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Synthesis of Polyphosphazenes with Ethyleneoxy-Containing Side Groups: New Solid Electrolyte Materials

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ABSTRACT: A series of mixed-substituent poly(organophosphazenes) with ethyleneoxy side groups has been synthesized. These polymers possess multiple electron-donor coordination sites that can form complexes with metal salts and generate "solid electrolyte" behavior. The polymers were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and elemental analysis. All the mixed-substituent polymers have low glass transition temperatures, from −70 to −56 °C, as well as at least one melting transition. Several polymer–lithium triflate complexes were examined by impedance analysis. The maximum conductivities for these polymers ranged from 1.6×10^{-6} to 3.9×10^{-5} S cm^{-1}.

Introduction

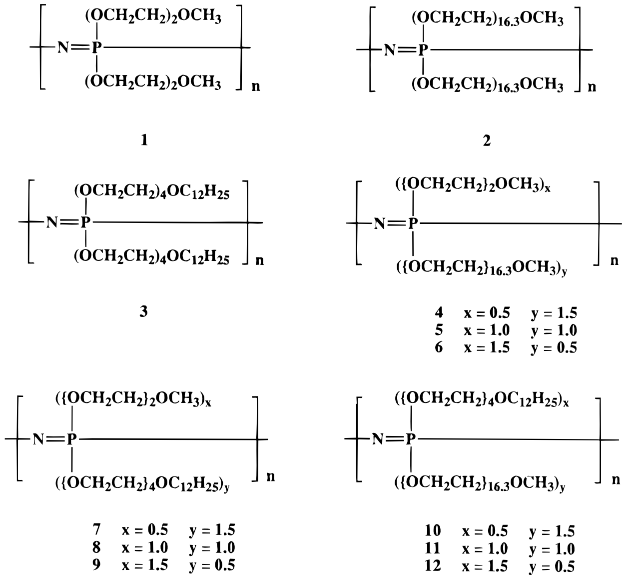
Poly(organophosphazenes) are a large class of macromolecules of the general formula $[NPR_2]_n$, where *R* may be any of a variety of amino, alkoxy, aryloxy, alkyl, or aryl units.[1–3] The properties of the polymers are highly dependent on the nature of the side group. As a result, poly(organophosphazenes) can be designed in a rational way to have a wide range of physical and chemical characteristics.

In recent years a growing interest has been evident in the development of polymers that can act as solvents for salts (solid polymer electrolytes).[4–6] This class of materials was first studied by Wright and co-workers, who described alkali metal salt complexes with poly(ethylene oxide).[7–9] Recognition of the potential of such systems as practical materials for applied electrochemistry, particularly in rechargeable lithium batteries, underlies much of the early work by Armand.[10,11] A number of reviews which detail the advancement of this field have been published by Shriver, Ratner, and coworkers.[12–14]

Several polymer characteristics aid in the formation of polymer–salt complexes. These include the presence of groups with sufficient electron-donor power to solvate the cations, low barriers to polymer bond rotation (low T_g), and a suitable distance between coordinating centers.[5,15] Polyphosphazenes may be designed to meet many of the requirements for a solid electrolyte material. For example, the phosphazene backbone is inherently flexible, and this allows facile polymer reorganization if flexible side groups are also present.[2] This segmental motion of the polymer appears to play a role in the ion transport of the system. In addition, various side groups with salt coordination sites may be incorporated.

A number of comb polymer systems with flexible backbones and short-chain polyether side groups have been investigated as solid polymer electrolyte materials. These include polyphosphazenes and polysiloxanes, among others.[16–27] It has been reported previously by Blonsky, Shriver, Austin, and Allcock that poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP) (**1**), forms complexes with salts such as lithium or silver triflate that have conductivities 100–1000 times higher than a poly(ethylene oxide)–lithium salt standard at room temperature.[16–19,28] One of the drawbacks of the MEEP system is its poor dimensional stability; the polymer flows under light pressure. Approaches to overcoming this problem include cross-linking by γ or ultraviolet radiation or through difunctional reagents and formation of blends, interpenetrating networks, or composites.[29–34]

Chart 1



$$\left[-N{=}\overset{(OCH_2CH_2)_2OCH_3}{\underset{(OCH_2CH_2)_2OCH_3}{P}}-\right]_n$$

1

$$\left[-N{=}\overset{(OCH_2CH_2)_{16.3}OCH_3}{\underset{(OCH_2CH_2)_{16.3}OCH_3}{P}}-\right]_n$$

2

$$\left[-N{=}\overset{(OCH_2CH_2)_4OC_{12}H_{25}}{\underset{(OCH_2CH_2)_4OC_{12}H_{25}}{P}}-\right]_n$$

3

$$\left[-N{=}\overset{(\{OCH_2CH_2\}_2OCH_3)_x}{\underset{(\{OCH_2CH_2\}_{16.3}OCH_3)_y}{P}}-\right]_n$$

4 x = 0.5 y = 1.5
5 x = 1.0 y = 1.0
6 x = 1.5 y = 0.5

$$\left[-N{=}\overset{(\{OCH_2CH_2\}_2OCH_3)_x}{\underset{(\{OCH_2CH_2\}_4OC_{12}H_{25})_y}{P}}-\right]_n$$

7 x = 0.5 y = 1.5
8 x = 1.0 y = 1.0
9 x = 1.5 y = 0.5

$$\left[-N{=}\overset{(\{OCH_2CH_2\}_4OC_{12}H_{25})_x}{\underset{(\{OCH_2CH_2\}_{16.3}OCH_3)_y}{P}}-\right]_n$$

10 x = 0.5 y = 1.5
11 x = 1.0 y = 1.0
12 x = 1.5 y = 0.5

In this paper we report the synthesis of cosubstituent polyphosphazenes and an investigation of their glass and melting transition temperatures. The polymers, shown in Chart 1, contain ethyleneoxy segments as potential sites for salt coordination. The side groups were 2-(2-methoxyethoxy)ethoxy, poly(ethylene glycol) methyl ether (average molecular weight of 750), and poly(oxyethylene(4)) lauryl ether units. The value of 16.3 for the number of ethyleneoxy repeat units in polymers **2**, **4–6**, and **10–12** reflects the average molecular weight of the poly(ethylene glycol) methyl ether starting material.

There were several objectives to this work. First, it was surmised that the incorporation of longer side groups might increase the opportunities for chain

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Table 1. ^{31}P, ^{1}H, and ^{13}C NMR Characterization Data for Polymers 1−12

polymer	^{31}P NMR δ (ppm)	^{1}H NMR^{a} δ (ppm)	^{13}C NMR^{a} δ (ppm)
1	−6.6	4.1, 3.7−3.6, 3.5, 3.3	72.7, 71.2, 71.0, 65.9, 58.9
2	−6.9	4.2, 3.6, 3.5, 3.3, 2.8, 2.7	72.0, 70.5, 59.1
3	−7.9	4.1, 3.6−3.4, 2.0, 1.6, 1.3, 0.9	71.7, 70.6, 70.1, 31.9, 29.7, 29.6, 29.4, 26.1, 22.7, 14.1
4	−6.8	4.1, 3.7−3.5, 3.3, 3.2	72.6, 71.2, 58.8
5	−6.7	4.1, 3.7−3.5, 3.3, 3.2	72.7, 72.6, 71.2, 71.0, 65.9, 59.0, 58.8
6	−6.6	4.1, 3.7−3.5, 3.3, 3.2	72.7, 71.2, 71.0, 65.9, 58.9
7	−6.7	4.2, 3.8−2.9, 1.7−0.8	72.7, 71.8, 71.3, 65.9, 59.0, 32.7, 30.5, 27.0, 23.4, 14.5
8	−6.3	4.2, 3.8−3.3, 1.8−1.2, 0.9	71.9, 71.5, 70.5, 70.2, 70.0, 65.0, 58.8, 31.9, 29.9, 29.4, 29.3, 26.5, 26.0, 22.6, 14.0
9	−6.6	4.2, 3.8−3.3, 1.6−1.2, 0.9	72.7, 71.7, 71.2, 71.0, 65.9, 58.9, 32.6, 26.9, 23.3, 14.3
10	−6.8	4.1, 3.8−3.4, 3.3, 1.6−1.2, 0.9	73.4, 72.6, 71.6, 71.2, 71.1, 58.8, 32.6, 26.9, 23.3, 14.3
11	−6.7	4.1, 3.8−3.4, 3.2, 1.6−1.2, 0.9	72.6, 71.2, 58.8, 32.6, 27.0, 23.3, 14.4
12	−6.7	4.2, 3.8−3.4, 3.2, 1.6−1.2, 0.9	73.5, 72.6, 71.2, 58.8, 32.6, 26.9, 23.3, 14.5

[a] Values represent the center of the peaks. In many cases, the peaks were broad.

entanglements and thereby increase the dimensional stability of the polymers, compared with MEEP. Second, poly(ethylene oxide) systems have been studied in great detail.[35,36] These macromolecules show good conductivities when heated above the melting transition temperature of the polymer (65 °C). However, at room temperature poly(ethylene oxide) is microcrystalline and conductivity is reduced. The use of a mixed-substituent system in phosphazene polymers may suppress or eliminate the tendency for microcrystallite formation. Finally, the poly(oxyethylene(4)) lauryl ether side group contains not only etheric sites for the coordination of cations but also a noncoordinative, alkyl tail. This alkyl segment could act as an incorporated "plasticizer" to hinder formation of microcrystalline domains. Alternatively, it could interfere with ionic conductivity due to its noncoordinative nature. A study of the influence of these two factors was a purpose of this research.

Table 2. GPC and Elemental Analyses for Polyphosphazenes 1−12

			elemental analysis^{a}			
polymer	M_n	M_w	% C	% H	% N	% Cl
1	4.1×10^5	9.4×10^5	(42.40)	(7.84)	(4.95)	(0.00)
			44.87	8.35	4.57	99 ppm
2	1.9×10^5	7.3×10^5	(52.26)	(8.91)	(0.907)	(0.00)
			52.29	8.96	0.87	0.0072
3	5.8×10^5	1.5×10^6	(62.49)	(10.76)	(1.82)	(0.00)
			60.74	10.88	1.09	0.0060
4	2.7×10^4	1.3×10^5	(50.81)	(8.70)	(1.14)	(0.00)
			51.16	9.02	1.01	0.016
5	2.5×10^4	9.4×10^4	(49.94)	(8.61)	(1.53)	(0.00)
			50.38	8.83	1.22	0.0048
6	1.3×10^4	5.5×10^4	(48.14)	(10.45)	(2.34)	(0.00)
			46.67	8.59	2.51	<0.03
7	8.4×10^3	2.8×10^4	(60.29)	(11.06)	(2.16)	(0.00)
			58.22	9.93	2.56	364 ppm
8	1.1×10^4	2.7×10^4	(57.07)	(11.50)	(2.66)	(0.00)
			56.48	10.39	2.96	686 ppm
9	9.0×10^3	3.6×10^4	(51.92)	(12.21)	(3.46)	(0.00)
			52.16	9.54	3.55	400 ppm
10	1.9×10^4	7.0×10^4	(52.92)	(9.04)	(1.04)	(0.00)
			54.39	9.41	1.07	446 ppm
11	1.7×10^4	4.5×10^4	(55.04)	(9.42)	(1.21)	(0.00)
			53.76	9.16	2.21	697 ppm
12	1.7×10^4	5.7×10^4	(58.01)	(9.96)	(1.46)	(0.00)
			57.35	9.75	1.71	87 ppm

[a] Calculated values in parentheses.

Results and Discussion

Preparation of Polymers. The polymers were synthesized according to the following protocol. Poly(dichlorophosphazene) dissolved in THF was allowed to react at 67 °C with a stoichiometric deficiency of the sodium alkoxide of the first side group. An excess of the second nucleophile was then added. The polymers were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, DSC, GPC, and elemental analysis. The results are shown in Tables 1−3. The ^{31}P NMR spectra of the polymers consisted of one peak in the −6 to −8 ppm region. The existence of only one peak in the spectra of the mixed-substituent polymers is presumably a result of the close relationships of the phosphorus atom environments due to the similarity of the side groups. Both the proton and the carbon NMR spectra indicated multiple environments which consisted of envelopes of overlapping peaks. However, these shifts correlate well with the carbon and proton NMR spectra of the alcohol starting materials. Elemental microanalysis detected only very small amounts (<0.03%) of residual chlorine in the polymers. This indicates that replacement of the chlorine by organic groups was essentially complete.

Thermal Transitions. (a) Glass Transition Temperatures. All the polymers had glass transition temperatures (T_g's) well below room temperature, specifically in the range of −84 to −54 °C (Table 3). These values indicate that the torsional mobility of the phosphazene backbone is not seriously hindered by the presence of these side groups. In general, the greater the percentage of methoxyethoxyethoxy units, the lower was the T_g.

Single-Substituent Polymers (1−3). Poly[bis((methoxyethoxy)ethoxy)phosphazene] (**1**) has the lowest glass transition temperature (−84.1 °C) of the polymers examined. The T_g of polymer **2**, $[\mathrm{NP}(\{\mathrm{OCH_2CH_2}\}_{16.3}\mathrm{OCH_3})_2]_n$, was approximately 22 °C higher. $[\mathrm{NP}(\{\mathrm{OCH_2CH_2}\}_4\mathrm{OC_{12}H_{25}})_2]_n$ (**3**), which contains side groups with less flexible alkyl segments in addition to the ethyleneoxy spacer, has a T_g at −53.6 °C.

(Methoxyethoxy)ethoxy/Poly(ethylene glycol) Methyl Ether Cosubstituent Polymers (4−6). The glass transition temperatures of **4**−**6** were similar to that of **2**. As the ratio of (methoxyethoxy)ethoxy to poly(ethylene glycol) methyl ether side groups increased from 1:3 to 3:1, the T_g decreased by approximately 5 °C. At only 25% loading of the $(\mathrm{OCH_2CH_2})_{16.3}\mathrm{OCH_3}$ units (polymer **6**), the T_g was increased by approximately 16 °C as compared to **1**. As the loading of poly(ethylene glycol) methyl ether increased, the T_g approached that of the single-substituent polymer **2** (−62.5 °C).

(Methoxyethoxy)ethoxy/Poly(oxyethylene(4)) Lauryl Ether Cosubstituent Polymers (7−9). The same trend was seen for this series. Polymer **7**, with 75% incorporation of poly(oxyethylene(4)) lauryl ether, has a T_g at approximately the same temperature as that of the single-substituent polymer **3**. As the ratio of (methoxyethoxy)ethoxy to $(\mathrm{OCH_2CH_2})_4\mathrm{OC_{12}H_{25}}$ groups

Table 3. Thermal Transitions for Polymers 1−12

polymer	T_g (°C)	T_1 (°C)	T_2 (°C)
$[NP(\{OCH_2CH_2\}_2OCH_3)_2]_n$ (**1**)	−84.1		
$[NP(\{OCH_2CH_2\}_{16.3}OCH_3)_2]_n$ (**2**)	−62.5	30.5	
$[NP(\{OCH_2CH_2\}_4OC_{12}H_{25})_2]_n$ (**3**)	−53.6	−1.1	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{0.5}(\{OCH_2CH_2\}_{16.3}OCH_3)_{1.5}]_n$ (**4**)	−63.3	32.6	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{1.0}(\{OCH_2CH_2\}_{16.3}OCH_3)_{1.0}]_n$ (**5**)	−66.0	27.2	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{1.5}(\{OCH_2CH_2\}_{16.3}OCH_3)_{0.5}]_n$ (**6**)	−68.7	20.6	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{0.5}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{1.5}]_n$ (**7**)	−55.6	−3.8	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{1.0}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{1.0}]_n$ (**8**)	−59.6	−8.2	
$[NP(\{OCH_2CH_2\}_2OCH_3)_{1.5}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{0.5}]_n$ (**9**)	−68.0	−12.7	
$[NP(\{OCH_2CH_2\}_{16.3}OCH_3)_{1.5}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{0.5}]_n$ (**10**)	−69.9	−5.5	29.1
$[NP(\{OCH_2CH_2\}_{16.3}OCH_3)_{1.0}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{1.0}]_n$ (**11**)	−68.1	−5.3	22.6
$[NP(\{OCH_2CH_2\}_{16.3}OCH_3)_{0.5}(\{OCH_2CH_2\}_4OC_{12}H_{25})_{1.5}]_n$ (**12**)	−59.8	−2.0	11.2

was increased, the glass transition temperature decreased by 4 °C, from −55.6 to −59.6 °C. A further increase in the (methoxyethoxy)ethoxy content lowered the T_g to −68.0 °C. As seen for copolymers **4**−**6**, even a 25% loading of the longer side group, in this case poly(oxyethylene(4)) lauryl ether, has a dramatic effect on the T_g and raises the transition by approximately 16 °C as compared to polymer **1**.

Poly(ethylene glycol) Methyl Ether/Poly(oxyethylene(4)) Lauryl Ether Cosubstituent Polymers (10−12). For this set of polymers, the glass transition temperatures increased from −69.9 to −59.8 °C with a decrease in the poly(ethylene glycol) methyl ether side group content. This may be due to the more flexible nature of the $(OCH_2CH_2)_{16.3}OCH_3$ side group, which consists entirely of ethyleneoxy units, whereas the poly(oxyethylene(4)) lauryl ether units contain stiffer, aliphatic segments.

(b) Melting Transition Temperatures. A disadvantage of polymer electrolytes based on poly(ethylene oxide) is that they generally contain crystalline phases which reduce the conductivity.[5] Thus, it is desirable to use amorphous polymers or those with very low melting temperatures. All the cosubstituent polymers discussed here, as well as the single-substituent polymers **2** and **3**, have melting transitions. These values range from as low as −12.7 to a high of +32.6 °C. The melting transitions were clearly influenced by the length and nature of the side groups (Table 3). $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (**1**) has no melting transition detectable by DSC. The flexible (methoxyethoxy)ethoxy side groups are randomly oriented and any coorientation of the side groups is minimal. Polymer **2**, with poly(ethylene glycol) methyl ether side groups, has a melting transition (T_m) at 30.5 °C. The single-substituent polymer of poly(oxyethylene(4)) lauryl ether has a T_m of −1.1 °C. The cosubstituent polymers with (methoxyethoxy)ethoxy and poly(ethylene glycol) methyl ether side groups had one T_m; the polymers with poly(ethylene glycol) methyl ether and poly(oxyethylene(4)) lauryl ether cosubstituents had two.

(Methoxyethoxy)ethoxy/Poly(ethylene glycol) Methyl Ether Cosubstituent Polymers (4−6). The copolymers with $OCH_2CH_2OCH_2CH_2OCH_3$ and $(OCH_2CH_2)_{16.3}OCH_3$ side groups had T_m's near room temperature (20.6 to 32.6 °C). As the (methoxyethoxy)ethoxy content increased, the T_m decreased from 32.6 °C, which corresponds approximately to the T_m of polymer **2**, to 20.6 °C for 75% loading. For **2**, the long ethyleneoxy segments favor microcrystalline domain formation. The presence of the (methoxyethoxy)ethoxy cosubstituents disrupts the stacking to some extent. By introducing some degree of conformational randomness, the entropy of fusion is increased and the melting temperature decreases. However, even a low incorporation of poly(ethylene glycol) methyl ether side units generates a melting transition close to room temperature.

(Methoxyethoxy)ethoxy/Poly(oxyethylene(4)) Lauryl Ether Cosubstituent Polymers (7−9). A similar trend in melting transition temperatures occurred for the (methoxyethoxy)ethoxy/poly(oxyethylene(4)) lauryl ether cosubstituent polymers. In general, the T_m's are lower than those for polymers **4**−**6**. This is probably because of the lower initial melting transition temperature of the homopolymer generated by the $(OCH_2CH_2)_4OC_{12}H_{25}$ side group itself. At 75% loading of the poly(oxyethylene(4)) lauryl ether side group, the T_m is −3.8 °C. Further incorporation of (methoxyethoxy)ethoxy cosubstituents for polymer **8** lowers the T_m to −8.2 °C. As the (methoxyethoxy)ethoxy content was increased to 75%, the melting transition decreased to −12.7 °C. The (methoxyethoxy)ethoxy side groups may be able to disrupt some of the side group associations and generate lower T_m's.

Poly(ethylene glycol) Methyl Ether/Poly(oxyethylene(4)) Lauryl Ether Cosubstituent Polymers (10−12). Polymers containing both poly(oxyethylene(4)) lauryl ether and poly(ethylene glycol) methyl ether side groups showed two melting transitions, one associated with the $(OCH_2CH_2)_4OC_{12}H_{25}$ units (T_1) and the other associated with the $(OCH_2CH_2)_{16.3}OCH_3$ side groups (T_2). As the poly(ethylene glycol) methyl ether content increased, T_1 decreased from −2.0 to −5.5 °C. The poly(ethylene glycol) methyl ether, despite its own ability to form microcrystalline domains, was still able to disrupt the packing of the poly(oxyethylene(4)) lauryl ether side groups and lower the melting transition. At 75% incorporation of poly(ethylene glycol) methyl ether (polymer **10**), T_2 was approximately the same as the T_m for **2**. As the percentage of poly(oxyethylene(4)) lauryl ether side group increased, the T_m decreased by a greater amount than in the analogous copolymers **4**−**6**. This may be due to more effective disruption of side group packing by poly(oxyethylene(4)) lauryl ether side units than (methoxyethoxy)ethoxy groups. (Methoxyethoxy)ethoxy side groups are much shorter than the poly(ethylene glycol) methyl ether substituents; thus the termini of the $(OCH_2CH_2)_{16.3}OCH_3$ units may still be able to associate with each other or perhaps with other (methoxyethoxy)ethoxy groups in an ordered array. However, poly(oxyethylene(4)) lauryl ether, with its long alkyl tail, appears to be able to disrupt the packing to a greater extent.

(c) Thermal Transitions of Lithium Triflate-Complexed Polyphosphazenes. The salt complexes of polymers **6**, **9**, and **12** were also analyzed by DSC (Table 4). As the percent loading of lithium triflate increased, the glass transition temperatures rose significantly. The glass transition temperature values for lithium triflate complexes of polymers **6**, **9**, and **12**

Table 4. DSC Data for Lithium Triflate-Complexed Polymers 6, 9, and 12

wt %[a] lithium triflate	polymer **6**		polymer **9**		polymer **12**		
	T_g (°C)	T_1 (°C)	T_g (°C)	T_1 (°C)	T_g (°C)	T_1 (°C)	T_2 (°C)
1	−68.5	17.2	−67.3	−12.0	−69.2	−0.8	8.4
2.5	−67.4	16.5	−65.1	−11.4	−65.5	−1.2	8.3
5	−67.8	14.0	−63.2	−11.3	−61.6	−0.3	11.1
10	−61.4	13.2	−57.4	−14.1	−52.7	0.9	
15	−55.2		−52.7	−18.8	−46.3	1.2	
20	−48.7		−45.7	−22.7	−42.2	−0.8	
25	−45.8		−46.2		−40.3	−1.2	
30	−43.0		−42.4		−42.1	−6.7	

[a] These wt % values correspond to the following mol % values for polymers **6**, **9**, and **12**, respectively: 5.6, 3.2, 6.9; 13.0, 7.9, 16.0; 23.5, 15.0, 28.1; 39.3, 27.2, 45.1; 50.8, 37.2, 56.5; 59.3, 45.7, 65.0; 66.1, 52.8, 71.1; 71.4, 59.1, 75.9.

ranged from approximately −70 °C, at 1 wt % lithium triflate, to −42 °C at the highest loading. This is attributed to cross-linking caused by the coordinated ions. The melting transition temperatures were less consistent in behavior, but overall tended to decrease slightly with increasing weight percent of the salt.

Impedance Analysis. Four polymers were examined further by impedance analysis at room temperature. Polymer **1** has been studied previously and was used here as a control.[16−18] Polymer **2** has been reported previously[37] and, due to its 30.5 °C melting transition temperature, was not examined. Polymer **3** and one polymer from each series (**6**, **9**, and **12**), with the lowest T_m values of their group, were investigated. The polymers were complexed with lithium triflate and the conductivities measured. The results are summarized in Figure 1. The maximum conductivity for polymers **3**, **6**, **9**, and **12** occurred at 35.4, 23.5, 7.9, and 45.1 mol % of lithium triflate, respectively. In each case, the conductivity decreased beyond these points with further increases in salt concentration. Again, this is ascribed to interchain coordination of ions that act as transient cross-links. This would reduce the overall segmental motion of the polymer and thus reduce the ion-transport process.[5]

Of the four polymers examined by impedance analysis, polymer **3**, $[NP(\{OCH_2CH_2\}_4OC_{12}H_{25})_2]_n$, possessed the lowest room temperature conductivity. This may be due to several factors. First, polymer **3** has the highest T_g of all of the polymers (−53.6 °C). As stated earlier, backbone flexibility appears to assist in the ion-transport process. However, a T_g of −53.6 °C is still indicative of a very high molecular flexibility, so other factors must play a role. It is likely that the presence of the long $-C_{12}H_{25}$ alkyl tail is detrimental to ionic conductivity. This segment possesses no ion coordinating sites and, due to its stiffness compared to ethoxy segments, may hinder the overall side group motion. These effects can also be seen in the poly(oxyethylene-(4)) lauryl ether-containing polymers **9** and **12**. Polymers **9** and **12** have a maximum conductivity values that are intermediate between those of polymer **1** (2.7×10^{-5} S cm^{-1}) and polymer **3**. Thus the poly(oxyethylene(4)) lauryl ether side group appears to hinder ion transport in these systems as well. We conclude that the additional free volume generated by the uneven lengths of the cosubstituents in polymers **7**−**9** does not make a significant contribution to the ionic conductivity. The incorporation of the flexible (methoxyethoxy)ethoxy cosubstituent clearly assists in the conductivity.

Polymer **6** has the highest conductivity of the polymers analyzed (3.9×10^{-5} S cm^{-1}). This value also exceeds the room temperature value for polymer **1**. Both substituents on polymer **6** consist entirely of ethyleneoxy units which are flexible and capable of transient ion coordination, factors that should favor ion transport. It is also possible that the free volume generated by the presence of different length ethyleneoxy side groups assists in ion transport. It must be remembered that the poly(ethylene glycol) methyl ether side group has an *average* length of 16.3 ethoxy units, so that the side group length varies in a random fashion along the polymer backbone. However, the dimensional stability of this polymer was no better than that of polymer **1**, since it flows under pressure at room temperature. Some of the cross-linking techniques which were used successfully to stabilize the dimensional stability of polymer **1** may also be useful for this system.[29,30]

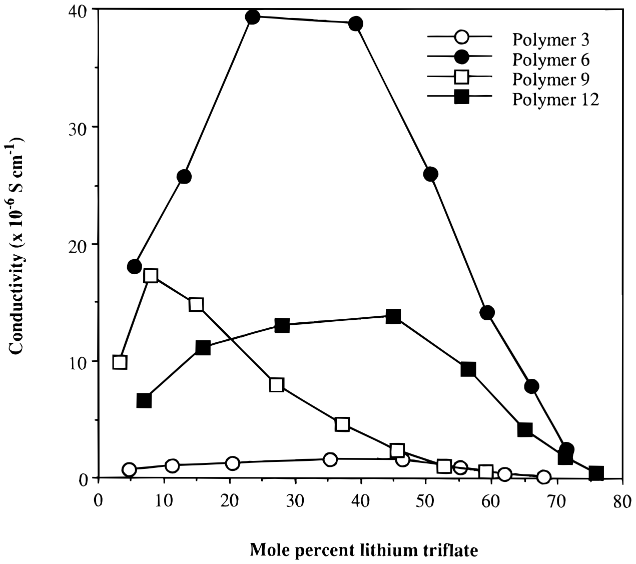

Figure 1. Ionic conductivity of lithium triflate-complexed polyphosphazenes **3**, **6**, **9**, and **12**.

Conclusions

A series of mixed-substituent polyphosphazenes bearing ethyleneoxy side groups has been synthesized. These polymers have low glass transition temperatures and, in the majority of cases, have melting transition temperatures that are below room temperature. These polymers are capable of serving as solvents for lithium triflate and can act as solid polymer electrolyte materials. Conductivity results indicate that those polymers with alkyl-containing side groups have poorer conductivities than systems that contain only ethyleneoxy units. By control of the cosubstituent ratios, the glass and melting transitions can be tuned over a range of temperatures. Cosubstituent polymers of (methoxyethoxy)ethoxy and poly(ethylene glycol) methyl ether appear to be the most promising of these systems for ionic conduction.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Nippon Fine Chemicals/Ethyl Corp.) was purified by recrystallization from heptane and by sublimation at 50 °C (0.05 mmHg). Poly(dichlorophosphazene) was prepared as described previously.[38] Sodium hydride (60% dispersion in mineral oil, Aldrich) was used as received. Tetrahydrofuran (Omnisolv) was dried over sodium benzophenone ketyl and was distilled under a nitrogen atmosphere. The 2-(2-methoxyethoxy)ethanol (Aldrich) was purified by vacuum distillation and stored over 4 Å molecular sieves. Poly(ethylene glycol) methyl ether (average molecular weight of 750) (Aldrich) and poly(oxyethylene(4)) lauryl ether (Brij 30) (Aldrich) were dried azeotropically with absolute ethanol/benzene (once) and benzene (twice)[37] and then stored over 4 Å molecular sieves. Lithium triflate (Aldrich) was dried under vacuum (60 °C, 0.01 mmHg) for 2 days. All reactions were performed under an atmosphere of dry argon using standard Schlenk techniques.

Equipment. ^{31}P NMR spectra were recorded by the use of a JEOL FX90Q NMR spectrometer operated at 36.2 MHz or with a Bruker WM-360 NMR spectrometer at 146 MHz. ^{31}P chemical shifts are relative to 85% phosphoric acid as an external reference with positive shift values downfield from the reference. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM-360 NMR spectrometer operated at 360 or 90.27 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to internal $CDCl_3$ or acetone-d_6. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and a Polymer Laboratories PL gel 10 μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium nitrate in THF (OmniSolv). The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. Glass transition temperatures were obtained by differential scanning calorimetry on a Perkin-Elmer DSC-7 unit controlled by a PE7500 computer. Heating rates of 10−25 °C/min and sample sizes of 15−30 mg were used.

Impedance Analysis. All the polymers were dried in a vacuum oven (40 °C, 1.0 mmHg) for 1 week before use. Solutions of the polymers and lithium triflate were prepared in THF, the solvent was removed by evaporation, and the complexed polymers were placed in a vacuum oven (40 °C, 1.0 mmHg) for 2 days. These complexes were dried further under vacuum (25 °C, 0.01 mmHg) for 2 days. Conductivity measurements were performed by use of a Hewlett-Packard 4192A LF impedance analyzer set at an a.c. potential of 1 V, with complex impedance techniques over a frequency range of 5 Hz to 13 MHz. All complex impedance analysis measurements were carried out in a constant-flow argon atmosphere glovebox. The complexed polymer samples were placed between platinum blocking electrodes and, due to their poor dimensional stability, were supported by a Teflon O-ring. The polymers were then placed in a fixture to which leads were attached, and complex impedance analyses were performed at 25 °C (±2 °C).

Synthesis of Poly[bis((methoxyethoxy)ethoxy)phosphazene] (1). The poly[bis((methoxyethoxy)ethoxy)phosphazene] was obtained by a method reported previously.[37] Sodium 2-(2-methoxyethoxy)ethoxide was prepared by reaction of 2-(2-methoxyethoxy)ethanol (18.5 mL, 154 mmol) with sodium hydride (9.32 g, 60% dispersion in mineral oil) in THF (200 mL) at reflux for 24 h. The reaction mixture was then filtered with use of an airless fritted funnel to obtain a light brown solution. Poly(dichlorophosphazene) (3.0 g, 25.9 mmol) in THF (200 mL) was added slowly to this solution. The reaction mixture was stirred for 36 h at reflux. The polymer was purified by dialysis in deionized water (4 days) and methanol (3 days). The solution was then filtered and the polymer collected by evaporation of the solvent.

Synthesis of poly[bis{poly(ethylene glycol) methyl ether}phosphazene] (2). Polymer **2** was obtained by a method reported in the literature.[37] The sodium salt of poly(ethylene glycol) methyl ether was prepared by reaction of poly(ethylene glycol) methyl ether 750 (32.33 g, 43.1 mmol) with sodium hydride (2.31 g, 60% dispersion in mineral oil) in THF (200 mL) at reflux for 24 h. The reaction mixture was then filtered with use of an airless fritted funnel. Poly(dichlorophosphazene) (0.5 g, 4.3 mmol) in THF (200 mL) was added slowly to the alkoxide solution. The reaction mixture was stirred for 36 h at reflux. The polymer was purified by dialysis in deionized water (4 days) and methanol (3 days). The solution was then filtered and the polymer collected by evaporation of the solvent.

Synthesis of Poly[bis{poly(oxyethylene(4)) lauryl ether}phosphazene] (3). Poly[bis{poly(oxyethylene(4)) lauryl ether}phosphazene] has been synthesized previously.[39] The following slightly altered procedure was used. The sodium salt of poly(oxyethylene(4)) lauryl ether was prepared by reaction of poly(oxyethylene(4)) lauryl ether (56.26 g, 155 mmol) with sodium hydride (9.30 g, 60% dispersion in mineral oil) in THF (200 mL) at reflux for 24 h. The reaction mixture was then filtered with use of an airless fritted funnel. Poly(dichlorophosphazene) (0.5 g, 4.3 mmol) in THF (200 mL) was added slowly to the sodium salt. The reaction mixture was stirred for 36 h at reflux. The polymer was purified by precipitation from THF into water and methanol.

Preparation of Polymers 4−12. Polymers **4**−**12** were prepared in the same manner. The procedure for the preparation of **9** is typical. The sodium salts were prepared as discussed previously. The poly(oxyethylene(4)) lauryl ether salt (4.69 g, 12.9 mmol) was added slowly and with vigorous stirring to the poly(dichlorophosphazene) (3.0 g, 25.9 mmol) in THF (700 mL). The reaction mixture was refluxed for 24 h before the slow addition of the sodium 2-(2-methoxyethoxy)-ethoxide (13.98 g, 116 mmol). The mixture was refluxed for an additional 48 h. The polymer was purified by dialysis in deionized water (4 days) and methanol (3 days). The solution was then filtered and the polymer collected by evaporation of the solvent.

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