

Review

Neat Linear Polysiloxane-Based Ionic Polymers: Insights into Structure-Based Property Modifications and Applications

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Abstract: A diverse range of linear polysiloxane-based ionic polymers that are hydrophobic and highly flexible can be obtained by substituting the polymers with varying amounts of ionic centers. The materials can be highly crystalline solids, amorphous soft solids, poly(ionic) liquids or viscous polymer liquids. A key to understanding how structural variations can lead to these different materials is the establishment of correlations between the physical (dynamic and static) properties and the structures of the polymers at different distance scales. This short review provides such correlations by examining the influence of structural properties (such as molecular weights, ion pair contents, and ion types) on key bulk properties of the materials.

Keywords: polysiloxane; ionomer; polyelectrolyte; ionic polymer; poly(ionic) liquid; polymer ionic liquid; ionic liquid

1. Introduction

1.1. A Brief History of Polysiloxanes, Including an Overview of Their Properties

Since the seminal work of Frederic Kipping on organosilanes, commencing more than 100 years ago [1], polysiloxanes and silicones have been used for an enormous range of applications [2–11]; they pervade our lives. The applications include electrical insulation [2–4], water repellents for leather [5], adhesives [6,8,11], surfactant agents for both foaming and anti-foaming [7,9], and personal care products [10]. The continued popularity of these materials can be attributed to their high stability to heat, light and many classes of chemicals [12–14], as well as their flexibility, and ease of modification of other mechanical properties. Neat polydimethylsiloxanes (PDMS) are structurally flexible due to the low torsional energy barrier around their Si-O-Si bonds (0–5 kJ/mol [15,16]) and the related glass transition temperatures (T_g) that are lower than those of linear polyacrylates of a similar molecular weight. The ability to synthesize polysiloxanes by polycondensation reactions [13] between cyclic oligosiloxanes and functionalized dichlorosilanes provides a plethora of materials with different chemical structures and mechanical behaviors that can be tuned for different applications. For example, the commonly employed Karstedt's catalyst [17,18] can be used to convert cyclic oligosiloxanes from liquids at room temperature into flexible plastic and gel-like materials that have been used as platforms for optoelectronics [19,20]. With appropriate polar functional groups, polysiloxanes become somewhat hydrophilic, making them useful as adhesives and sealants [11] despite the parent polymers being highly hydrophobic. For example, aminopropyl dimethicone and amodimethicone [21], classes of polysiloxane copolymers with aminopropyl and dimino-containing chains, form emulsions in water. Also, the amino groups can be protonated using mild acids, and even form crosslinks with diacids;

in both cases, ion pairs, that alter the local polarity of the polymers, are produced [22]. Although the use of amodimethicone and other polysiloxane-based copolymers in cosmetic [23] and textile products [24] appeared in the 1980s, functionalized ionic polysiloxanes have been introduced more recently. Recent developments in the field of polysiloxanes that exploit non-covalent (especially ionic) cross-links will be the focus of this mini-review. Also, the increasing number and type of applications of polysiloxane-based ionic polymers, in fields as diverse as fuel cells and electrolytic media for batteries [25,26], make a review of these materials especially pertinent at this time.

1.2. Ionic Polymers and Polysiloxanes

Ionomers are ionic polymers with a small fraction (defined formally by the International union of pure and applied chemistry (IUPAC) as 10%) of monomers containing charged groups. Ionic polymers with a higher fraction of monomers containing charged groups are defined by IUPAC as polyelectrolytes.

As a result of the charged centers, ionomers have a propensity to form microphases consisting of small ionic clusters (approximately 1–5 nm in size [27]) embedded in the amorphous regions. The physical properties of the polymers depend on the ion content because the strength of the electrostatic interactions between ion pairs exceeds the dispersive polymer–polymer chain polysiloxane interactions. When ionomers are dissolved in low dielectric solvents, the ionic interactions remain a dominant factor, but they are less important in solvents of high polarity. The distribution of the sizes is due to numerous factors related to the polymer architecture [27]: molecular weight, type of pendant groups, polymer backbone type, random versus block substituent placement, etc. One disadvantage of ionic aggregation is the lowering of conductivity relative to polymers without ionic clustering [28].

IUPAC provides only a qualitative definition of polyelectrolytes, and modifications of them include ionic polymers (ionomers) and their interactions with solvents [29,30]. Because this review focuses on neat ionic polymer melts, the original limit suggested by IUPAC of 10% by mole for the ion content will be used here to distinguish ionomers from polyelectrolytes. The greater number of non-covalent ionic interactions among the constituents of polyelectrolytes also helps to distinguish them from ionomers. Many ionomers are semi-crystalline solids whose packing can be discerned from analyses of X-ray diffraction data. In addition, when monomers of ionic liquids are polymerized, a special category of polyelectrolytes, called poly(ionic) liquids (or polymeric ionic liquids), is formed; many poly(ionic) liquids remain liquids at temperatures below 100 °C [31–33]. These materials have been studied for their potential to combine the benefits of polyelectrolytes (i.e., flexible macromolecular architectures) and ionic liquids (i.e., high thermal stabilities and ionic conductivities) [34,35].

The overview presented here focuses on the bulk and physico-chemical properties of neat linear polysiloxane-based ionic polymers and emphasizes their ion pair content and molecular weight as the principal macromolecular variables.

2. Types of Polysiloxane-Based Ionic Polymers

2.1. Polyelectrolytes Where All Monomers Except the Terminal Group Contain an Ion

Polysiloxane-based polyelectrolytes with inorganic counterions. The flexibility of the polysiloxane polymer chains can be decreased drastically by increasing the frequency of ionic cross-linker sites [31,36–40]. Polyelectrolyte examples of this effect, shown in Figure 1A, have been studied by Kaneko and coworkers [36–39,41]. This general structure is related to the polyelectrolyte ionomer (with far fewer ionic groups), aminopropyl dimethicone. Another key structural difference between the structures in Figure 1A and aminopropyl dimethicone is the presence of a hydroxyl group in the former instead of a methyl group in the siloxane monomer. Each of the aminopropyl-trimethoxysiloxane monomeric units (APTMO) used to form the resulting siloxane-based polyelectrolytes (PAPS) in Figure 1 contains a charged ammonium ion with either chloride or nitrate (PAPS-Cl or PAPS-NO₃, respectively) as the counterion. Neither the average

molecular weight nor the polydispersity was reported for either the **PAPS-Cl** or **PAPS-NO₃**; bulk characterization consisted of X-ray diffraction (XRD), transmission and scanning electron microscopies, and nitrogen porosimetry. Due to the high density of ion pairs and hydroxyl groups along the polymer chains, the formation of highly ordered structures is not surprising. XRD data showed that the chains of both **PAPS-Cl** and **PAPS-NO₃** pack in hexagonally ordered arrays that implicate somewhat extended polymer chains.

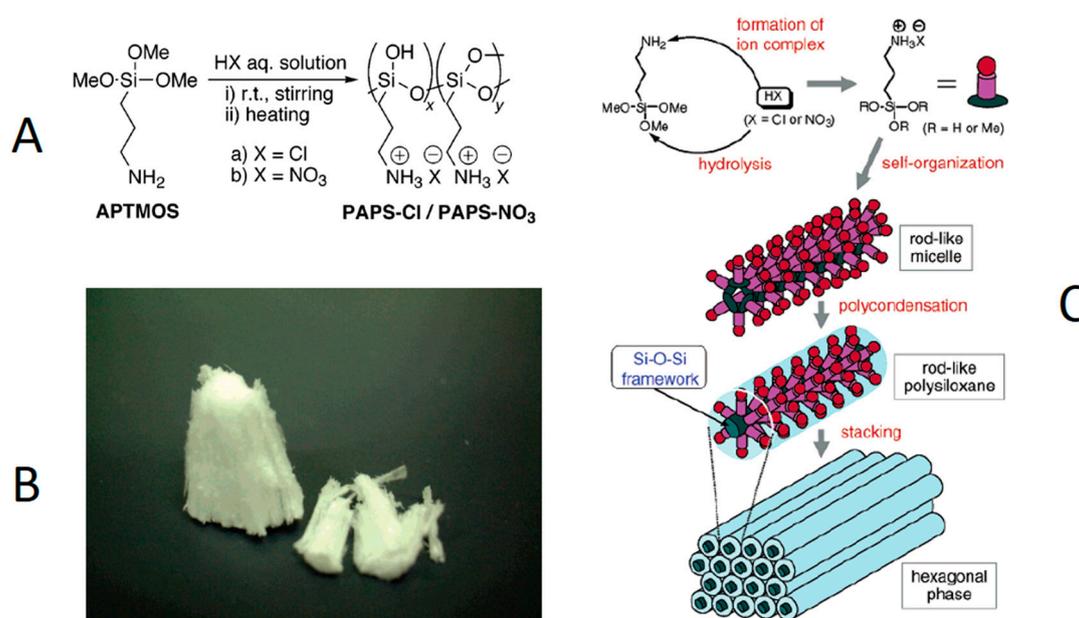


Figure 1. Neat polysiloxane-based polyelectrolytes with propylammonium chloride or nitrate pendant groups [36]. (A) The synthetic route to **PAPS-Cl** and **PAPS-NO₃**. (B) Photograph of neat **PAPS-Cl**. (C) Cartoon representation of the ordered layers based on X-ray diffraction (XRD) data. Reprinted with permission from [36]. Copyright (2004) (American Chemical Society).

The highly hydrophilic and hygroscopic nature of the **PAPS-Cl** or **PAPS-NO₃** salts also follows from the prevalence of the multiple ion pairs. The effects on the packing of the chloride salt, **PAPS-Cl**, was explored by dissolving it in water first and then recording the X-ray diffractograms at various stages of drying. Thus, it was found that the slow removal of water by drying in air does not change the overall packing motif.

PAPS-Cl and **PAPS-NO₃** are not soluble in low polarity, aprotic solvents such as chloroform and dichloromethane. Curiously, the polyelectrolytes can be dissolved in DMSO but not in some other polar (and some protic) solvents such as ethanol, methanol, acetone and *N,N*-dimethylformamide.

Polysiloxane-based polyelectrolytes with organic counterions. Organic counterions, such as long-chained carboxylates, in polysiloxane-based polyelectrolytes introduce another structural variable: an increased importance of London dispersion forces. Thus, Kaneko and coworkers [36,37] have combined **PAPS** with octanoate as the counterion (**PAPS-C8**). The neat material is a hygroscopic powder, similar in appearance and packing to **PAPS-Cl** and **PAPS-NO₃**. XRD indicates hexagonal packing, again, but with a wider cylindrical diameter due to the alkyl chains. Kaneko and coworkers [36] mention that **PAPS** with carboxylate counterion chains longer than octanoate (N.B., decanoate, dodecanoate, and tetradecanoate) do not maintain hexagonal packing, probably due to increased London dispersion interactions and entropic disorder. Also, **PAPS** with carboxylate chains shorter than octanoate (N.B., hexanoate and butanoate) remained liquids at room temperature; they are polymeric ionic liquids. Additionally, carboxylates as counterions make the **PAPS** electrolytes more hydrophobic; whereas **PAPS-C8** is soluble in ethanol, neither **PAPS-Cl** nor **PAPS-NO₃** can be dissolved in this alcohol.

The correlation between the bulk properties of polyelectrolytes and the length of the alkyl chain in the counterion is interesting, and has been found in other examples involving polyelectrolyte-surfactant complexes [42–45]. Polyacrylate-based polycations with hexanoate and shorter alkyl carboxylate anions are also ionic liquids at room temperature, but form ordered structures when the carboxylates are decanoate or longer.

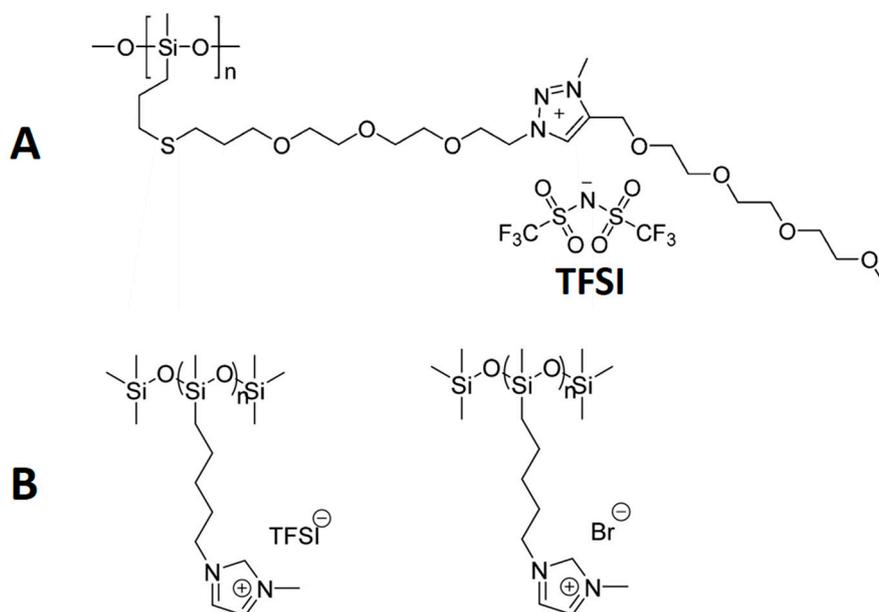
Polysiloxane-based polyelectrolytes with a polymeric counterions. To the best of our knowledge, there is only one report of a polysiloxane-based polyelectrolyte in which all monomeric units contain an ion pair [37]: **PAPS-Cl** has been combined with another polymeric polyelectrolyte, sodium polyacrylate (molecular weight of 250 KDa). The resultant nano-composite was heterogeneous because the two polymers exhibited minimal interactions. Their nearly complete separation allowed the rod-like polysiloxane to retain its hexagonal packing while being surrounded by layers of sodium polyacrylate.

Polysiloxane-based poly(ionic) liquids/polymer ionic liquids. Due to their flexibility, polysiloxane-copolymer chains have been shown to form polymeric ionic liquids (PILs). Both of the PILs shown in Scheme 1 [31,32] have pendant groups that lack sufficient non-covalent interactions to be in a semi-crystalline state at room temperature. In the PILs designed by Jourdain and coworkers [31], a triazolium bis(trifluoromethyl)sulfonamide ion pair is generated through click chemistry using a copper(I)-catalyzed azide-alkyne cycloaddition. The presence of the oligomeric ethylene oxide group promotes packing of the chains, although the glass transition temperature is still only ca. $-62\text{ }^{\circ}\text{C}$; by comparison, the glass transition temperature of neat, high molecular weight PDMS is $-123\text{ }^{\circ}\text{C}$ [12]. A similar result was found for the PILs made by Bocharova and coworkers [46], where the length of the alkyl chain is too short to generate lamellar packing that is stable at room temperature. The trends observed for both PILs can be summarized by a correlation of the monomer molar volume and glass transition temperature. For PILs with a flexible backbone, a smaller molar volume of the monomer (including the counterion) results in a higher glass transition temperature. This observation may explain why the polyelectrolyte salts of Kaneko and coworkers [36,38] did not form polymeric ionic liquids—their molar volumes are smaller. Lastly, one assumption implicit in this correlation is that the counterions of the PILs do not contribute significantly to the non-covalent interactions (i.e., bis(trifluoromethane)sulfonimide (TFSI) and the halide anions do not aggregate or phase separate into structures similar to those found for organic anions such as long-chain carboxylates). More examples will be needed to test this hypothesis adequately.

2.2. Polysiloxane-Based Polyelectrolytes with Some Monomers not Containing Ion Pairs

Influence of lowering the ion pair content. A decrease in the amount of non-covalent crosslinkers does not always translate to a decrease in their influence on the physical state of an ionic polymer; a broad range of possible materials can still be formed [40,47,48]. Much of the intermolecular interactions that influence the physical state of the material is now delegated to the pendant groups and counterion. Thus, a polysiloxane-based imidazolium bromide polyelectrolyte salt remains a liquid at room temperature even with 25% by mole of imidazolium bromide ion content. Beyond noting that this material is a Newtonian liquid at room temperature, not much else is known about the physical texture of the polyelectrolyte. Also using an imidazolium bromide (NL) ion pair, Zuo and coworkers [40] in 2017 synthesized polyelectrolytes (PNL1-n) with differing NL grafting densities using thiol-ene chemistry (Figure 2a). Ranging from 16% for PNL1-1 to 85% for PNL1-5 (Figure 2), the grafting density was calculated using the weight average molar mass provided. Surprisingly, at a higher grafting density, the authors found that the resulting polyelectrolyte remains a viscous liquid. The authors attribute this result to the disruption of entanglements that occurs for PNL1-4 and PNL1-5, but not for PNL1-3. This is interesting, as the polysiloxane copolymer with mercaptopropyl pendant groups (PMMS) is a liquid as noted by the rheological data. Thus, there appears to be an optimal grafting density range that results in a phase transition. An unanswered question in this work involves the 365 nm wavelength used to photo-initiate the thiol-ene click chemistry. This radiation can also

induce the formation of disulfide linkages in primary alkyl thiols [49], and they may also contribute to the different physical states of the materials.



Scheme 1. Two examples of potentially important polymeric ionic liquids [31,32]: (A) a TFSI-based polymeric ionic liquid (PIL) and (B) an imidazolium-based PIL. Reprinted with permission from [31,32]. Copyright (2016 and 2017) (American Chemical Society).

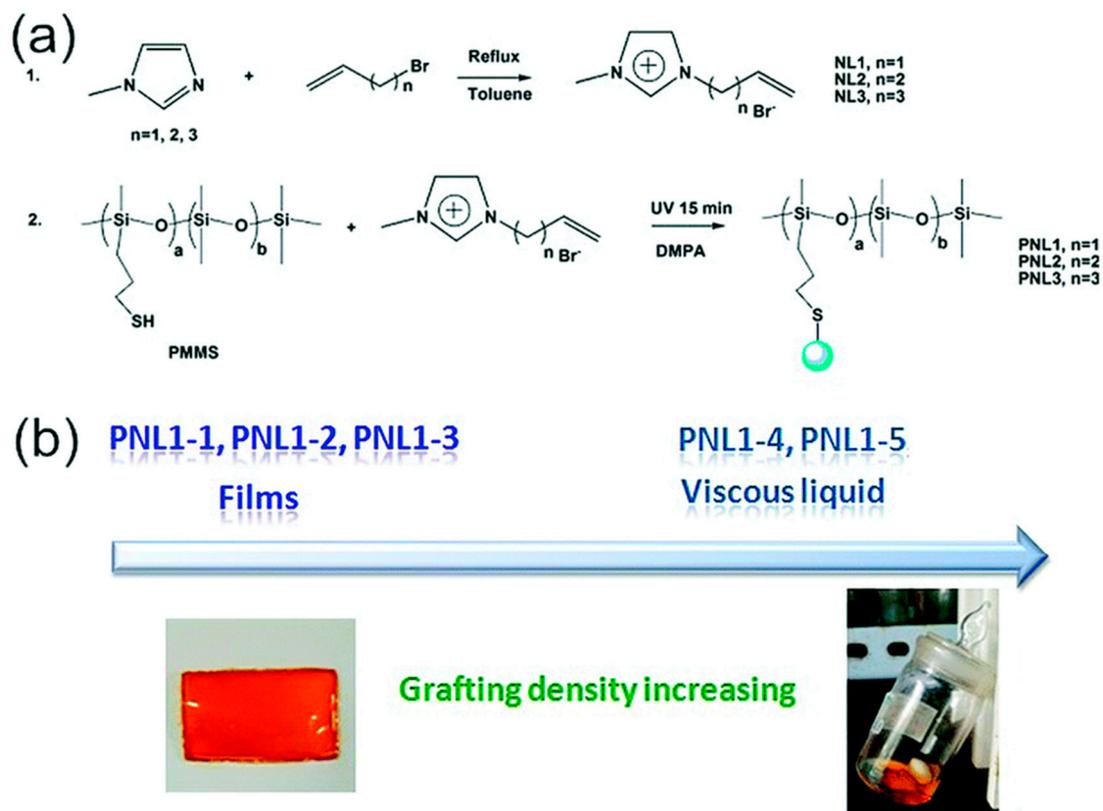


Figure 2. (a) Reaction schemes and (b) pictures involving an imidazolium bromide polyelectrolyte system [40]. Reproduced from [40] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Influence of alkyl chain lengths at lowered ion content [50]. Many researchers are exploiting the influence of pendant groups on the bulk properties of ionic polymeric systems. The highly flexible nature of the linear polysiloxane homopolymers and the type and amount of a pendant group can be used to tailor physical properties, such as the glass transition temperature. Exploring different types of pendant groups can be used to introduce new properties not normally seen with linear polysiloxane homopolymers. A good example is the liquid-crystalline polyelectrolyte made by Wang and coworkers [50]. A set of polysiloxane copolymers, $[P_nSO_3]$, were synthesized with two unique pendant groups: a phenylpropoxy sulfonate anion and a bulky cholesteric group. Amounts of these groups were varied and given as mole fractions of the sulfonate anion (Figure 3D). The lowest amount of sulfonate in the polysiloxane copolymer is denoted by $n = 1$ or $[P_1SO_3]$ and the highest amount by $n = 3$ or $[P_3SO_3]$. The former was used to crosslink two different dications: hexane-1,6-diyl diisonicotinate (HPy) and (1,1'-bipenyl)-4,4'-diisonicotinate (BPy) (Figure 3C), making the networks far more rigid than those observed for the inorganic salt crosslinked systems mentioned in the previous section. The bulky cholesteric group provides the van der Waals ordering responsible for the liquid crystalline properties observed in the optical microscope images (Figure 3A,B). Due to greater intermolecular interactions from the pendant groups, the glass transition of the polyelectrolyte increases to 50 °C, with minimal influences from the crosslinkers [HPy] or [BPy]. It is also not surprising that that a smectic A or cholesteric mesophase is observed. They are typical of cholesteric liquid crystals [51]. One conclusion of note is that the thermal stability of the smectic A mesophase can be correlated with the amount of cholesteric pendant groups. The flexibility of the crosslinkers, HPy and BPy, also influences the thermal stability of the polyelectrolyte. Thermogravimetric analyses showed that the onset of pyrolysis of the organic component was 50 °C lower for [HPy][P_1SO_3] than for [BPy][P_1SO_3].

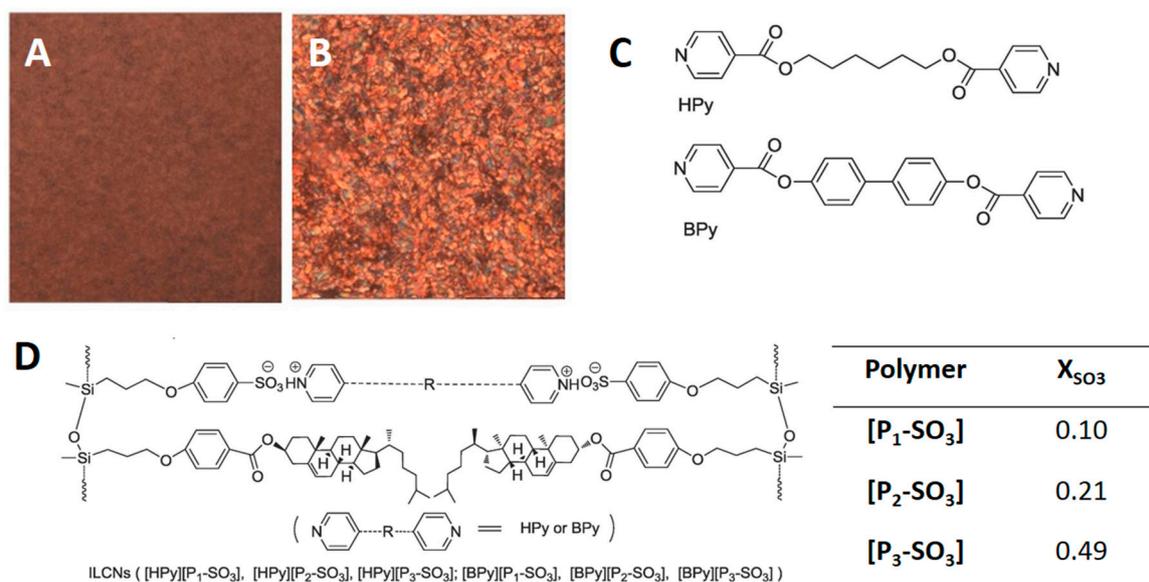


Figure 3. Optical microscope images of the liquid-crystalline polyelectrolyte salt $[BPy][P_1SO_3]$ in its cubic phase at 80 °C (A) and smectic phase at 120 °C. (B). The structures of hexane-1,6-diyl diisonicotinate (HPy) and (1,1'-bipenyl)-4,4'-diisonicotinate (BPy) (C) and the final polyelectrolyte salts (D) are also shown [50]. Note: X_{SO_3} is the molar fraction of each of the polymers. Adapted with permission from [50]. Copyright Elsevier (2018).

Polysiloxane-based ionomers. A key to categorizing the properties of ionic polymers is a determination of their propensity to form ion clusters (i.e., analysis of the regions rich and poor in ion pairs). Of the different types of ionic polymers, ionomers contain the fewest ion pairs and, for that reason, their bulk properties are the closest to those of unsubstituted polysiloxane homopolymers.

Microstructural properties of ionomers [48,52–56]. Because of their applications in single-ion conductivity, especially in materials containing lithium, understanding their microstructural properties has been a focus of ionomers research. Examples with polysiloxanes included here involve investigations of the microstructural consequences of changing the ion content of monomers with lithium perfluoroether sulfonate [48] and the nature of pendant groups [52–56]. One such example from the Colby group describes ionomers with halide counterions [52]. These ionomers cannot form covalent crosslinks. As a result, these ionomers remain liquids at room temperature [52]. Because polysiloxanes exhibit low glass transition temperatures, high hydrophobicity, and good thermal (Figure 4A) and chemical stability, Chen and coworkers targeted the ionomers for potential use as a media for ion transport [52]. The X-ray scattering data in Figure 4C show three unique peaks for this ionomer that can be attributed to the structural features in Figure 4B: the polysiloxane backbone (peak II), the oligo-ethylene oxide connecting groups that act as a plasticizer (peaks I and II), and the small quantity of phosphonium halide pendant groups that cluster (peak III). An interesting FT-IR method for following the progress of polysiloxane syntheses from non-ionic monomers has been reported recently [57,58]. It should be adaptable easily to follow the syntheses of ionic polymers reported here.

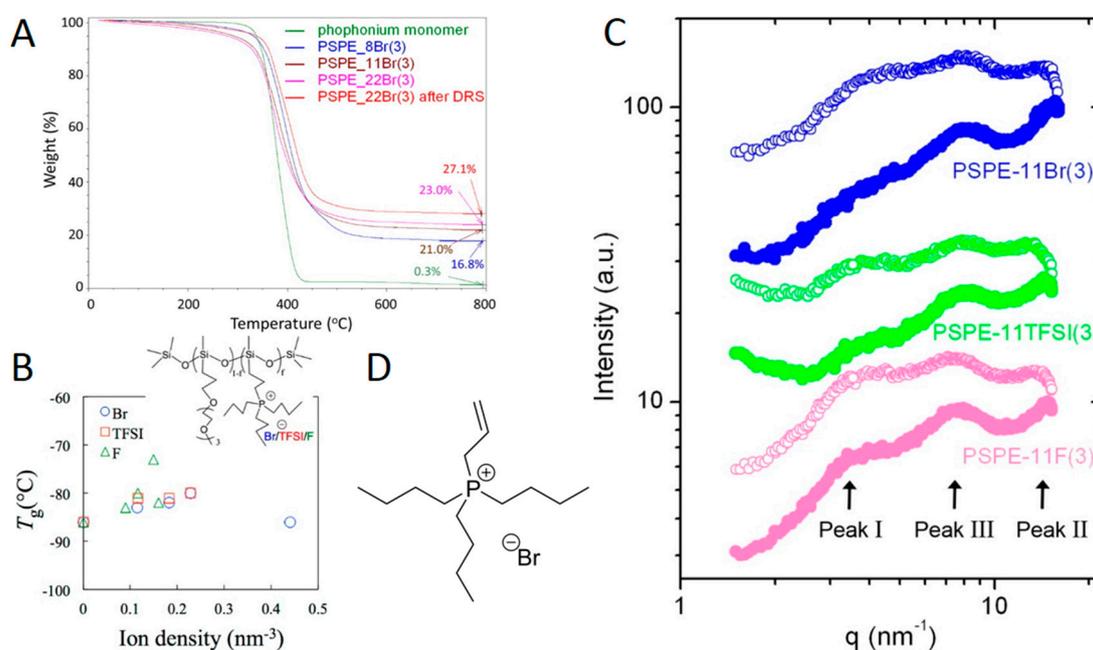


Figure 4. Polysiloxane-based ionomers with phosphonium halide pendant groups [52,53]. (A) Thermogravimetric (TGA) results for neat polysiloxane-based ionomers with phosphonium halide pendant groups. (B) Correlation between the glass transition temperature and ion density of the ionomers with various halide ions. (C) X-ray scattering spectra of polysiloxane-based ionomers with phosphonium bromide, bis(trifluoromethane)sulfonimide (TFSI), and fluoride pendant groups at varying temperatures; the filled and open circles are for data obtained at 25 and 125 °C, respectively. (D) Structure of the allyltributylphosphonium bromide monomer used for the TGA data in A. Reprinted with permission from [52,53]. Copyright (2013, 2014) (American Chemical Society).

3. Melt Rheology of Polysiloxane-Based Ionic Polymers

3.1. Melt Rheology

The effects of ion association and reptation in polysiloxane-based polymers will be discussed in this section [59–64]. Unlike neutral copolymers [62,64], the affinity of ionic polymers to associate has a significant influence on their chain dynamics and the resulting mechanical properties [59–61,63]. The ability of an ionic polymer to undergo chain relaxation is determined principally by (1) the ability of the pendant ions to dissociate from one position and re-associate with another and (2) the ability of

the entangled ionomer chains to undergo reptation. The first can be described as “ion-hopping” [59,65]: ions bound to a charged pendant group on an ionomer changes partners either by intra- or inter-chain processes. Association of ions in an ionomer is an equilibrium process and the rate of exchange depends on the nature of the solvation of the ions by the charged polymer pendant group. The importance of the second factor is related to the ease of relaxation of a polymer chain that depends on the microstructure of the polymer (including the flexibility of its backbone, the number of ionic or ionizable pendant groups, and the solvation ability of the ions [59,60,65]).

3.2. Melt Rheology of Polysiloxane-Based Ionic Ionomers

The melt rheology of polysiloxane-based ionic polymers has been investigated in numerous studies that involve phosphonium halide ionomers [52–54], zinc propanoate ionomers and polyelectrolytes [66], as well as ammonium carbamate and ammonium dithiocarbamate polyelectrolyte complexes [67]; the authors of [67,68] report rotationally sheared rheology of uncharged PDMS. A key study by Chen and coworkers [52] provides a good example of the effects of ion pairs on polysiloxane copolymers. Figure 5 is a time-temperature superposition master curve with a reference temperature of $-75\text{ }^{\circ}\text{C}$. The curves were correlated using the William–Landau–Ferry equations [69,70] and crossover points such as the onset of the glass transition from the glassy region to a transition region. The phosphonium bromide pendant group content ranged from 0 to 22% (by mole). Only samples with 5 and 11% were analyzed by gel permeation chromatography (GPC). They indicate an average molecular weight of 2500 to 5400 Da. This is a relatively small ionomer and, thus, it not surprising that the rubbery plateau could be missing in the 0% master curve. To obtain a plateau according to the sticky Rouse model, both strong ion association and significant polymer entanglement would be needed. The current system is far below the critical molecular weight for entanglements for systems such as PDMS and further rationalizes the absence of a rubbery plateau. As the ion association increases, the master curve changes in two ways. The first change occurs in the intermediate ion content range of 5–11%, where we observe an elongation of the transition region (i.e., where the storage and loss moduli are proportional to the angular frequency, suggesting the ionomer exhibits ion association preventing relaxation to the terminal region). The second change involves the decreased angular frequency for the onset of the glass transition. This occurs in the 5–26% region, suggesting that the glass transition is related to the ion content. The curves for 22–26% exhibit an extreme broadening of the glass transition temperature region that has been ascribed to slow β -relaxations (segmental motions in the glassy state [69–72]) and α_2 -transitions (polymer chain relaxations [73]).

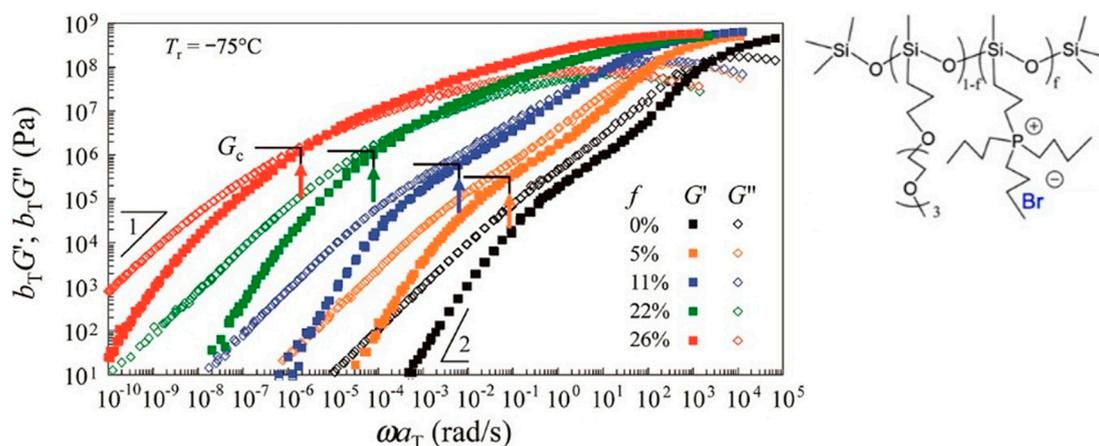


Figure 5. Time-temperature superposition master-curve of polysiloxane-based ionomers containing different contents of phosphonium bromide pendant groups [52] (from right to left: $f = 0\%$, 5% , 11% , 22% , and 26%). The reference temperature was set at $-75\text{ }^{\circ}\text{C}$. Reprinted with permission from [52]. Copyright (2013) (American Chemical Society).

4. Applications of Polysiloxane-Based Ionic Polymers

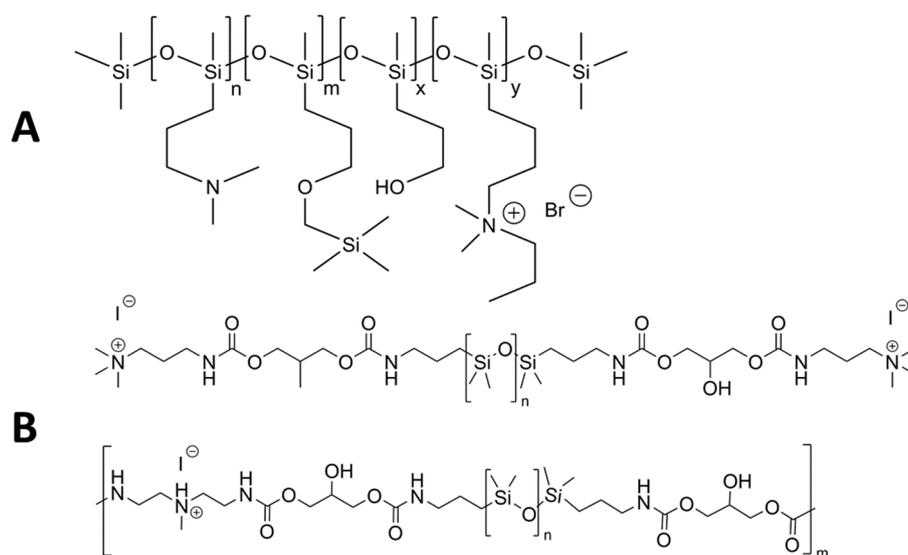
Polysiloxane-based polymers have been used in applications that range from food production to cosmetics to surfactants. Previous research has shown that many of the applications found for PDMS and similar polysiloxanes use the polymers in their charge-neutral forms (i.e., in which van der Waals interactions but no ionic interactions are present). Only since the late 1980s has research been conducted to explore possible applications of polysiloxane polymers with charged and ionizable pendant groups. Those efforts have resulted in significant applications that exploit the electrostatic forces and ionic crosslinking of an ionomer and its polyelectrolyte complexes.

Biocidal, and antimicrobial, properties [74–76]: Due to the hydrophobic nature of the polysiloxane backbone and its cationic-anionic domains, ionomers and polyelectrolytes have been shown to exhibit antimicrobial properties, working in a similar fashion to soap with hydrophobic and hydrophilic regions. Cationic disinfectants, which are quaternary ammonium salts (QAs), have been shown to be very effective in combating microbial growth [77,78]. These QAs are thought to interact with and damage the cell walls of a variety of microorganisms so that they may not replicate, ultimately killing the organism. Hazziza-Laskar and coworkers [74] showed that ionomers even with low QA compositions exhibit strong biocidal properties. Using polyurethane films based on copolymers with 3.9% and 12.4% QA groups with octyl alkyl substituents (corresponding to 0.4 mmol/g and 1.0 mmol/g, respectively), they found that the concentration of *Escherichia coli* decreased substantially even after only an hour of contact [74]. They also found that, after immersing the polyurethane film in water for 30 days, the biocidal activity remained relatively unchanged, and there was no evidence for the presence of toxic molecules; the anti-bacterial properties are an intrinsic property of the polymer surface. Similar findings were reported by Sauvet and coworkers [76] and Novi and coworkers [75], although using different siloxane-based ionomers that utilize QA pendants (Scheme 2). Sauvet and coworkers [76] used higher concentrations of QAs, ranging from 1.73 to 2.58 mmol/g, and conducted their bactericidal tests in solutions of both *E. coli* and *Staphylococcus aureus* instead of polyurethane films. They found that the minimum inhibitory concentration (MIC), associated with the largest dilution of soluble polymer, glucose broth, and incubated bacteria that appeared not cloudy, was similar in the five polymers that were employed. They noted that although the molar fractions of QAs in each ionomer were different, the moles of QAs per gram of polymer were small initially, and cited this as a potential explanation for the similarities. Regardless, their results show that all of the polymers examined exhibited antibacterial activity. MIC values, based on QA molar concentrations, were in range found usually for other antiseptics [79].

Novi and coworkers [75] employed a different method for the construction of their ionomers. They attached ammonium groups to the ends as well as along the PDMS chains. This provided hydrophobic environments in both the middle and cationic ends. Even with this change in molecular construction, they found in the patch tests performed on *Bacillus subtilis* and *E. coli* that the antibacterial effects were stronger on Gram-positive bacteria (*B. subtilis*) than on Gram-negative bacteria (*E. coli*) for end-chain ammonium groups, and vice versa for main-chain ammonium groups. However, both effects were comparable to those found for other antibacterial compounds and products. As shown by the studies [74–76], the addition of QA groups to PDMS backbones can yield ionomers with appreciable antibacterial activity.

Anti-fungal properties. A series of PDMS-based ABA triblock ionomers (Figure 6B) has been tested for antifungal activity [80]. The syntheses of the ionomers involved a ring opening polymerization of cyclic siloxanes into one of the block polymers and an amidation reaction to connect the blocks. Polydispersity indexes (PDI) ranging from 1.6 to 1.8 and molecular weights ranging from 4.0 to 8.0 KDa of the different triblock polymers were determined by GPC measurements before the attachment of the benzylammonium chloride group. Figure 6C shows results from experiments with one of the polymers (J2; Mw (copolymer backbone) = 4.0 KDa, PDI (copolymer backbone) = 1.79, 4 m = 20.8%) to determine the minimum inhibitory concentration (MIC, $\mu\text{g/mL}$) and the minimum fungal growth (MFC, $\mu\text{g/mL}$) of the fungal species, *Candida Albicans*. Good anti-fungal activity (an average MIC of

500 $\mu\text{g/mL}$) was found when the ratio of MFC/MIC was <4 . When larger triblock ionomers were used, the MFC decreased, suggesting that the ionomers are less effective. This result is not surprising because larger hydrophobic backbones make penetration into fungal cell walls more difficult. The siloxane backbone, being more hydrophobic than skin, inhibits the ionomer from being adsorbed through the skin while allowing the medicinally active pendant groups (i.e., the charged benzylammonium chloride) to interact at the dermal surface (Figure 6A). This selectivity was demonstrated by tests to determine the degree of skin penetration by the ionomers using a simplified Franz diffusion cell onto which a small piece of rat skin had been affixed [80]. A higher molecular weight ionomer, J7 (Mw (copolymer backbone) = 7.9 KDa, PDI (copolymer backbone) = 1.64, 4 m = 32.4%), was added to a saline solution and the donor cell. Rat skin permeation of the ionomer was measured using UV-vis absorbance from the benzylammonium cation of aliquots of the receptor cell. As indicated by a lack of change in the absorbance over a period of 8 h, the ionomer did not penetrate the epidermal layer.



Scheme 2. Ionomers studied by (A) Hazziza-Laskar and coworkers [74] and (B) Novi and coworkers [75]. Copyright (1995) Wiley. Used with permission from [74,75]. Copyright (2006) Wiley.

Single Ion Conductors. Other uses for polysiloxane-based ionic polymers explored more recently are in energy storage and energy conversion. As mentioned earlier, polysiloxanes and their respective ionomers and polyelectrolytes have low glass transition temperatures that allow many of the materials to conduct ions well and are considered highly flexible [15,16,81]. For this reason, polysiloxanes resist crystallization, a process which is known to hinder ionic conductivity.

Thus, materials with ionic side chain groups have been designed to increase the conductivity. In that regard, Liang and coworkers [55] added anionic borates to the PDMS backbone as a means to further lower the glass transition temperatures and, in so doing, increase conductivity. They used three types of borate side chains: lithium triphenylsilyl borate, lithium triphenylstyryl borate with three ethylene oxides, and one with perfluorinated phenyl rings. Because T_g typically increases as ionic concentration increases, there is a tradeoff between the deleterious effect on conductivity of increasing the glass transition temperature and the beneficial effect on ionic conductivity of increasing the ion content. Whereas the borate **A** (Scheme 3) showed maximum conductivity at 8% by mole ion content, the ethylene oxide separated borates lowered the T_g value and increased the conductivity, and the perfluorinated borate also substantially increased the conductivity [53]. Thus, the borate anions lower the ion association energy and are fairly good Li^+ conductors. This complements the low T_g values that are intrinsic to the flexible siloxane backbone. For these reasons, PDMS-based ionomers may become useful in lithium ion batteries if the ionomer designs can be improved for that purpose. Choi and coworkers [69] similarly found that adding weakly binding borates to a polyethylene glycol

(PEG) increased overall lithium ion conduction by increasing polymer flexibility and reducing T_g . The authors used dielectric relaxation spectroscopy to show that adding more PEG resulted in an increase in both dielectric constant and ionic conductivity. Furthermore, they showed that the PEG lowered the activation energy for ion transport from 14 to 8 kJ/mol [82]. They suggest that the small amount of added PEG solvates the ions and allows them to rearrange with less ionic aggregation [82].

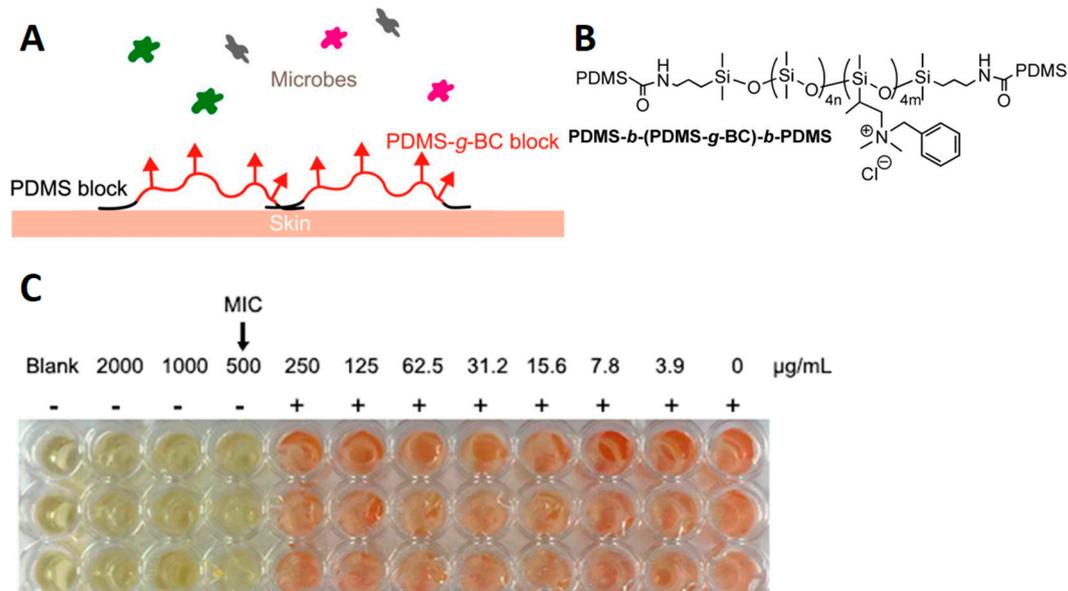
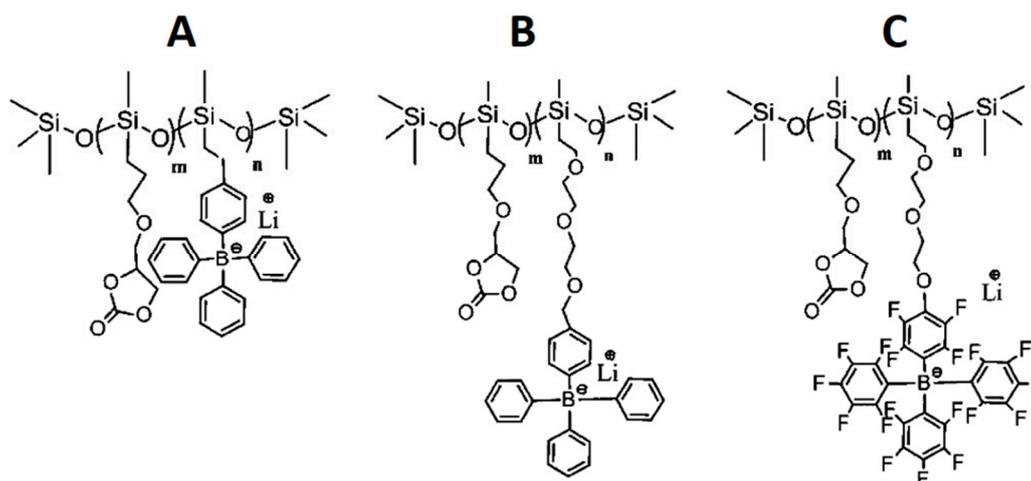


Figure 6. Polysiloxane-based triblock ionomer system [80] with a benzylammonium chloride pendant group used for antimicrobial and antifungal studies: (A) diagram describing the role of polysiloxane in preventing the microbial from entering the hydrophilic layer in human skin; (B) polysiloxane-based triblock ionomer used in this study; (C) images of Sabouraud dextrose petri plates containing fixed amounts of *Candida Albicans* while varying the amount of the polysiloxane-based triblock ionomer (4.0 kDa, $m = 20.8$). Adapted with permission from [80]. Copyright Elsevier (2018).



Scheme 3. Boron-containing ionomers studied for lithium-ion conduction with varying pendant groups [55,80]: lithium tetraphenyl borate pendant groups with (A) an ethylene linker and (B) with a triethyleneglycol linker; (C) a perfluorinated lithium tetraphenyl borate pendant group with a triethyleneglycol linker. Reprinted with permission from [55,82]: Copyright (2012, 2014) (American Chemical Society).

Both of these studies indicate that ionomers and polyelectrolytes based on polysiloxanes may have widespread use for facile ionic conduction, especially for conduction of lithium ions.

5. Summary

At the beginning of this review, a question was posed: How does changing the structure of the monomers in the ionic polymers affect the bulk properties of the resulting materials? The results cited show that increasing the ion content increases the ability of an ion pair to influence the bulk properties. The results from Kaneko and coworkers [36–39,41] show that the disorder in neat PAPS-C8 decreases as the length of the chains of the carboxylate counterions decreases, allowing the polymers to pack in a hexagonal phase. When an oligoethylene oxide is the connecting group, greater disorder is found in the system and a poly(ionic) liquid results. Even at low concentrations of ion pairs, they can play a decisive role in whether a polysiloxane-based material is more liquid, solid or even liquid crystal like [50].

We conjecture that future uses of polysiloxane-based ionic polymers will be very important in fields that exploit the intrinsic tunability—backbone flexibility, hydrophobicity, and charge content and type—of the polymers. Because the polymeric chains of these materials experience strong, localized non-covalent interactions, it may be possible to construct shape memory and self-healing materials from them. The potential for using semi-crystalline or liquid crystalline polysiloxane-based ionic polymers as adhesive films seems quite high as well. Obviously, this list is incomplete. We hope that readers will add to it.

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