Effect of Oligo(ethyleneoxy)cyclotriphosphazenes, Tetraglyme, and Other Small Molecules on the Ionic Conductivity of the Poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)/Lithium Triflate System

Harry R. Allcock,* Ramakrishna Ravikiran, and Stephen J. M. O'Connor

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

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ABSTRACT: Four small molecule cyclotriphosphazenes bearing linear and branched ethyleneoxy units have been synthesized as ion transport assistance (ITA) species to improve the ionic conductivity of poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)−lithium triflate systems. The cyclotriphosphazenes were characterized by ^{31}P, ^{1}H, and ^{13}C nuclear magnetic resonance spectroscopy and infrared spectroscopy. MEEP was complexed with lithium triflate and combined with different amounts of each of the ITA molecules. Room temperature conductivity measurements and differential scanning calorimetry experiments were carried out on each of these mixtures. The effect of concentration of the ITA molecules and salt on the ionic conductivity of MEEP is reported. The general trend observed is an increased conductivity with increasing ITA molecule concentration. The effect of branching in the ITA molecule on the ionic conductivity was studied by comparing influence of branched versus linear side groups. Differential scanning calorimetry data indicate that these small molecules play a role in ionic cross-linking. The influence of high dielectric solvents on the ionic conductivity of MEEP/$LiSO_3CF_3$ systems was also studied. These solvents generated higher conductivities at the same concentration than did the cyclotriphosphazene ITA species.

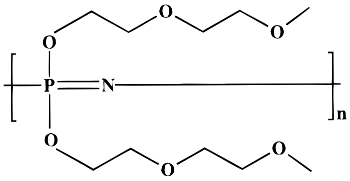
Introduction

The design of new solid polymer electrolytes is a major challenge that underlies future developments in lightweight robust energy storage devices, flat panel displays, light emitting devices, and supercapacitors. Solid polymer electrolytes are expected to permit the design of impact-resistant, safer devices that can readily be fabricated into intricate shapes. The fundamental composition of such materials is that of a salt dissolved in a suitable polymer.

Two basic requirements are needed for an effective solid polymer electrolyte. These are as follows: (1) the polymer should contain highly flexible macromolecules that provide a conduit for the passage of ions; (2) it should possess coordination sites that assist salt dissolution through ion solvation and thereby favor ion pair separation. A widely accepted theory is that, in such polymers, ionic conductivity occurs via a hand-to-hand transfer of ions from one transient coordination site to another facilitated by the thermal motions of the polymer chains and their side groups.[1−6] The use of a salt with a bulky counterion such as the triflate anion is usually necessary in order to assist the ion solvation and ion pair separation processes.

Most of the existing studies on solid polymer electrolytes have used poly(ethylene oxide) (PEO) as a matrix for salts such as lithium triflate. This follows an original discovery by Wright[7] that stimulated interest in the use of this phenomenon in battery research.[8,9] However PEO contains microcrystalline domains that inhibit ion transport. Thus, acceptable conductivities with salts such as lithium triflate can be achieved only when the material is heated to 80−100 °C. At room temperature the conductivity is only 5×10^{-8} S cm^{-1}. Attempts to outflank this problem have included the use of noncrystalline copolymers of ethylene oxide and propylene oxide, and the addition of organic solvents to the polymer-salt complex in order to disrupt crystallinity and generate a more liquid-like medium.[10−13] However this second approach carries with it the danger that significant amounts of flammable solvents could pose a hazard if the device is ruptured.

An entirely different approach is to design polymers that are specifically optimized for ion transport at room temperature or below. Poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) (**I**) is a macromolecule that was designed specifically to avoid the problems encountered with PEO.[14] MEEP shows a relatively high ionic conductivity under solvent-free conditions when complexed with lithium triflate.[15,16] For example, it gives a conductivity of 2.6×10^{-5} S cm^{-1} at 25 °C in the presence of one molecule of lithium triflate to four repeating units of the polymer. However, the use of MEEP in batteries and other devices requires that the polymer chains must be cross-linked to convert the gumlike material to a dimensionally stable substance.[10,17] An attempt has been made to generate a dimensionally stable system from blends of MEEP and PEO.[18,19] These blends yielded conductivities higher than those of PEO but well below the values for MEEP/lithium triflate alone.



MEEP

We have recently reported the synthesis of more than 30 analogues of MEEP that possess the same highly flexible backbone but with different linear and branched alkyl ether and alkoxy side chains. Some of these

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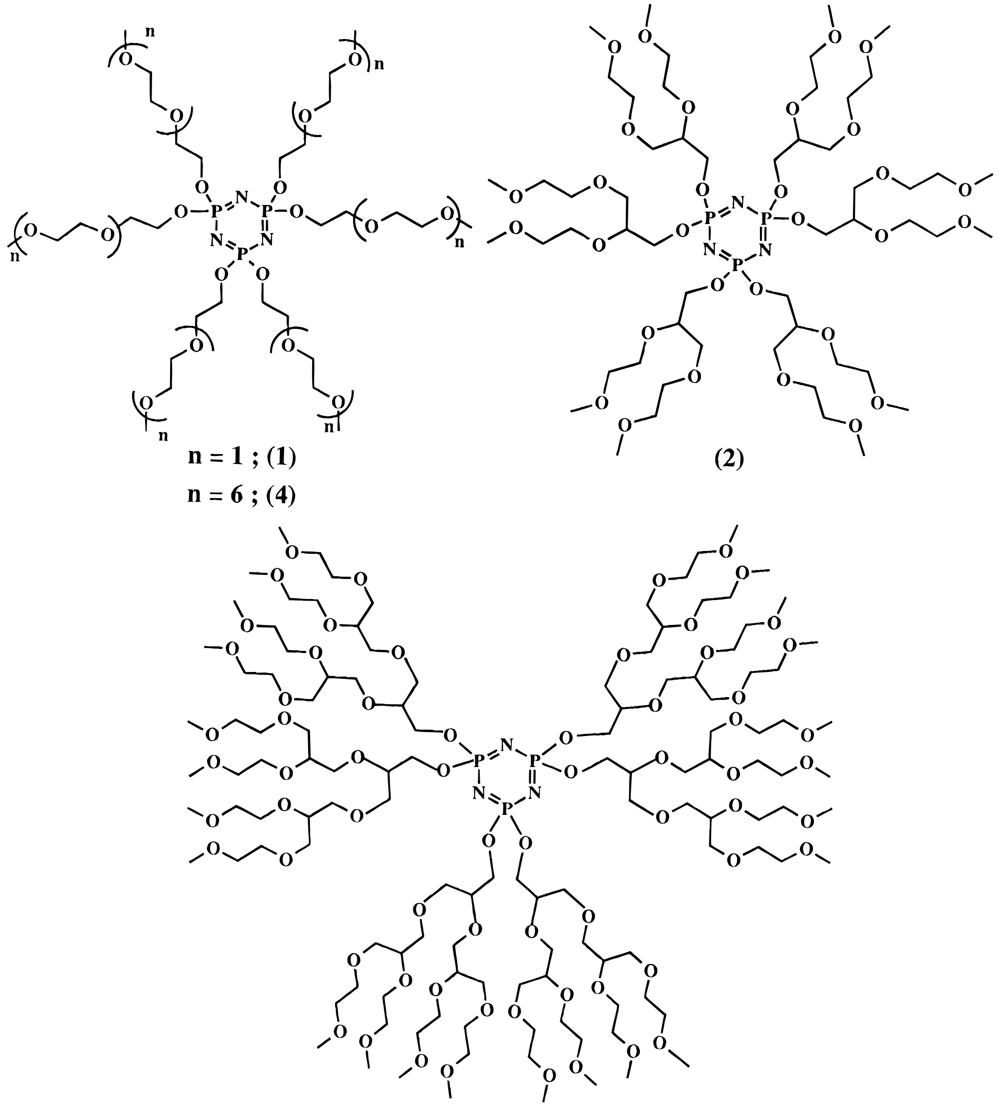
Chart 1. Cyclotriphosphazenes Synthesized



n = 1 ; (1)

n = 6 ; (4)

(2)

(3)

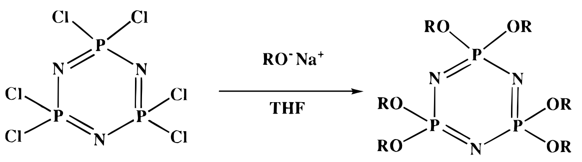
polymers yield slightly higher conductivities than found for MEEP (up to 4.8×10^{-5} S cm^{-1} at 25 °C), but the principal advantage of species with branched side chains is their dimensional stability. In other words, they can be used as the electrolyte in thin film devices without the need for polymer cross-linking. Nevertheless, even those conductivities at 25 °C fall somewhat lower than those generally preferred for device development (10^{-4}–10^{-3} S cm^{-1}). Thus, we have concluded that to achieve higher conductivities the addition of small molecules to the primary polymers may be required, hence improving ion pair separation, ion transport, or both of these factors at the same time.

With these facts in mind we have investigated the consequences of addition to MEEP/lithium triflate of small amounts of ion-coordinative small molecules in an attempt to increase the ion-pair separation and provide a more mobile coordination sphere within the polymer matrix. Two requirements were set. First, the additives should have a low volatility in order to reduce the possibility of hazards in working devices. Second, the concentrations of the additives should be small enough to avoid altering the physical state of the host polymer. Specifically, the polymer/salt/additive mixture should remain as a flexible solid and not become a liquid.

Two different approaches have been explored. First, we have designed and synthesized a series of four cyclic small molecule phosphazenes with alkyl ether side groups as possible ion transport assistance (ITA) species (Chart 1). These are molecules with low volatility, with ion-complexing abilities that should be comparable to or greater than those of MEEP and its analogues and with a compatibility with MEEP that allows solubility in the high polymer. Because these molecules have dimensions that are considerably smaller than those of the high polymers, it might be expected that their diffusion through the matrix might be higher than the reptation of a polymer. They might also assist in hand-to-hand ion transfer. Finally, as small molecules they may "plasticize" the polymer, create more free volume, and increase the overall mobility.[20,21]

Second, the influence of these cyclophosphazene ITA species was compared with that of several organic additives with high dielectric constants. These include tetraglyme, *N*-methylpyrrolidone and propylene carbonate. The concentrations of these organic additives were maintained at the same low molar levels as used for the cyclophosphazenes. In a sense, this biases the data against the organic small molecules since each cyclotriphosphazene bears multiple coordination sites. Nevertheless, the mobility of the organic small molecules

Scheme 1. General Scheme for the Synthesis of Phosphazenes 1−4



was expected to be higher than that of the cyclophosphazene ITA species.

Experimental Section

Equipment. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained by using a Bruker WM360 spectrometer. Both ^{13}C and ^{31}P spectra were proton decoupled unless otherwise specified. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield from the reference. ^{1}H and ^{13}C spectra were referenced to external tetramethylsilane. Elemental analyses were obtained by Galbraith Laboratories Knoxville, TN. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector. The samples were eluted with a 0.01 molar solution of tetra-*n*-butyl ammonium nitrate in THF. Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. All samples were heated from −100 to +75 °C. Heating rates of 10, 20, and 40 °C/min. under a nitrogen atmosphere were used. Conductivity measurements were made using a Hewlett Packard 4192A LF impedance analyzer with an ac frequency range of 5 Hz to 13 MHz. All conductivity measurements were carried out in an argon filled drybox.

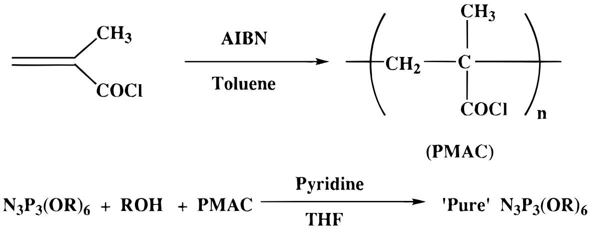
Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, (Ethyl Corp./Nippon Fine Chemical) was purified by recrystallization from hexane followed by sublimation at 40 °C (0.05 Torr). Poly(dichlorophosphazene) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[22] Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was distilled in an atmosphere of dry nitrogen before use. 2-Methoxyethanol and 2-(2-methoxyethoxy)ethanol (Aldrich) were distilled from anhydrous magnesium sulfate under vacuum onto molecular sieves. All other reagents (Aldrich) were used as received. Reactions that involved the use of chlorophosphazenes were carried out in an atmosphere of dry nitrogen or argon.

Synthesis of Poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP). The synthesis of this polymer was carried out according to a method reported previously.[15]

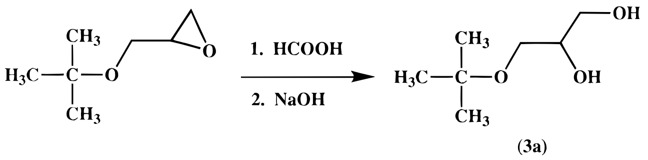
Synthesis of Cyclotriphosphazenes 1−4. The general method is shown in Scheme 1.

Hexakis(methoxyethoxyethoxy)cyclotriphosphazene (1). 2-(2-Methoxyethoxy)ethanol (9.42 mL, 0.08 mol) was added dropwise to a 500 mL 3-neck flask containing sodium (1.8 g, 0.08 mol) and freshly distilled THF (250 mL). The solution was then refluxed until all the sodium was consumed. The solution was then allowed to cool to room temperature, and to this was added hexachlorocyclotriphosphazene (4.0 g, 0.01 mol). The solution was stirred at room temperature. The reaction was complete in 2 h as indicated by ^{31}P NMR spectroscopy. The crude product was isolated by filtration and removal of the solvent under reduced pressure. The product was redissolved in chloroform and was washed with small quantities of water. The organic layer was then dried with anhydrous magnesium sulfate. The crude product was isolated by evaporation of the solvent. After purification (see later) the product was a colorless oil (8.39 g, 86%). ^{31}P NMR ($CDCl_3$), δ (ppm): 18.53 (s). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.07 (br, 2H), 3.69 (t, 2H), 3.64 (m, 2H), 3.5 (m, 2H), 3.33 (s, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 71.88, 70.49, 70.01, 65.03, 58.94. Mass spectrometry, *m*/*e*: 849 M$^+$ base peak.

Scheme 2. Purification of Phosphazenes 1−4



Scheme 3. Synthesis of 3-*tert*-Butoxy-1,2-propanediol



Hexakis[2,3-bis(2-methoxyethoxy)propoxy]cyclotriphosphazene (2). The synthesis was similar to that described for phosphazene **1**. The amounts of starting materials were as follows: 2,3-bis(2-methoxyethoxy)propanol, **3c** (16.5 g, 0.08 mol); sodium (1.8 g, 0.08 mol); hexachlorocyclotriphosphazene (3.0 g, 8 mmol). The hexachlorotriphosphazene solution was added to a warm solution of the sodium salt and the reaction was complete in a period of 2 h. After purification, a non distillable colorless oil was obtained (10.5 g, 89%). ^{31}P NMR ($CDCl_3$), δ (ppm): 18.39. ^{1}H NMR ($CDCl_3$), δ (ppm): 3.92 (br, 2H), 3.37−3.72 (m, 11H), 2.39−3.35 (br, 6H). ^{13}C NMR ($CDCl_3$), δ (ppm): 78.18, 77.78, 71.99, 71.74, 71.26, 70.60, 69.53, 67.41, 58.77. Mass spectrometry, *m*/*e*: 1377 M$^+$.

Synthesis of the starting alcohol **3d** is described later in this section.

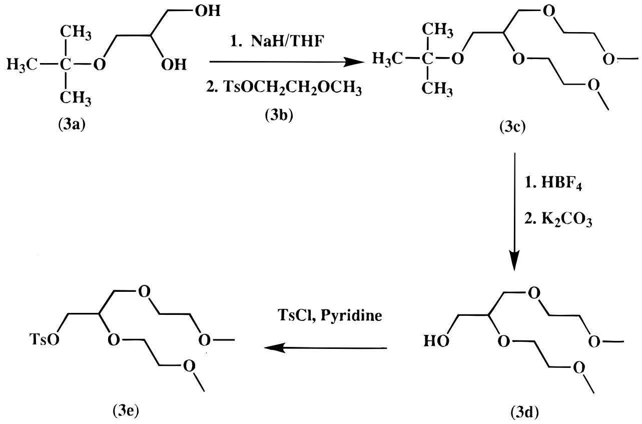
Phosphazene 3. Compound **3h** (5.0 g, 0.01 mol.) in THF was added to a mixture of sodium hydride dispersion in oil (0.5 g, 0.0125 mol) in 75 mL of freshly distilled tetrahydrofuran. To a warm solution of the sodium salt was added hexachlorocyclotriphosphazene (0.3 g, 0.86 mmol). The reaction mixture was then refluxed for a period of 3 h. The progress of the reaction was monitored by ^{31}P NMR. After completion of the reaction, the solution was filtered and the solvent removed under vacuum to obtain a yellow oil. After purification by the method described below, a viscous oil was obtained (2.01 g, 79%). ^{31}P NMR ($CDCl_3$), δ (ppm): 18.42(s). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.15 (br, 2H), 3.30−3.70 (m, 41H). ^{13}C NMR ($CDCl_3$), δ (ppm): 78.20, 75.11, 75.05, 68.60−72.91 (multiple peaks), 58.56.

Phosphazene 4. The synthesis and purification of this compound was similar to that of phosphazene **1**. The amounts of starting materials were as follows: poly(ethylene glycol) methyl ether (average $M_n \sim 350$), 27.7 g, 0.08 mol; sodium hydride (60% dispersion in mineral oil), 3.17 g, 0.08 mol; hexachlorocyclotriphosphazene, (2 g, 5 mmol). The hexachlorocyclotriphosphazene solution in THF was added to a warm solution of the sodium salt. The reaction was complete in 2 h. After purification (see below) a slightly yellow colored oil was isolated (10.04 g, 84%). ^{31}P NMR ($CDCl_3$), δ (ppm): 18.35 (s). ^{1}H NMR, δ (ppm): 4.20 (br, 2H), 3.32−3.92 (m, 31H); ^{13}C NMR ($CDCl_3$), δ (ppm): 70.56, 69.16, 68.66, 63.75, 57.48.

Purification of Phosphazenes 1−4, Using Poly(methacryloyl chloride). The technique used is illustrated in Scheme 2.[8] The crude reaction product (5.5 g), poly(methacryloyl chloride) (20.0 g, excess), pyridine (10 mL), and freshly distilled THF (300 mL) were mixed in a 500 mL, 3-neck flask. The mixture was stirred at room temperature for 24 h and then boiled at reflux for 2 h. The polymeric component was then precipitated into methanol. To precipitate the polymer completely, the mixture was heated to about 60 °C. The polymer was then removed by filtration. The product was isolated by evaporation of the solvent. Further purification was effected by either dialysis against water and methanol or by passage through a short silica gel column (10 cm, 2 cm) using hexane−THF (1:3) as the eluent.

Synthesis of Starting Alcohols 3a−h. 3-*tert*-Butoxy-1,2-propanediol (3a). Compound **3a** was prepared by the method described by Montanari and Tundo (Scheme 3).[23] *tert*-Butyl glycidyl ether (Aldrich), (141 mL, 1.0 mol) was added

Scheme 4. Synthesis of 2,3-Bis(2-methoxyethoxy)propyl Toluene-*p*-sulfonate



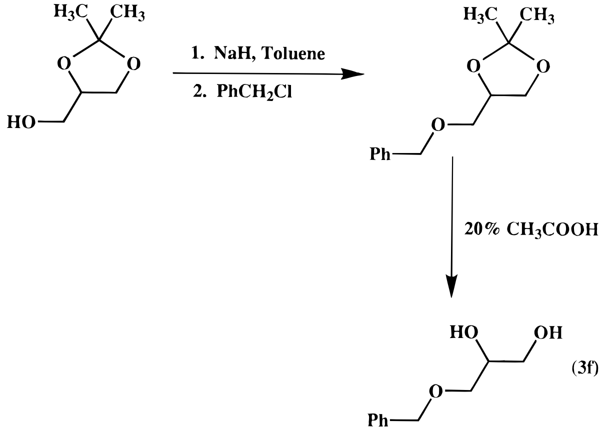
dropwise to 99% formic acid (83 mL, 2.2 mol). The reaction mixture was then stirred and the temperature was maintained below 30 °C. The mixture was stirred at room temperature for 12 h. A solution of sodium hydroxide (100 g, 2.5 mol) in 125 mL of water was added slowly, keeping the temperature below 40 °C. The organic fraction was separated, and the aqueous phase was extracted several times with dichloromethane. The combined organic fractions were dried ($MgSO_4$) and evaporated, and the oily residue was distilled under vacuum to give **3a** (75 g, 54%) as a colorless oil: (bp 55−60 °C, 0.015 Torr): IR 3400 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 3.25−4.0 (m, 7H), 1.2 (s, 9H); ^{13}C NMR ($CDCl_3$) δ (ppm) 73.5, 70.5, 64.4, 63.6, 27.16. Mass spectrometry, *m/e*: 149 MH^+ base peak.

2-Methoxyethyl Toluene-*p*-Sulfonate (3b). Compound **3b** was prepared according to a method described in the literature.[24] A slurry of *p*-toluenesulfonyl chloride (210.65 g, 1.1 mol) and pyridine (200 mL) was stirred mechanically in a three-necked, N_2-flushed flask. The temperature of the reaction mixture was maintained at approximately 5 °C (dry ice−ethanol bath), while 2-(methoxy)ethanol (76.0 g, 1.0 mol) was added slowly from an addition funnel. After the addition was complete, the mixture was stirred for 15 min. The mixture was poured into ice−water (900 mL) and was washed with dichloromethane (900 mL). The organic layer was washed with ice-cold 6 N HCl (3 × 500 mL) and dried ($MgSO_4$) and reduced to a minimum volume by evaporation under reduced pressure to yield a colorless oil (218 g, 95%) (bp 110−115 °C, 0.01 Torr): ^1H NMR ($CDCl_3$) δ (ppm) 7.3−7.7 (m, 4H, aromatic), 3.4−4.2 (m, 4H), 3.35 (s, 3H), 2.5 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) 144.5, 133.0, 129.8, 127.8, 70.0, 69.0, 58.9, 21.5. Mass spectrometry, *m/e*: 231 MH^+ base peak.

1-*tert*-Butyloxy-2,3-bis(2-methoxyethoxy)propane (3c). Compound **3** (31.0 g, 0.135 mol) was added to a slurry of the di sodium salt of 3-*tert*-butoxy-1,2-propanediol (0.062 mol), **2**, in dry THF (500 mL) (Scheme 4). The reaction mixture was stirred, heated, and maintained at reflux under an atmosphere of dry nitrogen for 24 h. The mixture was allowed to cool and was filtered, and the solvent was then removed by evaporation under vacuum. The residue was then extracted with chloroform, dried ($MgSO_4$), filtered, and solvent removed by vacuum rotary evaporation to yield a brown liquid (17.0 g). The crude product was washed with water (250 mL) and extracted with chloroform (300 mL). The organic fraction was separated from the aqueous layer and dried using anhydrous $MgSO_4$. The solvent was removed by rotary evaporation under vacuum to give a pale yellow oil (15.0 g, 94%). The crude product was distilled (bp 120−125 °C, 0.25 Torr) to give a colorless oily liquid (11.1 g, 67%): IR 2975, 2875 (CH) cm^{-1}, 1198 (COC) cm^{-1}, 1109 (COC) cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm) 3.3−3.85 (m, 19H), 1.3 (s, 9H, *tert*-butyl); ^{13}C NMR ($CDCl_3$), δ (ppm) 78.95, 72.94, 72.21, 71.92, 71.74, 70.64, 69.69, 61.73, 58.98, 58.8, 27.43. Mass spectrometry, *m/e*: 265 MH^+; 209 $(M - C(CH_3)_3)H^+$ base peak.

2,3-Bis(2-Methoxyethoxy)propanol (3d) (Scheme 4). To a solution of compound **3c** (10.0 g, 0.038 mol) in dichloromethane (100 mL) was added tetrafluoroboric acid (54% in diethyl ether), (13.7 mL). The mixture was stirred at room temperature for 20 min. The acid was neutralized with solid potassium carbonate, the inorganic salts were filtered off, and the solvent was removed by rotary evaporation to give a pale yellow oil. The crude product was distilled under vacuum (bp 94−95 °C, 0.02 Torr) to give a colorless liquid (18.75 g, 78%): ^1H NMR ($CDCl_3$) δ (ppm) 3.5−3.9 (m, 13H), 3.35−3.4 (s, 6H), 2.75−2.8 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) 79.56, 72.07, 71.73, 71.16, 70.59, 69.35, 62.40, 58.83, 58.75. Mass spectrometry, *m/e*: 209 MH^+ base peak.

Scheme 5. Synthesis of 3-(Benzyloxy)-1,2-propanediol

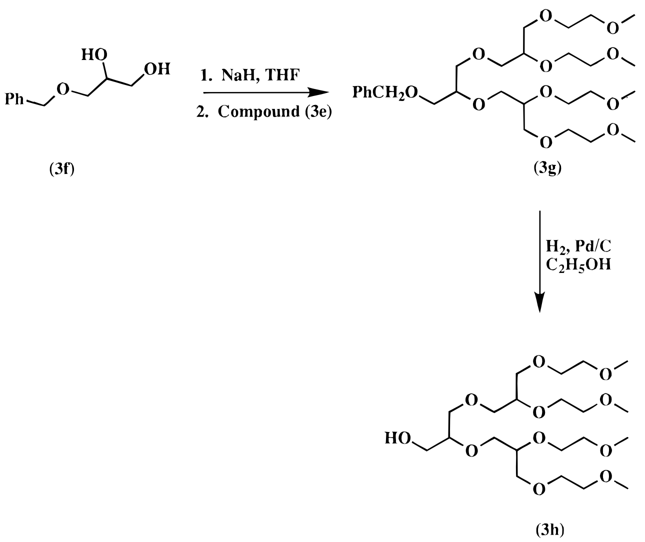


2,3-Bis(2-Methoxyethoxy)propyl Toluene-*p*-Sulfonate (3e). Compound **3e** was prepared using the same method described for the preparation of compound **3b**. The reagents and quantities used were as follows: *p*-toluenesulfonyl chloride (50.4 g, 0.26 mol); pyridine, 300 mL; and 2,3-bis(2-methoxyethoxy)propanol (50 g, 0.24 mol). The final product was a pale yellow oily liquid (83.5 g, 0.23 mol). The product was found to be pure and was used as such in the next reaction. ^1H NMR ($CDCl_3$), δ (ppm): 7.75 (d, 2H), 7.30 (d, 2H), 3.35−4.10 (m, 19H), 2.4 (s, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 144.72, 132.77, 129.69, 127.81, 79.50, 71.91, 71.67, 71.22, 70.67, 69.58, 62.49, 58.82, 58.70, 29.50.

3-(Benzyloxy)-1,2-propanediol (3f) (Scheme 5). The synthesis of compound **3f** involves the preparation of 3-(benzyloxy)solketal and deprotection of the acetonide functionality. Benzyl chloride (26.4 g, 0.2 mol) was added dropwise to a solution of the sodium salt of solketal (0.198 mol) in toluene (400 mL). Potassium iodide (3.1 g, 0.02 mol) was added to speed up the reaction. The reaction was stirred and refluxed under an atmosphere of argon for 16 h. The mixture was allowed to cool and was filtered, and the solvent was removed under reduced pressure to give a pale yellow liquid. The crude product was distilled (bp 120 °C, 0.002 mm), and a colorless oil (36.5 g, 85%) was obtained. Deprotection of the 3-(benzyloxy)solketal was carried out by refluxing (35 g, 0.16 mol) with 20% acetic acid (100 mL) for about 8 h. In that period of time the reaction mixture became homogenous. The water was removed under reduced pressure, and the product was distilled to obtain compound **3f** (22.9 g, 79.9%) as a colorless oil (bp 105−110 °C, 0.002 mmHg). ^1H NMR, δ (ppm): 7.31−7.42 (m, 5H), 4.55 (br, 2H), 4.0−4.35 (m, 2H), 3.75 (m, 1H), 3.41−3.61 (m, 2H). ^{13}C NMR, δ (ppm): 167.20, 137.63, 128.90, 128.50, 73.58, 71.79, 70.59, 64.06.

Compound 3g (Scheme 6). To a solution of the sodium salt of compound **3f** (0.14 mol) in toluene was added compound **3e** (66.3 g, 0.28 mol). The reaction mixture was stirred at room temperature for 2 h after which it was refluxed for a period of 24 h. The reaction mixture was then allowed to cool and was filtered. The solvent was removed by evaporation under reduced pressure to obtain a brown colored oil. Compound **3g** was purified by column chromatography using silica medium and methylene chloride−THF (1:1) as an eluent. The final product was a slightly yellow colored oil (70.0 g, 90.1%). ^1H NMR, δ (ppm): 7.35 (br, 5H), 4.52 (s, 2H), 3.30−3.72 (m, 41H). ^{13}C NMR ($CDCl_3$), δ (ppm): 167.33, 138.44, 129.72, 129.56, 78.62, 75.35, 75.16, 68.91−73.21.

Scheme 6. Synthesis of 3h



Compound 3h (Scheme 6). Compound **3g** (10 g) was deprotected by mixing with catalytic amounts (0.5 g) of palladium–carbon in 150 mL of 95% ethanol and the mixture was stirred in an atmosphere of hydrogen. The reaction was complete in 1 h. The product was isolated by removal of solvent under vacuum. Purification was accomplished by column chromatography using hexane–THF (1:3) as the eluent. About (7.5 g, 90%) of pure material was obtained. ^{1}H NMR, δ (ppm): 4.09 (s, 2H), 3.25–3.75 (m, 41H), 2.45 (s, 1H). ^{13}C NMR, δ (ppm): 78.31, 75.46, 75.28, 68.96–73.41.

Preparation of Samples for Ac Conductivity Measurements. As a typical example, the procedure for preparing a sample containing MEEP, lithium triflate, and phosphazene **1** was as follows: MEEP (0.5 g, 1.7 mmol) and lithium triflate (0.0663 g, 0.43 mmol) in an airless flask were dissolved in dry, distilled THF. To this was added phosphazene **1** (0.3651 g, 0.43 mmol), and the mixture was stirred for a half hour. This yielded a sample of composition 4:1:1 of MEEP:salt:phosphazene **1**. The THF was then evaporated, and the solid was placed in a vacuum oven with the temperature maintained at 60 °C for a period of 48 h. The oven was backfilled with argon before opening and the flasks were quickly transferred to a vacuum line and allowed to cool to room temperature. The samples were then transferred to an argon-filled drybox, where they were placed inbetween platinum electrodes for ac conductivity measurements.

Results and Discussion

Synthesis and Purification of Small Molecule Cyclotriphosphazenes. The synthesis of the cyclotriphosphazenes **1**–**4** (Scheme 1) was carried out as follows.

The sodium salt of the alcohols was formed by allowing the respective alcohols to react with sodium metal in refluxing THF. The sodium alkoxide (15 equiv) was then allowed to react with a solution of hexachlorocyclotriphosphazene (1 equiv) in THF at room temperature. The reactions were complete within a period of 2 h. The progress of the reactions was monitored by ^{31}P NMR spectroscopy.

Purification of the cyclotriphosphazenes was accomplished by the use of poly(methacryloyl chloride) (PMAC) and dialysis techniques. In order to separate the excess side group alcohol from the product, the crude product was treated with an excess of PMAC and a small excess of pyridine in THF. The PMAC was removed by precipitation into methanol. Pure cyclotriphosphazene was isolated by removal of the methanol. Further purification, when required, was accomplished by dialysis (MW cutoff of 500 or 1000) against water and methanol. The absence of the side group alcohol was confirmed by IR spectroscopy. The cyclotriphosphazenes **1**–**4** were almost colorless oily materials which could not be distilled. Phosphazenes **1**, **2**, and **3** displayed no thermal transitions in the range −100 to 75 °C. Compound **4** had a melting transition at −56 °C. The structures were confirmed by ^{31}P (145.8 MHz), ^{1}H (360 MHz) and ^{13}C (90 MHz) nuclear magnetic resonance (NMR) spectroscopy.

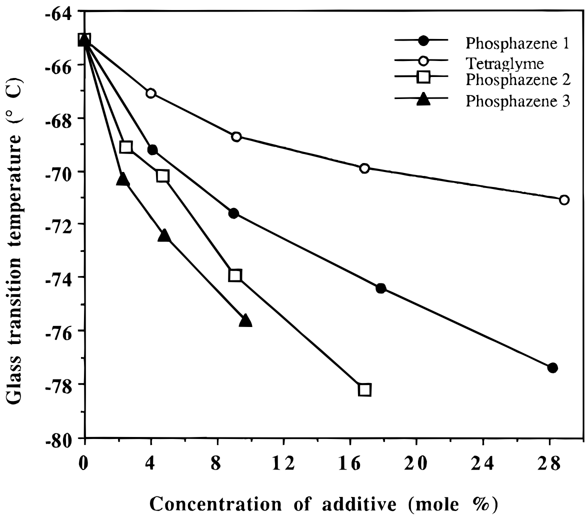


Figure 1. Variation of T_g with additive concentration.

The synthesis and purification of MEEP is as described in the literature.[15]

Physical Properties. All the polymer samples studied had good mechanical properties. The samples containing tetraglyme were extremely adhesive to glass but did not flow. At concentrations higher than those indicated in Figure 1, the materials underwent viscous flow. Among the four cyclotriphosphazenes, materials containing phosphazenes **3** and **4** were less susceptible to viscous flow at higher additive concentrations. Throughout this paper, the concentrations of the salts and plasticizers are described in mole percentages unless indicated otherwise. It should also be noted that complexes of the small molecule additives with lithium triflate were viscous liquids; hence, ionic conductivities were not be measured on these species alone. The addition of solvents of high dielectric constants (up to 30 wt %), like *N*-methylpyrrolidone (NMP) or propylene carbonate (PC), did not affect significantly the mechanical properties of the MEEP/lithium triflate.

The addition of a salt to MEEP results in transient ionic cross-linking by the coordination of metal ion to two or more oxygen atoms. This causes an increase in the T_g, especially at high loading of the salt. The addition of the small molecule additives to MEEP/salt complexes brought about a decrease in the T_g of the material. This is presumably due to the decrease in polymer–polymer interactions and an increase in polymer–additive interactions. It has also been proposed that the decline in T_g reflects an additive increase in free volume due to the addition of a plasticizer, hence causing a decrease in T_g. These concepts have been studied by positron annihilation lifetime spectroscopy (PALS).[20,21]

The glass transition temperature of uncomplexed MEEP is −84 °C. The T_g of MEEP complexed with lithium triflate in a ratio of four repeat units of the polymer to one salt molecule is −65 °C. The addition

Table 1. Conductivity and Thermal Data for the System Containing Phosphazene 4

ratio[a]	% phosphazene **4**	$\sigma \times 10^5$ (S cm^{-1})	T_g (°C)
4:1:0.125	2.34	2.04	−67.2, −42.4
4:1:0.25	4.67	2.60	−70.4, −43.4
4:1:0.5	9.12	2.92	−71.5, −44.1

[a] Mole ratio of MEEP:$LiSO_3CF_3$:Phosphazene **4**.

of small molecule phosphazenes to uncomplexed MEEP decreased the T_g. At the concentrations studied, the T_g ranged from −85 to −90 °C. Figure 1 shows the variation of T_g with the concentration of different small molecule additives. Increasing amounts of the small molecule additives resulted in a large decrease in the T_g. Tetraglyme gave the smallest decrease in T_g. For cyclotriphosphazenes **1**−**4** increases in the number of ethyleneoxy side arms bring about a larger decrease in T_g. Comparisons of the T_g's at one particular concentration, for example at 9% concentration, indicated that systems containing phosphazene **3** yielded the lowest T_g. This can be explained by free volume effects as described earlier.

The thermal behavior and ionic conductivity data for phosphazene **4** are shown in Table 1. The DSC thermogram for the samples containing phosphazene **4** contained evidence for two transitions—one corresponding to the MEEP−lithium triflate complex (around −70 °C) and the other which corresponded to a complex of phosphazene **4** with lithium triflate (near −40 °C). Small molecule phosphazene **4** by itself has a melting transition near −55 °C. By comparing these systems to those containing small molecule phosphazene **3**, because they are of comparable molecular weight, it was clear that the materials containing phosphazene **4** were partially crystalline.

Ac Ionic Conductivity Results. The systems studied generate a range of conductivities depending on the amounts of the small molecule added. The general trend is for an increase in conductivity to occur with increasing amounts of the small molecule additives. Most samples gave ionic conductivity values higher than that of the MEEP/$LiSO_3CF_3$ (4:1) system. Figure 2 shows the variation of conductivity with concentration of the small molecules. Samples containing tetraglyme exhibited higher conductivities than did the samples that contained phosphazenes **1-3** at all concentrations. Of the three cyclotriphosphazenes, phosphazene **3** gave the highest ionic conductivities, followed by phosphazene **2** and phosphazene **1**.

For the systems that contained tetraglyme, the high conductivities could reflect the influence of polymer−small molecule interactions or an additive free volume effect. The thermal analysis data showed that samples containing tetraglyme have the lowest T_g values. Because of its smaller size than phosphazenes **1**−**3**, tetraglyme may interact strongly with lithium ions to disrupt ionic cross-links between the polymer side chains. This would allow the Li^+ ions to be transported more rapidly either via mobile Li^+ tetraglyme complexes or through higher polymer side chain mobility.

In samples that contained phosphazenes **1**−**3**, the additive free volume effect apparently predominates over a polymer−plasticizer interaction effect. The polymer side chains are restricted by the presence of the additives and hence are less mobile. Due to the branching in phosphazenes **2** and **3**, the side groups appear to be extremely mobile. These side groups can participate in the transport of Li^+ ions. Hence phosphazenes **2** and **3** generate higher conductivity than does phosphazene **1**. Phosphazene **1** has the same side group as the polymer, which could lead to strong interactions between polymer and the cyclic trimer. This could be the reason for the low ionic conductivities for the systems that contain phosphazene **1**. However, the difference in conductivity between the different systems formed by phosphazenes **1**−**4** is not large, which indicates that the small molecules do not immobilize the cation, but actually aid in the ionic conduction.

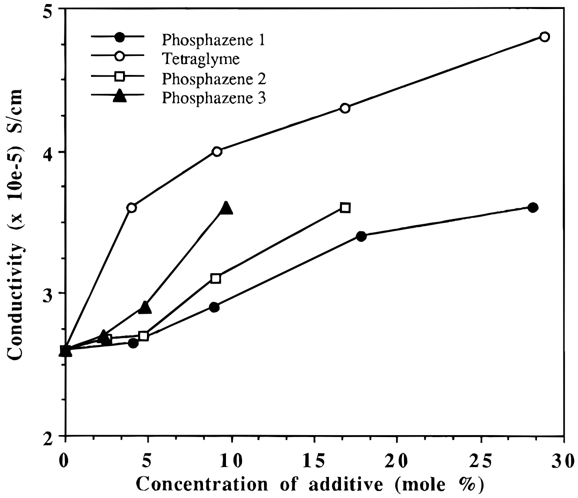


Figure 2. Variation of the conductivity with additive concentration.

Samples that contained phosphazene **4** gave conductivity values (Table 1) that were equal to or lower than that of the MEEP/ $LiSO_3CF_3$ (4:1) system. The Cole−Cole plots of these systems were not perfect semicircles. Indeed, at lower frequencies, the curve was almost a straight line, which suggests that phosphazene **4** may be facilitating ionic conductivity independently in addition to that of the MEEP component. This fact was further confirmed by the thermal data for these systems. The 4:1 ratio of MEEP to lithium triflate corresponds to one lithium ion for every 16 ethyleneoxy units. In this study we have considered two different salt concentrations. The first (the samples discussed above) contain amounts of lithium triflate that correspond to the 16 ethyleneoxy units on the polymer alone. In the second case, the total number of ethyleneoxy units (polymer and small molecules) is considered, and the corresponding amount of lithium triflate was added. *In all cases, the increase in the concentration of the lithium triflate resulted in decreased conductivity values.* The conductivity values in the case of phosphazene **1**, tetraglyme, and phosphazene **4** were lower than that of the MEEP/$LiSO_3CF_3$ (4:1) system. This is probably due to the saturation of the coordination sites with lithium ions. The DSC data of these systems confirm this interpretation. The data indicate increased T_g's. In the case of tetraglyme, the T_g was as high as −53 °C. In the case of the systems containing phosphazene **4**, the conductivity values are reduced to below that of MEEP/$LiSO_3CF_3$ (4:1) system (about 1.7×10^{-5} S cm^{-1}), indicating extensive cross-linking and saturation of the coordination sites. Both of the thermal transitions are shifted to a higher value.

In an attempt to study the possibility that the cyclic trimeric species might act as a cation transporting agent, samples containing poly[bis(hexyloxy)phosphazene] (**5**), lithium triflate, and phosphazene **1** were prepared, with the knowledge that polymer **5** is a poor

Table 2. Conductivity of MEEP−$LiSO_3CF_3$ (4:1) with Imbibed Organic Solvents

solvent[a]	wt % organic solvent	$\sigma \times 10^5$ (S cm^{-1})
NMP	8.1	20.6
NMP	15.2	30.4
NMP	30.6	89.6
PC	9.2	43.3
PC	14.3	70.2
PC	28.3	120

[a] NMP = *N*-methylpyrrolidone. PC = propylene carbonate.

ionic conductor. However, these components were physically incompatible and did not form uniform mixtures. As observed by ^1H NMR, different regions of the sample contained different amounts of the cyclotriphosphazene.

MEEP Plasticized with Solvents of High Dielectric Constant. It has been widely reported that PEO/salt samples have high ionic conductivities when plasticized with small amounts of solvents that have high dielectric constants.[3] This has been attributed to the ability of these solvents to facilitate ion pair separation. Two of these solvents, *N*-methylpyrrolidone (NMP) and propylene carbonate (PC) have been utilized in the present work. Table 2 lists the conductivity data for the MEEP/lithium triflate/solvent systems studied. The effect of these solvents on the mechanical properties of the samples was minimal. Because this study involved the use of uncross-linked MEEP, the amount of solvent incorporated in the samples was less than 30%. The T_g's of these materials (around −95 °C) were lower than the T_g's of the samples containing similar amounts of cyclotriphosphazenes **1**−**4**. This is probably due to the high solvation of the lithium ion and hence the reduced ionic cross-linking.

Conclusions

The synthesis and characterization of four different small molecule cyclotriphosphazenes are reported. These small molecules are used as additives in the well-studied MEEP−$LiSO_3CF_3$ system. Increasing amounts of these molecules bring about an increase in conductivity. Of the three cyclotriphosphazenes, phosphazene **3** gives the highest ionic conductivity. As deduced from DSC data, these small molecule polyether cyclotriphosphazenes probably decrease the degree of ionic cross-linking within the high polymer component. These trimers apparently do not enhance ion pair separation of the salt to an appreciable extent. As a result, the ionic conductivity of these systems is similar to that of the additive-free systems. The use of phosphazene **4**, decreased the conductivity, perhaps due to the partially crystalline nature of the mixture.

The MEEP(uncross-linked)−$LiSO_3CF_3$ system when plasticized with organic liquids such as propylene carbonate or NMP generated high ionic conductivities on the order of 10^{-3} S cm^{-1}. The T_g's of these systems are lower than those of the MEEP/$LiSO_3CF_3$ systems, presumably due to the high degree of cation solvation, and a presumed decrease in ionic cross-linking. Samples containing tetraglyme showed the least decrease in T_g but resulted in higher ionic conductivities than systems that contained the cyclotriphosphazenes at all concentrations. The amounts of the small molecules that can be added to the MEEP/lithium triflate system without inducing liquefaction are low due to the uncross-linked state of the polymer. However, the systems examined have good mechanical properties.

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