Influence of Terminal Phenyl Groups on the Side Chains of Phosphazene Polymers: Structure−Property Relationships and Polymer Electrolyte Behavior

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ABSTRACT: A series of single- and mixed-substituent polyphosphazenes with a combination of 2-(2-methoxyethoxy)ethoxy and 2-(2-phenoxyethoxy)ethoxy side groups were synthesized and evaluated to determine the effect of variations in side group ratios on the physical properties and ionic conductivity of gels. The 2-(2-phenoxyethoxy)ethoxy side groups increased the T_g values of both the solid polyphosphazenes and the gel electrolytes relative to the control polymer poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) but decreased the ionic conductivity. Specifically, as the content of 2-(2-phenoxyethoxy)ethoxy side groups increased, the glass transition temperatures (T_g) also increased, from −79 °C for MEEP to −21 °C for poly[bis(2-(2-phenoxyethoxy)ethoxy)phosphazene]. A gel polymer electrolyte derived from MEEP had an ionic conductivity of 3.9×10^{-4} S/cm at 25 °C, one of the highest measured for a MEEP-type system. The gel electrolyte derived from the polymer with all phenyl-terminated substituents had an ionic conductivity of 1.8×10^{-5} S/cm at 25 °C, and those from mixed-substituent polymers increased with increasing 2-(2-methoxyethoxy)ethoxy side group content. The gel electrolyte derived from a polymer with a 60:40 ratio of 2-(2-methoxyethoxy)ethoxy to 2-(2-phenoxyethoxy)ethoxy side groups gave the best compromise between dimensional stability and conductivity, with a T_g of −61 °C and an ionic conductivity of 1.2×10^{-4} S/cm.

Introduction

Polymer electrolyte systems offer numerous advantages over conventional liquid electrolytes in metallic lithium-based power storage and especially in large-scale applications. The flammability of liquid electrolytes and the need for electrolyte containment in many current lithium batteries are impediments for their use in many challenging applications.[1,2] Solid polymer electrolytes (SPEs) avoid the leakage and flammability problems of liquid systems but have limited ionic conductivity due to the slow rate of ion transport through the solid polymer matrix.[3] Gel polymer electrolytes (GPEs) incorporate an organic liquid electrolyte into a polymer−salt matrix to plasticize the polymer and increase ion transport. This achieves a compromise between the dimensional stability of solid electrolytes and the high conductivity of liquids.[4] The best solvent-free ion-conductive polymers are completely amorphous, have glass transition temperature (T_g) values well below room temperature, and have viscous, gumlike properties.[3] One of the best-known examples is poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP, **1**) (Figure 1), which is a soft, adhesive elastomer.[5,6] This polymer flows under slight pressure, and rechargeable batteries based on MEEP electrolytes often require a porous inert separator to prevent short circuiting of the electrodes. Here, we describe a modification of MEEP by the introduction of 2-(2-phenoxyethoxy)ethoxy cosubstituent groups to reduce the fluidity. The effect of this change on the T_g and on ionic conductivity was evaluated.

The mechanism of ion conduction in GPEs is a subject of keen interest. Studies of gels made from polymers which interact minimally with lithium salts support a mechanism for ion conduction that depends mainly on the participation of the liquid plasticizer.[7] However, investigations of GPEs that contain strongly ionically coordinating polymers support an alternative mechanism which depends on polymer segmental motion.[8,9] Some evidence also exists for a dependence of ionic conductivity on polymer motion in GPEs even in noncoordinative polymers.[10,11] Only when very high loadings of a solvent (>40% w/w) are reached do the liquid components play a significant role in ion conduction in ion-conductive polymers.[3,4]

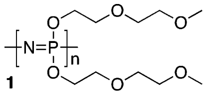

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Figure 1. Structure of MEEP.

Two of the most studied polymer electrolyte materials are poly(ethylene oxide) (PEO) and MEEP. Ionic conductivity values for MEEP of 2.6×10^{-5} S/cm for a 4:1 molar ratio of polymer repeat units to lithium triflate have been reported.[5,6] GPEs derived from this polymer have even higher conductivities, exceeding 7.0×10^{-4} S/cm with the same ratio of polymer to salt in the presence of 14% (w/w) propylene carbonate.[12] Comparable PEO systems conduct at 7.7×10^{-7} S/cm in the solid state[13] and 9.1×10^{-6} S/cm in gels that contain 50 mol % propylene carbonate.[14] The high conductivity of the MEEP system relative to PEO is due to the absence of crystallinity in MEEP as well as the high flexibility of the phosphazene polymer backbone.[2] However, gel electrolytes that meet the conductivity requirement for general-purpose batteries (10^{-3} S/cm) typically have low inherent dimensional stability due to the large amount of plasticizer required.[3] This complicates the design and construction of useful energy storage devices.

One challenge in the continuing search for superior GPE materials is the development of an ion-conductive polymer that has higher dimensional stability than MEEP without an adverse

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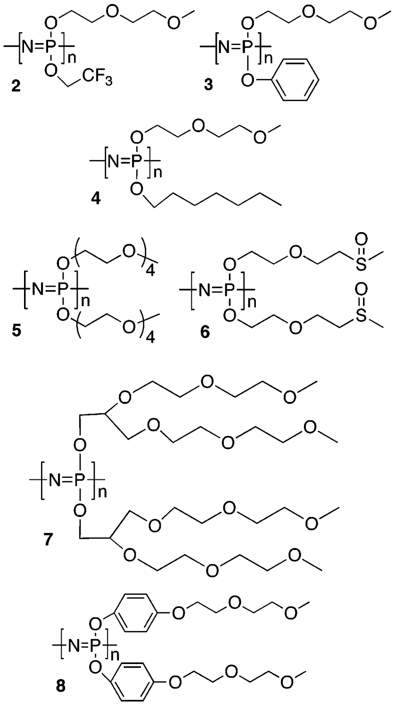


Figure 2. Polyphosphazene systems related to MEEP.

effect on the conductivity. Previous steps to combat dimensional instability and improve conductivity of MEEP-type polyphosphazenes included the incorporation of other side groups in addition to the 2-(2-methoxyethoxy)ethoxy substituent. Phenoxy,[15] alkoxy,[16,17] and 2,2,2-trifluoroethoxy[9] groups were examined as cosubstituents along with 2-(2-methoxyethoxy)ethoxy side groups (**2**−**4**) (Figure 2). The overall conclusion is that the incorporation of these cosubstituent groups decreases the ionic conductivity, particularly in cases where the cosubstituent contains no ion-coordinating sites. Previous work in our laboratory also introduced coordinative side groups that replace 2-(2-methoxyethoxy)ethoxy units entirely, such as longer linear and branched alkoxy ether chains,[18,19] alkyl ethers that bear sulfoxide and sulfone groups,[20] and phenoxy substituents with pendent oligoethyleneoxy units[15] (**5**−**8**) (Figure 2). Although approaches that focused on lengthening and branching the oligoethyleneoxy chain produced some materials that had higher dimensional stability without a strong negative effect on the ionic conductivity, the synthesis of these side groups is challenging, especially on a large scale. γ-rays[21] and UV[22] radiation have been used to cross-link MEEP to reduce its fluidity. Radiation cross-linking has a minimal effect on ionic conductivity, and this is a viable approach for the preparation of small-scale devices. Regardless of the side chain used, unplasticized polyphosphazenes still fall short of the 10^{-3} S/cm goal for ionic conductivity in practical systems.

Despite the various shortcomings of the polymers studied to date, polyphosphazenes remain an attractive platform for battery materials for numerous reasons. Primary advantages include the demonstrated thermooxidative and electrochemical stability of phosphazene materials and the inherent flexibility of the phosphazene polymer backbone, which imparts a high degree of macromolecular mobility, a key property for effective ion transport. Furthermore, the synthetic methodology of macromolecular substitution permits precise control over the ratio of side groups on a mixed-substituent polymer without the need to devise new polymerization procedures.[23] Polyphosphazenes, especially MEEP, have been shown previously to be compatible with common liquid electrolytes, such as propylene carbonate, *N*-methylpyrrolidone, and *N*,*N*-dimethylformamide in gel matrices, and to require smaller amounts of the organic additives than conventional liquid or gel electrolytes.[24]

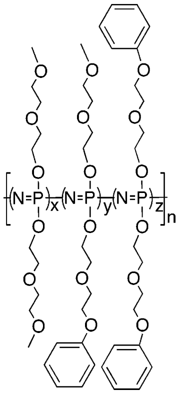


Figure 3. General structure of poly[2-(2-methoxyethoxy)ethoxy-*co*-2-(2-phenoxyethoxy)ethoxyphosphazenes] **9**−**14**.

The aim of this study was to assess the effect on T_g and on ionic conductivity following the linkage of a novel phenoxy-terminated oligoethyleneoxy side chain to a polyphosphazene skeleton (Figure 3). In previous research on cosubstituted systems based on MEEP, the best conductivities have consistently resulted from polymers that contain the most 2-(2-methoxyethoxy)ethoxy side groups.[9,17] The introduction of the 2-(2-phenoxyethoxy)ethoxy side group in the present work was intended to lower electrolyte fluidity without reducing the number of coordination sites available for ion conduction. Polyphosphazenes with phenoxy, 2-phenoxyethoxy, and short-chain phenylalkoxy substituents directly attached to the polymer backbone have much higher T_g values than MEEP,[25,26] but the linkage of phenyl or phenoxy units to the polymer backbone through tethers longer than a propoxy chain had not been investigated. The new polymers described here were studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry (DSC). Gel electrolyte samples were fabricated and were evaluated by DSC and complex impedance spectroscopy. A constant molar concentration of propylene carbonate was used in the gel samples to isolate the roles played by the liquid and polymer electrolyte.

Experimental Section

Materials. Reagent grade tetrahydrofuran (THF), methanol, hexanes, diethyl ether, NaOH (97%), and $MgSO_4$ (anhydrous, 98%) were obtained from EMD Chemicals, Inc. Lithium bis(trifluoromethanesulfonyl)imidate was obtained from 3M. *N*,*N*-Dimethylformamide (reagent grade), phenol (99%), 2-(2-chloroethoxy)ethanol (99%), 2-(2-methoxyethoxy)ethanol, NaH (95% and 60% dispersion in mineral oil), and propylene carbonate (anhydrous, 99.7%) were obtained from Aldrich Chemical Co. Potassium carbonate (anhydrous, 99.9%) was obtained from J.T. Baker. THF was purified by distillation over sodium metal and benzophenone. 2-(2-Methoxyethoxy)ethanol was dried over CaH_2 (Aldrich, 98%) and distilled under vacuum before use. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical) was recrystallized from heptane (EMD) and sublimed under vacuum (0.2 mmHg) before polymerization to form poly(dichlorophosphazene) by a previously published procedure.[27] All other reagents and solvents were used as received from the manufacturer. Substitution reactions took place under an atmosphere of dry nitrogen or argon. The polymers were exposed to air only after the substitution reactions were complete. Polymer **1** was synthesized according to a previously published procedure.[5,6]

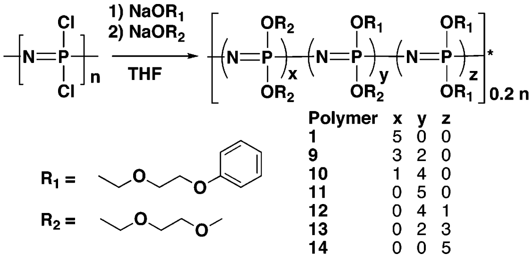
Equipment. Molecular weights were estimated using an HP 1090 gel permeation chromatograph with an HP 1047A refractive index detector by comparison of the elution times through two Phenomenex Phenogel columns to polystyrene standards using HP and Polymer Laboratories Chemstation software. Samples were eluted with a 10 mM solution of tetrabutylammonium nitrate in THF at a rate of 1.0 mL/min. Thermal analyses were performed using a Thermal Advantage DSC-Q10 differential scanning calorimeter. Thermal transitions for polymers and gel polymer electrolytes were examined between −100 and 100 °C at a heating rate of 10 °C/min. Polymer **1** was examined from −150 to 100 °C at the same heating rate. All NMR spectra were obtained using a Bruker AMX 360 spectrometer with multinuclear (^{1}H (360.13 MHz), ^{13}C (90.56 MHz), ^{31}P (145.47 MHz)) probe, except the ^{13}C spectra of polymers **1**, **11**, and **14**, which were obtained with use of a Bruker DRX-400 spectrometer (100.62 MHz). ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent, d_2-methylene chloride, or *d*-chloroform. ^{31}P NMR spectra were referenced externally to 85% phosphoric acid. Impedance data were acquired with an HP 4192A LF impedance analyzer with a measurement frequency range of 5 Hz−13 MHz. The operating potential was 0.1 V. Ionic conductivities were measured by complex impedance spectroscopy over a temperature range from 22 to 80 °C. GPE samples were sandwiched between platinum plates with a Teflon spacer, and this assembly was held between aluminum blocks in a Teflon holder.

2-(Phenoxyethoxy)ethanol. Phenol (24.9 g, 265 mmol) and K_2CO_3 (50.0 g, 361 mmol) were suspended in *N*,*N*-dimethylformamide (DMF) (500 mL) with vigorous stirring for 30 min before 2-(2-chloroethoxy)ethanol (29.88 g, 240 mmol) was added. The mixture was then stirred and heated at reflux for 24 h. The product solution was filtered, and the DMF was removed by vacuum distillation. The crude product was dissolved in diethyl ether (300 mL) and washed with 0.5 M NaOH(aq) (5 × 100 mL). The ether layer was dried over $MgSO_4$ for 18 h and filtered. The ether was removed by rotary evaporation, leaving 13.8 g of a pale yellow liquid product (31.4% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.20 (m, 2H, Ar *m-H*), 6.90 (m, 1H, Ar *p-H*), 6.87 (m, 2H, Ar *o-H*), 4.05 (t, $J = 4.7$ Hz, 2H, PhOCH_2CH$_2$O), 3.79 (t, $J = 4.7$ Hz, 2H, PhOCH$_2$CH_2O), 3.68 (t, $J = 4.7$ Hz, 2H, OCH_2CH$_2$OH), 3.59 (t, $J = 4.7$ Hz, 2H, OCH$_2$CH_2OH), 2.29 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ (ppm) 158.4 (Ar *o-C*), 129.2 (Ar *m-C*), 120.7 (Ar *p-C*), 114.7 (Ar C−O), 72.5 (OCH$_2$CH$_2$OH), 69.4 (PhOCH$_2$CH$_2$O), 67.0 (PhOCH$_2$CH$_2$OH), 61.4 (OCH$_2$CH$_2$OH).

60/40-Poly[(2-(2-methoxyethoxy)ethoxy)-*co*-(2-(2-phenoxyethoxy)ethoxy)phosphazene] (Polymer 10). This example is representative of the procedures used to synthesize a range of polymers (**9**−**13**) with different side group ratios. 2-(2-Phenoxyethoxy)ethanol (2.51 g, 13.8 mmol) was added to a suspension of 95% NaH (0.366 g, 14.5 mmol) in anhydrous THF (50 mL), and the mixture was stirred for 18 h. The burgundy-colored solution was added by syringe to a solution of poly(dichlorophosphazene) (2.00 g, 17.2 mmol) in THF (200 mL), and the mixture was held at a gentle reflux for 18 h. 2-(2-Methoxyethoxy)ethanol (3.18 g, 26.5 mmol) was added to a suspension of 95% NaH (0.610 g, 24.1 mmol) in anhydrous THF (50 mL) and stirred 18 h. This yellow solution was added by syringe to the partially substituted polymer reaction mixture, and the mixture was refluxed for 24 h. The reaction mixture was then transferred to dialysis tubing (MWCO 12−14 kDa) and dialyzed against deionized water (9 × 6 L). The dialysis solvent was then changed to THF (3 × 4 L). The solvent was evaporated, and the residual solid polymer was redissolved in a minimum amount of THF and precipitated into hexanes. The polymer was dried under vacuum (40 °C, 0.1 mmHg) for 3 days to yield 3.07 g (53.5% yield) of an adhesive elastomer.

Poly[bis(2-(2-phenoxyethoxy)ethoxy)phosphazene] (Polymer 14). 2-(2-Phenoxyethoxy)ethanol (11.1 g, 60.6 mmol) was added to a suspension of 95% NaH (1.53 g, 60.6 mmol) in anhydrous THF (100 mL) and allowed to react for 18 h. The resulting burgundy-colored solution was added to a solution of poly(dichlorophosphazene) (3.50 g, 22.5 mmol) in THF (300 mL), and the mixture was stirred at room temperature for 5 h. The mixture was then heated to 50 °C for an additional 5 h. The volume was reduced by rotary evaporation, and the product was precipitated into hexanes. The polymer was dialyzed (MWCO 12−14 kDa) against a mixture of deionized water and methanol (9 × 8 L). The solvent was removed, and the residual solid was redissolved in a minimal amount of THF and precipitated into hexanes. The polymer was then dried under vacuum (40 °C, 0.1 mmHg) for 3 days to give 8.13 g (88.7% yield) of a firm rubbery elastomer.

Scheme 1. Synthesis of Poly[(2-(2-methoxyethoxy)ethoxy)-*co*-(2-(2-phenoxyethoxy)ethoxy) phosphazenes] 1 and 9−14



Polymer	x	y	z
1	5	0	0
9	3	2	0
10	1	4	0
11	0	5	0
12	0	4	1
13	0	2	3
14	0	0	5

Fabrication of Polymer Electrolytes. Gel polymer electrolyte samples were fabricated to maintain an 8:1:6.3 mole ratio of polymer repeat units to lithium bis(trifluoromethanesulfonyl)imidate (LiTFSI) to propylene carbonate. This ratio of components corresponds to 15−20% (w/w) in propylene carbonate, depending on the molecular weight of the polymeric repeat unit. The 8:1 ratio of polymer to salt was chosen because it gave the highest conductivity in a preliminary evaluation of SPEs derived from polymer **10**. Polymer (0.3 g), LiTFSI, and propylene carbonate were combined in the appropriate amounts in 10 mL of anhydrous THF. The THF was then allowed to evaporate over 3 days under a blanket of dry nitrogen. The samples were dried under vacuum for 5 h at room temperature and were then transferred to a glovebox with an atmosphere of dry argon. The propylene carbonate content was estimated by ^{1}H NMR before and after the drying to verify minimal loss of this compound under vacuum conditions.

Solid polymer electrolyte samples were fabricated from polymer **10** by a similar method. Polymer (0.3 g) and LiTFSI were combined in 10 mL of anhydrous THF in mole ratios of 4:1, 8:1, and 16:1. The solvent was allowed to evaporate in a nitrogen-flushed environment over 3 days. The samples were dried under vacuum at 40 °C for 7 days and then transferred to a glovebox with an atmosphere of dry argon.

Results and Discussion

Polymer Synthesis and Characterization. All the polymers were synthesized according to the reactions shown in Scheme 1. Polymer **1** had been previously synthesized,[5,6] while polymers **9**−**14** were prepared for the first time. Poly(dichlorophosphazene) was obtained via the thermal ring-opening polymerization of hexachlorocyclotriphosphazene and was then treated sequentially with stoichiometric amounts of sodium 2-(2-phenoxyethoxy)ethoxide and excess sodium 2-(2-methoxyethoxy)ethoxide to ensure full substitution. NMR and molecular weight characterization data for polymers **1** and **9**−**14** are presented in Table 1. Several syntheses have been published for 2-(2-phenoxyethoxy)ethanol.[28−31] For this work, this compound was obtained by reaction of 2-(2-chloroethoxy)ethanol with phenol in a manner similar to that published by Ashton and co-workers.[31] Characterization data for this compound agreed with those published previously.

Polymer **1** was a soft gum, whereas polymer **14** was an adhesive elastomer. Polymers **9**−**13** had intermediate properties, becoming firmer with increasing content of the 2-(2-phenoxyethoxy)ethoxy side group. A single peak was detected in the ^{31}P NMR spectrum for the mixed-substituent polymers **9**−**13**, probably because the chemical shifts for the respective single-substituent polymers **1** and **14** were identical. In polymers **9**−**13**, 12 ^{13}C NMR peaks are detected, although 13 were expected.

Table 1. Characterization Data for Polymers 1 and 9−14

polymer	actual side group ratio (R_1:R_2)	^{1}H NMR δ (ppm)[a]	^{31}P NMR δ (ppm)	^{13}C NMR δ (ppm)	M_w (kDa)	M_n (kDa)	PDI
1	N/A	4.16 (br s, 2H), 3.74 (br m, 4H), 3.62 (br s, 2H), 3.46 (br s, 3H)	−8.0 (s)	72.3,70.7, 70.6, 65.5, 58.9	638	403	1.6
9	20:80	7.17 (br m, 2H$_P$), 6.90 (br m, 3H$_P$), 4.14 (br s, 2H$_P$), 3.98 (br s, 2H$_M$), 3.75 (br s, 2H$_P$), 3.65−3.50 (br m, 4H$_P$ + 4H$_M$), 3.41 (br s, 2H$_M$), 3.25 (br s, 3H$_M$)	−8.0 (s)	159.3, 129.8, 120.9, 114.8, 72.3, 70.9, 70.6, 70.4, 69.9, 67.6, 65.5, 59.2	418	178	2.4
10	37:63	7.4 (br m, 2H$_P$), 6.9 (br m, 3H$_P$), 4.2−4.0 (br m, 4H$_P$ + 2H$_M$), 3.87 (br s, 2H$_P$), 3.79 (br s, 2H$_P$), 3.70 (br s, 2H$_M$), 3.61 (br s, 2H$_M$), 3.48 (br s, 2H$_M$), 3.28 (br s, 3H$_M$)	−8.0 (s)	159.3, 129.8, 121.0, 114.8, 72.3, 71.0, 70.8, 70.7, 69.6, 67.7, 65.6, 59.0	703	351	2.0
11	45:55	7.20 (br s, 2H$_P$), 6.87 (br m, 3H$_P$), 4.2−4.0 (br m, 4H$_P$ + 2H$_M$), 3.8−3.5 (br m, 4H$_P$ + 6H$_M$), 3.4−3.3 (br m, 3H$_M$)	−8.0 (s)	159.2, 129.7, 120.9, 114.8, 72.2, 70.9, 70.8, 70.6, 69.9, 67.6, 65.5, 58.9	262	86	3.0
12	63:37	6.98 (br s, 2H$_P$), 6.67−6.60 (br m, 3H$_P$), 3.95−3.85 (br m, 2H$_P$ + 2H$_M$), 3.74 (br s, 2H$_P$), 3.4−3.3 (br m, 4H$_P$ + 2H$_M$), 3.28 (br s, 2H$_M$), 3.2−3.0 (br m, 5H$_M$)	−8.0 (s)	159.2, 129.8, 121.0, 114.8, 72.3, 71.0, 70.8, 70.6, 69.9, 67.6, 65.6, 59.0	309	124	2.5
13	83:17	7.29 (br s, 2H$_P$), 6.97 (br m, 3H$_P$), 4.26 (br m, 2H$_P$ + 2H$_M$), 4.03 (br s, 2H$_P$), 3.80 (br m, 4H$_P$ + 2H$_M$), 3.65−3.38 (br m, 5H$_M$)	−8.0 (s)	159.1, 129.8, 120.9, 114.7, 72.2, 70.9, 70.7, 70.6, 69.8, 67.5, 65.6, 58.9	546	155	3.5
14	N/A	7.14 (t, J = 7.1 Hz, 2H), 6.76 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 4.15 (br s, 2H), 3.80 (br s, 2H), 3.65−3.55 (br m, 4H)	−8.0 (s)	158.9, 129.5, 122.6, 120.7, 114.5, 70.6, 69.6, 67.3, 65.3	1220	442	2.7

[a] Peak integrations in the ^{1}H NMR spectra were identified by the number of protons from each side group: H$_M$ for the 2-(2-methoxyethoxy)ethoxy and H$_P$ for the 2-(2-phenoxyethoxy)ethoxy side groups.

Table 2. Ionic Conductivity and Glass Transition Temperature Data for Polymers 7−13 and their GPEs 7a−13a[a]

polymer	T_g (°C, neat)	T_g (°C, GPE)	σ (25 °C, 10^{-5} S/cm)
1	−79	−77	39
9	−66	−67	22
10	−56	−61	12
11	−48	−52	7.3
12	−37	−43	4.3
13	−27	−38	1.9
14	−21	−39	1.8

[a] The GPEs consist of an 8:1:6.3 molar ratio of polymer (by repeat unit), LiTFSI, and propylene carbonate.

Table 3. Glass Transition Temperatures for Polymers 1−6

polymer	T_g (°C)	ref
2	−75 to −55[a]	9
3	−55	15
8	−36	15
poly[bisphenoxyphosphazene] (**15**)	−7	25
poly[bis(2-phenoxyethoxy)phosphazene] (**16**)	−8	25
poly[bis(3-phenylpropoxy)phosphazene	−47	26

[a] This range refers to a set of polymers of type **2** with ratios of 2,2,2-trifluoroethoxy and 2-(2-methoxyethoxy)ethoxy substituents ranging from 4:1 to 1:4.

This may be due to an overlap of two peaks from the 2-(2-methoxyethoxy)ethoxy and 2-(2-phenoxyethoxy)ethoxy substituents because polymers **1** and **14** showed ^{13}C peaks at 70.6 ppm. Different batches of poly(dichlorophosphazene) were used in the synthesis of polymers **1** and **9−14**, and the variation of molecular weights (M_w 260−1200 kDa) is attributed to differences between individual batches of poly(dichorophosphazene). The organic-substituted polymers were soluble in common organic solvents, such as tetrahydrofuran (THF), dichloromethane, chloroform, or acetone. Polymers **1** and **9** were also soluble in methanol or water.

Thermal Analysis. *Glass Transitions of Polymers* ***1*** *and* ***9−14.*** A single T_g was detected for each of the pure polymers **1** and **9−14**, which suggested an amorphous morphology (Table 2). The T_g values of polymers **1** and **9−14** increased linearly with increasing content of the 2-(2-phenoxyethoxy)ethoxy side group (Figure 4), which is a typical behavior for a randomly substituted mixed-substituent polyphosphazene system. The following discussion will mainly address polymers **1** and **14** because these polymers best illustrate the contrast in properties across the series.

Comparisons to other polyphosphazenes that contain phenyl groups (Table 3) show that polymer **14** has a lower T_g than poly[bisphenoxyphosphazene] (**15**) and poly[bis(2-phenoxyethoxy)phosphazene] (**16**), but a higher T_g than poly[bis(3-phenylpropoxy)phosphazene] and polymers **3** and **8**. The decrease in T_g from polymers **15** and **16** is probably due to increased side group mobility brought about by the extension of the oligoethoxy chain. The lower T_g of polymer **8** relative to polymer **14** indicates that the chain-stiffening effect of substituents with similar oligoethyleneoxy content, but different phenyl ring placement is greater when the phenoxy group is not adjacent

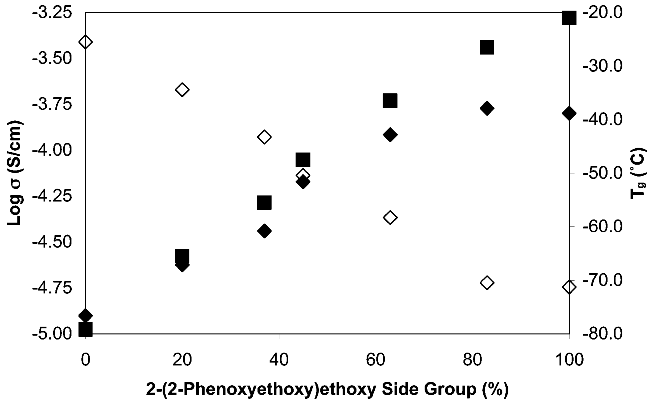


Figure 4. T_g values of polymers **1** and **9−14** (■) and of GPEs **1a** and **9a−14a** (◆) and ionic conductivity of GPEs **1a** and **9a−14a** at 25 °C (◇) as a function of 2-(2-phenoxyethoxy)ethoxy side group content.

Table 4. Glass Transition Temperatures and Ionic Conductivities of Several Comparable GPE Systems

polymer	Li + salt	mole ratio	plasticizer	T_g (°C)	σ_{25} (S/cm)	ref
10	LiTFSI	8:1	none	−45	1.9×10^{-5}	this work
PEO	LiTFSI	4:1	none	−40	5×10^{-5}	41
PEO	$LiSO_3CF_3$	9:1	PC (50%)[a]	none reported	9.0×10^{-6}	14
1	$LiSO_3CF_3$	4:1	PC (14%)	−95	7×10^{-4}	12
2	$LiSO_3CF_3$	9:1	PC (22%)	−74 to −76[b]	5.1×10^{-5}–2.9×10^{-4} [b]	9

[a] PC stands for propylene carbonate. The value in parentheses is the weight percent. [b] This range refers to a set of polymers of type **2** with ratios of 2,2,2-trifluoroethoxy and 2-(2-methoxyethoxy)ethoxy substituents ranging from 4:1 to 1:4.

to the polymer backbone. The similarity in T_g values of polymers **3** and **10** also suggests strong interactions between the aromatic portions of the side groups, even when the phenoxy units are not constrained by the motions of the polymer backbone.

The high T_g of polymer **14** relative to polymers **1**, **2**, **3**, and **8**, and the steady increase in T_g with increasing content of the 2-(2-phenoxyethoxy)ethoxy side group, is attributed to increased interactions between side chains, which may include both side chain entanglement and π-stacking of the phenyl rings. In polymers of type **2**, the T_g increased by 20 °C when the long, flexible 2-(2-methoxyethoxy)ethoxy side groups were replaced by the shorter 2,2,2-trifluoroethoxy side groups.[9] A larger increase in T_g ($\Delta T = 35$ °C) was measured as the proportion of bulky 2-(2-phenoxyethoxy)ethoxy substituents increased from 20% in polymer **9** to 100% in polymer **14**. In this series of polymers, the phenoxy termini of the 2-(2-phenoxyethoxy)ethoxy side groups may impede motion of the smaller 2-(2-methoxyethoxy)ethoxy cosubstituents. Evidence of $\pi-\pi$ interactions has been reported for polyphosphazene **15** and the analogous cyclophosphazene trimer ($n = 3$) in solution and in the solid state by excimer fluorescence.[32−35] There is additional evidence for π-stacking in organic polymers with a high proportion of phenyl rings. π-Stacking behavior has been predicted in polystyrene by computational modeling[36,37] and confirmed by excimer fluorescence,[38] by scanning tunneling microscopy of nanoparticles,[39] and by X-ray diffraction studies of bulk polymer.[40] Although polymer **15** is semicrystalline, the π-stacking in polystyrene is short-range and does not affect the amorphous morphology, which suggests that a polymer such as **14** need not be crystalline in order to experience strong short-range interactions among its side groups.

*Glass Transitions of GPEs from Polymers **1** and **9**−**14** with LiTFSI and Propylene Carbonate.* A single T_g was detected for each of the GPEs derived from polymers **1** and **9**−**14** (referred to as GPEs **1a** and **9a**−**14a**, respectively), which suggests a homogeneous composition and a retention of the amorphous morphology found in the pure polymers (Table 2). The T_g values of the GPEs that contain propylene carbonate and LiTFSI increased progressively with increasing 2-(2-phenoxyethoxy)ethoxy side group content, and the viscosity increased with the T_g, as was the case with the solvent-free polymers (Figure 4). The T_g values for all the GPEs, except **1a**, were lower than those of the pure polymers. The plasticizing effect of propylene carbonate was enhanced with increasing 2-(2-phenoxyethoxy)ethoxy side group content. A similar effect was detected in polymers of type **2** with increasing proportions of 2,2,2-trifluoroethoxy substituents.[9] The increase in plasticization could be due to several effects. The bulk of the phenyl ring of the 2-(2-phenoxyethoxy)ethoxy side group could decrease the availability of the adjacent etheric oxygens for interaction with lithium ions and reduce transient cross-link formation. Alternatively, stronger solvation of the 2-(2-phenoxyethoxy)ethoxy side group by propylene carbonate might better disrupt the interactions between the phenyl rings on the substituents, which are suspected to induce the high T_g values in the pure polymers.

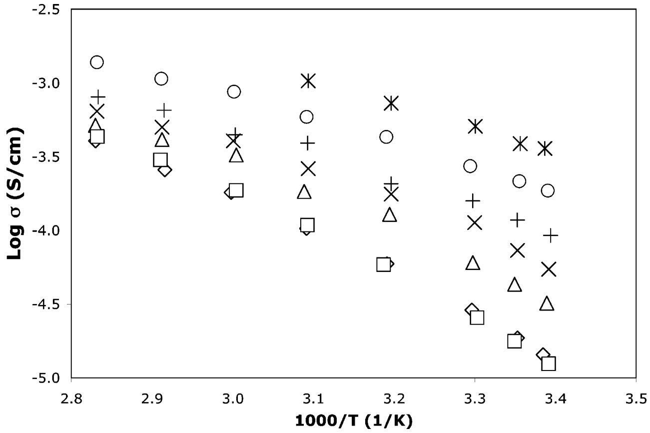


Figure 5. Arrhenius plot of the conductivity of GPEs **1a** (*), **9a** (○), **10a** (+), **11a** (×), **12a** (△), **13a** (◇), and **14a** (□).

Although LiTFSI apparently plasticizes PEO,[41] the decrease in T_g for the polymers discussed here with significant amounts of 2-(2-phenoxyethoxy)ethoxy side groups is not primarily due to this effect. The T_g of the SPE derived from polymer **10** (Table 4) was higher than that of the pure polymer. The addition of propylene carbonate lowered the T_g below that of the pure polymer. The T_g of a MEEP GPE decreased with higher lithium triflate content and slightly lower weight percent of propylene carbonate compared to the pure polymer (Table 4),[12] whereas in this study a slight increase in T_g was found for GPE **1a**. On the basis of these observations, it is unlikely that the LiTFSI has a significant plasticizing effect on polymers **1** and **9**−**14**.

Ionic Conductivity. As observed in previous studies,[9,17] the most highly conductive GPEs in the series **1a** and **9a**−**14a** contained the highest proportion of 2-(2-methoxyethoxy)ethoxy side groups. GPE **1a** had the highest ionic conductivity of these seven systems, with a value of 3.9×10^{-4} S/cm at 25 °C. The conductivity of GPE **14a** was 1.8×10^{-5} S/cm, and those of GPEs **1a** and **9a**−**14a** decreased linearly with increasing 2-(2-phenoxyethoxy)ethoxy side group content, a trend which correlates well with increasing T_g (Figure 4). The room temperature conductivity data are summarized in Table 2.

As shown in Figure 5, the log conductivity of each GPE increased linearly with increasing temperature. At temperatures above 25 °C, the variation in conductivity between the polymers became less pronounced. The conductivities span one and a half orders of magnitude at 25 °C, whereas at 80 °C the conductivity values span only one-third of that range. This trend mirrors the increased plasticization effect of propylene carbonate as the content of the 2-(2-phenoxyethoxy)ethoxy side group increased and bolsters the idea that side group interactions are a major factor in the increased T_g values in the bulk polymers.

The elevated ionic conductivities of GPEs with increasing percentages of 2-(2-methoxyethoxy)ethoxy cosubstituents in this study suggest that the mechanism of ion conduction is strongly dependent on the local motions of the polymer chains. The constant molar concentration of the sample components eliminates the plasticizer and salt concentrations as variables that determine the origins of effects on ionic conductivity. This corroborates previous work in which GPEs of various ion-conductive polymers were examined at a constant weight percentages of plasticizer.[4,8,9]

The room temperature conductivities of the GPEs in this study compare favorably to previously studied systems based on MEEP, polymers of type **2**, or PEO (Table 3). The conductivity of GPE **1a** is half that of the highest reported conductivity for MEEP at this concentration of additive.[12] Delocalization of the charge in the TFSI anion generally leads to increased dissociation of the lithium salt, to better ion solvation by polymeric media, and ultimately to a greater availability of lithium ions for transport through polymer or gel matrices relative to more traditional species such as lithium triflate or lithium perchlorate;[4,13,41] however, the larger concentration of lithium triflate in the previously studied sample of polymer **1** may account for its greater measured conductivity. GPEs **1a** and **9a−11a** exceed the room temperature conductivities of polymers of type **2**, though the conductivities of the present system decreased more sharply as the content of 2-(2-methoxyethoxy)ethoxy cosubstituent decreased despite the presence of ion-coordinating sites on the 2-(2-phenoxyethoxy)ethoxy side group. GPEs **1a** and **9a−14a** all exceeded the room temperature conductivity of a PEO GPE with lithium triflate and propylene carbonate,[14] but only GPEs **1a** and **9a−11a** exceeded those of a PEO SPE which used LiTFSI as the salt.[41] The relatively poor performance of GPEs **12a−14a** in comparison to solid PEO:LiTFSI systems is possibly due to (a) the decreased crystallinity in the PEO caused by the plasticizing effect of LiTFSI and (b) the disruption of polymer chain and ion motion by the large proportion of bulky, non-ion-coordinating terminal phenoxy units in polymers **12−14**, despite the similarity in T_g values for all four electrolyte systems.

Conclusions

Polymers **1** and **9−14** were synthesized as amorphous elastomers and were evaluated for use as dimensionally stable gel polymer electrolytes (GPEs). The polymers were characterized by standard techniques, including multinuclear NMR, gel permeation chromatography, and differential scanning calorimetry (DSC). A linear correlation was found between increasing content of the 2-(2-phenoxyethoxy)ethoxy side groups and increased T_g, which is consistent with the structure of a randomly cosubstituted polyphosphazene system. The dimensional stability, as determined by visual inspection and handling, increased with T_g.

GPEs of polymers **1** and **9−14** containing propylene carbonate and LiTFSI were evaluated by DSC and complex impedance analysis. Most GPEs had lower T_g values than the respective pure polymers, which is consistent with plasticization by propylene carbonate. The same linear increase in T_g with 2-(2-phenoxyethoxy)ethoxy side group content was detected for the GPE samples as for the pure polymers. The ionic conductivities of GPE samples at 25 °C ranged from 1.8×10^{-5} S/cm (GPE **14a**) to 3.9×10^{-4} S/cm (GPE **1a**). GPEs with intermediate side group compositions showed a linear increase in conductivity with increasing 2-(2-methoxyethoxy)ethoxy side group content and decreasing T_g. The ionic conductivity values measured for these GPEs compare well those of GPE systems derived from polymer **2** or PEO. GPE **10a** provided the best compromise between high ionic conductivity and dimensional stability, with a T_g of −61 °C and an ionic conductivity of 1.2×10^{-4} S/cm at 25 °C. The dimensional stability of this polymer system could be increased further by light cross-linking using UV or γ-ray radiation techniques, as described previously for MEEP (**7**).[21,22] Further experiments are necessary to determine the exact nature of the side group interactions that lead to the dramatic increase in T_g from polymer **1** (−79 °C) to polymer **14** (−21 °C).

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