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Synthesis and Characterization of Novel Segmented Polyionenes Based on Polydimethylsiloxane Soft Segments

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Novel polydimethylsiloxane (PDMS) based polyionenes were synthesized by a modified Menschutkin reaction involving reaction between bromo-terminated PDMS oligomers and various ditertiary amino compounds. In this study, the nature of the hard segment was varied by using various ditertiary amino compounds and in some cases by incorporating chain extenders, while the soft segment content was varied by changing the molecular weight of the PDMS oligomers. The mechanical properties of these materials were found to be dependent on both the nature and amount of the hard segments. These materials also showed distinct evidence of a microphase-separated morphology where under normal conditions, the hard segments formed in what are believed to be cylindrical ion-rich microdomains dispersed randomly in the soft PDMS matrix. When subjected to uniaxial deformation, the ionic cylinders were found to orient along their long axes in the stretch direction.

Keywords: Polyionene, siloxane, microphase separated morphology, mechanical properties

1 Introduction

Polyionenes are ion-containing polymers that possess quaternary amine linkages in the chain backbones. The term "ionene" was coined by Rembaum and his co-workers (1, 2), who first synthesized them by the Menschutkin reaction, which involves polymerization of dihaloalkanes and ditertiary amines as schematically shown in Scheme 1.

The charge density in such materials can be controlled by varying the number of methylene spacer units in both the ditertiary amine (m) and dihaloalkane (n) monomers, and the counter anion is varied through selection of the halogen substituent in the dihaloalkane. Smaller values of m and n lead to ionenes with higher ionic character, and they become more hydrophilic and less soluble in organic solvents with increasing ionic content (3). It has been found that the polymerization rates and ultimate molecular weights of polyionenes are influenced by the dihalide structure (4). Highly reactive dihalides, such as benzyl dihalides, have been employed to synthesize high molecular weight ionenes (4, 5). The reactivities of benzyldihalides can be further enhanced by incorporating *para* substituents on the phenyl rings that can donate electron density through resonance (4). High molecular weight ionenes have also been synthesized by direct coupling of telechelic poly(tetramethylene oxide) (PTMO) synthesized with triflic anhydride as the initiator with ditertiary amines (6), and also via homopolymerization of A-B monomers such as ω-haloalkyldialkylamines (7, 8).

Segmented polyionenes have received considerable attention due to their high tensile strengths and thermoplastic elastomeric nature, and they have been considered for biomedical/biocidal (9, 10) and conductive polymer (11, 12) applications. Leir and Stark (4) synthesized a series of segmented polyionenes based on PTMO soft segments and different hard segments. These elastomeric materials displayed high strength which was shown to be due to a high degree of microphase separation of the hard and soft segments in conjunction with the ability to promote strain induced crystallization of the PTMO soft segments (observation made by performing DMA, stress-strain, TMA, TEM and SAXS analysis) (13, 14). TEM and SAXS results both showed that the hard segment ionic domains formed long-range periodic cylindrical or rod-like structures. This structure was attributed to the very strong coulombic or electrostatic interactions between the short dibenzyl containing segments and halogen counterions as well as the

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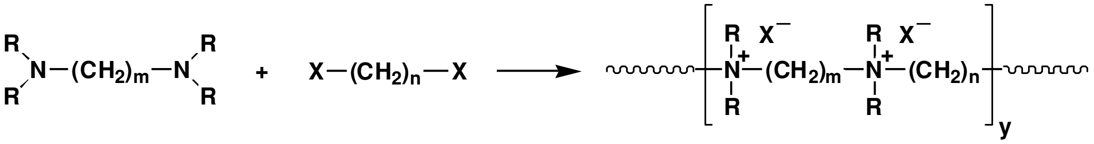


Scheme 1. Generic Menschutkin reaction for synthesizing polyionenes. The letters R and X represent alkyl and halide groups, respectively.

incompatibility of the ionic groups between the PTMO chains and ionic hard segments. The morphologies of these segmented polyionenes depended on their ionic content and could be systematically altered by changing the molecular weight of the PTMO soft segments. It was also shown that their morphological textures were influenced by the solution casting procedure, even at a very low ionic content (<6.4 vol%). When cast on glass plates from solution, the cylindrical ionic domains were surprisingly found to preferentially orient perpendicular to the casting surface.

In the present study, we report the synthesis, morphological and mechanical analysis of segmented polyionenes based on polydimethylsiloxane (PDMS) soft segments. The distinguishing features of PDMS segments are their low T_gs, flexible backbone, low surface energy and exceptional thermal stabilities under neutral conditions. These polyionenes were synthesized by a modified Menshutkin reaction between bromoalkyl-terminated PDMS and various ditertiary amines. Effects of varying the nature of the hard segments and ionic content by changing the PDMS molecular weight and employing chain extension on the structure-property behavior of these PDMS-polyionenes were addressed. The mechanical properties were analyzed by DMA, TMA and uniaxial tensile analysis, while the morphologies were probed with tapping-mode AFM and small and wide angle X-Ray analysis (SAXS and WAXS). The rationale behind the synthesis of PDMS-based segmented polyionenes was that it might to possible to induce morphologies in these materials where the ionic domains associate to form ionic channels that will assist in ion conduction while being embedded in a hydrophobic PDMS matrix. The hydrophobic nature of the PDMS matrix stabilizes the materials in the presence of moisture. Such materials should potentially find uses in actuators, biocidal and other applications.

2 Experimental

2.1 Materials

Celite, standard Supercel (Alfa Aesar) was used as received. 6-Bromohexanoyl chloride (97%), 1,4-diazabicyclo [2.2.2]octane (DABCO, 98%), 1,4-dibromobutane (99%), sodium hydroxide (1 N, aq) and triethylamine (TEA, $\geq$ 99.5%) were purchased from Aldrich and used as received. Chloroform and dichloromethane (EMD, Drisolv) were used as received. Tetrahydrofuran (THF, EMD Chemicals, 99.5%) was refluxed over sodium with benzophenone until the solution reached a deep purple, and fractionally distilled just prior to use. 1,4-Bis(bromomethyl)benzene ($\geq$98%) and dimethylamine solution (60% in water) were purchased from Fluka and used as received. α, ω-Aminopropyl-PDMS oligomers (Gelest, Inc.) were vacuum-stripped to remove any cyclics prior to use. Magnesium sulfate (Mallinckrodt Chemicals, anhydrous powder) was used as received.

2.2 Synthesis

2.2.1. *Bromoalkyl-terminated PDMS*

A representative procedure for synthesizing a 1982 g mol^{-1} bromoalkyl-terminated PDMS oligomer is provided. α, ω-Aminopropyl-terminated PDMS (20 g, 0.0118 mol) was dissolved in dry dichloromethane (300 mL) in a 500-mL, flame-dried, two-necked round-bottom flask fitted with an addition funnel. The reaction mixture was cooled to 0°C with an ice-water bath under dry N_2. TEA (3.84 g, 0.0379 mol) was added via a syringe. A solution of 6-bromohexanoyl chloride (5.79 g, 0.027 mol) in dichloromethane (20 mL) was added to the addition funnel under dry N_2. The acid chloride solution was added dropwise to the stirring PDMS solution. The mixture was allowed to warm to room temperature and reacted for 24 h with stirring. The reaction mixture was passed through a Celite column, then washed 3X with DI water. The dichloromethane was removed under vacuum, and the difunctional bromoalkyl-terminated PDMS was dried at 60°C under vacuum for 12 h. ^{1}H-NMR was used to confirm the expected structure of the product.

2.2.2. *Dimethylamino-functional xylene*

1,4-(N,N′-dimethylaminomethyl)benzene was prepared according to a procedure adapted from Spencer et al. (15). 1,4-(Bromomethyl)benzene (6.0 g, 0.023 mol) was dissolved in THF (150 mL) in a round-bottom flask. The reaction mixture was cooled to −78°C with an acetone/dry ice bath. A 60% aqueous solution of dimethylamine (397 mL, 4.37 mol) was added to the cooled reaction via cannula. The reaction mixture was stirred at −78°C for 30 min, followed by stirring at room temperature for 4 days. The solvents were removed under vacuum, and the product was dissolved in diethyl ether. The diethyl ether solution was washed with a

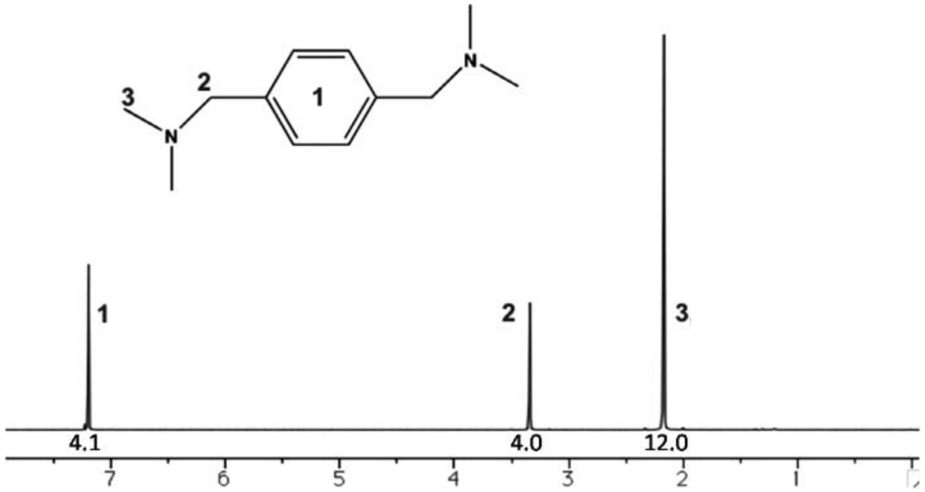


Figure 1. ^{1}H-NMR of 1,4-(N,N′-dimethylaminomethyl)benzene.

2 M solution of sodium hydroxide (3X) and DI water (3X). The diethyl ether layer was dried over magnesium sulfate, then filtered and concentrated under vacuum, yielding 1,4-(N,N′-dimethylaminomethyl)benzene. ^{1}H-NMR was used to confirm the structure of the product (Fig. 1).

2.2.3. *Polyionene synthesis*

A characteristic procedure for the synthesis of a PDMS polyionene with a xylene hard segment is provided. A difunctional bromoalkyl-terminated PDMS oligomer (1982 g mol^{-1}, 5.1 g, 2.6 mmol) and 1,4-(N,N′-dimethylaminomethyl)benzene (0.50 g, 2.6 mmol) were dissolved in dry chloroform (18.5 mL) in a flame-dried round-bottom flask fitted with a reflux condenser. The reaction mixture (20 wt% solids) was refluxed at 75°C for 24 h. Films were cast into Teflon molds and were slowly air-dried for 24 h. The polyionene films were then dried in a vacuum oven at 60°C for 12 h. The films were gently removed from the Teflon molds and stored in a desiccator under a dry nitrogen atmosphere until analyzed.

2.3 Polymer Characterization

2.3.1. *Dynamic mechanical analysis (DMA)*

Tests were performed on a Seiko DMS 210 tensile module with auto-cooler for precise temperature control. Rectangular samples were cut (12 mm in length and 4–6 mm in width) from cast film and deformed (1 Hz frequency, 10 μm amplitude) under a dry nitrogen atmosphere. The temperature was increased from -150 to 250°C, at a heating rate of 2°C/min.

2.3.2. *Thermomechanical analysis (TMA)*

Tests were performed on a TA Instruments TMA 2940. Square samples (*ca.* 4 mm^2) were cut from solvent cast films and loaded into the instrument with a preload force of 0.05 N. The temperature was ramped from room temperature at a heating rate of 2°C/min under a dry air atmosphere until the sample flowed and/or the ability to measure force accurately was lost.

2.3.3. *Thermogravimetric analysis (TGA)*

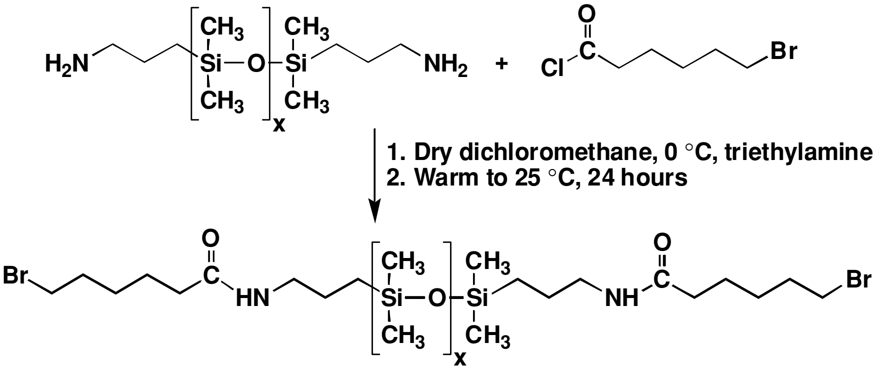
Tests were performed on a TA Instruments Q400 TGA. Samples were initially dried in the TGA at 120°C for 15 min. They were then heated at 5°C/min from 30° to 700°C in a dry air atmosphere.

2.3.4. *Atomic force microscopy (AFM)*

AFM images of the air-free surfaces of the solution cast ionene films were obtained using a Veeco Dimension 3000 atomic force microscope with a Nanoscope IIIa controller. Images were obtained under a nitrogen atmosphere using Nanodevices TAP150 silicon cantilever probe tips (5 N/m spring constant, ~100 kHz resonant frequency). The free air amplitude was normally set at 4.0 V and the set point ratio was in the range of 0.4 to 0.7, which constitutes hard to medium tapping, respectively. The phase images of the samples were obtained by performing AFM analysis on the free air side of the solvent cast films. In all cases, the samples were investigated as quickly as possible to minimize any absorption of moisture from the ambient atmosphere.

2.3.5. *Tensile testing*

Dog-bone samples (13 × 2.9 × 0.5–0.8 mm) were cut from solvent cast films and their tensile properties were measured under ambient conditions (50% RH and 26°C) with an Instron model 5500R machine controlled by Bluehill V2.1 software. Samples were elongated at 50 mm/min until failure. In all cases, the samples were mounted and tested as quickly as possible to minimize any absorption of moisture from the ambient atmosphere.



Scheme 2. Outline of the synthesis of bromoalkyl-terminated PDMS oligomers.

2.3.6. *X-Ray scattering analysis*

X-ray scattering was performed with the multi-angle X-ray scattering system (MAXS) at the University of Pennsylvania. The MAXS system generates Cu K_αX-rays from a Nonius FR 591 rotating-anode 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 Brukers Hi Star two-dimensional detector with a sample to detector distance of 11, 54 and 150 cm. Using Datasqueeze software (16), the 2-D data was converted to 1-D data, intensity corrected for primary beam intensity, and background scattering was subtracted.

2.3.7. *Gel Permeation Chromatography (GPC)*

GPC analyses were performed on an Alliance Waters 2690 Separations Module with a Viscotek T60A dual viscosity detector and laser refractometer equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set. The GPC data collected in chloroform at 30°C was analyzed using a Universal calibration, allowing for determination of absolute molecular weights.

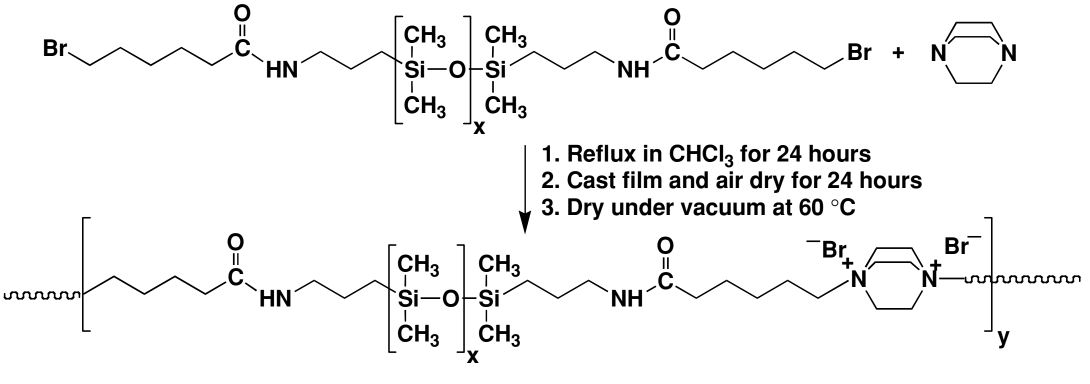
3 Results and Discussion

Difunctional PDMS oligomers suitable for polyionene syntheses were prepared by reacting aminopropyl-functional PDMS precursors with 6-bromohexanoyl chloride, thus forming amide linkages to the PDMS with bromoalkyl endgroups (Scheme 2). A slight excess of triethylamine relative to acid chloride was utilized as an acid scavenger in these derivatizations to avoid any reaction of an acid by-product with the acid-sensitive PDMS backbone. Oligomers with approximately 2000 and 3000 g mole^{-1} number average molecular weights were prepared to investigate polyionene properties as a function of the oligomer segment length. Molecular weights and distributions of the bromoalkyl-functional PDMS oligomers were analyzed by NMR and GPC with good agreement between both methods (Table 1).

A representative ^{1}H-NMR spectrum demonstrates the quantitative addition of 6-bromohexanoyl chloride to aminopropyl-terminated PDMS using this approach (Fig. 2). The precursor oligomers had been synthesized by a polysiloxane redistribution reaction, so the molecular weight distributions were close to two as expected.

PDMS-based polyionenes were prepared in step growth polymerizations by chain extending the bromoalkyl-functional oligomers with either 1,4-(N,N′-dimethylamino-methyl)benzene or diaminobicyclooctane (DABCO) utilizing Menshutkin reactions (Scheme 3).

The determination of the absolute molecular weights and molecular weight distributions of polyionenes by conventional techniques such as GPC or viscometry (17) is



Scheme 3. Synthesis of segmented PDMS-polyionenes containing DABCO hard segments.

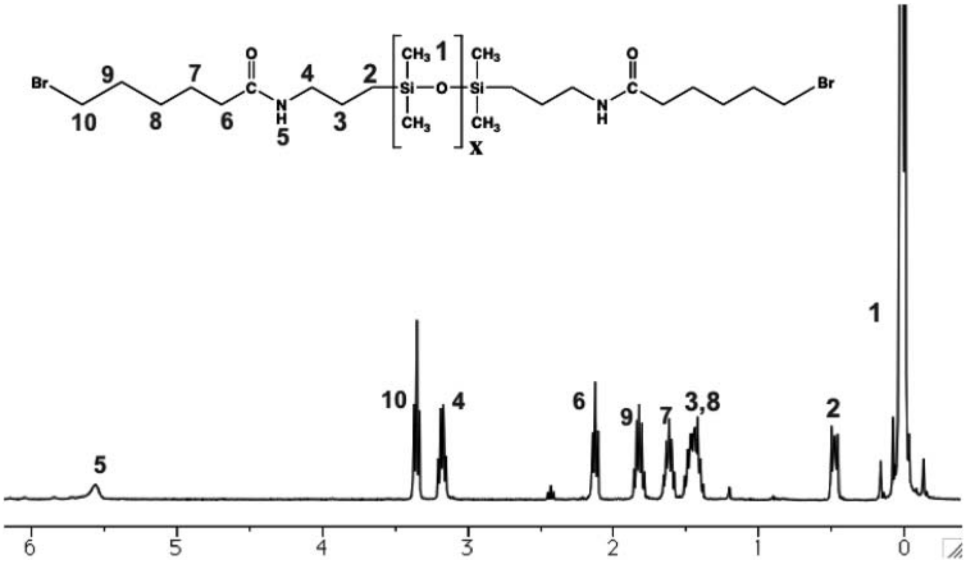


Figure 2. ^{1}H-NMR of a 1982 g mole^{-1}bromoalkyl-terminated PDMS.

complicated by polymer-polymer and polymer-stationary phase interactions. Recently, Layman *et al.* (18) developed an aqueous-based SEC-MALLS technique coupled with a suitable mobile phase which reduces various interactions present in the system to determine the absolute molecular weights of various aliphatic polyionenes. In the present study, however, neither the relative nor the absolute molecular weights of the polyionenes were determined.

The hard segments used in this study were either xylene or DABCO, while the PDMS oligomer molecular weight was either ∼2000 or ∼3000 g/mole. Dibromobutane was also employed in select cases with DABCO as a chain extender to increase the hard segment length. Careful attention was given to maintaining 1:1 stoichiometries between the amino and bromoalkyl groups to obtain high molecular weights.

3.1 Thermo Gravimetric Analysis of PDMS Polyionenes

Figure 3 shows the results of the weight loss with temperature of the segmented PDMS polyionenes in air. All of the polymers showed similar degradation patterns, with initial degradation starting around 225°C. Interestingly, the two polymers comprised of only the PDMS and the bicyclic amine had unusually high char yields, and this suggests that the bicyclic structure may lead to enhanced crosslinking upon exposure to elevated temperatures relative to the other systems.

Table 1. Bis(bromoalkyl-terminated) PDMS molecular weights

	M_n *(gmole^{-1})*		
Polymer	*^{1}H-NMR*	*GPC*	*PDI**
PDMS(2000)	1982	2100	2.1
PDMS(3000)	3082	3400	1.9

*PDI = Polydispersity index.

3.2 Temperature Dependent Moduli of PDMS Polyionenes

The temperature-dependent moduli of the PDMS polyionenes were analyzed by DMA under an inert dry nitrogen atmosphere. Samples were removed from the desiccator and loaded into the instrument in less than 5 min in order to minimize absorption of moisture from the ambient air during mounting. Figure 4 shows the DMA spectra of solvent cast films of the polyionenes depicting effects of the

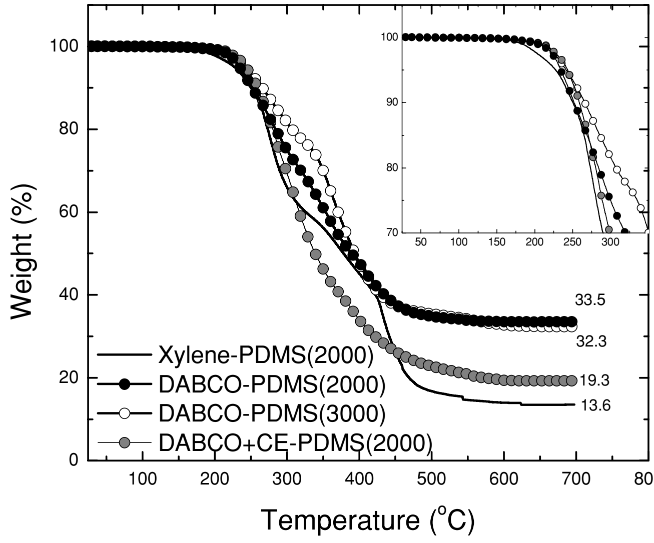


Figure 3. Thermo gravimetric analysis of PDMS-polyionenes.

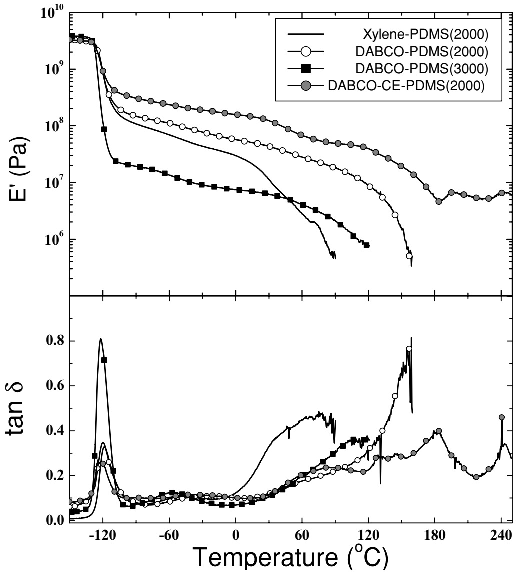


Figure 4. Dynamic mechanical spectra of films of the PDMS polyionenes.

variation of hard segment content, soft segment molecular weight and chemical nature of the hard segment on their temperature-dependent modulus profiles.

All the polyionenes showed high moduli ($>10^9$ Pa) at low temperatures, and this was followed by a sharp drop in modulus (and a corresponding Tan δ peak) at *ca.*−120°C due to the glass transition of the PDMS soft segment. This was followed by a downward sloping temperature-dependent rubbery plateau for all systems studied. The results also showed that the nature of the hard segment had a distinct effect on the DMA profiles of the polyionenes. The copolymers with xylene and DABCO hard segments had similar hard segment contents (HS content ∼22 wt% for xylene and ∼ 20 wt% for DABCO) and soft segment molecular weights (∼ 2000 g mole^{-1}). However, the former had a slightly lower rubbery plateau modulus and the temperature at which the modulus starts decreasing due to weakening of the ionic group association in the hard segments (may be attributed to ion-hopping [19]) was lower relative to the corresponding DABCO-based polyionene. This difference may possibly be attributed to better packing of the DABCO-based polyionene chains than the corresponding xylene-based chains.

The hard segment content was varied by both increasing the molecular weight of the PDMS soft segments (from ∼2000 to ∼3000 g/mole, which reduced the HS content from ∼20 to ∼13 wt%, respectively) and/or by the incorporation of the chain extender, dibromobutane (which increased the HS content from ∼20 to ∼30 wt%). Figure 4 shows that the increase in SS content leads to a systematic increase in the heat capacity change at the PDMS T_g, and breadth of the rubbery plateau modulus and the temperature at which the ionic association started weakening in the hard domains.

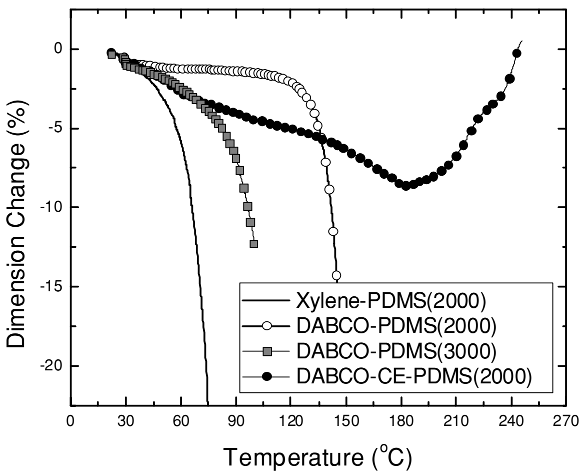


Figure 5. Thermo-mechanical analysis (TMA) of PDMS-polyionenes.

3.3 Thermo-Mechanical Analysis of PDMS Polyionenes

The softening temperatures of the polyionenes were further verified by performing thermo-mechanical analysis (TMA) under a nitrogen atmosphere (Fig. 5). The softening points of the polyionenes obtained from TMA were similar to those obtained from DMA. The chain-extended polyionene also showed an increase in film thickness after the initial softening (highly reproducible), which is believed to be due to the complex degradation reactions which occur at these temperatures and which appeared to promote some "foaming" of the initial film (confirmed by TGA analysis).

3.4 Tensile Properties of PDMS Polyionenes

Figure 6 shows the uniaxial tensile analysis of the PDMS polyionenes obtained at ambient conditions. The trend in

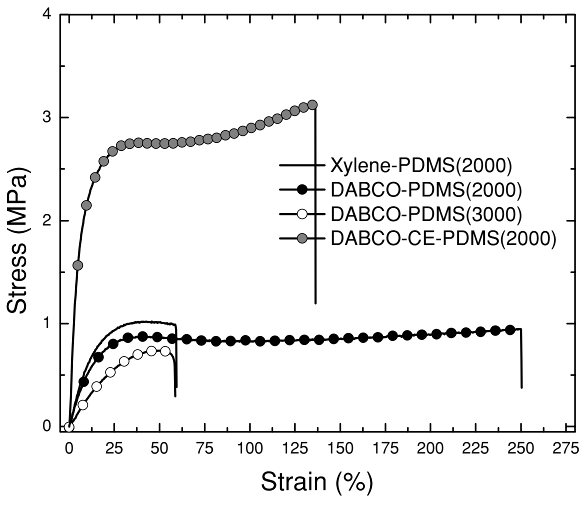


Figure 6. Tensile properties of PDMS polyionenes.

the variation of the tensile moduli of the polyionenes was the same as observed in the DMA analysis in the same temperature range as utilized for the stress-strain analysis (26°C - recall Fig. 4). The xylene based polyionene showed a slightly higher modulus than the corresponding DABCO based copolymer (with ~2000 g/mole PDMS). As the hard segment content was increased, the modulus of the DABCO polyionenes increased as expected. The chain extended ionene showed a weak yield point suggesting the presence of some long-range connectivity between the hard segments—see later discussion.

3.5 Morphological Analysis of PDMS Polyionenes by Tapping-mode AFM

The DMA results in Figure 4 clearly suggested the presence of a microphase-separated morphology, which was further analyzed by ambient tapping mode AFM (Fig. 7) under a nitrogen atmosphere. The polyionene based on DABCO hard segments and ~2000 g/mol PDMS soft segments in fact did provide evidence of a microphase-separated morphology where the hard segments were found to form thread-like domains which were dispersed in the soft PDMS matrix. With an increase in the soft segment molecular weight from 2000 (Fig. 7a) to 3000 g/mole (Fig. 7b), the film became softer (darker phase image) and the somewhat thread-like hard domains were found to be further dispersed from each other. The presence of the microphase separated morphology in the other polyionenes was confirmed by performing further characterization by X-Ray scattering analysis, which is presented in the following section.

3.6 Morphological Analysis of PDMS Polyionenes by X-Ray Scattering

While the AFM results indicate that at least two of the polyionene materials possessed some signs of microphase separation at the film surface, the data was limited. Thus, additional evidence of microphase separation was sought by use of two dimensional (2D) X-ray scattering. In addition, some samples were also investigated in both the unstretched as well as the stretched state (150%)—the latter being done by stretching at 100°C and then holding the deformed films at ambient condition while the X-ray measurements were undertaken. The precursor bromo-terminated PDMS material was also investigated in the unstretched state. Three different angular regions were explored and these included the small angle (SAXS), intermediate angle (IAXS) and wide angle (WAXS) regions. The 2D data for the undeformed samples showed no azimuthal dependence. In these initial experiments, the beam was passed normal to the plane of each cast film. This data was then integrated over the azimuthal angle and the three different angular regions were combined to give continuous plots of the log of the scattering intensity as a function of the log of the scattering vector ***q*** for the four polyionene samples and the PDMS precursor—see Figure 8a.

At high ***q*** (wide angle scattering), a peak was noted at 8.36 nm^{-1} which was associated with the amorphous halo from the PDMS component since this matched the peak from the PDMS precursor. A weaker peak at the higher q value of ca.14.74 nm^{-1} was attributed also to the local amorphous packing within the polyionene.

Of particular importance was the observation of scattering peaks within the small and intermediate angle regions as is best addressed by replotting the data from the four ionene containing materials into the form of log intensity versus ***q*** as is given in Figure 8b. Here, the reader notes that there are at least two scattering peaks in the range of ***q*** of 0.7 – 4.0 nm^{-1}. As seen in Figure 8b, these peaks have been labeled as **1**, **2**, and in the case of sample DABCO+CE-PDMS(2000), there is a very weak third order peak labeled **3**. These peaks are higher order reflections that arise from the high electron density ionene regions comprised of the N+ and Br- ion pairs (or groups of such ion pairs).

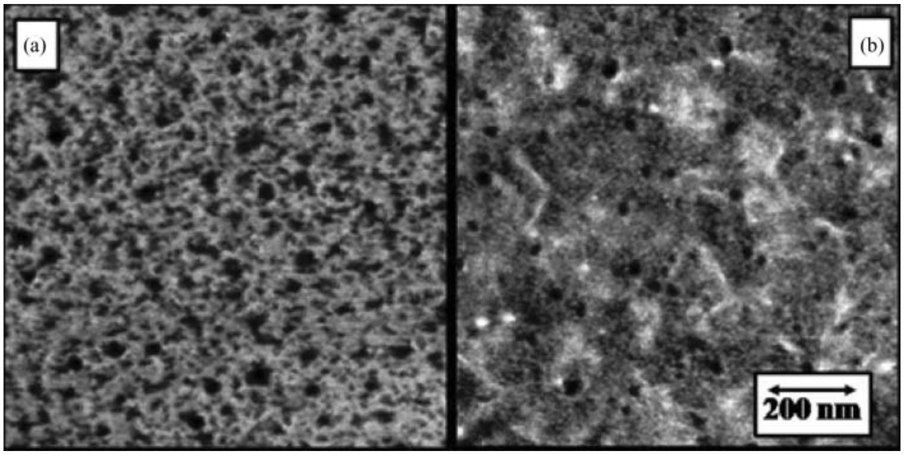


Figure 7. Tapping mode AFM phase images of PDMS polyionenes at room temperature: a. DABCO-PDMS(2000), b. DABCO-PDMS(3000).

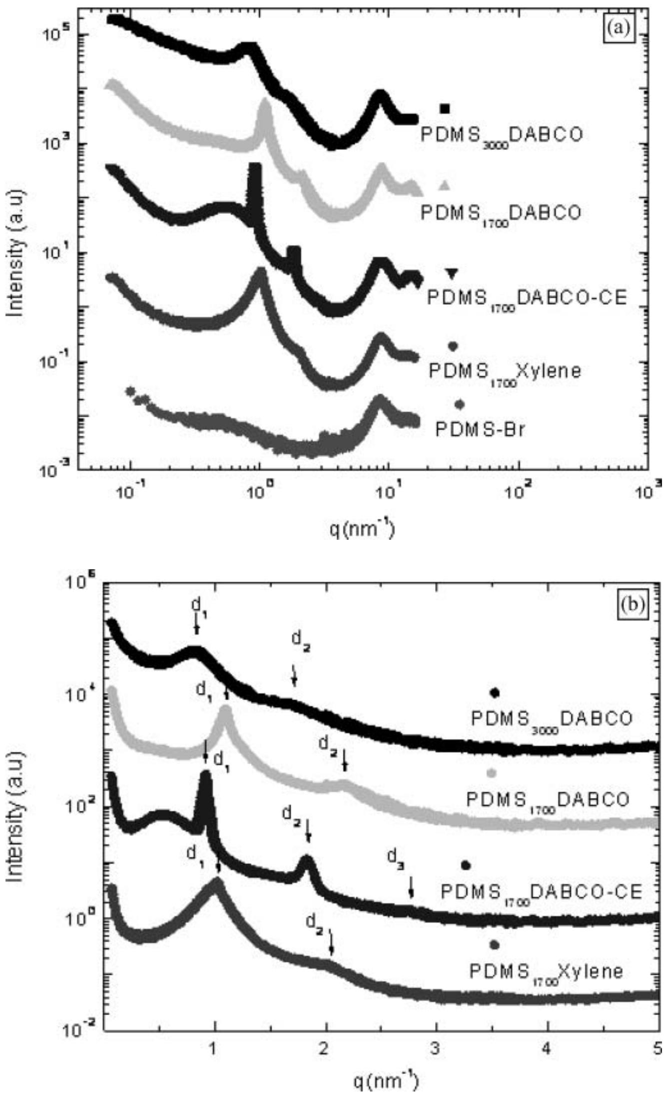


Figure 8. Intensity vs. scattering vector in a log-log plot for PDMS polyionenes at wide (WAXS), intermediate (IAXS) and small (SAXS) angle region (a) and similar data replotted on a log-linear scale showing only multiple reflections (b).

The periodicity between the ionic domains depends on the PDMS length. Self assembly (microphase separation) of the ionene regions may also be partially influenced by the development of hydrogen bonding between the amide linkages, but we suggest that the ionic interactions (microphase separation) will likely dominate the ordering process. It is also noted that for the non-chain extended DABCO containing ionene, the lower soft segment PDMS molecular weight (2000 vs. 3000 g/mol) provides a sharper first order peak than does the corresponding 3000 g/mol PDMS containing system and this sharper peak occurs at a lower spacing than does the 3000 g/mol PDMS system as would be expected (5.7 nm w/o DABCO vs. 8.2 nm with DABCO). Furthermore, when the chain extender is utilized within the DABCO+CE-PDMS(2000) system, it also leads to a slight increase in the spacing relative to the non-chain extended analog as would also be expected (6.9 nm w/ chain extended vs. 5.7 nm w/o chain extended). The **d**-spacings are summarized in Table 2.

Table 2. Comparison table between the unstretched, stretched and calculated real space distances for all polyionenes studied

Sample	d_1 *(unstretched) (nm)*	d_1 *(stretched) (nm)*	$d_{1(calc.)}$ *(nm)*
PDMS-3000-DABCO	8.0	8.0	8.2
PDMS-1700-DABCO	5.7	5.8	5.7
PDMS-1700-DABCO-CE	6.6	6.6	6.9
PDMS-1700-Xylene	6.3	6.2	6.6

The origin of the suggested microphase separation of the ionene containing regions extends from the earlier work of Feng from one of the present author's (GLW) laboratory (14). While the ionene chemistry was a bit different from that given in the present report in that the soft segment was based on polytetramethylene oxide (PTMO) and the ionene units were based on dibenzyl halides, that work clearly showed using SAXS and TEM that the ionene regions led to distinct association which constructed cylindrical domains. Furthermore, these cylindrical domains underwent hexagonal packing within the PTMO matrix when the composition ratios of hard and soft segment were in the same general range as those addressed in the present study. Finally, up to four orders of scattering were noted for these systems particularly when the PTMO segment molecular weight was in the range of 1000 g/mol. Using a similar argument in the present work suggests that the local packing might be represented by the simplified schematic shown in Figure 9.

Here it is noted that the value of $\mathbf{d}_1$ relates to the center-to-center distance of the ionene containing cylindrical

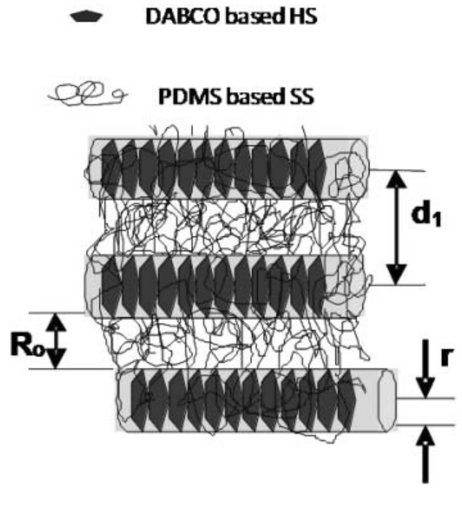


Figure 9. Schematic drawing of PDMS-based ionenes forming cylindrical aggregates.

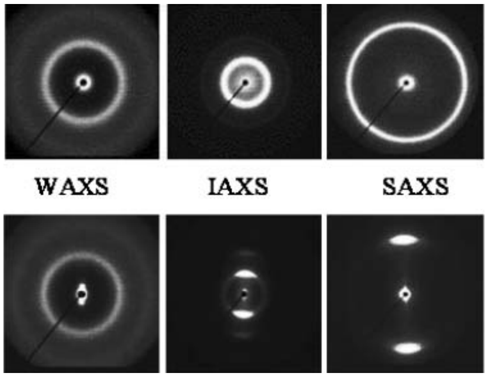


Figure 10. 2D scattering for unstretched (top) and stretched (bottom) DABCO-PDMS(2000). The spacing d_1 correspond to the multiple reflections at $q{\sim}0.7$–4 nm^{-1}. The stretch direction is horizontal.

aggregates while the parameter $\mathbf{R}_0$ represents the average dimension associated with the intervening PDMS soft segment matrix regions between the aggregates. The characteristic spacing ($\mathbf{d}_1$) between the cylindrical aggregates appears to increase with the end-to-end distance (R_0) of PDMS (as controlled by the molecular weight) and the size of the hard segments (r): $d_{calc} = Ro + 2r \sim d_1$ where r is *calculated* by assuming a simple cube and infinite long cylinders, as shown in Table 2.

Turning briefly to the scattering behavior of the uniaxially deformed ionene materials, we first show Figure 10. This figure provides the 2D WAXS, IASX and SAXS patterns for the representative sample of DABCO-PDMS(2000). Here both the 2D patterns for the undeformed and deformed sample are given where the stretch direction is along the horizontal direction and the beam in all cases was passed normal to the plane of the cast film. The important feature of these patterns is that when the first order spacing is calculated from either SAXS pattern of the deformed or the undeformed sample, no significant difference existed suggesting that the PDMS segments still remain relatively unperturbed—see Table 2. Furthermore, at least at this level of deformation (150%), ordering of the local cylindrical ion containing domains occurs such that their long axis aligns quite well along the stretch direction as based on the azimuthal dependence of the scattered intensity for the deformed sample. As might be expected, when the SAXS patterns were determined by passing the beam along each of the three orthogonal axes of the film for both the undeformed and the deformed sample of the same ionene, it is noted that there was no azimuthal dependence for any of the patterns obtained for the unstretched film. However, there is an equal azimuthal dependence observed for the two patterns when the beam is orthogonal to the stretch direction and no dependence when the beam is parallel to the stretch direction—see Figure 11.

This of course confirms that the initial morphological texture is isotropic prior to deformation and becomes uniaxial in nature with deformation as expected. The cause and justification for this latter experiment was that in the earlier work of Feng et al. (14) on the PTMO ionenes mentioned earlier, those systems did show that upon film casting, ordering of the cylindrical ion containing domains led to some ordering perpendicular to the film plane. As shown

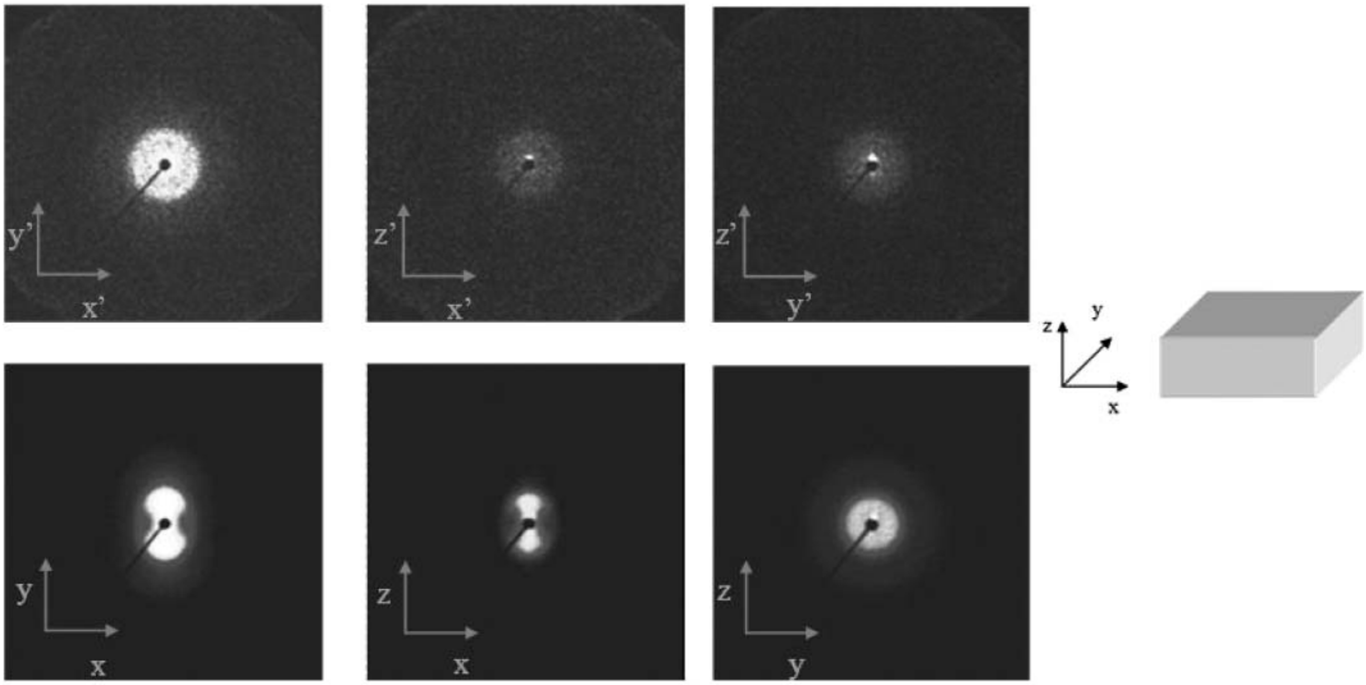


Figure 11. 2D scattering between the un-stretch (top) and stretch (bottom) DABCO-PDMS(3000) at each orthogonal plane.

by the results given in Figure 11 above, such ordering upon film casting did not occur in the PDMS ionene systems addressed in the present report.

4 Conclusions

In this paper, we presented the successful synthesis and characterization of novel ionene polymers based on PDMS soft segments. The polymers were synthesized by a modified Menshutkin reaction between bromo-terminated PDMS oligomers and various ditertiary amino compounds. Thermal analysis (DMA and TMA) of the polyionenes showed that the value and breadth of the rubbery plateau moduli and their final softening temperatures changed systematically with the nature and content of the hard segments of the copolymers, as expected. Uniaxial tensile analysis showed the systematic increase in the modulus of the polyionenes with their hard segment content. Evidence of long range connectivity of the hard segments in the highest hard segment content polyionene was also observed. The morphology of the polyionenes was analyzed with both AFM and X-ray scattering analysis, which showed the presence of a microphase separated morphology in all the polymers. Based on X-ray analysis in both unstretched and stretched conditions, we propose a morphological model for these novel polyionene copolymers, where the hard domains formed high electron density cylindrically packed ionene regions comprised of the packing of the N^+ and Br^- ion pairs, due to their incompatibility with the PDMS soft segments that comprise the soft domains. Though in the undeformed state, these cylinders were oriented isotropically, when deformed uniaxially, the cylinders were found to orient along their long axes in the stretch direction.

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