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Ionene segmented block copolymers containing imidazolium cations: Structure–property relationships as a function of hard segment content

Sharlene R. Williams [a], David Salas-de la Cruz [b], Karen I. Winey [c], Timothy E. Long [a,*]

[a] Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061, USA
[b] Chemical and Biomolecular Engineering Department, University of Pennsylvania, Philadelphia, PA 19104, USA
[c] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

ABSTRACT

Imidazolium ionene segmented block copolymers were synthesized from 1,1′-(1,4-butanediyl)bis(imidazole) and 1,12-dibromododecane hard segments and 2000 g/mol PTMO dibromide soft segments. The polymeric structures were confirmed using ^{1}H NMR spectroscopy, and resonances associated with methylene spacers from 1,12-dibromododecane became more apparent as the hard segment content increased. TGA revealed thermal stabilities $\geq 250\,^\circ$C for all imidazolium ionene segmented block copolymers. These ionene segmented block copolymers containing imidazolium cations showed evidence of microphase separation when the hard segment was 6–38 wt%. The thermal transitions found by DSC and DMA analysis found that the T_g and T_m of the PTMO segments were comparable to PTMO polymers, namely approximately $-80\,^\circ$C and $22\,^\circ$C, respectively. In the absence of PTMO soft segments the T_g increased to $27\,^\circ$C The crystallinity of the PTMO segments was further evidence of microphase separation and was particularly evident at 6, 9 and 20 wt% hard segment, as indicated in X-ray scattering. The periodicity of the microphase separation was well-defined at 20 and 38 wt% hard segment and found to be approximately 10.5 and 13.0 nm, respectively, for these ionenes wherein the PTMO soft segment is 2000 g/mol. Finally, the 38 and 100 wt% hard segment ionenes exhibited scattering from correlations within the hard segment on a length scale of approximately 2–2.3 nm. These new materials present structure on a variety of length scales and thereby provide various routes to controlling mechanical and transport properties.

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1. Introduction

Ammonium ionenes are ion-containing polymers that contain quaternary nitrogen atoms in the macromolecular main chain, as opposed to a pendant site, and are synthesized through a Menschutkin reaction of ditertiary amines and alkyl dihalides. Ammonium ionenes are widely reported in literature [1–10], but the synthesis and structure–property relationships of imidazolium ionenes are not well-documented. In fact, only a few examples in the literature exist. For example, although the researchers did not refer to their polymers as imidazolium ionenes, only two research groups have reported the preparation of quasi-solid state dye-sensitized solar cells containing imidazolium salts within the repeating unit of the polymer backbone [11,12]. Yanagida et al. were the first to report the synthesis of imidazolium cation-containing ionenes from alkyl bis(imidazoles) and alkyl diiodides for this

purpose [12]. The second report originated from the group of Chen et al. [11], and the researchers conducted investigations with imidazolium ionenes containing ethylene oxide chains, which are known for improving charge-transport properties [13]. The resulting dye-sensitized solar cells, which contained ethylene oxide repeating units, possessed light-to-electricity conversion efficiencies of 1.56%.

Typically, imidazolium cation-containing polymers are prepared from vinyl, acrylate, and methacrylate monomers using conventional free radical polymerization techniques. Ohno et al. synthesized organoboron and imidazolium salt-containing polymers via hydroboration polymerization for lithium cation transport purposes [14]. The resulting polymers possessed ionic conductivities of 3.74×10^{-5}–1.93×10^{-5} S/cm at $50\,^\circ$C when combined with equimolar concentrations of lithium bis(trifluoromethylsulfonyl)imide. In addition, Ohno et al. reported the synthesis of polymer brushes that contained imidazolium salts and poly(ethylene oxide) (PEO) [15]. The imidazolium polymer exhibited a conductivity of 1.49×10^{-4} S/cm at $30\,^\circ$C and a T_g that was consistent with pure PEO.

Imidazolium cation-containing ionenes offer many advantages compared to conventional imidazole-containing polymers. The reactivity and charge density are easily controlled through variation in the alkylene spacer length between the bis(imidazole) monomer and the alkyl dihalide. In addition, the polymerization process does not require initiators or produce by-products. Segmented ionenes offer many interesting thermal, mechanical, and morphological properties due to the availability of oligomeric precursors. Poly-(tetramethylene oxide) (PTMO) is a suitable oligomer for ionenes, and Kohjiya et al [16]. reported the first segmented ammonium ionene based on PTMO. The ammonium ionenes exhibited promising elastomeric behavior, namely, 1.37 MPa tensile stress at break and 510% elongation at break. Since then, many researchers have conducted ammonium ionene syntheses using PTMO segments. Leir and Stark conducted investigations on the reactivity of various dihalides with ditertiary amine end-capped PTMO [17]. However, in their synthetic strategy, further alkylation can occur in the presence of dimethylamine. Therefore, the PTMO segment was not well-defined before the ionene polymerization. In a later collaboration with Wilkes et al., they determined the effect PTMO molecular weight, counteranion (Br$^-$ vs. Cl$^-$), and structural differences of the ionene hard segment on the thermal and mechanical properties of the ammonium ionenes. Overall, they concluded that PTMO ionenes behaved similar to polyurethane ionomers, despite the absence of hydrogen bonding that polyurethane ionomers have within their hard segments [1]. Furthermore, Wilkes et al. discovered that reacting an amino-terminated PTMO oligomer with 1,4-dibromo-p-xylene resulted in an ionene that microphase separated into rod-like structures [18].

In this manuscript, the synthesis of novel imidazolium ionene segmented block copolymers containing PTMO soft segments is reported. The PTMO soft segment was prepared using a quantitative derivatization of PTMO using 6-bromohexanoyl chloride. This superior synthetic strategy avoids potential further alkylation, which was a possible side reaction from a previously reported synthetic route [17]. To enhance the film formation properties, segmented block copolymers containing 1,12-dibromododecane hard segments were also synthesized. Thermal and mechanical properties were evaluated, and structure–property relationships were established as a function of hard segment content.

2. Experimental

2.1. Materials

Poly(tetramethylene oxide) (PTMO) oligomer (Terathane, Du Pont) with number-average molecular weight of 2000 g/mol was purchased from Aldrich and dried in vacuo (0.1 mm Hg) at 23 °C for 24 h prior to use. 1,12-Dibromododecane (Aldrich, 98%) was recrystallized from ethanol. Imidazole (Aldrich, ≥99%), dimethyl ether solution (Aldrich, 60% in water), 6-bromohexanoyl chloride (Alfa Aesar, 97%), toluene (EMD Chemicals, 99.5%), dimethylsulfoxide (DMSO, Aldrich, anhydrous grade), and diethyl ether (Fisher Scientific, 99.9%, anhydrous) were used as received. Sodium hydroxide pellets (Aldrich, ≥98%) were used to prepare a 50 wt % aqueous solution. 1,4-Dibromobutane (Aldrich, 99%) and

triethylamine (TEA, Aldrich, 99%) were distilled prior to use. Dimethylformamide (DMF, Aldrich, 99.8%, anhydrous) and tetrahydrofuran (THF, EMD Science, HPLC grade) were passed through alumina and molecular sieves columns before use. Chloroform (CHCl$_3$, Fisher, Optima grade) was distilled from sodium/benzophenone immediately prior to use. 1,12-Bis(N,N-dimethylamino)-dodecane was synthesized according to a modified literature procedure [10,19].

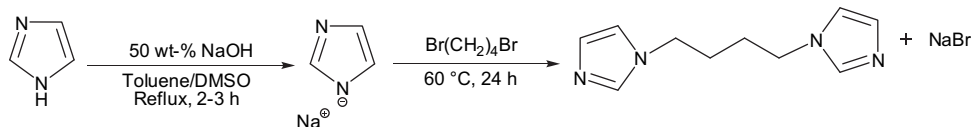### 2.2. Synthesis of 1,1'-(1,4-butanediyl)bis(imidazole)

The procedure of So et al. [20] was used to synthesize 1,1'-(1,4-butanediyl)bis(imidazole), except 1,4-dibromobutane was used rather than 1,4-dichlorobutane. The final product was obtained in 89% yield. ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO) δ = 7.58 (s, 2H), 7.11 (s, 2H), 6.86 (s, 2H), 3.92 (m, 4H), 1.59 (m, 4H). FAB-MS: M + H = 191.12 (found), molecular weight = 190.12 (calculated).

### 2.3. Synthesis of poly(tetramethylene oxide) dibromide

PTMO (10.0 g, 0.005 mol) was dissolved in 200 mL dry CHCl$_3$ in a 500-mL, round-bottomed flask containing a magnetic stir bar. TEA (1.53 mL, 0.011 mol, 2.2 eq) was added via syringe. The flask was equipped with an addition funnel and 100 mL of dry CHCl$_3$ was added to the funnel. 6-Bromohexanoyl chloride (1.68 mL, 0.011 mol, 2.2 eq) was syringed into the addition funnel. The reaction flask was cooled with an ice bath and the acid chloride was added dropwise to the reaction, and the reaction was allowed to warm to room temperature (23 °C). Stirring was continued for 18 h. When the reaction was complete, the solution was filtered through a Celite column to ensure complete removal of the triethylamine salt, and the reaction mixture was evaporated. The final product was obtained in 44% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.13 (t, 4H), 3.35 (m, 134H), 2.26 (t, 4H), 1.82 (q, 4H) 1.61 (q, 4H), 1.56 (m, 134 H), 1.42 (q, 4H). SEC-MALLS M_n = 2850 g/mol, M_w = 4000 g/mol, M_w/M_n = 1.39.

2.4. Synthesis of imidazolium ionene containing 100 wt % hard segment

1,12-dibromododecane (1.0 g, 3.05 mmol) and 1,1'-(1,4-butanediyl)bis(imidazole) (0.58 g, 3.05 mmol) were added to a two-neck, round-bottomed flask equipped with a stir bar, condenser, and nitrogen inlet. Dry DMF (20 wt % solids) was added to the flask via syringe. The reaction was allowed to proceed for 24 h at 80 °C. Upon completion, the polymer was cast into a film for further characterization. The drying procedure for film preparation was critical, and slow removal of DMF was required to avoid formation of film defects. DMF was allowed to evaporate in ambient conditions for 1 day. Subsequently, the films were heated in the Teflon™ molds at approximately 80 °C for at least 2–3 days. Finally, the polymer films were subsequently dried in vacuo (0.1 mm Hg) at 80 °C for 72 h to ensure complete removal of DMF. ^{1}H NMR (400 MHz, CD$_3$OD) δ = 9.17 (2H per repeating unit), 7.69 (4H per repeating unit), 4.23–4.33 (8H per repeating unit), 1.90–1.98 (8H per repeating unit), 1.30–1.35 (16H per repeating unit).

Scheme 1. Synthesis of 1,1'-(1,4-butanediyl)bis(imidazole).
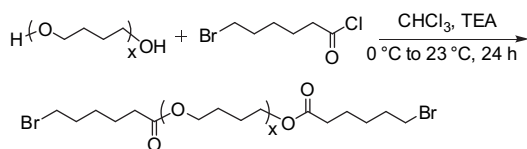
Scheme 2. Synthesis of bromine-terminated PTMO.

2.5. Synthesis of imidazolium ionene segmented block copolymers containing PTMO soft segments

The copolymer containing 38 wt % hard segment is used as an example; however, all copolymers were prepared in a similar fashion. 1,12-dibromododecane (0.194 g, 0.591 mmol), PTMO dibromide (0.562, 0.197 mmol), and 1,1′-(1,4-butanediyl)bis(imidazole) (0.15 g, 0.788 mmol) were added to a two-neck, round-bottomed flask equipped with a stir bar, condenser, and nitrogen inlet. Dry DMF (20 wt % solids) was added to the flask via syringe. The reaction was allowed to proceed for 24 h at 80 °C. Upon completion, the polymer was cast into a film for further characterization using the same drying method described above. ^{1}H NMR (400 MHz, CD$_3$OD) $\delta = 9.17$ (2H per repeating unit), 7.68 (4H per repeating unit), 4.23–4.33 (8H per repeating unit), 4.10 (t, 4H per repeating unit), 3.44 (m, 134H PTMO), 2.35 (t, 4H per repeating unit), 1.91–1.98 (8H per repeating unit), 1.89 (q, 4H per repeating unit) 1.66 (q, 4H per repeating unit), 1.62 (m, 134 H PTMO), 1.40 (q, 4H), 1.30–1.36 (16H per repeating unit).

2.6. Characterization

^{1}H NMR spectroscopy was utilized to determine monomer composition in CDCl$_3$ at 23 °C with a 400 MHz Varian UNITY spectrometer. FAB-MS was obtained on a JOEL HX110 dual focusing mass spectrometer. The molecular weight was determined at 40 °C in THF (ACS grade) at a flow rate of 1 mL/min using polystyrene standards on a Waters Alliance SEC system equipped with a Waters 2410 refractive index detector, a Wyatt Technology MiniDAWN MALLS detector, and a Viscotek 270 viscosity detector. Reported molecular weights are based on absolute measurements using the MALLS detector. In addition, potentiometric titrations were performed to confirm the hydroxyl number. A TA Instruments Hi-Res TGA 2950 with a temperature ramp of 10 °C/min in a nitrogen atmosphere was used for thermogravimetric analysis (TGA). Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800 dynamic mechanical analyzer in tension mode at a frequency of 1 Hz and temperature ramp of 3 °C/min. The sample was cooled from room temperature to −100 °C prior to heating. The glass transition temperature (T_g) was determined at the peak of the tan δ curve. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q100 differential scanning calorimeter under a nitrogen flow of 50 mL/min. The sample was first heated from −100 °C to 125 °C at a heating rate of

10 °C/min. The cooling rate was 20 °C/min, and a subsequent heating from −100 °C to 125 °C at a heating rate of 10 °C/min was conducted.

The solvent-cast and dried imidazolium ionene films were used directly for X-ray scattering characterization. The polymer films were dried in vacuo (0.1 mm Hg) at 60 °C for 24 h to ensure complete removal of solvent. The multi-angle X-ray scattering system (MAXS) generated Cu X-ray from a Nonius FR 591 rotating-anode generator operated at 40 kV and 85 mA. The bright, highly collimated beam was obtained via Osmic Max-Flux optics and pinhole collimation in an integral vacuum system. The scattering data were collected using a Bruker Hi-Star multiwire detector with sample to detector distances of 11, 54 and 150 cm. The 2-D data reduction and analysis were performed using Datasqueeze software [21]. The spacings were calculated using $d = 2\pi/q$. The MAXS system provides an uncommonly wide range of scattering angles that was critical in evaluating the morphology of these segmented copolymers.

3. Results and discussion

The bisimidazole monomer, (1,1′-(1,4-butanediyl)bis(imidazole)), was prepared from imidazole and 1,4-dibromobutane, according to a literature procedure (Scheme 1) [20]. In the first step, imidazole was deprotonated, and in the subsequent step, the anionic nucleophile attacked the primary alkyl bromide, yielding the final structure shown in Scheme 1 The final structure, confirmed with ^{1}H NMR spectroscopy and FAB-MS, corresponded well to previous literature results.

The soft segment precursor, bromine-terminated PTMO, was prepared via quantitative derivatization of 2000 g/mol PTMO with 6-bromohexanoyl chloride to yield an oligomeric dibromide (Scheme 2). This novel structure was confirmed using ^{1}H NMR spectroscopy, and the absolute molecular weights were determined from SEC-MALLS and ^{1}H NMR spectroscopy. After derivatization, SEC-MALLS revealed a typical M_n of 2850 g/mol, M_w of 4000 g/mol, and M_w/M_n of 1.39. These values correlated well to the ^{1}H NMR M_n of 2800 g/mol. This synthetic route was facile and the soft segment molecular weight was easily varied with perfect difunctionality PTMO diols that have low polydispersity and were readily available. It is important to note that the five methylene spacer was not critical for successful oligomeric dibromide synthesis when the reaction was conducted in CHCl$_3$. Other acid chlorides are commercially available, including bromoacetyl chloride. However, Schneider et al. reported that bromoacetyl bromide cleaved ethers, including THF [22]. Therefore, all quantitative derivatizations of PTMO were conducted in CHCl$_3$ to prevent any deleterious side reactions. Synthesis of this bromine-terminated soft segment is novel, since Sukhyy et al. were the only researchers to report the synthesis of oligomeric ionene precursors using chloroacetyl chloride and poly(ethylene glycol); however, the exact synthetic details were omitted from their manuscript, and different starting materials were utilized.
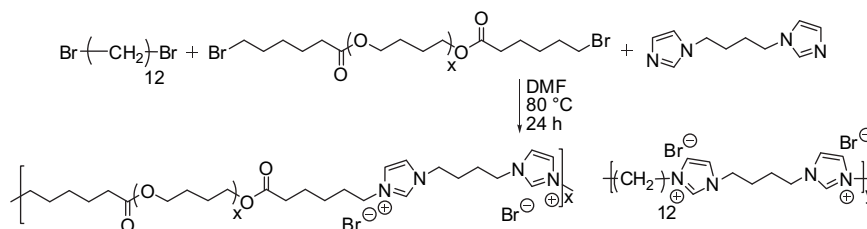
Scheme 3. Synthesis of imidazolium ionene segmented block copolymers containing 1,12-dibromododecane and bromine-terminated PTMO.

Table 1
Segmented block copolymer compositions based on molar equivalents of monomer and HS/SS content.

PTMO Dibromide (mol eq.)	1,12-Dibromide (mol eq.)	Bisimidazole (mol eq.)	HS (wt %)	SS (wt %)
1.00	0.00	1.00	6	94
0.75	0.25	1.00	9	91
0.50	0.50	1.00	20	80
0.25	0.75	1.00	38	62
0.00	1.00	1.00	100	0

Table 2
TGA and DSC results of imidazolium ionene segmented block copolymers.

HS (wt %)	SS (wt %)	$T_{d5\%}$ (°C)	T_g (°C)	T_m (°C)
6	94	262	−82	23
9	91	263	−80	24
20	80	266	−83	22
38	62	270	−84	22
100	0	257	27	–

Imidazolium ionenes were prepared according to Scheme 3. The amount of soft segment (SS) and hard segment (HS) were varied, while maintaining a 1:1 molar ratio of bisimidazole:dibromide. In all, five novel polymer compositions were synthesized, as shown in Table 1. HS compositions were calculated from the amount of 1,12-dibromododecane and 1,1′-(1,4-butanediyl)bis(imidazole) added; the HS content varied from 6 to 100 wt %. The 1:1 molar ratios of monomers, shown in Table 1, were required to achieve high molecular weight step-growth polymers.[23,24] From previous studies, we have demonstrated that in-situ FT-IR spectroscopy is a useful tool for monitoring the FT-IR spectrum of a reaction over time, particularly because it eliminates the need for removing samples from the reaction flask. Small molecule model reactions performed in our lab indicated that the reaction rate for quaternization of the imidazole and ammonium functional groups were relatively similar. Thus, the polymerization was allowed to proceed in a similar fashion to that of ammonium ionenes.

Segmented block copolymer composition was evaluated using ^{1}H NMR spectroscopy. The HS/SS ratio corresponded well to the feed ratios of monomers. Fig. 1 demonstrates the change in ^{1}H NMR spectra as the hard segment content was varied. As expected, the resonances associated with the methylene spacers (∼1.2 ppm) of 1,12-dibromododecane became more apparent as the hard segment content increased.

Thermogravimetric analysis (TGA) of the ionenes demonstrated high thermal stability for these polymers (Table 2). An exact trend in thermal stability as a function of HS content was not observed, but all imidazolium segmented block copolymers were stable to ≥250 °C. These values were slightly greater than those previously reported for conventional ammonium ionenes [10,25]. However, the ionenes were not as thermally stable as imidazole-containing acrylate copolymers, which reportedly possessed onset degradation temperatures approaching 400 °C [26].

The effect of hard segment content on thermal transitions was investigated using DSC, and the results for the imidazolium ionene segmented block copolymers are shown in Table 2. Each copolymer that contained PTMO soft segments possessed a T_g near −80 °C, which was similar to the T_g of pure PTMO. All imidazolium ionenes containing PTMO segments also possessed T_ms, which were similar to the T_m of pure PTMO, indicating that the imidazolium ionenes containing PTMO segments possessed crystallinity. The data in Table 2 strongly suggested that these ionene segmented block copolymers were microphase separated.

Scattering patterns were recorded at the small-, intermediate- and wide-angle positions with sample to detector distances of 150, 54 and 11 cm, respectively, to capture a broad range of morphological features in these materials. Fig. 2 shows the combined multi-angle X-ray scattering intensity versus scattering vector (q) plotted on a log–log scale for these imidazolium ionenes with 6–100 wt% HS. At the lowest level of hard segment content, the PTMO crystallinity dominated the scattering pattern. The peaks at scattering vectors of $q = 14.2$ nm^{-1} and 17.3 nm^{-1} corresponded to the (020) and (110) peaks of PTMO crystals, respectively [27]. This mark of PTMO crystallinity was evident when the ionenes had 6, 8, and 20 wt% HS, and with increasing hard segment content the peaks weakened relative to the amorphous polymer peak at the same position. At both 6 and 9 wt% hard segment, the broad peaks below $q = 1$ nm^{-1}, corresponded to interlamellae spacings and again weakened with increasing hard segment, as expected. The imidazolium ionene containing only 6 wt% HS, exhibited two orders of scattering at 0.42 nm^{-1} and 0.87 nm^{-1} that corresponded to an interlamellae spacing of 15.0 nm. For comparison, consider the monoclinic crystal structure of PTMO having a planar zig–zag conformation along the c-axis cell [28]. The length of a fully extended crystalline PTMO chain of 2000 g/mol is approximately 16.8 nm, which is only 12% larger than the inter-lamellar spacing given via X-ray scattering and thereby consistent with well-developed PTMO crystals in the imidazolium ionenes with only 6 wt% HS.
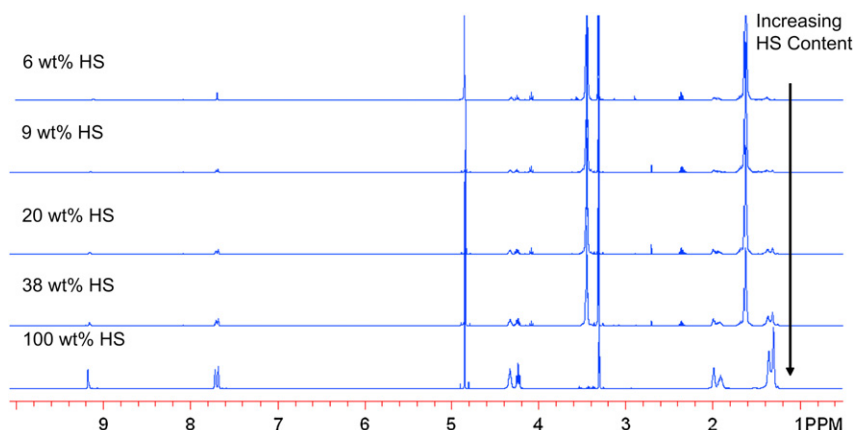

Fig. 1. ^{1}H NMR spectroscopy of imidazolium ionene segmented block copolymers as a function of hard segment content.
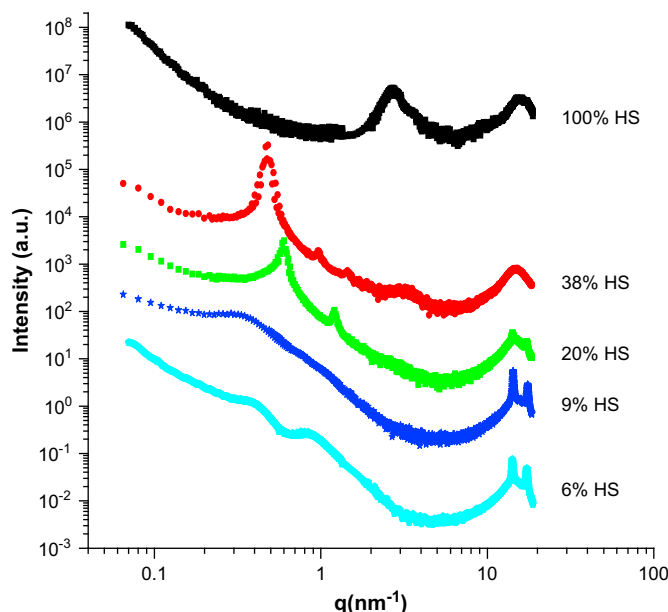
Fig. 2. Multi-angle X-ray scattering intensity vs. scattering vector q plotted on a log–log scale for PTMO-based imidazolium ionene films containing different concentrations of hard segment.

Fig. 3. Dynamic mechanical behavior of PTMO-based imidazolium ionenes. Dashed line = 38 wt% HS, solid line = 20 wt% HS.

When the hard segment content was 20 and 38 wt%, the imidazolium ionenes clearly showed microphase separation. Multiple scattering peaks were evident at scattering vectors from 0.2 to 2 nm^{-1}. For 20 wt% HS, the microphase separation peaks occurred at $q = 0.6$ and 1.2 nm^{-1}, which corresponded to a periodicity of ~10.5 nm. For 38 wt% HS, the microphase separation peaks occurred at $q = 0.48$, 0.96 and 1.44 nm^{-1}, which corresponded to a periodicity of ~13.0 nm. The observed microphase separation peaks were at the ratios of 1:2:3, which suggested the presence of a layered-morphology. Others have observed the incompatibility between soft and hard segments, resulting in microphase separation in various segmented polymers [29–33]. The driving force for the microphase separation in the PTMO imidazolium ionenes arose from the incompatibility of the PTMO segments and the ionic domains.

A broad correlation peak was also present at ~3 nm^{-1} when the imidazolium ionenes contained 38 and 100 wt% HS. The correlation peak originated from the periodicity between the bisimidazole monomeric units when they were separated by the dodecane hard segments. For 38 and 100 wt% HS, the correlation peaks occurred at $q = 3.2$ and 2.7 nm^{-1}, which corresponded to a spacing of ~2.0 and 2.3 nm. A 12-carbon alkane chain in an all *trans* conformation is 1.6 nm. As expected, the observed correlation distances were somewhat larger than the alkane chain alone to accommodate the bisimidazolium groups. A similar correlation peak was previously reported in 12,12-ammonium ionenes ($q = 4.38$ nm^{-1}, $d = 1.4$ nm), wherein the ammonium groups are separated by 12-carbon alkane linkages [10]. As expected, the correlation distances were larger for the imidazolium ionenes compared to those for the ammonium ionenes, because each repeating unit of the imidazolium ionenes contained two imidazolium salt units separated by a 4-carbon alkane linkage.

The mechanical properties of films made from these imidazolium ionene segmented block copolymers reflected the underlying multiscale morphologies described by DSC and X-ray scattering analysis. As the hard segment concentration increased, the toughness of the polymer film increased to a critical level and then decreased as the materials became brittle with further increases in hard segment. The two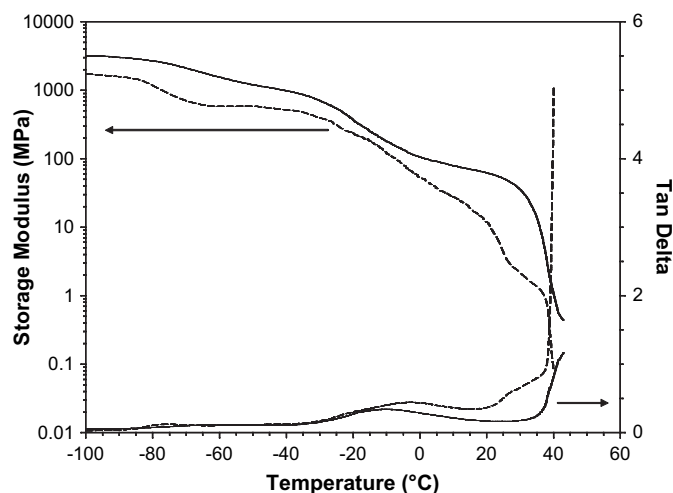 copolymers containing 20 and 38 wt % hard segment formed free-standing films and were easily characterized using DMA (Fig. 3). However, the imidazolium ionene consisting of 100 wt % hard segment was too brittle to examine using DMA. In the glassy regime at −100 °C, the imidazolium ionene with 20 wt % HS content possessed a higher glassy modulus (3200 MPa) as compared to the 38 wt % HS imidazolium ionene (1700 MPa), because the ionene with less HS contained more PTMO crystallinity, as shown above. This is in agreement with Wilkes et al. [34] and Long et al. [35] where both research groups reported that the presence of PTMO crystals increased the glassy modulus. The imidazolium ionenes did not show an extended rubbery plateau, and many transitions were observed as temperature increased. Three transitions were observed in the 20 wt % HS imidazolium ionene: (1) a modest decrease in modulus at −75 °C associated with a PTMO T_g, (2) a broad decrease in modulus centered near −20 °C probably associated with the dodecane linkages, and (3) a large decrease in modulus at 33 °C attributed to both the melting of the PTMO crystals and the onset of liquid-like flow similar to a disordered block copolymer [36]. The dynamic mechanical response of the 38 wt % HS imidazolium ionene had similar transitions at −75 °C and −20 °C, but the higher temperature transition presented as two separate transitions corresponding to PTMO melting at 24 °C and liquid-like flow at 39 °C. To further correlate the dynamic mechanical properties and the multiscale morphology, which includes PTMO crystallinity and microphase separation, the X-ray scattering experiments can be performed as a function of temperature.

4. Conclusions

This paper reports the first synthesis of imidazolium cation-containing ionene segmented block copolymers. The copolymers were prepared from novel PTMO dibromide oligomers, 1,12-dibromododecane, and 1,1′-(1,4-butanediyl)bis(imidazole), with hard segment contents ranging from 6 to 100 wt %. Thermal stabilities were ≥250 °C. Structure–property relationships were established as a function of hard segment content. DSC indicated that the imidazolium ionenes containing PTMO segments with 6 to 38 wt% hard segment possessed a T_g similar to pure PTMO (−80 °C), while the imidazolium ionene containing 100 wt % HS possessed a T_g of 27 °C. Both DSC and X-ray scattering found evidence of PTMO crystallites in these segmented block copolymers. At 20 and 38 wt% hard segment, the ammonium ionenes were microphase separated with lamellar-type morphologies with periodicities of ~10.5 and

13.0 nm, respectively. Although the segmented block copolymer without PTMO was too brittle to evaluate, the microphase separated ammonium ionenes (20 and 38 wt% hard segment) formed tough films with transitions in moduli consistent with a glass transition in PTMO, a glass transition in the dodecane linkage, the melting of PTMO crystallites, and the order–disorder transition. These new materials present structure on a variety of length scales and this work provides insights to controlling their mechanical and transport properties. Performing successful aqueous SEC on polyelectrolytes is often difficult due to problems associated with polymer–column interactions and sample aggregation in the mobile phase. There is evidence that high molecular weight structures were formed, for example: solution and melt viscosity increase during polymerization, ductile film formation, and higher order structures observed via X-ray scattering. The subject of SEC characterization will be investigated in a future publication.

Acknowledgments

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