5216 *Macromolecules* **2008**, *41*, 5216−5222

Synthesis and Characterization of Well-Defined 12,12-Ammonium Ionenes: Evaluating Mechanical Properties as a Function of Molecular Weight

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Received March 19, 2008; Revised Manuscript Received May 20, 2008

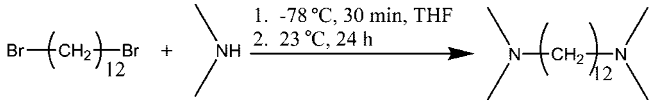
ABSTRACT: Water-soluble 12,12-ammonium ionenes were prepared via the Menschutkin reaction from 1,12-dibromododecane and 1,12-bis(*N*,*N*-dimethylamino)dodecane. A stoichiometric imbalance of monomers controlled the final molecular weights of the polymers. The absolute molecular weights were determined for the first time using an online multiangle laser light scattering (MALLS) detector in aqueous size exclusion chromatography (SEC). Weight-average molecular weights ranged from 4300 to 20 900 g/mol. Relationships between weight-average molecular weight and mechanical properties were established for a series of 12,12-ammonium ionenes using both tensile testing and dynamic mechanical analysis (DMA). Tensile analysis of the higher molecular weight ionenes revealed an average tensile strength of 20 MPa and elongations ranging from 230 to 440%. Dissociation of ionic aggregates was observed at 85−88 °C in DMA experiments, and the glass transition temperatures increased with increasing molecular weight (61−88 °C). X-ray scattering revealed an amorphous polyethylene peak at ≈14 nm^{-1} and a sharp ionic group correlation peak at 4.38 nm^{-1}. These correlations agreed well with the proposed macromolecular structure.

Introduction

Ammonium polyionenes, or ionenes, are ion-containing polymers that contain quaternary nitrogen atoms in the macromolecular main chain as opposed to a pendant site. In 1933, Gibbs and co-workers were the first to report the synthesis of ionenes from dimethylamino-*n*-alkyl halides via a step-growth polymerization process.[1] Ionene synthesis also occurs via polymerization of an alkyl dihalide and a ditertiary amine according to the Menschutkin reaction.[2] Rembaum et al. used the Menschutkin reaction to synthesize ionenes with a variety of methylene spacers and extensively explored their solution properties.[3–5] The polymer is commonly named from the number of methylene units, which correspond to the diamine and dihalide monomers, respectively (i.e., *x*,*y*-ionene).[5] Rembaum et al. studied the solution properties of high-charge density ionenes with structures of 3,4- and 6,6-ionenes.[3] They reported that both ionenes exhibited rodlike behavior in solutions without additional salt, which is known as the polyelectrolyte effect.[6] Upon addition of 0.4 M KBr, the polyelectrolyte effect was suppressed and the ionenes behaved as uncharged polymers. Ander et al. also studied the transition of polyelectrolyte to polysoap behavior of N,N-disubstituted ionenes.[7,8] They observed that as the length of the substituent on the nitrogen atoms increased from methyl to *n*-octyl, the ionene behaved as a polysoap rather than a polyelectrolyte. Salamone et al. demonstrated the successful synthesis of ionenes via the Menschutkin reaction using bulky ditertiary amines such as 1,4-diaza-[2.2.2]bicyclooctane.[9] This article established that there are a wide range of possibilities for ionene synthesis because of the number of ditertiary amines and dibromoalkanes available in sufficient purity for polymerization.

Wilkes et al. analyzed the structure−property relationships of ionenes prepared from a dimethylamino-terminated poly(tetramethylene oxide) (PTMO) oligomer that was reacted with 1,4-dibromo-*p*-xylene.[10] The ionenes possessed elastomeric behavior due to the microphase separation of ionic aggregates with adjacent low glass transition temperature soft segments. Multiple peaks were observed in small-angle X-ray scattering (SAXS) profiles, which indicated that ionic aggregation was present in the ionene films. Rodlike structures were observed with transmission electron microscopy (TEM), which further demonstrated microphase separation of the ionic domains from the PTMO soft segment. Later, Wilkes et al. prepared ionenes from a reaction of telechelic PTMO dioxonium ions and either 4,4′-bipyridine or 1,2-bis(4-pyridinium)ethylene.[11] These ionenes showed a single scattering peak in SAXS profiles, which indicated the presence of ionic aggregates. The absence of higher order scattering peaks indicated that a long-range ordered structure was not formed. However, the ionenes still possessed excellent mechanical properties, including tensile strengths greater than 30 MPa and elongations greater than 800%.

Scheme 1. Synthesis of 1,12-Bis(*N*,*N*-dimethylamino)dodecane



Ionenes offer many potential uses in emerging biomedical applications. Earlier research in nonviral gene delivery vectors has typically involved cationic polymers such as poly(ethylene imine) (PEI),[12] poly(L-lysine),[13] and poly(2-(dimethylamino)-ethyl methacrylate) (PDMAEMA).[14,15] Since DNA does not efficiently cross cell membranes in the absence of a vector due to charge repulsion, cationic ionenes also complex DNA, which allows DNA to be transported across the cell membrane.[16] Izumrudov et al. formed polyelectrolyte complexes (PEC) of symmetric and asymmetric aliphatic ionenes with calf thymus DNA to explore the influence of added salt on PEC stability.[17] Later, in collaboration with Langer et al., Izumrudov explored the effect of polymer chain length and charge density on

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10.1021/ma8006152 CCC: $40.75

Scheme 2. Synthesis of Bromine-Terminated 12,12-Ammonium Ionenes

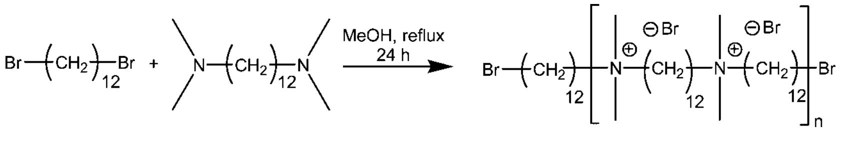


Table 1. Ionene Ditertiary Amine Monomer:Dihalide Monomer Molar Ratios and Corresponding Molecular Weights[a]

monomer molar ratio	calcd mol wt (g/mol)	M_w (g/mol)[b]	M_n (g/mol)[c]	M_w (g/mol)[c]	M_w/M_n[c]
1.00:1.00		20 900	10 700	26 900	2.52
1.00:1.03	19 800	17 800	9 700	23 000	2.36
1.00:1.05	12 000	14 600	6 900	17 000	2.45
1.00:1.07	8 600	12 300	6 800	17 000	2.50
1.00:1.10	3 200	4 300	1 900	4 900	2.63

[a] Calculated molecular weights for offset stoichiometry determined from Carother's equation. [b] Molecular weights are absolute and determined from the MALLS detector. [c] PEO/PEG equivalent molecular weights determined using dRI retention volumes/times.

effective gene delivery.[18] Ionenes are also used in antimicrobial applications due to their ability to disrupt bacterial cellular membranes.[19] The concentration, charge density, hydrophobicity, and molecular weight dictate whether an ionene is suitable for DNA delivery or antimicrobial applications.[20,21]

One potential limitation of conventional ionenes compared to pendant tertiary amines, such as PDMAEMA, is the presence of permanent positive charge on all quaternary nitrogens. The endosome must release the polyplex to deliver the therapeutic DNA.[22,23] Polymers containing tertiary amines allow for pH sensitivity since the presence of a charge is pH-dependent. It is hypothesized that the polymers buffer the endosome and release the polyplex that contains the therapeutic DNA through a pH-controlled mechanism.[22,23] However, ionenes, which bear a permanent positive charge, perhaps are not suitable for efficient gene therapy due to the lack of pH control and corresponding mode of endosomal release. Nevertheless, ionenes are useful in gene therapy as model polyelectrolytes, as the charge density and molecular weight are easily adjusted.[18] In addition, the delivery of DNA from PECs based on ionene vectors does suggest a more complex endosomal release mechanism.

Ion-containing polymers typically exhibit moduli and glass transition temperatures (T_g) that are significantly higher than their nonionic counterparts. This is primarily attributed to ionic aggregates that form physical cross-links.[24,25] For example, Eisenberg et al. studied the aggregation phenomenon in vinylpyridinium cationic ionomers.[26] The ionic aggregates decreased the mobility of the main chain, and increasing ionic content subsequently raised the T_g. An ion-containing polymer has a higher apparent molecular weight and possesses similar mechanical properties and thermal transitions as nonionic polymers of higher molecular weight. Reversible cross-links, formed from ionic aggregates, allow for easier melt processability, higher melt stability, and lower melt viscosity than nonionic polymers. The effect of added salt has a profound effect on the chain conformation of the polyelectrolyte, and this is well-documented within the literature, including the works of Dobrynin, Rubinstein, Eisenberg, and Holliday.[24,25,27,28] Briefly, the expanded polymer chains collapse in the presence of added salt, allowing the salt to effectively screen electrostatic interactions. Previous work in our laboratory has focused on the synthesis of telechelic poly(ethylene terephthalate) sodium sulfonate ionomers.[29] Melt rheology confirmed that the ionic end groups increased the melt viscosity compared to uncharged analogues at equivalent molecular weights. In addition, we have recently reported the novel synthesis of polymers containing complementary hydrogen bonding and cationic phosphonium salts.[30] The addition of the cationic guest drastically changed the dynamic mechanical behavior and morphology compared to the polymer in the absence of the cationic phosphonium salt. In this work, we describe the synthesis and mechanical properties of 12,12-ammonium ionenes as a function of weight-average molecular weight, and X-ray scattering revealed for the first time the morphology of 12,12-ionenes.

Experimental Section

Materials. 1,12-Dibromododecane (98%) was purchased from Aldrich and recrystallized from ethanol. Dimethylamine solution (60% in water) was purchased from Aldrich and used as received. Methanol (MeOH, Fisher, HPLC grade) was distilled from calcium hydride. Tetrahydrofuran (THF, EMD Science, HPLC grade), diethyl ether (Fisher, 99.9%, anhydrous), and sodium hydroxide (Mallinckrodt Chemicals, 99%) were used as received.

Synthesis of 1,12-Bis(*N,N*-dimethylamino)dodecane. A modified literature procedure was used to synthesize 1,12-bis(*N,N*-dimethylamino)dodecane.[31] THF (125 mL) and 1,12-dibromododecane (10.10 g, 0.0308 mol) were introduced into a one-neck, round-bottomed flask, equipped with a stir bar. The flask was cooled to −78 °C for 30 min. The solution of dimethylamine (478 mL total solution) was slowly added to the flask. The flask was warmed to room temperature, and the reaction was allowed to proceed for 24 h. Upon completion, the solvent was removed via rotary evaporation. The product was redissolved in ether and subsequently stirred with 2 M NaOH(aq). The layers were separated, and the ether layer was dried over magnesium sulfate and evaporated to yield a pale yellow oil. The oil was further purified via vacuum distillation (100 °C and 150 mTorr) to yield a colorless liquid. The final product was obtained in 47% yield. ^{1}H NMR (400 MHz, CD_3OD): $\delta = 2.81$ (t, 4H), 2.16 (s, 12H), 1.39 (dd, 4H), 1.22 (m, 16H). ^{13}C NMR (100 MHz, CD_3OD): $\delta = 123.8, 59.7, 44.3, 29.6, 29.5, 27.5, 27.2$. FAB MS: $m/z = 257.29$ (found); $m/z = 256.48$ (calculated).

Synthesis of 12,12-Ammonium Ionenes. 1,12-Dibromododecane (1.28 g, 0.0039 mol) and 1,12-bis(*N,N*-dimethylamino)dodecane (1.00 g, 0.0039 mol) were added to a two-neck, round-bottomed flask equipped with a stir bar, condenser, and nitrogen inlet. Freshly distilled MeOH 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 methanol was required to avoid formation of film defects. First, the polymer was dissolved in MeOH (≈50 wt %) and poured in a Teflon mold. Methanol was allowed to evaporate in ambient conditions for 3 days. Subsequently, the films were heated in the Teflon molds at ≈60−70 °C for at least 2−3 days. Finally, the polymer films were subsequently dried in vacuo (0.1 mmHg) at room temperature for 24 h to ensure complete removal of MeOH. ^{1}H NMR (400 MHz, CD_3OD): $\delta = 3.31$ (m, 8H per repeating unit, $CH_2N^+(CH_3)_2CH_2$), 3.05 (s, 12H per repeating unit, $CH_2N^+(CH_3)_2CH_2$), 1.75 (m, 8H per repeating unit, $CH_2CH_2N^+(CH_3)_2CH_2CH_2$), 1.3−1,4 (m, 32H per repeating unit, $(CH_2)_8CH_2CH_2N^+(CH_3)_2$).

Characterization. ^{1}H NMR was utilized to determine monomer and polymer composition in $CDCl_3$ or CD_3OD at 23 °C with a 400 MHz Varian UNITY spectrometer. FAB-MS was obtained on a JEOL HX110 dual focusing mass spectrometer. Thermogravimetric analysis (TGA) was conducted on a TA Instruments Hi-Res TGA 2950 with a temperature ramp of 10 °C/min in a nitrogen atmosphere. 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.

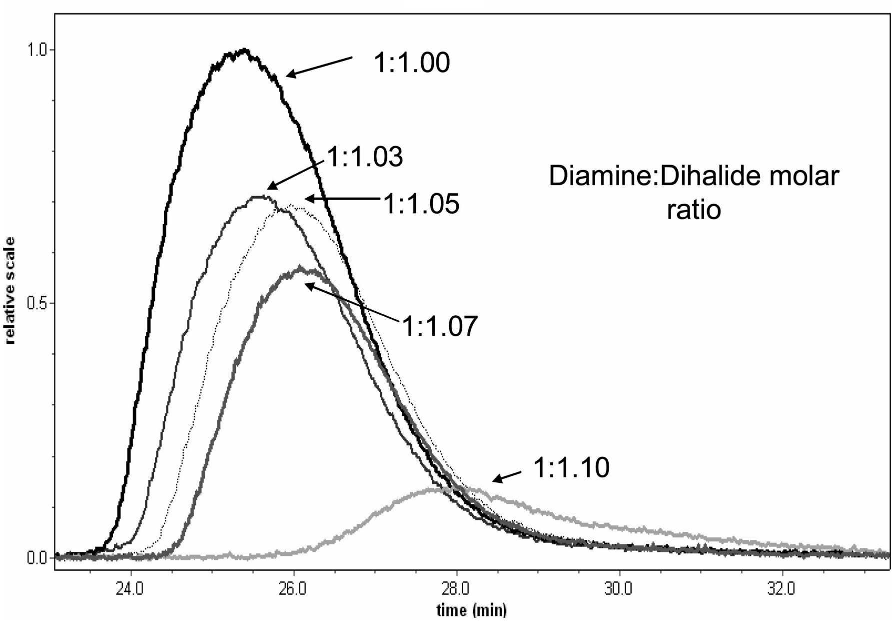


Figure 1. SEC MALLS traces of the bromine-terminated 12,12-ammonium ionenes.

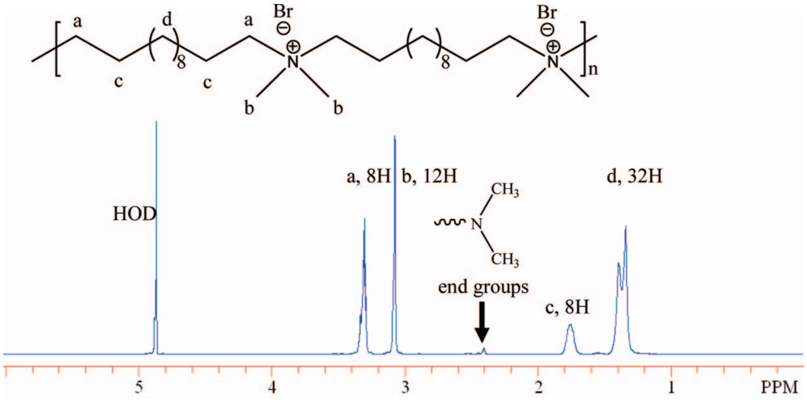


Figure 2. ^{1}H NMR spectrum of an amino-terminated 12,12-ammonium ionene.

The glass transition temperature (T_g) was determined at the peak of the tan δ curve. Stress−strain experiments were conducted with dogbone-shaped film specimens, which were cut with a die according to ASTM D3368 specifications. Tensile tests were performed on a 5500R Instron universal testing instrument with a cross-head speed of 13 mm/min using manual grips at ambient temperature.

Size exclusion chromatography (SEC) was performed using a Waters size exclusion chromatograph. The instrument was equipped with a Waters 1515 isocratic HPLC pump, a Waters 717plus autosampler, a Wyatt miniDAWN multiangle laser light scattering (MALLS) detector operating a He−Ne laser at 690 nm, a Viscotek 270 viscosity detector, and a Waters 2414 differential refractive index detector operating at 880 nm and 35 °C. A flow rate of 0.8 mL/min in 54:23:23 H_2O:MeOH:acetic acid (v/v/v), 0.54 M NaAc, 200 ppm NaN_3, pH = 4 was used. Reported weight-average molecular weights are based on absolute measurements using the MALLS detector. The specific refractive index increment (d*n*/d*c*) was calculated using a Wyatt OptiRex differential/absolute refractive index detector operating at 690 nm and 30 °C. After allowing the polymers to dissolve in the SEC solvent for 18 h, samples were injected via a syringe pump that was equipped with a 0.45 μm PTFE syringe filter into the RI detector at a rate of 0.8 mL/min. The d*n*/d*c* values were determined using the Wyatt Astra V software package.

The solvent-cast and dried ionene films were used directly for X-ray scattering characterization. The multiangle 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 beam was focused by doubly focusing mirror−monochromator optics in an integral vacuum system. The scattering data were collected over an interval of 1 h using a Bruker Hi-Star multiwire detector with a sample-to-detector distance of 11 and 54 cm. The 2-D data reduction and analysis were performed using *Datasqueeze* software.[32]

Results and Discussion

The synthetic strategy (Scheme 1) for the preparation of 1,12-bis(*N*,*N*-dimethylamino)dodecane was adapted from Spencer et al.[31] ^{1}H NMR spectroscopy confirmed the structures of the diamine and dihalide. 1,12-Dibromododecane was recrystallized from ethanol and subsequently dried in vacuo (0.1 mmHg) at room temperature for 24 h prior to polymerization. A series of 12,12-ammonium ionenes were successfully synthesized via the Menschutkin reaction in a single step from the dihalide and diamine (Scheme 2). The reactions were allowed to proceed for 24 h in refluxing methanol. ^{1}H NMR spectroscopy confirmed the final polymer structure.

It is well-known that a 1:1 stoichiometry is required to obtain high molecular weight polymers via step growth polymerizations;[33] however, in some cases, it is advantageous to limit molecular weight. One can achieve molecular weight control

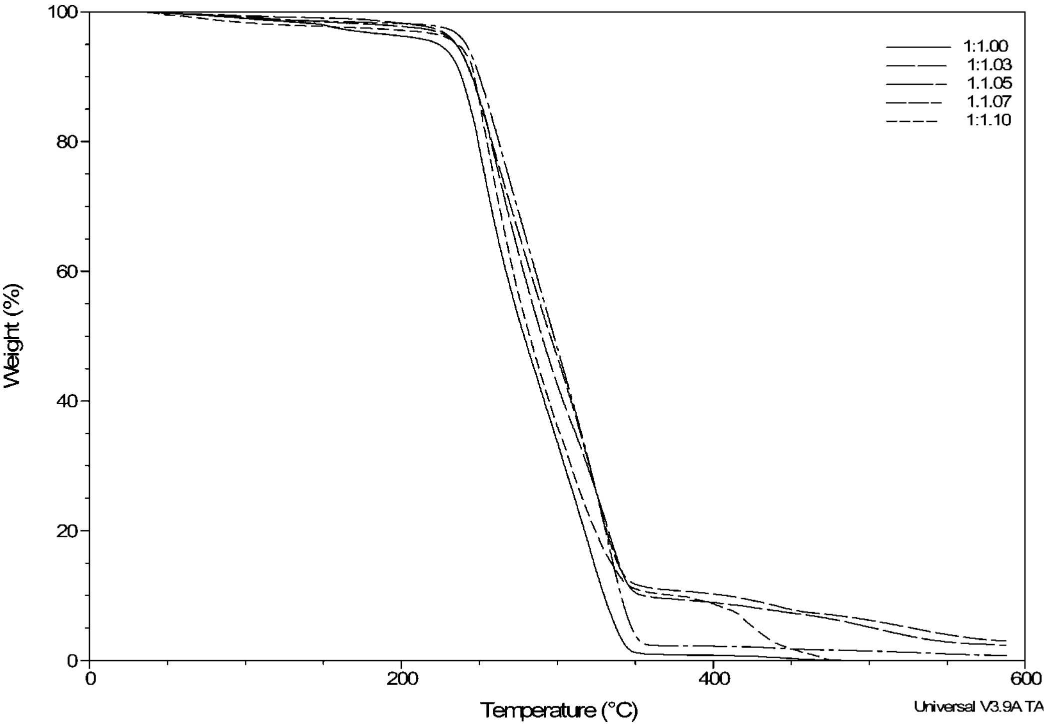
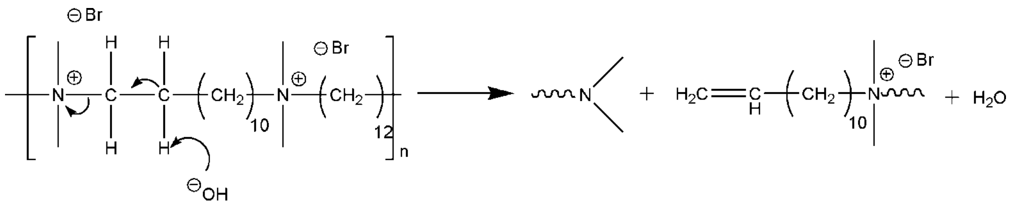


Figure 3. TGA curves for bromine-terminated 12,12-ammonium ionenes. Molar ratios in graph legend correspond to the diamine:dihalide molar ratios.

Scheme 3. Mechanism of the Base-Promoted Hofmann Elimination Reaction for 12,12-Ionenes



in step-growth polymerization through the addition of monofunctional reagents, through limited difunctional monomer conversion, or through a nonstoichiometric imbalance of difunctional monomers.[34] The latter method is preferred because the resulting polymers possess chain ends with the same functionality as the excess monomer. In this case, both monomers are completely consumed, and this results in a stable polymer that cannot increase in molecular weight during a postpolymerization process.[34,35] In our work, excess dihalide resulted in polymers possessing alkyl bromide end groups. Carother's equation was utilized to predict molecular weights as a function of the monomer stoichiometry.[35] As shown in

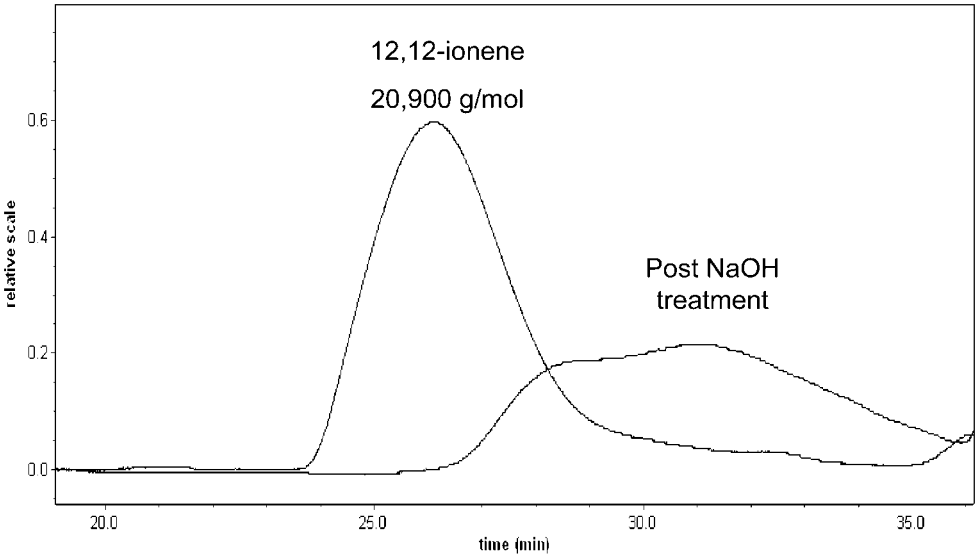


Figure 4. SEC dRI traces of the 12,12-ammonium ionene before and after degradation in the presence of base.

Table 2. Ionene Molecular Weight and Corresponding Thermal Transitions[a]

M_w (g/mol)	T_g (°C)	ionic dissociation (°C)
20 900	88	88
17 800	69	85
14 600	69	88
12 300	61	87

[a] The T_g was determined from maximum in tan δ vs temperature graphs. Second transition corresponds to the ionic aggregate disassociation.

Table 3. Tensile Data for 12,12-Ammonium Ionene Films as a Function of Molecular Weight

M_w (g/mol)	stress at break (MPa)	strain at break (%)	stress at yield (MPa)
20 900	26.4 ± 1.0	440 ± 45	21.5 ± 2.8
17 800	33.0 ± 3.0	360 ± 42	22.9 ± 3.9
14 600	16.2 ± 2.4	230 ± 31	22.9 ± 9.2

Table 1, the obtained experimental M_w values were consistent with the calculated molecular weight values, as expected for a controlled step-growth polymerization process. Controlled weight-average molecular weights ranging from 4300 to 20 900 g/mol (Table 1 and Figure 1) were obtained using a stoichiometric imbalance. The chromatograms based on the light scattering detector are shown in Figure 1. It is important to note that the chromatograms are monomodal, and significant interaction of the polymer with the stationary phase of the column was not observed. Performing successful aqueous SEC on polyelectrolytes is often difficult due to problems associated with polymer−column interactions and sample aggregation in the mobile phase.[36] A manuscript, which describes the establishment of these suitable chromatographic conditions in more detail, was recently submitted.[37]

An amino-terminated polymer was also synthesized using a 1.05:1.00 molar ratio of 1,12-bis(*N*,*N*-dimethylamino)dodecane and 1,12-dibromododecane. The reaction was allowed to proceed for 24 h in refluxing methanol. The amino-terminated polymer was prepared to compare ^{1}H NMR spectroscopy number-average molecular weights and SEC molecular weights and thus determine whether the SEC measurements were reliable. The methyl groups attached to the amino nitrogen end group were easily detected with ^{1}H NMR spectroscopy. End-group analysis indicated a number-average molecular weight of 7600 g/mol (Figure 2). Aqueous SEC was utilized to determine the molecular weight of the identical polymer, and the resulting M_n was 8400 g/mol. Saito and co-workers examined the reliability of SEC-MALLS and ^{1}H NMR to confirm the molecular weight of low molecular weight polystyrene standards that ranged from 500 to 2400 g/mol.[38] Their study concluded that MALLS detection was reliable, even at low molecular weights. Thus, the results obtained with ^{1}H NMR and SEC-MALLS were comparable for the amino-terminated 12,12-ammonium ionene and supported the reliability of the SEC-MALLS reported herein.

Thermal stability was measured via thermogravimetric analysis (TGA), and all polymers typically exhibited 5% weight loss at ≈225 °C (Figure 3). The thermal degradation occurred in a single step, which Ruckenstein et al.[39] and Jerome et al.[40] attributed to the dequaternization of the nitrogen, although the actual mechanism of thermal decomposition is complex.[41] Charlier and co-workers extensively studied the thermal stability of telechelic polystyrene containing quaternary ammonium ionic groups.[42] They concluded that the Hofmann elimination occurred at the end groups of the telechelic polymers via the analysis of both pristine and degraded polymers using a combination of TGA, high-performance liquid chromatography (HPLC), and mass spectroscopy. The onset degradation values reported herein are similar to those reported by Tanaka et al. for various ionenes including 12,*n*-ionenes (250 °C).[43]

It is well-documented in the literature that the Hofmann elimination also occurs in the presence of base, converting tetraalkylammonium salts to an alkenes and dimethylamines (Scheme 3).[44,45] Chemical degradation of the 20 900 g/mol 12,12-ionene was also observed in the presence base. An experiment was conducted in 1 M NaOH solution at 23 °C for 24 h. After the reaction was complete, the SEC results indicated that the polymer was partially degraded, as the M_n decreased from 20 900 to 2500 g/mol. Differential RI traces before and after the reaction are shown in Figure 4. The monomodal, symmetrical peak for the 20 900 g/mol 12,12-ammonium ionene became multimodal and unsymmetrical after the reaction. Furthermore, the presence of dimethylamino groups was observed in the ^{1}H NMR spectrum, which indicated that the nitrogen of the tetraalkylammonium salt was the site of degradation. The degradation study was performed at a concentration of 0.01 g/mL. Although concentration was not addressed in this study, it is presumed that concentration may influence the formation of various side products including cyclic species at more dilute concentrations. This will be the focus of a future study. Ionene degradation in the presence of base shows promise as a means to convert mechanically strong films and coatings to low mass monomers in the presence of base upon disposal. In fact, our current efforts involve monomer selection to ensure more environmentally friendly byproducts upon degradation.

DSC analysis revealed the expected dependence of T_g on molecular weight. The highest molecular weight ionene had the greatest T_g, and the values ranged from 24 to 69 °C. A melting transition was not observed to 200 °C. Thus, the presence of a crystalline melting point would have to occur above 200 °C, which is near the degradation temperature (∼225 °C). DMA of the ammonium ionenes revealed two transitions, as expected for ion-containing polymers that form ionic aggregates.[28,46,47] The lower temperature transition was assigned to the T_g, and the second higher temperature transition was attributed to ionic aggregate dissociation (Table 2). The dissociation of ionic aggregates in aliphatic ionenes has not been previously reported. Eisenberg and co-workers have extensively studied the dynamic mechanical properties of ionomers with various ionic contents.[48] At lower ionic content, a second transition occurred at temperatures above the matrix T_g, and this transition was termed the cluster T_g. As the ionic content increased, both the matrix and cluster T_g increased. Kim and co-workers studied the dynamic mechanical behavior of sulfonated poly(butylene succinate) ionomers and found that ion-pair associations caused the polymer chains to collapse and cause a decrease in the viscosity and radius of gyration.[49,50] Eisenberg and co-workers determined with sodium salts of styrene−methacrylic acid copolymers that macromolecular ionic dissociation only occurred if the ion content was sufficient for aggregates to form.[28,46,47] In the case of ionenes, the T_g (tan δ maximum) increased with increasing molecular weight and ranged from 61 to 88 °C, and the ionic aggregate dissociation occurred at higher temperatures, typically 85−88 °C. It is interesting to note that the ionic aggregate dissociation was independent of molecular weight. The T_g was not reported from the onset of storage modulus loss, since the transition was broad. In fact, the temperature that corresponded to the onset of storage modulus loss was approximately the same temperature as T_g midpoint as determined via DSC. Interestingly, there was overlap of the T_g and the ionic aggregate dissociation temperature for the 20 900 g/mol ionene due to increasing molecular weight. It was presumed that the ionic aggregate dissociation temperature remained nearly constant, since the ion content remained unchanged as molecular weight increased. In addition, the presence of end groups is presumed to have an insignificant effect on the ionic aggregate dissociation

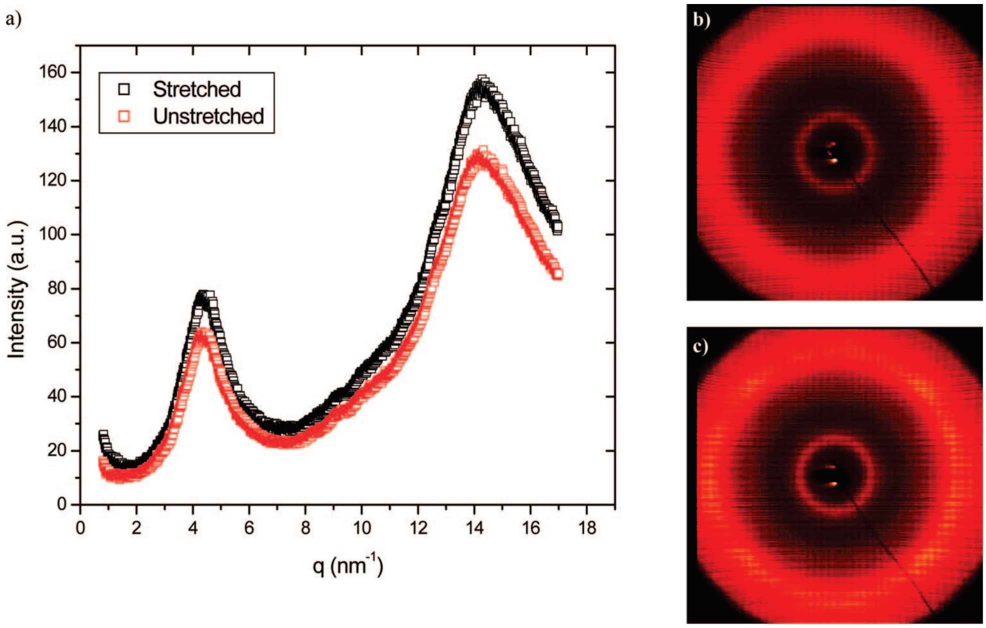


Figure 5. X-ray scattering profiles of the 1:1 12,12-ionene: (a) scattering intensity vs q for stretched and unstretched 12,12-ammonium ionenes films; (b) wide-angle X-ray scattering pattern of stretched ionene film; (c) wide-angle X-ray scattering pattern of unstretched ionene film.

temperature, since over the range of molecular weights, the aggregate dissociation temperature did not change. Furthermore, all of the ionenes have equal equivalent molecular weight and ion content.

Tensile properties revealed high ultimate mechanical strength, as shown in Table 3. This is the first report of tensile analysis of 12,12-ionenes to the best of our knowledge. As the M_n of the ionene decreased, the stress at break decreased from 26.4 to 16.2 MPa. Furthermore, the strain at break decreased from 440% to 230%. Yield stress was approximately identical for all three polymers (22 MPa). The relaxation of the polymer chains during tensile testing and subsequent collapse of the ionic aggregates may cause similar yield points, despite the variation in polymer molecular weights.[51] Tensile analysis was not performed on the lower molecular weight samples due to their brittle nature. The tensile performance of 12,12-ionene compared well to the earlier literature for polyurethane ionene rotaxanes.[51] In Wilkes' earlier work, the stress at break ranged from 17 to 34 MPa, and the elongation ranged from 114 to 807%.

X-ray scattering was performed on stretched and unstretched 20 900 g/mol 12,12-ionene films. The stretched sample was elongated ~200% with heating at 70 °C. Both stretched and unstretched films were isotropic as evident in the two-dimensional scattering patterns (Figure 5). Both films were also amorphous with a broad amorphous peak at ~14 nm^{-1}, and crystalline peaks corresponding to polyethylene were not observed. This result was consistent with DSC and DMA data. In addition, there was a scattering peak at 4.38 nm^{-1}, which corresponded to a real-space distance of 1.43 nm. While the ammonium groups prevented crystallization, these ionic groups assembled into ionic domains. The correlation distance between these domains was well-defined because the separation between ionic groups was exactly 12 methylene groups. If this polyethylene segment was in the *all-trans* crystalline conformation, the ammonium−ammonium separation would be 1.60 nm. The somewhat smaller separation observed here was consistent with the amorphous morphology.

Wagener and co-workers have also synthesized a periodic ionomer, and their reported morphology was similar to this work.[52] The poly(ethylene-*co*-acrylic acid) (EAA) copolymer had 9, 15, or 21 methylene groups between pendant carboxylic acid groups. As in the 12,12-ionene, the correlation lengths between acid groups was comparable to or somewhat smaller than the *all-trans*-polyethylene conformation. However, in sharp contrast to the 12,12-ionene, the EAA copolymer with the longest polyethylene spacer (21 methylene units) exhibited crystallinity, and multiple reflections indicated that packing was more regular. In a similar fashion to the 12,12-ionene, the EAA copolymer with the 15 methylene units between acid groups remained anisotropic upon stretching. In both the EAA copolymers and 12,12-ionenes, the primary structure of the polymers dictated the nanoscale morphology. The comparison of ammonium ionenes to EAA copolymers may also suggest the relatively more efficient aggregation of metal carboxylates vs large, organic ammonium cations as reported earlier.[53,54]

Conclusions

The Menschutkin reaction was used to prepare a series of water-soluble 12,12-ammonium ionenes from 1,12-dibromododecane and 1,12-bis(*N,N*-dimethylamino)dodecane. The macromolecular structures were confirmed with ^{1}H NMR spectroscopy, and the absolute weight-average molecular weights were determined for the first time using multiangle laser light scattering (MALLS) with aqueous size exclusion chromatography (SEC). Relationships between molecular weight and mechanical performance were established for a series of 12,12-ammonium ionenes using tensile testing and dynamic mechanical analysis (DMA). The water-soluble polymers possessed greater than room temperature glass transition temperatures and ionic aggregate disassociation temperatures of 85−88 °C. Tensile analysis of the higher molecular weight ionenes revealed an average yield stress of 22 MPa and elongations ranging from 230 to 440%. The morphology was examined with X-ray scattering, and it was discovered that the steric hindrance of ammonium groups inhibited the close packing and crystallization of the relatively short polyethylene segment between the charges. Specifically, X-ray scattering indicated the formation of ion-rich domains, with an average separation that correlated with the methylene spacer length between the charged groups. Degradation studies in the presence of base support the possibility for water-soluble coatings with excellent mechanical durability that are amenable to triggered depolymerization.

Acknowledgment. This material is based upon work supported in part by the Macromolecular Interfaces with Life Sciences (MILES) Integrative Graduate Education and Research Traineeship (IGERT) of the National Science Foundation under Agreement DGE-0333378. This material is based upon work supported in part by the U.S. Army Research Office under Grant W911NF-07-1-0452 Ionic Liquids in Electro-Active Devices (ILEAD) MURI. This material is based upon work supported in part by the Kimberly Clark Corporation, and we acknowledge helpful discussions with Dr. Clay Bunyard.

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MA8006152