containing block ratios of 1:0.90; 1:0.66; and 1:0.42 (alkyl:imidazolium repeat units) (i.e., 25-*b*-23; 30-*b*-20; and 35-*b*-15 alkyl:imidazolium BCP lengths) revealed that all three diblock copolymer compositions exhibited diffraction patterns indicative of ordered microphase-separation in the solvent-free melt state, with all three forming highly periodic lamellar phases. Extensive control experiments indicated that the ordered phase-separation of

these new alkyl-imidazolium copolymers is due to block architecture, and that these copolymers behave very differently from a physical blend of the analogous homopolymers in solution and the melt state. To our knowledge, this system is one of the first documented examples of a poly(IL)-containing BCP that forms phase-separated, ordered nanostructures in the melt state.

3.2 Introduction

Polymerized ionic liquids (poly(IL)s) are a new class of polyelectrolytes that are valuable for a number of engineering applications.¹ These cationic polymers are typically made via the covalent polymerization of imidazolium-based organic salt monomers that are liquids at ≤ 100 °C.¹ Imidazolium-based poly(IL)s are particularly useful as functional materials because of their unique combination of physical properties, such as high intrinsic CO₂ gas solubility and ion conductivity.¹ Consequently, these poly(IL)s have been applied as new membrane materials for separating CO₂ from other light gases,² as solid-state ion conductors,³ as specialty dispersants/surfactants,⁴ and as platforms for electrochemical devices,⁵ to name just a few. Unfortunately, imidazolium-based poly(IL)s have only been synthesized in a limited number of polymer architectures so far. The majority of examples have been linear sidechain homopolymers (including sidechain liquid-crystalline (LC) derivatives).¹ Only a handful of examples of other homopolymer architectures (e.g., main-chain polymers;⁶ amorphous⁷ and ordered (LC)⁸ cross-linked networks) and copolymer architectures (e.g., random⁹ and blocky¹⁰) have been reported. Since differences in polymer architecture and composition often lead to different physical properties and morphologies, this represents an opportunity to explore and synthesize

new imidazolium poly(IL)s with potentially enhanced performance in the aforementioned applications.

Phase-separated block copolymers (BCPs) represent an interesting polymer architecture for exploration of new imidazolium-based poly(IL) materials, especially for gas and ionic transport applications. Prior work with conventional, non-ionic, phase-separated diblock copolymers have shown that orientation of the ordered phases can affect light gas transport.¹¹ If constructed with ionic blocks, copolymers with anisotropic ion-conducting domains may be produced, similar to the LC-sidechain poly(IL) electrolytes described in the literature.¹ An added benefit of BCPs is that their chemical composition can be altered to obtain different mechanical properties and morphologies and incorporate the ability to selectively transport a secondary solute, without affecting the basic properties of the individual domains. In contrast, composition changes in alternating and random copolymers often result in dilution or significant modification of the overall polymer properties. Prior work documenting the solution¹²⁻¹⁵ and melt-state¹⁶⁻¹⁸ assembly of BCPs containing an ionic component have primarily focused on more traditional polyelectrolyte systems, such as those containing acrylic acid,¹²⁻¹⁵ sulfonated styrene,¹⁶⁻¹⁸ or protonated lysine residues.^{13,14} However, the demonstrated formation of phase-separated ordered nanostructures in a solvent-free melt state by poly(IL)-containing BCPs is largely unprecedented. This is particularly true for the very few examples of imidazolium-containing BCPs reported in the literature so far.¹⁰

Herein, we present a new type of imidazolium-based, alkyl-ionic diblock copolymer (**1**) synthesized using living ring-opening metathesis polymerization (ROMP) that forms ordered nanostructures via phase-separation in the solvent-free melt state at 25

°C (Figure 3.1). Control of the relative composition and molecular weights of the hydrophobic alkyl and imidazolium blocks in these BCPs afforded initial compositions of **1** (i.e., samples **1A–C** with block ratios of 1:0.90 to 1:0.42 (alkyl:imidazolium repeat units); total polymer length: 50 repeat units) that all exhibit phase separation and form highly periodic lamellar phases. Furthermore, in solution, these alkyl-imidazolium diblock copolymers all show surfactant behavior in several non-aqueous solvents. Control experiments with physical blends of the two homopolymers do not show this ordered phase-separation in the melt state nor surfactant behavior in solution.

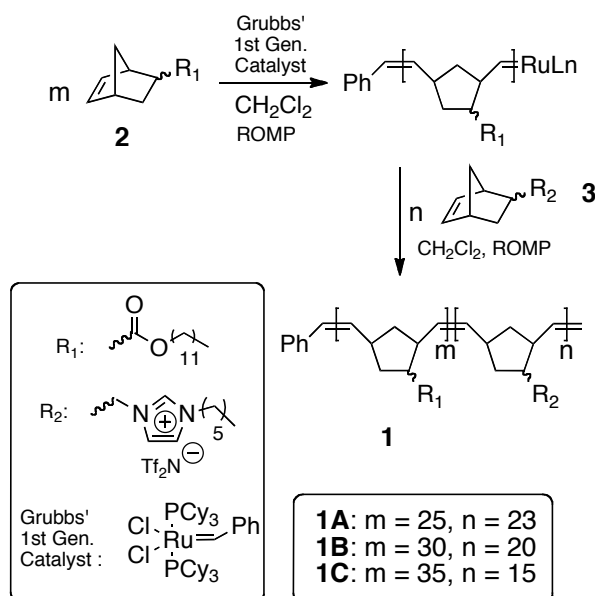


Figure 3.1. The synthesis and structures of alkyl-imidazolium diblock copolymers **1A–C** made via ROMP that show ordered phase-separation in the melt-state. The values of m and n depicted in **1A–C** are derived from the observed NMR block length ratios of the BCPs and the monomer-to-catalyst ratios as used in the living ROMP of **2** and **3**.

3.3 Results and Discussion

Imidazolium BCPs **1A–C** were synthesized via sequential living ROMP of hydrophobic alkyl monomer **2** and cationic imidazolium IL monomer **3** using Grubbs' 1st-generation olefin metathesis catalyst in CH_2Cl_2 solution as shown in Figure 1 (see the

Supporting Information for details).¹⁹ Monomers **2** and **3** were both synthesized from commercially available starting materials in relatively high yields (see Supporting Information). ROMP was the desired polymerization technique for making phase-separated alkyl-imidazolium BCPs due to its living and linear character, precise molecular weight control, low polydispersity (PDI), and tolerance of a diverse range of functional groups, including imidazolium units.²⁰ Norbornene derivatives are ideal monomers for ROMP because of their facile synthesis and modularity for functional group attachment, as well as their relatively high ring strain (27.2 kcal/mol, the relief of which drives the ROMP reaction).²¹ In our block copolymerizations, **2** was first polymerized to form an initial hydrophobic block, followed by living addition of **3** to form the subsequent ionic block. This order of copolymerization was used because the living polymerization of monomer **2** proceeds faster than the ionic monomer **3** (ca. 3–4 times faster at room temp.). By varying the molar ratios of **2** and **3** in the sequential ROMP reactions, alkyl-imidazolium BCPs with different alkyl vs. imidazolium block length ratios were successfully formed.

The ability to polymerize monomers **2** and **3** sequentially to afford BCPs **1A–C** with distinct block composition ratios and lengths was confirmed by ¹H NMR analysis on the polymers and experimental confirmation of living ROMP behavior for the two monomers. The alkyl:imidazolium repeat unit molar ratios for each BCP prepared were directly determined by integrating and comparing distinct ¹H NMR signals indicative of each block. The block lengths (Figure 3.1) were then calculated from the NMR-based repeat unit ratios and the copolymerization monomer-to-catalyst ratios, after confirming living ROMP homopolymerization character for each monomer (see the Supporting

Information for details).²² The M_n values for BCPs **1A–C** were then approximated by multiplying the calculated block lengths by the repeat unit molecular weights. The approximate M_n values for **1A**, **1B**, and **1C** are 20100, 20000, and 18800 g/mol, respectively (see Supporting Info). The absolute M_n values for the BCPs **1A–C** could not be determined directly using ^1H NMR endgroup analysis as in the case of the individual homopolymers because the imidazolium proton signals are shifted slightly in the BCPs and overlap with the five phenyl end-group protons. Unfortunately, conventional methods used to typically determine the molecular weight, molecular weight distribution, and block architecture of copolymers (e.g., GPC, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and dynamic light scattering) were attempted on **1A–C**, but all yielded inconclusive results. These difficulties were largely associated with the challenges inherent in the characterization of such highly charged macromolecules.¹ Since the block architecture of **1A–C** could not be determined using conventional polymer molecular weight characterization methods, a combination of alternative methods was used to verify a block architecture and to differentiate their behavior from that of a simple physical blend of homopolymers of **2** and **3**. These alternative methods included surfactant behavior and solubility analysis, diffusion-ordered spectroscopy (DOSY), differential scanning calorimetry (DSC), rheological measurements, and small-angle X-ray scattering (SAXS) studies.

With respect to surfactant and solubility behavior, it was found that copolymers **1A–C** all show surfactant behavior (i.e., extensive foaming when agitated) when mixed in hexanes, THF, CHCl_3 , EtOAc, MeOH, and CH_3CN , as would be expected from amphiphilic BCPs. Control experiments with physical blends of poly(**2**) and poly(**3**) of

the same length as in the copolymers do not show this behavior. Copolymers **1A–C** also show very different solubility behavior compared to physical blends of the two homopolymers, poly(**2**) and poly(**3**). For example, when mixed with hexanes (10 mg/mL) **1A** forms opaque heterogeneous suspensions, whereas the physical blend yields a brown solid within a clear solution on top (i.e., poly(**2**) is soluble in hexanes while poly(**3**) is insoluble) (Figure 3.2). Similar results were observed when comparing samples **1A–C** to their physical blends in ethyl acetate and acetonitrile, where poly(**3**) is soluble and poly(**2**) is insoluble.

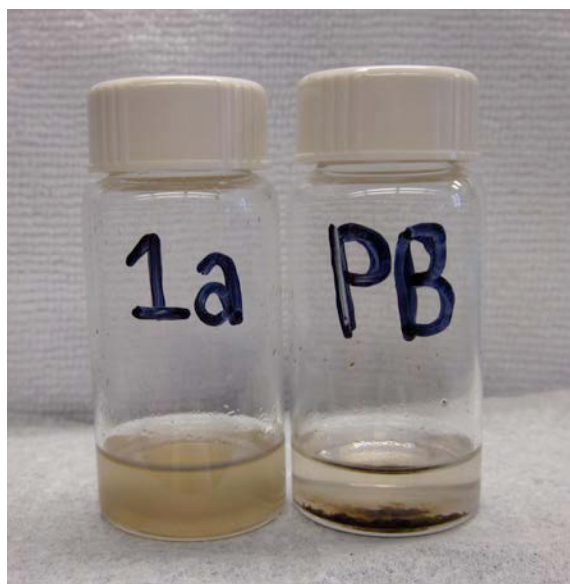


Figure 3.2. Different solubilities of copolymer **1A** and a physical blend (PB) of poly(**2**) + poly(**3**) in hexanes at room temperature.

In NMR DOSY studies, it was found that copolymer **1A** in CD_2Cl_2 (10 mg/mL) only showed one room-temperature diffusion coefficient ($3.68 \times 10^{-10} \text{ m}^2/\text{s}$) whereas a physical blend of the two homopolymers of comparable length exhibited two distinct diffusion coefficients ($8.8 \times 10^{-10} \text{ m}^2/\text{s}$ and $10.6 \times 10^{-10} \text{ m}^2/\text{s}$). **1A** consists of only one macromolecular species and is different than the physical blend of two distinct

macromolecular species. Collectively, the results of these comparative studies are consistent with a covalently-linked BCP architecture for **1A–C**, instead of a physical blend of the two homopolymers.

Further verification of the block architecture of copolymers **1A–C** and their collective ability to form phase-separated structures was established via a combination of DSC, dynamic rheology, and SAXS data collection. DSC studies on samples of **1A–C** revealed the presence of two broad but distinct thermal transitions near -28 and 7 °C, consistent with crystallization of the *n*-dodecyl sidechains and the vitrification of the imidazolium blocks, respectively (see Supporting Information). The thermal transitions at ca. 7 °C for BCPs **1B** and **1C** exhibit decreased intensity since they are associated with smaller imidazolium block regions. These DSC results do not directly verify connectivity between the polymer blocks but do establish their phase-separated state in the melt. Slight shifts in the transition temperatures of the BCPs of several degrees relative to those of the individual homopolymers are also consistent with restricted domain sizes and finite interfacial widths typical of ordered BCP morphologies.

While the combination of solubility, NMR DOSY, DSC, and rheology studies confirmed the connected block structure and phase-separated state of **1A–C**, SAXS analysis was used to establish the length scale (and thus block connectivity) and domain geometry of the ordered melts of these samples. SAXS analysis on each of the compositionally unique BCPs verified phase separation on the nanoscale and thus block connectivity with absolute certainty.

Representative 25 °C SAXS data are shown in Figure 3.3 for each of the alkyl-imidazolium BCPs synthesized, together with data collected for the physical blend (PB)

of the two homopolymers for comparison. At each of the block ratios synthesized, prominent principal diffraction peaks plus multiple higher order reflections are consistent with melt-state lamellar (L) phase morphologies.²³ Notably, the domain spacings ($d = 2\pi/q$) for the three BCP species are very similar (**1A**: 28.6 nm, **1B**: 29.4 nm, **1C**: 32.1 nm), although increasing slightly as the composition shifts towards greater fractions of the non-ionic block (poly(**2**)). Interestingly, the principal domain spacings ($d = 2\pi/q$) in the range of 30 nm are quite large compared to many traditional BCP systems, considering both the targeted degree of polymerization (~ 50) and approximate average molecular weights in the 20000 g/mol range. For comparison, a PS-PVP lamellar block copolymer of similar molecular weight would be expected to have a domain spacing around only 20 nm.²⁴ However, the manner in which mass is distributed along these two BCP chains is quite different, with the PS-PVP chain described above having a contour length about 60% longer than **1A–C**. Thus, mass (and volume) is concentrated more densely along the length of **1A–C** (repeat unit molecular weights of monomer **2** and **3** of 307 and 540 g/mol, respectively), resulting in stiffer, “fatter” chains that favor larger domain spacings. Notably, the mass fraction of the imidazolium block in BCPs **1A–C** ranges from 0.43 (**1C**) to 0.54 (**1B**) to 0.62 (**1A**) which, while difficult to accurately correlate to volume fractions without known homopolymer densities, appears highly consistent with the expected location of the L phase window exhibited by other classic BCP systems.²³

The variations in higher-order diffraction peak intensities for the three samples is also consistent with changes in composition, as the relative thicknesses of the alkyl and ionic domains making up the lamellar period directly affect the superposition product of

the form (particle) and structure (lattice) factor scattering contributions. For example, the notable absence of the reflections at $q/q^* = \sqrt{4}$ and $\sqrt{16}$ in sample **1B** suggests the 1:0.66 repeat unit ratio is approaching a nearly symmetric volume fraction of 0.5, in which the minima in the form factor scattering cancels out the diffraction intensity associated with the lamellar periodicity for even-order diffraction maxima.²⁵

Dynamic rheological measurements on BCPs **1A–C** also revealed behavior prototypical of traditional lamellar BCP melts, exhibiting elastic and loss moduli of similar magnitudes, with a tendency to decrease together monotonically with increasing temperature (see Supporting Information).²³ None of the systems revealed any order-order transitions below 150 °C. Importantly, a physical blend of the two homopolymers (poly(**2**) + poly(**3**)) does not exhibit any observable scattering or diffraction, confirming the necessity of the covalent bond between the blocks for microphase separation.

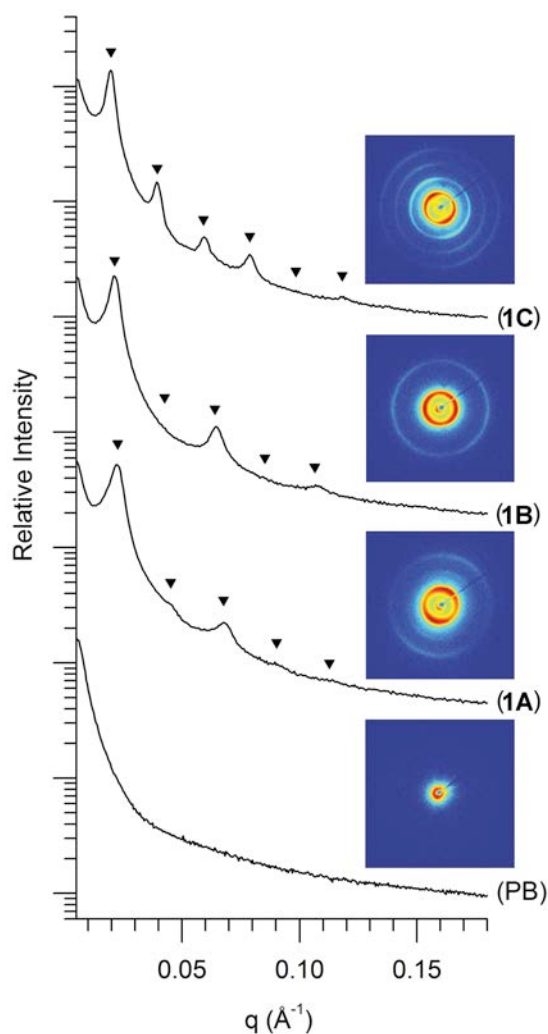


Figure 3.3. Representative SAXS data for imidazolium BCPs containing block ratios of 1: 0.90 (**1A**), 1:0.66 (**1B**), and 1:0.42 (**1C**), with the corresponding 2D detector images (inset). Inverted triangles represent the location of the allowed reflections for the lamellar morphology, calculated based on the position of the primary scattering wave vector q_{100} : (L) q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc. The physical blend (PB) of poly(**2**) and poly(**3**) shows no observable diffraction peaks, in contrast to the BCPs.

3.4 Summary

In summary, a new type of imidazolium-based, alkyl-ionic BCP has been synthesized that undergoes ordered phase separation in the melt state and exhibits surfactant behavior in non-aqueous solvent. This new BCP platform is based on the

sequential ROMP of alkyl- and imidazolium IL-norbornene monomers, which provides convenient block ratio and length control. Extensive control experiments indicated that the ordered phase separation of these new alkyl-imidazolium copolymers is due to a block architecture, and that these copolymers behave very differently from a physical blend of the analogous homopolymers in solution and the melt state. To our knowledge, this system is one of the first examples of a poly(IL)-containing BCP that forms phase-separated, ordered nanostructures in the melt state. We are in the process of exploring a wider range of block length ratios for this BCP system in order to map out its full phase behavior. We are also currently extending this project to new monomer systems and ROMP catalysts, testing the performance of these nanostructured imidazolium BCPs as gas separation membranes, and exploring the synthesis of imidazolium triblock copolymers.

3.5 Acknowledgments

Primary financial support for the work performed at CU Boulder was provided by the Defense Threat Reduction Agency (grant: HDTRA1-08-1-0028) and the Advanced Research Projects Agency – Energy (grant: DE-AR0000098). E.E.F. thanks M. Moran, Dr. R. K. Shoemaker, and B. Norris for their extensive help with the DSC, DOSY NMR, and attempted GPC work. J.P.E. thanks the Undergraduate Research Opportunities Program at CU Boulder for support of his work in this effort. Primary financial support for the work performed at CSU was provided by the National Science Foundation (grant: DMR-0645781). SAXS studies were performed at CSU using a regional instrument supported by National Science Foundation MRI Program (grant: DMR-0821799).

3.6 Supporting Information

3.6.1 Materials and General Procedures

1-Bromohexane, 1-dodecanol, 5-norbornene-2-carboxylic acid, ethyl vinyl ether, and oxalyl dichloride were purchased from the Sigma-Aldrich Co., and used as received. Dicyclopentadiene and 1-vinylimidazole were purchased from TCI America, and used as received. Lithium bis(trifluoromethylsulfonyl)amide (LiTf_2N) 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 N_2 -pressurized activated alumina columns, and de-gassed. Additionally, the CH_2Cl_2 used as the solvent in ring-opening metathesis polymerization (ROMP) reactions was purified by re-filtering over activated alumina prior to de-gassing. The H_2O used for synthesis was purified and de-ionized, with resistivity greater than $12 \text{ M}\Omega \text{ cm}^1$. All chemical syntheses were carried out in a dry argon atmosphere using standard Schlenk line techniques, unless otherwise noted. Silica gel purification was performed using 230–400 mesh, normal-phase silica gel purchased from Sorbent Technologies.

3.6.2 Instrumentation

^1H and ^{13}C 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. Fourier-transform infrared spectroscopy (FT-IR) measurements were performed using a Matteson Satellite series spectrometer (neat, thin film samples on Ge crystals). HRMS (ES) analysis was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado, Boulder. Differential

scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC823[°] and a Julabo FT100 Intracooler. Gel permeation chromatography (GPC) spectra were collected 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). Molecular weight data obtained on this GPC system were referenced to polystyrene molecular weight standards. NMR diffusion ordered spectroscopy (DOSY) experiments were performed using a Varian Inova-400 NMR spectrometer. Small-angle X-ray scattering (SAXS) data was collected using a Rigaku S-Max 3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_α), Confocal Max-Flux Optic, Gabriel multiwire area detector, and a Linkam thermal stage. Polymer samples were sandwiched between Kapton discs. Exposure times for samples were typically on the order of 600–1200 s. Rheological experiments were run using a TA Instruments Advanced Rheometric Expansion System (ARES) rheometer. Samples were roughly formed as discs and then positioned between two parallel plates (8 mm diameter). The gap was reduced and adjusted to ensure even distribution of the sample. Gaps were ~0.5 mm. Dynamic temperature ramp tests were performed while heating and cooling at 1 °C min⁻¹ at an angular frequency of 1 rad s⁻¹ and a strain of 1% (linear viscoelastic regime).

3.6.3 Synthesis

3.6.3.1 Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (endo:exo 80:20) (2)

5-Norbornene-2-carboxylic acid (5.01 g, 0.0366 mol, predominantly endo) and DMF (2 mL) were stirred in CH₂Cl₂ (100 mL). Oxalyl dichloride (6.9 g, 0.055 mol) was added dropwise to the mixture at 0 °C, and the reaction mixture was stirred at room temperature for 18 h. The reaction mixture was then concentrated in vacuo (35 °C, 100 mtorr) before the addition of THF (70 mL), triethylamine (5 mL) and 1-dodecanol (6.6803 g, 0.035850 mol) at room temperature. After stirring for 24 h, the reaction mixture was then dried with anhydrous MgSO₄, filtered, and concentrated in vacuo (20 °C, 100 mtorr). The crude product was purified by silica gel column chromatography using a 75/25 hexanes/ethyl acetate (v/v) solution as the eluent. The final product was concentrated from the eluate in vacuo as a yellow oil (8.645 g, 78%). ¹H NMR (300 MHz, CDCl₃): δ 6.36–5.76 (m, 2H), 4.26–3.81 (m, 2H), 3.40–2.12 (m, 3H), 2.10–1.77 (m, 1H), 1.77–0.70 (m, 26H). ¹³C NMR (75 MHz, CDCl₃): δ 176.3, 174.8, 138.0, 137.7, 135.8, 132.4, 64.6, 64.3, 49.6, 46.6, 46.4, 45.7, 43.4, 43.2, 42.5, 41.6, 31.9, 30.3, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 28.7, 25.9, 22.7, 14.1. IR (neat): 3064.1, 2952.9, 2929.6, 2854.4, 1735.6, 1467.6, 1384.5, 1334.9, 1272.2, 1184.8 cm⁻¹. HRMS (ES) calcd. for C₂₀H₃₄O₂Na (M Na⁺): 329.2451; observed: 329.2440.

3.6.3.2 1-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1*H*-imidazole (endo:exo 80:20) (4)

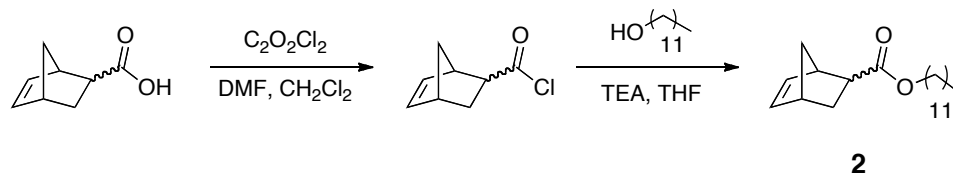
1-Allylimidazole (12.4 g, 0.115 mol) and dicyclopentadiene (3.79 g, 0.0287 mol) were stirred neat at 172 °C for 24 h. Excess 1-vinylimidazole was removed from the reaction mixture via vacuum distillation (100 mtorr, 40 °C). The remaining distillant was loaded onto a silica gel separation column, rinsed with hexanes (400 mL), and eluted with

10:4:0.8 (v/v/v) mixture of acetone/CH₂Cl₂/MeOH. After removal of the solvent in vacuo, pure **4** was isolated as a brown oil (8.47 g, 85%). ¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, *J* = 15.5, 1H), 7.17–6.97 (m, 1H), 6.92 (dt, *J* = 5.4, 1.2, 1H), 6.35–5.93 (m, 2H), 3.78 (dddd, *J* = 33.8, 22.9, 13.8, 8.1, 2H), 2.99–2.20 (m, 3H), 1.89 (ddd, *J* = 11.8, 9.2, 3.8, 1H), 1.59–1.07 (m, 2H), 0.63 (ddd, *J* = 11.8, 4.4, 2.6, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 138.5, 137.2, 137.1, 137.0, 136.0, 131.6, 129.4, 129.3, 118.9, 118.8, 52.2, 50.9, 49.5, 44.8, 44.1, 44.1, 42.4, 41.8, 40.4, 40.6, 31.0, 30.1. IR (neat): 3131.6, 3105.4, 3057.4, 2960.0, 2940.4, 2868.5, 1648.2, 1568.8, 1505.4, 1448.4, 1394.1 cm⁻¹ HRMS (ES) calcd. for C₁₁H₁₄N₂Na (M Na⁺): 197.1049; observed: 197.1053.

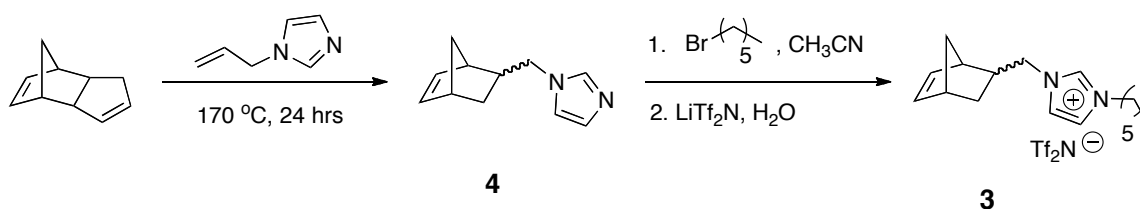
3.6.3.3 3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3*H*-imidazolium bis(trifluoromethylsulfonyl)amide (endo:exo 80:20) (3)

Compound **4** (2.00 g, 0.0115 mol) and 1-bromohexane (3.79 g, 0.0230 mol) were stirred in acetonitrile at reflux for 18 h. Upon cooling, the reaction mixture was concentrated to form a yellow viscous oil and washed with Et₂O (3 x 100 mL). The resulting oil was then dissolved in H₂O (100 mL), LiTf₂N (3.63 g, 0.0127 mol) was added, and the mixture stirred at room temperature for 12 h. A yellow oil was then extracted from this aqueous mixture with CH₂Cl₂ (3 x 50 mL). The CH₂Cl₂ layer was then washed with H₂O (3 x 150 mL), dried with anhydrous MgSO₄, filtered, and concentrated to give monomer **3** as a yellow oil (yield: 5.33 g, 83%). ¹H NMR (300 MHz, CDCl₃): δ 8.83 (d, *J* = 23.9, 1H), 7.36 (ddd, *J* = 7.2, 4.0, 1.9, 2H), 6.47–5.87 (m, 2H), 4.46–3.73 (m, 4H), 3.07–2.42 (m, 3H), 2.09–1.72 (m, 3H), 1.61–0.52 (m, 11H). ¹³C NMR (75 MHz, CDCl₃): δ 139.3, 137.5, 135.6, 135.4, 135.2, 130.8, 126.1, 122.4, 122.4,

122.3, 122.2, 121.8, 117.6, 113.3, 54.8, 54.0, 50.1, 49.5, 44.9, 44.1, 42.4, 41.8, 39.8, 30.9, 30.6, 30.1, 29.8, 25.7, 22.3, 13.8. IR (neat): 3147.47, 3114.20, 3089.90, 2960.89, 2937.45, 2872.85, 1563.32, 1456.09, 1348.19, 1331.51, 1225.74, 1183.60, 1135.87, 1054.68 cm^{-1} . HRMS (ES) calcd. for $\text{C}_{19}\text{H}_{27}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$ (M^+ M^+ Tf_2N^-): 798.3516; observed: 798.3498.



Scheme 3.S1. Synthesis scheme for hydrophobic alkyl-functionalized norbonene monomer **2**.

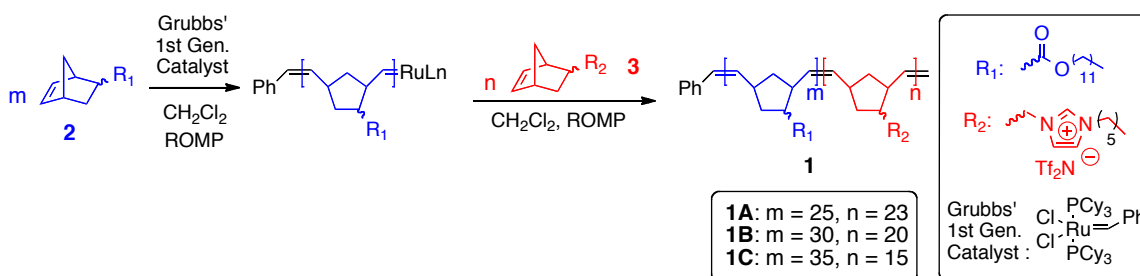


Scheme 3.S2. Synthesis scheme for imidazolium-functionalized norbonene monomer **3**.

3.6.4 General Procedure for ROMP of Monomers **2** and **3** to Form Diblock Copolymers

A flame-dried Schlenk flask was charged with the desired amount of Grubbs 1st-generation catalyst and a stirbar under argon. The appropriate amount of CH_2Cl_2 was then added to the Schlenk flask to form a catalyst solution with the desired concentration. The appropriate amount of the first monomer (**2**) was then added to the catalyst solution from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe under argon atmosphere. Upon consumption of all of the monomer (as verified by ^1H NMR analysis) to form the

first copolymer block, the second monomer (**3**) was added from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe. Upon complete consumption of monomer **3** (as verified by ^1H NMR analysis), the ROMP diblock copolymerization mixture was quenched with excess of ethyl vinyl ether. The resulting diblock copolymer was then isolated by removal of the solvent in vacuo. NMR analysis of polymers **1A–C** confirmed the absence of any residual monomers.



Scheme 3.S3. ROMP polymerization of diblock copolymers **1A**, **1B**, and **1C**.

3.6.4.1 Procedure for Sequential ROMP of Monomers **2** and **3** to Form Diblock Copolymer **1A**

Under argon atmosphere, Grubbs' 1st-generation catalyst (16.4 mg, 0.0199 mmol) was dissolved in dry, degassed CH_2Cl_2 (0.75 mL). Monomer **2** (7.65 g, 24.9 mmol) was diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, 0.49 mL (0.49 mmol) was added to the catalyst solution, and the reaction mixture stirred at room temperature until the polymerization of **2** was complete (3 h). Monomer **3** (13.5 g, 25.1 mmol) was diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, monomer **3** (0.49 mL, 0.49 mmol) was then added to the living ROMP polymerization mixture containing polymerized **2**, and the reaction stirred at room temperature for 12 h. The ROMP copolymerization mixture was

then quenched by addition of excess ethyl vinyl ether (1 mL). The resulting diblock copolymer **1A** was isolated by removal of the solvent and other volatile compounds in vacuo at ambient temperature for 24 h (0.435 g, 99%). ^1H NMR (300 MHz, CDCl_3) δ 8.50–8.75 (br s, imidazolium C2), 7.47–7.27 (br s, imidazolium C4 and C5), 5.27–5.52 (b, $-\text{C}(\text{H})=\text{C}(\text{H})-$), 3.75–4.45 (b, $-\text{COO}-\text{CH}_2-$, $-\text{C}(\text{H})_2-\text{N}-\text{CH}-\text{N}-\text{C}(\text{H})_2-(\text{CH}_2)_4\text{CH}_3$), 2.35–3.15 (br m, $-\text{imidazolium}-(\text{CH}_2)_5-\text{CH}_3$), 1.50–2.25 (b, $-\text{COO}-(\text{CH}_2)_{11}-\text{CH}_3$), 0.95–1.45 (br m, $-\text{COO}-\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3$), 0.72–0.90 (br m, $-\text{imidazolium}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3) δ 121.9, 117.7, 76.6, 31.9, 30.8, 29.5, 28.7, 26.1, 25.6, 22.7, 22.2, 14.1, 13.7. Block repeat unit molar ratio = 1:0.90 (alkyl:imidazolium); block length composition = 25-*b*-23; estimated $M_n = 20,100 \text{ g mol}^{-1}$ (calculated based on ^1H NMR repeat unit integrals, monomer-to-catalyst ratio for a living polymerization, and repeat unit molecular weights. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

3.6.4.2 Procedure for Sequential ROMP of Monomers **2** and **3** to Form Diblock Copolymer **1B**:

Under argon atmosphere, Grubbs' 1st-generation catalyst (22.3 mg, 0.0271 mmol) was dissolved in dry, gas-free CH_2Cl_2 (2.0 mL). Monomer **2** (3.07 g, 10.0 mmol) was diluted to a total volume of 10 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, monomer **2** (0.81 mL, 0.81 mmol) was added to the catalyst solution, and the reaction was mixture stirred at room temperature until the polymerization of **2** was complete as determined by ^1H NMR analysis (5 h). Monomer **3** (5.38 g, 9.98 mmol) was then diluted to a total volume of 10 mL with dry, gas-free CH_2Cl_2 . From this monomer

solution, monomer **3** (0.54 mL, 0.54 mmol) was then added to the living ROMP reaction mixture containing polymerized **2**, and the reaction mixture stirred at room temperature for 12 h. The ROMP copolymerization reaction was then quenched by adding ethyl vinyl ether (1 mL). The resulting diblock copolymer **1B** was isolated by removal of the solvent and other volatile compounds in vacuo at ambient temperature for 24 h (0.561 g, 99%). ^1H NMR (300 MHz, CDCl_3) δ 8.50–8.75 (br s, imidazolium C2), 7.47–7.27 (br s, imidazolium C4 and C5), 5.27–5.52 (b, $-\text{C}(\text{H})=\text{C}(\text{H})-$), 3.75–4.45 (b, $-\text{COO}-\text{CH}_2-$, $-\text{C}(\text{H})_2-\text{N}-\text{CH}-\text{N}-\text{C}(\text{H})_2-(\text{CH}_2)_4\text{CH}_3$), 2.35–3.15 (br m, $-\text{imidazolium}-(\text{CH}_2)_5-\text{CH}_3$), 1.50–2.25 (b, $-\text{COO}-(\text{CH}_2)_{11}-\text{CH}_3$), 0.95–1.45 (br m, $-\text{COO}-\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3$), 0.72–0.90 (br m, $-\text{imidazolium}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3) δ 121.9, 117.7, 76.6, 31.9, 30.8, 29.5, 28.7, 26.1, 25.6, 22.7, 22.2, 14.1, 13.7. Block repeat unit molar ratio = 1:0.66 (alkyl:imidazolium); block length composition = 30-*b*-20; estimated M_n = 20,000 g mol^{-1} (calculated based on ^1H NMR repeat unit integrals, monomer-to-catalyst ratio for a living polymerization, and repeat unit molecular weights. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

3.6.4.3 Procedure for Sequential ROMP of Monomers **2** and **3** to Form Diblock Copolymer **1C**:

Under argon atmosphere, Grubbs' 1st-generation catalyst (18.6 mg, 0.0226 mmol) was dissolved in dry, degassed CH_2Cl_2 (2.0 mL). Monomer **2** (3.07 g, 10.0 mmol) was diluted to a total volume of 10 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, monomer **2** (0.79 mL, 0.79 mmol) was added to the catalyst solution, and the

reaction mixture was stirred at room temperature until the polymerization of **2** was complete as determined by ^1H NMR analysis (5 h). Monomer **3** (5.38 g, 9.98 mmol) was then diluted to a total volume of 10 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, monomer **3** (0.34 mL, 0.34 mmol) was added to the living ROMP polymerization mixture containing polymerized **2**, and the reaction stirred at room temperature until the polymerization of **3** was complete by ^1H NMR analysis (12 h). The ROMP copolymerization reaction was then quenched by addition of ethyl vinyl ether (1 mL). The resulting diblock copolymer **1C** was isolated by removal of the solvent and other volatile compounds in vacuo at ambient temperature for 24 h (0.431 g, 98%). ^1H NMR (300 MHz, CDCl_3) δ 8.50–8.75 (br s, imidazolium C2), 7.47–7.27 (br s, imidazolium C4 and C5), 5.27–5.52 (b, $-\text{C}(\text{H})=\text{C}(\text{H})-$), 3.75–4.45 (b, $-\text{COO}-\text{CH}_2-$, $-\text{C}(\text{H})_2-\text{N}-\text{CH}-\text{N}-\text{C}(\text{H})_2-(\text{CH}_2)_4\text{CH}_3$), 2.35–3.15 (br m, $-\text{imidazolium}-(\text{CH}_2)_5-\text{CH}_3$), 1.50–2.25 (b, $-\text{COO}-(\text{CH}_2)_{11}-\text{CH}_3$), 0.95–1.45 (br m, $-\text{COO}-\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3$), 0.72–0.90 (br m, $-\text{imidazolium}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3) δ 121.9, 117.7, 76.6, 31.9, 30.8, 29.5, 28.7, 26.1, 25.6, 22.7, 22.2, 14.1, 13.7. Block repeat unit length molar ratio = 1:0.42; block length composition = 35-*b*-15; estimated $M_n = 18,800 \text{ g mol}^{-1}$ (calculated based ^1H NMR repeat unit integrals, monomer-to-catalyst ratio for a living polymerization, and repeat unit molecular weight. See following sections for details on how the copolymer block composition, block lengths, and M_n were determined).

Note on the use of solvents for NMR analysis of the BCPs. Even though the BCPs show foaming behavior in CDCl_3 when agitated, we were able to use CDCl_3 as NMR solvent because we used lower BCP loading levels, minimized the amount of solution agitation,

and allowed the CDCl₃ solutions to settle and reach a non-foaming steady state before NMR analysis.

3.6.5 Determination of BCP Composition and Molecular Weights.

Conventional methods used to experimentally and directly determine the molecular weights values of **1A–C** (e.g., GPC, NMR endgroup analysis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and dynamic light scattering) were attempted, but all yielded inconclusive results. These difficulties were largely associated with the very different physical properties of these highly charged macromolecules (e.g., solubility) compared to typical non-charged polymers.^{26d} Consequently, the block composition ratios, overall lengths, and estimated M_n values of BCPs **1A–C** were determined via a combination of ¹H NMR-based repeat unit/block length composition analysis and confirmation of living polymerization behavior with predictable molecular weight control for both monomers, as described below:

3.6.5.1 Determination of BCP Alkyl:Imidazolium Block Composition Ratios via ¹H NMR Analysis.

Block composition ratios were determined to compare the block length of the hydrophobic (alkyl) block to the block length of the imidazolium (ionic) block via ¹H NMR analysis. The signals for the unstrained backbone protons for both blocks overlap to create a broad peak between 5.00–5.75 ppm (signal C in Figures 3.S1–3.S3). The signals for the protons adjacent to the ester linker of the hydrophobic block (made by ROMP of monomer **2**) and the protons adjacent to the imidazolium ring of the ionic

block (made by ROMP of monomer **3**) appear as a broad peak between 3.75–4.50 ppm (signal D in Figures 3.S1–3.S3). There are 2 unstrained backbone protons per repeat unit for the hydrophobic block (m) and 2 unstrained backbone protons per repeat unit for the ionic block (n) (see Equation 3.S1). There are 2 methylene protons adjacent to the ester linker per repeat unit for the hydrophobic block (m) and 4 methylene protons adjacent to the imidazolium ring per repeat unit for the ionic block (n) (see Equation 3.S2).

$$2\mathbf{m} + 2\mathbf{n} = \mathbf{C}_{1\text{H NMR Integration}} \quad (\text{Eq. 3.S1})$$

$$2\mathbf{m} + 4\mathbf{n} = \mathbf{D}_{1\text{H NMR Integration}} \quad (\text{Eq. 3.S2})$$

Using the two equations to solve for the two unknowns, m and n, the alkyl:imidazolium block composition ratios (m, n) can be quantified for each BCP sample **1A**, **1B**, and **1C**, as shown below:

Block Composition Ratio for BCP **1A** (Figure 3.S1):

$$2m + 2n = 4.07$$

$$2m + 4n = 6.00$$

$$m = 1.0, n = 0.90$$

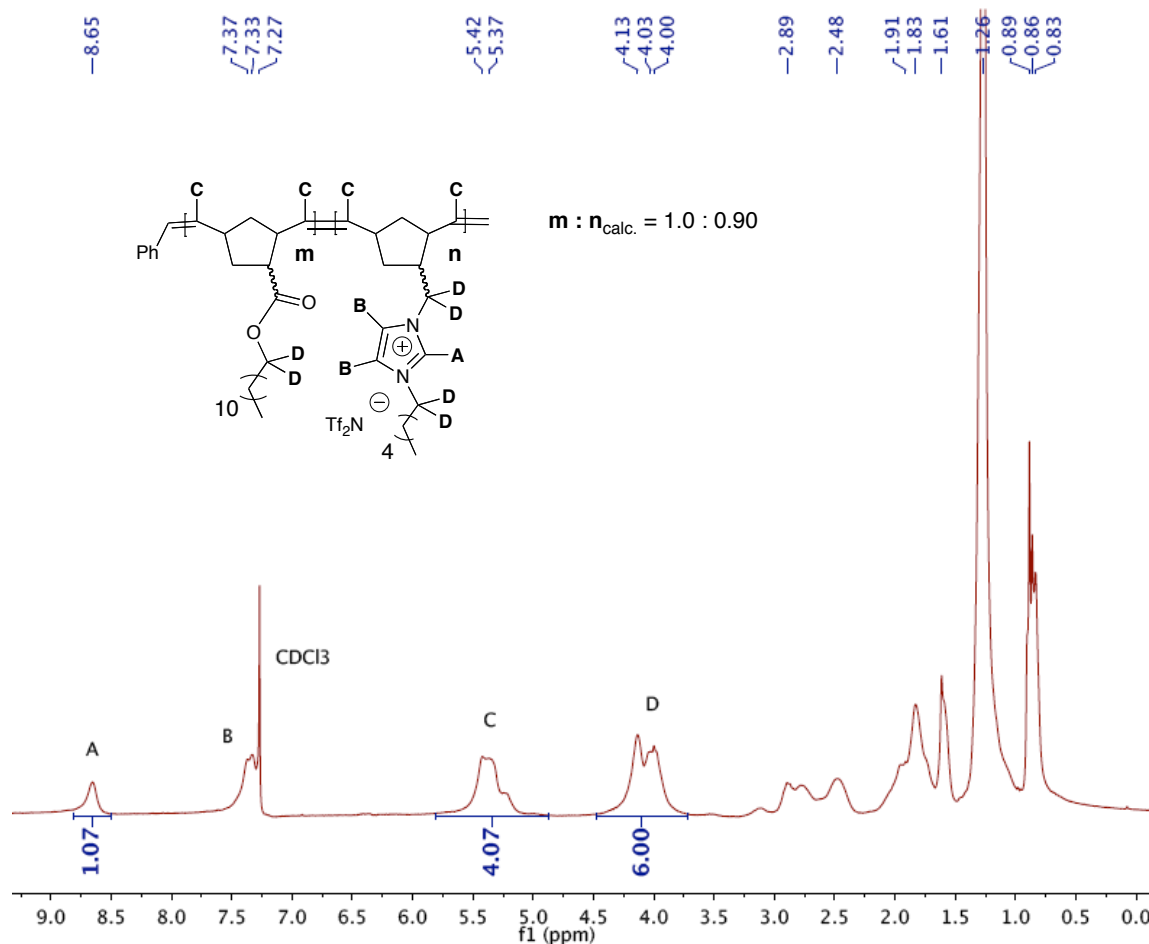


Figure 3.S1. An example ^1H NMR spectrum of BCP **1A**, and the ^1H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in **1A**.

Block Composition Ratio for BCP **1B** (Figure 3.S2):

$$2m + 2n = 4.29$$

$$2m + 4n = 6.00$$

$$m = 1.0, n = 0.66$$

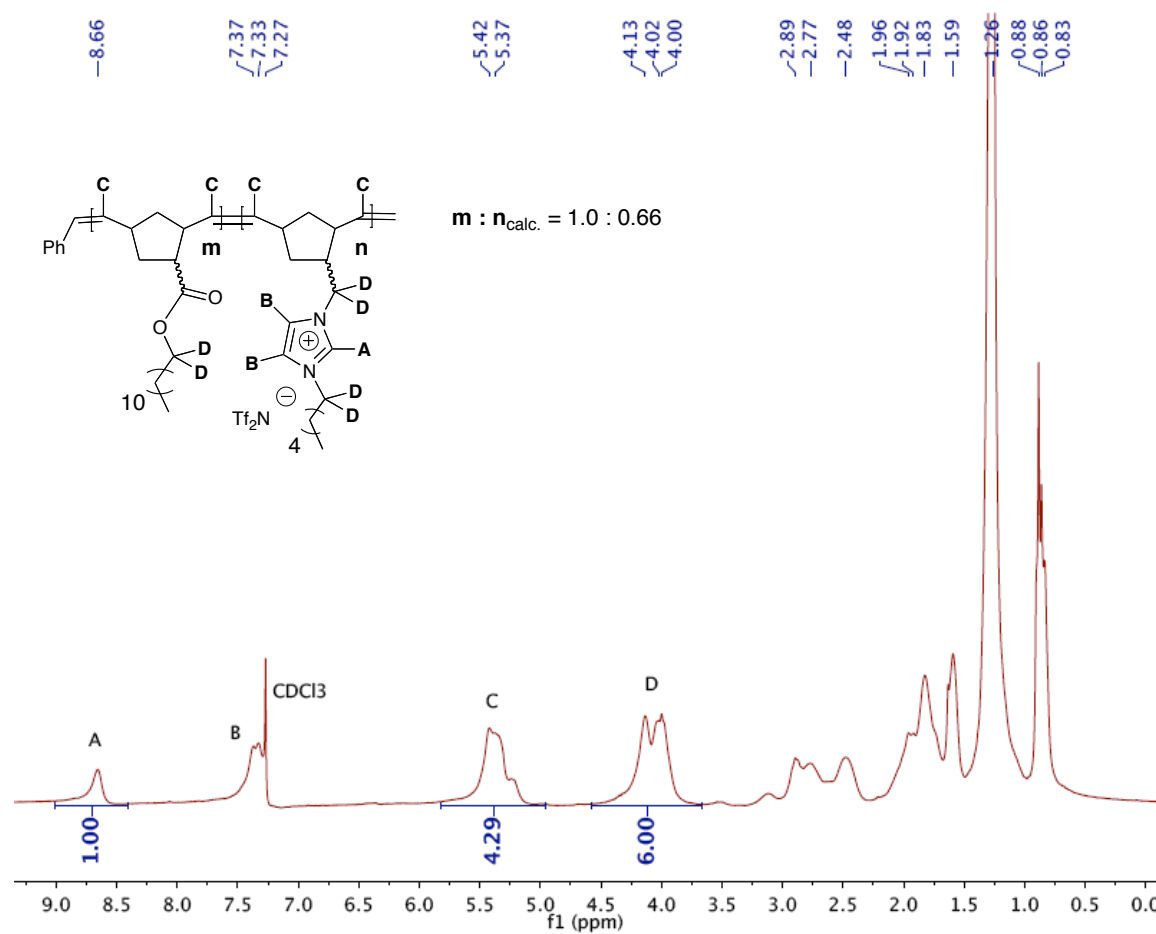


Figure 3.S2. An example ¹H NMR spectrum of BCP **1B**, and the ¹H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in **1B**.

Block Composition Ratio for BCP **1C** (Figure 3.S3):

$$2m + 2n = 4.63$$

$$2m + 4n = 6.00$$

$$m = 1.0, n = 0.42$$

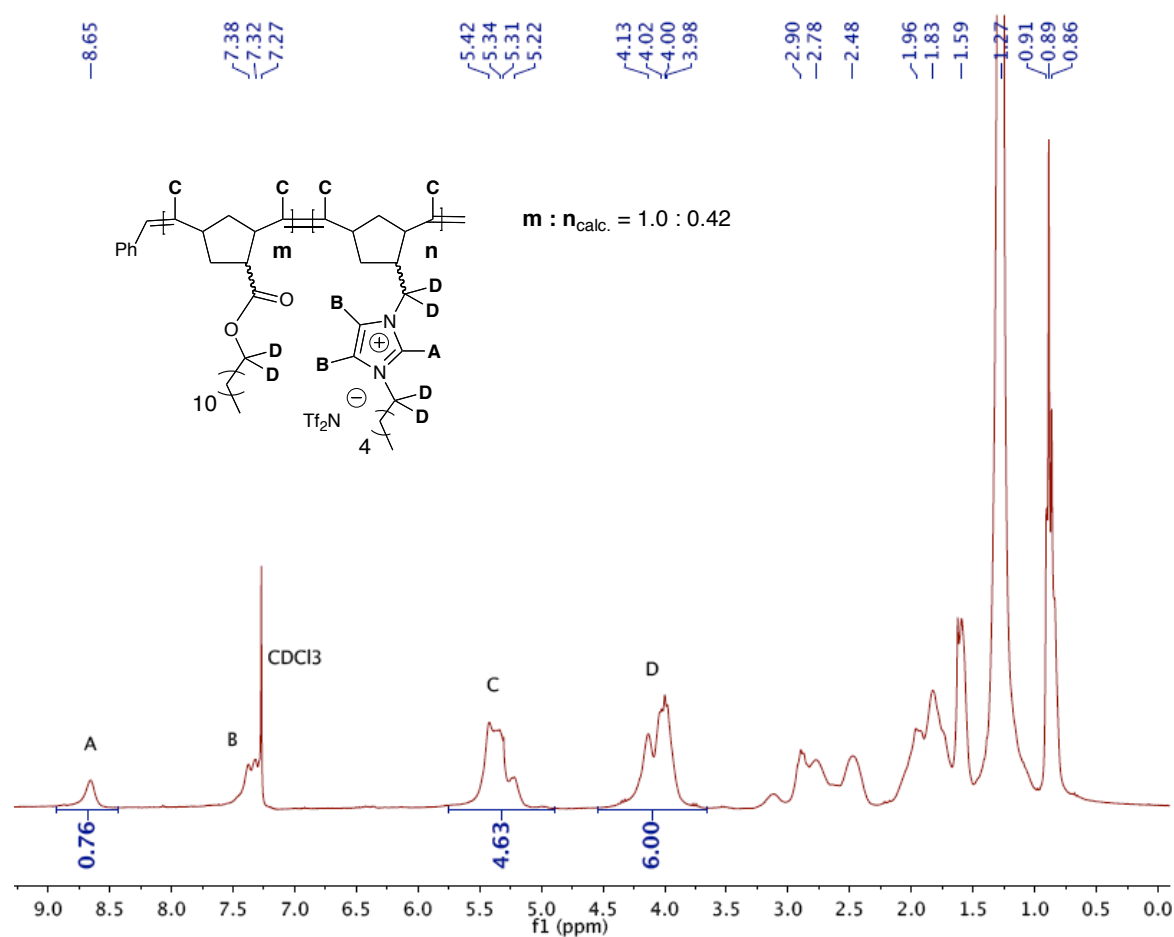
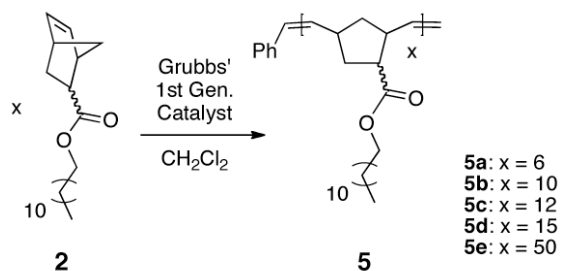


Figure 3.S3. An example ^1H NMR spectrum of BCP **1C**, and the ^1H NMR peak assignments used for calculating the alkyl:imidazolium block composition (i.e., repeat unit) ratio in **1C**.

3.6.5.2 Verification of Living Character with Molecular Weight Control

Systematic ROMP homopolymerizations of hydrophobic monomer **2** and imidazolium monomer **3** were used to help verify the linear molecular weight control and low PDI nature of these polymerization systems, in order to prepare the compositions and lengths of BCPs **1A–C**.

ROMP experiments with monomer **2** showed that increasing the monomer-to-catalyst ratio increases the (absolute) molecular weight of poly(**2**) samples in a linear fashion by ^1H NMR endgroup analysis, indicative of a living polymerization with predictable molecular weight control. As can be seen in Figure 3.S4, five samples of poly(**2**) (**5a–e**) were synthesized by polymerizing **2** with varying mole ratios of Grubbs' 1st-generation catalyst (Scheme 3.S4). The absolute number-average molecular weight (M_n) values of these model homopolymers were directly determined with ^1H NMR spectroscopy by integrating the distinct unstrained alkene backbone protons in the repeat units and comparing to those of the five phenyl endgroup protons from the catalyst initiation step. A linear relationship was observed between monomer-to-catalyst molar ratio used in the ROMP reactions and the absolute M_n values of the poly(**2**) samples formed (Figure 3.S4).



Scheme 3.S4. Hydrophobic poly(**2**) oligomers used for absolute M_n determination via ^1H NMR endgroup analysis in order to confirm living polymerization behavior.

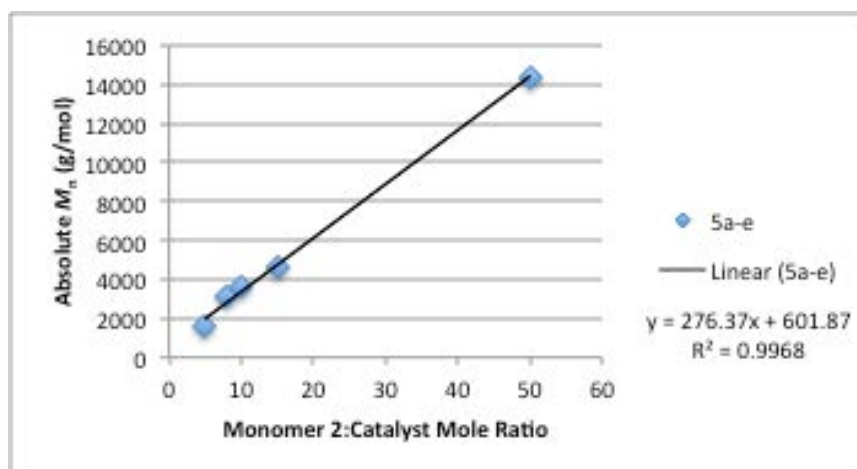


Figure 3.S4. Linear relationship between monomer-to-catalyst molar ratio used and absolute M_n from ^1H NMR endgroup analysis for various poly(**2**) oligomers. Note: this NMR-based polymer molecular weight data does not provide PDI information.

In order to help verify the living character of the monomer **2** ROMP system with Grubbs' 1st generation catalyst, GPC analysis to obtain PDI information (THF solvent, polystyrene standards) of poly(**2**) prior to the addition of monomer **3** during sequential polymerizations yielded low PDI values (1.15–1.17) (Table 3.S1). This is also consistent with living polymerization behavior.

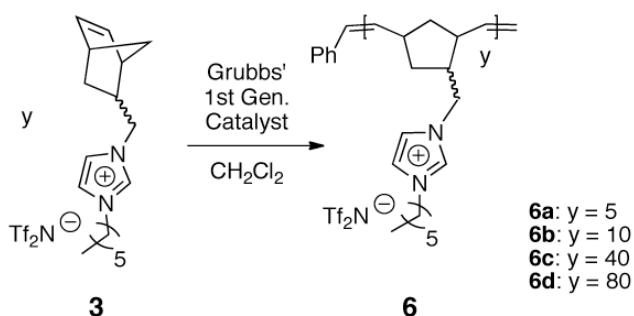
Table 3.S1. Relative M_n and M_w GPC Data (vs. Polystyrene Standards) and PDI Values For Confirming The Living ROMP of Monomer **2**.

Poly(2) ROMP Experiment	Mon 2 :Cat Ratio	Relative M_n vs. PS stds ^a (g/mol)	Relative M_w vs. PS stds ^a (g/mol)	PDI
1 (Precursor to 1A)	25:1	14500	16800	1.16
2 (Precursor to 1B)	30:1	15800	18400	1.17
3 (Precursor to 1C)	35:1	21000	24000	1.15

a.) The raw M_n and M_w values obtained by GPC vs. PS stds are different than the expected absolute M_n and M_w values based on repeat unit molecular weights because poly(**2**) is different than PS in solution.

Analogous experiments to verify the living ROMP character of monomer **3** with the Grubbs' 1st-generation catalyst were also performed. Unfortunately, the ionic poly(**3**)

samples (like the BCPs) had sufficiently different solubility properties from conventional non-charged polymers^{26d} that GPC analysis was inconclusive and did not yield any definitive PDI results. However, similar ¹H NMR endgroup molecular weight analysis of model oligomers of poly(**3**) formed using varying monomer-to-catalyst ratios (**6a–d**) showed linearly increasing M_n values, again consistent with a living polymerization process (see Scheme 3.S5 and Figure 3.S5). This trend, coupled with the fact that a large number of norbornene-based monomers (including those with ionic substituents) are known to exhibit living ROMP behavior with Grubbs-type olefin metathesis catalysts,²⁶ suggests that the ROMP of **3** is living as well.



Scheme 3.S5. Imidazolium poly(**3**) oligomers used for absolute M_n determination via ¹H NMR endgroup analysis in order to confirm living polymerization behavior.

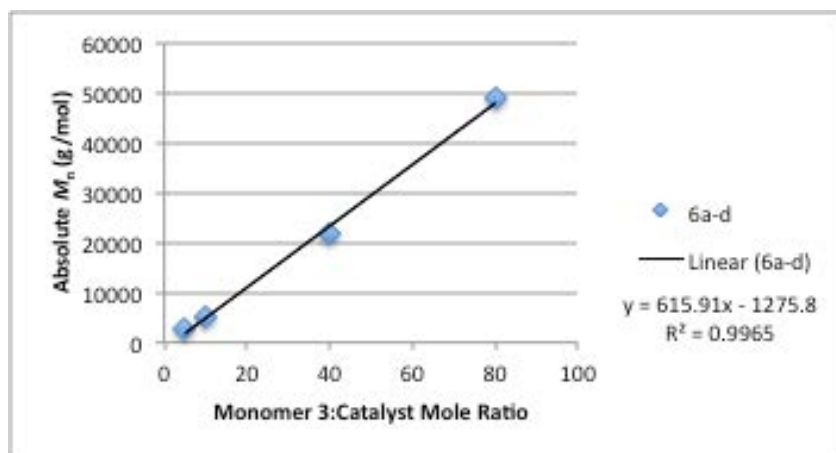


Figure 3.S5. Linear relationship between monomer-to-catalyst molar ratio used and absolute M_n from ¹H NMR endgroup analysis for various and poly(**3**) oligomers.

*It is important to note that while the endgroup protons (used to determine absolute M_n) for poly(**3**) homopolymers were distinct and separate from the imidazolium crown protons on ^1H NMR, endgroup analysis could not be performed on the BCPs. This is because the formation of each BCP alters the chemical shift of the imidazolium crown protons such that they shift to overlap the endgroup protons.*

3.6.5.3 Calculating Block Length Composition

Based on the observed living characteristics for the ROMP of monomers **2** and **3** by the Grubbs 1st-generation catalyst, the block length compositions for the BCPs **1A–C** were calculated using the monomer-to-catalyst loading ratios (with complete monomer consumption as per a living polymerization), and the observed block composition (i.e., repeat unit) ratios for each BCP via ^1H NMR analysis (see Equation 3.S3). The blocky polymer architecture and connectivity of **1A–C** are discussed and substantiated by the data presented in the main manuscript.

$$[(\text{Mon:Cat loading ratio})(m_{\text{block ratio}})]-b-[(\text{Mon:Cat loading ratio})(n_{\text{block ratio}})] \quad (\text{Eq. 3.S3})$$

Block Length Composition for BCP **1A**:

$$[(25)(1.0)]-b-[(25)(0.90)] = 25-b-23$$

Block Length Composition for BCP **1B**:

$$[(30)(1.0)]-b-[(30)(0.66)] = 30-b-20$$

Block Length Composition for BCP **1C**:

$$[(35)(1.0)]-b-[(35)(0.42)] = 35-b-15$$

3.6.5.4 Calculating BCP Molecular Weight

As mentioned previously, conventional methods used to directly determine the molecular weights of BCPs **1A–C** (e.g., GPC, endgroup analysis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and dynamic light scattering) were attempted, but all yielded inconclusive results. Consequently, the M_n value for each BCP **1A–C** was estimated by multiplying the calculated lengths of each block (as described in the preceding sections) with the molecular weight value of the appropriate repeat unit.

$$\text{BCP } \mathbf{1A}: 25(307 \text{ g/mol}) + 25(540 \text{ g/mol}) \approx 20,100 \text{ g/mol}$$

$$\text{BCP } \mathbf{1B}: 30(307 \text{ g/mol}) + 20(540 \text{ g/mol}) \approx 20,000 \text{ g/mol}$$

$$\text{BCP } \mathbf{1C}: 35(307 \text{ g/mol}) + 15(540 \text{ g/mol}) \approx 18,800 \text{ g/mol}$$

3.6.6 Differential Scanning Calorimetry (DSC)

DSC studies on BCP **1A** revealed the presence of two distinct but broad thermal transitions near -28°C and 7°C , consistent with crystallization of the *n*-dodecyl side chains on the poly(**2**) segments and the vitrification of the imidazolium blocks, respectively (Figure 3.S6). In comparison, DSC analysis of the two independent homopolymers showed that poly(**2**) has a thermal transition near -35°C , and that poly(**3**) has a broad thermal transition at ca. -4°C (Figure 3.S6). BCPs **1B** and **1C** also show thermal transitions similar to BCP **1A**, with strong transitions at ca. -28°C and weaker transitions at ca. 7°C .

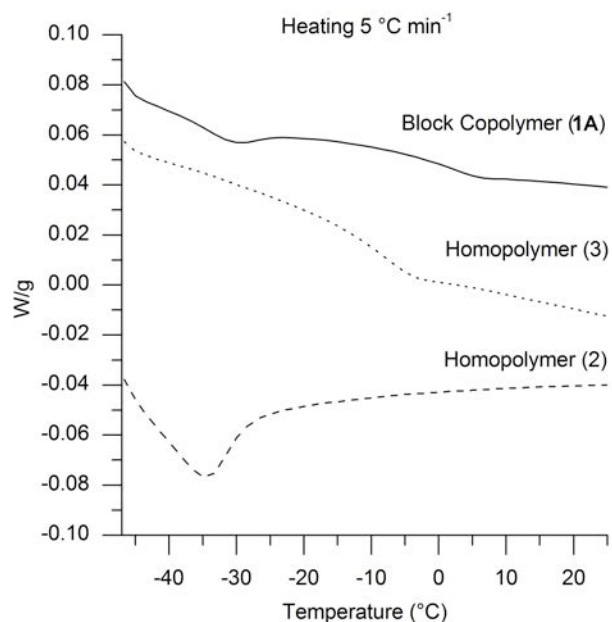


Figure 3.S6. DSC profiles of BCP **1A** and the respective homopolymers of **2** and **3**, performed at heating and cooling rates of 5 °C min⁻¹.

3.6.7 NMR DOSY Studies

NMR DOSY experiments were performed using a Varian Inova-400 NMR spectrometer at 400.157 MHz for ¹H observation in CD₂Cl₂ at 10 mg/mL. Gradients were calibrated to pure H₂O at 25.0 °C such that $D_{(\text{H}_2\text{O})} = 29.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Specific parameters were chosen as optimum to achieve nearly complete decay, and NMR diffusion data were processed using local covariance order DOSY (LOCODOSY).²⁷

BCP 1A. The total gradient time (δ) used was 2.5 ms, the diffusion delay (Δ) was 90 ms, and 90° pulse-width (pw90) was 14.75 ms.

Physical Blend of (poly(2) + poly(3)). The total gradient time (δ) used was 2.0 ms, the diffusion delay (Δ) was 40 ms, and 90° pulse-width (pw90) was 13.8 ms.

3.6.8 Rheology

Measured dynamic elastic and loss moduli measured for BCPs **1A–C** were consistent with ordered block copolymer melts, with the general behavior typical of that observed for lamellar structured systems. Figure 3.S7 depicts the temperature dependence of those moduli for sample **1C**, as an example. Increased noise at higher temperatures is associated with instrument torque limitations prevalent when using the small sample (8mm diameter) parallel plate tool configuration.

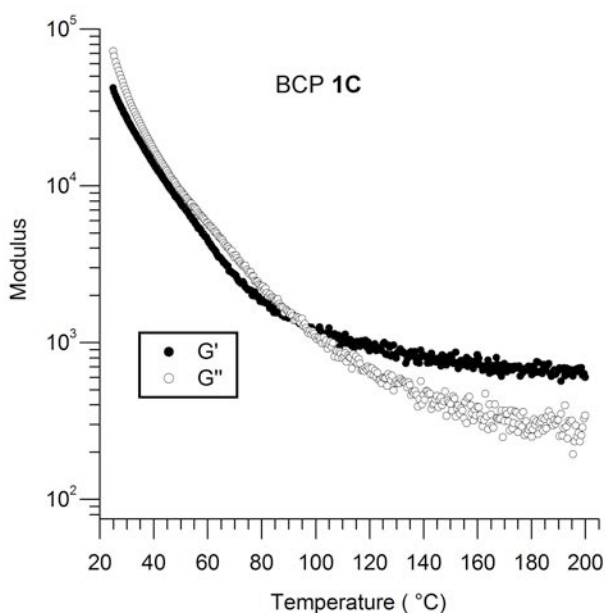


Figure 3.S7. Dynamic temperature ramp experiment data for **1C** performed while heating at $1\text{ }^{\circ}\text{C min}^{-1}$ at an angular frequency of 1 rad s^{-1} and a strain of 1%.

3.6.9 Preparation and Purification of Higher Length Homologues of BCPs **1A–C**

It is possible to prepare longer homologues of BCP platform **1** (e.g., 150–250 total repeat units) using the above procedures; however, with longer overall chain lengths, residual monomer has been observed in the resulting BCPs (2.5–9 mol%), thereby

compromising sample purity. This residual monomer is very difficult to completely remove due to solubility complications and the ionic nature of the BCPs and monomer **3**.

3.7 References

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distribution of poly(**2**) was symmetric and monomodal, with PDI values consistently in the 1.15–1.17 range for all samples.

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CHAPTER 4

Morphological Phase Behavior of Poly(RTIL)-Containing Diblock Copolymer Melts

(Manuscript published under the same title in *Macromolecules* **2012**, *45*, 4262–4276,
co-authored with Scalfani, V. F.; Ekblad, J. R.; Edwards, J. P.; Gin, D. L; Bailey, T. S.)

4.1 Abstract

The development of nanostructured polymeric systems containing directionally continuous poly(ionic liquid) (poly(IL)) domains has considerable implications toward a range of transport-dependent, energy-based technology applications. The controlled, synthetic integration of poly(IL)s into block copolymer (BCP) architectures provides a promising means to this end, based on their inherent ability to self-assemble into a range of defined, periodic morphologies. In this work, we report the melt-state phase behavior of an imidazolium-containing alkyl–ionic BCP system, derived from the sequential ring-opening metathesis polymerization (ROMP) of imidazolium- and alkyl-substituted norbornene monomer derivatives. A series of 16 BCP samples were synthesized, varying both the relative volume fraction of the poly(norbornene dodecyl ester) block ($f_{\text{DOD}} = 0.42\text{--}0.96$) and the overall molecular weights of the block copolymers (M_n values from 5000–20100 g mol^{−1}). Through a combination of small-angle X-ray scattering (SAXS) and dynamic rheology, we were able to delineate clear compositional phase boundaries

for each of the classic BCP phases, including lamellae (Lam), hexagonally packed cylinders (Hex), and spheres on a body-centered-cubic lattice (SBCC). Additionally, a liquid-like packing (LLP) of spheres was found for samples located in the extreme asymmetric region of the phase diagram, and a persistent coexistence of Lam and Hex domains was found in lieu of the bicontinuous cubic gyroid phase for samples located at the intersection of Hex and Lam regions. Thermal disordering was opposed even in very low molecular weight samples, detected only when the composition was highly asymmetric ($f_{\text{DOD}} = 0.96$). Annealing experiments on samples exhibiting Lam and Hex coexistence revealed the presence of extremely slow transition kinetics, ultimately selective for one or the other but not the more complex gyroid phase. In fact, no evidence of the bicontinuous network was detected over a 2-month annealing period. The ramifications of these results for transport-dependent applications targeting the use of highly segregated poly(IL)-containing BCP systems are carefully considered.

4.2 Introduction

Polymerized ionic liquids (poly(IL)s) are a relatively new class of charged polymers (typically cationic) that combine the unique thermal, chemical, and transport properties of ionic liquids (ILs) with the physical and mechanical properties of polymeric materials. The result is a macromolecular system implicitly suited for a range of valuable engineering applications, most notably those involving selective transport phenomena in energy and energy industry related technologies.¹⁻⁵ The predominance of the recent synthetic efforts to produce poly(IL)s have focused on repeat units containing charged imidazolium groups,^{4,6-21} some of which have already shown considerable promise as

membrane materials for CO₂/light gas separations,^{22,23} solid-state ion conductors,^{24–26} and electrochemical devices.^{27,28} Such target applications are predicated on exploiting the inherent CO₂ gas solubility, ion conductivity, and tunable amphiphilicity associated with the charged imidazolium species. However, true performance optimization in these applications requires an ability to tune not only the charge or gas molecule transport behavior but the mechanical properties as well. In such singular, homopolymer-based materials, this becomes largely impractical, given the opposing dependence of mechanical response and transport on local chain mobility. That is, the integration of high cross-link densities, entanglements, or crystalline domains to provide the robust mechanical performance needed for long-term usage is inherently deleterious to the ability of the material to simultaneously achieve high ion and gas molecule transport rates.

One very promising solution to this dilemma can be achieved through direct integration of poly(IL)s into block copolymer (BCP) architectures with other, nonionic polymer species. Such an arrangement can provide access to single molecule systems capable of phase-separating into a range of morphologies, in which the ionic and nonionic polymer segments occupy separate domains spatially organized on the 5–50 nm length scale. Through the phase separation, the bulk mechanical property and transport characteristics of each polymer block can be largely retained, although the intra- and intergrain domain continuity associated with the morphology ultimately determines the macroscopic behavior of the sample. With the exception of the network phases such as gyroid,^{29,30} most identified BCP morphologies have geometries that constrain intragrain continuity in at least one block to two or fewer dimensions.³¹ However, arbitrary

intergrain orientation randomizes this intragrain orientational preference and can effectively restore three-dimensional continuity.³² Of course, net transport rates are reduced by the added tortuosity imposed on the transport process as well as defects and dead ends generated at grain boundary interfaces. These effects on ion conductivity have been studied in detail by Balsara and coworkers in lithium-^{33,34} and imidazolium³⁴-doped poly-(styrene)-*b*-poly(ethylene oxide) BCPs and more recently by Mahanthappa and coworkers in BCPs containing pendant charged imidazolium groups prepared via postpolymerization modification.²¹ Processing methods in BCPs that produce increased orientational order and larger grain sizes can theoretically improve performance and have been the subject of significant study.³⁵⁻⁴³ Such methods have been recently applied to the orientation of ordered phases in conventional, nonionic, phase-separated diblock copolymers and shown to affect transport for both light gas⁴⁴ and ethanol⁴⁵ separations. It is worth mentioning that much of the processing effort associated with producing preferred domain orientations can be potentially eliminated using one of the continuous network phases, such as the bicontinuous cubic gyroid phase found in AB diblock copolymer melts.²⁹ The continuity in both domains, combined with an inherent propensity to form very large grain sizes during annealing, creates a potential advantage for transport applications, making it a worthy target. Unfortunately, the gyroid phase has often been found to be experimentally confined to weakly segregated systems, making its use challenging in systems for which the Flory interaction parameter between blocks is high or the molecular weight is large.

Over the past several years, we have been particularly interested in the application of imidazolium-based poly(room-temperature ionic liquids), poly(RTIL)s, as selective

components in CO₂/light gas separation membranes. In this regard, we have been focused on developing BCP systems containing imidazolium-based poly(RTIL)s that can ultimately produce the combined mechanical properties and gas molecule transport performance necessary for efficient high volume separations. To this end, our groups recently reported the direct synthesis of an imidazolium-based alkyl–ionic diblock copolymer employing sequential ring-opening metathesis polymerization (ROMP) polymerization of alkyl ester and charged imidazolium norbornene monomer derivatives.⁴⁶ This synthetic route stands as one of the first examples of poly(RTIL)-based BCP synthesis that does not require postpolymerization modification to introduce the IL component.^{16–18,20,21}

Given the importance of morphology on transport processes in these materials, a detailed characterization of the thermal and compositional BCP phase behavior for these highly charged molecules is the subject of this report. In general, the presence of the charged–uncharged architecture and its influence on the classically observed phase behavior exhibited by uncharged systems have received only limited attention. This is particularly true for poly(IL)-containing BCPs. Prior work documenting solution^{47–50} and melt-state^{51–53} phase separation of ionic-containing BCPs have primarily focused on different polyelectrolyte systems, such as those containing acrylic acid,^{47–51} sulfonated styrene,^{51–53} or protonated lysine residues.^{48,49} Documented phase separation in imidazolium-based poly(IL) BCPs in the solvent-free melt state is largely unprecedented and limited only to recent work by Mahanthappa and coworkers²¹ and our preliminary report focused on the BCP synthesis.⁴⁶ In any event, the ability to access each of the different phases classically observed in BCP systems has not yet been established for

these unusual systems. Of particular interest is the impact of the charged–uncharged architecture on the ability of the BCP to form the idealized (for transport applications) gyroid network. We believe this is the first detailed investigation into the phase behavior of imidazolium-based poly(RTIL)-containing BCPs.

In this report, we present the melt-state phase behavior of a series of 16 imidazolium-based poly(RTIL) BCPs spanning the composition range of 42–96 vol % poly(norbornene dodecyl ester), characterized through a combination of small-angle X-ray scattering (SAXS) and dynamic rheology. Of the 16 BCPs studied, 14 were found to have a high degree of long-range order, even those having relatively low molecular weights. A detailed morphological analysis of each sample is presented in this report, and the impact of the charged–uncharged architecture on the degree of segregation and the resulting phase behavior is discussed. The implications for the apparent absence of the gyroid phase from this and other charged–uncharged BCP systems are also considered.

4.3 Results and Discussion

4.3.1 Synthesis of Alkyl–Imidazolium DOD–IMD Diblock Copolymers

A total of 16 block copolymer samples (**1D–1S**) were synthesized via the sequential ROMP using Grubbs' first-generation catalyst of two norbornene monomer derivatives (Figure 4.1): one substituted with a hydrophobic dodecyl ester (**2**) and the other with a cationically charged imidazolium-based norbornene RTIL (**3**). The synthesis and characterization details can be found in our recent communication.⁴⁶ The majority of BCP samples synthesized (13 out of 16) were targeted to contain 50 total repeat units while varying the relative volume fraction of the poly(norbornene dodecyl ester) block from 0.42 to 0.96. As discussed in our previous communication, M_n values were targeted

through monomer/catalyst ratios and verified through end-group analysis on a sample of poly(norbornene dodecyl ester) homopolymer taken from the reactor just prior to the addition of the second (**3**) monomer. The final BCP M_n values were then inferred using these homopolymer M_n values and the ^1H NMR spectra for the corresponding BCP. Direct analysis of M_n of the BCP through ^1H NMR was not possible due to peak overlap with the initiator fragment protons. Final BCP molecular weights (M_n) varied from 5000 to 20,100 g mol^{-1} (Table 4.1). SEC analysis of the BCPs could not be performed due to the inherent complications of charged species interacting with the columns. Poly(norbornene dodecyl ester) homopolymer samples extracted prior to addition of the imidazolium block were found to have typical PDI values of 1.15–1.2.⁴⁶

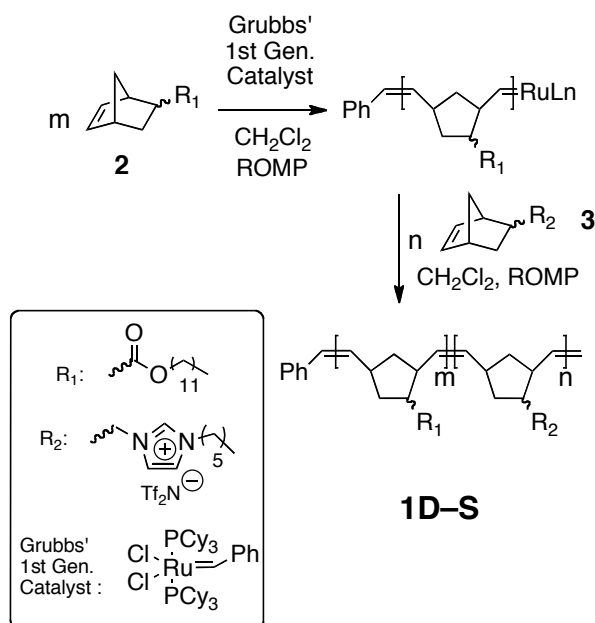


Figure 4.1. Sequential ROMP of monomers **2** and **3** to yield imidazolium-based DOD-IMD BCPs **1D-S**.

Table 4.1. Summary of synthesized imidazolium-based alkyl-ionic BCPs and their corresponding phase behavior.

Sample	$m : n^a$	$M_n(\text{DOD})^b$	$M_n(\text{IMD})^c$	wt % $(\text{DOD})^d$	f_{DOD}^e	Morphological Behavior
1D	48.5 : 1.4	14900	800	0.95	0.96	LLP → Dis
1E	47.0 : 3.8	14400	2000	0.88	0.89	LLP
1F	45.0 : 5.6	13800	3000	0.82	0.84	LLP → S _{BCC}
1G	43.5 : 6.9	13400	3700	0.78	0.81	LLP → Hex
1H	42.0 : 9.5	12900	5100	0.71 ₆	0.74 ₇	LLP → Hex
1I	40.0 : 9.1	12300	4900	0.71 ₅	0.74 ₆	LLP → Hex
1J	38.5 : 11.3	11800	6100	0.66	0.69	Lam + Hex
1K	37.5 : 12.8	11500	6900	0.63	0.66	Lam + Hex
1L	36.5 : 13.9	11200	7500	0.60	0.64	Lam + Hex
1M	35.6 : 14.4	10900	7800	0.58	0.62	Lam
1N	30.0 : 12.8	9200	6900	0.57	0.61	Lam
1O	32.0 : 18.0	9800	9700	0.50	0.54	Lam
1P	7.5 : 5.0	2300	2650	0.46 ₅	0.50 ₄	Lam
1Q	30.0 : 20.0	9200	10800	0.46 ₀	0.50 ₀	Lam
1R	15.0 : 10.3	4600	5600	0.45	0.49	Lam
1S	25.0 : 23.0	7700	12400	0.38	0.42	Lam

^am:n ratio determined from relative ¹H NMR peak integrations in combination with poly(DOD) M_n values.⁴⁶ ^b M_n of DOD were calculated from monomer-to-catalyst loading ratios (with complete monomer consumption as per a living polymerization) and verified by ¹H NMR. ^c M_n of poly(IMD) inferred from ¹H NMR of DOD homopolymer and final BCP. ^dWeight fraction of DOD calculated as $M_n(\text{DOD})/[M_n(\text{DOD}) + M_n(\text{IMD})]$. ^eVolume fraction of DOD calculated with $f_{\text{DOD}} = kM_n(\text{DOD})/[kM_n(\text{DOD}) + M_n(\text{IMD})]$, with $k = \rho(\text{IMD})/\rho(\text{DOD}) = 1.173$, determined using SAXS of sample 1Q, as described in the main text. LLP = liquid-like packing, Dis = disordered, SBCC = spheres on a body-centered cubic lattice, Hex = hexagonally packed cylinders, Lam = lamellae.

4.3.2 Overview of Melt State Phase Behavior

A combination of dynamic rheology and SAXS analysis was utilized to study the self-assembled melt-state phase behavior of the 16 DOD–IMD BCP samples spanning

42–96 vol % poly(norbornene dodecyl ester) (DOD). The systematic characterization of the BCP phase behavior was carried out by first measuring the elastic (G') and loss modulus (G'') response as a function of temperature with dynamic rheology (in the linear viscoelastic regime) under a complete thermal heating (up to 200 °C) and cooling (back to RT) cycle. The cooling cycle was then immediately followed by a second heating ramp. In an effort to probe each sample for additional thermal transitions and in particular a transition to the isotropic disordered state, the second heating ramp in the cycle was extended past 200 °C. However all samples exhibited a rapid and irreversible increase in modulus in the range of 210–240 °C, which appears to be associated, not with a phase transition, but thermally induced cross-linking of the samples. TGA analysis confirmed degradation (loss of mass) onset temperatures around 350 °C, suggesting the observed spike in modulus is likely a crosslinking, not an early degradation event (Supporting Information). Preliminary experiments with adding 0.02 wt % butylated hydroxytoluene (BHT, a radical trap) to prevent cross-linking appeared to substantially alter the rheological response, presumably through the interaction with the charged imidazolium block. Since such a change in rheological response is indicative of a potential morphological change, it was decided to restrict study of the morphological behavior to temperatures less than 200 °C, to avoid the potential interference associated with additives. Samples prepared for SAXS analysis were restricted to a single, complete heating and cooling cycle up to a maximum of 200 °C, based on the theologically established instability above this temperature. We note, however, that for the most asymmetric samples **1D** and **1E** the rheological experiments were limited to ~140 °C. These limits were imposed due to disordering in the former and reaching the low torque

resolution limits of the rheometer in the latter. In both cases the increased liquid-like nature of and degree of disorder in these samples (**1D** and **1E**) at such moderate temperatures made use of the full cycle unnecessary.

A phase diagram plotted as a function of temperature and volume fraction of the DOD block has been assembled in Figure 4.2 from the rheological and SAXS data collected. For clarity, only data from the 13 BCPs having ~50 combined repeat units are included in this diagram. Generally, direct morphological assignments were possible by comparing multiple diffracted reflections obtained from SAXS to those calculated for symmetries of documented diblock copolymer morphologies. Importantly, the SAXS data presented in this report contain data markers located at specific positions in q . These data markers are not pointing to features in the data but more appropriately to the calculated positions of the allowed reflections for the particular assigned morphology. The vertical dotted line boundaries in Figure 4.2 are visual guides to separate the observed morphologies and have been chosen arbitrarily, not experimentally. In general, different shaped symbols have been used to designate the specific morphology located at each point in the diagram. Weakly ordered morphologies, such as LLP spheres, have been designated using open symbols. Highly ordered morphologies assigned from multiple higher reflections in the SAXS data have been designated using solid symbols. While only one sample in the very asymmetric region ($f_{\text{DOD}} = 0.96$) clearly disordered in an experimentally accessible temperature range, disordered sample locations are designated with a cross symbol. In many of the BCP samples, there was a sufficient delay upon heating before obtaining highly ordered structures, defined here as scattering patterns with multiple well-resolved reflections. Upon further cooling or reheating, the

high level of order established during initial heating was retained, with no reversion to the initial weakly ordered state. This behavior was also reflected in the rheological response of the materials, in which subtle transitions in moduli detected during the initial heating ramp were consistent with the evolution of a highly ordered state. In these cases, subsequent cooling and heating ramps were nearly identical, absent of the “ordering” transitions observed on first heating, and with little hysteresis over the range of temperatures studied (27–200 °C). Because of the apparent importance of the thermal processing history on the degree of order in these samples, however, we have chosen to indicate the region of slow ordering kinetics on the phase diagram, directly. The temperature ranges over which weakly ordered samples were initially observed (as assigned from broad reflections observed in the SAXS patterns) are represented by semi-filled symbols. A transition from semi-filled to solid symbols (at a particular volume fraction) is indicative of the location at which the high degree of order finally develops in that particular sample. Again, the high degree of order developed above this transition point is retained upon subsequent cooling of the sample. The dependence of the sample order on the thermal history is thus signified by the semi-filled symbols.

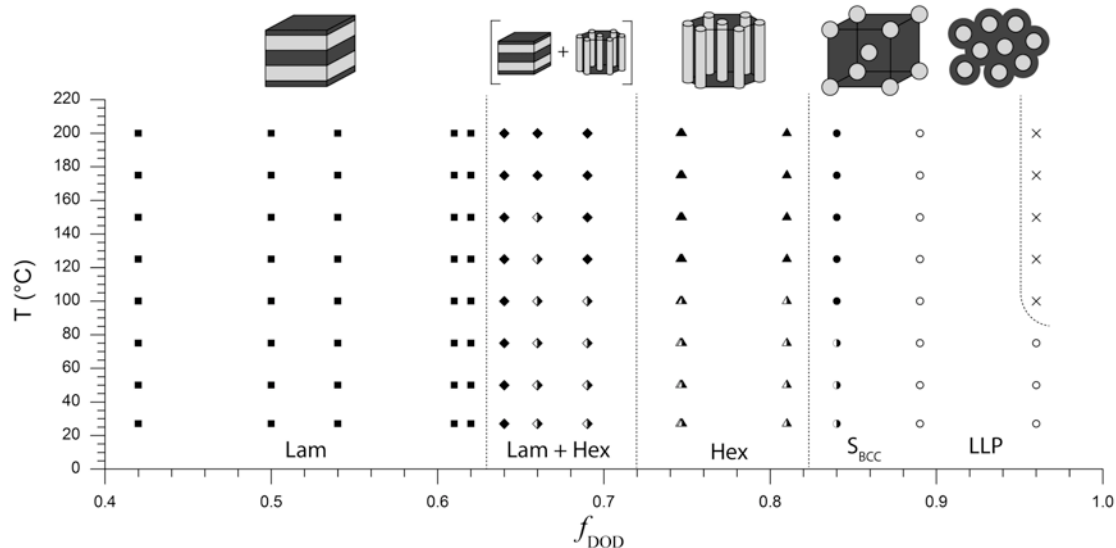


Figure 4.2. Phase diagram of morphologies observed in the imidazolium-based alkyl-ionic copolymer melt system including lamellae (Lam), hexagonally packed cylinders (Hex), coexisting Lam and Hex, spheres on a body-centered cubic lattice (SBCC), and a liquid-like packing (LLP) of spheres. Solid symbols represent regions of well-defined ordered structures, observed by multiple resolved SAXS diffraction reflections, semi-filled and open circles represent regions of poorly ordered structures, evident by broad peaks in SAXS, and cross symbols depict the disordered region.

Across the 16 samples studied, three of the four classically observed equilibrium diblock morphologies were identified, including lamellae (Lam), hexagonally packed cylinders (Hex), and spheres on a body-centered-cubic lattice (SBCC). The bicontinuous gyroid phase was not detected; instead, a metastable coexistence of lamellae and hexagonally packed cylinders was found to occupy volume fractions within the traditional gyroid boundaries. In addition, we observed at least one sample (**1E**) in which a LLP of spheres was persistent and failed to develop into an ordered BCC lattice over the temperature range studied. Thermodynamic order-to-order transitions (OOTs) between phases were not observed directly in rheological time scales for any of the BCPs studied, although in at least one sample showing phase coexistence, very slow (months) transition kinetics favoring one phase over the other (Hex over Lam in **1J**) appeared to be

present. In the following sections, we present and discuss a subset of the characterization data collected for samples **1D–1S** in order to generate the phase diagram in Figure 4.2. For the interested reader we have included complete rheological temperature ramp data along with the complete SAXS analysis (heating and cooling up to 200 °C with data collected every 25 °C) for all BCPs studied in this report within the Supporting Information. It is also worth noting that direct imaging of these samples using AFM and TEM were unsuccessful due to the inherent stickiness of the BCP samples. In general, direct imaging is advantageous for characterization of morphology when assignment through SAXS is ambiguous, which fortunately is not the case with regard to these samples. As such, the absence of characterization by direct imaging, while unfortunate, does not affect our conclusions about the phase behavior of this BCP system.

4.3.2.1 Lamellae

Samples exhibiting lamellar morphologies include BCPs **1M–1S** which represents a composition range of 42–62 vol % DOD. Dynamic rheological temperature ramp data collected for samples **1M–1S** are presented in Figure 4.3. Each of these samples shows elastic and loss response behavior prototypical of Lam BCP phases, with G' and G'' values that remain similar in magnitude and parallel, with a steady decrease in both moduli upon heating.^{46,54} In the melt, each displayed numerous higher ordered SAXS diffraction reflections at q/q^* ratios of $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc. (where q^* is the position of the primary scattering wave vector, $\text{Lam} = q_{100}$), consistent with the allowed reflection conditions for layered periodic symmetry (Figure 4.3). Domain spacings (d_{100}) for samples, **1S**, **1Q**, **1O**, and **1M**, each with ~50 total norbornene repeat

units (M_n values of centered around 20 000 g mol⁻¹), were all nearly identical with a mean value of 26.5 ± 2.6 nm (at 125 °C). The shorter lamellae forming samples, including **1N** ($M_n = 16\ 100$ g mol⁻¹), **1R** ($M_n = 10\ 200$ g mol⁻¹), and **1P** ($M_n = 5000$ g mol⁻¹) had interplanar domain spacings of 22.5, 16.6, and 13.1 nm at 125 °C, respectively. Notably, the domain spacings were found to be considerably larger (~30%) than that expected for a lamellar structure formed in typical BCPs such as PS–PVP of comparable molecular weights.^{46,55} The increase is likely attributable to chain stiffness associated with the inherent bulkiness of the imidazolium and dodecyl ester substituents compressed along the polynorbornene backbone in combination with the strong chemical dissimilarity (large χ parameter) between the two blocks. Both attributions would favor a strong degree of segregation and associated larger domain spacings.⁵⁶ The variations in the relative intensities of the observed SAXS reflections are consistent with changes in chemical composition, as the relative ratio of domain thicknesses comprising the lamellar period directly affects the net product of the form and structure factor contributions to the scattered signal. The suppression of the even-order reflections at q/q^* ratios of $\sqrt{4}$, $\sqrt{16}$, and $\sqrt{36}$ in samples **1R**, **1Q**, and **1P** suggests an almost perfectly symmetric volume fraction of 0.5, where the near-zero minima in the particle form factor coincide with the even-order diffraction positions produced by the lamellar structure, such that reflections at these positions are effectively extinguished in the final scattering product.^{46,57,58}

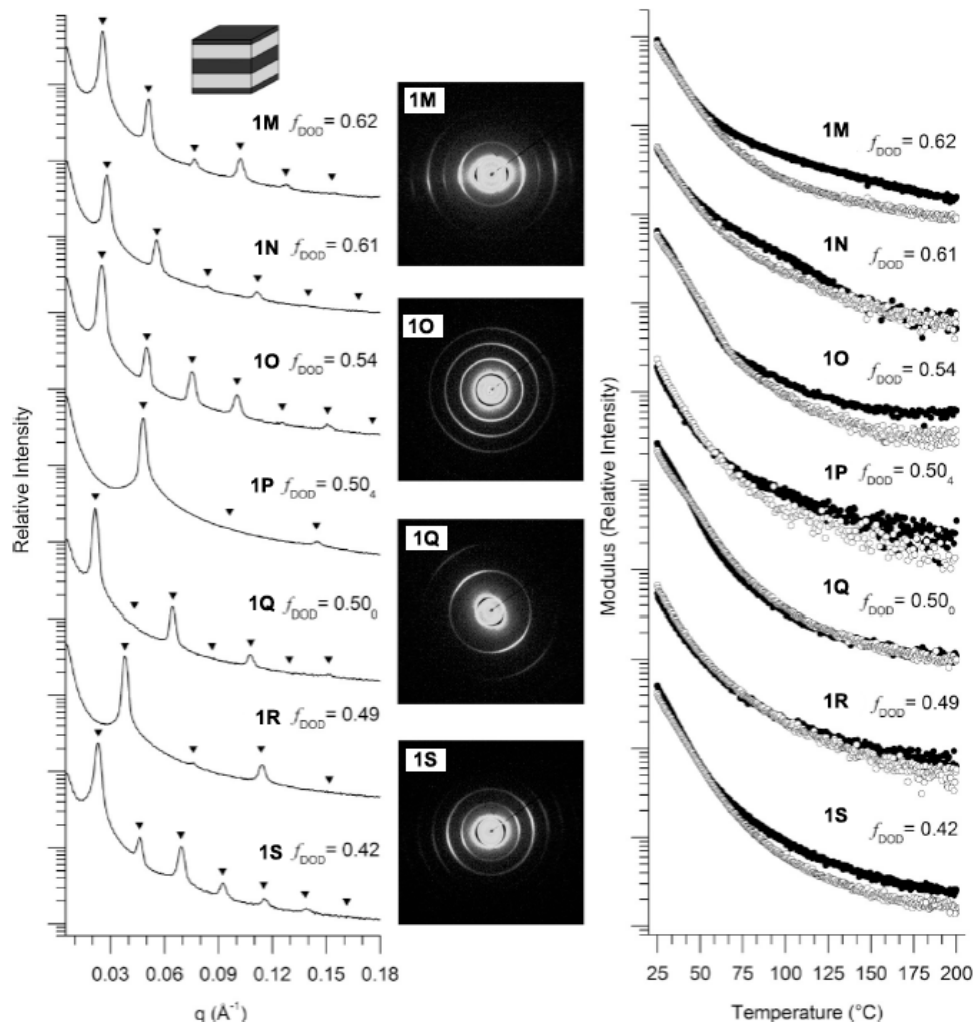


Figure 4.3. SAXS data at 125 $^{\circ}\text{C}$ (first heating cycle) for Lam forming BCPs **1M–1S**. Inverted solid triangles represent the locations of allowed reflections for the Lam morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc. The near complete suppression of even-order reflections in samples **1R**, **1Q**, and **1P** suggests an almost perfect symmetric volume fraction of 0.5 (left).^{57,58} Samples of 2D scattering patterns (center). Dynamic temperature ramps (first heating cycle) of BCPs **1M–1S** at 1 $^{\circ}\text{C min}^{-1}$, 1 rad s^{-1} and with strain values of 2.5–8% (within the linear viscoelastic regime). Solid and open circles represent G' and G'' , respectively (right).

Generally speaking, the relative block volume fraction of a BCP is estimated using known homopolymer densities at an arbitrarily selected temperature, usually constrained by the availability of tabulated data⁵⁹ for the polymers comprising the BCP. The use of fixed temperature density data is typically justified recognizing that, although

the densities themselves can be temperature dependent, the ratio of densities, which sets the volume fraction, is much less sensitive to changes in temperature. Unfortunately, due to the lack of available data tabulating the imidazolium and norbornene dodecyl ester functional polymers densities, we were unable to estimate the volume fraction of the DOD–IMD BCPs via this method. However, the noted absence of even-order diffraction reflections in several of the lamellae forming BCP samples provided a unique opportunity to independently establish the relative ratio of densities for the two blocks. From this ratio, then, the relative block volume fractions in each of the remaining DOD–IMD BCPs could be assigned. BCP **1Q** was selected for its near complete suppression of the even order (q/q^* ratios = $\sqrt{4}$, $\sqrt{16}$, and $\sqrt{36}$) reflections over a large temperature range and the relative volume fraction set to be exactly 0.500. A relative ratio of the block densities was then estimated ($k = \rho(\text{IMD})/\rho(\text{DOD}) = 1.173$) using this assigned volume fraction in combination with the ^1H NMR-calculated molecular weights for the individual blocks. This ratio of densities (k) was then used to determine the relative volume fractions of BCPs **1D–1S**. We note that the region of composition space where the even-order reflections are absent in the lamellar forming BCP samples appears to be fairly narrow, based on the reemergence of the even-order reflections in samples **1O** ($f_{\text{DOD}} = 0.54$) and, in particular, **1R** ($f_{\text{DOD}} = 0.49$). Based on this level of sensitivity, the calculated volume fractions are believed to be at least as accurate, if not more accurate, than estimations based on tabulated homopolymer densities at arbitrary temperatures. Reassuringly, the assigned morphologies for all remaining samples fall within ranges of relative volume fractions reported for other experimental BCP systems.^{60,61}

In an attempt to measure the Flory interaction parameter, χ , for these DOD-IMD BCPs, we synthesized three BCPs with nearly symmetric volume fractions of $f_{\text{DOD}} = 0.5$ but of varied overall molecular weights. These included BCPs **1Q**, **1R**, and **1P** with M_n values of 20,000, 10,200, and 5000 g mol⁻¹, respectively (Figure 4.3). We initially targeted two methods generally used to experimentally determine $\chi(T)$ in BCP systems.^{62,63} The first is to measure the order-to-disorder transition (ODT) temperatures in a series of BCPs, typically using dynamic rheology to quantify the transition temperature.⁶⁴⁻⁶⁷ The value of $\chi(T)$ can then be extracted by the use of a theoretically predicted (χ_N)ODT value at $f_A = f_B = 0.5$, defined by the mean-field theory (MF theory) developed by Liebler⁶⁸ or the adjusted fluctuation theory developed by Brazovskii,⁶⁹ Fredrickson, and Helfand⁷⁰ (BLFH theory). The second method for extracting $\chi(T)$ for BCPs involves collecting SAXS or SANS data for a single molecular weight sample at various temperatures above the TODT, that is, the correlation hole scattering⁷¹ of the mixed isotropic disordered melt.^{62,63,72} The value of $\chi(T)$ is then extracted from the disordered state structure factor predicted by MF⁶⁸ or BLFH theory.^{62,69,70} Both approaches require BCPs that can become disordered at experimentally accessible temperatures. While a symmetric BCP is not a necessity in either method, it offers the most accurate calculation as the error associated with composition is minimized by the plateau behavior of the phase diagram at the ODT boundary. Unfortunately, all three BCPs remained ordered up to the experimentally determined limit of 200 °C, which was confirmed through the persistence of intense diffraction over the complete temperature range. The inability to disorder the samples prevented the determination of $\chi(T)$ with either of the aforementioned methods. Notably, the smallest BCP, **1P**, with an average

M_n of 5000 g/mol has just 12 total repeat units, suggesting the Flory interaction parameter, χ , is extremely large, forcing even low molecular weight materials into the strongly segregated regime. An estimation of χ for strongly segregated BCPs systems is possible through a comparison of domain spacings measured via SAXS and those predicted using strong segregation theory by Semenov^{73,74} which depend on a range of BCP parameters characterizing the balance between interfacial energy (χ) and entropic chain stretching penalties. Unfortunately, the expressions for predicting domain spacing^{73,74} require statistical segment lengths of each of the blocks in order to calculate χ . To our knowledge, accurate chain dimensions of substituted polynorbornene polymers are absent in the literature and therefore preclude the estimation of χ via this approach as well. At the very least, the inability to disorder these materials at such low degrees of polymerization confirms the system is very strongly segregated. As discussed below, this has significant consequences with respect to the ability of the system to adopt balance of curvatures required by more complex morphologies, such as the gyroid network.

4.3.2.2 Hexagonally Packed Cylinders

This region of phase space is defined by samples **1G**, **1H**, and **1I** with a range of composition of 74–81 vol % DOD. SAXS data revealed diffraction reflections consistent with hexagonally packed cylinders at q/q^* ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. (where q^* is the position of the primary scattering wave vector, Hex = q_{100}), consistent with the allowed reflections conditions for hexagonal symmetry (Figure 4.4). As was discussed for the Lam phase-forming samples, relative differences in the reflection intensities are a result of changes in the distribution of volume as the relative block

composition is changed. The shifting distribution of volume affects the superposition of the form and structure factor scattering contributions, affecting the composite intensity produced from the scattering experiment. Most notably, the near complete suppression of the $\sqrt{4}$ reflection in sample **1I** ($f_{\text{DOD}} = 0.746$) is consistent with its predicted extinction at a volume fraction of 0.726,^{75,76} based on coincidence of the cylinder particle form factor minima (functionally approaching zero) and the position of the (200) structure factor reflections. One can clearly see the trend toward extinction by following the relative intensity changes across the three samples **1G–I** in Figure 4.4. The inter-cylinder distance ($2d_{100}/\sqrt{3}$) for BCPs **1G–I** is fairly consistent between these three samples based on the consistent overall polynorbornene degree of polymerization of ca. 50 units, having an average spacing of 22 ± 1 nm (at 125 °C). Molecular weights in these samples do shift to smaller values (average M_n of 17400 g mol⁻¹) relative to the lamellar samples of similar degree of polymerization just discussed, due to the reduction in the relative number of heavier IMD repeat units found in the BCP.

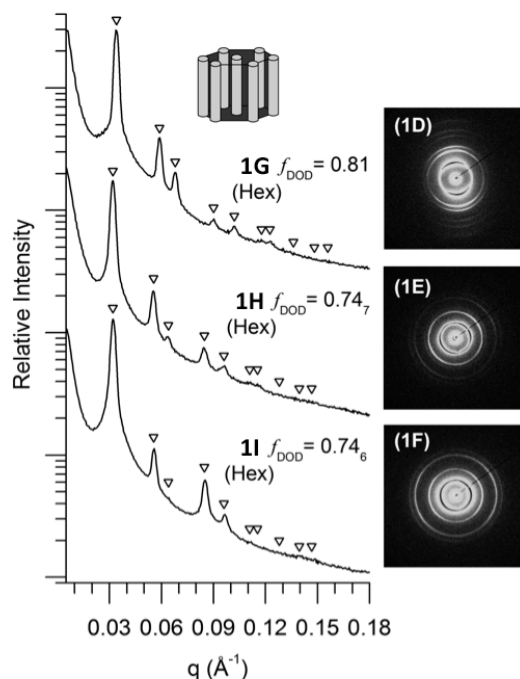


Figure 4.4. SAXS data at 150 °C (upon cooling) for Hex forming BCPs **1G–II**. Inverted open triangles represent the locations of allowed reflections for the Hex morphology based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. Relative intensity differences are consistent with variations in composition, most notably the near complete suppression of the $\sqrt{4}$ reflection in sample **1I**, which is suggestive of approaching a volume fraction of 0.726.^{75,76} Inset pictures are the 2D scattering patterns.

In contrast to the lamellar-forming BCPs, where highly ordered structures are present without any extended thermal processing (see complete thermal SAXS cycles in the Supporting Information), the hexagonally packed cylinder forming BCPs require an initial heating step to achieve a level of order that produces highly resolved diffraction patterns. As shown in Figure 4.5 for BCP **1G**, there is a sufficient delay in obtaining highly ordered hexagonally packed cylinders during the first heating cycle. The gradual ordering process evident by an evolution of the diffraction pattern from one with broad, poorly defined reflections at room temperature to one with multiple, easily resolved reflections at 125 °C and above. The rheological behavior is also consistent with the

observed delay in the ordering process, evident by a decade relaxation in shear moduli starting at 90 °C and ending at 130 °C in the dynamic temperature ramp experiment (Figure 4.5). These characteristically broad reflections have been observed previously in cylindrical systems^{77,78} and have been attributed to scattering off a non-lattice structure comprised of individual cylinders with an underdeveloped, weakly ordered, liquid-like packing (LLP). This behavior is also prevalent in spherical forming BCPs where liquid-like packing often predominates prior to adopting a fully developed SBCC lattice.^{79–81} The initial weakly ordered structure is presumably an artifact of slow ordering kinetics and not a true equilibrium phase in the thermodynamic sense. In support of this claim, once the highly ordered structure is established through thermal annealing, the order is preserved during subsequent cooling and heating cycles with no further evidence of any rheological transitions or decay in diffraction intensity which would accompany any return to the weakly ordered state (Figure 4.5).

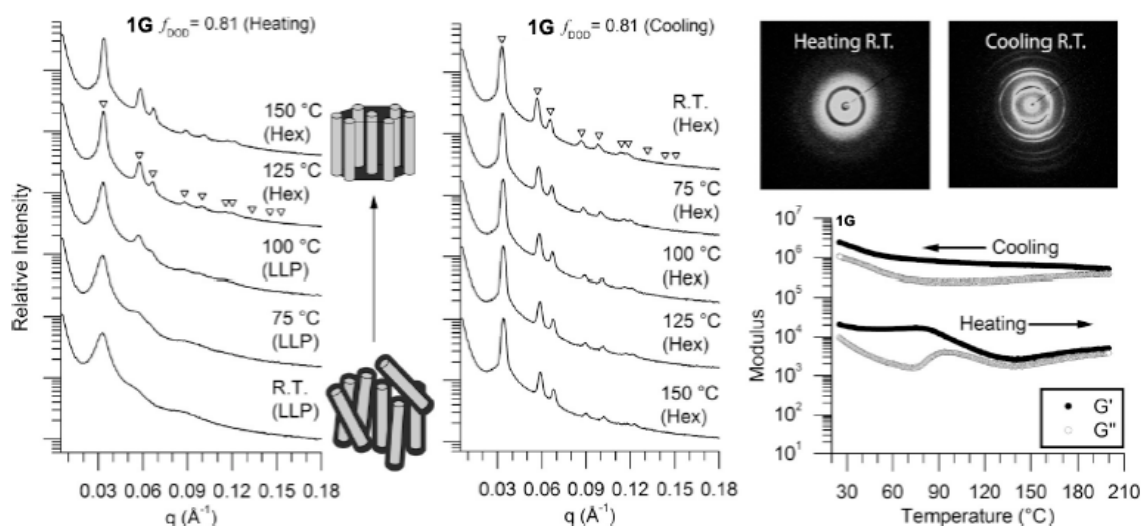


Figure 4.5. SAXS data of sample **1G** along a complete heating (left) and cooling (center) thermal cycle. Morphologies observed during heating include a distorted poorly ordered LLP of cylindrical domains before obtaining the well-ordered Hex morphology. Upon

cooling, the highly ordered Hex phase is preserved. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. Dynamic temperature ramp heating and cooling cycle of **1G** (right) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} , and 8% strain (within the linear viscoelastic regime). The cooling cycle has been shifted vertically 2 orders of magnitude for clarity. The rheological behavior mimics that of the SAXS, where a subtle transition is observed upon obtaining the well-ordered Hex morphology during heating, while any transitions are notably absent upon cooling. Insets are 2D scattering patterns depicting the initial weakly ordered morphology and final highly ordered morphology after the melt-processing.

4.3.2.3 Coexistence of Lamellae and Hexagonally Packed Cylinders

Samples **1J–1L**, with a range in composition spanning 60–66 vol % DOD, were found to exhibit a persistent coexistence of both lamellae and hexagonally packed cylinders. The SAXS patterns for samples defining this region of phase space (Figure 4.6) contain two sets of reflections at $q/q^{*,\text{lam}}$ ratios of $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc., and $q/q^{*,\text{hex}}$ ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc., where $q^{*,\text{lam}}$ and $q^{*,\text{hex}}$ are slightly shifted in position relative to one another. Importantly, the reflection positions were not consistent with the metastable hexagonally perforated lamellae phase in either the ABAB ($P6_3/mmc$) or ABCABC ($R3m$) stacking pattern.^{82–85} Notably, the allowed reflections for either of these HPL morphologies are not simple superpositions of those expected for the Lam and Hex morphologies taken independently, and so a clear distinction between simple coexistence and either of the HPL phases can be conclusively made for strongly diffracting materials. Each of the SAXS patterns for samples **1J–1L** have been presented in Figure 4.6 with separate labeling of expected reflection positions for both the Lam and Hex phases. For convenience, the SAXS patterns for single-phase Lam and Hex samples located just outside the coexistence region (**1M** and **1I**, respectively) have also been included in Figure 4.6. A comparison of the relative intensities of hexagonal phase,

reveals a clear composition dependence across the three samples. More specifically, the relative intensity of a set increase as it approaches the phase boundary with its pure state. We interpret these differences in intensity between the two sets of reflections as a direct indicator of the relative amounts of each phase present. For example, BCP **1L** is the closest to the pure Lam boundary and has a diffraction pattern in which the lamellar reflections, particularly those at $q/q^{*,\text{lam}}$ ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{16}$, dominate the scattering, while the hexagonal reflections are far less pronounced, with only $q/q^{*,\text{hex}}$ ratios of $\sqrt{1}$ and $\sqrt{7}$ observed. In contrast, sample **1J**, which is nearest to the Hex phase boundary, has a scattering profile that most closely resembles the Hex phase, with well-resolved reflections at $q/q^{*,\text{hex}}$ ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{7}$, and $\sqrt{9}$. Some lamellae character is also present with superimposed reflections at $q/q^{*,\text{lam}}$ ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{16}$; these reflections are far less pronounced compared with the same reflections in samples **1L** and **1K**. In addition, samples **1J** and **1K** exhibited the same delay in ordering kinetics found to exist in the hexagonal phase BCPs **1G–1I**, where an initial heating cycle was required to induce high levels of diffraction. This is consistent with the conclusion that samples **1J** and **1K** have a higher content of hexagonally packed cylindrical domains and share the slower ordering kinetics associated with that phase. On the other hand, sample **1L**, which is closer to the lamellar boundary, exhibited high levels of lamellar diffraction without any thermal treatment necessary, similar to the pure lamellar BCPs (**1M–1S**) discussed earlier. This result is consistent with conclusion sample **1L** is enriched in lamellae and contains far fewer hexagonally packed cylinder domains.

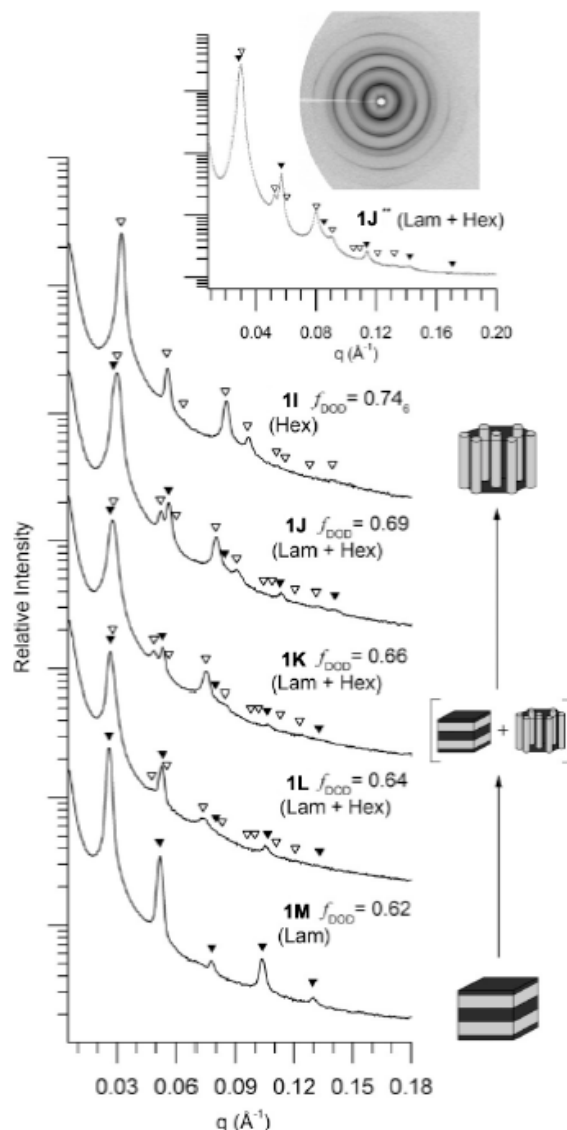


Figure 4.6. SAXS data at 150 °C (upon cooling) for coexisting (Lam + Hex)-forming BCPs **1J**–**1L**, plotted with the samples **1M** and **1I**, that exhibit a fully developed pure Lam and Hex phase, respectively, for comparison. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: $q/q^{*,\text{hex}}$ at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc., and inverted solid triangles represent the locations of allowed reflections for the Lam morphology, $q^* = q_{100}$: $q/q^{*,\text{lam}}$ at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc. Relative diffraction intensity differences are consistent with variations in composition (relative amounts of coexisting (Lam + Hex) domains), most notably the scattering profile of **1L** most closely resembles that of **1M** (pure Lam), while **1J** most closely resembles sample **1I** (pure Hex). Inset figure is the high-resolution synchrotron integrated and 2D SAXS data of sample **1J**, donated with double asterisks, showing the primary peak could not be resolved.

As shown in the overlaid data markers of Figure 4.6, the assignment of phase coexistence requires $q^{*,\text{lam}}$ and $q^{*,\text{hex}}$ positions that are in very close proximity to one another but do not, in fact, coincide. Qualitatively, a comparison of the primary peak widths for samples **1J–1L** with the primary peak widths for the adjacent single-phase Hex and Lam samples **1I** and **1M** shows a broadening in the former that suggests the overlap of two primary peaks is plausible. In an effort to resolve these two primary peaks definitively, we collected high-resolution synchrotron data for sample **1J**. The scattering data are presented in the inset of Figure 4.6. Unfortunately, the proposed Hex and Lam principal reflections could not be resolved, with the synchrotron source providing little improvement over the laboratory-grade Rigaku S-Max 3000 SAXS instrument used for the initial data collection. Despite our inability to resolve these two peaks, the quality of the peak assignments across the SAXS data from all three samples, combined with the results of additional rheology and annealing experiments (presented below), gives us great confidence in the conclusion of phase coexistence in these samples.

The rheological temperature ramp profiles of samples **1J–1L** are presented in Figure 4.7, bracketed again by the corresponding pure Hex and Lam data from adjacent samples **1I** and **1M**. Similar to that found in the SAXS, these samples present rheology profiles that appear intermediate to that typical of the two pure phases, with a consistent shift in character as one traverses across the coexistence region. For example, sample **1L** more closely resembles the rheology profile of the adjacent pure lamellar phase sample, **1M**, having similar magnitudes of G' and G'' with a steady relaxation in both moduli with heating. Likewise, sample **1J** more closely resembles the rheology profile of the adjacent pure hexagonal phase sample, **1I**, where there is only a slight decrease in G' and slight

recovery of G'' with heating. While the determination of actual phase coexistence by rheology is not particularly warranted, the data are at least consistent with the more convincing SAXS data for these samples. Notably, however, in contrast to the rheology of Hex samples **1G–1I** where subtle rheological transitions could be observed for the delay in ordering kinetics (double arrows in Figure 4.7 mark this transition for Hex sample **1I**), no such transitions were observed for samples in the coexistence region, despite the kinetic delay in ordering clearly demonstrated in the SAXS data for two of the samples (**1K** and **1J**). We note that while the temperature ramp profiles used by rheology (continuous) and SAXS (stepped) were fundamentally different, both ramp rates produced an average heating rate of $\sim 1\text{ }^{\circ}\text{C min}^{-1}$.

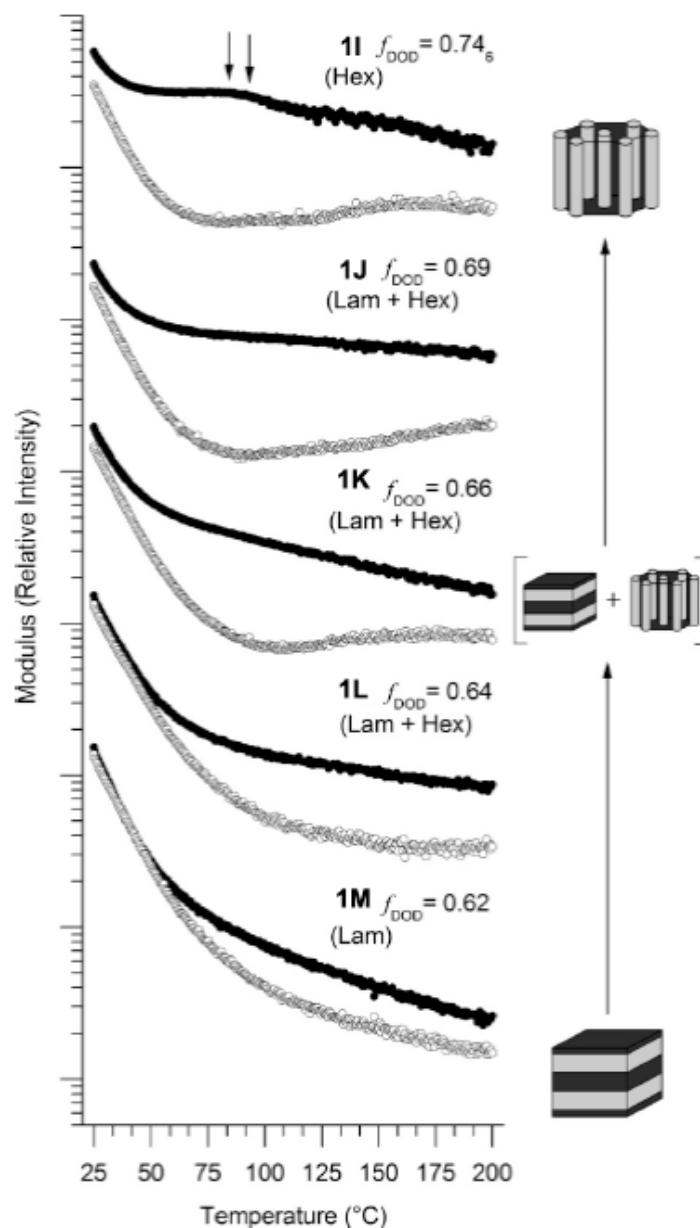


Figure 4.7. Dynamic temperature ramps (first heating cycle) at $1\text{ }^{\circ}\text{C min}^{-1}$, 1 rad s^{-1} , and with strain values of 6–8% (within the linear viscoelastic regime) for coexisting (Lam + Hex)-forming BCPs **1J**–**1L**, plotted with samples **1M** and **1I** that exhibit a fully developed pure Lam and Hex phase, respectively, for comparison. Solid circles represent G' , and open circles represent G'' . Differences in rheological response is consistent with variations in composition (relative amounts of coexisting (Lam + Hex) domains), most notably the temperature ramp profile of **1L** most closely resembles that of **1M** (pure Lam), while **1J** most closely resembles the profile of sample **1I** (pure Hex). Double arrows mark the subtle rheological transition present in the pure Hex **1I** sample arising from a delay in ordering kinetics. No such transitions were observed in rheology for samples in the coexistence region, despite the kinetic delay in ordering observed in SAXS

data for samples **1K** and **1J** (see Supporting Information for temperature-dependent SAXS data).

Theoretically, the composition region located between lamellae and hexagonally packed cylinders should be occupied, at equilibrium, by the bicontinuous gyroid phase.^{29,30,86,87} However, in many experimental systems, the gyroid network is often replaced by alternate morphologies, such as the near free energy equivalent, but metastable HPL phase,^{86,88,89} or a coexistence of Lam and Hex phases like that observed here.^{21,52,75,78,90–95} Typically, such metastable phases or phase coexistence are generated as a byproduct of postsynthesis, nonequilibrium solvent removal,^{75,78,91} and have been shown in several cases to eventually adopt the equilibrium gyroid morphology with extended annealing.^{90,94} However, recent theoretical efforts by Matsen⁹⁶ have shown that high levels of polydispersity can give rise to thermodynamically favored phase coexistence. In addition, phase coexistence is preferred and replaces the gyroid region at higher segregations in polydisperse samples.⁹⁶ Such polydispersity-driven phase coexistence has now been suspected in a number of recently studied experimental systems.^{97–100} Given the limited knowledge of the overall polydispersity in our samples, both solvent-induced (nonequilibrium) and polydispersity-driven (equilibrium) coexistence stand as possible explanations for the coexistence region. In an attempt to shed light on the true nature and stability of the observed phase coexistence, sample **1J** was annealed (under vacuum) at 150 °C for a total of 2-months. As shown in Figure 4.8, the relative intensities of Hex and Lam reflection sets change quite dramatically. In the initial scattering collected after only 5 min annealing, the primary scattering peak is fairly broad with strong reflections at $q/q^{*,\text{lam}}$ ratios of $\sqrt{1}$, $\sqrt{4}$, and $\sqrt{16}$ and $q/q^{*,\text{hex}}$ ratios of $\sqrt{1}$, $\sqrt{3}$, $\sqrt{7}$, and $\sqrt{9}$, indicating the presence of both phases in relatively significant quantities.

After 10 days of annealing, the primary scattering peak has begun to sharpen, with hexagonal phase reflections increasing in magnitude and becoming more easily resolved. In contrast, the lamellae scattering intensity has begun to decrease, revealing the sample composition shift toward the hexagonal phase. Most notably, the Lam diffraction peak at $q/q^{*,\text{lam}} = \sqrt{4}$ changes from being more intense than the hexagonal diffraction peak at $q/q^{*,\text{hex}} = \sqrt{3}$ to being nearly equal. At 2-months, the Lam character has decreased further, with the lamellae diffraction peak at $q/q^{*,\text{lam}} = \sqrt{4}$ now much less intense compared to the hexagonal diffraction peak at $q/q^{*,\text{hex}} = \sqrt{3}$ and the lamellae diffraction peak at $q/q^{*,\text{lam}} = \sqrt{16}$ now completely absent. In addition, the primary peak continues to sharpen, and the hexagonal diffraction peak at $q/q^{*,\text{hex}} = \sqrt{4}$ has become more pronounced. The sharpening of the primary peak throughout the annealing process is assumed to be a consequence of the decreasing contribution by $q^{*,\text{lam}}$. From this data, it is clear that the sample is evolving toward a higher concentration of the Hex phase. However, the 2-month experiment does not provide sufficient evidence to determine whether a new (equilibrium), Hex-rich distribution of Hex and Lam is simply being established or the sample is evolving exclusively toward the Hex phase as its equilibrium morphology. It appears, at least, that the initial concentration of Lam and Hex phases is likely influenced by rapid removal of CH_2Cl_2 during the synthetic work-up, and the sample thermodynamically prefers larger concentrations of the hexagonal phase. Clearly, however, the phase coexistence is quite persistent in these DOD-IMD BCPs and cannot be easily displaced even if it is a non-equilibrium state.

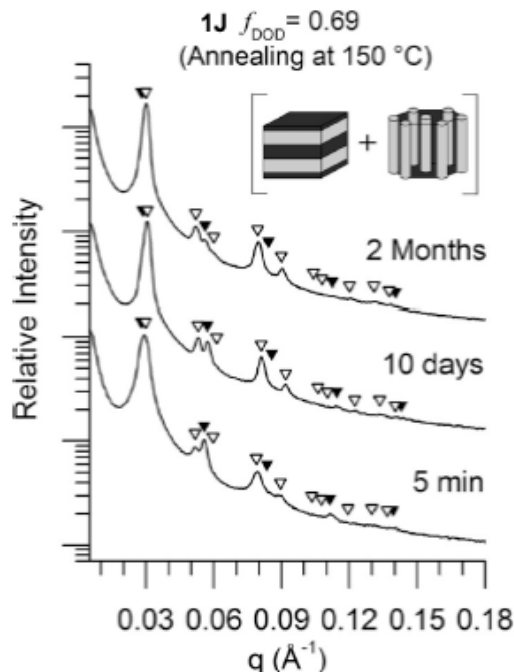


Figure 4.8. SAXS data of sample **1J** annealing at 150 °C for a total of 2 months, depicting the very slow ordering kinetics that suppresses the Lam phase and transitions toward a pure Hex phase, which is evident by the increased intensity of Hex reflections coupled with the substantial decrease in Lam reflection intensity with time. Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: $q/q^{*,\text{hex}}$ at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. Inverted solid triangles represent the locations of allowed reflections for the Lam morphology, $q^* = q_{100}$: $q/q^{*,\text{lam}}$ at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, etc.

Importantly, no evidence of any evolution toward the gyroid phase was found in sample **1J** after the 2-month annealing experiment. Persistent Hex and Lam phase coexistence in the gyroid region has been reported for a number of experimental diblock copolymer systems.^{21,90,94} The majority of incidences are associated with BCPs that, due to high degrees of polymerization or high values of χ , are inherently strongly segregated in the phase-separated state. Not coincidentally, the gyroid phase boundaries were originally suspected to converge upon reaching the intermediate segregation regime,^{86,101} which appeared to be supported by experimental results. However, it has been more

recently shown by Cochran et al.¹⁰² that the gyroid phase window actually extends deep into the intermediate to strong segregation regime, albeit over a very narrow composition window. These new results seem to bolster an earlier report by Lodge and co-workers,⁷⁴ in which they had conclusively identified the existence of the gyroid phase in strongly segregated polybutadiene-*b*-poly(hexafluoropropylene oxide) BCPs. However, that report appears to be the exception, not the rule, for most highly segregated systems studied thus far. Of particular relevance in that list are the very recent studies by Mahanthappa²¹ on BCPs containing charged imidazolium-based IL derivatives of polystyrene, where they found persistent Hex and Lam coexistence at the apparent expense of the gyroid morphology. Somewhat related, Lodge and co-workers⁹³ also just reported Hex and Lam coexistence in solutions of uncharged BCPs dissolved in charged IL solvents. The persistence of Hex and Lam coexistence in samples **1J–1L**, considered with the coexistence behavior documented in these other ionic BCP systems,^{21,93} suggests that strong degree of segregation imposed by the charged–uncharged architecture severely hinders gyroid formation. The significant penalties for mixing, and therefore chain rearrangement, effectively create a large activation energy for the transformation of the Hex/Lam mixture to the gyroid phase.¹⁰³ This is, of course, compounded by the (predicted) narrowness of the gyroid phase window in the strong segregation regime.¹⁰²

It is also worth mentioning the DOD–IMD BCPs likely exhibit a significant degree of conformational asymmetry arising from large differences in the DOD (dodecyl ester side chain) and IMD (substituted imidazole) block statistical segment lengths. It is possible that due to conformational asymmetry, the gyroid region may exist on the opposite side of the phase diagram (majority component IMD), which we have yet to

explore. The effects of conformationally asymmetric BCPs have been studied both theoretically¹⁰⁴ and experimentally.^{60,105} Theoretically, the results of conformational asymmetry reveal a shift in phase boundaries and a narrowing of the gyroid region on one side of the phase diagram. However, the overall trend of phase boundaries remain intact; that is, the gyroid region exists between the lamellae and hexagonal phase boundaries on both sides of the phase diagram. In support of the theoretical work by Matsen,¹⁰⁴ experimental studies by Hamley¹⁰⁵ and Floudas⁶⁰ with highly asymmetric BCPs showed the gyroid region exists on both sides of the phase diagram, albeit in shifted nontraditional composition windows. Interestingly, in the experimental work by Hamley,¹⁰⁵ a coexistence of Hex and Lam domains was suspected (from SAXS data) in addition to the confirmed gyroid morphology within the region of space between the pure Hex and Lam boundaries. It is possible that conformational asymmetry is contributing to the difficulty in locating the gyroid region in our DOD–IMD BCP system. However, in both prior experimental studies^{60,105} with highly conformationally asymmetric BCPs, the gyroid region was still identified on both sides of the phase diagram. Thus, in our DOD–IMD BCP system, which contains an exclusive region of Hex and Lam domains in place of the gyroid region on one side of the phase diagram, locating a gyroid region on the opposite side based on conformational asymmetry arguments alone may prove unlikely.

In brief, there are three contributing factors we considered for the absence of the gyroid phase including polydispersity, high segregation strength, and conformational asymmetry. We believe the most probable and dominant culprit responsible for the absence of the gyroid phase is the high segregation strength between the DOD and IMD

blocks. Access to the gyroid morphology may require highly controlled synthetic methodologies able to pinpoint compositions precisely as well as extensive combinations of solvent, thermal, and mechanical annealing treatments to facilitate its formation from non-equilibrium starting positions. Applications targeting co-continuous networks such as the gyroid phase in imidazolium poly(RTIL)-containing diblock copolymers may ultimately prove impractical.

4.3.2.4 Spherical

This region of the phase diagram is defined by the most asymmetric samples **1D–1F** with a composition range of 84–96 vol % DOD. Samples **1D** and **1E** both exhibited scattering characterized by broad, subtle oscillations typical of form factor scattering from individual spheres. The absence of clear diffraction peaks other than the primary reflection (Figure 4.9) is consistent with a poorly ordered LLP morphology commonly observed at such asymmetric BCP compositions. The absence of an organized lattice is typically attributed to sphere polydispersity associated with limited chain diffusion and mobility.^{106–111} Rheological temperature ramp tests of samples **1D** and **1E** show viscoelastic properties indicative of enhanced liquid-like behavior, characterized by a loss modulus (G'') exceeding the storage modulus (G') throughout the temperature ramp profile. There is no evidence of a sharp decrease in moduli characteristic of a traditional order-to-disorder (ODT) transition; in contrast, both samples **1D** and **1E** show a steady decrease in moduli with heating. The noise in the rheology profiles of samples **1D** and **1E** at higher temperatures is an artifact of torque resolution limits associated with the rheology instrumentation using the 8 mm, parallel plate configuration. Use of larger

diameter plates to improve the signal-to-noise ratio was constrained by limited material availability. As an alternative, the presence of an ODT in samples **1D** and **1E** was probed by looking for a clear transition SAXS. This transition, marked by increased broadness in the primary peak location, and a sharp decrease in intensity as the BCP becomes a homogeneous isotropic liquid, can be difficult to identify in the absence of a strongly diffracting ordered phase. For sample **1D**, there appears to be a significant change in the SAXS profile upon heating past 75 °C, where the intensity of the scattering is severely reduced and the second oscillation in the particle form factor becomes indistinguishable from the broad primary peak. Evidence of disordering was even more ambiguous in sample **1E**, where around 175 °C there is a 2-fold decrease in scattering intensity, but the primary scattering reflection seems to maintain some degree of sharpness. We suspect that sample **1E** may be exhibiting a persistence of disordered spherical micelles¹⁰⁹ across a large temperature range due in part to the very strong segregation of the DOD and IMD blocks. Because of the ambiguity of order in both samples **1D** and **1E**, coupled with the extreme asymmetry in composition, no efforts were made to extract $\chi(T)$ from the scattering data for these samples (as previously discussed).

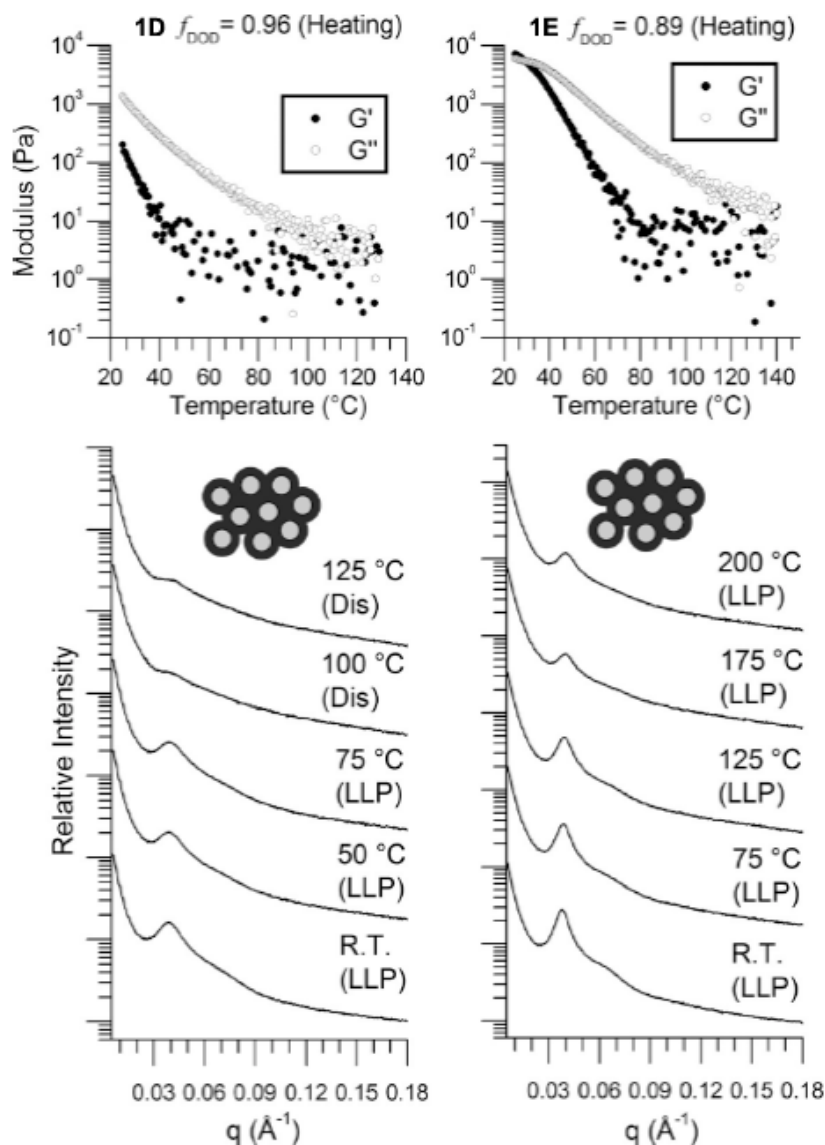


Figure 4.9. Dynamic temperature ramp (first heating cycle) for samples **1D** (left) and **1E** (right) at $1\text{ }^{\circ}\text{C min}^{-1}$, 1 rad s^{-1} with 30 and 8% strain, respectively (within the linear viscoelastic regime). The rheological behavior of both samples is characteristic of enhanced liquid-like properties where G'' is greater than G' . No clear ODT is observed via rheology in either sample. SAXS data of sample **1D** (left) and **1E** (right) along a complete heating thermal cycle are both indicative of a LLP of spheres, evident by broadness of scattering and absence of higher order diffraction reflections. Sample **1D** appears to clearly disorder upon heating marked by the drastic decrease in intensity and enhanced broadness of the scattering. In contrast, sample **1E** retains a fairly intense primary scattering peak throughout the entire heating cycle.

Highly ordered spheres on a body-centered-cubic lattice (SBCC) were observed in sample **1F** with a volume fraction of 0.84 DOD. SAXS data are plotted in Figure 4.10 for sample **1F** and show diffraction peaks consistent with the symmetry of the SBCC lattice with q/q^* ratios of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$, etc. Here, $q^* = q_{100}$ which is absent due to the reflection conditions associated with the BCC symmetry. The q_{110} interplanar spacing at 125 °C is 16.4 nm. Similar to the Hex forming BCPs, sample **1F** required an initial heating step to achieve a level of order that produces highly resolved SBCC diffraction patterns. As shown in the SAXS data of Figure 4.10, there is a sufficient delay in obtaining highly ordered BCC spheres in the first heating cycle. The gradual ordering process, evident by an evolution of the diffraction pattern from one with broad, form factor oscillations at room temperature, to one with multiple, easily resolved diffraction peaks at 100 °C and above. The rheological behavior is also consistent with the observed delay in the ordering process, evident by clear transition at 100 °C in the dynamic temperature ramp experiment (also Figure 4.10). As mentioned previously, this type of behavior in which LLP of spheres often exists prior to development of the fully organized SBCC lattice is fairly common in other BCP systems.^{79–81} As with the Hex-forming samples, the highly ordered structure established during the initial heating remains preserved during subsequent cooling and heating cycles, with no further evidence of any rheological transitions or decay in diffraction intensity signaling a return to the weakly ordered state (Figure 4.10).

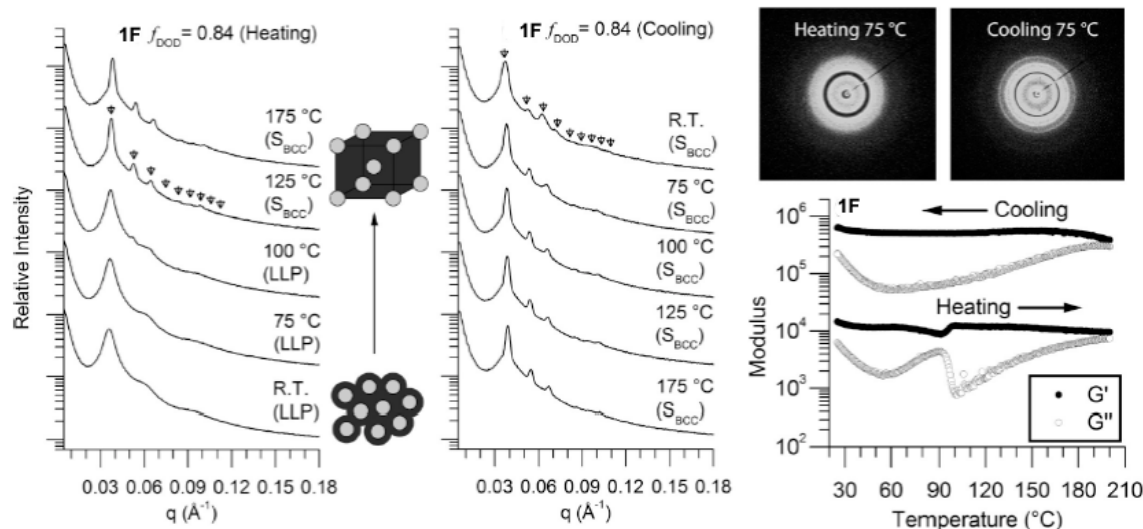


Figure 4.10. SAXS data of sample **1F** along a complete heating (left) and cooling (center) thermal cycle. Morphologies observed during heating include a distorted poorly ordered LLP of spherical domains before obtaining the well-ordered SBCC morphology. Upon cooling, the highly ordered SBCC phase is preserved. Inverted triangles with a strikethrough represent the locations of allowed reflections for the SBCC morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$ (absent for SBCC): q/q^* at $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$, etc. Dynamic temperature ramp heating and cooling cycle of **1F** (right) at $1\text{ }^\circ\text{C min}^{-1}$, 1 rad s^{-1} , and 8% strain (within the linear viscoelastic regime). The cooling cycle has been shifted vertically 2 orders of magnitude for clarity. The rheological behavior mimics that of the SAXS, where a subtle transition is observed upon obtaining the well-ordered SBCC morphology during heating, while any transitions are notably absent upon cooling. Insets are 2D scattering patterns depicting the initial weakly ordered morphology and final highly ordered morphology after the melt-processing.

4.4 Summary

A total of 16 alkyl–ionic DOD–IMD BCPs spanning compositions of 42–96 vol % DOD were extensively characterized using SAXS and rheology to develop a clear picture of the morphological phase behavior in these novel poly(RTIL)-containing BCP systems. The unique charged–uncharged BCP architecture produced each of the classic equilibrium morphologies (including lamellae (Lam), hexagonally packed cylinders (Hex), and spheres on a body-centered cubic lattice (SBCC) with the exception of the

bicontinuous gyroid phase. In general, the level of order achieved by the samples was exceptional, routinely producing diffraction patterns with numerous higher order reflections. Hex- and SBCC-forming DOD–IMD BCPs were found to require an initial heating step to induce highly periodic lattice formation but showed no signs of structure degradation during subsequent cooling and heating cycles. Lam samples showed no kinetic delay in ordering. Importantly, all samples (outside of the two most asymmetric) showed excellent preservation of structural order at room temperature, which is extremely important for the future preparation of functional materials built from these poly(RTIL)-based BCPs. Additional morphologies identified include a coexistence of Hex and Lam phases in three samples occupying the traditional gyroid region and a poorly defined liquid-like packing of spheres in the two most asymmetric samples. Annealing experiments on one of the three samples exhibiting Hex and Lam phase coexistence revealed extremely slow transition kinetics favoring increased Hex phase concentrations. Complete elimination of the coexisting Lam phase was not possible over a 2-month annealing period. Likewise, no evidence of gyroid formation was detected in the coexistence region or any other sample investigated. Ultimately, the strong degree of segregation inherent to the charged–uncharged architecture may limit the ability of the system to form the idealized gyroid network often sought for transport-related applications. Additional experiments involving advanced solvent, thermal, and mechanical annealing combinations may be necessary to achieve its formation. The inherent segregation strength also resulted in difficulties accessing order-to-disorder transitions and therefore complicated the measurement of a Flory interaction parameter, χ , for the system. Failure to disorder even the lowest molecular weight symmetric sample

with degree of polymerization of ~ 12 confirmed that accessible phase behavior for these BCPs is likely constrained to that of the strongly segregated regime. Investigation of these DOD–IMD BCPs as membranes for use in CO₂/light gas separations is currently underway.

4.5 Experimental section

4.5.1 Materials and Methods

1-Bromohexane, 1-dodecanol, 5-norbornene-2-carboxylic acid, ethyl vinyl ether, and oxalyl dichloride (Sigma-Aldrich) as well as dicyclopentadiene and 1-vinylimidazole (TCI America) were used as received without further purification. Lithium bis(trifluoromethylsulfonyl)amide (LiTf₂N) was purchased as Fluorad lithium trifluoromethanesulfonimide from the 3M Company. All solvents were purchased from Sigma-Aldrich or Mallinckrodt, Inc., and purified/dehydrated via N₂-pressurized activated alumina columns and subsequently degassed. Additionally, the CH₂Cl₂ used as the solvent in ring-opening metathesis polymerization (ROMP) reactions was purified by refiltering over activated alumina prior to degassing. H₂O used for synthesis was purified and deionized, with resistivity greater than 12 MΩ cm⁻¹. All chemical syntheses were carried out in a dry argon atmosphere using standard Schlenk line techniques, unless otherwise noted. Silica gel purification was performed using 230–400 mesh, normal-phase silica gel purchased from Sorbent Technologies.

4.5.2 General Synthetic Procedures for the Synthesis of Imidazolium-Based Alkyl-Ionic BCPs

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (endo:exo 80:20) (monomer **2**) and 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3*H*-imidazoliumbis-(trifluoromethylsulfonyl) amide (endo:exo 80:20) (monomer **3**) were prepared as previously described in the literature and found to have consistent spectroscopic and purity analysis.⁴⁶ In a procedure adapted from Wiesenauer et al.,⁴⁶ a flame-dried Schlenk flask with a PTFE stirbar was charged with the desired amount of Grubbs first-generation catalyst CH₂Cl₂ solution under a positive pressure of argon. Monomer **2** was then added to the catalyst solution from a dry degassed CH₂Cl₂ stock solution via syringe under argon atmosphere. Upon complete consumption of monomer **2** (as verified by ¹H NMR analysis) to form the first copolymer block, the second monomer **3** was added from a dry, degassed stock CH₂Cl₂ solution via syringe. After complete consumption of monomer **3** (as verified by ¹H NMR analysis), the ROMP diblock copolymerization mixture was quenched with an excess of ethyl vinyl ether. The resulting diblock copolymer was then isolated by removal of the solvent *in vacuo* (48 h, 25 °C). ¹H NMR analysis of BCPs **1D–S** also confirmed the absence of any residual monomer. The alkyl-imidazolium block fractions were determined by relative integrations of the ¹H NMR signals of each block. The number of repeat units of the dodecyl and imidazolium blocks were calculated based on the predetermined catalyst-to-monomer loading ratios assuming complete conversion of monomers **2** and **3**, evident by the absence of monomer by ¹H NMR analysis and living character determined in our previous report. Lastly, the M_n values are estimated by multiplying the block lengths by the corresponding monomer repeat unit molecular weight values.⁴⁶

4.5.3 Representative Synthesis of Diblock Copolymer 1S

Under an argon atmosphere, Grubbs' first-generation catalyst (16.4 mg, 0.0199 mmol) was dissolved in dry, degassed CH_2Cl_2 (0.75 mL). Monomer **2** (7.65 g, 24.9 mmol) was diluted to a total volume of 25 mL with CH_2Cl_2 . From this monomer solution, 0.49 mL (0.49 mmol) was added to the catalyst solution, and the reaction mixture was stirred at room temperature until the polymerization of **2** was complete (~ 3 h). Monomer **3** (13.5 g, 25.1 mmol) was diluted to a total volume of 25 mL with CH_2Cl_2 . Monomer **3** (0.49 mL, 0.49 mmol) was then added to the living ROMP polymerization mixture containing polymerized **2**, and the reaction mixture was stirred at room temperature for 12 h. The ROMP copolymerization mixture was then quenched by addition of excess ethyl vinyl ether (1 mL). The resulting diblock copolymer **1S** was isolated by removal of excess solvent and other volatile compounds in vacuo (48 h, 25 °C). Yield: 0.435 g (99%). ^1H NMR (300 MHz, CDCl_3) δ : 8.50–8.75 (br s, imidazolium C2), 7.27–7.47 (br s, imidazolium C4 and C5), 5.27–5.52 (b, $-\text{C}(\text{H})=\text{C}(\text{H})-$), 3.75–4.45 (b, $-\text{COO}-\text{CH}_2-$, $-\text{C}(\text{H})_2-\text{N}-\text{CH}-\text{N}-\text{C}(\text{H})_2-(\text{CH}_2)_4\text{CH}_3$), 2.35–3.15 (br m, $-\text{imidazolium}-(\text{CH}_2)_5-\text{CH}_3$), 1.50–2.25 (b, $-\text{COO}-(\text{CH}_2)_{11}-\text{CH}_3$), 0.95–1.45 (br m, $-\text{COO}-\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3$), 0.72–0.90 (br m, $-\text{imidazolium}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$). Block repeat unit molar ratio = 1:0.90 (alkyl:imidazolium); block length composition = 25-*b*-23; estimated $M_n = 20\,100\text{ g mol}^{-1}$.

4.5.4 Physical Measurements

^1H and ^{13}C NMR spectra were obtained using a Bruker 300 Ultrashield (300 MHz for ^1H) spectrometer. Chemical shifts are reported in ppm relative to residual protio

solvent, CHCl_3 . Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC 1 series thermal gravimetric analyzer. For TGA, samples were tested from 30–500 °C at a temperature ramp rate of 20 °C min^{-1} in an aluminum pan under a N_2 atmosphere.

4.5.5 Sample Preparation for Morphological Analysis

Samples were studied largely as synthesis products (after verifying absence of any unreacted monomer via ^1H NMR). Diblock copolymers were ultimately isolated in vials by removal of excess CH_2Cl_2 solvent and other volatile compounds *in vacuo*. The samples were then stored at room temperature prior to collection of data. No special solvent casting or thermal annealing was performed prior to dynamic mechanical spectroscopy and small-angle X-ray scattering.

4.5.6 Dynamic Mechanical Spectroscopy

Rheological experiments were run using a TA Instruments Advanced Rheometric Expansion System (ARES) rheometer outfitted with a nitrogen purged oven. Samples were roughly formed as disks by hand and then positioned between two parallel plates (8 mm diameter). The gap was reduced and adjusted to ensure even distribution of the sample. Typical gaps were 0.3–0.5 mm. Dynamic temperature ramp tests were performed under nitrogen while heating and cooling at 1 °C min^{-1} at an angular frequency of 1 rad s^{-1} and a constant strain (generally 6–8% for the majority of BCP samples studied herein) depending on the linear viscoelastic regime of each copolymer that provides high enough torque values ($>0.01 \text{ g}\cdot\text{cm}$) for acceptable signal-to-noise ratios. Larger parallel plates

(>8 mm) could be used to increase torque (and subsequently increase signal-to-noise); however, such measurements were avoided due to the significant amount of material required.

4.5.7 Small-Angle X-ray Scattering (SAXS)

Small-angle X-ray scattering (SAXS) data were collected using a Rigaku S-Max 3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K α , $\lambda = 1.54 \text{ \AA}$), sample-to-detector distance of 2.19 m, Confocal Max-Flux Optics, Gabriel multiwire area detector (1024×1024 pixel resolution), and a Linkam thermal stage. Copolymer samples were sandwiched between Kapton windows (0.05 mm thick $\times$ 10 mm diameter). Before collection of temperature dependent SAXS data, the sample stage temperature was allowed to equilibrate for 5 min under vacuum, unless otherwise stated. Data were collected under vacuum (~ 100 mtorr) with exposure times for samples typically on the order of 1200–1800 s. 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.

4.5.8 Synchrotron SAXS Characterization

Synchrotron SAXS measurements were performed at the 5-ID-D beamline of the DuPont–Northwestern–DOW Collaborative Access Team (DNDCAT) at the Advanced Photon Source (Argonne, IL). Experiments employed a beam energy of 17 keV ($\lambda = 0.7293 \text{ \AA}$) and a sample-to-detector distance of 2.979 m. Two-dimensional SAXS

patterns were recorded on a MAR-CCD detector (133 mm diameter active circular area) with 2048×2048 pixel resolution. Samples were heated to the desired temperature in a Linkam DSC and allowed to equilibrate for 5 or 10 min prior to data collection with exposure times of 0.1–0.2 s.

4.6 Acknowledgments

T.S.B., V.F.S., and J.R.E. thank the National Science Foundation (grant DMR-0645781) and the Colorado State University (CSU) for supporting the portion of this work performed at CSU. D.L.G., E.F.W., and J.P.E. thank the Advanced Research Projects Agency – Energy (grant DE-AR0000098) and the Defense Threat Reduction Agency (grant HDTRA1-08-1-0028) for support of the portion of this work performed at CU Boulder. The SAXS instrument at CSU is supported by the Central Instrument Facility of the Chemistry Department and the National Science Foundation MRI Program (grant DMR-0821799). We also gratefully thank Adam K. Schmitt and Prof. Mahesh K. Mahanthappa of the University of Wisconsin-Madison for collection of the synchrotron SAXS data on sample **1J**.

4.7 Supporting Information

4.7.1 Morphological Behavior

Table 4.S1. Summary of synthesized imidazolium-based alkyl-ionic BCPs and their corresponding morphological phase behavior.

Lab Notebook Sample Name	Published Sample Name	$m : n$	M_n (DOD)	M_n (DMD)	wt % (DOD)	f_{DOD}	Morphological Behavior
III-064	1D	48.5 : 1.4	14900	800	0.95	0.96	LLP $\rightarrow$ Dis
III-065	1E	47.0 : 3.8	14400	2000	0.88	0.89	LLP
III-066	1F	45.0 : 5.6	13800	3000	0.82	0.84	LLP $\rightarrow$ S _{BCC}
III-067	1G	43.5 : 6.9	13400	3700	0.78	0.81	LLP $\rightarrow$ Hex
III-068	1H	42.0 : 9.5	12900	5100	0.71 ₆	0.74 ₇	LLP $\rightarrow$ Hex
III-069	1I	40.0 : 9.1	12300	4900	0.71 ₅	0.74 ₆	LLP $\rightarrow$ Hex
III-070	1J	38.5 : 11.3	11800	6100	0.66	0.69	Lam + Hex
III-091	1K	37.5 : 12.8	11500	6900	0.63	0.66	Lam + Hex
III-074	1L	36.5 : 13.9	11200	7500	0.60	0.64	Lam + Hex
III-092	1M	35.6 : 14.4	10900	7800	0.58	0.62	Lam
III-076	1N	30.0 : 12.8	9200	6900	0.57	0.61	Lam
III-072	1O	32.0 : 18.0	9800	9700	0.50	0.54	Lam
III-093	1P	7.5 : 5.0	2300	2650	0.46 ₅	0.50 ₄	Lam
III-037	1Q	30.0 : 20.0	9200	10800	0.46 ₀	0.50 ₀	Lam
III-075	1R	15.0 : 10.3	4600	5600	0.45	0.49	Lam
III-107	1S	25.0 : 23.0	7700	12400	0.38	0.42	Lam

4.7.2 Thermogravimetric Analysis (TGA)

TGA was performed on BCPs **1D-S** in order to determine decomposition temperatures for each BCP. Decomposition onset temperatures were similar and ranged in value from 341.8 °C to 353.7 °C, with an average decomposition onset temperature of 347.8 °C.

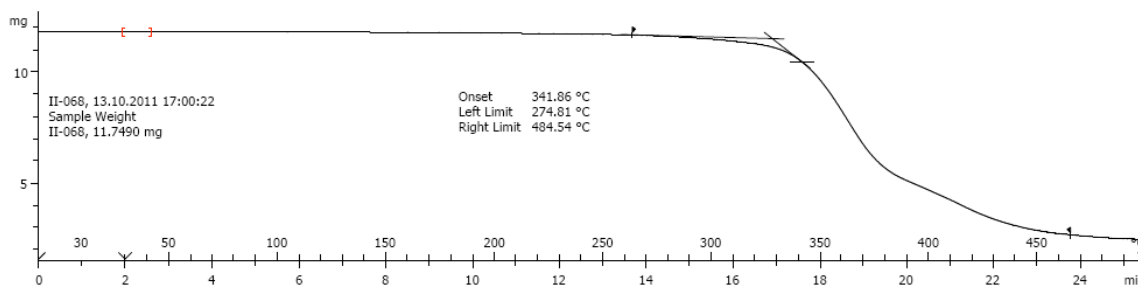


Figure 4.S1. Example TGA analysis profile of BCP **1H** under N₂ (temperature ramp rate: 20 °C min⁻¹).

4.7.3 Temperature-Dependent SAXS and Rheology Data

The following pages include thorough SAXS and rheological temperature dependent data for BCPs 1D-1S (labeled accordingly):

- 1.) Temperature dependent SAXS data (heating and cooling) for BCPs **1D-1S**.

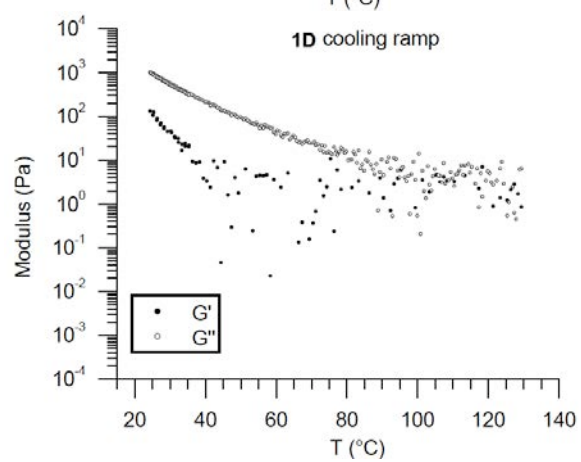
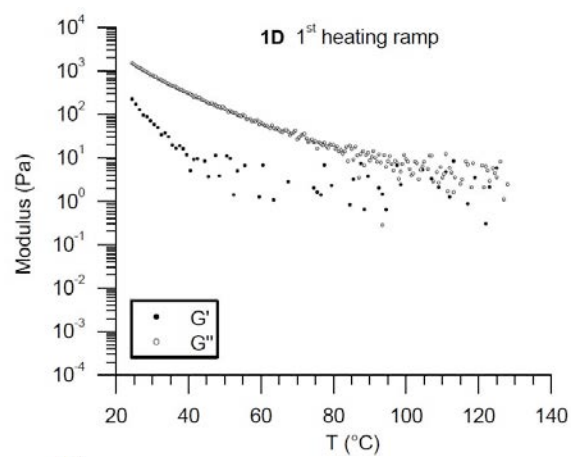
Inverted open triangles represent the locations of allowed reflections for the Hex morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$ etc, inverted solid triangles represent the locations of allowed reflections for the Lam morphology, $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, $\sqrt{36}$, and inverted triangles with a center vertical line represent the locations of allowed reflections for the SBCC morphology, based on the position of the primary scattering wave vector $q^* = q_{100}$ (absent for SBCC): q/q^* at $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, 12, $\sqrt{14}$ etc.

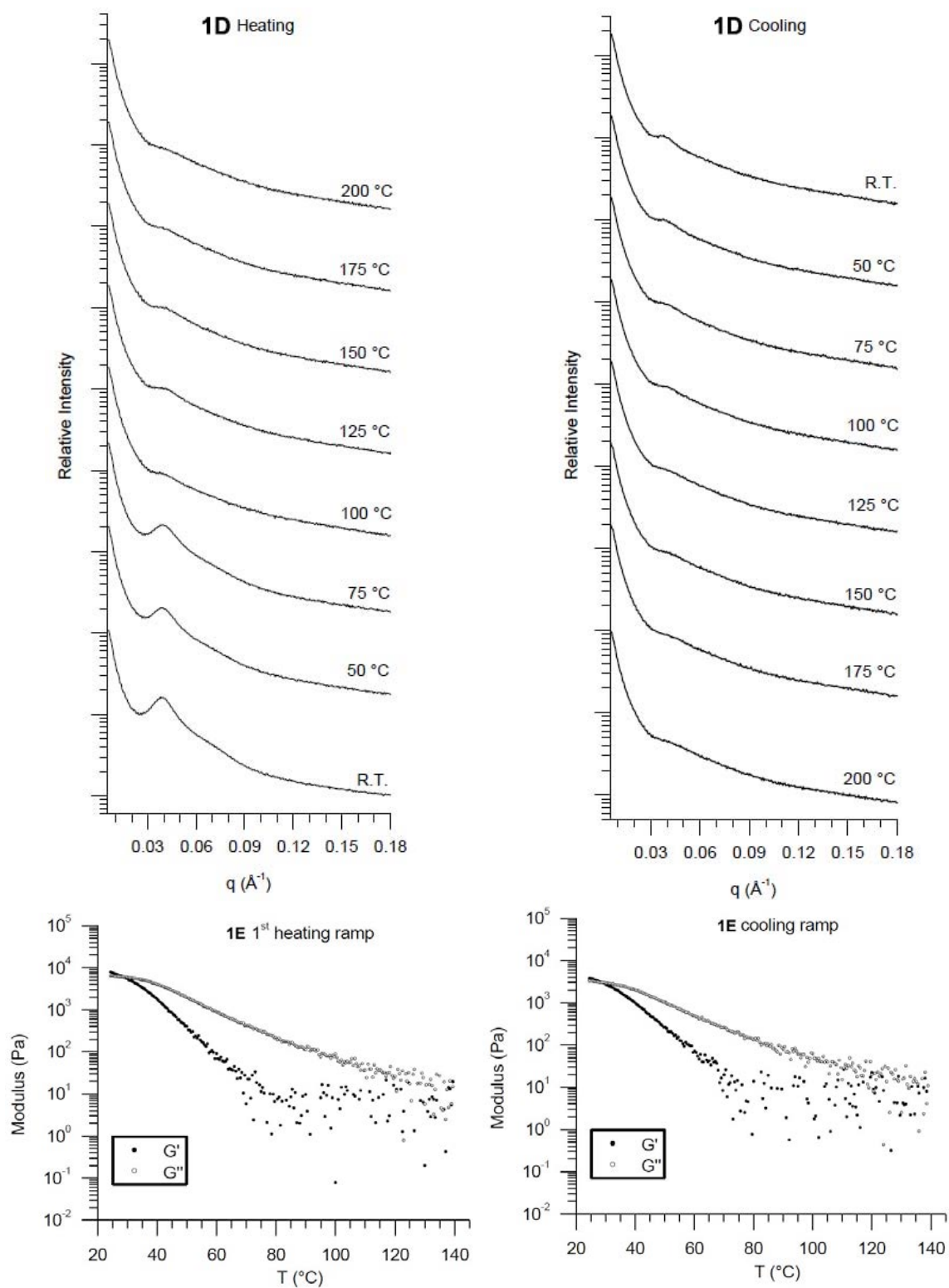
- 2.) Dynamic temperature ramps for BCPs **1D-1S** at 1 °C min⁻¹, 1 rad s⁻¹ and a chosen strain rate within the linear viscoelastic regime (Tabulated below).

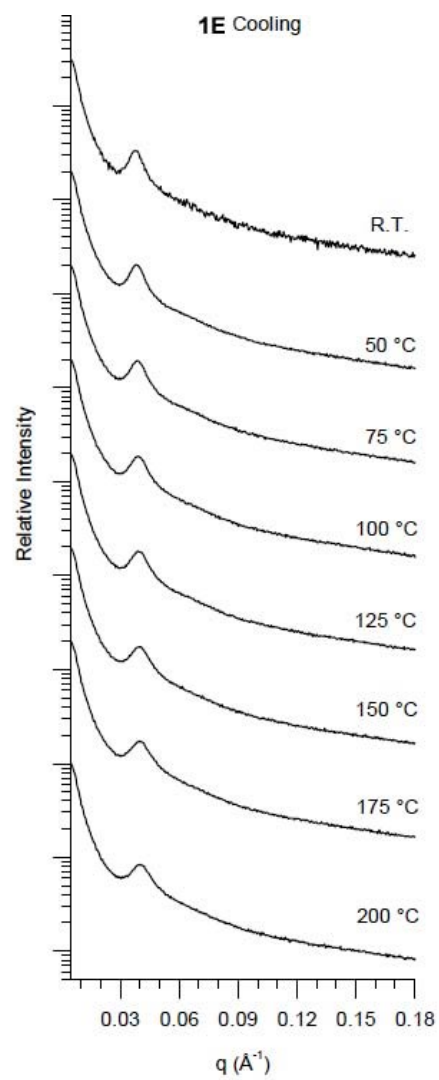
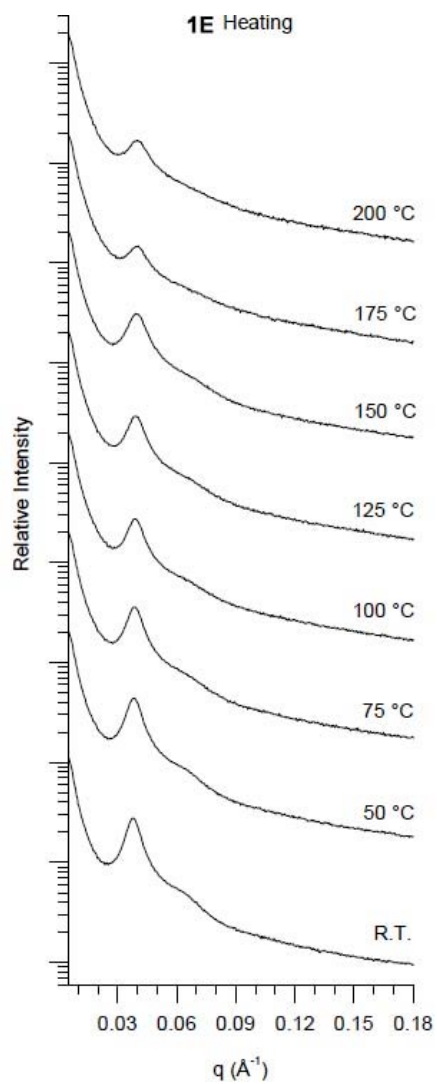
Table 4.S2. Summarized dynamic rheological data for BCPs **1D-1S** at a chosen strain rate within the linear viscoelastic regime.

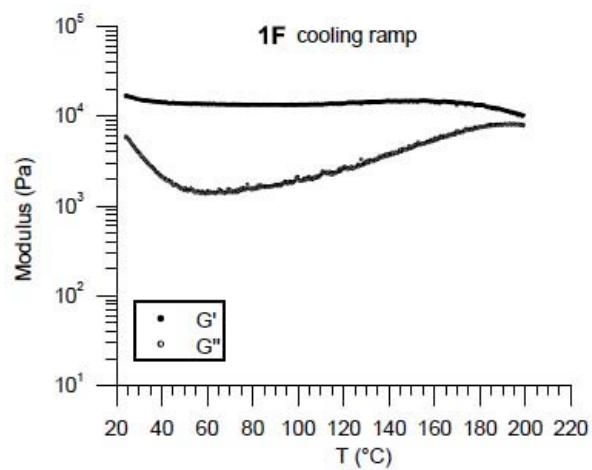
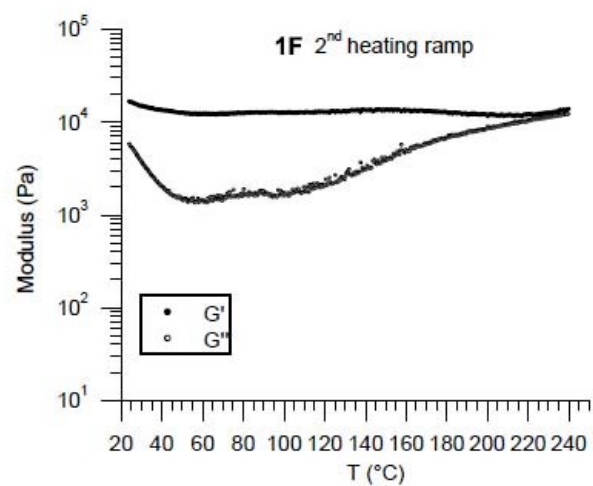
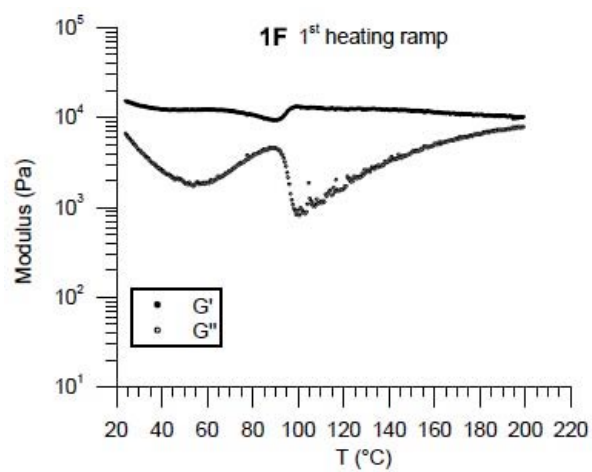
Sample	Rheology strain rate (%) ^a	G' (25 °C, 1 rad s ⁻¹) ^b	G''(25 °C, 1 rad s ⁻¹) ^b
1D	30.0	201	1370
1E	8.0	7210	5930
1F	8.0	14600	6340
1G	8.0	20800	9570
1H	7.0	18900	9400
1I	7.0	13900	8460
1J	7.0	14000	9990
1K	8.0	19700	14600
1L	7.0	15400	13400
1M	8.0	15300	13800
1N	7.0	6650	7080
1O	6.0	25600	23300
1P	2.5	7590	9350
1Q	7.0	31200	26300
1R	7.0	7160	8840
1S	8.0	51000	41900

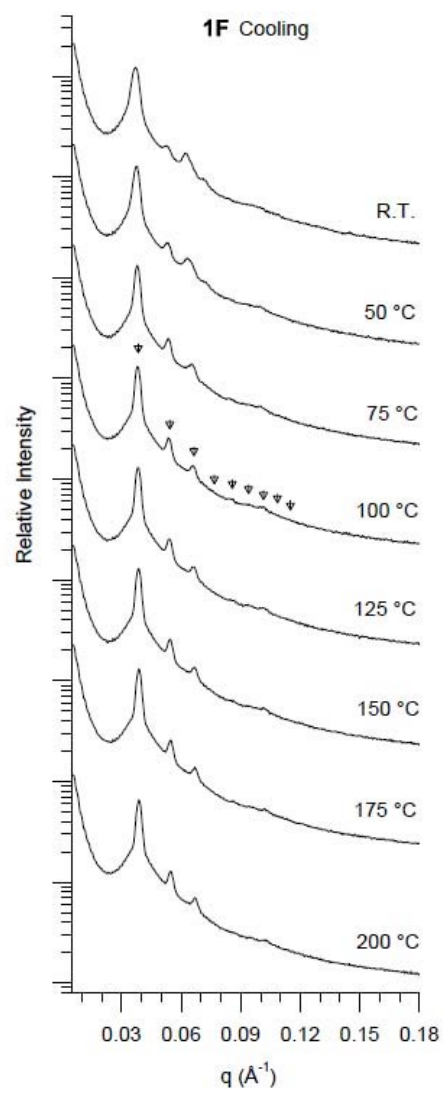
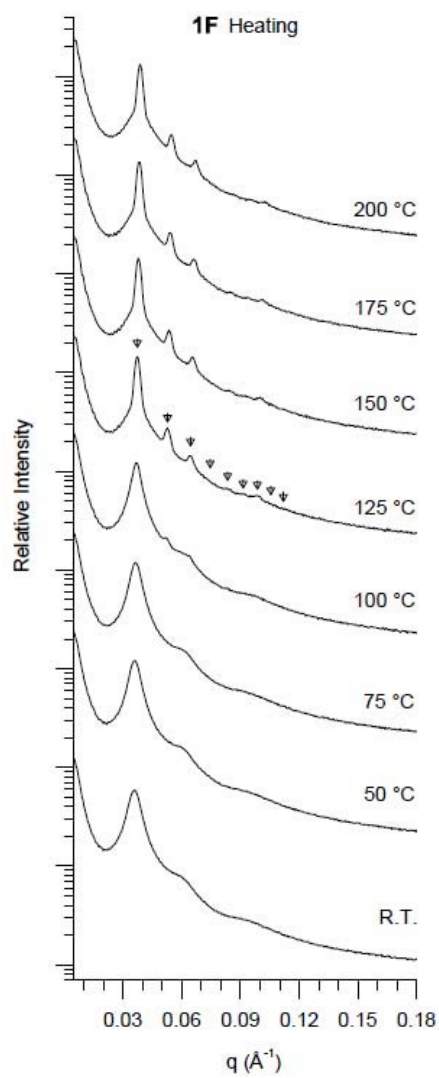
^aStrain rates from dynamic strain sweep experiments (25 °C, 1 rad s⁻¹) used for the dynamic temperature ramp experiments. The strain rates utilized were within the linear viscoelastic regime of each copolymer, and produced high enough torque values (> 0.01 g • cm) for acceptable signal-to-noise ratios. ^bTabulated data of G' and G'' (25 °C, 1 rad s⁻¹) are provided for reference. Complete dynamic temperature ramp data is shown on the following pages.

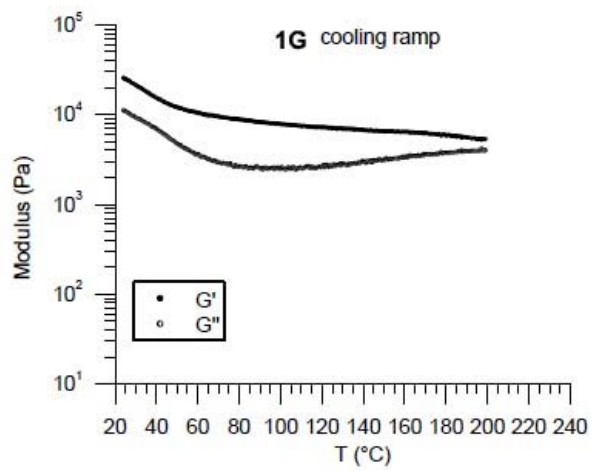
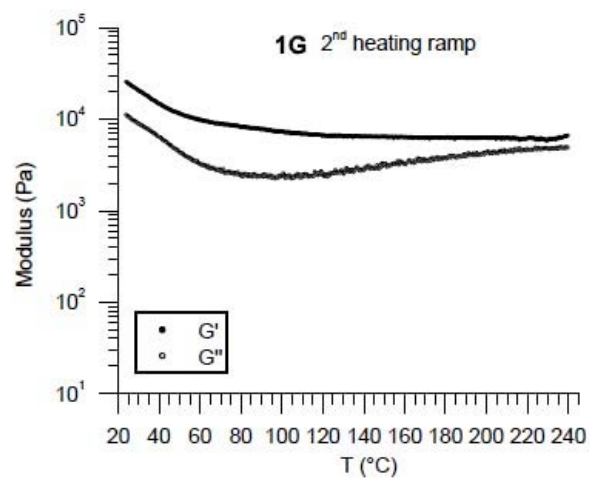
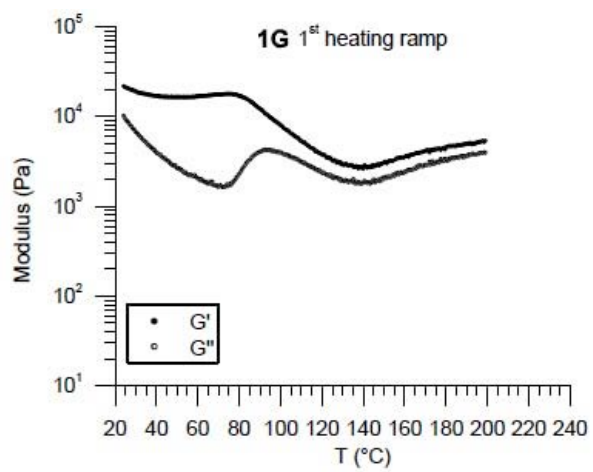


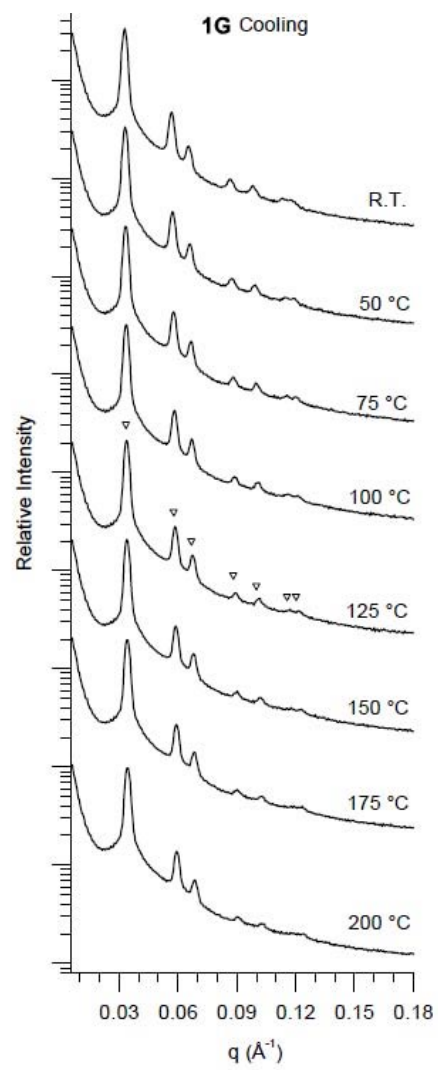
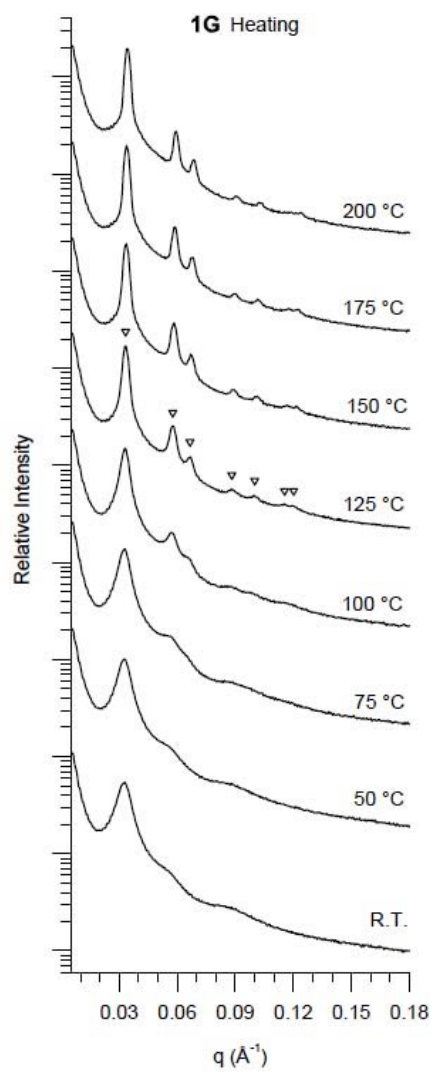


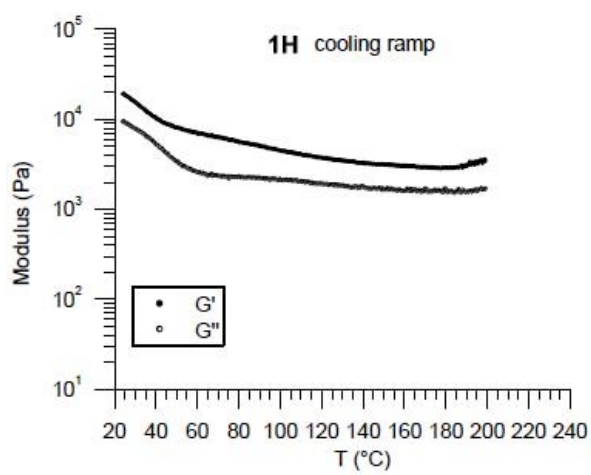
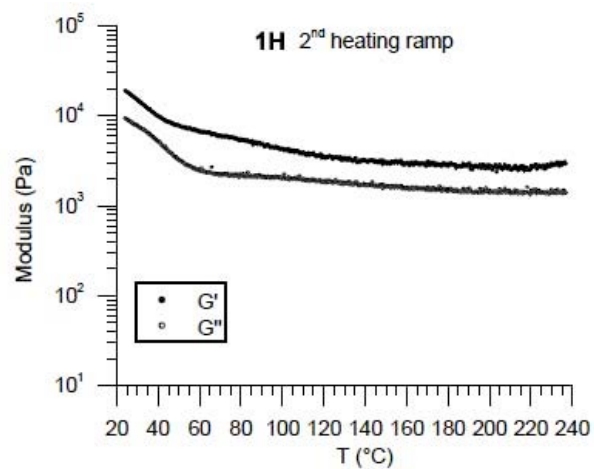
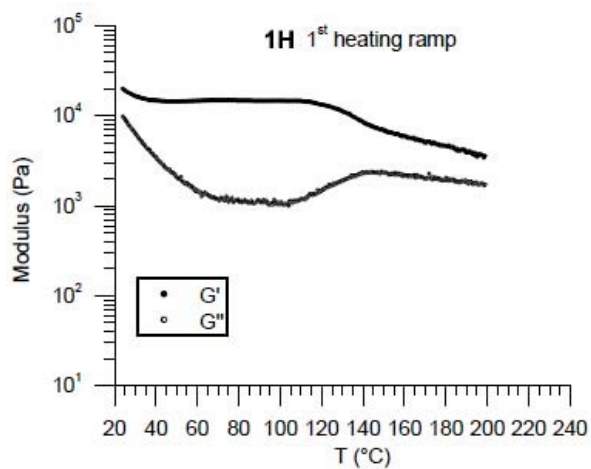


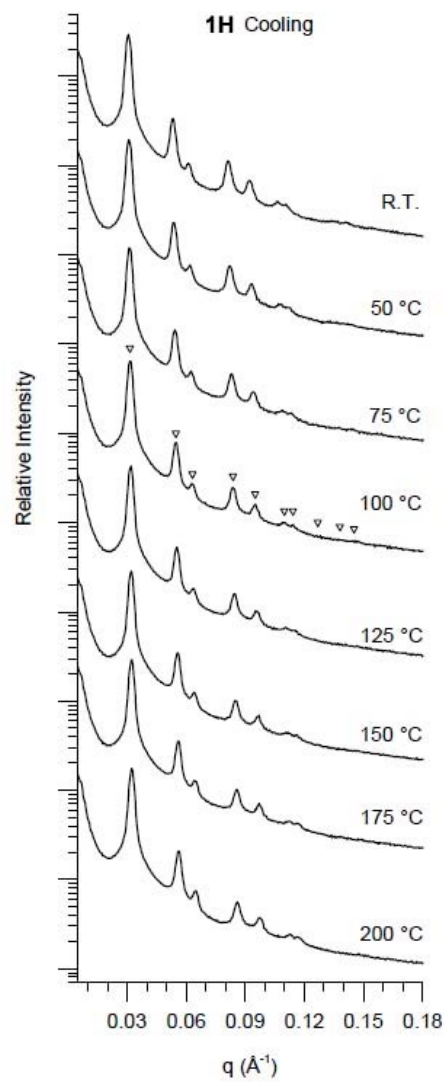
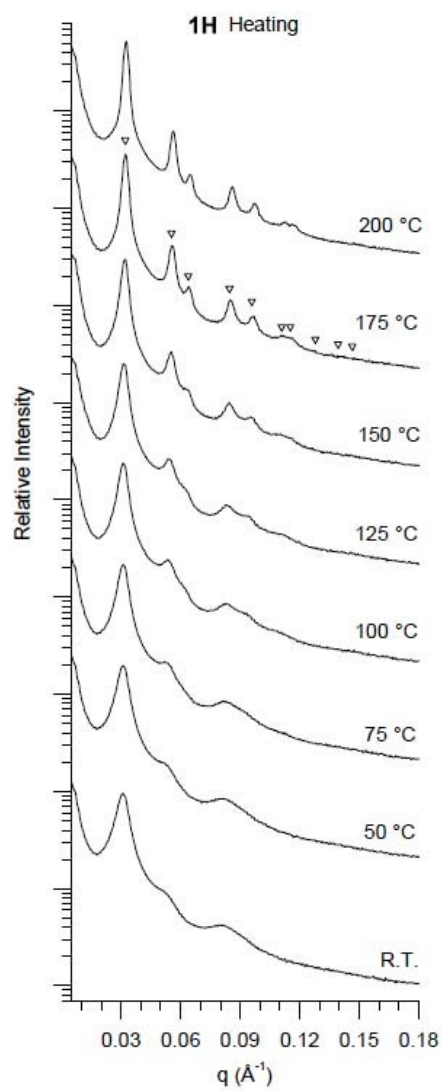


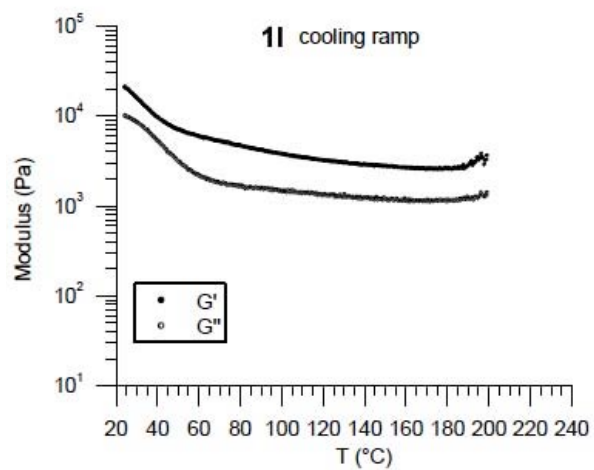
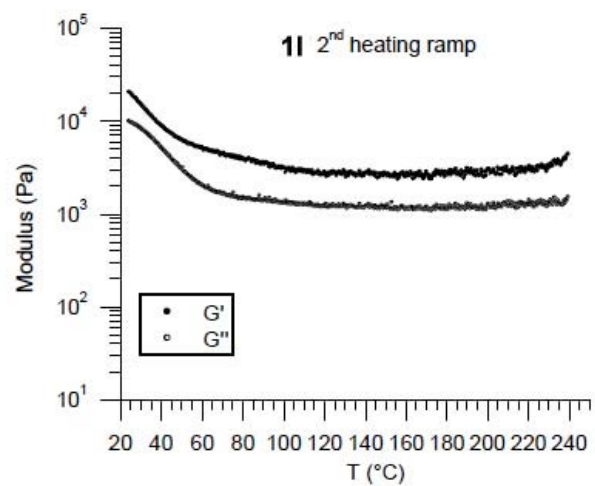
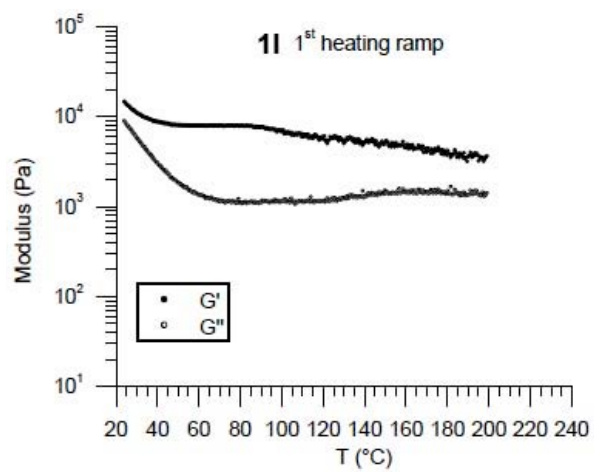


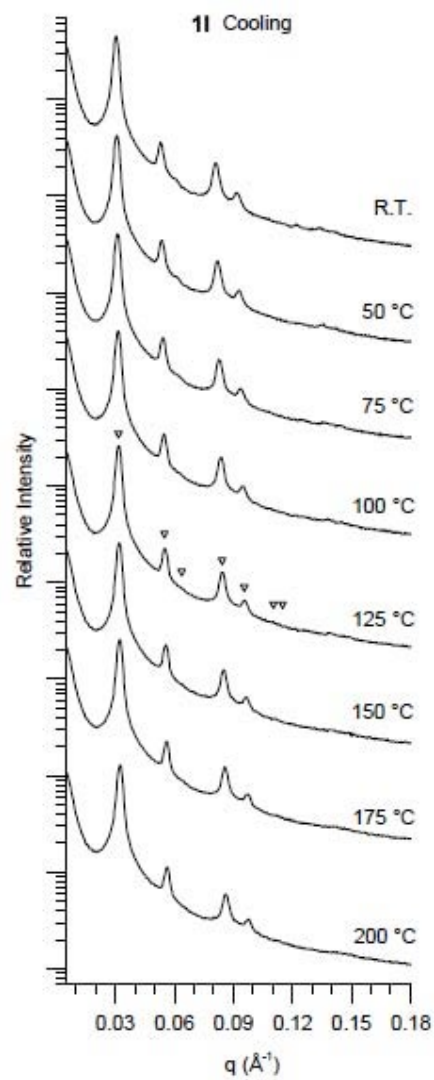
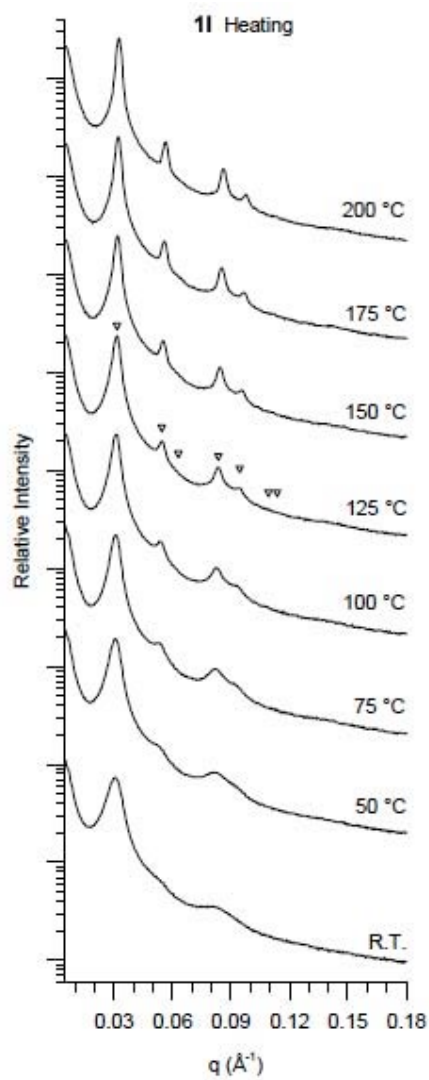


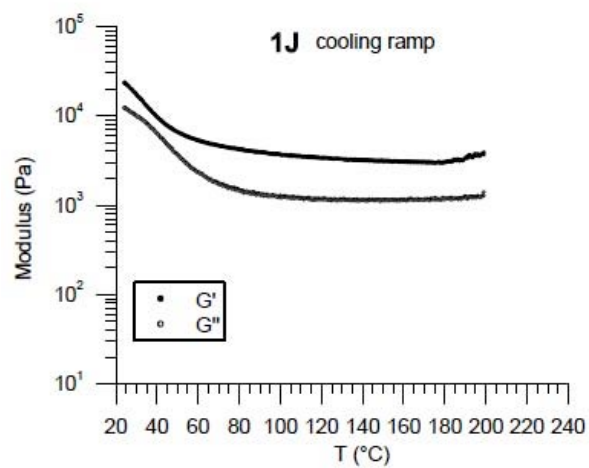
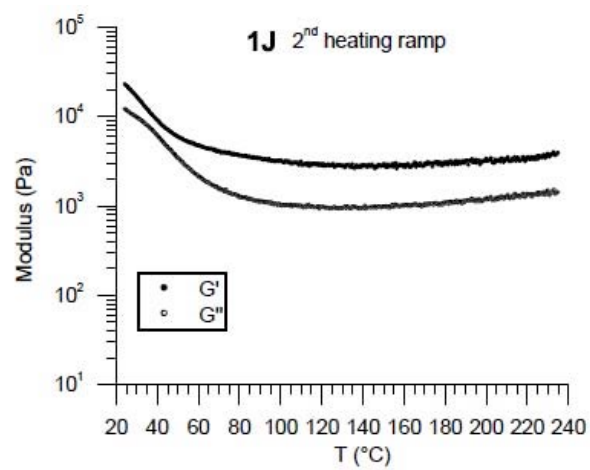
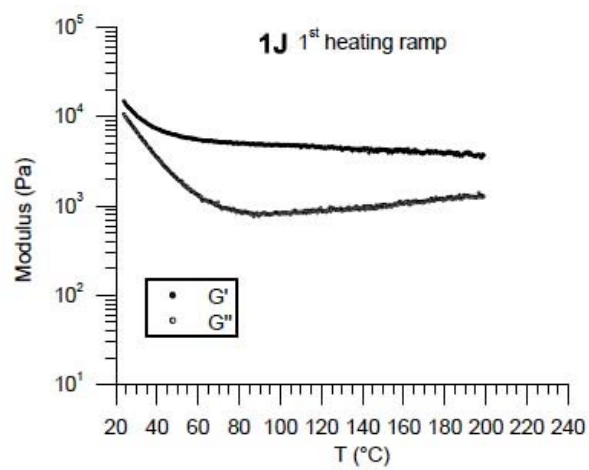


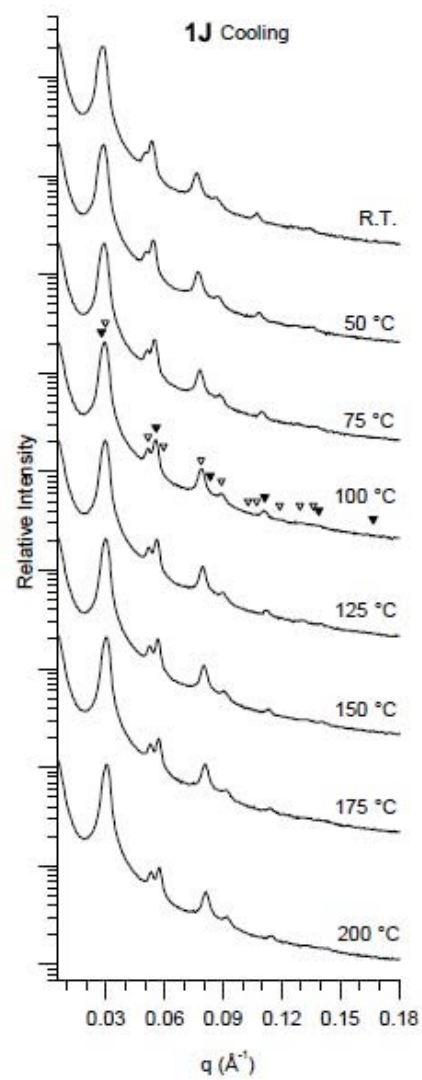
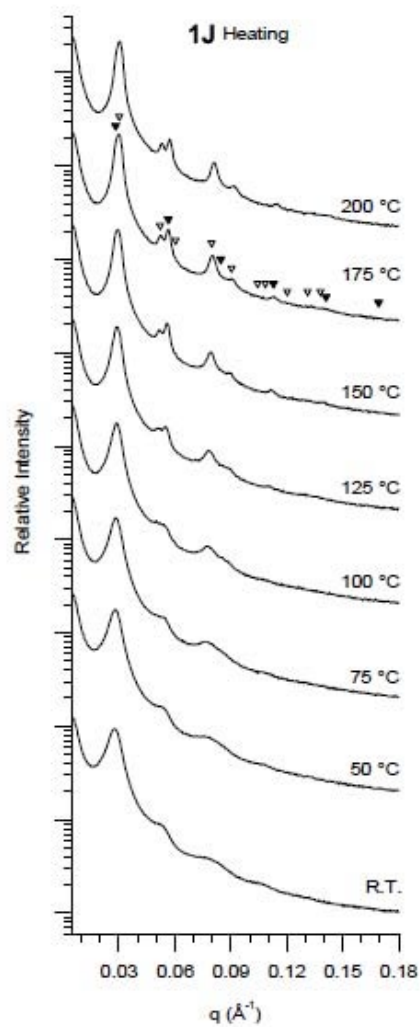


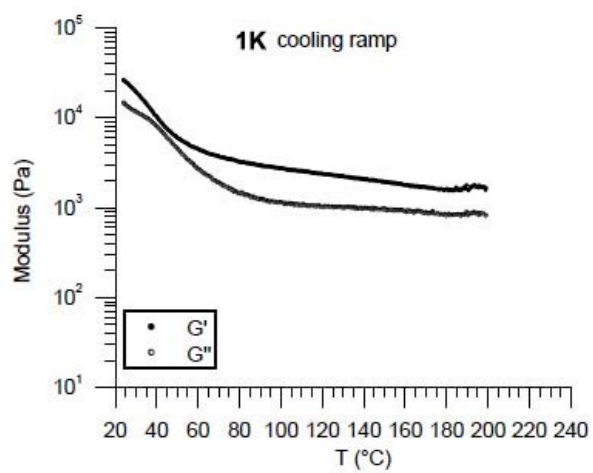
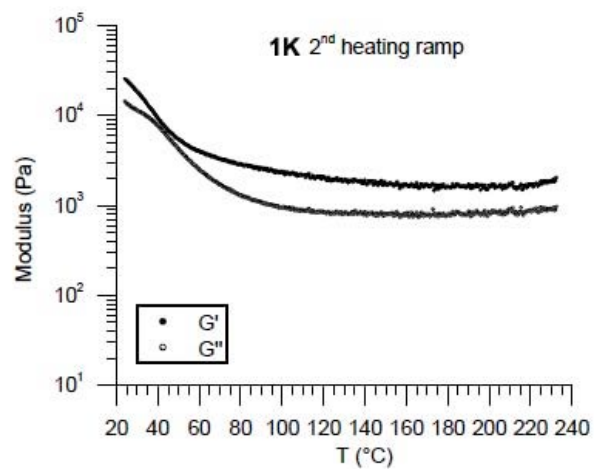
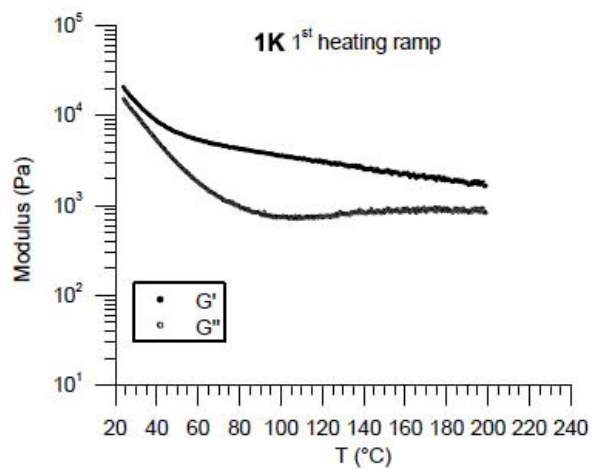


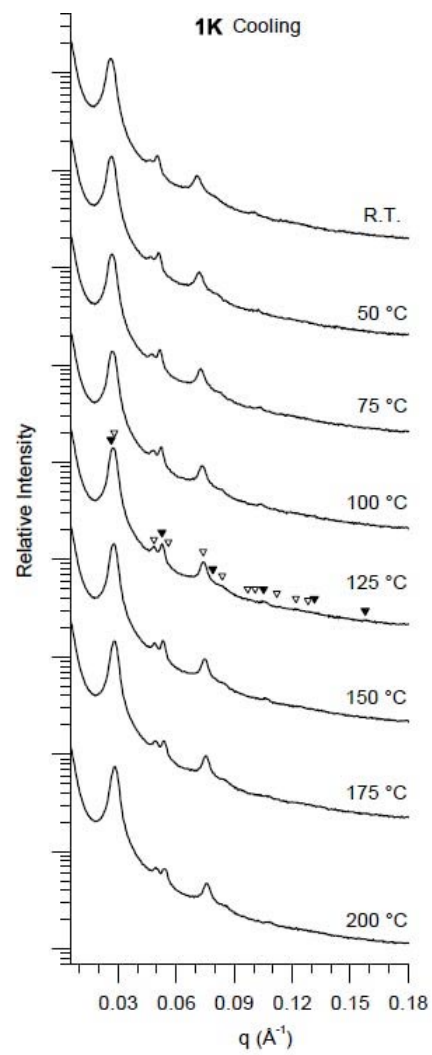
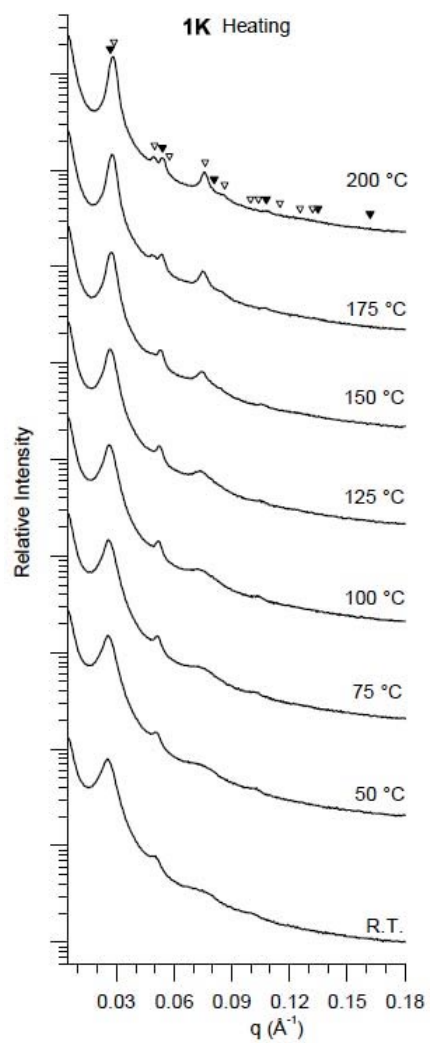


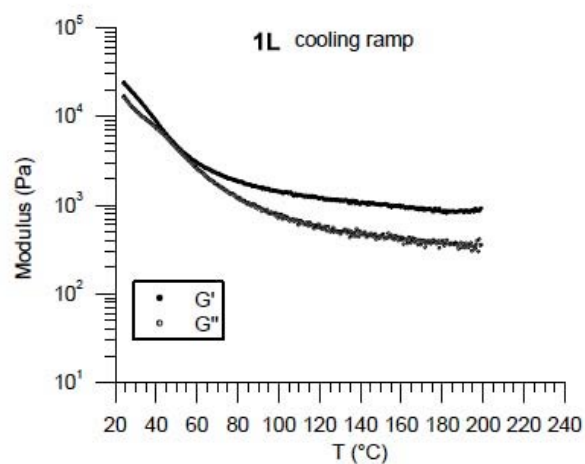
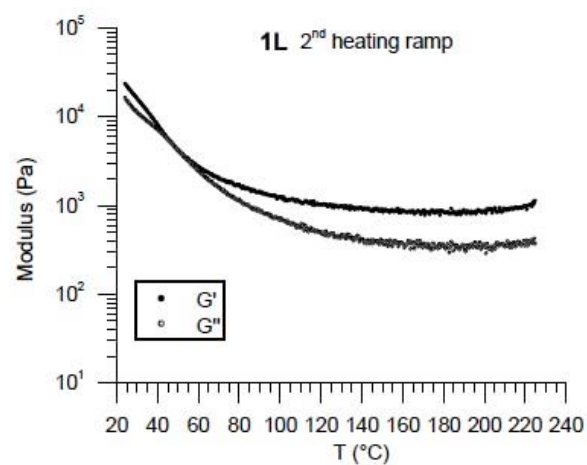
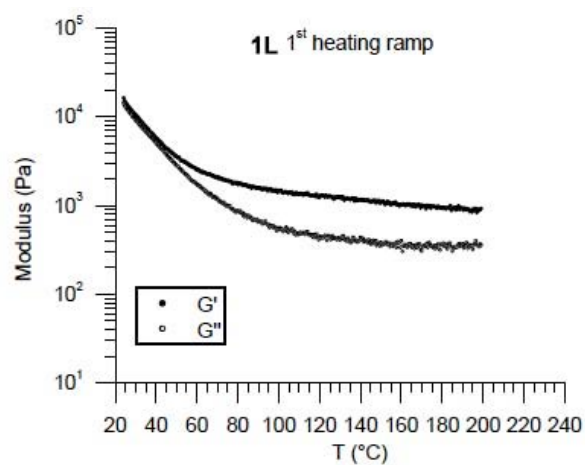


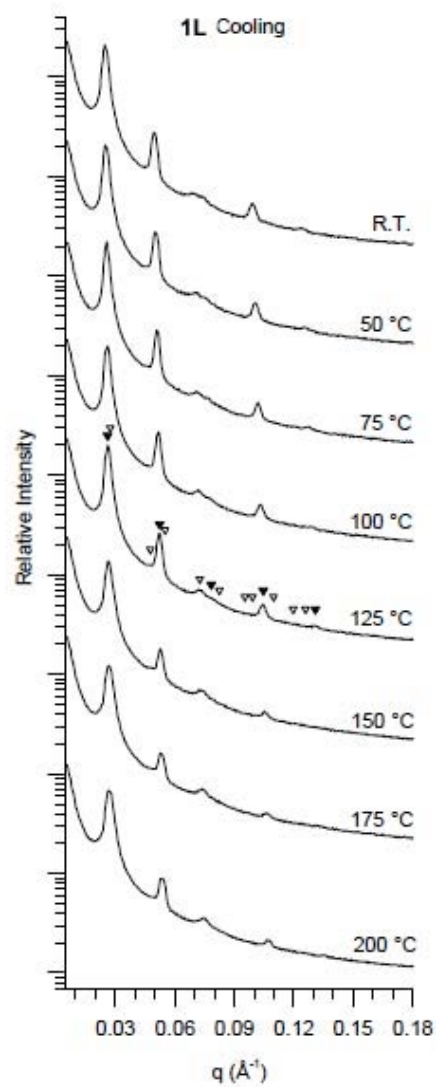
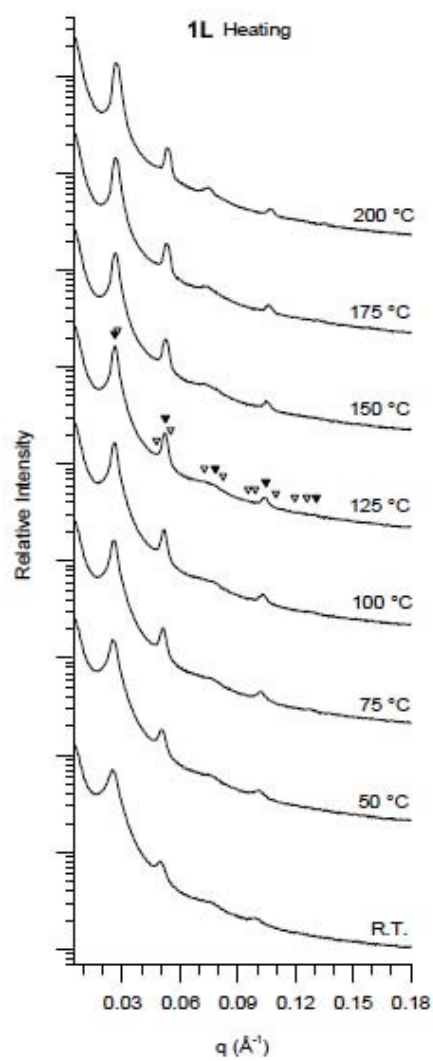


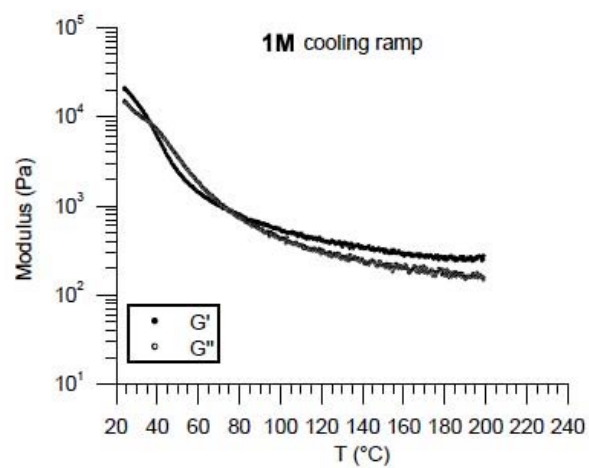
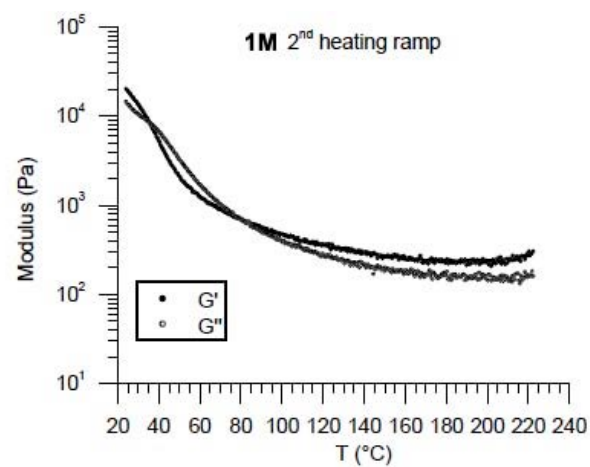
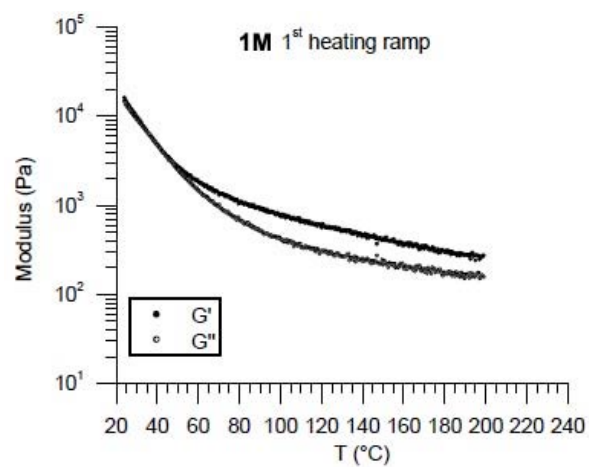


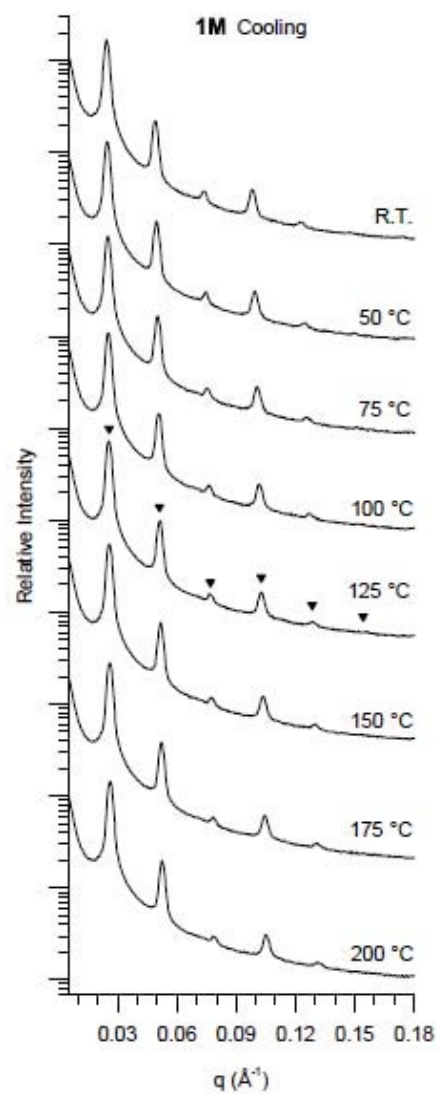
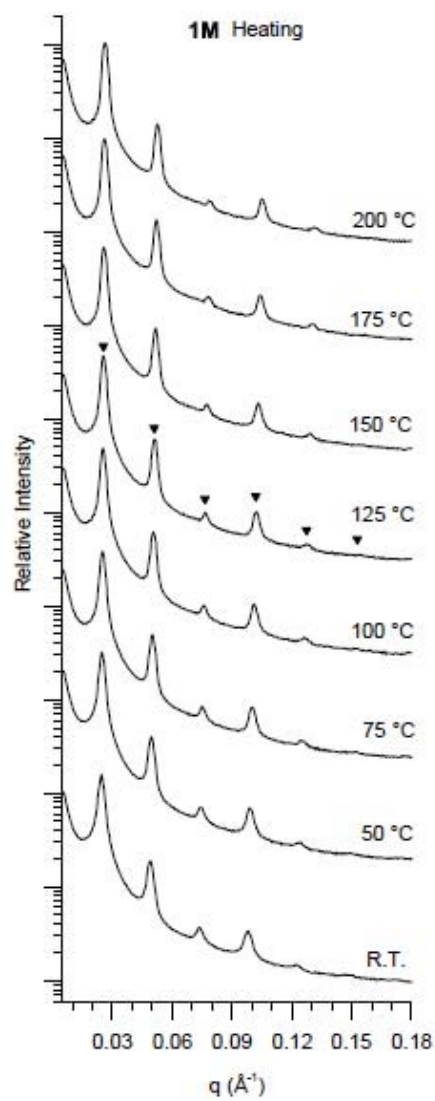


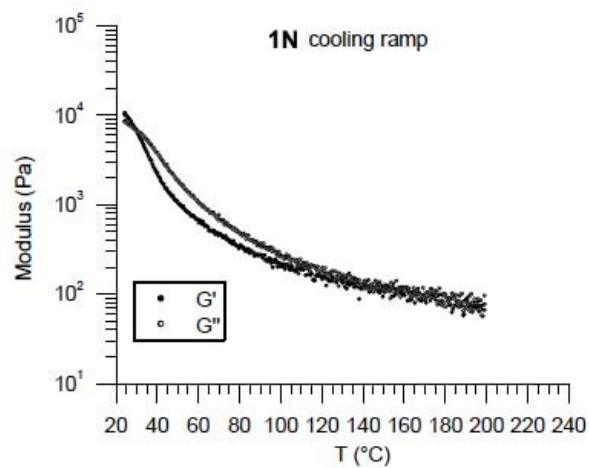
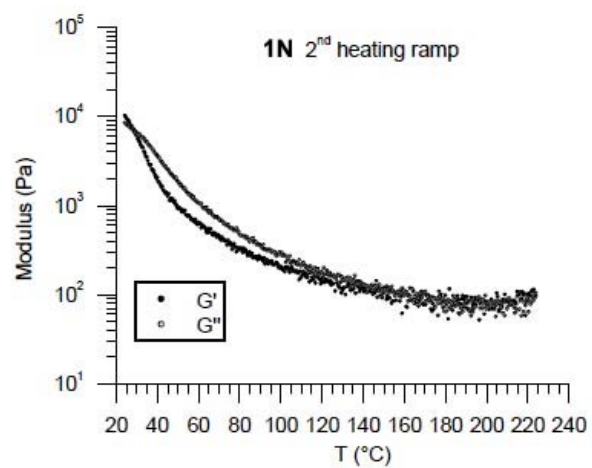
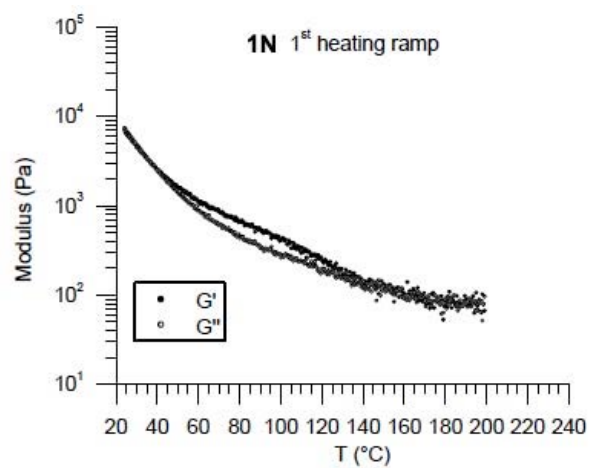


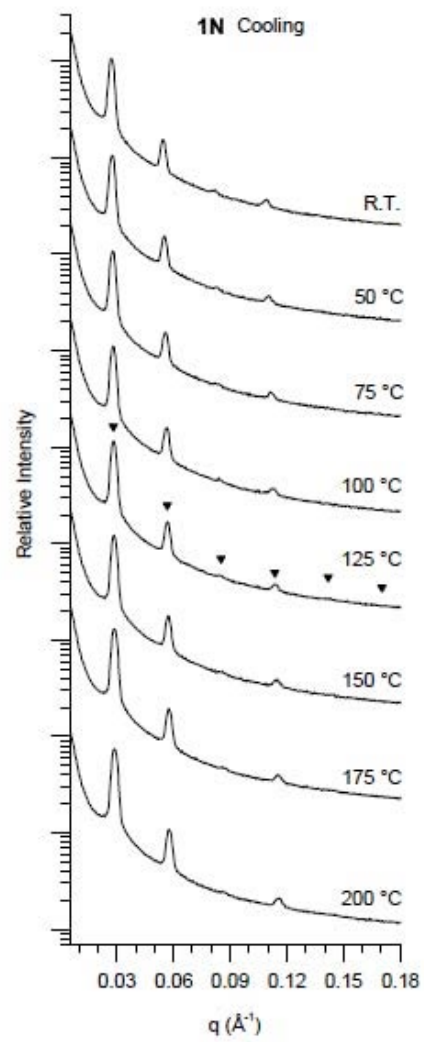
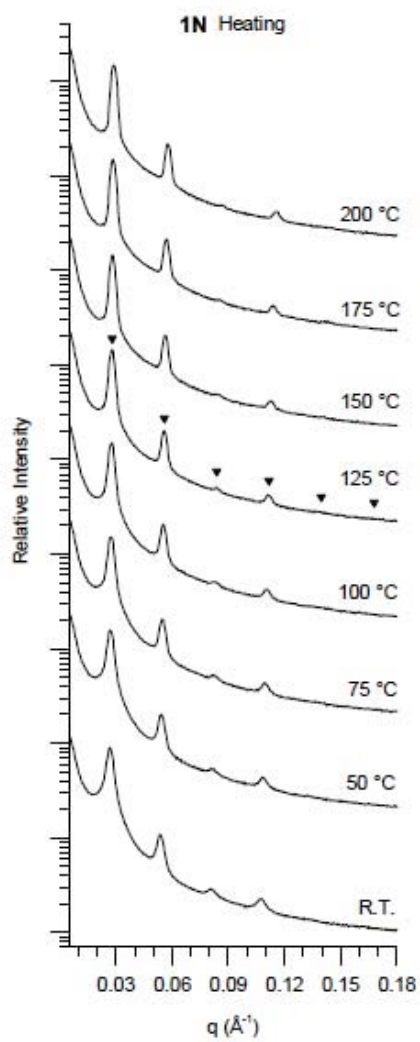


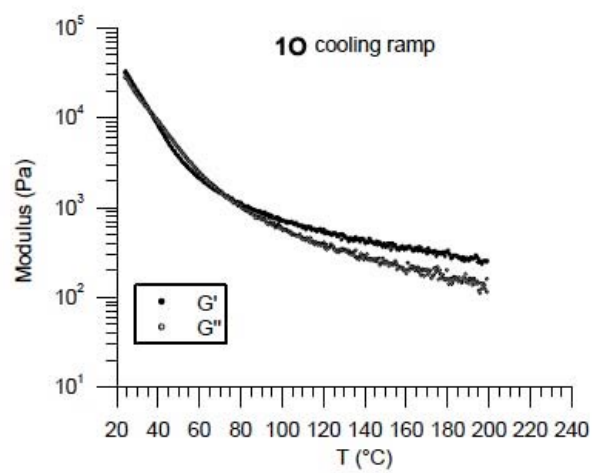
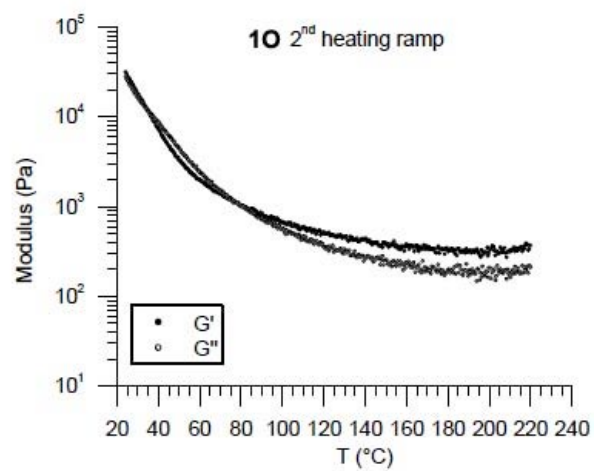
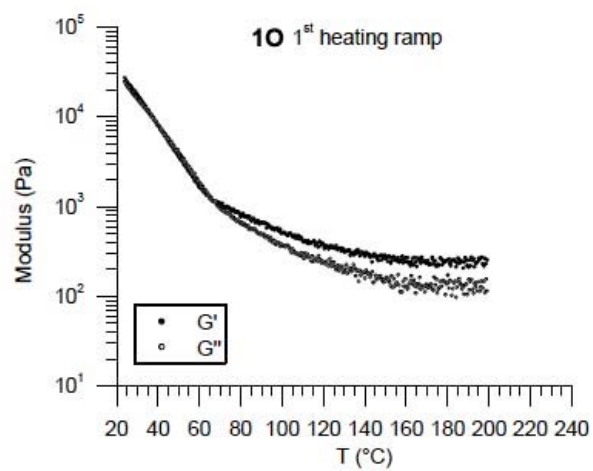


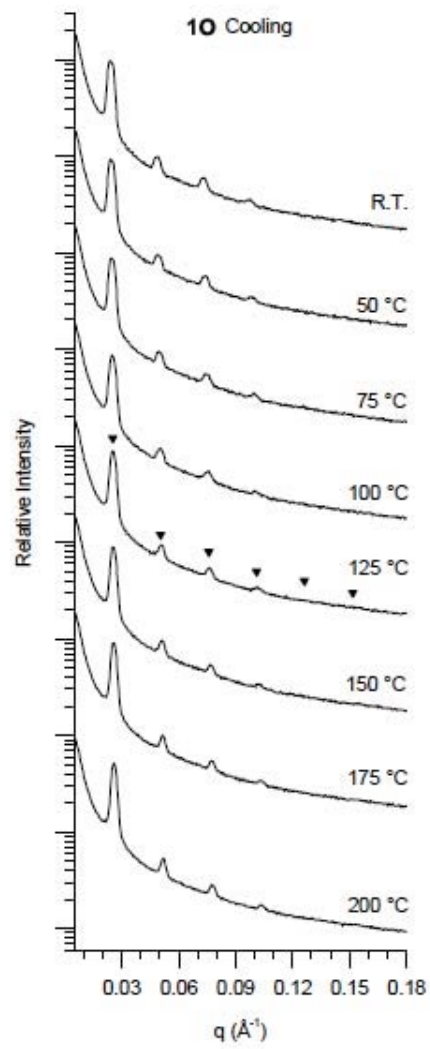
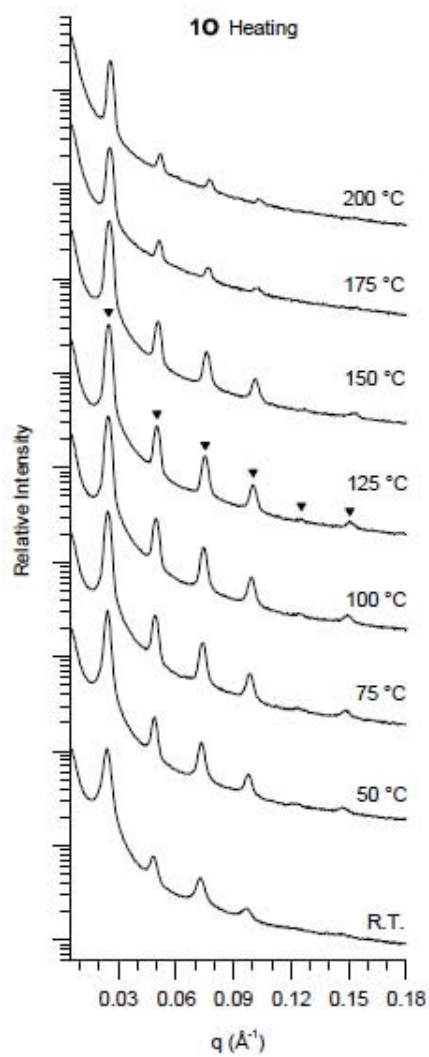


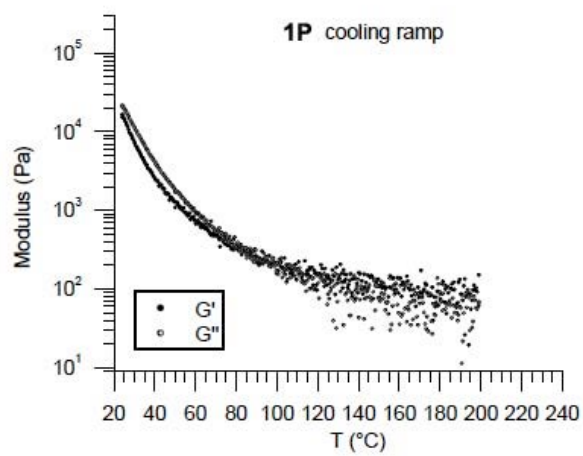
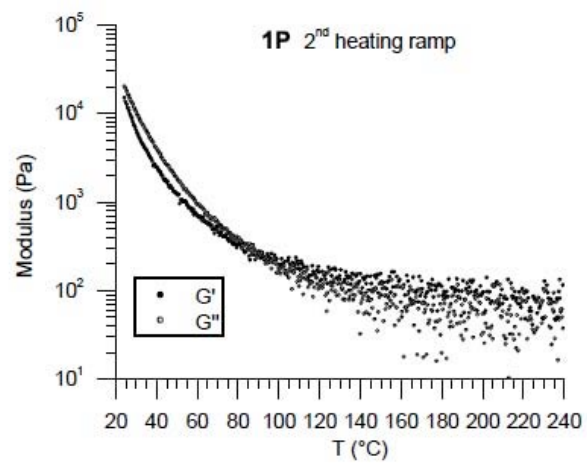
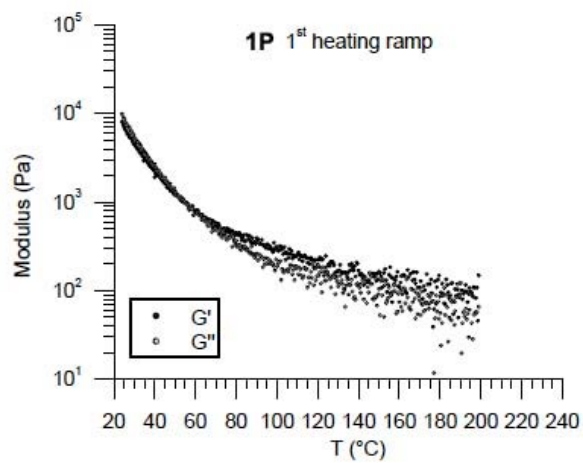


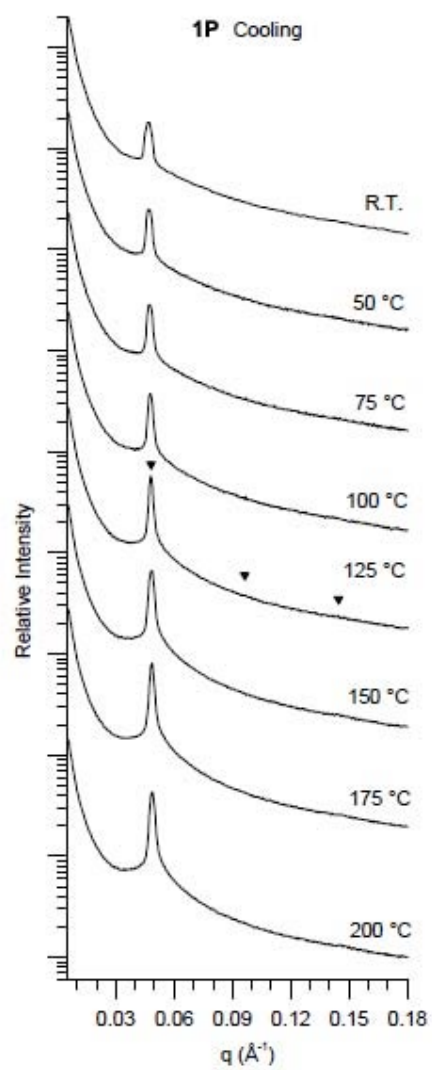
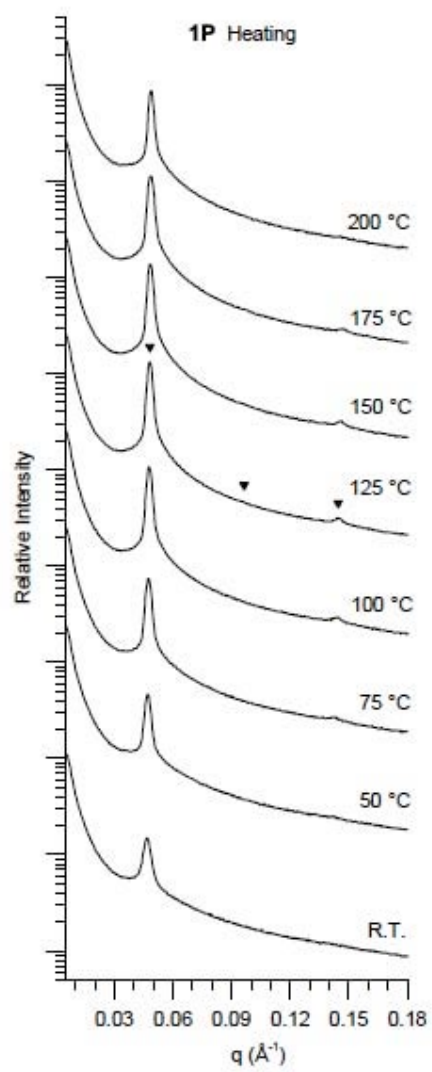


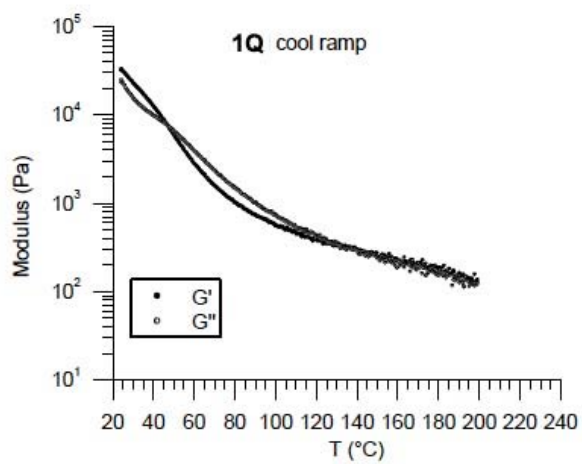
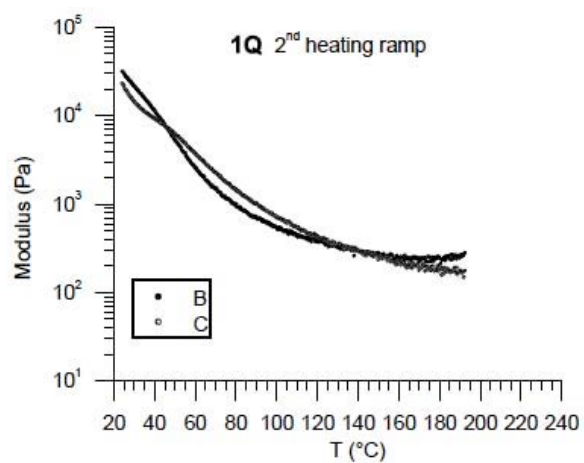
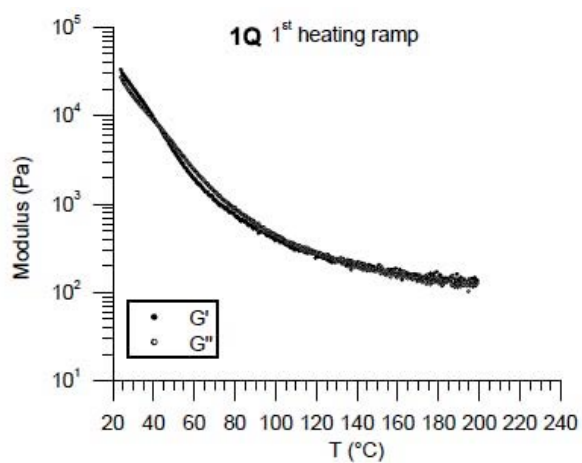


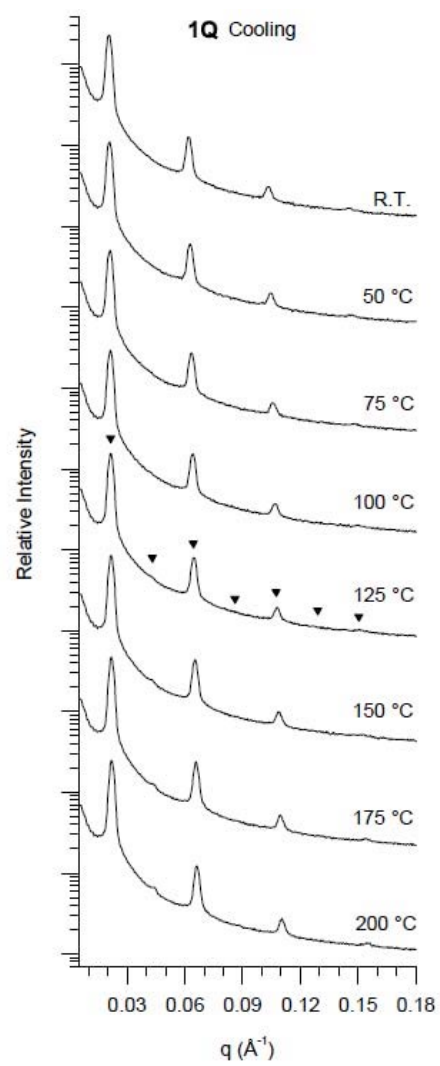
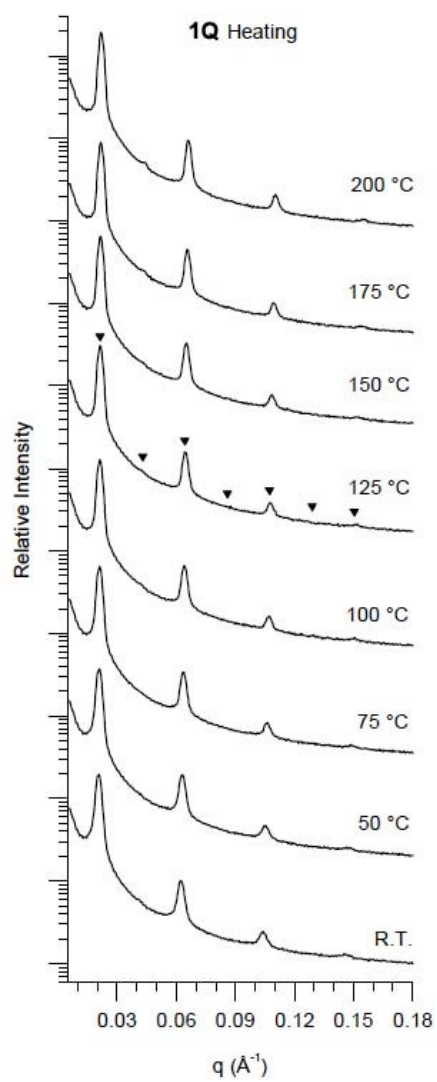


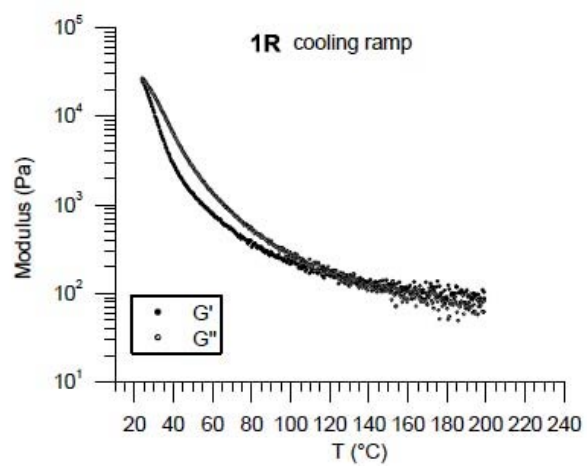
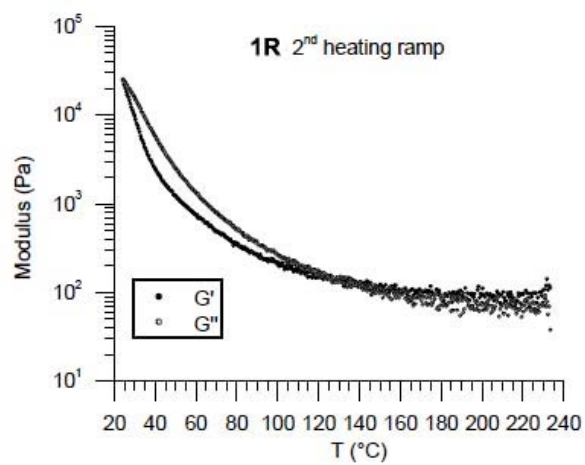
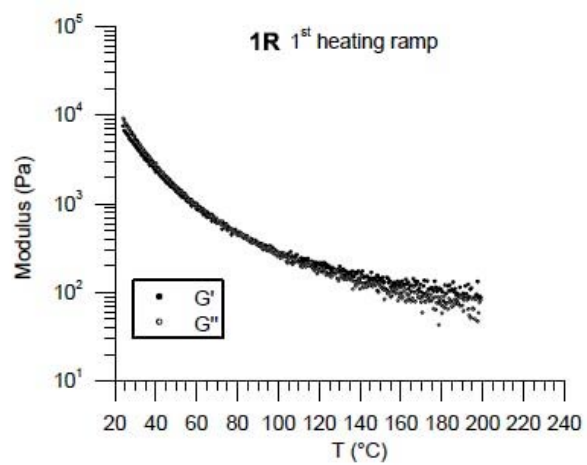


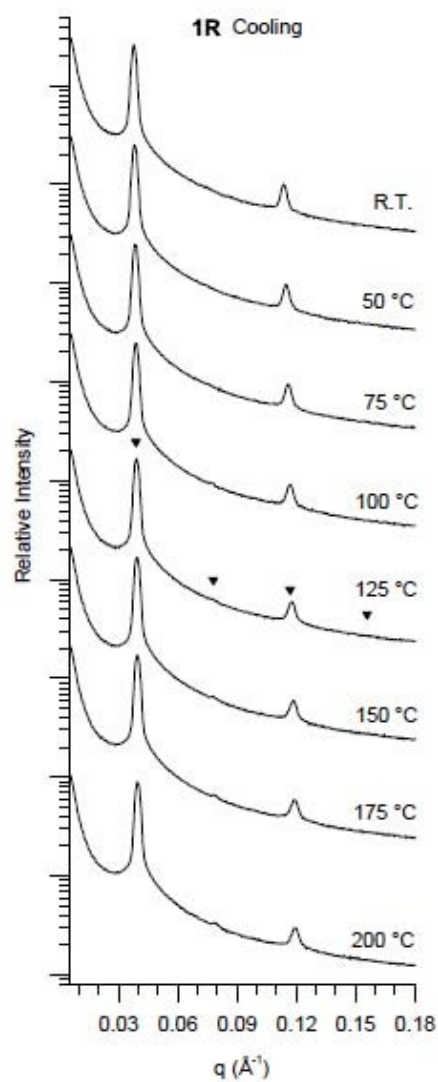
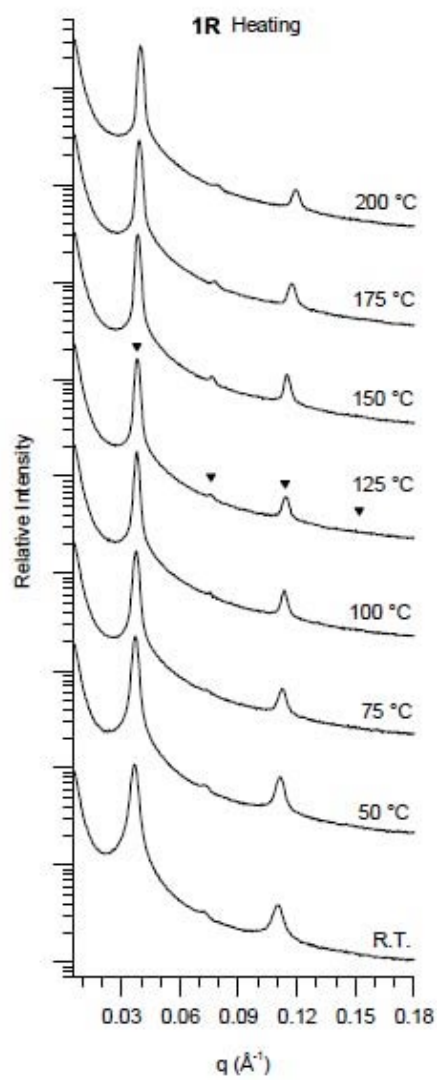


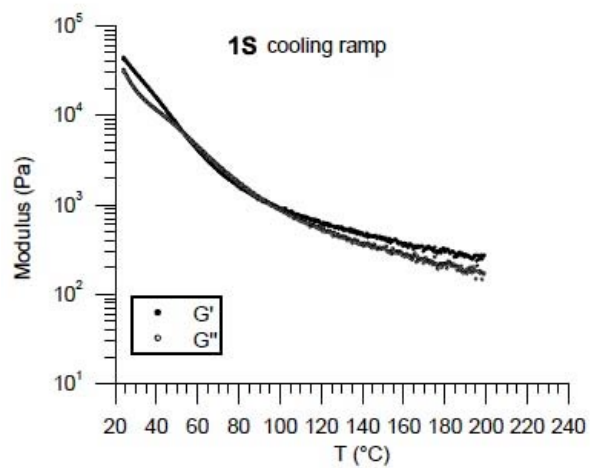
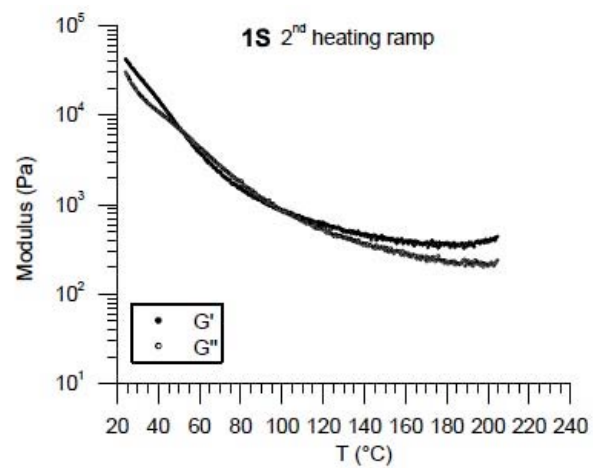
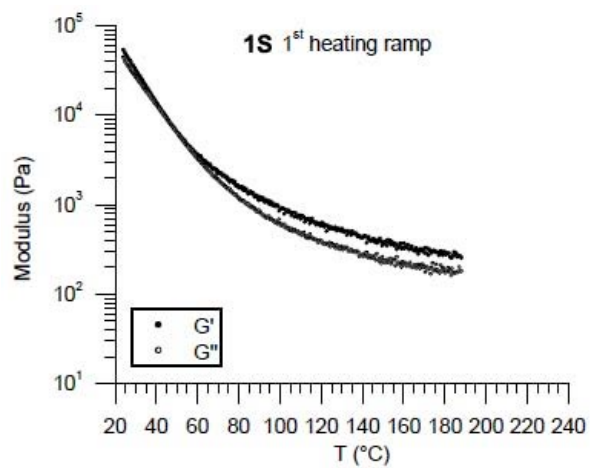


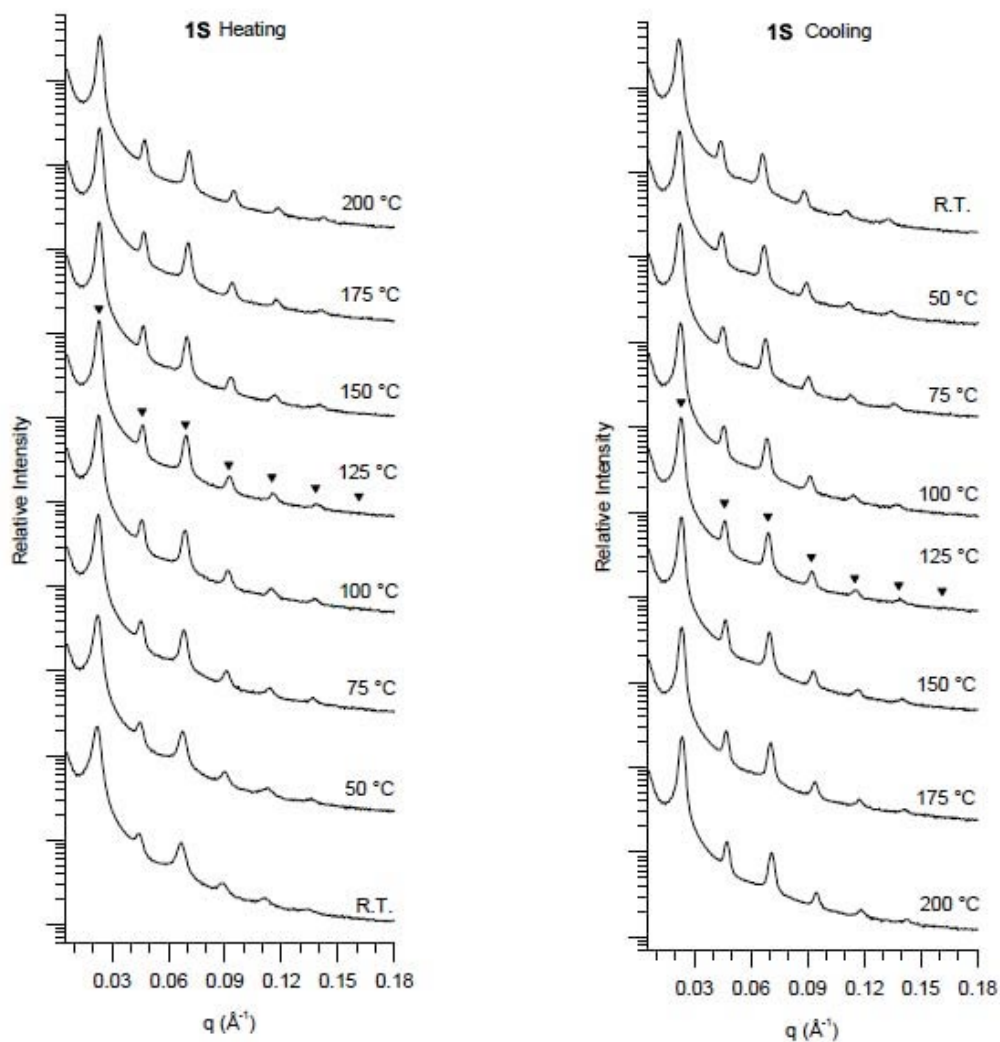












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CHAPTER 5

Effect of Composition and Nanostructure on CO₂/N₂ Transport Properties of Supported Alkyl-Imidazolium Block Copolymer Membranes

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5.1 Abstract

Polymerized room-temperature ionic liquids (poly(RTIL)s) have garnered attention as new and interesting membrane materials for CO₂/light gas separations because they combine the high CO₂ affinity and thermal and chemical stability of RTILs, with the physical and mechanical properties of polymeric materials. Our group recently synthesized a new type of block copolymer (BCP) combining an imidazolium-based poly(RTIL) and an alkyl non-ionic polymer. These alkyl-*b*-ionic BCPs phase-separate into ordered nanostructures. Prior work investigating gas transport through phase-separated BCPs is very limited, and none has included RTIL-based BCP systems. However it has been shown that nanoscale phase-separation could facilitate gas transport via nanostructure orientation control or phase connectivity improvement. We have successfully made defect-free, thin-film composite membranes with these novel alkyl-imidazolium BCPs as a 3–20 μm thick top layer, and determined their CO₂/N₂ separation

properties via single-gas permeability measurements and selectivity calculations. These new BCP materials were found to have distinct advantages over the analogous physical blends of the parent homopolymers with respect to membrane fabrication. The composition of the BCP top layer, which is directly connected to the type of nanostructure formed, was found to have a significant effect on CO₂ permeability (i.e., it can increase CO₂ permeability by two orders of magnitude up to an observed value of 9300 barrer). This improvement is mainly due to a large increase in the diffusion coefficient in the ordered nanostructures compared to amorphous BCP materials.

5.2 Introduction

CO₂ capture process development is a key technical, economical, and environmental challenge, since many applications require the separation of CO₂ from other light gases such as N₂, CH₄ and H₂. CO₂ and N₂ are the main compounds of flue gas resulting from the combustion of fossil fuels and air (post-combustion processes). Electric power generation is still dominated by coal combustion because of its accessibility and low cost, even though this method releases more CO₂ than the combustion of other fuels.¹ Natural gas production also needs a purification step because mined natural gas (principally composed of CH₄) contains around 10% CO₂.² This amount of CO₂ considerably decreases the value of the mined natural gas because CO₂ is not combustible. Moreover, CO₂ is highly corrosive and its removal is necessary for natural gas pipeline transport. Another important gas separation application concerns CO₂ and H₂, since CO₂ is an impurity in syngas production.

A number of different technologies, such as pressure swing adsorption, cryogenic distillation, membrane-based processes and gas-liquid absorption, have been developed to perform these CO₂/light gas separations. Gas-liquid absorption processes, which consist in washing the flue gas with a chemical solvent in a scrubbing column, have been largely studied as they provide high efficiency and high purity. However, direct contact between the gas and the liquid induces problems like fouling, plugging and entrainment. Membrane-based processes have recently gained a great deal of attention for this application because they provide large interfacial areas, are more flexible and easier to scale-up. Numerous studies have shown their potential to seriously compete with absorption processes.³⁻⁵

Polymeric membrane-based processes have been largely studied and have been the topic of several reviews.⁶⁻⁹ In general, polymer materials are mechanically stable, show good gas separation properties, and can be manufactured under different configurations such as flat sheets or hollow fibers.¹⁰ Some polymers are commercially available like poly(dimethylsiloxane) (PDMS), poly(imide) (PI) or cellulose acetate. However, these polymers do not meet industrial requirements in that they do not afford high CO₂ flux (i.e., CO₂ permeability) as well as high purity (i.e., CO₂/light gas selectivity). Indeed, as dense separation materials, polymers typically exhibit a tradeoff between permeability and selectivity that is represented by the so-called “upper-bound” in a Robeson Plot.¹¹ Moreover, polymeric membranes cannot withstand high temperatures and aggressive chemical environments.

Room-temperature ionic liquids (RTILs) are very attractive for CO₂/light gas separations. RTILs are organic salts, liquid at or below 298 K. These charged solvents

remain liquid at low temperature because of the large size and asymmetry of the cations, coupled with non-basic and often charge delocalized anions. The interest in RTILs as new CO₂/light gas separation membrane materials is based mainly on their intrinsically very low vapor pressure, their high thermal stability and the almost infinite possibilities to tune them chemically and structurally, as well as several variations morphologically. Moreover, they present a favorable solubility selectivity because of their inherent high CO₂ solubility compared to other light gases.¹²⁻¹⁴ The nature of the cation and anion has a large impact on the gas transport properties of these materials. The most studied RTILs for CO₂/light gas separations are based on imidazolium cation and bis(trifluoromethylsulfonyl)amide (Tf₂N) anion systems since they possess a very high solubility affinity for CO₂.¹⁵

To take advantage of the excellent chemical and physical properties of RTILs, different types of RTIL-based membranes have been fabricated.¹⁶ One easy way to obtain a membrane from these charged liquid materials is to fabricate supported ionic liquid membranes (SILMs) by completely infusing a non-selective, highly microporous polymer support with an RTIL.¹⁷⁻¹⁹ These SILMs exhibit high CO₂/light gas selectivity and high CO₂ permeability similar to the neat RTILs. A review by Scovazzo highlights the performances of these SILMs: CO₂ permeabilities range from 100 to 1700 barrer and CO₂/N₂ selectivities from 10 to 50.²⁰ However the retention of the RTIL in the microporous support only depends on the weak capillary forces and loss of RTIL is observed for low transmembrane pressure (0.2 to 2 bar).^{17,18,21} Gan et al. showed that nanoporous supports can help to increase the mechanical stability of SILMs, and tested their membranes up to 7 bar.²² Even so, the thickness of these SILMs is limited by the

support thickness itself (approximately 150 μm),^{19,22} whereas the industrial target is an active separation layer thickness of $\leq 1 \mu\text{m}$ to achieve the desired permeabilities and selectivities.²³

Over the past several years, polymerizable versions of RTILs (i.e., poly(RTIL)s) have been synthesized. Poly(RTIL)s combine the high CO_2 affinity and chemical and thermal stability of RTILs with the mechanical and physical properties of polymers. Our groups have developed numerous versions of these poly(RTIL)s, ranging from simple neat poly(RTIL)s, to gemini and polar-substituted poly(RTIL)s.²⁴⁻²⁶ These dense, solid poly(RTIL)s demonstrate excellent mechanical properties and high CO_2 /light gas selectivities but have lower permeabilities than the analogous liquid-phase RTILs because of a large decrease in the gas diffusivity after polymerization. Poly(RTIL)s CO_2 permeability values range from 4 to 30 barrer, and their CO_2/N_2 selectivity values are about 30–40.²⁴⁻²⁶

To improve the gas separation performance of these poly(RTIL)s, amine functionalities can be tethered to the poly(RTIL) to create task-specific materials and facilitate the transport of CO_2 .^{27,28} Another solution is to add non-polymerizable RTIL to create composite poly(RTIL)-RTIL materials. It has been shown that incorporating 20 wt% of a free liquid RTIL leads to an enhancement of the permeability up to 400%.^{29,30} To increase the amount of free RTIL without severely compromising mechanical stability, RTIL-based cross-linkers can be integrated in the membrane. Li et al. added up to 60 wt% of free RTIL in their poly(vinyl-RTIL) materials,³¹ and Carlisle et al. were able to make cross-linked poly(vinylimidazolium) membranes with up to 75 wt% of

added free RTIL.³² However, these composite RTIL-based membranes were found to still have lower CO₂/light gas separation performance than SILMs.

Keeping in mind the advantages of poly(RTIL)s and some initial reports in the literature on the effect of nanostructured, phase-separated block copolymer (BCP) systems on gas transport,³³ our group recently synthesized novel imidazolium-based alkyl-*b*-ionic diblock copolymers (BCPs) via sequential ring-opening metathesis polymerization (ROMP).³⁴ We then fully characterized the morphological phase behavior of short runs of these new RTIL-based BCPs as a function of composition and block length ratio³⁵ as a prelude to investigating these materials for use in membranes for CO₂/light gas separations.

In terms of related work, documented phase-separation in poly(RTIL)-based BCPs is largely unprecedented.^{34–41} Li et al., Stancik et al., and Weber et al. have developed and characterized polystyrene-*b*-poly(RTIL) BCPs^{36,39,41} while Gu and Lodge synthesized triblock copolymer systems with RTIL mid-block.⁴⁰ Most of these BCPs do not show phase separation in a solvent-free melt state like our alkyl-ionic BCPs but require added solvent that interacts with the different blocks and controls the ability to form well-defined nanostructures. Using this method, it seems that the morphology of these BCPs is limited to micelles.^{36,38,39} With respect to applications, none of these systems were tested for gas separation but were mostly investigated for their ion conductivity.⁴¹

Prior work investigating gas transport through phase-separated BCPs is very limited, and none has included RTIL-based BCP systems.^{33,42,43} For example, Kinning et al. studied the transport of CO₂ in poly(styrene-*co*-butadiene) BCPs and have observed

that the diffusion coefficient is highly dependent of the composition, morphology and connectivity of the most conductive phase.³³ In the work of Barbi et al., it was demonstrated that poor phase separation or nanostructure defects in polyether-*b*-polyamide lead to a decrease in gas permeabilities.⁴² Drzal et al. evaluated the effect of the microstructure orientation on CO₂ permeability in ordered ethylene/ethylene-propylene BCPs.⁴³ Finally Xue et al. showed that the functional block units and the cylindrical structure of their poly(ethylene oxide)-*b*-polystyrene have a deep impact on the CO₂ permeability and CO₂/N₂ selectivity.⁴⁴

In this report, we evaluated the potential of a novel poly(RTIL)-based BCP material for CO₂/light gas separations with a specific focus on CO₂/N₂ separation. Specifically, we found that in contrast to analogous physical blends of the parent homopolymers, our poly(RTIL)-based BCPs can be fabricated into defect-free, supported, thin-film composite (TFC) membranes. By varying the imidazolium content and the corresponding ordered nanostructure in the BCP TFC membranes, we were able to obtain a greater than two orders of magnitude increase in CO₂ gas permeability.

5.3 Experimental Section

5.3.1 Materials and General Synthetic Procedures

5.3.1.1 Materials and Methods

Dicyclopentadiene and 1-vinylimidazole (from TCI America), as well as 1-bromohexane, 1-dodecanol, 5-norbornene-2-carboxylic acid, ethyl vinyl ether, and oxalyl dichloride (all from Sigma-Aldrich) were used as received. Lithium bis(trifluoromethylsulfonyl)amide (LiTf₂N) was purchased as FluoradTM lithium

trifluoromethanesulfonimide from the 3M company. All solvents were purchased from Sigma-Aldrich or Mallinckrodt, Inc., and purified/dehydrated via N₂-pressurized activated alumina columns and degassed. Additionally, the CH₂Cl₂ used as the solvent in ring-opening metathesis polymerization (ROMP) reactions was purified by re-filtering over activated alumina prior to degassing. Tetrahydrofuran (THF) for BCP membrane fabrication was purchased from Mallinckrodt, Inc. and used without further purification. H₂O used for synthesis was purified and de-ionized, with a resistivity value greater than 12 MΩ cm⁻¹. All chemical syntheses were carried out in a dry argon atmosphere using standard Schlenk line techniques, unless otherwise noted. Silica gel purification was performed using 230-400 mesh, normal-phase silica gel purchased from Sorbent Technologies.

5.3.2 General Synthesis and Polymerization of Alkyl-Imidazolium BCPs 1T-W³⁴

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (endo:exo 80:20) (monomer **2**) and 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3*H*-imidazolium bis-(trifluoromethylsulfonyl)amide (endo:exo 80:20) (monomer **3**) were prepared and purified according to literature. In a procedure adapted from Wiesenauer et al.,³⁴ a flame-dried Schlenk flask was charged with argon, the desired amount of Grubbs' first generation catalyst, and dry, degassed CH₂Cl₂. Monomer **2** was then added via needle and syringe under argon from a dry, degassed stock solution. Upon complete consumption of monomer **2** (as verified by ¹H NMR analysis) to form the first copolymer block, the monomer **3** was added from a dry, degassed stock solution via syringe. Upon complete consumption of monomer **3** (as verified by ¹H NMR analysis), the ROMP

diblock copolymerization was quenched with excess ethyl vinyl ether. The resulting diblock copolymer was isolated by removal of the solvent in vacuum (48 h, 25 °C). Number-average molecular weights (M_n) are as follows: **1T** ($M_n = 106,300 \text{ g mol}^{-1}$), **1U** ($M_n = 19,152 \text{ g mol}^{-1}$), **1V** ($M_n = 17,680 \text{ g mol}^{-1}$), **1W** ($M_n = 17,669 \text{ g mol}^{-1}$). ^1H NMR analysis of BCPs **1T–1W** also confirmed the absence of any residual monomer. The alkyl:imidazolium block fractions were determined by relative integrations of the ^1H NMR signals of each block. The number of repeat units of the dodecyl and imidazolium blocks was calculated based on the catalyst-to-monomer loading ratios, complete monomer conversion (as verified by the absence of monomer from ^1H NMR analysis), and living polymerization character as determined in our previous report.³⁴ Lastly, M_n values were estimated by multiplying the block lengths by the corresponding monomer repeat unit molecular-weight values.³⁴

5.3.3 Alkyl-Imidazolium Block Copolymer Membrane Fabrication

35 wt% BCP in THF solutions were prepared at room temperature and stirred until homogeneous. A large range of concentrations was tested (5–50 wt% BCP in THF), but minimal amount of solvent lead to viscous solutions that were difficult to cast and created thick, uneven membranes. On the other hand, using higher THF content resulted in non defect-free membranes. Thus, we found the most suitable concentration was 35 wt%, with the exception of BCP **1A**, where the overall BCP has a substantially larger number of monomer repeat units, and a solution of 8 wt% BCP was used to decrease viscosity.

Thin, self-standing BCP membranes could not be fabricated because of the physical and mechanical properties of the materials. For this reason, several types of supports were tested. Two hydrophilic supports, Nylon (MFS-Life Science, N022A047A) and PTFE (Polytetrafluoroethylene, Millipore, Omnipore®, JGWP04700) were coated with the BCPs but the resulting membranes exhibited defects. Hydrophobic PTFE supports (Advantec membrane filters, T020A047A) repelled the BCP solutions, so homogeneous layers of BCP could not be made. Only polyacrylonitrile (PAN) ultrafiltration membranes supplied by MTR (Membrane Technology & Research) afforded thin, defect-free, supported BCP membranes.

Spray-coating and roller-coating fabrication methods were tested, but defect-free membranes could not be obtained. Instead, the BCP membranes were fabricated by dispensing approximately 1 mL of the BCP solution on top of a 50 mm x 50 mm square of PAN support via glass pipette. The solution quickly spread on the support by tilting the membrane, and the THF evaporated slowly at room temperature before drying under vacuum overnight.

5.3.4 Supported Thin-Film BCP Membrane Characterization

5.3.4.1 Small Angle X-ray Scattering (SAXS)

SAXS data were collected using a Rigaku S-Max 3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu K_{α} , $\lambda = 1.54 \text{ \AA}$), a sample-to-detector distance of $\sim 2.19 \text{ m}$, a Confocal Max-Flux Optics, a Gabriel multiwire area detector (1024 x 1024 pixel resolution), and a Linkam thermal stage. Bulk alkyl-imidazolium block copolymer samples were sandwiched between

Kapton windows (0.05 mm thick x 10 mm diameter). Data was collected at room temperature under vacuum (<100 mtorr) with exposure times of 1200 s for bulk samples, and 14400 s for membrane samples.

5.3.4.2 Scanning Electron Microscope (SEM) Imaging

In order to determine BCP layer thickness and quality (i.e., defect-free, homogeneous, good adhesion with the PAN support), SEM images of the films and membranes were acquired. SEM imaging was performed using a JEOL JSM-6480LV, with the acceleration voltage set to 10-15 kV and a spot size of 50 nm. Samples were fractured in liquid nitrogen, dried under vacuum over night, and then coated with gold by sputtering deposition to enhance the conductivity (thickness of the gold layer approximately 30 nm). At least two samples of each membrane were prepared for SEM imaging, and the thicknesses were measured at 3 different spots and averaged.

5.3.5 Gas Transport Properties Measurements via the Time-Lag Method

Single-gas permeabilities and diffusivities were measured by a time-lag apparatus. Before testing, membranes were degassed under dynamic vacuum over night and each experiment began under vacuum conditions (pressure below 10^{-2} mbar). All experiments were performed at room temperature (20 °C). Pure gas was applied at feed pressure around 1 bar, measured by an Omega pressure transducer (0–7 bar). The gas absorbed into the membrane, diffused through it, and desorbed from it on the permeate side. The permeate pressure (p_p) increased with time (t) and was recorded by an Omega pressure transducer (0–1 bar). The feed volume was considerably larger than the permeate volume

which kept the driving force (Δp) nearly constant throughout the experiment. Permeability measurements of every gas were carried out three times for each membrane, and the experimental error was less than 4%.

The permeability of gas i (P_i) is calculated from the membrane thickness (l), the average transmembrane pressure drop (Δp) and the volume flux (J_i). The quantity J_i is determined by Equation 5.1, where V_p is the permeate volume, A is the membrane area, R is the Ideal Gas Law constant, T is the absolute temperature, V_m is the gas molar volume, and (dp_p/dt) is the slope of the linear portion of the p_p vs. t plot.

$$P_i = J_i \frac{l}{\Delta p} = \frac{V_p V_m}{ART} \left(\frac{dp_p}{dt} \right) \frac{l}{\Delta p} \quad (\text{Equation 5.1})$$

The diffusivity of gas i (D_i) can be deduced by extrapolating the slope of the linear portion of the p_p vs. t plot back to the time axis. This intercept is the “time-lag” (θ) of the gas through the membrane and is related to D_i by Equation 5.2:

$$D_i = \frac{l^2}{6\theta} \quad (\text{Equation 5.2})$$

Gas transport through the BCP membrane is assumed to follow a solution-diffusion mechanism whereby the permeability is function of the diffusivity (D_i) and the solubility (S_i) of each gas through the dense membrane material¹⁰:

$$P_i = D_i \times S_i \quad (\text{Equation 5.3})$$

Knowing P_i and D_i allows for the calculation of S_i via Equation 5.3.

The ideal permeability selectivity ($\alpha_{i/j}$) is defined as the ratio of the permeability of the more permeable species *i* to the permeability of the less permeable species *j*. As shown in Equation 5.4, the selectivity can be written as the product of the diffusivity and solubility selectivity.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \quad (\text{Equation 5.4})$$

5.4 Results and Discussion

5.4.1 Synthesis and SAXS Characterization of Alkyl-Imidazolium BCPs

5.4.1.1 BCP Structure and Synthesis

A total of 4 BCP samples (**1T–1W**) were synthesized via sequential, living ROMP of hydrophobic alkyl monomer **2** and cationic imidazolium RTIL monomer **3** using Grubbs' first-generation catalyst (Figure 5.1). Two analogous pure homopolymers, poly(**2**) and poly(**3**), were also synthesized via ROMP using Grubbs' first-generation catalyst for membrane comparison studies with the BCP samples. Monomer and BCP synthesis and characterization details can be found in our recent publication.³⁴ The BCP compositions tested were chosen for their predicted nanostructures, based on our previous work where the phase diagram was elucidated for this unique alkyl-imidazolium BCP system.³⁵ The weight percent content of the imidazolium (IMID) component in the BCP test samples ranged from 100 wt% (poly(**3**)) to 18 wt% (BCP **1W**), as calculated as $M_{n(\text{IMID})}/[M_{n(\text{DOD})} + M_{n(\text{IMID})}]$. As discussed in our previous publication, the M_n values and alkyl:RTIL compositions were targeted by monomer/catalyst ratios in the ROMP polymerization and verified by ¹H NMR analysis on the resulting BCPs.

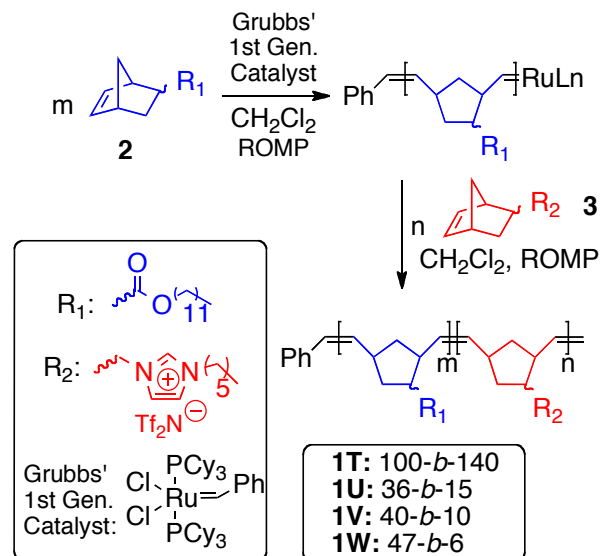


Figure 5.1. Sequential ROMP of monomers **2** and **3** to yield alkyl-imidazolium BCPs **1T–1W**.

5.4.1.2 SAXS Characterization

The morphological phase behavior of samples **1T–1W** was analyzed with SAXS. For sample **1T** (71 wt% IMID), SAXS analysis showed scattering identical to the background, consistent with an amorphous unordered sample (data not shown). SAXS data for samples **1U–1W** (bulk and membrane) at room temperature are presented in Figure 5.2, along with a blank membrane support for comparison. Scattering from sample **1U** (42 wt% IMID) bulk and membrane revealed multiple well-resolved diffraction peaks consistent with the lamellae morphology. There was a slight increase in the domain spacing (d_{100}) from 25.1 nm in the bulk, to 25.9 nm in the cast membrane sample, which is likely a result of slight differences in solvent casting conditions. Bulk samples were isolated by removing the CH_2Cl_2 reaction solvent, while membrane samples were drop-cast from THF as a 35 wt% solution before drying under vacuum. Nonetheless, the lamellae morphology is completely preserved when solvent cast onto the membrane

support as evident by the presence of multiple higher order diffraction reflections (Figure 5.2, **1U** inset).

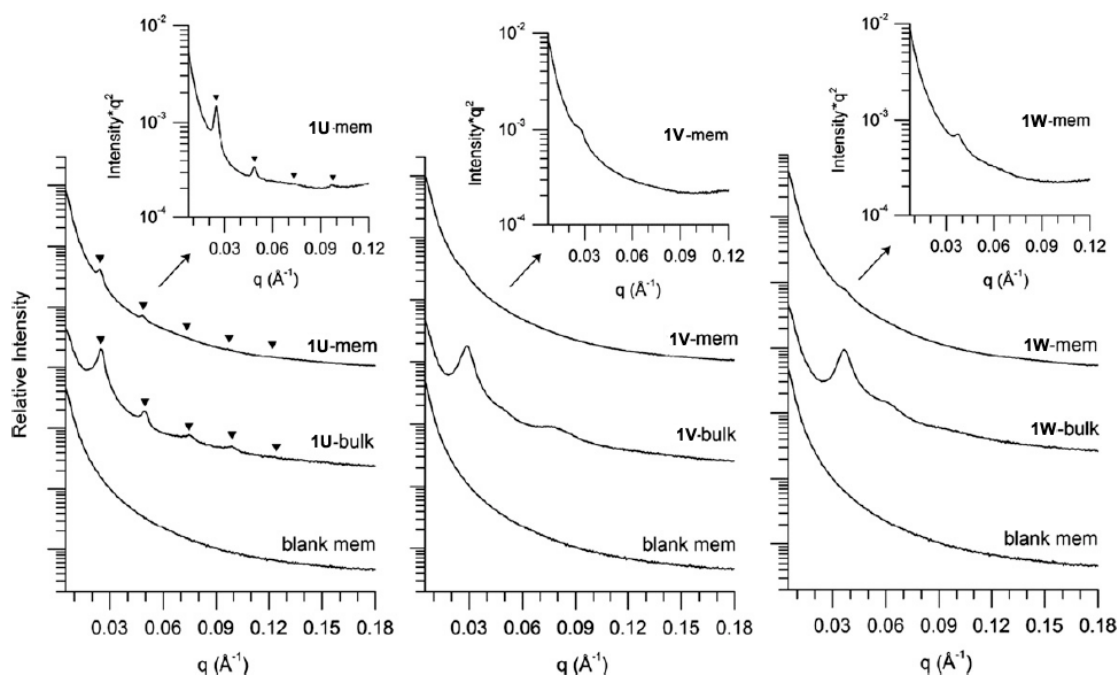


Figure 5.2. SAXS data at room temperature for **1U–1W** bulk and membrane samples. Sample **1U** bulk and membrane nanoscale structures are consistent with the lamellae phase. Inverted solid triangles represent the calculated locations of allowed reflections for the lamellae morphology based on the position of the primary scattering wave vector, $q^* = q_{100}$: q/q^* at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. Samples **1V** and **1W** bulk morphologies exhibit a weakly-ordered liquid-like packing of the phase-separated domains. Membrane samples **1V** and **1W** show phase separation evident by the observed primary scattering reflection. Insets accentuate scattering observed in membrane samples by plotting intensity $\cdot q^2$ vs. q .

In contrast to sample **1U** where a well-resolved diffraction pattern was observed, samples **1V** (31 wt% IMID) and **1W** (18 wt% IMID) bulk samples were characterized by a primary SAXS peak (bulk d -spacings: **1V** = 21.8 nm, **1W** = 17.1 nm), followed by broad, undefined, higher-order scattering peaks. This broad X-ray scattering behavior has been observed previously in our comprehensive morphological study of alkyl-imidazolium BCPs of similar composition, and is typical for a liquid-like packing (LLP) of phase-separated spherical aggregates.³⁵ In all previous alkyl-imidazolium hexagonal

and spherical domain-forming samples reported,³⁵ there exists an induction time for obtaining highly ordered structures, that can be overcome or reduced via thermal annealing of the samples. Based on the overall composition of samples **1V** (31 wt% IMID) and **1W** (18 wt% IMID) and previously obtained scattering data of similar alkyl-imidazolium samples,³⁵ we suspect that the morphologies of the **1V** and **1W** bulk samples are likely a LLP of hexagonal (sample **1V**) and LLP of spherical (sample **1W**) domains. In support of this claim, we annealed bulk samples **1V** and **1W** under vacuum at 150 °C for 1.5 h. After annealing, bulk **1V** exhibited SAXS peaks consistent with hexagonally-packed cylinders, while bulk **1W** exhibited multiple diffraction reflections consistent with spheres on a body-centered cubic lattice (verified with SAXS, data not shown). Scattering from the **1V** and **1W** TFC membranes revealed only a single subtle primary SAXS peak. Again, there are slight differences in the SAXS *d*-spacings from the bulk form to the corresponding supported TFC membrane configuration for both **1V** and **1W**. For **1V**, there was an increase in the SAXS *d*-spacing from 21.8 in the bulk to 23.3 nm in the TFC membrane, while there was very little change in *d*-spacing for **1W** on going from the bulk state (17.0 nm) to the TFC membrane form (16.8 nm). As mentioned previously, we attribute slight variations in SAXS *d*-spacing to the different solvent casting conditions used in the preparation of the bulk and supported membrane samples. The appearance of the primary scattering peak in the **1V** and **1W** TFC membranes confirms an ordered, phase-separated structure; however any further identification of the formed nanostructure could not be determined with a single SAXS peak alone. Lastly, we wish to emphasize that a microphase-separated morphology is present in three of the four

TFC membrane samples (**1U**, **1V**, and **1W**), despite not being able to identify the specific nanostructures of membranes formed with **1V** and **1W**.

5.4.2 Membrane Fabrication

BCPs **1T–1W** were found to have better processability compared to physical blend (PB) analogues of their parent homopolymers (poly(**2**) and poly(**3**)) in terms of thin, supported-membrane fabrication. In fact, the BCPs were essential for good thin-film membrane formation. The PB samples exhibited macroscopic phase-segregation on the support due to material incompatibility, whereas BCPs **1T–1W** created thin, uniform, defect-free layers on the PAN support (Figure 5.3 A and B). We believe this is because the imidazolium section interacts favorably with the support, and though the hydrophobic alkyl block is incompatible with either component, the covalent bond connecting the two blocks allows for sufficient wetting of the support. Several supports (hydrophilic and hydrophobic), solvent choices (CH_2Cl_2 and THF), and casting methods were attempted with our BCP systems, but only the method outlined in Section 5.3.3 using 35 wt% BCP in THF on PAN ultrafiltration support membranes lead to thin, defect-free, supported BCP membranes.

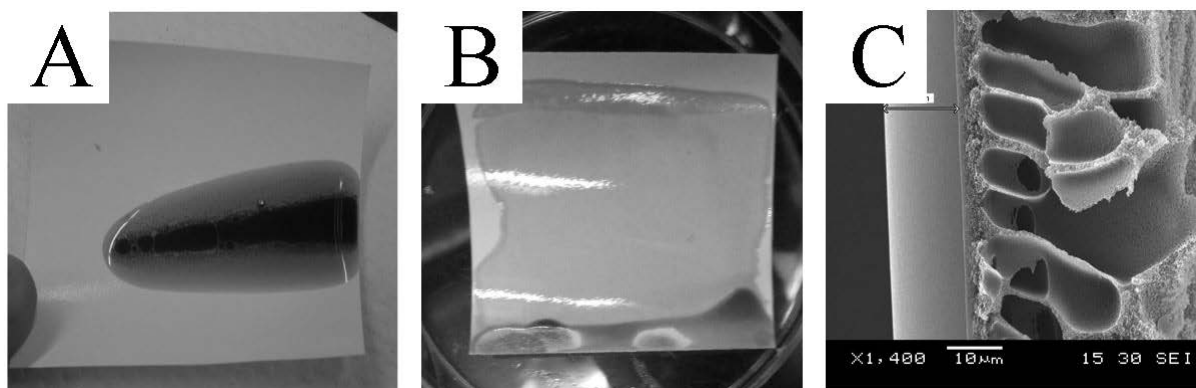


Figure 5.3. (A) Physical blend of poly(2) + poly(3) macroscale phase-separating on the PAN membrane support. (B) An example of a thin, uniform coating made possible with our BCP materials on the PAN membrane support. (C) SEM cross-sectional image of BCP 1U showing a uniform, defect-free surface (13.4 μm).

SEM was used to determine BCP layer thickness and quality (Figure 5.3 C). Using the aforementioned method, BCPs 1U, 1V, and 1W, had uniform average thicknesses of 13.6 μm , 13.5 μm , and 18.2 μm , whereas BCP 1T had an average sample thickness of 2.7 μm . The increased viscosity of BCP 1T required a lower BCP concentration in THF, which resulted in a thinner membrane layer in comparison to BCPs 1U–1W. Even though these BCP membranes are supported, the active layers are thin compared to non-supported membranes.^{33,42}

5.4.3 CO₂/N₂ Transport Studies

5.4.3.1 Permeabilities and Selectivity Measurement

Pure CO₂ and N₂ gas permeabilities were measured by a time-lag apparatus. The results are presented on a so-called Robeson plot where the ideal selectivity between CO₂ and N₂ is represented vs. the CO₂ permeability (see Figure 5.4). The “upper bound” shows the tradeoff between permeability and selectivity that has been observed for polymers, and corresponds to the gas separation performance limit of these materials.^{11,45}

Gas transport measurements indicate that the imidazolium-based homopolymer (poly(**3**)) presents a high selectivity for CO₂/N₂ (27) but a low CO₂ permeability (30 barrer). These numbers are in accordance with previous work on neat poly(RTIL)s.²⁶ A general trend can be deduced from Figure 5.4: modifying the composition of BCPs by decreasing the amount of poly(RTIL) (i.e., increasing the amount of dodecyl ester block) leads to lower CO₂/N₂ selectivities but improves the CO₂ permeability considerably. It appears that the BCP layer morphology plays an important role in gas transport as well. Indeed, the two amorphous materials, homopolymer poly(**3**) and BCP **1T**, exhibit comparable performances even though they have very different compositions, whereas the ordered nanostructures of BCPs **1U**, **1V** and **1W** contribute to an increase of the CO₂ permeability by one to two orders of magnitude. A large improvement in CO₂ permeability can be observed for BCP **1W** (9300 barrer), even if the CO₂/N₂ selectivity is divided by 3.

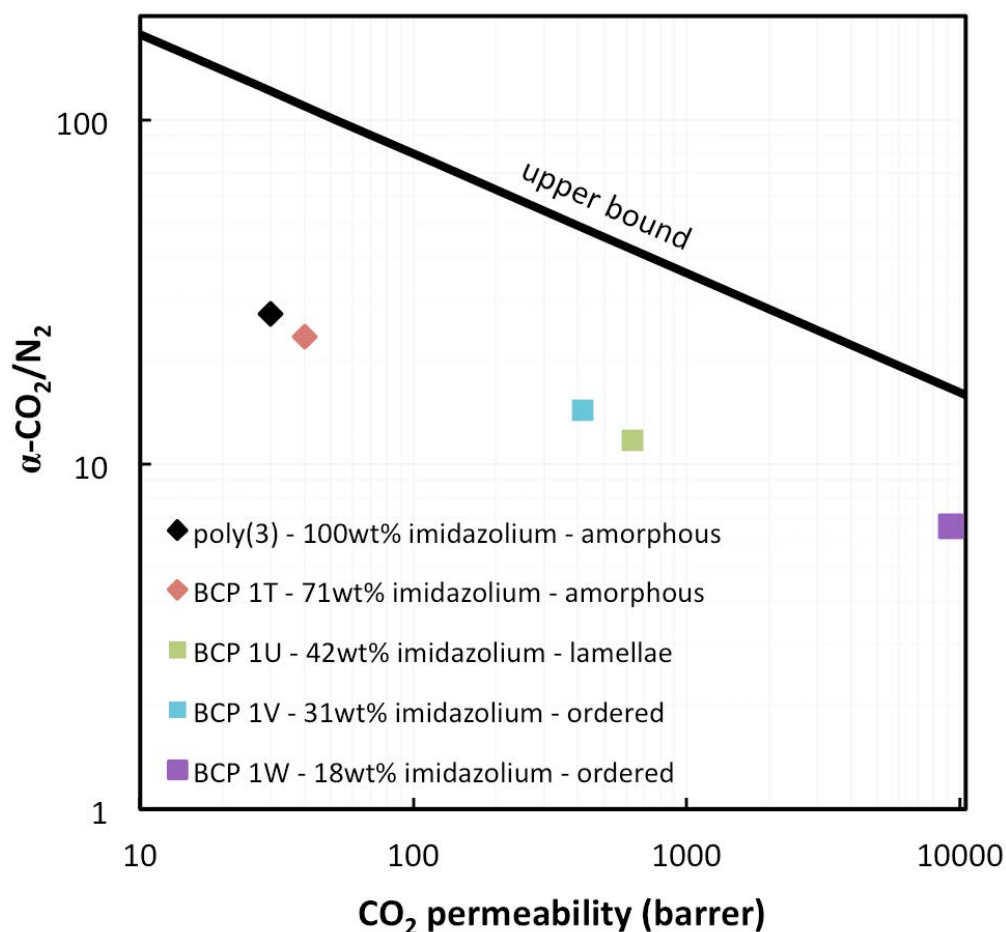


Figure 5.4. CO₂/N₂ selectivity vs. CO₂ permeability (Robeson plot) of alkyl-imidazolium BCP membranes. Content of imidazolium block in the block copolymer active layer is indicated in wt% and the type of nanostructure is identified. Experimental error is within the data points and represents less than 4%.

It is important to note that the PAN ultrafiltration membranes (supplied by MTR) that were used as supports for the BCPs coating, were found to not provide any gas selectivity. Consequently, the observed values of $\alpha_{\text{CO}_2/\text{N}_2}$ measured for the porous PAN-supported TFC BCP membranes can be attributed entirely to the thin layers of BCPs (and confirm the absence of pin-hole defects in the applied BCP coatings as well).

Additionally, a control experiment was carried out in order to check the effect of Grubbs' first-generation ROMP catalyst used during the synthesis of the BCPs. When

quenched after polymerization, this decomposed catalyst is responsible for the brown color of the BCPs. On this control experiment, two membranes of PDMS were cast: a blank sample and a membrane in which we introduced deactivated Grubbs' catalyst. The two samples were found to exhibit very similar CO₂ permeability (2990 barrer and 2670 barrer, respectively, for the blank sample and the membrane containing deactivated Grubbs' first-generation catalyst). Consequently, the deactivated catalyst does not seem to have any significant effect on CO₂ transport.

5.4.3.2 CO₂ Solubility Coefficient Determination

CO₂ solubility coefficients were determined from the measurement of CO₂ permeabilities and CO₂ diffusion coefficients and applying Equation 5.3. Figure 5.5 shows the CO₂ solubility coefficient (S_{CO_2}) vs. the imidazolium block content (wt%) in the BCPs. The dotted line has been added only to facilitate the comprehension of the figure. As can be seen in Figure 5.5, the imidazolium-based homopolymer poly(**3**) has a very high S_{CO_2} value due to the imidazolium cation and the Tf₂N⁻ anion⁴⁶ present in all of the polymer repeat units. The values of S_{CO_2} measured for the BCPs and poly(**3**) are also high (1.1 to 21.8 cm³ atm⁻¹ cm³) compared to other poly(RTIL)s (ca. 4 cm³ atm⁻¹ cm³).^{24,26} Finally, it appears that the polymer selective layer composition mainly influences the CO₂ solubility, since there is a linear trend between the amount of imidazolium block and the value of S_{CO_2} in the imidazolium-containing homopolymer and BCPs.

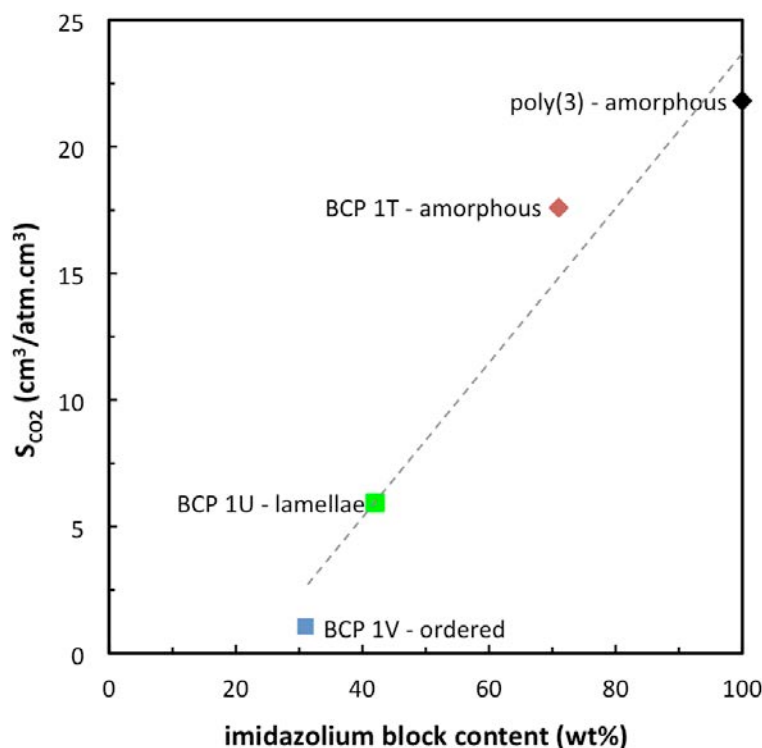


Figure 5.5. CO₂ solubility coefficient vs. imidazolium block content in the block copolymer active layer.

5.4.3.3 CO₂ Diffusion Coefficient Measurement

Figure 5.6 shows the trend in CO₂ diffusion coefficient (D_{CO_2}) (as determined by the time-lag method) vs. the imidazolium block content (wt%). Again, the dotted line has been added only to help the reading of the figure. The plot in Figure 5.6 shows that the value of D_{CO_2} increases when the imidazolium content decreases; however, it is a non-linear relationship. The amorphous materials (poly(**3**) and BCP **1T**) exhibit very low D_{CO_2} values ($1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $1.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively) that are similar to literature data (i.e., styrene-based poly(RTIL)s have D_{CO_2} values of 1.7 to $7.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$).²⁶ These values are in accordance with the work of Morgan et al. on diffusivities of gases in RTILs.⁴⁷ The rearrangement of the BCPs into ordered nanostructures has a

significant effect on D_{CO_2} values since they increase by two orders of magnitude compared to D_{CO_2} values of amorphous materials. It should be noted that it was not possible to determine the D_{CO_2} value of BCP **1W** (and subsequently S_{CO_2}) because the apparatus used was not precise enough to measure a time-lag shorter than 1 s. However, the D_{CO_2} of BCP **1W** must be higher than the D_{CO_2} of the other BCPs since its time-lag is much shorter. Consequently, we assume that the non-linear relationship between D_{CO_2} and imidazolium content must be due to morphological effects. Similar results have also been observed by Weber et al.⁴¹ These high D_{CO_2} values can be rationalized in different ways. First, the BCPs synthesized are not hard solids but present more the texture of a paste, which might favor better polymer chain or segment mobility. Moreover, BCPs **1U**, **1V**, and **1W** have shorter block lengths than BCP **1T** and poly(**3**), which may also facilitate the diffusion of gas molecules in the polymer. Finally, we believe that the ordered nanostructures of the BCPs increase the void volume content in the polymers and induce a better connectivity between the free volume elements.^{33,42} The super-glassy polymers like poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and Teflon® AF2400 and the rubbery polymer PDMS are well-known for their extremely high CO_2 permeability values due to large free volumes (Figure 5.7). Even if the BCPs present very high D_{CO_2} values (up to $3.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), these values are still low compared to those measured for PTMSP and PDMS ($2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).⁴⁸ This result allows us to be more confident in the reliability of our experimental data.

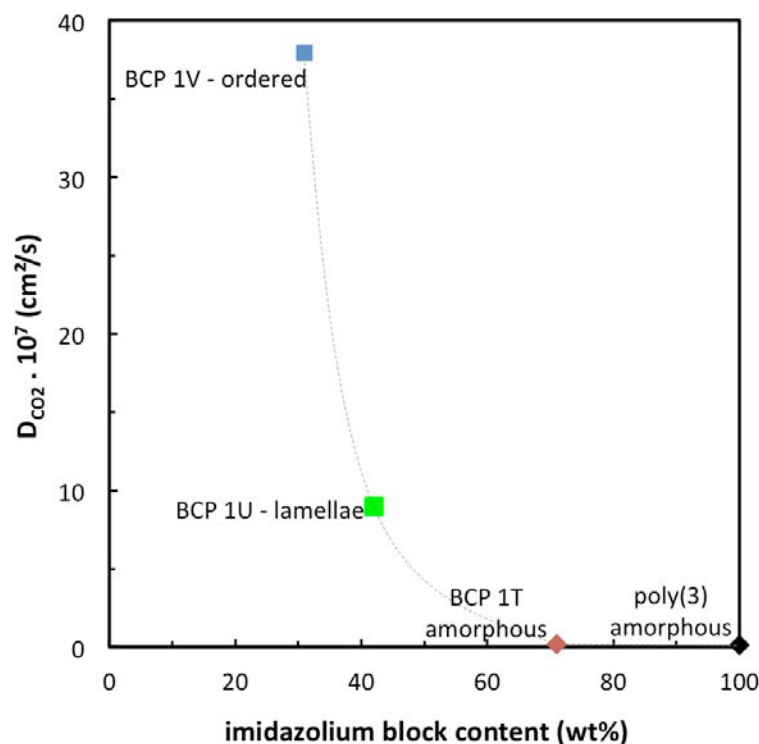


Figure 5.6. CO_2 diffusion coefficient vs. imidazolium block content in the block copolymer active layer.

Comparing Figures 5.5 and 5.6, we can see that the S_{CO_2} value decreases by a factor of 20 when the imidazolium content decreases from 100 wt% (homopolymer) to 31 wt% (BCP), but the D_{CO_2} value increases by a factor of 370. This large increase of D_{CO_2} is probably due to high polymer chain mobility and high free volume that are more interconnected, thus promoting both CO_2 and N_2 transport but inducing low selectivities. The change in free volume and/or connectivity could be confirmed by positron annihilation lifetime spectroscopy (PALS) measurements, and these studies are currently being investigated.

Even if BCPs with lower relative imidazolium content show better CO_2 permeability, the presence of the RTIL repeat units is absolutely necessary because they

greatly influence the gas permeability. Indeed, BCP **1V** has a higher diffusion coefficient than BCP **1U** but a lower permeability because the amount of RTIL-block is lower and so is the solubility coefficient.

Finally, it is crucial to emphasize that in these BCP materials, the composition and the ordered nanostructure of BCPs cannot be dissociated because changing the ratio alkyl block/ionic liquid block induces a modification of the morphology.

5.5 Comparison with Other Polymers Tested for CO₂/light Gas Separation; Future Work

Figure 5.7 represents the Robeson plot (data obtained at room temperature) for the three BCPs with ordered nanostructures and other materials with CO₂/light gas separation performance values. As can be seen in Figure 5.7, BCP **1W** has comparable gas transport properties than PTMSP, PDMS, or Teflon® AF2400, which are polymers characterized by high free volumes. The BCPs studied in this work exhibit higher CO₂ permeability than pure poly(RTIL) homopolymers and similar values compared to SILMs. However, their selectivity for CO₂/N₂ is lower.

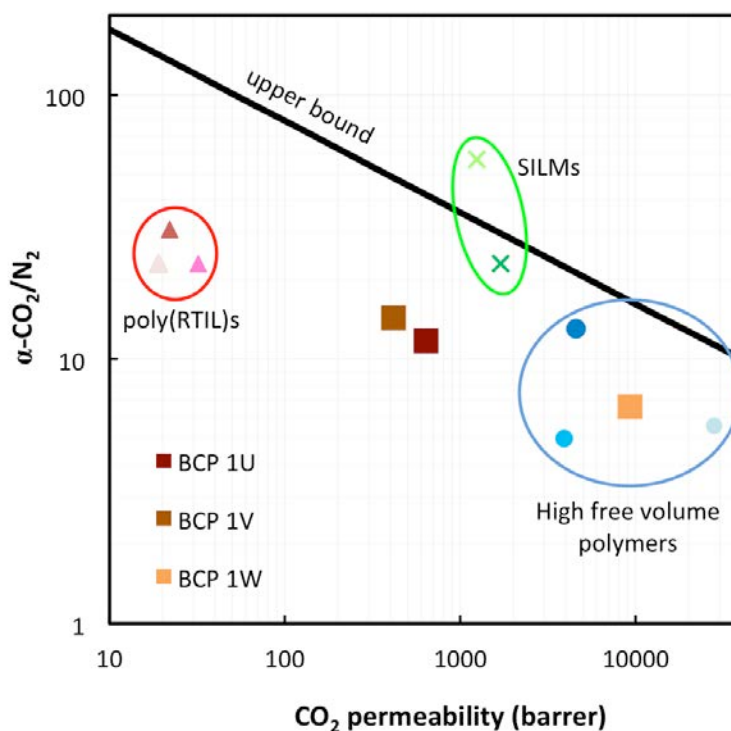


Figure 5.7. Comparison of the performance at room temperature of block copolymer membranes and other materials for CO₂/light gas separation on a Robeson plot.

● PTMSP,⁴⁸ ● PDMS,⁴⁸ ● Teflon® AF2400⁵² ▲ styrene-based poly(RTIL),²⁶ ▲ acrylate-based poly(RTIL),²⁶ ▲ poly(RTIL)-RTIL³² x and x SILMs²⁰

In order to increase the selectivity of the BCPs, non-polymerizable free RTIL can be introduced in the material: Hoarfrost et al. added RTIL to their BCP poly(styrene-*b*-2-vinyl pyridine) and observed a significant increase in proton transfer.⁴⁹ Similarly, Gu et al. blended a triblock copolymer with RTIL and obtained a material with similar properties to the neat RTIL.⁴⁰ Other functional additives can also be incorporated into the BCPs such as amines or poly(ethylene glycol)s (PEGs) that intrinsically present a large CO₂ affinity.⁵⁰ Preliminary tests have been carried out by adding free RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf₂N]) or triethylenetetramine (TETA, a tetraamine compound) to the alkyl-imidazolium BCPs, but we could not obtain defect-free membranes with these composite materials. Further study

needs to be done in order to understand the effect of these additives on the morphology and properties of these new BCPs.

Most of studies on nanostructured BCPs describe an annealing step at the end of the synthesis^{36,41,51} to help optimize the morphology. We also tried to anneal our alkyl-imidazolium BCP membranes by heating them at 150 °C for 1.5 h. We noticed a slight increase of the CO₂/N₂ selectivity after doing so but also an important decrease of the CO₂ permeability. Indeed, the heating step appears to have increased the density and packing of the BCP chains/segments, making the diffusion of gas molecules through the material more difficult.

Finally, the performances of the BCPs may be improved by tuning or using different monomers, for example, by employing monomers with pendant amine groups to create task-specific materials. One great advantage of RTILs is that the chemical and structural tuning possibilities are extremely broad.

Ongoing experiments on these TFC BCP membranes include evaluating their stability over time, confirming the increase in free volume and/or connectivity via PALS measurements, performing mechanical tests, and optimizing (i.e., reducing) the BCP active thickness in order to increase the membrane permeance.

5.6 Summary

The potential of novel imidazolium-based alkyl-ionic BCP membranes for CO₂/light gas separations has been evaluated through the example of CO₂/N₂ separation. These BCPs represent a new class of RTIL-based membrane materials combining the advantages of RTILs and ordered nanostructured polymers. BCPs containing a RTIL

component have been scarcely studied. The few examples detailed in the literature require a post-treatment and do not present the large range of nanophase-separated morphologies (i.e., lamellae, hexagonal, cubic, liquid-like packing, etc.) that we have with our BCPs. Moreover, none of the previous work considers the application of imidazolium-based BCPs for gas separation.

In comparison to analogous PBs of independent homopolymers (which macrophase-separate on the PAN support), the BCPs were successfully fabricated into defect-free, thin (3–20 μm), supported membranes. SAXS characterizations confirmed the ordered nanostructures in the active layers of BCPs. The type of morphology formed is directly linked to the alkyl:RTIL composition of the BCPs.

As far as we know, the effects of nanostructure and composition for BCPs containing RTIL units on gas transport have never been investigated. In performing such studies, we found that the CO_2 solubility is strongly impacted by the imidazolium content in the BCPs. Compared to the alkyl block, the RTIL block exhibits a high CO_2 affinity and is mainly responsible of the CO_2 solubility in the material, as expected. We also found that gas diffusion, which is path-dependent, is greatly influenced by the nanostructure/morphology of the BCPs. Indeed, the D_{CO_2} values of the ordered BCPs were two orders of magnitude higher than those measured for the amorphous polymers. These high diffusivity differences might be explained by the increased free volume or void elements that are well-interconnected, perhaps induced by the nanoscale phase-separation of the two blocks. This interpretation has been inspired by the gas transport mechanism in high free volume polymers such as PTMSP or Teflon® AF2400. The combined effects of composition and nanostructure of the BCPs have an important

impact on the CO₂ permeability and the CO₂/N₂ selectivity. The decrease of the amount of RTIL block, which goes together with the formation of ordered nanostructures, leads to a high improvement of the CO₂ permeability but decreases the selectivity as the diffusion of both CO₂ and N₂ are favor by the nanostructures. One of the ordered BCP exhibits an extremely high CO₂ permeability of 9300 barrer and could be an excellent candidate for CO₂/light gas separations if the CO₂ selectivity could be improve by adding RTILs or other CO₂-selective additives such as amines, or by tuning the different blocks.

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CHAPTER 6

Imidazolium-Containing, Hydrophobic-Ionic-Hydrophilic ABC Triblock Copolymers: Synthesis, Ordered Phase-Separation, and Supported Membrane Fabrication

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6.1 Abstract

Novel ABC triblock copolymers containing hydrophobic, imidazolium ionic liquid (IL)-based ionic, and non-charged hydrophilic blocks were synthesized by direct sequential, ring-opening metathesis polymerization (ROMP) of three chemically immiscible norbornene monomers. The resulting ABC triblock copolymers were found by small-angle X-ray scattering to phase-separate into different nanostructures in their pure melt states, depending on their block sequence and compositions. Supported composite membranes of these triblock copolymers were successfully fabricated with defect-free, ≤ 20 microns thick top coatings. Preliminary CO₂/light gas transport studies demonstrated the potential of this new type of IL-based block copolymer material for gas separation applications.

6.2 Introduction

Phase-separated block copolymers (BCPs) have been of intense interest in the materials community because of the physics of their ordered phase-separation and their potential for enhanced transport-related applications.¹⁻³ Recently, a new class of ionic liquid (IL)-containing BCPs has been prepared in which one block is hydrophobic (i.e., the repeat units contain uncharged alkyl sidechains) while the other block is charged (i.e., the repeat units contain IL-based sidegroups). These new IL-containing diblock copolymers (CPs) were prepared via either the direct, sequential living chain-addition polymerization of hydrophobic and IL-based monomers, or the post-polymerization incorporation of IL-based side-groups onto a pre-made, reactive diblock CP.^{4,5} The general premise of this work was to explore the incorporation of polymerized IL (poly(IL)) block segments into BCPs in order to examine their effect on nanophase separation as well as CO₂ gas transport and ion conductivity properties. This is because poly(IL)s inherently have high intrinsic CO₂ gas solubility and ion conductivity⁴, making them particularly useful as new functional materials for CO₂/light gas separations,^{6,7} solid-state ion conductors,⁸⁻¹⁰ and electrochemical devices.^{11,12} Prior work has shown several unique benefits from ordered phase-separation among BCPs with respect to improved light gas¹ and ethanol² transport, as well as ion conductivity.^{5,13,14} However, solvent-free, ordered phase-separation of poly(IL)-containing BCPs is largely undocumented, and this is particularly true of imidazolium-containing poly(IL)- based BCPs reported in the literature thus far.¹⁵⁻¹⁸

ABC *triblock* CPs are largely unexplored for applications but are uniquely sophisticated in comparison to commonly studied AB diblock CP systems. With the

addition of a third chemically unique block, ABC-type CP systems have the potential to form more complex nanostructured morphologies due to the competing interactions and constraints (i.e., “frustration”) between three mutually incompatible block units instead of two.³ Exclusive to ABC triblock CP systems, block sequence (i.e., ABC vs. ACB vs. CAB) can play an important role in phase-separation, and the dramatic expansion of parameter space can theoretically improve materials performances and stabilize emulsion phases in ternary solvent or polymeric blends.^{3,19}

Moreover, the study of *ionic* triblock CP systems is rare and has primarily been limited to ABA structures with the A or B block comprised of sulfonated polystyrene.¹⁹ Very recently, cationic imidazolium monomers were successfully polymerized into ABA-type triblock CP systems.²⁰⁻²⁴ In particular, reversible addition-fragmentation chain transfer polymerization (RAFT),^{20,21} nitroxide-mediated polymerization (NMP),^{22,23} and atom-transfer radical polymerization (ATRP)²⁴ techniques were used on vinyl- or acrylate-containing imidazolium monomers to form these ionic triblock CPs. While these ionic functional groups have demonstrated potential for ion conductivity^{20,22,23} and membrane gas transport²¹ applications, solvent-free, ordered phase-separation and thin-film composite membranes have not yet been realized for imidazolium-containing ABC triblock CP materials.

Herein, we present the first example of an ordered, nanophase-separated ABC triblock CP system containing hydrophobic, hydrophilic, and imidazolium-based ionic moieties. Defect-free, supported composite membranes were successfully fabricated with retention of the ordered morphology. Preliminary gas permeation results on these

membranes demonstrate the potential of this novel type of nanostructured ABC block copolymer material for CO₂/light gas separations.

6.3 Results and Discussion

6.3.1 Block Copolymer Synthesis

These triphasic ABC-type triblock CPs (**7A–C**) were synthesized via sequential, living ring-opening metathesis polymerization (ROMP) of norbornene-containing hydrophobic alkyl (**2**), cationic imidazolium (**3**), and non-charged hydrophilic polyethylene glycol (**8**) monomers using Grubbs' first-generation olefin metathesis catalyst in CH₂Cl₂ as the solvent under a water and O₂-free environment (Figure 6.1) (see the Supporting Information for more details). All three monomers were synthesized from commercially available starting materials in relatively high yields (see the Supporting Information). The overall compositions of triblock CPs **7A–C** were set to an initial 1:1:1 (hydrophobic:non-charged hydrophilic:ionic) block length ratio, with the total polymer length close to 60 overall repeat units. Therefore, each block length had roughly 20 monomer-specific repeat units per segment. To study the effect of triblock order sequence (i.e., ABC vs. CAB vs. ACB) on BCP nanostructure and gas transport, triblock CPs **7A–C** were synthesized by varying the sequence of monomer polymerization. In other words, the order of each domain (e.g., hydrophobic blocks made from monomer **2**, ionic blocks made from monomer **3**, and non-charged hydrophilic blocks made from monomer **8**) is different for **7A–C**. Triblock CP **7A** has the block sequence of (hydrophobic-ionic-uncharged hydrophilic) (i.e., ABC), **7B** has the sequence (uncharged hydrophilic-hydrophobic-ionic) (i.e., CAB), and **7C** has the sequence (hydrophobic-

uncharged hydrophilic-ionic) (i.e., ACB). In order to understand block incompatibility and nanophase-separation in this initial imidazolium triblock CP test platform, control experiments with monomers **2**, **3**, and **8** and their synthesized diblock CPs were explored to show phase-separation (see the Supporting Information).

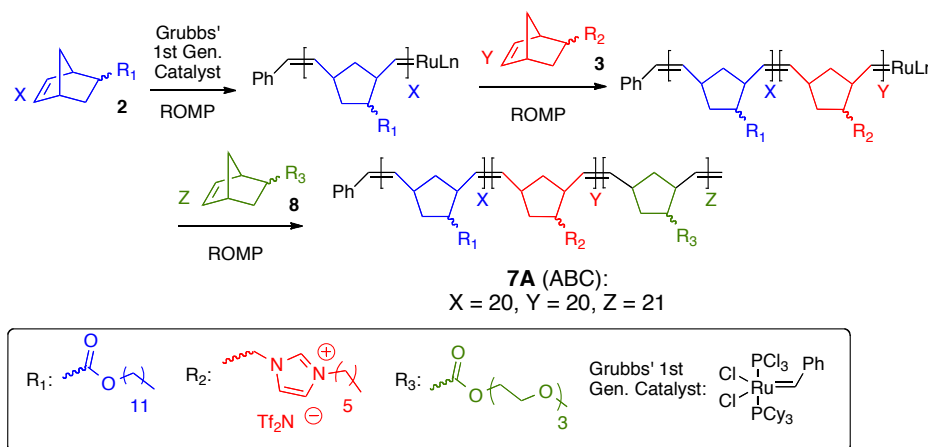


Figure 6.1. Example sequential ROMP of imidazolium-containing ABC triblock CP **7A**.

6.3.2 ^1H NMR Analysis to Determine Block Composition Ratios

After the sequential polymerization of monomers **2**, **3**, and **8** to afford triblock CPs **7A–C** with distinct block domains and lengths, ^1H NMR analysis was used to calculate their repeat unit block composition ratios (see the Supporting Information). The (hydrophobic:ionic:uncharged hydrophilic) ratios for each BCP were directly determined by integrating and comparing unique ^1H NMR signals distinct to each block domain. The block lengths were calculated from the block composition ratios and the monomer-to-catalyst loading ratios, after confirming molecular weight control and living homopolymerization character for each monomer (see the Supporting Information). Multiplying the repeat unit molecular weight by the calculated block length of each block segment gives the approximate number-average molecular weight (M_n) values for BCPs

7A–C. The approximate M_n values for **7A**, **7B**, and **7C** were determined to be 22,800 g/mol, 20,800 g/mol, and 22,800 g/mol, respectively (see the Supporting Information). Since the block length composition ratios were consistent (e.g., 1:1:1), the mass fractions for each block were also consistent and calculated to be as follows: 26.4 wt% hydrophobic block A, 46.1 wt% ionic block B, 27.5 wt% non-charged hydrophilic block C.

As discussed in our previous publication,¹⁶ absolute M_n values cannot be determined using conventional polymer molecular weight determination methods (e.g., GPC, mass spectrometry, light scattering) due to the highly charged nature of these macromolecules. Consequently, the use of these polymer molecular weight determination methods could also not be used to confirm a BCP primary structure via systematic M_n increases after the polymerization of each sequential block. To characterize this unconventional triblock CP system, **7A–C** block architecture was determined using alternative methods such as solubility and emulsion formation analysis, diffusion-ordered spectroscopy (DOSY), and small-angle X-ray scattering (SAXS).

6.3.3 Block Copolymer Morphology Characterization

6.3.3.1 Solubility Testing

In terms of their behavior with common solvents, samples **7A–C** all do not completely dissolve in hexanes, CH_2Cl_2 , ethyl acetate, THF, and methanol, rather, they show foaming behavior upon agitation ((i.e., surfactant-like behavior). In contrast, a physical blend (PB) analogue of the A, B, and C homopolymers does not show surfactant-like foaming behavior in the same solvents, consistent with samples **7A–C**

being covalently connected triblock CPs instead of non-connected mixtures of the homopolymers. Additionally, triblock CPs **7A–C** have distinct solubility differences than varying homopolymer or (diblock + homopolymer) physical blend analogues. For example, when mixed with methanol at 10 wt% polymer, each triblock CP forms an opaque suspension whereas the (poly(**2**) + poly(**3**) + poly(**4**)) homopolymer PB forms a clear, brown solution with an insoluble sticky, brown precipitate, and the (diblock + homopolymer) PBs form an off-white precipitate in the brown solution (see the Supporting Information).

6.3.3.2 ^1H NMR DOSY Analysis

With ^1H NMR DOSY analysis, one diffusion coefficient was found for each triblock CP sample, which is indicative of only one polymeric species in solution. On average, the diffusion coefficient for triblock CP samples **7A–C** was ca. $6.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. In contrast, the (poly(**2**) + poly(**3**) + poly(**4**)) PB control mixture in the same NMR solvent exhibited three distinct diffusion coefficients (see the Supporting Information), whereas the (diblock + homopolymer) PB control mixtures exhibited two, indicating clearly the structural difference between the triblock CP and PB samples.

6.3.3.3 Small Angle X-ray Scattering (SAXS) Analysis

In addition to solubility and NMR DOSY studies, small-angle X-ray scattering (SAXS) analysis was used to help to confirm block connectivity with absolute certainty. SAXS analysis of triblock CPs **7A–C** verified distinct phase-separation on the nanoscale, which is unique to covalently tethered BCPs. Each of the three variations in block

sequence for samples **7A–C** yielded BCPs with identifiable ordered morphologies (Figure 6.2). Representative SAXS data ($T = 100\text{ }^{\circ}\text{C}$) are shown in Figure 6.2 for each of the triblock CPs synthesized, along with SAXS data collected for the PB control sample containing the three homopolymers for comparison. For triblock CPs **7A** (ABC) and **7C** (ACB), prominent principal X-ray diffraction peaks, in addition to multiple higher-order reflections, are present that are consistent with a melt-state lamellar (L) phase morphology. For triblock **7B** (CAB), the observed prominent principal diffraction peaks and multiple higher order reflections are consistent with the hexagonally packed cylinder (HPC) morphology. Notably, the domain spacings ($d = 2\pi/q$) for the three triblock CP species are very similar (i.e., **7A**: 26.2 nm, **7B**: 28.6 nm, **7C**: 24.7 nm). The differences in phase behavior can be attributed to the differences in chain packing due to presumably asymmetric Flory interaction parameters ($\chi_{AB}, \chi_{AC} \gg \chi_{BC}$).³ We propose that the separation of the B-*b*-C interface in **7B** causes a unique difference in system frustration, resulting in the dissimilar morphology. This phenomenon has been known to explain differences in well-documented PS-PI-PEO vs. PI-PSPEO triblock CP systems.³ (For a more in-depth discussion about the phase-separation between the A-*b*-B vs. A-*b*-C vs. B-*b*-C interfaces, please see the Supporting Information.)

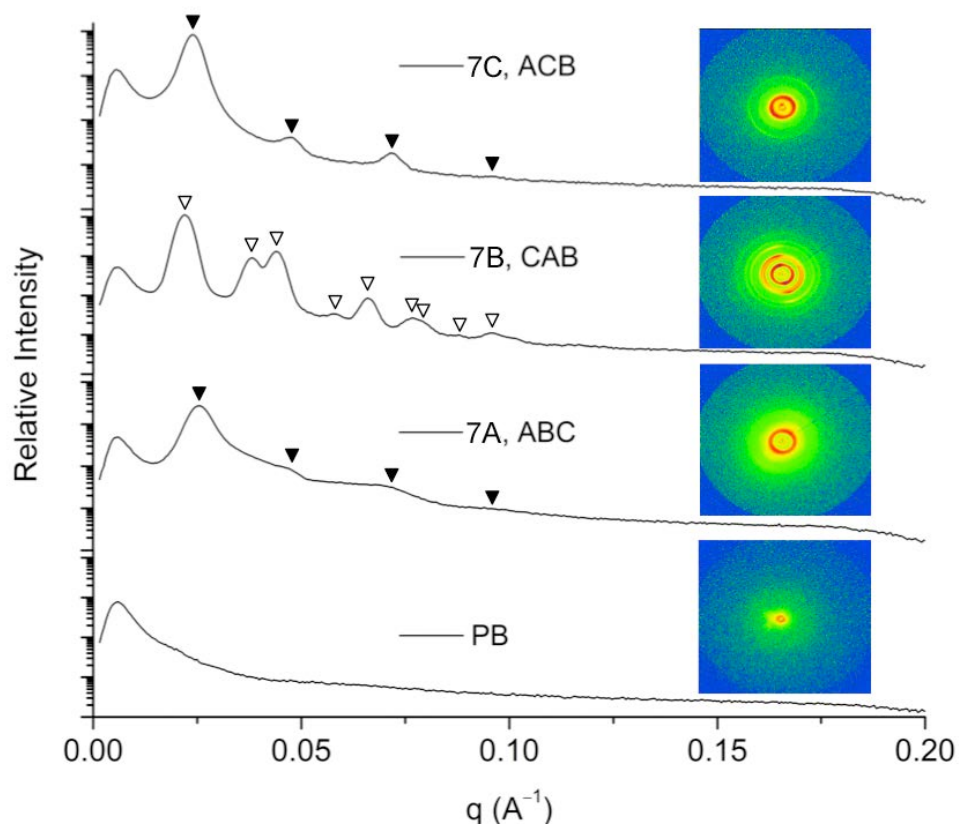


Figure 6.2. SAXS data for imidazolium-containing triblock CPs **7A–C**, with corresponding 2D detector images (inset). The inverted filled triangles represent the location of allowed reflections for the L morphology, calculated from the primary scattering wave vector $\mathbf{q}_{100}$: (L) $\mathbf{q}/\mathbf{q}^*$ at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. The inverted open triangles represent the location of allowed reflections for the HCP phase, calculated from the primary scattering wave vector $\mathbf{q}_{100}$: (L) $\mathbf{q}/\mathbf{q}^*$ at $\sqrt{1}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$, etc. The PB sample of poly(**2**), poly(**3**), and poly(**8**) shows no observable SAXS peaks, in contrast to the triblock CPs.

6.3.4 Composite Membrane Fabrication and Analysis

In terms of physical properties for film formation, triblock CPs **7A–C** were found to have better processability compared to the PB control sample. It was possible to form defect-free composite membranes of **7A** and **7B** via coating onto the surface of a commercial porous poly(acrylonitrile) (PAN) membrane support, whereas it was not possible to do so with the PB control mixture. The PB control mixture macrophase-

separated on the PAN support due to materials incompatibility, thereby preventing the formation of a continuous thin layer. In contrast, **7A** and **7B** completely wetted the PAN support when solvent-cast as a 10 wt% triblock CP in THF solution, and they formed thin, uniform, defect-free layers on the support. Unfortunately, we could not fabricate **7C** into a defect-free composite membrane in the same fashion. We believe this is due to the unique material properties caused by the block order sequence (hydrophobic:uncharged hydrophilic:ionic) in **7C**, since triblock CPs **7A** (hydrophobic:ionic:uncharged hydrophilic) and **7B** (uncharged hydrophilic:hydrophobic:ionic) were both successfully fabricated into composite membranes. The average triblock CP layer thickness for **7A** and **7B** was found to be 12.5 μm by cross-sectional scanning electron microscopy (SEM) analysis, which is an order of magnitude thinner than the only previously reported imidazolium-BCP membrane reported in literature.²¹ SEM cross-section images for the composite membranes of **7A** and **7B** are shown as insets in Figure 6.3.

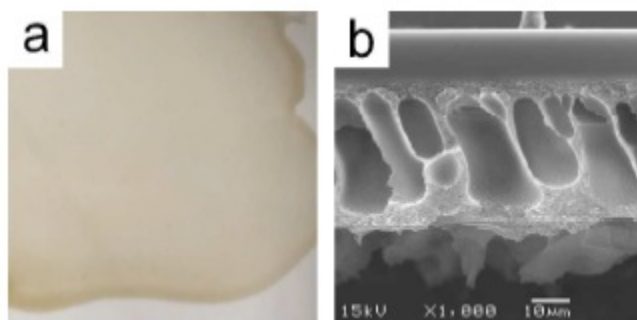


Figure 6.3. (a) Picture (top view) of a thin, uniform coating of our triblock CP **7B** on a porous PAN membrane support. (b) Cross-sectional SEM image of triblock CP **7B** coated on a porous PAN support showing a uniform, defect-free coating.

Representative SAXS data were collected for the triblock CP composite membranes **7A** and **7B**, and primary scattering peaks indicate an ordered, phase-

separated nanostructure (see the Supporting Information). However, the lack of higher-order SAXS peaks for the composite membranes prevents the assignment of any specific morphology. This is most likely due to the thin layer of the triblock CP (5–20 μm thick) on top of the membrane support (which is roughly 150 μm thick). However, regardless of the poorer signal-to-noise in the SAXS data of these coated composite membranes, the single SAXS peak observed indicate that a phase-separated morphology with a degree of nanoscale order is present in membrane samples of **7A** and **7B**.

6.3.5 Membrane Permeation Analysis

In order to show the potential of these new imidazolium-containing triblock CPs for CO_2 /light gas separations, we performed a series of preliminary permeation experiments on the composite membranes of **7A** and **7B** using four different gases (i.e., CO_2 , N_2 , CH_4 , and H_2). The results of these preliminary gas permeation studies are shown in Table 6.1. The apparatus and procedures for these gas permeation experiments are described in the Supporting Information. As can be seen from the data in Table 6.1, the composite membranes of **7A** (ABC sequence) and **7B** (CAB sequence) exhibit large differences in terms of their gas permeability values but show similar selectivity values. The gas permeability values of the **7A** (ABC)-based membrane are approximately 6 to 8 times higher than those measured for the **7B** (CAB)-based membrane. This difference could be explained by their different polymer nanostructures and/or domain orientation (i.e., L vs. HPC phases) due to the various affinities between the A (hydrophobic), B (ionic), and C (uncharged hydrophilic) blocks and the different position of the C block in the triblock CP.¹⁸ In this particular case, triblock CPs **7A** and **7B** have similar

compositions and overall block and total polymer lengths (just different block sequences), which could explain the comparable gas selectivities.

Table 6.1. Gas permeabilities (in barrers) and selectivities of **7A** (ABC) and **7B** (CAB) triblock CP-based composite membranes. Experimental error was less than 1.5%. Thicknesses of the active layers were 12.4 μm and 12.6 μm for **7A** and **7B**.

	P(CO ₂) [barrers]	P(N ₂) [barrers]	P(CH ₄) [barrers]	P(H ₂) [barrers]	$\alpha(\text{CO}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{CH}_4)$	$\alpha(\text{CO}_2/\text{H}_2)$
7A (ABC)	2340	230	820	740	10.2	2.9	3.2
7B (CAB)	410	30	100	140	137	4.1	2.9

The selectivity values for the gas pairs CO₂/CH₄ and CO₂/H₂ are low, but the CO₂/N₂ selectivity of the **7A** and **7B** composite membranes are very respectable, in 10–13 range. The CO₂ permeability values measured are up to 2300 barrer (Table 6.1). We want to highlight the value of this triblock CP architecture, as gas transport measurements for the homopolymerization of monomer **3** (i.e., poly(**3**)) present low CO₂ permeability (30 barrers) but high selectivity for CO₂/N₂ ($\alpha = 27$) as previously reported.¹⁷ The gas separation performance values are still far from those of current commercial membranes, but the potential for optimization and improvement of our materials is extremely high. The main parameter to increase in these triblock CPs is the CO₂/light gas selectivity (e.g., $\alpha > 20$ for CO₂/N₂), and several avenues can be explored to try and achieve this. For example, triblock CPs can be synthesized with different block lengths and block composition ratios, which should affect tremendously the nanostructures and the gas transport properties.¹⁷ Moreover, this casting technique can be optimized, and free ILs can be added to create mixed-matrix systems²¹ and improve these novel materials performances.

6.4 Summary

In summary, a new type of imidazolium-based ABC *triblock* CP system has been synthesized that undergoes ordered phase-separation in the solvent-free melt state and exhibits surfactant-like behavior in common organic solvents. This system was synthesized from the sequential, living ROMP of three chemically unique hydrophobic, imidazolium-based ionic, and uncharged hydrophilic norbornene-based monomers to afford triblock CPs with similar composition, block lengths, and total chain length but with three different block sequences (ABC, CAB, and ACB). Two of the resulting triblock CPs (i.e. **7A** (ABC) and **7B** (CAB)) were successfully fabricated into defect-free supported composite membranes, and preliminary gas permeation tests showed that these new imidazolium-containing triblock CP membranes have potential for CO₂/light gas separations. We believe this is the first investigation into the nanophase-separation and gas transport potential of an imidazolium-containing ABC-type triblock CP system. Given the importance of imidazolium character on CO₂ gas separations and ion conductivity and the potential of nanophase-separation on transport properties, we foresee great potential for this unprecedented, nanostructured poly(imidazolium)-containing system. Exploration of a wider range of block length ratios for this system is currently underway in order to map out a complete phase diagram. We are currently investigating the benefits of incorporating free IL and amines into these triblock CP systems as a means of increasing CO₂ permeability and selectivity values via the use of additives.

6.5 Acknowledgments

Primary financial support for the work performed at CU Boulder was provided by the DOE ARPA-E program (grant DE-AR0000098). Financial support for the work performed at CSU was provided in part by core funding from the Office of the Vice President. SAXS studies were performed at CSU using a regional instrument supported by the National Science Foundation MRI Program (grant DMR-0821799).

6.6 Supporting information

6.6.1 Materials and General Procedures

1-Bromohexane, 1-dodecanol, 5-norbornene-2-carboxylic acid, triethylene glycol monomethyl ether, *p*-toluenesulfonyl chloride, potassium carbonate, triethylamine, ethyl vinyl ether, and oxalyl dichloride were all purchased from the Sigma-Aldrich Co., and used as received. Dicyclopentadiene and 1-vinylimidazole were purchased from TCI America, and used as received. Lithium bis(trifluoromethylsulfonyl)amide (LiTf₂N) was purchased as Fluorad™ Lithium Trifluoromethanesulfonimide 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. Additionally, the CH₂Cl₂ used as the solvent in ring-opening metathesis polymerization (ROMP) reactions was purified by re-filtering over activated alumina prior to de-gassing. The H₂O used for synthesis was purified and de-ionized, with a resistivity value greater than 12 MΩ cm⁻¹. All chemical syntheses were carried out in a dry argon atmosphere using standard Schlenk line techniques, unless otherwise noted. Silica gel purification

was performed using 230–400 mesh, normal-phase silica gel purchased from Sorbent Technologies.

6.6.2 Instrumentation

^1H and ^{13}C 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. Fourier-transform infrared spectroscopy (FT-IR) measurements were performed using a Matteson Satellite series spectrometer (neat, thin film samples on Ge crystals). High-resolution mass spectrometry (HRMS) with electrospray (ES) analysis was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado, Boulder. SAXS data were collected using a Rigaku S-Max 3000 High Brilliance three-pinhole SAXS system outfitted with a MicroMax-007HFM rotating anode (Cu $K\alpha$), Confocal Max-Flux Optic, Gabriel multi-wire area detector, and a Linkam thermal stage. For SAXS analysis, the BCP samples were sandwiched between Kapton discs. Exposure times for the samples were typically on the order of 1800–43200 s.

6.6.3 Synthesis

6.6.3.1 Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid dodecyl ester (endo:exo 80:20) (2)¹⁵

Monomer **2** was prepared as previously described in the literature.¹⁵ Spectroscopic and purity analysis data were consistent with those previously reported.¹⁵

6.6.3.2 3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-hexyl-3*H*-imidazolium bis(trifluoromethyl-sulfonyl)amide (endo:exo 80:20) (**3**)¹⁵

Monomer **3** was prepared as previously described in the literature.¹⁵ Spectroscopic and purity analysis data were consistent with those previously reported.¹⁵

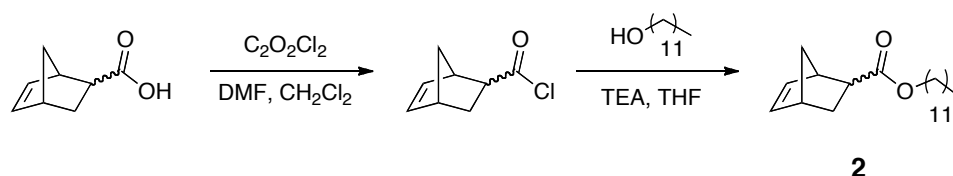
6.6.3.3 Triethylene glycol monomethyl ether tosylate (**9**)

In a procedure adapted from the literature,²⁵ triethylene glycol monomethyl ether (20.5 g, 125 mmol) and dry triethylamine (35.0 mL, 251 mmol) were added under air-free conditions to a 500-mL round-bottom flask containing CH₂Cl₂ (50 mL). Tosyl chloride (41.8 g, 219 mmol) dissolved in THF (50 mL) was added to the solution, and stirred at 0 °C before warming to room temperature overnight. The crude product was extracted with CH₂Cl₂ (3 x 100 mL), washed with 1 M HCl (2 x 250 mL), dried with anhydrous MgSO₄, and concentrated to a yellow oil. The product was isolated from excess TsCl via column chromatography (CH₂Cl₂, EtOAc) resulting in a clear, yellow oil matching literature characterization data (29.1 g, 73% yield). ¹H NMR (300MHz, CDCl₃): δ 7.82-7.80 (d, 2H), 7.37-7.34 (d, 2H), 4.16 (t, 2H), 3.71-3.54 (m, 10H), 3.38 (s, 3H), 2.46 (s, 3H).

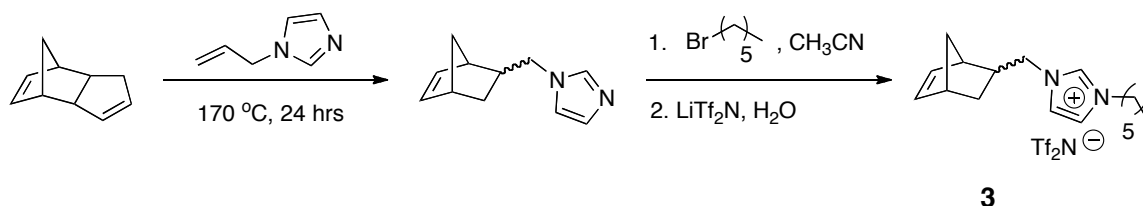
6.6.3.4 2-(2-(2-Methoxyethoxy)ethoxy) ethyl bicycle[2.2.1]hept-5-ene-2-carboxylate (**8**).

Norbornene-2-carboxylic acid (8.68 g, 62.8 mmol) and K₂CO₃ (17.4 g, 126 mmol) were stirred in CH₃CN (64 mL) before adding tosylate **9** (10.0 g, 31.4 mmol) and heating the mixture to reflux for 48 h. The crude product was then extracted with EtOAc (3 x 100 mL), washed with NaHCO₃ (2 x 300 mL) and H₂O (2 x 300 mL), dried with

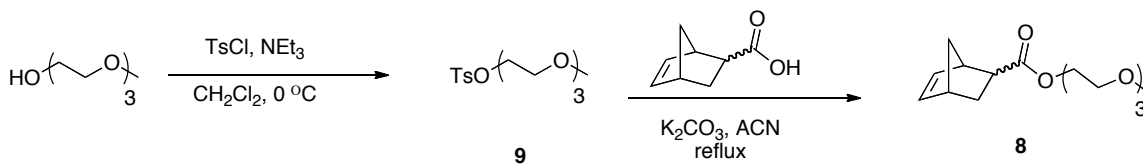
anhydrous MgSO_4 , and concentrated to a clear, yellow oil (8.93 g, 85% yield). ^1H NMR (300MHz, CDCl_3): δ 6.20-5.93 (m, 2H), 4.24-4.16 (m, 2H), 3.70-3.54 (m, 10H), 3.39 (s, 3H), 3.23-2.90 (m, 3H), 1.91-1.26 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 176.2, 174.7, 138.0, 137.7, 135.7, 132.4, 71.9, 70.5, 69.2, 63.5, 63.3, 59.1, 49.6, 46.7, 46.3, 45.7, 43.2, 43.0, 42.5, 41.6, 30.4, 29.3. IR (neat): 2944.7, 2874.2, 1728.8, 1450.8, 1335.5, 1271.1, 1251.8, 1176.2, 1106.5, 1068.7, 1041.6, 942.5 cm^{-1} . HRMS (ES) calcd. for (MH^+) : 285.1702; observed 285.1702.



Scheme 6.S1. Synthesis scheme for hydrophobic alkyl-functionalized norbonene monomer **2**.



Scheme 6.S2. Synthesis scheme for imidazolium-functionalized norbonene monomer **3**.

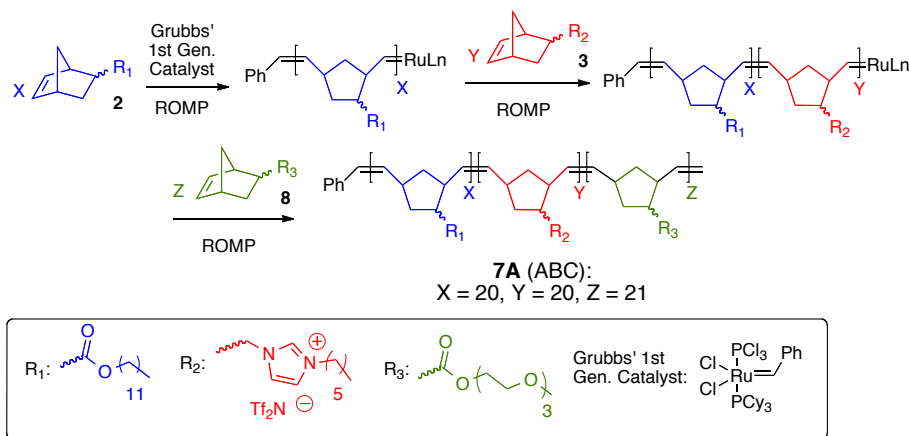


Scheme 6.S3. Synthesis scheme for polyethylene glycol-functionalized norbornene monomer **8**.

6.6.4 General Procedure for ROMP of Monomers **2**, **3**, and **8** to Form Triblock Copolymers¹⁵

A flame-dried Schlenk flask was charged with the desired amount of Grubbs 1st-generation catalyst and a stir bar under argon. The appropriate amount of CH_2Cl_2 was

then added to the Schlenk flask to form a catalyst solution with the desired concentration. The appropriate amount of the first monomer was then added to the catalyst solution from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe under argon atmosphere. Upon consumption of all of the monomer (as verified by ^1H NMR analysis) to form the first copolymer block, the second monomer was added from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe. Upon complete consumption of the second monomer (as verified by ^1H NMR analysis) to form the second copolymer block, the third monomer was added from a dry, degassed stock solution (CH_2Cl_2 solvent) via syringe. Upon completion of the third and final monomer, the ROMP triblock copolymerization mixture was quenched with excess of ethyl vinyl ether. The resulting triblock copolymer was then isolated by removal of the solvent in vacuo. ^1H NMR analysis of triblock copolymers **7A–C** confirmed the absence of any residual monomer.



Scheme 6.S4. Sequential ROMP of monomers **2**, **3**, and **8** to yield triblock copolymer **7A**.

6.6.5 Sample Procedure for Sequential ROMP of Monomers **2**, **3**, and **8** to Form Triblock Copolymer **7A**

Under argon atmosphere, Grubbs' 1st-generation catalyst (39.3 mg, 0.0478 mmol) was dissolved in dry, degassed CH_2Cl_2 (2.3 mL). Monomer **2** (7.72 g, 25.2 mmol) was diluted to a total volume of 25 mL with dry, degassed CH_2Cl_2 . From this monomer solution, 0.95 mL (0.956 mmol) was added to the catalyst solution, and the reaction mixture was stirred at room temperature until the polymerization of **2** was complete (4 h). Monomer **3** (13.5 g, 25.0 mmol) was then diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, 0.96 mL (0.96 mmol) was then added to the living ROMP polymerization mixture containing polymerized **2**, and the reaction was stirred at room temperature for 17 h. Monomer **8** (9.58 g, 33.7 mmol) was diluted to a total volume of 25 mL with dry, gas-free CH_2Cl_2 . From this monomer solution, 0.71 mL (0.96 mmol) was added as the final sequential addition to the living ROMP triblock copolymerization, and the reaction was stirred at room temperature for 7 h. The ROMP copolymerization mixture was then quenched by addition of excess ethyl vinyl ether (3 mL). The resulting triblock copolymer **7A** was isolated by removal of the solvent and other volatile compounds in vacuo at ambient temperature for 24 h (1.10 g, 98% yield).

*Note: The synthetic procedure for triblock copolymers **7B** and **7C** used the same quantities of Grubbs' catalyst and monomers from the above listed monomer stock solutions, as well as block polymerization reaction times with the only procedural difference being the sequence of monomer addition. For **7B**, the monomer addition/block polymerization sequence order was **8**, **2**, and then **3**. For **7C**, the monomer addition/block polymerization sequence order was **2**, **8**, and then **3**.*

Triblock copolymers **7A–C**, albeit with varying alkyl hydrophobic:ionic:non-charge hydrophilic block sequences, have the same chemical shifts in ^1H and ^{13}C NMR within ± 0.05 ppm due to being based on the same repeat units, so only one set of ^1H and ^{13}C NMR chemical shifts is presented for the sake of being non-repetitive. Copolymer block composition, block lengths, and extrapolated copolymer M_n values were determined via the combined use of ^1H NMR integration analysis, experimental confirmation of living ROMP character, and several control/comparison experiments against homopolymer physical blends, as detailed in our initial publication on the synthesis and basic characterization of these alkyl-imidazolium BCPs.¹⁵ See the following sections for summaries of the spectroscopic, compositional, and M_n values of the triblock copolymer samples **7A–C** prepared in this paper and analyzed by these prior procedures, as well as examples of the determination methods.

(7A) ^1H NMR (300 MHz, CDCl_3): δ 8.67 (br s, imidazolium C2), 7.28 (br s, imidazolium C4 and C5), 5.42–5.34 (b, $-\text{C}(\text{H})=\text{C}(\text{H})-$), 4.22–4.00 (b, $-\text{COO}-\text{CH}_2-$, $-\text{C}(\text{H})_2-\text{N}-\text{CH}-\text{N}-\text{C}(\text{H})_2-(\text{CH}_2)_4\text{CH}_3$), 3.66–3.38 (b, $-\text{O}-(\text{CH}_2)_2-\text{O}-$, $-\text{O}-\text{CH}_3$), 3.25–2.40 (br m, $-\text{imidazolium}-(\text{CH}_2)_5-\text{CH}_3$), 2.00–1.50 (b, $-\text{COO}-(\text{CH}_2)_{11}-\text{CH}_3$), 1.45–0.95 (br m, $-\text{COOCH}_2-(\text{CH}_2)_{10}-\text{CH}_3$), 0.90–0.86 (br m, $-\text{imidazolium}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 171.2, 162.8, 103.8, 71.9, 70.5, 69.2, 63.2, 59.1, 31.9, 30.8, 29.7, 29.4, 28.7, 22.7, 22.2, 14.1, 13.8. Block repeat unit molar ratio = 1:0.98:1.07 (alkyl hydrophobic:imidazolium ionic:non-charged hydrophilic); block length composition = 20-*b*-19.6-*b*-21.4; estimated $M_n = 22,800 \text{ g mol}^{-1}$.

(7B) Block repeat unit molar ratio = 1:0.86:0.91 (non-charged hydrophilic:alkyl hydrophobic:imidazolium ionic); block length composition = 20-*b*-17.2-*b*-18.2; estimated $M_n = 20,800 \text{ g mol}^{-1}$.

(7C) Block repeat unit molar ratio = 1:1.14:0.94 (alkyl hydrophobic:non-charged hydrophilic:imidazolium ionic); block length composition = 20-*b*-22.8-*b*-18.9; estimated $M_n = 22,800 \text{ g mol}^{-1}$.

6.6.6 Determination of BCP Composition and Molecular Weights

As discussed in our previous paper,¹⁵ conventional methods used to directly determine polymer molecular weights (e.g., GPC, NMR endgroup analysis, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and light scattering) of our imidazolium-containing BCPs yielded inconclusive results. These difficulties are likely associated with the very different physical properties of these BCPs due to their highly ionic nature, compared to conventional non-charged polymers.²⁶ Consequently, the block composition ratios, block lengths, and estimated M_n values for triblock copolymers **7A–C** were determined via a combination of ^1H NMR repeat unit/block length composition analysis and confirmation of living polymerization behavior with observed molecular weight control for each monomer.

(a) Sample calculation for determining hydrophobic:imidazolium:noncharged hydrophilic block composition ratios (for 7A)

Block composition ratios were determined via ^1H NMR in order to compare the hydrophobic (alkyl), ionic (imidazolium), and non-charged hydrophilic blocks for

each triblock copolymer. The signals for the unstrained alkene polymer backbone protons for all three blocks overlap between 5.34–5.42 ppm to create a broad peak (signal B in Figures 6.S1–6.S3). The signals for the methylene protons adjacent to the ester linkers in the hydrophobic and noncharged hydrophilic blocks and the methylene protons adjacent to the imidazolium unit in the ionic block overlap to create a broad signal between 4.00–4.22 ppm (signal C in Figures 6.S1–6.S3). The signals for the methylene protons in the ether chain in the noncharged hydrophilic block overlap to create a broad signal between 3.66–3.38 ppm (signal D in Figures 6.S1–6.S3). There are 2 unstrained protons per repeat unit for the hydrophobic block (x), 2 unstrained protons per repeat unit for the imidazolium block (y), and 2 unstrained protons per repeat unit for the non-charged hydrophilic block (z) (see Equation 6.S1). There are 2 methylene protons per repeat unit for the hydrophobic block (x), 2 methylene protons per repeat unit for the non-charged hydrophilic block (z), and 4 methylene protons per repeat unit for the imidazolium block (y) (see Equation 6.S2). There are 13 methylene protons in the ether chain per repeat unit for the non-charged hydrophilic block (z) (see Equation 6.S3).

$$2x + 2y + 2z = B_{1H \text{ NMR Integration}} \quad \text{Equation 6.S1}$$

$$2x + 4y + 2z = C_{1H \text{ NMR Integration}} \quad \text{Equation 6.S2}$$

$$13 = D_{1H \text{ NMR Integration}} \quad \text{Equation 6.S3}$$

Using the three equations to solve for the three unknowns, x, y, and z, the hydrophobic:imidazolium:non-charged hydrophilic block compositions (x, y, z) can be quantified for each triblock copolymer sample **7A**, **7B**, and **7C**, as shown below:

Block Composition Ratio for triblock copolymer 7A (Figure 6.S1):

$$\begin{aligned} 2x + 2y + 2z &= 6.04 \\ 2x + 4y + 2z &= 7.97 \\ 13z &= 13.83 \\ x &= 1.0, y = 0.98, z = 1.07 \end{aligned}$$

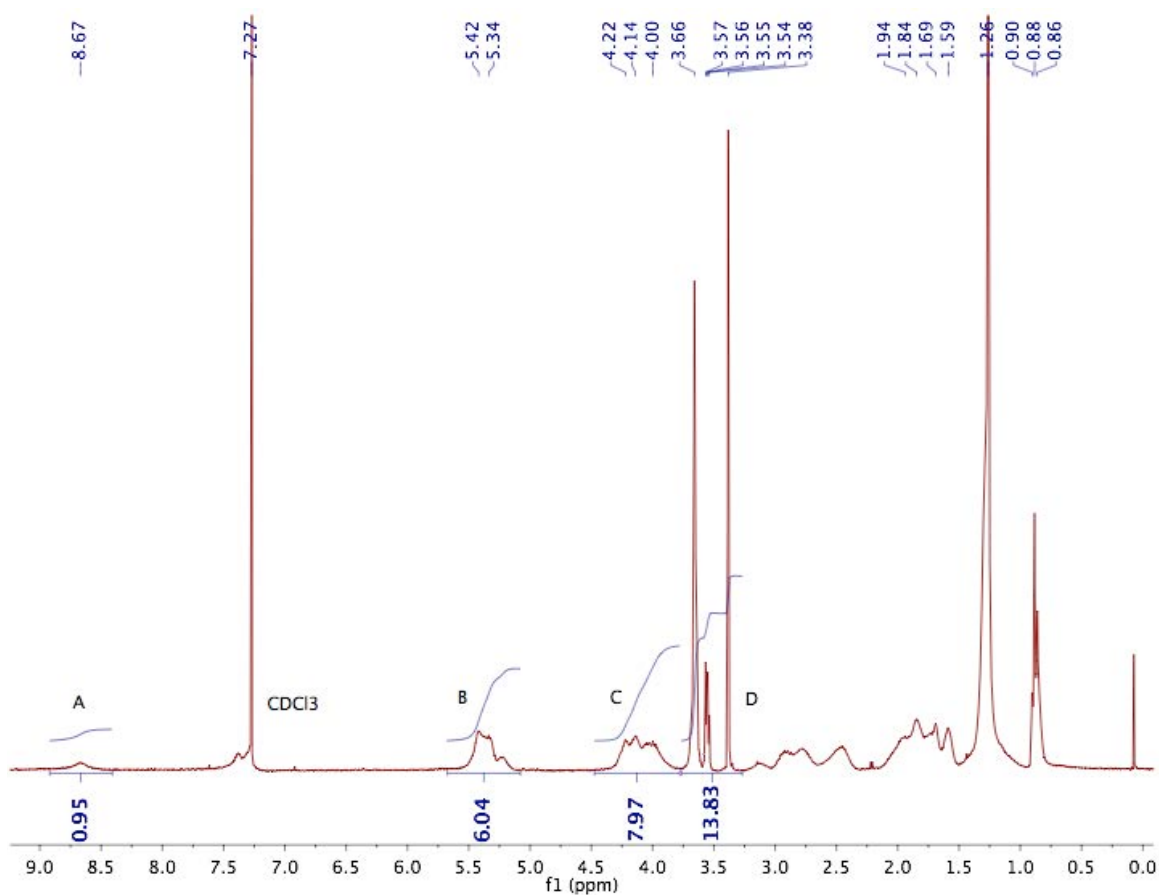
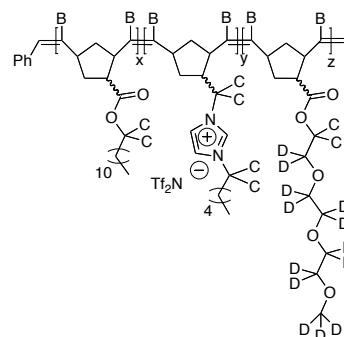


Figure 6.S1. An example ^1H NMR spectrum of triblock copolymer **7A**, and the ^1H NMR peak assignments used to calculate the hydrophobic:ionic:non-charged hydrophilic block composition (i.e., repeat unit) ratio in **7A**.

Block Composition Ratio for triblock copolymer 7B (Figure 6.S2):

$$\begin{aligned} 2x + 2y + 2z &= 6.30 \\ 2x + 4y + 2z &= 8.37 \\ 13z &= 14.85 \\ z &= 1.00, x = 0.86, y = 0.91 \end{aligned}$$

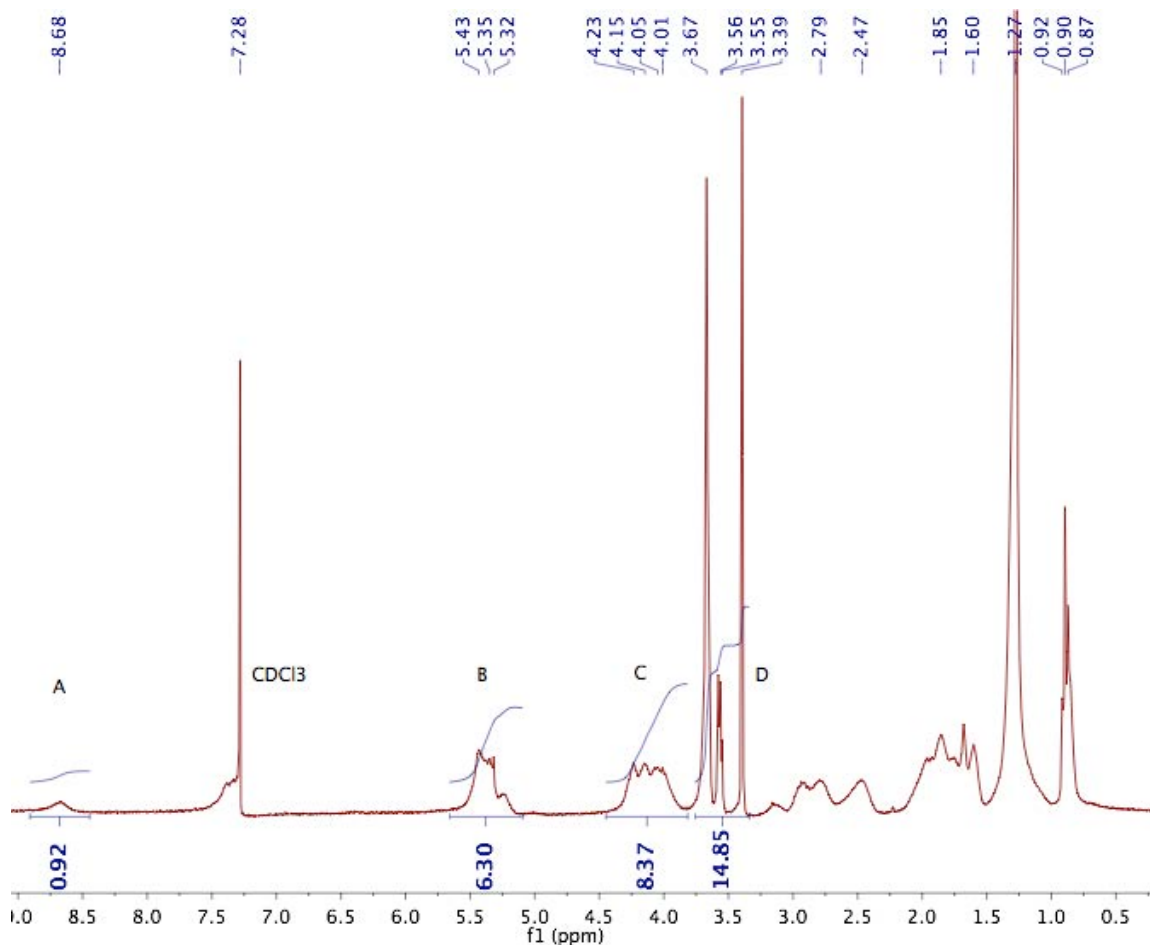
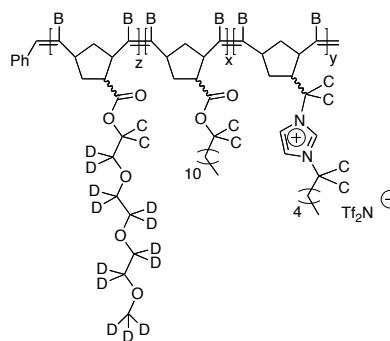


Figure 6.S2. An example ^1H NMR spectrum of triblock copolymer **7B**, and the ^1H NMR peak assignments used to calculate the non-charged hydrophilic:hydrophobic:ionic block composition (i.e., repeat unit) ratio in **7B**.

Block Composition Ratio for triblock copolymer 7C (Figure 6.S3):

$$\begin{aligned} 2x + 2y + 2z &= 7.51 \\ 2x + 4y + 2z &= 9.80 \\ 13z &= 18.08 \\ x &= 1.0, z = 1.14, y = 0.94 \end{aligned}$$

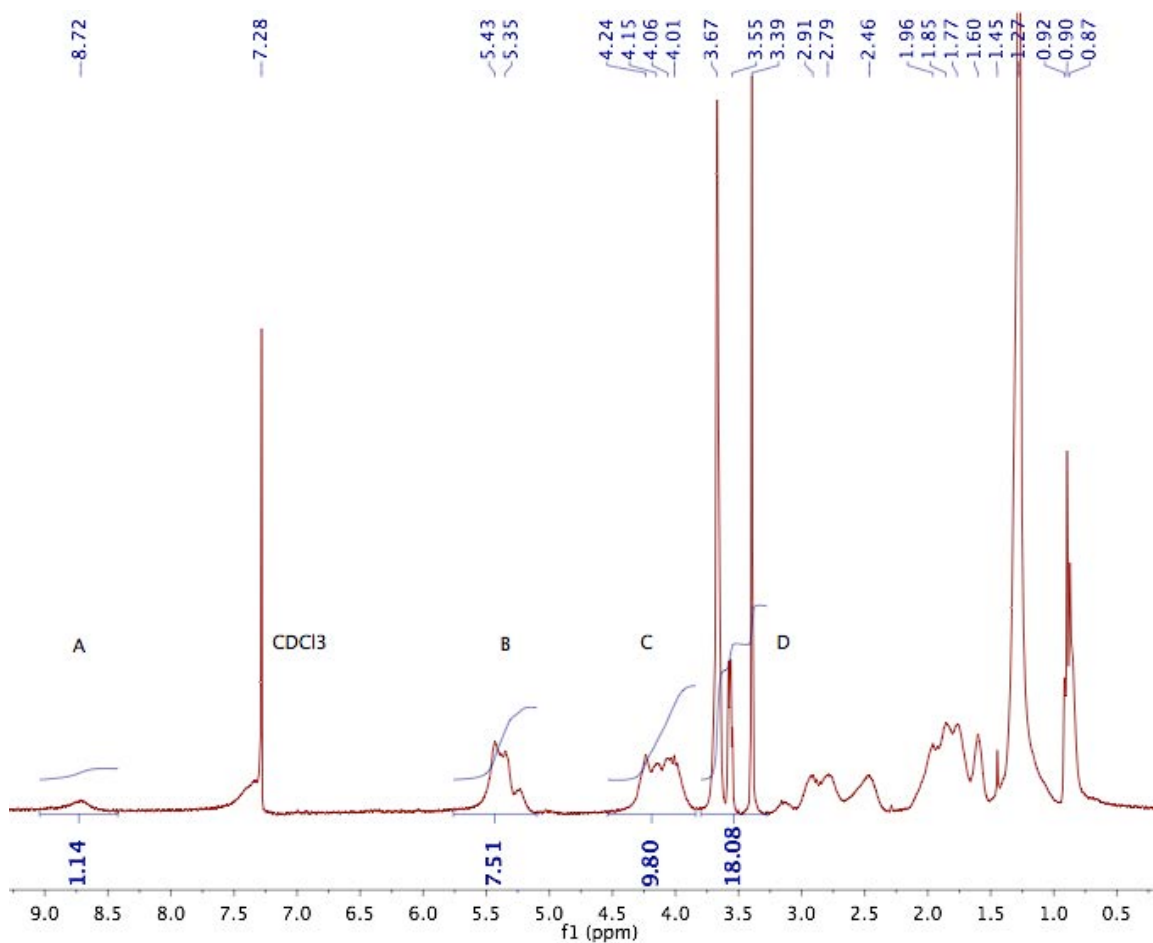
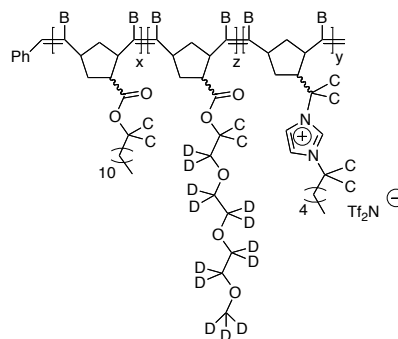
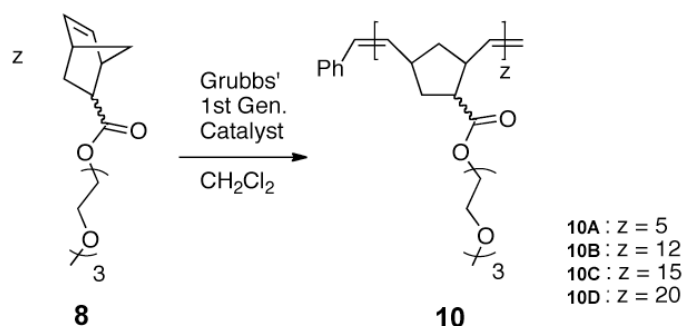


Figure 6.S3. An example ^1H NMR spectrum of triblock copolymer 7C, and the ^1H NMR peak assignments used to calculate the hydrophobic:non-charged hydrophilic:ionic block composition (i.e., repeat unit) ratio in 7C.

- (b) **Monomer 8 verification of living polymerization character with molecular weight control.** Living character and molecular weight control for ROMP homopolymerizations of monomers **2** and **3** are thoroughly discussed in our previous paper.¹⁵ The same systematic ROMP homopolymerizations to verify linear molecular weight control, living character, and low-PDI nature of monomer **8** were performed and described here.

ROMP experiments with monomer **8** showed that increasing the monomer-to-catalyst ratio increases the (absolute) molecular weight while maintaining low PDI of poly(**8**) samples in a linear fashion by GPC analysis, indicative of a living polymerization with predictable molecular weight control. Four samples of poly(**8**) oligomers (i.e., **10A–D**) were synthesized by polymerizing **8** with varying mole ratios of Grubbs' 1st-generation catalyst (Scheme 6.S5). The number-average molecular weight (M_n) and PDI values of these model homopolymers were determined using GPC with polystyrene (PS) molecular weight standards in THF (Figure 6.S4). The GPC M_n values were then compared to the absolute M_n values determined via ^1H NMR endgroup analysis. The GPC M_n values (vs. PS standards) for each homopolymer were found to be slightly different than the absolute M_n values determined by NMR endgroup analysis because poly(**8**) has a different chemical structure and thus a different hydrodynamic volume than PS in the same solvent. The measured PDI values ranged from 1.14–1.26, and a linear relationship was observed between monomer-to-catalyst molar ratio used in the ROMP reactions and the M_n values of the poly(**8**) samples formed (Figure 6.S4).



Scheme 6.S5. Non-charged hydrophilic oligomers (**10A–D**) used for M_n determination via GPC analysis (and substantiated by NMR endgroup analysis) in order to confirm living polymerization behavior.

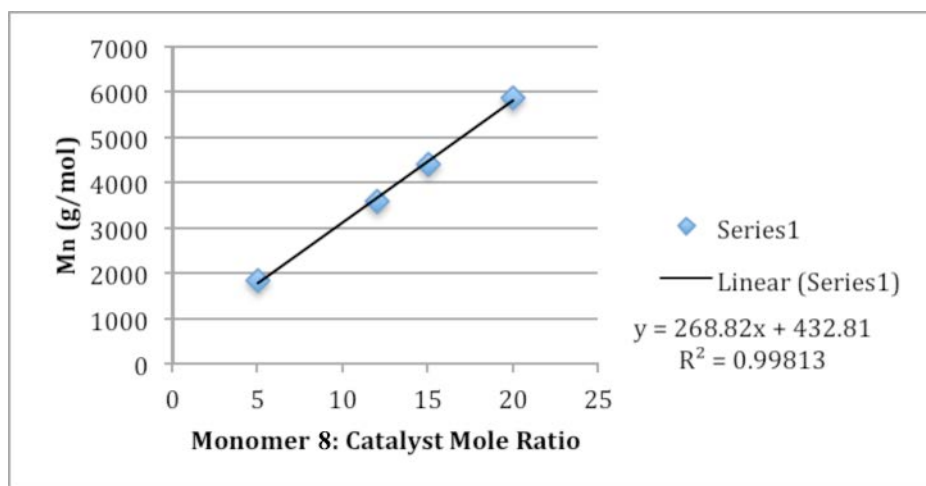


Figure 6.S4. Linear relationship between monomer-to-catalyst molar ratio used and M_n from GPC analysis for various poly(**8**) oligomers (**10A–D**). PDI values were consistent and ranged from 1.14–1.26, indicative of living polymerization with molecular weight control.

(c) **Calculating Block Length Compositions.** Based on the observed living characteristics for the ROMP of monomers **2**, **3**, and **8** by the Grubbs' 1st-generation catalyst, the block length compositions for triblock copolymers **7A–C** were calculated using the monomer-to-catalyst loading ratios (with complete monomer consumption), and the observed block composition (i.e., repeat unit) ratios for each triblock copolymer via ^1H NMR analysis (see Equations 6.S4–

6.S6). The blocky architecture and connectivity of **7A–C** are discussed and substantiated by the data presented in the main manuscript.

i. Block Length Composition for triblock copolymer 7A:

$$[(\text{Mon:Cat})(x_{\text{block ratio}})]-b-[(\text{Mon:Cat})(y_{\text{block ratio}})]-b-[(\text{Mon:Cat})(z_{\text{block ratio}})] \text{ (Eq. 6.S4)}$$

$$[(20)(1.0)]-b-[(20)(0.98)]-b-[(20)(1.07)] = 20-b-19.6-b-21.4$$

ii. Block Length Composition for triblock copolymer 7B:

$$[(\text{Mon:Cat})(z_{\text{block ratio}})]-b-[(\text{Mon:Cat})(x_{\text{block ratio}})]-b-[(\text{Mon:Cat})(y_{\text{block ratio}})] \text{ (Eq. 6.S5)}$$

$$[(20)(1.0)]-b-[(20)(0.86)]-b-[(20)(0.91)] = 20-b-17.2-b-18.2$$

iii. Block Length Composition for triblock copolymer 7C:

$$[(\text{Mon:Cat})(x_{\text{block ratio}})]-b-[(\text{Mon:Cat})(z_{\text{block ratio}})]-b-[(\text{Mon:Cat})(y_{\text{block ratio}})] \text{ (Eq. 6.S6)}$$

$$[(20)(1.0)]-b-[(20)(1.14)]-b-[(20)(0.94)] = 20-b-22.8-b-18.9$$

(d) Calculating Triblock copolymer Molecular Weight. As mentioned previously, conventional methods used to directly determine the molecular weights of triblock copolymers **7A–C** (e.g., GPC, end group analysis) were attempted, but all yielded inconclusive results. The M_n value for each triblock copolymer **7A–C** was estimated by multiplying the calculated lengths of each block with the molecular weight value of the appropriate repeat unit:

i. Triblock copolymer 7A:

$$20(307 \text{ g/mol}) + 19.6(540 \text{ g/mol}) + 21.4(285 \text{ g/mol}) \approx 22,800 \text{ g/mol}$$

ii. Triblock copolymer **7B**:

$$20(285 \text{ g/mol}) + 17.2(307 \text{ g/mol}) + 18.2(540 \text{ g/mol}) \approx 20,800 \text{ g/mol}$$

iii. Triblock copolymer **7C**:

$$20(307 \text{ g/mol}) + 22.8(285 \text{ g/mol}) + 18.9(540 \text{ g/mol}) \approx 22,800 \text{ g/mol}$$

6.6.6.1 Solubility Analysis

Triblock copolymers **7A–C** have unique solubility characteristics compared to an analogous physical blend (PB) mixture of (poly(**2**) + poly(**3**) + poly(**4**)). When mixed with MeOH at 10 wt %, triblock copolymers **7A–C** form lightly colored solutions, whereas PB analogues show clearly different behavior by forming heterogeneous mixtures (Figure 6.S5).

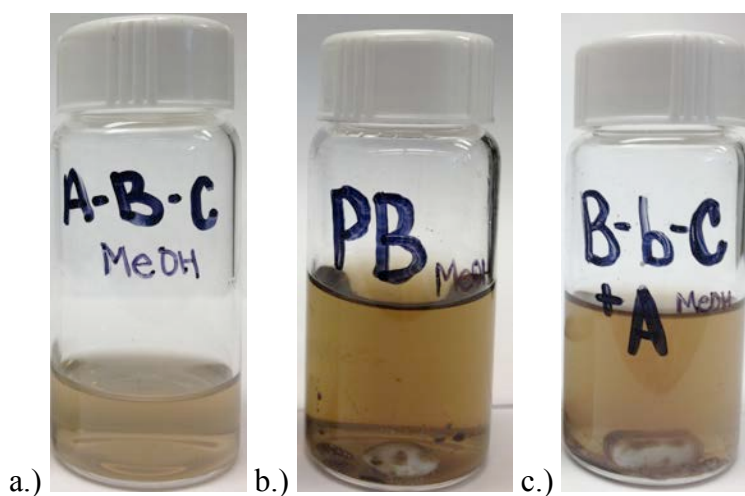


Figure 6.S5. Photographs showing the difference in solubility behavior at 10 wt% loading in MeOH between: (a) triblock copolymer **7A**; (b) a (poly(**A**) + poly(**B**) + poly(**C**)) homopolymer physical blend; and (c) a (B-*b*-C diblock CP + poly(**2**)) physical blend.

6.6.6.2 NMR DOSY Studies

NMR DOSY experiments were performed using a Varian Inova- 400 NMR spectrometer at 400.157 MHz for ^1H observation in $\text{DMSO-}d_6$ at 10 mg/mL sample concentration. Specific parameters were chosen as optimum to achieve nearly complete decay. Diffusion coefficients are listed below. As expected, the triblock copolymers **7A–C** each exhibit only one diffusion coefficient, indicative of only one species in solution, whereas the various PB control samples exhibit more than one diffusion coefficient, indicative of multiple polymer species present.

- i. Triblock copolymer **7A**: $0.06 \times 10^{-10} \text{ m}^2/\text{s}$
- ii. Triblock copolymer **7B**: $0.07 \times 10^{-10} \text{ m}^2/\text{s}$
- iii. Triblock copolymer **7C**: $0.06 \times 10^{-10} \text{ m}^2/\text{s}$
- iv. PB of (poly(**2**) + poly(**3**) + poly(**8**)): 0.24×10^{-10} ; 0.33×10^{-10} ; $0.39 \times 10^{-10} \text{ m}^2/\text{s}$
- v. PB of (B-*b*-C diblock copolymer + poly(**2**)): 0.19×10^{-10} ; $0.44 \times 10^{-10} \text{ m}^2/\text{s}$

6.6.6.3 SAXS Analysis

In order to understand the phase separation between each interface (e.g., hydrophobic:ionic, hydrophobic:non-charged hydrophilic, ionic:non-charged hydrophilic), SAXS data was collected for 3 synthesized diblock copolymers with 25-*b*-25 block length compositions: AC (hydrophobic-*b*-non-charged hydrophilic), BC (ionic-*b*-non-charged hydrophilic), AB (hydrophobic-*b*-ionic). Representative SAXS data (100 °C) are shown in Figure 6.S6 for each of the diblock copolymers synthesized. For AC and AB, prominent principal diffraction peaks in addition to multiple higher order reflections are consistent with melt-state lamellar (L) phase morphologies. For BC,

neither a prominent principal diffraction peak nor any higher order reflections are observed. Therefore, no specific morphology can be assigned to BC. Notably, the d spacings ($d = 2\pi/q$) for the BCP species AC and AB are similar (AC: 22.9 nm and AB: 27.9 nm).

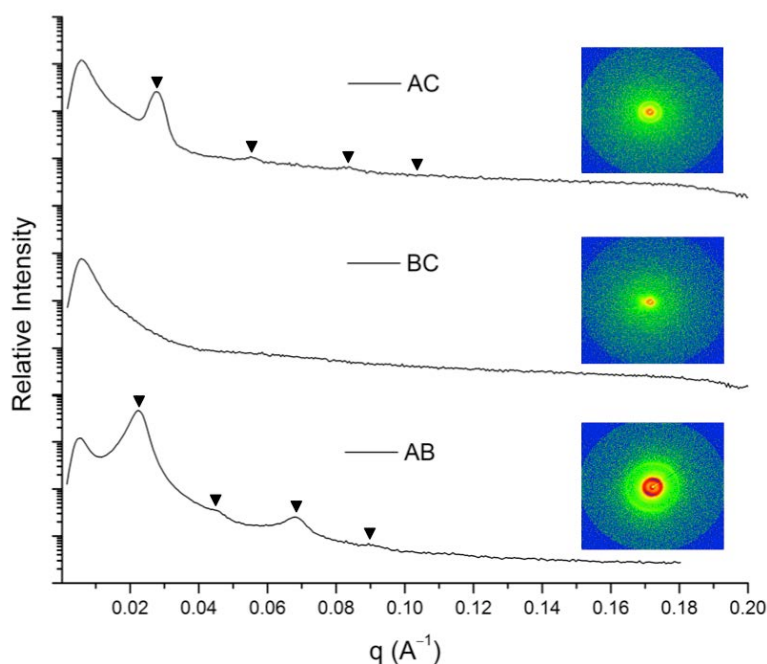


Figure 6.S6. Comparison of SAXS data (collected at 100 °C from heating). Inverted filled triangles represent the location of the allowed reflections for the lamellar morphology, calculated based on the position of the primary scattering wave vector $\mathbf{q}_{100}$: (L) $\mathbf{q}/\mathbf{q}^*$ at $\sqrt{1}$, $\sqrt{4}$, $\sqrt{9}$, $\sqrt{16}$, $\sqrt{25}$, etc. Inset pictures are the 2D scattering patterns.

SAXS data were collected for the fabricated triblock CP composite membranes **7A** and **7B** (Figure 6.S7). The appearance of the primary scattering peak confirms an ordered, phase-separated structure; however, further identification of an assigned morphology could not be assigned due to the absence of higher-order SAXS peaks. We believe this absence is due to the thin layer of the triblock CP (5–20 μm -thick) on top of the much thicker membrane support (which is roughly 150 μm -thick).

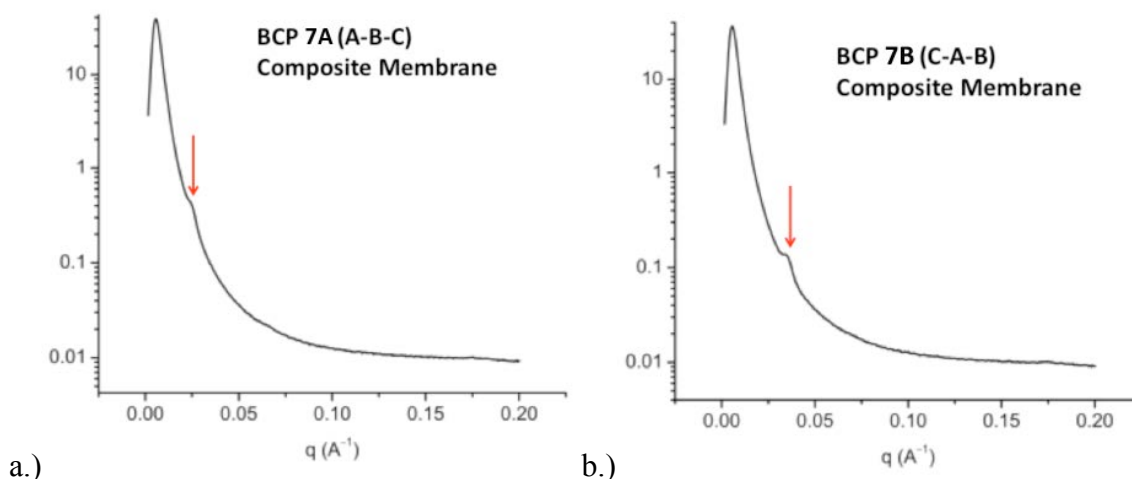


Figure 6.S7. SAXS data (collected at 100 °C from heating) of triblock CP composite membranes samples show phase separation evident by the observed primary scattering reflections of (a) triblock CP composite membrane **7A** and (b) triblock CP composite membrane **7B**.

6.6.7 Supported Membrane Fabrication

Supported triblock copolymer membranes were fabricated with a 10 wt % triblock copolymer in THF solution, coated on top of a PAN support (supplied by Membrane Technology and Research). The solution quickly spread on the support by tilting the membrane, and the THF evaporated slowly at room temperature before drying under vacuum overnight.

6.6.8. Scanning Electron Microscope (SEM) Imaging

SEM imaging was performed using a JEOL JSM-6480LV, with the acceleration voltage set to 10–15 kV and a spot size of 50 nm. Samples were fractured in liquid nitrogen, dried under vacuum overnight, and then coated with gold. At least two samples of each membrane were prepared and the thicknesses were measured at 3 different spots and averaged.

6.6.9 Gas Transport Properties Measurements via the Time-Lag Method

Single-gas permeability values for the supported triblock copolymer membranes were measured by a time-lag apparatus as previously reported.¹⁷ Each experiment began under vacuum conditions and was performed at room temperature (20 °C). Pure gas was applied at feed pressure around 1 bar, measured by an Omega pressure transducer (0–7 bar). The permeate pressure increased with time and was recorded by an Omega pressure transducer (0–1 bar). Permeability measurements of every gas were carried out three times for each membrane, and the experimental error was found to be less than 1.5%. The ideal permeability selectivity (α) is defined as the ratio of the permeability of the more permeable species to the permeability of the less permeable species.

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CHAPTER 7

Summary and Recommendations for Future Work

7.1 Thesis Objectives

The overall objective of this thesis research project was to design, synthesize, and characterize unprecedented room-temperature ionic liquid (RTIL)-based AB- and ABC-type block copolymers (BCPs) that can self-assemble into nanostructures in their melt states for potential use as CO₂/light gas separation materials. RTIL-based materials have many intrinsic properties such as high CO₂ uptake over other light gases that make them ideal for CO₂/light gas separation applications. BCPs are unique polymers in that they can phase-separate into nanostructured morphologies that can affect molecular gas transport. By combining these features into a single material, the premise was that a new type of material could be constructed that act as a unique membrane material with enhanced properties for CO₂/light gas separations.

The first goal of this first-generation project was to synthesize an RTIL-based monomer and one or more mutually immiscible co-monomers that could be sequentially co-polymerized with length control via ring-opening metathesis polymerization (ROMP). ROMP was chosen as the preferred polymerization method because it is a known functional group-tolerant, living (i.e., controlled) polymerization technique that can provide the uniform, low polydispersity polymer samples needed for consistent, ordered

phase-separation. However, the use of ROMP in preparing RTIL-based BCPs capable of ordered phase separation had not been reported prior to the work in this thesis.

Secondary goals of this project were to characterize the morphological behavior of these new, RTIL-based BCPs and to explore the correlation between BCP morphology and CO₂/light gas transport behavior through these materials. Due to the highly ionic nature of these RTIL-based BCPs, traditional polymer characterization techniques were not feasible. Consequently, alternative polymer characterization techniques were explored.

7.2 Summary of Thesis Accomplishments

A new imidazolium-RTIL-based, charged norbornene monomer was successfully synthesized. In addition, a hydrophobic alkyl ester norbornene monomer as well as an uncharged hydrophilic oligo(ethylene oxide) norbornene monomer were also successfully designed and synthesized. It was then demonstrated that each of these three mutually immiscible monomers can be polymerized by ROMP in a controlled, living fashion to form mutually immiscible homopolymers, before sequential copolymerization trials were attempted to make BCPs.

To verify individual monomer molecular weight control, a series of oligomers were polymerized by varying the molar ratio of monomer to Grubbs' catalyst. Absolute molecular weight was calculated via ¹H NMR end group analysis for all three homopolymers systems (e.g., poly(hydrophobic alkyl ester), poly(RTIL), poly(uncharged hydrophilic oligo(ethylene oxide))) and plotted versus the monomer-to-catalyst ratio. A linear trend was observed for each monomer, indicative of molecular weight control.^{1,2} Furthermore, living polymerization character was observed for each homopolymerization

when more of the same monomer was introduced, and the active (i.e., “living”) homopolymers continued to grow. This increase in homopolymer molecular weight, again, was verified via ^1H NMR analysis and is indicative of living polymerization character.^{1,2}

After it was demonstrated that each of the monomers could be polymerized via ROMP in a controlled, living fashion, a library of novel AB hydrophobic-ionic di-BCPs and ABC hydrophobic-ionic-uncharged hydrophilic tri-BCPs were successfully synthesized. Block ratios and block lengths were systematically varied, and the BCPs were extensively characterized using solubility analysis, diffusion ordered spectroscopy nuclear magnetic resonance (DOSY NMR), rheology, and small-angle X-ray scattering (SAXS) to confirm block connectivity compared to physical blends (PBs) of analogous homopolymers. The unique charged-uncharged BCP architecture produced each of the classic nanostructured morphologies, including lamellae, hexagonally packed cylinders, and spheres on a body-centered cubic lattice with the exception of the bicontinuous cubic gyroid phase. The strong degree of segregation and chemical immiscibility between the ionic-hydrophobic blocks may limit the ability of the BCP system to form the idealized gyroid network often sought after for transport-related applications. Furthermore, tri-BCP block sequence (e.g., ABC vs. CAB vs. ACB) was found to have a direct effect on nanostructured morphology.

Following thorough characterization, the RTIL-based di- and tri-BCPs were successfully fabricated into defect-free, thin (3–20- μm -thick) supported membranes and tested for CO_2 /light gas transport behavior. CO_2 solubility was strongly impacted by the imidazolium content in the BCPs, and gas diffusion, which is path-dependent, was also

greatly influenced by the morphology of the BCPs. Specifically, the CO₂ diffusion coefficient values of ordered BCPs were two orders of magnitude higher than those measured for synthesized, amorphous IL-based BCPs. One of the ordered BCP species exhibits an extremely high CO₂ permeability of 9300 barrer and could be an excellent candidate for CO₂/light gas separations if the CO₂ selectivity could be improved.

7.3 Recommendations for Future Work

7.3.1 (BCP + free RTIL) Composites

Following successful RTIL-based BCP synthesis, block connectivity characterization, and membrane gas transport work described in Chapters 3–6, an important future goal is to develop methods for improving the membrane performance (e.g., higher CO₂/N₂ selectivity and CO₂ permeability) in these BCP systems. There are multiple variables that could be adjusted to improve gas transport across RTIL-based polymeric membranes, such as modification of the RTIL cation (e.g., imidazolium vs. ammonium) and anion (Tf₂N⁻ vs. BF₄⁻) chemical structures,³ incorporating polar substituents,⁴ or adding free (i.e., non-polymerizable) RTIL to the polymer matrix.^{3,5} In the later case, previous work involving the blending of free RTIL into poly(RTIL) homopolymers^{6,7} (see Chapter 1) has shown that substantial increases in CO₂ permeability and some improvement in CO₂/N₂ selectivity can be achieved via fluidization/incorporation of more free volume in the resulting RTIL/poly(RTIL) composite. The analogous blending of free RTIL into RTIL-based BCPs should be able to do the same (Figure 7.1). However, one of the caveats in doing so is that incorporation of free RTIL into the imidazolium-containing BCP domains may change or disrupt the

ordered, phase-separated nanostructures formed, similar to a composition-dependent lyotropic liquid crystal system.

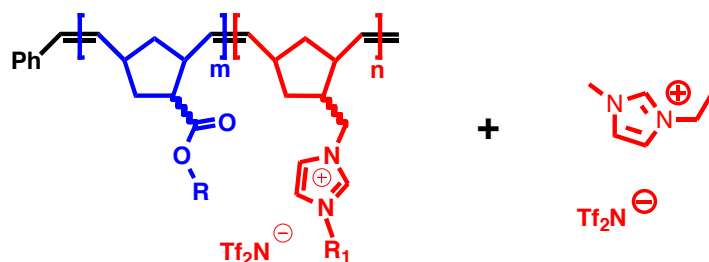


Figure 7.1. Chemical structures of an example (RTIL-based BCP + free RTIL) composite system consisting of a hydrophobic-*b*-imidazolium di-BCP and free EMIM Tf₂N RTIL. Such a composite material could possess improved membrane gas transport properties.

7.3.2 Cross-linkable RTIL-based Block Copolymer Architectures

Future work in this area should include the design and synthesis of a curable (i.e., cross-linkable) BCP system. In other words, after self-assembled phase separation of the BCP architecture, a cross-linking polymerization reaction would take place to “lock” the nanostructure into place (Figure 7.2). This concept would lend itself to substantially higher loadings of free RTIL, which in turn would most likely increase gas solubility selectivity while maintaining the BCP membrane permeability performance.

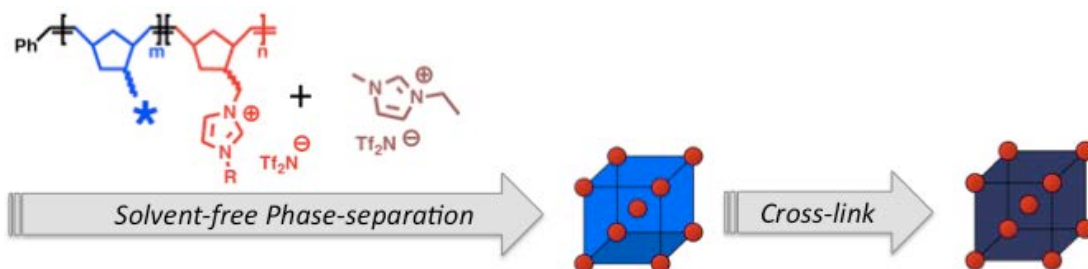


Figure 7.2. Potential design of a curable, post-polymerization BCP system that can incorporate high loadings of non-polymerizable “free” RTIL, phase-separate, and later cross-link to lock morphology into place. The blue * symbol denotes an orthogonal

chain-addition polymerizable group that can be activated for chain-cross-linking after initial BCP synthesis and phase-separation with RTIL inclusion.

Very preliminary work in this area has shown that a sequential ROMP-compatible, yet post-polymerization cross-linkable norbornene monomer can be designed and synthesized (Figure 7.3). The requirements for such a monomer are not trivial. The monomer must contain a norbornene derivative for compatibility with ring-opening metathesis polymerization, yet the pendent cross-linkable moiety cannot interfere with the Grubbs catalyst used in the ROMP reactions. Ideally, the monomer and subsequent polymer must show molecular weight control and living character while maintaining thermal stability. This is necessary due to the importance of thermal processing on the degree of order in BCP systems.⁸ One promising test candidate for this monomer design is one that possesses a cinnamoyl functionality.⁹⁻¹²

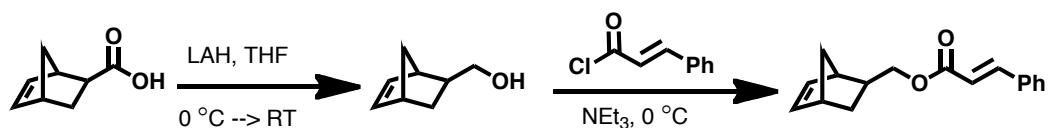


Figure 7.3. Successful synthesis of a cinnamate ester-functionalized norbornene monomer that is compatible with ring-opening metathesis polymerization and shows molecular weight control and living character, with the potential to photochemically cross-link upon UV irradiation.

The cinnamate ester moiety can perform [2+2] photo-cycloaddition upon irradiation of UV light (Figure 7.4).¹⁰ This photo-transformation phenomena is well-controlled and can occur under ambient conditions in solution^{10,12} or as a thin film^{9,11} material. Additionally, the disappearance of the cinnamoyl alkene group can be monitored via IR, making percent conversion easy to determine. Very little literature

exists on utilizing cinnamoyl groups for photo-cross-linking polymeric materials, especially ROMP-compatible. However, Wright et al.⁹ were able to synthesize a norbornene, ROMP-compatible dicinnamate monomer. While they did not synthesize di-BCPs, they reported the post-polymerization photo-cross-linking of the cinnamoyl groups using a 400 W Hanovia lamp UV source. Other research groups that have used cross-linking cinnamoyl groups in their curable polymers^{10–12} have reported up to 100% cross-linking conversion upon UV irradiation for 1–60 minutes with 275 or 365 nm light sources. Consequently, there is great potential in this functional group for post-ROMP cross-linking applications, and its use in making “stabilized” RTIL-based BCP composite materials warrants future work.

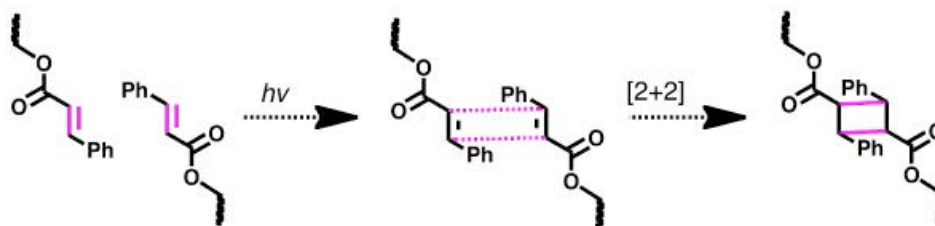


Figure 7.4 [2+2] photochemically allowed coupling of the cinnamate ester alkene bond that is not ROMP active. This functional group and coupling chemistry can thus be used for ROMP-prepared BCP post-polymerization chain cross-linking.

7.3.3 Alternative Living Polymerization Platforms and Techniques

Future work in this area could focus on exploring and utilizing other known controlled (i.e., living) polymerization techniques to synthesize ionic-based AB and ABC di- and tri-BCPs. Two problems with the use of ROMP for imidazolium-based BCP synthesis is the high cost of the Grubbs’ catalysts used compared to other types of living polymerization methods, and the fact that colored transition-metal residue is left in the

resulting polymers even after catalyst quenching and polymer precipitation and washing.¹³ The use of alternative, non-metal-based living polymerization techniques such as controlled/living radical polymerization of different monomers (i.e., activated terminal olefin monomers instead of strained cyclic alkene monomers) should be able to overcome these problems. They may also afford better scalability as well. The introduction of ionic blocks into well-defined BCPs via nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) has only just recently emerged thanks to the advances in these controlled radical polymerizations.^{14,15}

Unlike the Grubbs' catalyst necessary for ring-opening metathesis polymerization (ROMP) used throughout the entirety of this thesis, NMP, ATRP, and RAFT offer the opportunity to use less expensive nitroxyl radical (NMP), copper (ATRP), and dithioester (RAFT) catalysts or initiators.² After initiation, the controlled nature of these three living radical polymerization techniques are propagated by stable radicals, compared to the ruthenium-ligand complex propagation intermediate of ROMP.¹ In the case of NMP and RAFT, metal residue in the formed polymers from the catalyst/initiator system can also be avoided.

One obvious future direction of research would be to explore the direct sequential controlled/living radical polymerization of imidazolium-based styrene or acrylate monomers with hydrophobic and uncharged hydrophilic styrene or acrylate monomers. Although limited, there is some literature precedent for the successful living polymerization of styrene- or acrylate-containing imidazolium monomers via NMP^{16,17}, ATRP^{18,19}, and RAFT^{7,20} to form poly(RTIL)s and BCPs. While the Wang,²⁰ Lodge,⁷

and Long^{16,17} research groups have independently demonstrated the potential for ionic conductivity and membrane gas transport applications in these ionic-based BCP systems, phase-separated nanostructured morphologies have not yet been explored nor utilized for said applications.

A related direction for future research in this area is to explore the modification of nitroxide-mediated living block copolymerization of styrene and chloromethylstyrene.²¹ The resulting poly(chloromethylstyrene) (PCMS) blocks would be amenable to post-polymerization modification to form ionic blocks. Simple S_N2 chemistries can take place on the PCMS block to create imidazolium-functionalized styrene-based BCPs. Likewise, PMCS could be post-polymerization modified with vinyl imidazole to afford photo-curable, imidazolium-containing BCPs (Figure 7.5).

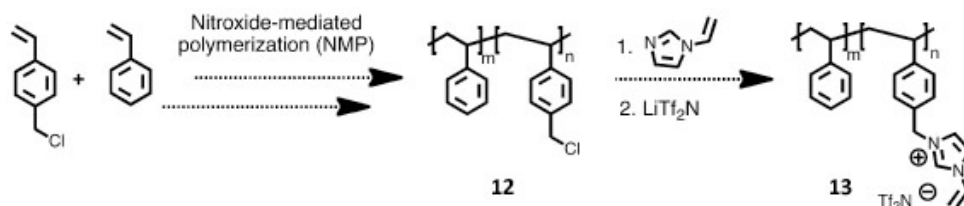


Figure 7.5. Proposed imidazolium-based BCP system synthesized via NMP that could undergo post-polymerization chemical modification to afford photo-cross-linkable BCPs.

Collectively, these alternative living/controlled polymerization techniques may prove to be more versatile, inexpensive, and industrially viable for future RTIL-based BCP design and warrant further exploration.

7.4 References

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