Cation Complexation and Conductivity in Crown Ether Bearing Polyphosphazenes

Harry R. Allcock,* David L. Olmeijer, and Stephen J. M. O'Connor

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received November 12, 1997

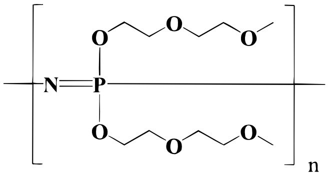
ABSTRACT: An attempt has been made to understand the mechanism of ionic conductivity in polyphosphazene−salt complexes by the synthesis and study of systems with crown ether side groups and salts with different cations. Amorphous phosphazene polymers, bearing either (12-crown-4)-methoxy, (15-crown-5)-methoxy, or (18-crown-6)-methoxy pendent groups, either as single-substituent polymers or mixed-substituent species in a 1:3 ratio with 2-(2-methoxyethoxy)ethoxy groups, were synthesized and characterized. The polymers in which all the side groups are crown ether units have glass transition temperatures higher than other oligo(ethyleneoxy) polyphosphazenes. They generate relatively low ionic conductivities at ambient temperatures when complexed with lithium triflate or lithium perchlorate. This suggests that the cation carries a significant part of the current in ether-type polymers. The ambient temperature ionic conductivity of the cosubstituent polyphosphazenes, as well as of poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) (**3**), when complexed with $MClO_4$ (M = Li, Na, K, Rb, Cs), was measured. The ionic conductivity is reduced when a favorable 1:1 or 2:1 crown ether−cation complex is formed. The thermal behavior of these polymer−salt complexes was also investigated. The polymers exhibit an increased glass transition temperature when a favorable 2:1 crown ether−cation complex is formed. The relationships between the ionic conductivity and the glass transition temperature of the host polymer electrolytes and the stability of the crown ether−cation complexes formed are discussed.

Introduction

The study of solid polymer electrolytes has its origins in the early 1970s when Wright reported the formation of complexes between poly(ethylene oxide) (PEO) and potassium thiocyanate.[1−3] In 1978, Armand suggested the use of polymer electrolytes as solid solvents for lightweight, rechargeable lithium batteries.[4,5] Since then, the study of polymer electrolytes has grown to include the synthesis of new polymers, the investigation of the mechanisms of conductivity,[6,7] and the engineering of potentially useful energy storage devices.

Poly(ethylene oxide) has been studied extensively as an ionically conducting medium during the last 20 years. The oxygen atoms in the backbone of PEO can coordinate to metal cations and thus facilitate ion-pair separation of dissolved salts. However, the ambient temperature application of PEO as a solid electrolyte is limited by the presence of microcrystalline domains. Microcrystallites impede ion mobility by both blocking the paths of ions and reducing overall polymer flexibility. PEO has a melting transition at 65 °C and does not become completely amorphous until heated above 100 °C. This has prompted many researchers to attempt to modify PEO with the aim of eliminating crystallinity.[8−19]

A significant development in the field of solid polymer electrolytes was the synthesis and study in 1984 of poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) (**3**) by Blonsky, Shriver, Austin, and Allcock.[20,21] For a polymer to be a useful solid polymer electrolyte, it must (a) possess anion or cation coordinating sites, (b) be completely amorphous, and (c) have a flexible backbone and therefore a low glass transition temperature. MEEP fulfills all these requirements. It contains six oxygen atoms per repeat unit, at least four of which play a role in cation complexation and salt dissolution. MEEP is amorphous at all temperatures and, due to the high flexibility of the polyphosphazene backbone and the side groups, displays a very low glass transition temperature (−84 °C). When complexed with $LiSO_3CF_3$ or $AgSO_3CF_3$ salts, MEEP has ambient temperature ionic conductivities 2−3 orders of magnitude higher than PEO.


MEEP (3)

Recently, new polyphosphazenes for use as solid polymer electrolytes have been reported from our laboratory, including examples that use non-ion-coordinating cosubstituents to increase the free volume of the polymer, species with side groups that increase the number of oxygen atoms per repeat unit, and others that utilize branched rather than linear oligo(oxyethylene) side groups.[22−25]

Some reports have appeared about the effect on ionic conductivity of polymers complexed with the salts of various alkali metals (Li, Na, K, Rb, and Cs).[26,27] Smaller cations such as Li^+ may have the ability to migrate faster through an electrolyte medium due to the small size of the ions and the high rate of diffusion. However, larger cations such as Rb^+ and Cs^+ are softer acids than their smaller counterparts. These larger cations will have less of an affinity for the oxygen atoms in an etheric polymer electrolyte, such as PEO or MEEP, and may be transported through the polymer faster. These two competing effects determine whether larger or smaller alkali metal cations migrate faster. However, it has generally been reported that the larger cation will generate a higher ionic conductivity when its salts are

S0024-9297(97)01666-5 CCC: $15.00

Table 1. Ionic Diameters and Crown Ether Cavity Sizes[32]

cation	ionic diameter (Å)	crown ether	cavity size (Å)
Li^+	1.36	12-crown-4	1.2−1.5
Na^+	1.94	15-crown-5	1.7−2.2
K^+	2.66	18-crown-6	2.6−3.2
Rb^+	2.94		
Cs^+	3.34		

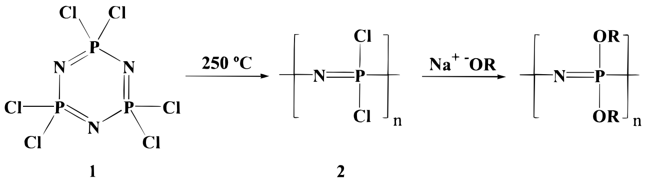
complexed within an oligoether-based polymer electrolyte.

Crown ethers were discovered by Pedersen in 1967 and are known to form relatively strong complexes with alkali metal cations.[28,29] As a general rule, a crown ether will form its most stable complex with a cation whose diameter is closest in size to the cavity in the center of the macrocycle.[30,31] Table 1 lists the ionic diameters of the first five alkali metal cations as well as the approximate cavity diameters of some common crown ether macrocycles.[32] Thus, the 12-crown-4 macrocycle forms its most stable 1:1 complex with a lithium cation, which rests just above the plane of the ring when coordinated to the four oxygen atoms. Similarly, 15-crown-5 forms its most stable complex with sodium ions, and 18-crown-6 is known to yield very stable 1:1 complexes with both potassium and sodium, with potassium being the more favored cation. Furthermore, 2:1 “sandwich” structures are possible when the cation is slightly larger than the diameter of the cavity of the crown ether.[33,34] Sodium forms the most stable 2:1 complex with 12-crown-4. Potassium forms the most stable 2:1 complex with 15-crown-5. For 18-crown-6, it is the cesium 2:1 complex that is most stable. Rubidium is a borderline case, capable of sometimes forming 1:1 and sometimes 2:1 complexes with 18-crown-6 ethers.

The incorporation of covalently bound crown ethers into a polymer electrolyte host material could have conflicting effects on the conductivity by cations. Stable complex formation between cations and crown ethers will facilitate solvation and ion-pair separation of dissolved salts. This would increase the number of charge carriers. Indeed, researchers have shown that the incorporation of free small-molecule crown ethers into polymer electrolytes enhances ionic conductivity.[35,36] However, when bound to a macromolecule, a crown ether that forms stable 1:1 complexes with the cations may inhibit the migration of those ions through the material. Furthermore, the existence of 2:1 “sandwich” complexes in a polymer electrolyte with covalently linked crown ethers, in addition to inhibiting cation migration, will increase the possibility of ionic cross-linking throughout the material. Thus, it is unclear whether the presence of a polymer-bound crown ether will increase or decrease ionic conductivity.

Some crown ether bearing polymers have been investigated for solid electrolyte applications. Ohno and coworkers reported the synthesis of organic backbone polymers bearing diaza-15-crown-5, diaza-18-crown-6, and diaza-21-crown-7 units and studied the ionic conductivities of these polymers when complexed with a series of alkali metal perchlorate salts.[37,38] They concluded that ionic conductivity was lowest when a particular cation formed the most stable complex with the crown ether present. For example, the ionic conductivity of a poly(diaza-18-crown-6 ether) system was lower when complexed with potassium perchlorate than with analogous sodium or rubidium salts. Therefore, it was suggested that the cation is the primary charge carrier.

Scheme 1. General Synthesis of Alkoxy-Substituted Polyphosphazenes



Parker and co-workers reported the synthesis of polyacrylates and polymethacrylates bearing 12- and 14-crown-4 ethers and the measurement of the ionic conductivity of these polymers when complexed with lithium perchlorate and triflate salts.[39−41] Of these two macrocylces, 14-crown-4 forms the more stable 1:1 complex with lithium. The polymers bearing 12-crown-4 units showed the higher ionic conductivities.

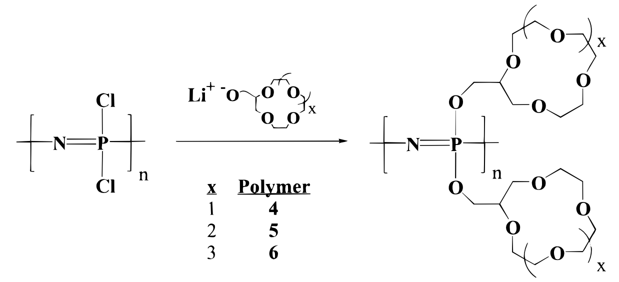
Polyphosphazenes bearing pendent crown ether groups have also been synthesized previously and their ionic conductivities studied.[41−44] Cowie and co-workers synthesized polyphosphazenes with pendent 16-crown-5 and 12-crown-4 ethers, all spaced from the main polymer backbone by 0, 3, or 6 methylene units, but they did not succeed in producing polymers in which all the side groups bore crown ethers. These investigators generally obtained a 50−80% loading of the crown ether moieties onto the phosphazene backbone by displacement of trifluoroethoxy groups with the sodium salts of various crown ether alcohols. Thus, a significant number of residual trifluoroethoxy groups remained on the polymer. Trifluoroethoxy groups are ineffective as coordinating ligands for cations.[21] When these polymers were complexed with alkali metal salts it was found that the ionic conductivity at elevated temperatures was highest for the cation that formed the most stable 1:1 complex with the crown ether present (Li^+ in 12-crown-4 and Na^+ in 16-crown-5 polymer). It was suggested that this was the result of the polymer’s increased capacity for inducing ion-pair separation, and this would imply that the *anion* is the main charge-carrying species in this system.

Because conflicting interpretations of the mechanism of ionic conductivity in polymers seem to exist, an aim of this project was to synthesize and characterize a series of polyphosphazenes with 12-crown-4, 15-crown-5, and 18-crown-6 moieties in the side groups and utilizing 2-(2-methoxyethoxy)ethoxy cosubstituents. The ionic conductivities of these polymers, when complexed with $MClO_4$ (M = Li, Na, K, Rb, Cs), were measured to determine if conductivity increases or decreases with optimum crown ether−cation complex formation. Another goal of this project was to develop an experimental technique to obtain polymers in which all or most of the side groups bore crown ether units.

Results and Discussion

Single-Substituent Polymer Synthesis. Alkoxy-substituted polyphosphazenes are normally synthesized by macromoleuclar substitution reactions carried out between sodium alkoxides and poly(dichlorophosphazene), as shown in Scheme 1.[45] However, because sodium readily forms 1:1 or 2:1 complexes with 12-crown-4, 15-crown-5, and 18-crown-6 groups, complications existed to synthesis by this route. The reaction of sodium hydride with hydroxymethyl-(12-crown-4), followed by the addition of poly(dichlorophosphazene), resulted in gelation of the reaction mixture and pre-

Scheme 2. Synthesis of Crown Ether Single-Substituent Polymers



x	Polymer
1	4
2	5
3	6

Table 2. Loading of Crown Ether Groups for Synthesis of Single-Substituent Polymers 4−6

polymer	crown ether	nucleophile	C−N ratio found	C−N ratio expected	% substitution
4	12-crown-4	Na alkoxide	12.36	15.41	80.1
4	12-crown-4	Li alkoxide	14.24	15.41	92.3
5	15-crown-5	Li alkoxide	17.82	18.86	94.4
6	18-crown-6	Li alkoxide	21.44	22.27	96.1

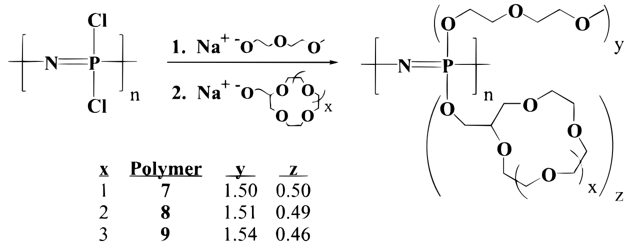
cipitation of the polymer. It is presumed that this was the result of 2:1 "sandwich" structures between the sodium ion and the 12-crown-4 unit in the tetrahydrofuran reaction mixture, which served to cross-link the polymer ionically, thus lowering solubility and preventing complete substitution.

The synthesis of polymers in which all the side groups are crown ether units was therefore performed by utilizing the *lithium* salt of the various hydroxymethyl crown ethers, as shown in Scheme 2. Synthesis of the 15-crown-5 (**5**) and 18-crown-6 (**6**) single-substituent polymers was performed in this manner. However, synthesis of the 12-crown-4 homopolymer (**4**) by this route was still difficult. Because the lithium ion rests above the cavity of the 12-crown-4 macrocycle, 2:1 complexes between this cation and the crown ether are possible. Thus, coordinative cross-links and the insolubility of the polymer in the reaction mixture proved to be a problem. The best results were obtained by a slow addition of a solution of poly(dichlorophosphazene) to a very dilute reaction mixture containing the lithium salt of the hydroxymethyl-(12-crown-4) side group.

Table 2 lists the extent to which each crown ether unit was able to replace the chlorine atoms along the polyphosphazene backbone. These values were calculated by comparing the percent carbon to percent nitrogen ratios, as determined by elemental analysis, with the theoretical values. The density of the crown ether side groups along the polymer backbone increased with increasing crown ether size. Presumably, as the crown ether becomes larger, its affinity for the lithium cation used in the substitution reaction decreases, causing fewer reaction complications. Although none of these polymers underwent 100% chlorine replacement by crown ether units, they represent a significant improvement over the 50−80% loading reported previously.[42−44] A distinct difference exists in the loading of (12-crown-4)-methoxy side groups when lithium is used as opposed to sodium.

The molecular weights of these polymers could not be estimated accurately by gel permeation chromatography. When samples of these polymers were passed through GPC columns eluted with 0.1 wt % tetra-*n*-butylammonium nitrate in THF, they were not detected by the refractive index detector. Apparently, the crown ether bearing polymers precipitated on the chromatography gel.

Scheme 3. Synthesis of Crown Ether−MEEP Cosubstituent Polymers



x	Polymer	y	z
1	7	1.50	0.50
2	8	1.51	0.49
3	9	1.54	0.46

Cosubstituent Polymer Synthesis. Mixed-substituent polymer synthesis involved fewer problems than did the formation of single-substituent polymers. Polyphosphazenes **7−9**, substituted with 75% 2-(2-methoxyethoxy)ethoxy groups and 25% crown ether groups, were obtained easily by the sequential reaction of the sodium salts of the two nucleophiles with poly(dichlorophosphazene). As shown in Scheme 3, the 2-(2-methoxyethoxy)ethoxy groups were introduced first, and the partially substituted polyphosphazene was then added to a reaction mixture that contained an excess of the sodium salt of a hydroxymethyl crown ether. No gelation or insolubility of the polymer was apparent.

The actual stoichiometric ratios of the two substituents on polymers **7−9**, as shown in Scheme 3, were calculated on the basis of the amount of 2-(2-methoxyethoxy)ethanol used in the initial substitution reaction. Polymer **9** was the only one that differed slightly from the intended 3:1 ratio. These discrepancies were taken into account when reaction yields and cation−repeat unit ratios were calculated for the polymer complexed with alkali metal salts.

Ionic Conductivity. The ambient temperature ionic conductivity of MEEP (**3**), both pure and complexed with lithium perchlorate, was measured with repeat unit−cation ratios that ranged from 16:1 to 2:1. As shown in Figure 1, the highest ambient temperature ionic conductivity, which occurred at an 8:1 repeat unit−cation ratio, was 5.1×10^{-5} S cm^{-1}. This is slightly higher than previously reported values for MEEP−lithium triflate complexes.

Similar ionic conductivity experiments, also shown in Figure 1, were carried out for the cosubstituent polyphosphazenes **7−9**, in which 25% of the side groups are crown ether substituents. The ambient temperature ionic conductivity was decreased by a factor of at least half an order of magnitude. If the coordination behavior of the crown ether is ignored, this effect might be attributed to a lower overall polymer molecular mobility since the glass transition temperatures of these cosubstituent polymers are approximately 20 °C higher than that of MEEP. The ionic conductivity data show that polymer **7**, which bears the 12-crown-4 groups, had the lowest conductivity of these three polymers when complexed to lithium perchlorate (approximately 6.6×10^{-6} S cm^{-1}). The 12-crown-4 macrocycle forms more stable complexes with lithium ions than do the larger crown ethers. Polymers **8** and **9** bear the 15-crown-5 and 18-crown-6 groups, respectively. When complexed with $LiClO_4$, they demonstrate maximum ambient temperature ionic conductivities slightly higher than 1.0×10^{-5} S cm^{-1}. Thus, it appears that the formation of stable crown ether−cation complexes inhibits ionic conductivity. This is despite the fact that 12-crown-4 units are

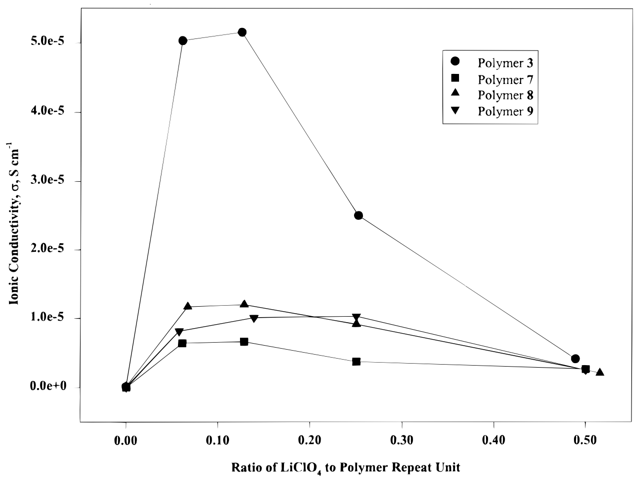


Figure 1. Ionic conductivity of polymers **3** and **7**−**9** complexed with $LiClO_4$ (25 °C).

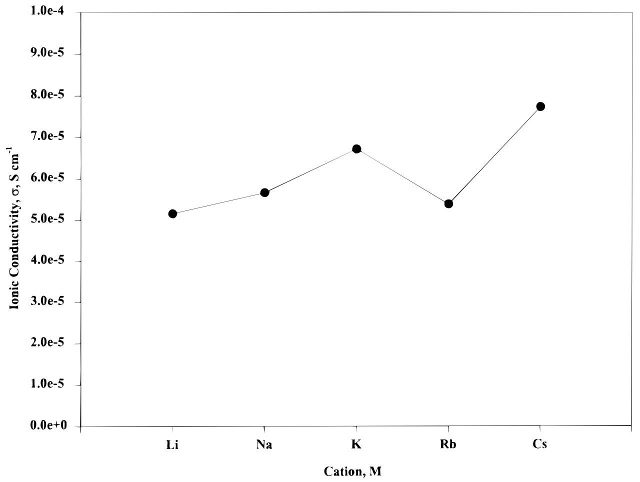


Figure 2. Ionic conductivity of polymer **3** complexed with alkali metal perchlorates in an 8:1 repeat unit to $MClO_4$ ratio (25 °C).

expected to increase the degree of ion-pair separation of lithium-based salts.

A repeat unit-to-cation ratio of 8:1 was chosen as a standard to compare the ionic conductivities of MEEP with the mixed-substituent polymers **7**−**9** when complexed with $MClO_4$ (M = Li, Na, K, Rb, Cs). For MEEP, the trend in conductivity with increasing cation size is demonstrated in Figure 2. The conductivity generally increases as the cation size increases from Li^+ to Cs^+. The decreased affinity of the larger cations for the etheric oxygen atoms presumably allows the cation more freedom to migrate through the polymer. The $RbClO_4$−MEEP complex does not fall into this pattern for reasons that are not understood.

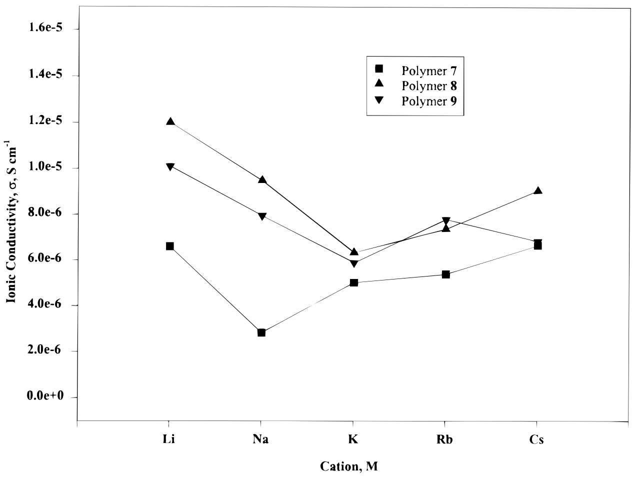


Figure 3. Ionic conductivity of polymers **7**−**9** complexed with alkali metal perchlorates in an 8:1 repeat unit to $MClO_4$ ratio (25 °C).

Figure 3 demonstrates the ionic conductivities of polymers **7**−**9** when complexed to $MClO_4$ (M = Li, Na, K, Rb, Cs). For polymer **7**, which contains the 12-crown-4 side group, the ambient temperature ionic conductivity decreased as the cation changed from Li^+ to Na^+, in contrast to the observation for MEEP. Sodium forms a stable 2:1 complex with 12-crown-4 ethers. It appears that 2:1 12-crown-4:Na^+ complexes both impede the migration of cations and serve as sites for more effective ionic cross-linking of the polymer. Both of these factors probably contribute to the decrease in the ionic conductivity of the host polymer. In fact, the sodium ion gave the lowest ionic conductivity of all the alkali metal cations in this polymer. When the polymer was complexed with the salts of the heavier cations, K^+, Rb^+, and Cs^+, the ambient temperature ionic conductivity rose once again.

The ionic conductivity of polymer **8**, which contains the 15-crown-5 group, follows a pattern similar to that of polymer **7** when complexed with the alkali metal perchlorate series. First, a decrease in conductivity occurred as the cation was changed from Li^+ to Na^+, once again in contrast to the behavior of MEEP. 15-Crown-5 forms its most stable 1:1 complexes with the sodium ion. Thus, the formation of these stable 1:1 complexes inhibits the transmission of cations through the polymer. As the cation is changed from Na^+ to K^+, the ionic conductivity decreases even further. In fact, potassium demonstrates the lowest ionic conductivity of any alkali metal cation in this polymer. Significantly, potassium readily forms 2:1 complexes with the 15-crown-5 ether. Thus, the increased ionic cross-linking via 2:1 complex formation appears to play an even greater role in lowering ionic conductivity than does 1:1 complex formation. Both rubidium and cesium salts generated higher conductivities.

18-Crown-6 forms stable 1:1 complexes with both sodium and potassium ions. Its most stable 2:1 complex is with cesium. Thus, it is not surprising that the ionic conductivity of polymer **9** decreased steadily as the cation was changed from Li^+ to Na^+ to K^+, which is the opposite trend to the one found for MEEP. The most stable 1:1 complex is with potassium, which demonstrated the lowest conductivity of all the alkali metal cations in this polymer. The 2:1 complex formation is possible with rubidium but is most likely with cesium. Although the conductivity of polymer **9** increases as the cation is changed from K^+ to Rb^+, it once again falls off when complexed to Cs^+.

Conductivity experiments were also performed on the three single-substituent polymers **4-6**, when complexed with lithium triflate and lithium perchlorate. None of these three polymers showed evidence of any ionic conductivity that could be measured at ambient temperatures by our apparatus. These conductivity values must be below 10^{-8} S cm^{-1}, which was the lower limit of detection for the surface area and thickness of samples used in our experimental protocol.

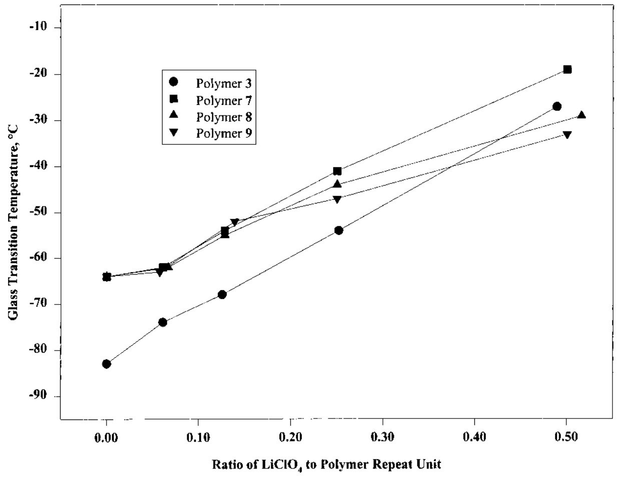


Figure 4. Glass transition temperature of polymers **3** and **7**−**9** complexed with $LiClO_4$.

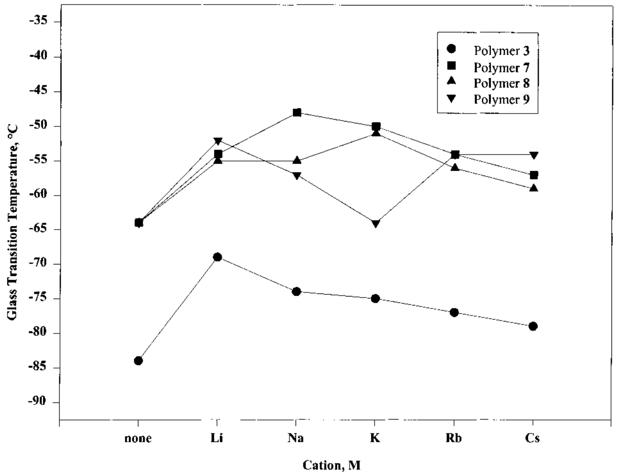


Figure 5. Glass transition temperature of polymers **3** and **7**−**9** complexed with alkali metal perchlorates in an 8:1 repeat unit to $MClO_4$ ratio.

Thermal Analysis. Single-substituent polymers **4-6** all possessed glass transition temperatures at −40 °C when measured by DSC analysis. No difference in T_g was evident for the various sizes of crown ether substituents. These values are significantly higher than for MEEP, which has a glass transition at −84 °C. The bulky nature of the crown ether side groups probably inhibits torsional motion about the phosphorus−nitrogen backbone, thereby raising the T_g.

The cosubstituent polymers **7**−**9** all have a glass transition temperature at approximately −64 °C by DSC. This is 20 °C higher than the T_g of the single-substituent polymer MEEP. Once again, the specific size of the crown ether side group does not affect the T_g. The complexes of MEEP and these polymers with $LiClO_4$ at various ratios of repeat units to cations alters the T_g as shown in Figure 4. The salt concentration directly affects the glass transition temperature. Higher concentrations of salt increase ionic cross-linking and increase the glass transition temperature.

The glass transition temperature of MEEP, when complexed to $MClO_4$ (M = Li, Na, K, Rb, Cs) at an 8:1 repeat unit-to-cation ratio, was measured. As demonstrated in Figure 5, the glass transition temperatures of these complexes decreased steadily as the cation was changed from Li^+ ($T_g = -71$ °C) to Cs^+ ($T_g = -79$ °C). This is a small change which indicates that the larger cations, due to their softer acid nature, have less of an affinity for the etheric oxygen coordination sites of MEEP than do the smaller ones. Thus, ionic cross-linking in this polymer is less influential for the larger cations, even at the same salt concentration, and this results in lower glass transition temperatures.

The glass transition temperatures of polymers **7**−**9**, when complexed to $MClO_4$ (M = Li, Na, K, Rb, Cs) at an 8:1 repeat unit-to-cation ratio, were also measured by DSC, and these results are included in Figure 5. The thermal behavior of these polymer−salt complexes does not necessarily follow the same pattern as it does for MEEP. Polymer **7**, which bears the 12-crown-4 cosubstituents, showed a higher glass transition temperature when complexed with sodium than when complexed with lithium. Presumably, increased ionic cross-linking occurs via the 2:1 complexes that form between 12-crown-4 and the Na^+ cations. The falloff in glass transition temperature for complexes of alkali metal salts with cations larger than Na^+ in polymer **7** indicates the lack of stable 2:1 complexes between the cation and the pendent crown ether.

Polymer **8** achieved its highest glass transition temperature when complexed with potassium. This polymer bears pendent 15-crown-5 groups. The 2:1 complex formation between the 15-crown-5 moieties and the potassium cations probably causes the increased ionic cross-linking, which is responsible for the elevated glass transition temperature. For cations heavier than potassium, the T_g begins to decrease with increasing cation size, in the same manner as with MEEP, and this indicates the lack of stable 2:1 complexes.

Polymer **9**, with 18-crown-6 side groups, follows a similar trend. As shown in Figure 5, the decrease in glass transition temperature for this polymer is easily detected as the cation increases in size from Li^+ to Na^+ to K^+. This phenomenon, a lower glass transition temperature with increasing cation size and acid softness, is also found in MEEP over the entire alkali metal sequence. However, for polymer **9**, the glass transition temperature increases in the presence of rubidium and cesium salts. 2:1 complexes between 18-crown-6 and rubidium are possible and are especially stable with cesium. Thus, it is probable that these cations contribute to enhanced ionic cross-linking in polymer **9** and a raised glass transition temperature.

Conclusions

The synthesis of single-substituent phosphazene polymers that bear crown ether containing side groups only is subject to serious complications. A loading of more than 92% of the crown ether moieties was accomplished when lithium alkoxide nucleophiles were used. Higher loadings were obtained with the larger crown ether substituents. These polymers showed no measurable ambient temperature ionic conductvitiy when complexed with lithium triflate or lithium perchlorate and it appears that the incorporation of crown ethers into the structure of these polymer electrolytes inhibits the transmission of cations.

Cosubstituent polyphosphazenes bearing both 2-(2-methoxyethoxy)ethoxy and crown ether side groups in a 3:1 ratio have higher glass transition temperatures than the single-substituent polyphosphazene MEEP. They also have lower ambient temperature ionic conductivities than MEEP when complexed to lithium perchlorate.

In MEEP, the larger cations in the series (Li, Na, K, Rb, Cs) generally give rise to higher ionic conductivities, presumably because of their increased acid softness and decreased affinity for oxygen atoms. However, in the cosubstituent polymers, the ionic conductivity was decreased when a particular cation was known to form stable 1:1 complexes with the pendent crown ethers. Complex formation of this type inhibits cation migration. An even greater effect was found when the crown ether−cation pair is capable of forming strong 2:1 complexes, for example, polymer **7** with $NaClO_4$ or polymer **8** with $KClO_4$. Both decreased the ambient temperature ionic conductivities and increased the glass transition temperatures. Complex formation of this type inhibits cation migration and increases the ionic cross-linking of the material.

It can be inferred from these experiments that, in polymer electrolytes such as MEEP, a large fraction of the current is carried by the cations rather than the anions. The incorporation of crown ethers into the structure of this polymer may increase the degree of ion-pair separation and thus increase the number of potential charge carriers. However, any benefits brought about by such an effect are overpowered by the negative influence of stable crown ether−cation complexation. Cations are prevented from migrating and the conductivity is decreased despite the increased number of free ionic species present. Thus, it seems likely that a significant portion of the current passage through polymer electrolytes such as MEEP is due to movement of the cations. An alternative explanation, that cation immobilization also restricts the mobility of the anion by electrostatic effects, cannot be ruled out. On the basis of the overall assessment of the results reported here, this explanation appears to be unlikely because ion-pair separation should be enhanced.

Experimental Section

Equipment. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained by using a Bruker WM360 spectrometer. Both ^{31}P and ^{13}C NMR spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield of the reference. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. All polymer samples were heated from −100 to +110 °C. Heating rates of 10, 20, and 40 °C/min were used and the glass transition temperatures determined by extrapolation to zero heating rate. Sample sizes were between 10 and 30 mg. Conductivity measurements were made using a Hewlett-Packard 4192A LF Impedance Analyzer with an ac frequency range of 5 Hz to 13 MHz. All conductivity measurements were carried out in an argon-filled drybox.

Materials. Hexachlorocyclotriphosphazene (**1**) (Ethyl Corp.) was purified by recrystallization from hot heptane followed by sublimation at 40 °C (0.05 Torr). Poly(dichlorophosphazene) (**2**) was prepared by the thermal ring-opening polymerization of **1** in the melt at 250 °C, as reported previously.[46] Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was distilled in an atmosphere of dry argon before use. The hydroxymethyl-functionalized crown ethers and 2-(2-methoxyethoxy)ethanol were obtained from Aldrich, distilled under vacuum from anhydrous calcium hydride onto activated molecular sieves, and stored under argon prior to use. Sodium hydride (approximately 60% emulsion in mineral oil) (Fluka) and lithium metal (Aldrich) were used as received. All alkali metal salts (Aldrich) were dried under vacuum and stored in an argon-filled drybox before use. Reactions that involved the use of chlorophosphazenes were carried out in an atmosphere of dry argon.

Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (3). Polymer **3** was prepared as reported previously.[47] 2-(2-methoxyethoxy)ethanol (15.55 g, 0.129 mol) was added to sodium metal (3.0 g, 0.124 mol) in dry tetrahydrofuran (800 mL). Once the sodium had reacted completely, the solution was treated with a solution of poly(dichlorophosphazene) (**2**) (5.0 g, 0.043 mol) in dry THF (400 mL) under an atmosphere of argon. The reaction mixture was stirred and refluxed for 24 h under argon and allowed to cool to room temperature. The reaction mixture was dialyzed against water (2 weeks) and then methanol (1 week). The polymer was recovered by rotary evaporation of the dialysis solvent. The recovered material was dried under vacuum at approximately 40 °C. The final product, polymer **3** was obtained as a white gum (7.3 g, 60%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.30−3.40 (s, 6H), 3.45−3.55 (t, 4H), 3.60−3.70 (m, 8H), 4.00−4.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm) 72.0, 70.4, 70.3, 65.0, 58.8; ^{31}P NMR ($CDCl_3$) δ (ppm) −7.7. Anal. Calcd: C, 42.4; H, 7.8; N, 5.0. Found: C, 41.6; H, 7.8; N, 4.8.

Poly[bis((12-crown-4)-2-methoxy)phosphazene] (4). Freshly distilled 2-(hydroxymethyl)-12-crown-4 (2.98 g, 0.0144 mol) dissolved in THF (25 mL) was added to lithium metal (0.095 g, 0.0137 mol). The reaction mixture was refluxed under dry argon for 3 days until the lithium had reacted completely. Additional THF (400 mL) was then added to the lithium salt reaction mixture. Poly(dichlorophosphazene) (**2**) (0.46 g, 0.0040 mol) in dry THF (300 mL) was added dropwise to the stirring reaction mixture. After the addition was complete, the mixture was heated and maintained at reflux with stirring for 4 days. The reaction mixture was then dialyzed against water (2 weeks) and methanol (1 week). The polymer was recovered by rotary evaportation and dried under vacuum at 40 °C. The final product, polymer **4**, was recovered as a brown material (1.23 g, 68%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.40−3.50 (broad), 3.55−3.70 (broad), 3.70−3.80 (broad), 3.80−4.10 (broad); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.4, 71.4, 70.8, 70.4, 70.3, 65.3; ^{31}P NMR ($CDCl_3$) δ (ppm), −8.0. Anal. Calcd: C, 47.5; H, 7.5; N, 3.1. Found: C, 45.6; H, 7.6; N, 3.2.

Poly[bis((15-crown-5)-2-methoxy)phosphazene] (5). Freshly distilled 2-(hydroxymethyl)-15-crown-5 (6.00 g, 0.0240 mol) dissolved in THF (25 mL) was added to lithium metal (0.15 g, 0.0216 mol) in THF (100 mL). The reaction mixture was refluxed under dry argon for 3 days until the lithium had reacted completely. Poly(dichlorophosphazene) (**2**) (0.54 g, 0.0047 mol) in dry THF (150 mL) was added dropwise to the stirring reaction mixture. After the addition was complete, the mixture was heated and maintained at reflux with stirring for 4 days. The reaction mixture was then dialyzed against water (2 weeks) and methanol (1 week). The polymer was recovered by rotary evaporation and dried under vacuum at 40 °C. The final product, polymer **5**, was recovered as a brown material (1.20 g, 47%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.50−3.80 (broad), 3.80−4.00 (broad); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.6, 71.5, 70.9, 70.7, 70.6, 70.4, 65.4; ^{31}P NMR ($CDCl_3$) δ (ppm) −8.2. Anal. Calcd: C, 48.6; H, 7.8; N, 2.6. Found: C, 47.6; H, 7.9; N, 2.7.

Poly[bis((18-crown-6)-2-methoxy)phosphazene] (6). Polymer **6** was prepared as described for polymer **5**. The reagents and quantities used were 2-(hydroxymethyl)-18-crown-6 (9.94 g, 0.0338 mol), lithium metal (0.21 g, 0.0303 mol), and poly(dichlorophosphazene) (**2**) (1.00 g, 0.0086 mol). Polymer **6** was purified by dialysis against water and methanol and recovered as a brown material (4.40 g, 81%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.50−3.75 (broad), 3.75−3.85 (broad), 3.85−4.00 (broad); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.4, 71.7, 70.8, 70.7, 70.5, 70.1, 65.3; ^{31}P NMR ($CDCl_3$) δ (ppm) −8.4. Anal. Calcd: C, 49.4; H, 8.0; N, 2.2. Found: C, 48.3; H, 8.0; N, 2.3.

Poly[((12-crown-4)-2-methoxy)-*co*-(2-(2-methoxyethoxy)-ethoxy)phosphazene] (7). Freshly distilled 2-(2-methoxyethoxy)ethanol) (3.92 g, 0.0326 mol) was added to sodium hydride (1.40 g of a 60% emulsion in mineral oil, 0.0350 mol) in THF (200 mL). After 1 day with heating and stirring under an atmosphere of dry argon, the sodium salt reaction mixture was added dropwise to a solution of poly(dichlorophosphazene) (**2**) (2.52 g, 0.0217 mol) in THF (700 mL). This mixture was heated with stirring for 1 day under an atmosphere of dry argon. In a separate reaction vessel, freshly distilled 2-(hydroxymethyl)-12-crown-4 (5.00 g, 0.0242 mol) dissolved in THF (50 mL) was added to sodium hydride (1.10 g of a 60% emulsion in mineral oil, 0.0275 mol) in THF (150 mL). To this mixture, after it was heated with stirring for 1 day under an atmosphere of dry argon, was added, dropwise, the reaction mixture of the polyphosphazene partially substituted with 2-(2-methoxyethoxy)ethanol. The final reaction mixture was heated at reflux for 24 h and was dialyzed against water (2 weeks) and methanol (1 week). Following rotary evaporation of the dialysis solvent, polymer **7** was recovered as a brown gum (6.36 g, 90%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.30−3.35 (s), 3.45−3.50 (t), 3.55−3.75 (m), 3.80−3.95 (m), 4.00−4.05 (m); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.4, 71.9, 71.5, 70.7, 70.4, 70.3, 65.0, 58.8; ^{31}P NMR ($CDCl_3$) δ (ppm), −7.9. Anal. Calcd: C, 44.2; H, 7.7; N, 4.3. Found: C, 43.0; H, 7.6; N, 4.1.

Poly[((15-crown-5)-2-methoxy)-*co*-(2-(2-methoxyethoxy)-ethoxy)phosphazene] (8). Polymer **8** was prepared as described for polymer **7**. The reagents and quantities used were 2-(2-methoxyethoxy)ethanol (3.90 g, 0.0325 mol), sodium hydride (1.40 g of a 60% emulsion in mineral oil, 0.0350 mol), poly(dichlorophosphazene) (**2**) (2.50 g, 0.0216 mol), 2-(hydroxymethyl)-15-crown-5 (4.57 g, 0.0183 mol), and sodium hydride (0.80 g, 0.0200 mol). Polymer **8** was purified by dialysis against water and methanol and recovered as a brown gum (5.63 g, 75%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.30−3.35 (s), 3.50−3.55 (t), 3.55−3.75 (m), 3.80−3.95 (m), 4.00−4.10 (m); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.6, 71.9, 71.6, 70.9, 70.8, 70.6, 70.4, 70.3, 65.0, 58.8; ^{31}P NMR ($CDCl_3$) δ (ppm) −7.8. Anal. Calcd: C, 44.8; H, 7.8; N, 4.0. Found: C, 43.7; H, 7.8; N, 4.0.

Poly[((18-crown-6)-2-methoxy)-*co*-(2-(2-methoxyethoxy)-ethoxy)phosphazene] (9). Polymer **9** was prepared as described for polymer **7**. The reagents and quantities used were 2-(2-methoxyethoxy)ethanol (4.25 g, 0.0354 mol), sodium hydride (1.50 g of a 60% emulsion in mineral oil, 0.0375 mol), poly(dichlorophosphazene) (**2**) (2.67 g, 0.0230 mol), 2-(hydroxymethyl)-18-crown-6 (8.00 g, 0.0272 mol), and sodium hydride (1.20 g, 0.0300 mol). Polymer **9** was purified by dialysis against water and methanol and recovered as a brown gum (5.28 g, 63%): ^{1}H NMR ($CDCl_3$) δ (ppm) 3.30−3.40 (s), 3.50−3.55 (t), 3.55−3.75 (m), 3,75−3.80 (m), 3.85−3.95 (m), 4.00−4.10 (m); ^{13}C NMR ($CDCl_3$) δ (ppm) 78.4, 71.9, 71.8, 70.9, 70.7, 70.6, 70.4, 70.3, 70.0, 65.0, 58.8; ^{31}P NMR ($CDCl_3$) δ (ppm) −7.8. Anal. Calcd: C, 45.4; H, 7.9; N, 3.8. Found: C, 44.3; H, 8.0; N, 3.8.

Acknowledgment. We thank the National Science Foundation E.P.R.I. (Joint Advanced Polymeric Materials Program) and the Department of Energy (Grant No. DE-FG02-93) for the support of this work. We also thank Gregory S. McCarty for his technical assistance with the impedance analysis equipment.

References and Notes

(1) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589.
(2) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319.
(3) Wright, P. V. *J. Polym. Sci., Polym. Phys.* **1976**, *14*, 955.
(4) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. Second International Conference on Solid Electrolytes; St. Andrews, Scotland, 1978.
(5) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Duclot, M. J., Vashishta, P., Mundy, J. N.; Shenoy, G. K., Eds.; North-Holland: Amsterdam, 1979.
(6) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.
(7) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89* (17), 3187.
(8) Foos, J. S.; Erker, S. M. *J. Electrochem. Soc.* **1987**, *134*, 1724.
(9) Goulart, G.; Sylla, S.; Sanchez, J. V.; Armand, M. B. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: London, 1990.
(10) Giles, J. R. M.; Booth, C.; Mobbs, R. H. In *Proceedings, Sixth Risø International Symposium on Metallurgy and Materials Science*; Poulsen, F. W., Anderson, N. H., Clausen, K., Skaarup, S., Sorensen, O. T., Eds.; Risø National Laboratories: Roskilde, Denmark, 1985.
(11) Craven, J. R.; Mobbs, R. H.; Booth, C.; Giles, J. R. M. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 81.
(12) Nicholas, C. V.; Wilson, D. J.; Booth, C.; Giles, J. R. M. *Br. Polym. J.* **1988**, *20*, 289.
(13) Linden, E.; Owen, J. R. *Solid State Ionics* **1988**, *28−30*, 994.
(14) Gray, F. M. *Solid State Ionics* **1990**, *40/41*, 637.
(15) Passiniem, P.; Takkumaki, S.; Kankare, J.; Syrjama, M. *Solid State Ionics* **1988**, *28−30*, 1001.
(16) Przyluski, J.; Wieczorek, W.; Florjanczyk, Z.; Krawiec, W. Second International Symposium on Polymer Electrolytes; Siena, Italy, 1989.
(17) Thatcher, J. H.; Thanapprapas, K.; Nagee, S. I.; Mai, S. M.; Booth, C.; Owen, J. R. *J. Mater. Chem.* **1994**, *4*, 591.
(18) Takebe, Y.; Hochi, K.; Matsuba, T.; Shirota, Y. *J. Mater. Chem.* **1994**, *4*, 599.
(19) Selvaraji, I. I.; Chaklanobis, S.; Manoravi, P.; Chandrasekhar, V. *Polymer* **1995**, *36* (13), 2603.
(20) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
(21) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *Solid State Ionics* **1986**, *18/19*, 258.
(22) Allcock, H. R.; O'Connor, S. J. M.; Olmeijer, D. L.; Napierala, M. E.; Cameron, C. G. *Macromolecules* **1996**, *29*, 7544.
(23) Allcock, H. R.; Napierala, M. E.; Cameron, C. G.; O'Connor, S. J. M. *Macromolecules* **1996**, *29*, 1951.
(24) Allcock, H. R.; Kuharcik, S. E.; Reed, C. S.; Napierala, M. E. *Macromolecules* **1996**, *29*, 3384.
(25) Allcock, H. R.; Napierala, M. E.; Olmeijer, D. L.; Cameron, C. G.; Kuharcik, S. E.; Reed, C. S.; O'Connor, S. J. M. Proceedings of the International Conference on Solid Polymer Electrolytes. *Electrochim. Acta*, in press.
(26) Rietman, E. A.; Kaplan, M. L.; Cava, R. J. *Solid State Ionics* **1987**, *25*, 41.
(27) Ohno, H.; Kobayashi, N.; Takeoka, S.; Ishizaka, H.; Tsuchida, E. *Solid State Ionics* **1990**, *40/41*, 655.
(28) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495.
(29) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(30) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.
(31) Popov, A. I.; Lehn, J. M. In *Coordination Chemistry of Macrocyclic Compounds;* Nelson, G. A., Ed.; Plenum Press: New York, 1979.
(32) Weber E.; Vogtle, F. In *Host−Guest Complex Chemistry: Macrocycles*; Vogtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, 1985.
(33) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386.
(34) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.
(35) Kaplan, M. L.; Rietman, E. A.; Cava, R. J.; Holt, L. K.; Chandross, E. A. *Solid State Ionics* **1987**, *25*, 37.
(36) Chen, K.; Doan, K.; Ganapathiappan, S.; Ratner, M.; Shriver, D. F. *Mater. Res. Soc. Symp. Proc.* **1991**, *210*, 211.
(37) Ohno, H.; Yamazaki, H.; Tsukube, H. *Polymer* **1993**, *34*, 1533.
(38) Ohno, H.; Inoue, Y.; Tsukube, H. *Polymer* **1994**, *35*, 5753.
(39) Collie, L.; Denness, E.; Parker, D.; O'Carroll, F.; Tachon, C. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 1747.
(40) Collie, L.; Parker, D.; Tachon, C.; Hubbard, H. V. St. A.; Davies, G. R.; Wood, I. M.; Wellings, S. C. *Polym. Commun.* **1993**, *34*, 1541.
(41) Denness, J. E.; Parker, D.; Hubbard, H. St. V. A. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 1445.
(42) Cowie, J. M. G.; Sadaghianizadeh, K. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 387.
(43) Cowie, J. M. G.; Sadaghianizadeh, K. *Polym. Commun.* **1988**, *29*, 126.
(44) Andrei, M.; Cowie, J. M. G.; Prosperi, P. *Electrochim. Acta* **1992**, *37*, 1545.
(45) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992; Chapter 3.
(46) Allcock, H. R.; Kugel, R. L. *J. Am.Chem. Soc.* **1965**, *87*, 4216.
(47) Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

MA971666P