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Synthesis and Characterization of Ionically Conducting Alkoxy Ether/Alkoxy Mixed-Substituent Poly(organophosphazenes) and Their Use as Solid Solvents for Ionic Conduction

Harry R. Allcock,* Mark E. Napierala, Charles G. Cameron, and Stephen J. M. O'Connor

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

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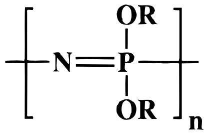
ABSTRACT: A series of mixed-substituent poly(organophosphazenes) with the general structure $\{NP[OCH_2CH_2OCH_2CH_2OCH_3]_x[O(CH_2)_yCH_3]_{2-x}\}_n$, where $x = 1$ and $y = 2-9$ was synthesized. These polymers are candidates for use as solid polymeric, ionic conduction media. The polymers were characterized by ^1H, ^{13}C, and ^{31}P nuclear magnetic resonance spectroscopy, gel permeation chromatography, elemental microanalysis, infrared spectroscopy, and differential scanning calorimetry. The polymers were complexed with $LiSO_3CF_3$ and ambient temperature (25 °C) ionic conductivity studies were performed with the use of complex impedance analysis. The effect of changes in the length of the alkyl component of the alkoxy groups on conductivity was examined. A maximum conductivity as a function of the concentration of lithium triflate was found for each system. The conductivity decreased with an increase in the alkyl group side-chain length. These polymers were compared to the polyphosphazene single-substituent polymer $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$, as well as to the *n*-alkyloxy single-substituent polymers $\{NP[O(CH_2)_xCH_3]_2\}_n$, where $x = 2-9$.

Introduction

The study of solid polymeric electrolytes (SPEs) has grown rapidly since the early 1970s. One of the major objectives is to produce a polymer-based electrolyte material that has a high ionic conductivity and is stable mechanically as well as electrochemically. In 1973, Wright and co-workers reported that poly(ethylene oxide) (PEO) and KSCN form a crystalline, stoichiometric polymer−salt complex.[1] In 1978, Armand recognized that solvent-free polymer−salt complexes might be excellent electrolytes for high-energy-density, solid-state batteries.[2] Since that time, PEO has been studied extensively for use in ionically conducting SPEs. The mechanism of conduction in such systems has been discussed by Ratner, Shriver, Vincent, and others.[3−5]

These studies have helped to develop basic property requirements that polymers must possess to be used as SPE media. First, the polymer should possess cation or anion coordination sites to assist in the process of salt solvation and ion pair separation. In PEO this is achieved by the oxygen atoms in the polymer backbone. Second, a polymer should have a low glass transition temperature, which is a manifestation of high molecular flexibility at ambient temperatures. A flexible polymer will allow high ion mobility and, thus, high ionic conductivity. Third, the polymer should be amorphous. The presence of crystalline domains in the polymer will not only reduce the overall flexibility of the system but will also act as barriers to the transport of ions. PEO has a crystalline melting temperature at 65 °C and does not become wholly amorphous until heated above 100 °C. Thus, the crystallinity of PEO is a major disadvantage because the operational temperature for most SPE applications is below the melting transition of PEO. This has prompted many workers to attempt to modify the properties of PEO with the aim of eliminating the presence of crystallinity.[6−15]

Poly(organophosphazenes) such as **1** comprise a broad class of macromolecules where the side group may be any of a variety of alkyl, aryl, amino, alkyloxy, or aryloxy side groups.[16−18] The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with additional physical or chemical characteristics imposed by the side group structure.[16,19,20] The ability of chemists to tailor the macroscopic properties of polyphosphazenes by the incorporation of various side groups is the basis for the belief that specific phosphazene derivatives may be useful in the area of SPEs.



$$\left[N{=}P(OR)_2 \right]_n$$

1

The first polyphosphazene shown to have a significant level of ionic conductivity was reported by Blonsky, Shriver, Austin, and Allcock in 1984.[21] This polymer is poly[bis[2-(2′-methoxyethoxy)ethoxy]phosphazene] (MEEP). It is amorphous at room temperature and below and functions as an excellent solid solvent for metal salts such as $LiSO_3CF_3$ or $AgSO_3CF_3$. The polymer−salt systems formed by MEEP were found to have room temperature conductivities 2−3 orders of magnitude higher than PEO. This level of ionic conductivity is attributed to the high flexibility of the polymer backbone, good solvation (coordinative power) by the oxygen atoms in the etheric side groups to cations, the presence of six oxygen atoms per repeat unit, and the amorphous character of MEEP at room temperature.

The relationship between ionic conductivity and polymer chain flexibility, as manifest in the glass transition temperature, is a matter of interest. However, the separation of this effect from the influence of gross coordination power by the polymer has not been ad-

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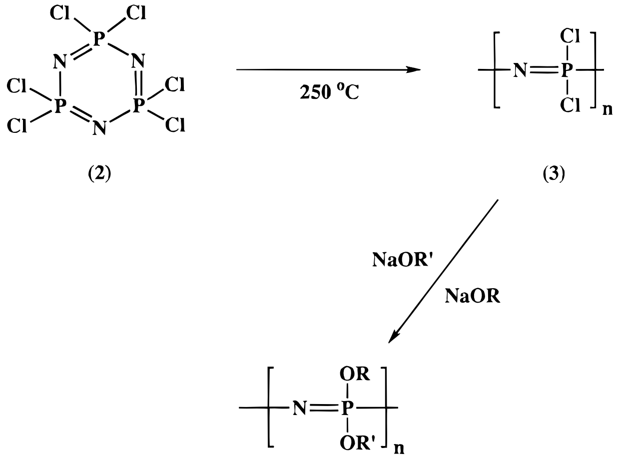
Scheme 1. Synthesis of Mixed-Substituent Polymers



R'= $CH_2CH_2OCH_2CH_2OCH_3$

(4) R=$(CH_2)_2CH_3$

(5) R=$(CH_2)_3CH_3$

(6) R=$(CH_2)_4CH_3$

(7) R=$(CH_2)_5CH_3$

(8) R=$(CH_2)_6CH_3$

(9) R=$(CH_2)_7CH_3$

(10) R=$(CH_2)_8CH_3$

(11) R=$(CH_2)_9CH_3$

dressed up to this point. A way to address this question is to synthesize mixed-substituent polymers with both *n*-alkyloxy and alkyl ether side groups. The single-substituent polymer $\{NP[O(CH_2)_xCH_3]_2\}_n$, where $x = 4$, has a glass transition temperature of −105 °C, which is roughly 20 °C lower than that of MEEP.[22] Thus, through the replacement of some of the ethyleneoxy substituents in MEEP by alkyloxy substituents, it might be possible to decrease the glass transition of the polymer system, which would allow for greater amorphous character and possibly generate higher conductivities. At the same time, the presence of a certain percentage of alkyl ether side groups would maintain the solvation capability and coordination power of the MEEP single-substituent polymer.

Results and Discussion

Polymer Synthesis and Characterization. The syntheses of the mixed-substituent copolymers **4**−**11** (see Scheme 1 and Experimental Section) were carried out as follows: One equivalent of sodium (methoxyethoxy)ethoxide was allowed to react with poly(dichlorophophazene) (**3**) in THF to generate $[NPCl(OCH_2CH_2OCH_2CH_2OCH_3)]_n$. This intermediate was then treated with an excess of the sodium salt of the second alcohol.

The polymer structures were examined with the use of ^{31}P (145.8 MHz), ^{1}H (360 MHz), and ^{13}C (90 MHz) nuclear magnetic resonance (NMR) spectroscopy, elemental microanalysis, and gel permeation chromatography (see Tables 2 and 3 and Experimental Section). ^{1}H NMR spectroscopy and elemental microanalysis were used to estimate the ratios of the different side groups. For ^{1}H NMR spectroscopy, the integration of the signal representative of the terminal methoxy group protons on the (methoxyethoxy)ethoxy side chain was compared to the signal representative of the terminal methyl group protons on the *n*-alkyl group side chain.

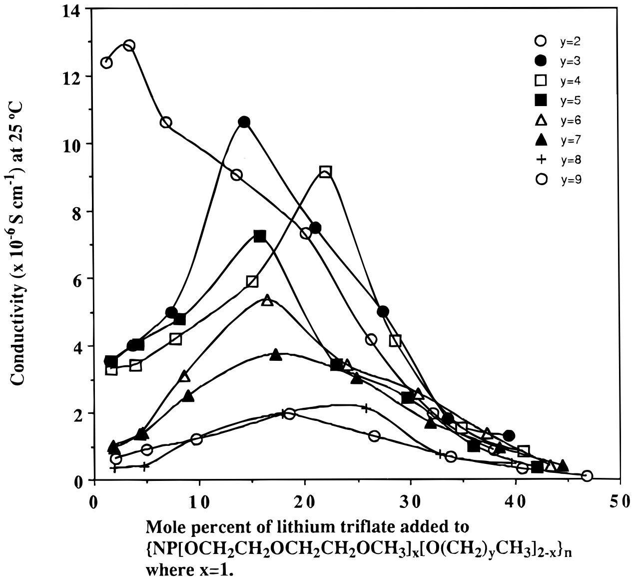


Figure 1. Conductivity values for the mixed-substituent polymers at 25 °C determined by complex impedance analysis compared to the mole percent of lithium triflate added.

Electrochemical Results. The poly(organophosphazenes) investigated in this work gave a range of conductivity values that varied with the side group structure (see Figure 1). First, the level of conductivity of each mixed-substituent polymer was affected by the concentration of $LiSO_3CF_3$. The total range of $LiSO_3CF_3$ concentrations used for complexation of all mixed-substituent systems was from 1.4 to 46.8% (the concentration of salt throughout this paper is expressed in terms of a mole percentage). Salt-free polymer samples gave conductivity values in the range of 10^{-8} S cm^{-1}. The addition of 1.4−2.0% $LiSO_3CF_3$ increased the conductivity at least 1 order of magnitude for all of the polymers. For example, polymer **8** has a conductivity value that increases from 5.67×10^{-8} S cm^{-1} for the pure material to 1.03×10^{-6} S cm^{-1} for a system with 1.8% $LiSO_3CF_3$. At these low salt concentrations the polymers demonstrate an ability for solvation and coordination with ions that is quite remarkable. It is for this reason that each polymer shows an additional increase in conductivity as more salt is added. As the concentration of salt rises, each polymer reaches a point of maximum conductivity. This point occurred for polymer **8** at 16.5% $LiSO_3CF_3$ with a conductivity value of 5.36×10^{-6} S cm^{-1}, which corresponds to a 5.1:1 molar ratio (all molar ratios throughout this paper are expressed in terms of polymer repeat unit to $LiSO_3CF_3$ unit). The addition of more salt reduced the conductivity for each system. This occurs because of a decrease in the number of coordinating sites available as more ions are added to the system. Moreover, the polymer molecules become less flexible as the amount of salt is increased. Salt aggregates probably reduce ion mobility and decrease conductivity. In addition, the glass transition of the polymer will increase steadily as the salt concentration is raised because the number of ionic cross-links will increase correspondingly.

Second, the maximum conductivities for each polymer system decreased with an increase in the length of the alkyl group side chain (see Figure 2 and Table 1). Polymer **4**, with the shortest alkyl group side chain, had a maximum conductivity of 1.29×10^{-5} S cm^{-1} while

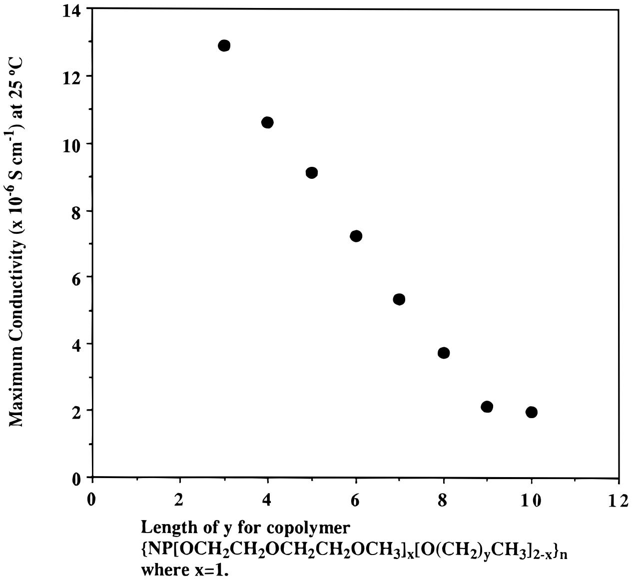


Figure 2. Maximum conductivity values for the mixed-substituent polymers at 25 °C determined by complex impedance analysis as a function of the length of the alkyloxy side group.

Table 1. Maximum Conductivity Data for $\{NP[OCH_2CH_2OCH_2CH_2OCH_3]_x[O(CH_2)_yCH_3]_{2-x}\}_n$ at 25 °C

polymer	max conductivity (S/cm)	mol % $LiSO_3CF_3$ added	mole ratio polymer:salt
4	1.29×10^{-5} ±2.33%	3.5	27.3:1
5	1.06×10^{-5} ±5.94%	14.4	5.9:1
6	9.13×10^{-6} ±2.67%	22.1	3.5:1
7	7.24×10^{-6} ±4.83%	15.9	5.3:1
8	5.36×10^{-6} ±3.17%	16.5	5.0:1
9	3.74×10^{-6} ±3.21%	17.3	4.8:1
10	2.14×10^{-6} ±12.3%	25.8	2.9:1
11	1.96×10^{-6} ±12.1%	18.6	4.4:1

polymer **11**, which contains the longest alkyl group side chain, had a maximum conductivity of 1.96×10^{-6} S cm^{-1}. This is nearly 1 order of magnitude difference in conductivity. It may reflect the presence of an increased molar volume of etheric sites compared to methylene sites in the polymer. This would affect the solvation and ion pair separation characteristics directly.

It was shown previously through solid-state NMR studies carried out with polyether-substituted siloxane-based and phosphazene-based polymer electrolyte materials that the two oxygen atoms closest to the backbone of the polymer play a very minor role in the coordination of metal cations such as lithium or sodium.[3,23] Thus, for a single-substituent polymer such as MEEP with six oxygen atoms per polymer repeat unit, there are probably only four coordination sites per polymer repeat unit available for metal ions. The polymers studied in this present work contain four oxygen atoms per repeat unit, two of which are close to the backbone. Therefore, only two coordination sites are probably available for metal ions. Thus, the theoretical maximum coordinative ability of all the polymers is 2 mol of polymer repeat unit to 1 mol of salt. The maximum conductivities of all systems studied here were found at ratios of polymer to salt above this level, which suggests that ion-free coordination sites must be present to allow for the movement of ions through the polymer matrix. In general, except for polymer **4**, maximum conductivities for the mixed substituent polymers occurred at an average concentration of roughly 18.6% $LiSO_3CF_3$. These conductivities were within a molar ratio range of 2.9:1−5.9:1. Polymer **4** had a maximum conductivity at 3.53% $LiSO_3CF_3$, which corresponds to a molar ratio of 27.3:1. Also, in general, the molar ratios of polymer to salt at the maximum conductivities decreased with an increase in the length of the alkyl group side chain.

Third, complex impedance analysis studies performed previously on MEEP demonstrated conductivity values higher than those for the systems examined here.[21] MEEP has a conductivity of twice the value of polymer **4**. This could be due to the presence of more oxygen atoms per repeat unit in MEEP, which could provide more coordination sites for metal ions. However, as was mentioned previously, the conductivities for the polymers studied vary over a range of 1 order of magnitude. The alkyloxy side-chain length responsible for this variation, when used in conjunction with another side chain which may possess better polymer electrolyte characteristics, can be viewed as a tool for tunable conductivity.

Polymer Thermal Behavior. The glass transition temperatures (T_g's) and melting transitions (T_m's) of the poly(organophosphazenes) used in this work were determined by differential scanning calorimetry (DSC) (see Table 4 and Experimental Section). DSC studies confirmed that polymers **4**−**9**, both salt-free and salt-complexed, were amorphous over the temperature range of −120 to +80 °C. These same studies also showed that crystallinity does not occur if the alkyloxy side-chain length is below nine carbons. Above this limit crystallinity is detected, as in the case of polymers **10** and **11**.

The T_g's of the salt-free polymers ranged in value from −95 to −85 °C with no apparent trend in terms of the length of the alkyl side chain. In general, the T_g's of the polymer−salt complexes increased with an increase in the amount of dissolved salt in the system. Polymer **10** showed a T_g and a melting transition temperature (T_m) at salt concentrations of 17.9% and below. This polymer, when salt-free, showed a T_g and two T_m's. Polymer **11**, both salt-free and complexed, had two T_m's and did not show a T_g until the salt concentration reached 18.6%. At this point, a T_g was detected together with the two T_m's. The T_m's for both polymers **10** and **11** were no longer present above 17.9 and 18.6% salt concentration, respectively. This is possibly due to the ability of the salt to disrupt the micocrystallinity of the polymer.

In general, all polymers had a T_g roughly 10 °C below that of the single-substituent polymer MEEP. This suggests that the polymers are highly flexible. Thus, the conductivities must reflect a difference in the coordination or solvation abilities, rather than inherent chain flexibility. Salt-free polymer **4** has a T_g of −91 °C, which is 8 °C lower than that of MEEP. However, the conductivities of the polymer **4** salt complexes were lower than those of MEEP. A comparison of these two systems seems to indicate that, although polymer **4** may be more flexible than MEEP, the larger number of oxygen atoms in MEEP per unit volume, acting as sites for ion coordination, play a significant role in the ability to produce a higher conductivity. Moreover, polymers **5**−**9** have slightly lower T_g's than polymer **4** and yet show even lower conductivities, again due to fewer coordination sites per unit volume of polymer. Thus, the incorporation of noncoordinating alkyloxy-based side chains at the expense of coordinating alkyl ether based side chains results in a decrease in ionic conductivity

Table 2. NMR Characterization Data for $\{NP[OCH_2CH_2OCH_2CH_2OCH_3]_x[O(CH_2)_yCH_3]_{2-x}\}_n$

polymer	x	y	^{31}P NMR, ppm	^1H NMR, ppm	^{13}C NMR, ppm
4	1.03	2	−7.63	0.87 (t), 1.55 (m), 3.33 (s), 3.49 (m), 3.61 (br), 3.84 (br), 4.03 (br)	72.0, 70.4, 70.3, 64.9, 58.9, 32.5, 19.0, 13.9
5	0.96	3	−7.61	0.90 (t), 1.37 (m), 1.54 (m), 3.35 (m), 3.50 (m), 3.63 (m), 3.90 (br), 4.03 (br)	72.0, 70.5, 70.3, 65.4, 64.6, 58.9, 32.5, 19.0, 13.9
6	1.02	4	−7.63	0.86 (t), 1.28 (m), 1.54 (br), 3.33 (s), 3.47 (m), 3.61 (br), 3.87 (br), 4.02 (br)	14.1, 22.5, 28.1, 30.2, 58.9, 64.7, 65.7, 70.4, 70.6, 72.0
7	1.03	5	−7.64	0.85 (t), 1.25 (br), 1.55 (br), 3.33 (s), 3.47 (br), 3.61 (br), 3.85 (br), 4.02 (br)	14.1, 22.7, 25.7, 30.6, 31.8, 58.9, 64.7, 65.7, 70.4, 70.6, 72.0
8	0.98	6	−7.60	4.05 (br), 3.90 (br), 3.65 (br), 3.50 (m), 3.40 (s), 1.65 (br), 1.30 (br), 0.90 (t)	72.0, 70.5, 70.3, 65.7, 64.7, 58.9, 32.0, 30.7, 29.4, 26.0, 22.7, 14.1
9	0.94	7	−7.60	4.04 (br), 3.87 (br), 3.63 (m), 3.49 (m), 3.35 (s), 1.56 (m), 1.25 (m), 0.89 (t)	72.0, 70.6, 70.3, 65.7, 64.7, 58.9, 32.0, 30.7, 29.8, 29.5, 26.1, 22.7, 14.1
10	0.96	8	−7.60	4.00 (br), 3.90 (br), 3.65 (m), 3.50 (m), 3.35 (s), 1.60 (br), 1.30 (br), 0.90 (t)	72.0, 70.5, 70.3, 65.7, 64.7, 58.9, 32.0, 30.7, 29.9, 29.5, 26.1, 22.7, 14.1
11	0.98	9	−7.60	4.10 (br), 3.90 (br), 3.65 (m), 3.50 (m), 3.30 (s), 1.70 (br), 1.55 (br), 1.30 (br), 0.90 (t)	72.0, 70.5, 70.3, 66.3, 61.2, 32.0, 29.6, 29.5, 26.1, 22.7, 14.1

Table 3. Characterization Data for $\{NP[OCH_2CH_2OCH_2CH_2OCH_3]_x[O(CH_2)_yCH_3]_{2-x}\}_n$

polymer	IR (cm^{-1})	M_n/M_w ($\times 10^{-5}$)		elemental anal. (%)			% Cl (ppm)
				C	H	N	
4	2861−2966, 1456, 1240, 1066	1.56/2.79	calcd	43.05	8.07	6.28	0
			found	42.17	8.33	6.40	175
5	2875−2960, 1457, 1236, 1067	1.57/2.77	calcd	45.57	8.44	5.91	0
			found	45.67	7.99	5.91	233
6	2848−2957, 1456, 1240, 1057	1.68/3.10	calcd	47.81	8.76	5.58	0
			found	44.69	9.06	5.68	284
7	2853−2962, 1456, 1236, 1100	0.791/1.90	calcd	49.81	9.06	5.28	0
			found	48.54	9.18	5.75	<318
8	2855−2964, 1456, 1239, 1069	3.70/6.67	calcd	51.61	9.32	5.02	0
			found	51.36	9.80	5.05	209
9	2854−2963, 1456, 1240, 1070	4.12/6.98	calcd	53.24	9.56	4.78	0
			found	51.74	8.99	4.88	156
10	2856−2965, 1467, 1240, 1062	4.80/7.61	calcd	54.72	9.77	4.56	0
			found	55.06	9.78	3.98	118
11	2855−2964, 1467, 1240, 1065	3.22/5.41	calcd	56.07	9.97	4.36	0
			found	54.78	10.13	4.80	469

Table 4. Thermal Transition Data for $\{NP[OCH_2CH_2OCH_2CH_2OCH_3]_x[O(CH_2)_yCH_3]_{2-x}\}_n$ (°C)[a]

polymer		mol % lithium triflate added to polymers[b]								
		0	*1.4*	*3.5*	*7.0*	*13.7*	*20.2*	*26.3*	*32.3*	*37.9*
4	T_g	−91	−89	−88	−86	−77	−73	−60	−51	−54
		0	*1.5*	*3.8*	*7.4*	*14.4*	*21.1*	*27.5*	*33.6*	*39.4*
5	T_g	−95	−93	−91	−88	−82	−73	−71	−65	−55
		0	*1.6*	*4.0*	*7.8*	*15.2*	*22.1*	*28.6*	*34.9*	*40.8*
6	T_g	−95	−94	−92	−86	−77	−72	−71	−71	−67
		0	*1.7*	*4.2*	*8.2*	*15.9*	*23.1*	*29.8*	*36.1*	*42.1*
7	T_g	−95	−95	−92	−90	−72	−75	−71	−69	−58
		0	*1.8*	*4.4*	*8.6*	*16.5*	*24.0*	*30.8*	*37.3*	*43.3*
8	T_g	−94	−92	−93	−87	−75	−76	−69	−54	−47
		0	*1.9*	*4.6*	*9.0*	*17.3*	*24.9*	*31.9*	*38.5*	*44.6*
9	T_g	−90	−90	−90	−84	−78	−68	−62	−55	−59
		0	*2.0*	*4.8*	*9.4*	*17.9*	*25.8*	*32.9*	*39.6*	*45.7*
10	T_g	−85	−82	−81	−77	−71	−63	−60	−64	−64
	$T_m{}^1$	−68	−56	−56	−51	−47				
	$T_m{}^2$	−60								
		0	*2.0*	*5.0*	*9.8*	*18.6*	*26.6*	*34.0*	*40.6*	*46.8*
11	T_g					−64	−51	−40	−43	−42
	$T_m{}^1$	−43	−43	−41	−40	−36				
	$T_m{}^2$	−37	−37	−36	−35	−29				

[a] Estimated uncertainty values: T_g, ±3 °C; T_m, ±3 °C. [b] Values in italic type.

because there are fewer coordinated ions per volume of polymer, in spite of the higher polymer flexibility.

The T_g's of polymers **4**−**7** were higher than those of the previously reported corresponding single-substituent alkoxy polymers with the general formula $\{NP[O(CH_2)_xCH_3]_2\}_n$, where $x = 2-5$.[22] The alkyl ether cosubstituent units probably introduce a weak dipolar interaction into the polymers and raise the T_g's. The T_g's of polymers **8**−**10** are lower than those of the single-substituent alkoxy polymers and MEEP. This is possibly due to a free-volume effect that is introduced into the system by the longer alkoxy side chains. The corresponding single-substituent polymers $\{NP[O(CH_2)_8CH_3]_2\}_n$ and $\{NP[O(CH_2)_9CH_3]_2\}_n$ each have a single T_m transition at 10 and 22 °C, respectively, which is significantly higher than those observed for polymers **10** and **11**.[24] The presence of (methoxyethoxy)ethoxy side chains in the mixed-substituent polymers possibly causes a disruption in the crystal packing of the longer and less flexible *n*-nonyl and *n*-decyl side chains, thus lowering, but not eliminating, the T_m transition.

Conclusions

A study of the relationship between polymer side-chain structure and measured conductivities for a selected series of poly(organophosphazene) polymers was carried out. The effects of salt concentration, alkyl side-chain length, and glass transition temperature were examined. In general, the conductivity values for each mixed-substituent polymer system were affected by the concentration of dissolved salt. A maximum conductivity was found that was specific for each system, and this value decreased as the length of the alkyl group side chain increased. The glass transition temperatures of polymer−salt complexes within the same polymer increased with rising salt concentrations. The incorporation of noncoordinating alkyloxy based side chains at the expense of coordinating alkyl ether based side chains results in a decrease in ionic conductivity because fewer ions are coordinated per volume of polymer. This leads to the conclusion that increased free volume *per se* does not enhance conductivity unless the number of donor coordination sites is increased correspondingly. Overall, the polyphosphazenes used in this study allow the conductivity to be varied over a range of 1 order of magnitude.

Experimental Section

Equipment. ^{1}H NMR (360.0 MHz), ^{13}C NMR (90.0 MHz), and ^{31}P NMR (145.8 MHz) spectra were obtained using a Bruker WM-360 spectrometer. Chemical shifts are relative to tetramethylsilane at $\delta = 0$ for protons and carbon. The phosphorous chemical shifts are relative to external 85% H_3PO_4 at $\delta = 0$ with positive shift values downfield from the reference. All heteronuclear NMR spectra were proton decoupled. Molecular weights were determined using an HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and Polymer Laboratories PL gel 10 μm columns. The injection volume was 5 μL of a solution prepared from 20 mg of polymer dissolved in 1 mL of dry THF. The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate in THF. 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. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Infrared spectra were obtained by the use of a Perkin-Elmer 1600 series FT-IR spectrophotometer. Thermal analyses were carried out with the use of a Perkin-Elmer thermal analysis system 7 equipped with a Perkin-Elmer 7500 computer. For the determination of glass transition temperatures by differential scanning calorimetry, heating rates of 10, 20, and 40 °C/min under a nitrogen atmosphere were used and the values were extrapolated to 0 °C/min. A sample size between 10 and 30 mg was used. Conductivity measurements were carried out with the use of a Hewlett-Packard 4192A LF impedance analyzer set at an ac potential of 1 V with complex impedance techniques used over a frequency range of 5 Hz to 13 MHz.

Materials and Procedures. All reactions were carried out under an atmosphere of dry argon (Matheson) with the use of standard Schlenk line and drybox techniques. Tetrahydrofuran (THF) was dried and distilled from sodium benzophenone ketyl. Fractional sublimation (30 °C, 0.01 mmHg) was utilized to purify the hexachlorocyclotriphosphazene, which was provided by Ethyl Corp. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of the cyclic trimer at 250 °C.[16] The alcohols (Aldrich) were distilled under vacuum onto 4 Å molecular sieves and were stored under argon.

All polymers were dried in a vacuum oven (40 °C, 1 mmHg) for 1 week before use in complex impedance analysis measurements. The $LiSO_3CF_3$ was dried under vacuum (60 °C, 0.01 mmHg) for 2 days and was stored under argon. Solutions of polymer and salt were prepared with the use of dry THF. The THF was removed by evaporation, and the complexed polymers were placed in a vacuum oven (40 °C, 1 mmHg) for 2 days. These complexes were further dried under vacuum (25 °C, 0.01 mmHg) for 2 days. All complex impedance analysis measurements were made in a constant-flow argon atmosphere glovebox. The complexed polymer samples were placed between platinum blocking electrodes and were supported by a Teflon O-ring due to their tendency to undergo viscous flow under an applied pressure. The polymers were then placed in a fixture to which leads were attached and complex impedance analyses performed.

Synthesis of Polymers 4−11. Polymers **4**−**11** were all prepared in a similar manner. The following preparation of **6** is typical. A suspension of 60% NaH in mineral oil (0.69 g, 17 mmol) and 2-(2′-methoxyethoxy)ethanol (2.07 g, 17 mmol) in THF (75 mL) was stirred overnight at room temperature. A suspension of 60% NaH in mineral oil (1.03 g, 26 mmol) and 1-pentanol (2.28 g, 26 mmol) was stirred (50−65 °C) overnight. Poly(dichlorophosphazene) (2.0 g, 17 mmol) was dissolved in THF (450 mL) and the mixture was stirred (40−50 °C) overnight. The THF solution of the sodium salt of 2-(2′-methoxyethoxy)ethanol was added dropwise to the warm (40−50 °C) polymer solution, and the mixture was stirred overnight. The THF solution of the sodium salt of 1-pentanol was allowed to cool and was then added dropwise to the partially substituted polymer solution, and the mixture was stirred warm (50−65 °C) overnight. The solvent was removed by rotary evaporation to leave a viscous solution which was dialyzed against water (7 days). All the polymers showed some degree of insolubility in water because of the presence of the alkyl side chains. Polymers **4**−**10** were then dialyzed in methanol (7 days) and polymer **11** in 1-propanol (7 days). Full characterization is given in Tables 2−4.

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