Polyphosphazenes with Novel Architectures: Influence on Physical Properties and Behavior as Solid Polymer Electrolytes

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ABSTRACT: Three types of polyphosphazenes with different architectures have been synthesized and characterized. The influence of the polymer architecture on solid ionic conductivity was of particular interest. The first type includes linear oligo- and polyphosphazenes with the general formula $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) with different chain lengths. The second type consists of a series of triarmed star-branched polyphosphazenes with the general formula $N\{CH_2CH_2NH(CF_3CH_2O)_2P[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n\}_3$ with different arm lengths. These were synthesized via the reaction of the tridentate initiator $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}N{-}PCl_3^+\}_3][PCl_6^-]_3$ with the phosphoranimine $Cl_3P{=}NSiMe_3$ in CH_2Cl_2 followed by halogen replacement with sodium (methoxyethoxy)ethoxide. The molecular weights in this system were carefully controlled by variation of the monomer-to-initiator ratios, and the effect of polymer molecular weight on solid ionic conductivity was examined. The third polymer system was designed to examine the effect of complex branching on ionic conductivity. Thus, a highly branched polymer containing five branches from a cyclotriphosphazene pendent side group (with 26 ethyleneoxy units per repeat unit) was synthesized. The conductivity of this polymer in the presence of three different salts has been measured and compared to the behavior of MEEP with a corresponding molecular weight. The mechanism of ion transport in these systems is discussed.

Introduction

Polymer architecture controls properties such as solubility, thermal behavior, viscosity, glass transition temperature (T_g), etc. An objective of this work was to determine how changes in polymer architecture affect ion transport in a solid polymer electrolyte (SPE). Solid polymer electrolytes are of considerable interest as prospective light-weight, thin-film media for applications such as high-energy density solid-state batteries, supercapacitors, or flat panel electroluminescent devices.[1] Most of the earlier work in this area has involved the use of poly(ethylene oxide) (PEO) for use as an SPE. Initial studies by Wright showed that alkali metal salts form stoichiometric salt complexes with PEO.[2] Later, papers by Armand emphasized the potential of such systems for use in electrochemical applications.[1] Studies of the mechanism of conduction, and extensive reviews of the development of this area, have been published by Shriver, Vincent, Ratner, and others.[3−5]

As a result of these various studies, critical polymer property relationships have been identified to aid in the assessment of the utility of a polymer as an SPE. The polymer should possess: (1) cation or anion coordination sites to assist in salt solvation and ion pair separation, (2) a low barrier to backbone bond rotation, as found in flexible low glass transition temperature (T_g) materials which permit high ion mobility, and (3) an amorphous structure, because crystalline domains will reduce polymer flexibility and impede the transport of ions.[6] PEO has a crystalline melting temperature at 65 °C and allows a room temperature conductivity with lithium salts in the range of only 10^{-8} S cm^{-1}. Maximum conductivity is obtained only when the polymer is heated to 100 °C, which is well above the preferred operational temperature of most SPE-based devices. This has prompted much research on methods to alter the properties of PEO to eliminate the presence of crystallites.[7−16]

During the past decade, polyphosphazenes such as poly[bis(methoxyethoxy)ethoxy)phosphazene] $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) (**1**) and similar derivatives have been examined for use as improved solid polymer electrolyte materials.[17−20] These polymers show great promise as SPEs due to the amorphous nature of the solid materials and their ability to function as excellent solid solvents for salts such as $LiSO_3CF_3$ or $AgSO_3CF_3$. Solid solutions of high molecular weight ($M_n \sim 10^6$) MEEP-based polymers with these salts show conductivities at 25 °C that are 2−3 orders of magnitude higher than similar complexes with PEO. This higher level of conductivity is attributed to the amorphous character of MEEP, the presence of a highly flexible polyphosphazene backbone as manifested by a low glass transition temperature (−83 °C), and the large number of etheric solvation/coordination sites per repeat unit. The major drawback of MEEP is its poor dimensional stability because the polymer flows under light pressure. This problem has been overcome by the use of γ and ultraviolet irradiation to cross-link the polymer,[21] by the use of longer and branched ethyleneoxy side substituents,[22] and by the formation of blends,[23] interpenetrating networks, or composites.[24]

Polyphosphazenes such as MEEP are normally prepared by the macromolecular substitution process developed in our program over the last 30 years. This process involves two steps. A reactive macromolecular intermediate, poly(dichlorophosphazene) (**5**), is first produced. Second, the chlorine atoms in this polymer are replaced by organic side groups by treatment with organic nucleophiles.[25−27] Two methods exist for the preparation of $(NPCl_2)_n$. In the classical approach,[28]

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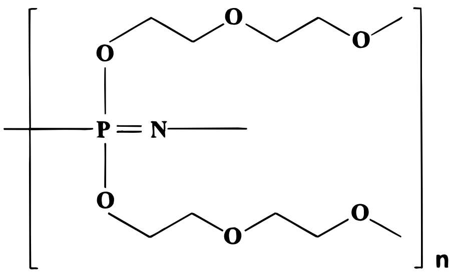

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hexachlorocyclotriphosphazene $(NPCl_2)_3$ is polymerized thermally in a ring-opening process. An alternative approach is the recently developed living, cationic, condensation process.[29,30]

The new method for the preparation of poly(dichlorophosphazene) involves the reaction of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**4**) with small amounts of PCl_5 in CH_2Cl_2 at 25 °C (Scheme 1).[29,30] This allows an ambient temperature synthesis of poly(dichlorophosphazene) via a "living" cationic-induced polymerization, with molecular weight control and low polydispersities. This polymerization route also serves as an efficient method for the direct preparation of a variety of poly(organophosphazenes)[31,32] via the PCl_5-induced polymerization of *organo*phosphoranimines at ambient temperature. Phosphazene-based block copolymers are also accessible by this method.[33] In addition, extensions of this process that employ initiators with multiple cationic sites, such as $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}N{-}PCl_3^+\}_3][PCl_6^-]_3$ (**7**), have recently led to the development of the first free-standing triarmed star-branched polyphosphazenes of the general structure $N\{CH_2CH_2NH(CF_3CH_2O)_2P[N{=}P(OR)_2]_n\}_3$ (**2**).[34]

This ability to control molecular weight and branching opened up several new approaches to improving the performance of MEEP−lithium salt complexes.

The objective of this present work was to answer the following questions: (a) What is the effect of variations in polymer chain length on the ionic conductivity and thermal behavior of MEEP/lithium triflate systems? (b) What is the effect of star branching on the dimensional stability of MEEP? For example, is it comparable to previously synthesized branched ethyleneoxy-containing polyphosphazenes? (c) How do the ionic conductivities of star-branched MEEP differ from those of (i) linear MEEP with a molecular weight equal to that of one branch and (ii) linear MEEP with a molecular weight equal to that of all three branches combined? (d) How does extensive branching in the side chain affect the ionic conductivity and mechanical properties of the polymer and how do these properties compare to that of MEEP of comparable molecular weight? Polymer **3** was synthesized in order to compare its properties to the MEEP/lithium triflate/additive systems studied previously.[35] The additives used in that study were various oligoethyleneoxy cyclotriphosphazenes.

Scheme 1. Synthesis of Linear Polyphosphazenes

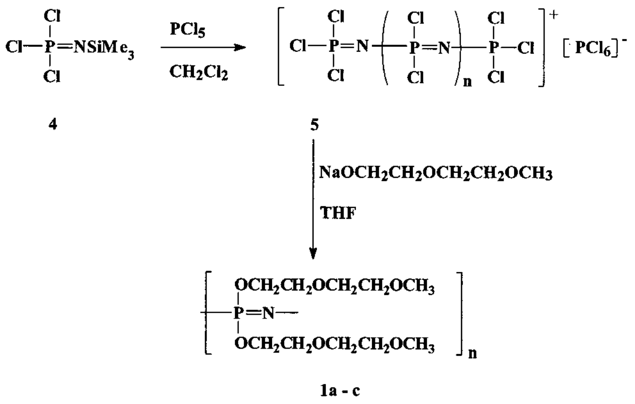
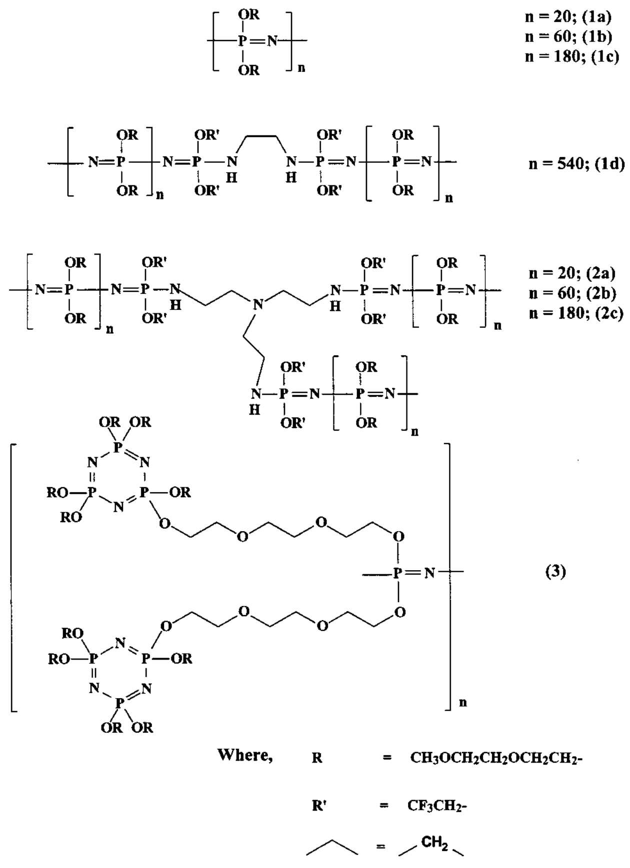


Chart 1. Polyphosphazenes Studied



In this paper, we report the synthesis of a series of linear MEEP (**1a**−**d**) and triarmed star MEEP polymers (**2a**−**c**) via the cationic-induced polymerization of phosphoranimines at ambient temperatures (Chart 1). This method yields linear polyphosphazenes or arm branches with excellent molecular weight control and low polydispersities. Also reported here is the synthesis, by conventional ring opening polymerization methods, of a highly branched side group containing polyphosphazene, **3**. The ionic conductivities of these polymers have been measured and their T_g values are reported.

Results and Discussion

(A) Polymer Synthesis and Characterization. Synthesis and Characterization of Linear $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) (1a−d). Previous studies involving the monomer $Cl_3P{=}NSiMe_3$ (**4**) have shown that this species reacts with 2 equiv of PCl_5 to form the salt complex $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$ with the elimination of Me_3SiCl.[30] Addition of further equivalents of **4** to this initiator will eliminate Me_3SiCl and form the linear oligomer or polymer $[Cl_3P{=}N(Cl_2P{=}N)_nPCl_3]^+[PCl_6]^-$. Thus, trace quantities of PCl_5 can be used as an efficient catalyst for the polymerization of **4** to produce "living" samples of $(N{=}PCl_2)_n$ (**5**) (Scheme 1). For example, linear $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (**1a**) was synthesized by the addition of 1

Table 1. Molecular Weights of Polymers

polymer	M_n found[a] $\times 10^{-3}$	(PDI)	M_n found[b] $\times 10^{-3}$	PCl_5 or **7**: $Cl_3PNSiMe_3$
1a	7.6	1.04	9.1	1:10
1b	11.3	1.11	13.0	1:30
1c	17.0	1.29	NA	1:90
1d[c]	124.6	1.08	NA	1:270
	9.4	1.28		
2a	9.3	1.07	18.7	1:60
2b	22.9	1.12	55.2	1:180
2c	29.9	1.23	NA	1:540
3	735	3.21	NA	NA

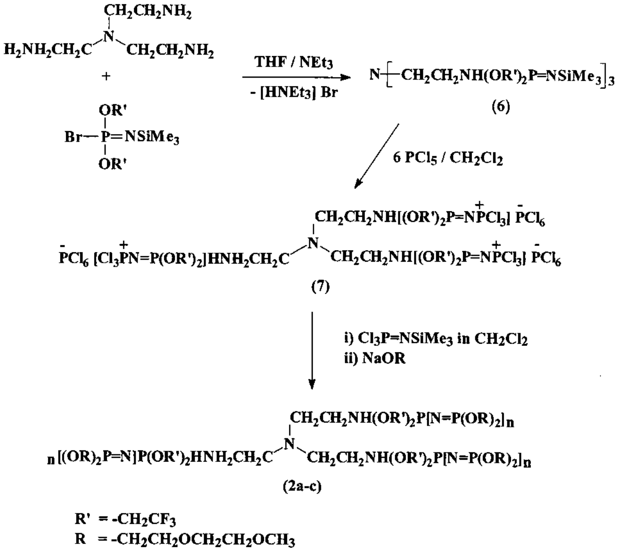
[a] Molecular weights determined by GPC following replacement of Cl by $^{-}OCH_2CH_2OCH_2CH_2OCH_3$. [b] Molecular weights determined by end-group analysis using ^{31}P NMR spectroscopy. [c] Bimodal distribution of molecular weight.

molar equiv of PCl_5 to 10 of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**4**) in CH_2Cl_2 at 25 °C. This yielded oligo(dichlorophosphazene) (**5**) identified by ^{31}P NMR spectroscopy from the characteristic resonance for this polymer at -17 ppm. Integration of the resonances associated with the linear polymer confirmed the initial 10:1 $Cl_3P{=}NSiMe_3$:PCl_5 ratio. In other words, the oligomer contained 20 repeating units and a $PCl_3^+PCl_6^-$ end unit. The molecular weights of these oligomers and polymers were controlled by variations in the $Cl_3P{=}NSiMe_3$:PCl_5 ratios (see Table 1). Treatment of these samples of $(N{=}PCl_2)_n$ (**5**) with an excess of sodium 2-(2-methoxyethoxy)ethoxide in THF at 40 °C produced the linear polymers **1a**−**d**. These substitution reactions were complete within a period of 2 h as monitored by ^{31}P NMR spectroscopy.

Purification of the resultant linear MEEP oligomers and polymers was accomplished by dialysis against water and methanol for 3 days. Analysis of **1a** by gel permeation chromatography (GPC) revealed a number average molecular weight $M_n = 7.6 \times 10^3$ and a polydispersity index (PDI $= M_w/M_n$) of 1.04. The structures of these linear macromolecules were confirmed by multinuclear magnetic resonance spectroscopy. Where applicable, end groups analysis by ^{31}P NMR spectroscopy was used to provide a second estimate of molecular weights.

Previous ambient temperature PCl_5-induced polymerizations of $Cl_3P{=}NSiMe_3$ (**4**) at ratios of $Cl_3P{=}NSiMe_3$:PCl_5 higher than 150:1 were found to be only poorly reproducible and required lengthy polymerization times. They often gave high molecular weight polymers with bimodal molecular weight distributions.[30] In an effort to circumvent this problem, the difunctional initiator $[-CH_2NH[(CF_3CH_2O)_2P{=}NPCl_3^+]_2[PCl_6^-]_2$, prepared from ethylenediamine, was used to initiate the polymerization of $Cl_3P{=}NSiMe_3$ (**4**). It was considered possible that the ability of this difunctional species to initiate polymerization in two directions may reduce polymerization times and perhaps lower the tendency for formation of polymers with broad or bimodal molecular weight distributions brought about by chain termination over prolonged polymerization times. However, the higher molecular weight polymer **1d** (ca. 540 repeat unit linear), synthesized by use of the difunctional initiator, still possessed a bimodal molecular weight distribution. Thus, the use of the difunctional initiator reduces polymerization times for the formation of medium molecular weight polymers, but the polydispersities are still broad or bimodal in nature.

Scheme 2. Synthesis of Triarmed Star Polyphosphazenes

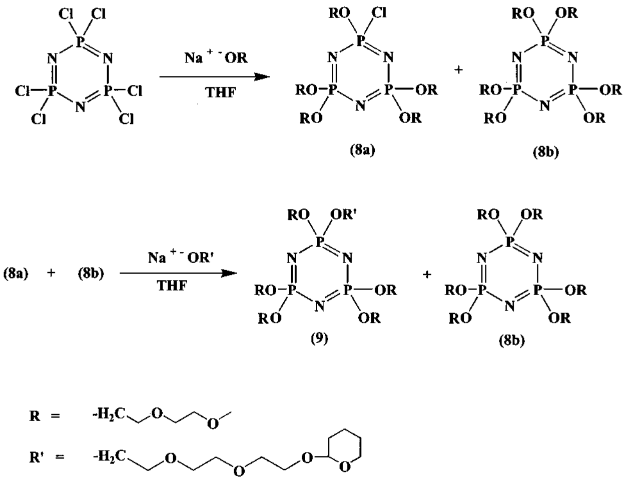


Synthesis and Characterization of Triarmed Star-Branched MEEP-Based Polyphosphazenes. $N\{CH_2CH_2NH(CF_3CH_2O)_2P[N{=}P(OCH_2CH_2OCH_2CH_2\text{-}OCH_3)_2]_n\}_3$ (2a−c). Previous work in our program has shown that the trifunctional phosphoranimine $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NSiMe_3\}_3$ (**6**) can be prepared by treatment of the tridentate primary amine $N(CH_2CH_2NH_2)_3$ with $(CF_3CH_2O)_2BrP{=}NSiMe_3$ in the presence of triethylamine.[34] Subsequent reaction of **6** with 6 molar equiv of PCl_5 at -78 °C results in the formation of the trifunctional cationic initiator $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+\}_3][PCl_6^-]_3$ (**7**). Triarmed poly(dichlorophosphazenes) with controlled molecular weights and low polydispersities were then prepared by treatment of **7** with $Cl_3P{=}NSiMe_3$ (**4**) in CH_2Cl_2.[34]

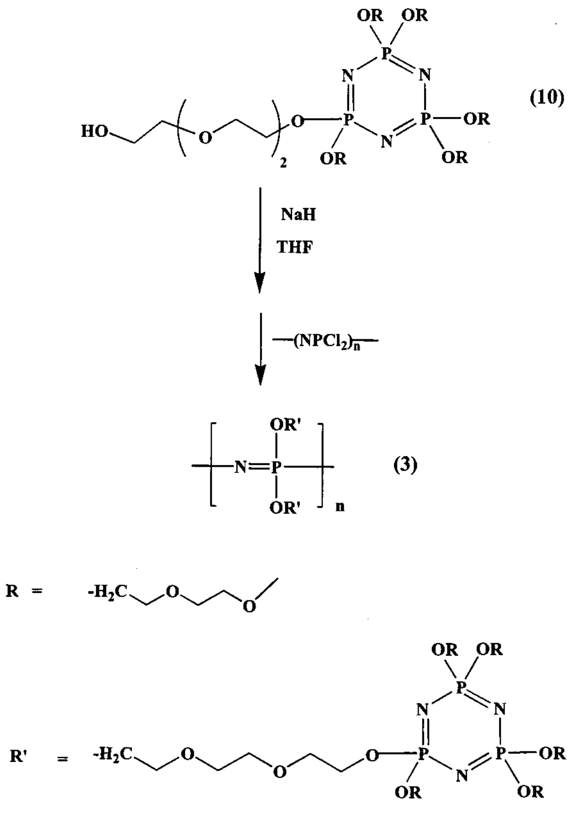
The preparation of polymer **2a** is typical and is illustrated in Scheme 2. The cationic initiator (**7**) was treated with a 20-fold excess (per reactive site) of $Cl_3P{=}NSiMe_3$ (**4**) in CH_2Cl_2. After 3 h at 25 °C, examination of the reaction mixture by ^{31}P NMR spectroscopy revealed the complete reaction of **4** with **7** to yield $N\{CH_2CH_2NH(CF_3CH_2O)_2P[N{=}PCl_2]_n\}_3$. This product was treated with an excess of sodium (methoxyethoxy)ethoxide (1.3 equiv per chlorine) to replace the chlorine atoms and generate the MEEP-analogue star polymer $N\{CH_2CH_2NH(CF_3CH_2O)_2P[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n\}_3$ (**2a**). Analysis of **2a** by GPC indicated that it possessed an $M_n = 9.3 \times 10^4$ and a PDI of 1.07. The molecular weights of these star polymers can be controlled by variation of the monomer-to-initiator ratios (Table 1).

Synthesis of Complex-Branched Side-Group-Containing Polyphosphazene (3). The synthesis of polymer **3** was accomplished as follows. First, penta(methoxyethoxyethoxy)monochlorocyclotriphosphazene (**8a**) was synthesized by the treatment of hexachlorocyclotriphosphazene with 5.3 equiv of sodium methoxy(ethoxy)ethoxide (Scheme 3). Mixtures of the hexasubstituted compound (MEET) (**8b**) and the pentasubstituted species (**8a**) were obtained. No attempt to separate these two compounds was made at this stage because of the hydrolytic sensitivity of compound **8a**. This mixture was then treated with the sodium salt of mono(tetrahydropyranyl)triethylene glycol, synthesized by the slow addition of 2,3-dihydropyran to a solution containing triethylene glycol in methylene chloride in the presence of a catalytic amount of pyridinium *p*-

Scheme 3. Synthesis of Compound 9



Scheme 4. Synthesis of Polymer 3



toluenesulfonate (PPTS). The monoprotected compound was separated from the diprotected compound by column chromatography. The product now contained a mixture of hexakis(methoxyethoxyethoxy)cyclotriphosphazene (**8b**) and compound **9**. The THP-protected cyclotriphosphazene (**9**) was deprotected by use of a catalytic amount of PPTS in 95% ethanol at 55 °C to obtain alcohol **10**. Compound **10** was then separated from **8b** by column chromatography. The absence of **8b** was confirmed by mass spectrometry. The sodium salt of the alcohol **10** (3.0 equiv) was then added dropwise to a warm solution of poly(dichlorophosphazene) (Scheme 4). The reaction was completed during a period of 12 h to yield polymer **3**.

Purification of this polymer involved dialysis against water for 3 days and against methanol for another 3 days in order to remove the salts and excess unreacted side group. On evaporation of the solvent, a slightly off-white, dimensionally stable polymer was obtained, which was soluble in common solvents such as chloroform, THF, and water.

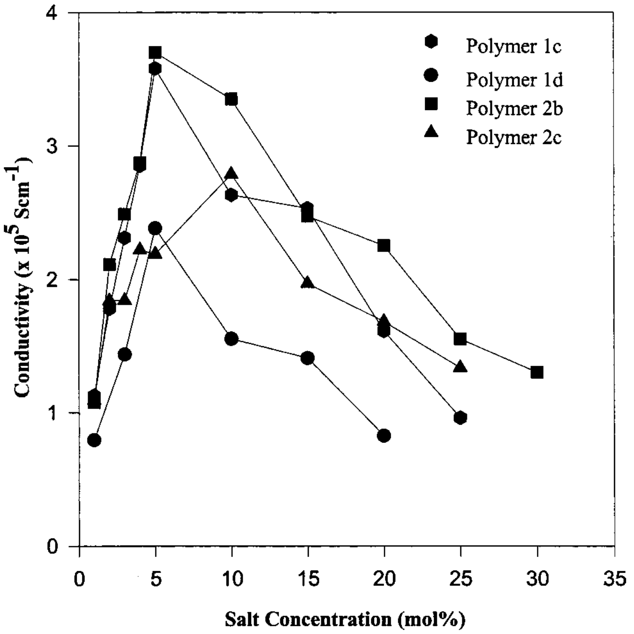


Figure 1. Variation of conductivity of linear and star MEEP with salt concentration.

Ionic Conductivity. The MEEP-type phosphazene/lithium triflate systems investigated in this work gave a range of conductivity values that depended on both the molecular weight and structure (linear vs star-branched, linear vs complex-branched side group) of the material. The low molecular weight polymers **1a**, **1b**, and **2a** ($M_n = 7.6 \times 10^3$, 1.1×10^4, and 9.3×10^3, respectively) showed a tendency to undergo viscous flow, and because of this, their ionic conductivities could not be measured accurately with the available equipment. The higher molecular weight polymers **1c**−**d** and **2b**−**c** ($M_n > 1.7 \times 10^4$) were less susceptible to viscous flow, and their ionic conductivities could be examined. The ionic conductivity of each polymer was measured as a function of variations in lithium triflate concentration (1−30 mol %). Most of the polymers studied displayed a maximum ionic conductivity at a salt concentration of about 5 mol % lithium triflate per polymer repeat unit. For example, polymer **2b** had a conductivity of 1.08×10^{-5} S cm^{-1} at 1 mol % $LiSO_3CF_3$. The addition of more salt increased the conductivity of all the polymers up to a maximum. This point occurred at 5 mol % for polymer **2b**, with a conductivity value of 3.70 $\times 10^{-5}$ S cm^{-1}. This corresponded to a 19:1 molar ratio of polymer repeat unit to salt. As more salt is added beyond this point, fewer coordination sites presumably are available to foster ion pair separation. Moreover, the number of ionic cross-links would increase correspondingly and this could restrict the motion of the ethyleneoxy side groups and thereby cause a reduction in the conductivity. This phenomenon has been observed with other polymer electrolytes.[17−19] Figure 1 indicates that both the lower molecular weight linear (**1c**) and star-branched (**2b**) polymers show higher conductivities than the moderate (**1d, 2c**) to high molecular weight MEEP/$LiSO_3CF_3$ systems. The reasons for this are discussed in the following section.

Long-Range Ion Transport in MEEP. To understand why the low molecular weight MEEP polymers generate higher conductivities than the high molecular weight counterparts, it is necessary to take into account the motion of the polymer chains. Two current models describe the motions of low and high molecular weight polymers: (1) the DeGennes model,[36] which accounts for motions in higher molecular weight polymers (above a "critical entanglement limit"), and (2) the Rouse model,[37] which describes motions of linear low molecular weight polymers (below the "critical entanglement limit").

Studies performed on poly(ethylene oxide) (PEO) with various molecular weights ($M_n = 400$ to 4×10^6) have shown that the transport of cations is indeed governed by the dynamic relaxational modes proposed by the above two models.[38] It appears that, above the critical entanglement limit, long-range cation transport occurs mainly through polymer segmental motion and site percolation. In this model, the lateral motion of a polymer chain is impeded by adjoining chains. Ratner and co-workers[39] have adapted the DeGennes model to propose a mechanism for long-range ion transport by suggesting two distinct processes: (i) local segmental motion of the chains carry the cations which are temporarily attached to the coordination sites, and (ii) ions occasionally "hop" to and from different coordination sites. Nonlabile cations such as magnesium displayed negligible ionic conductivity. Below the critical entanglement limit, as suggested by Ratner et al.,[39] the cation can diffuse or migrate through the polymer electrolyte while remaining attached to the host polymer. Both labile (lithium) and nonlabile cations displayed appreciable ionic conductivities. This critical entanglement limit for PEO was estimated to be around a molecular weight of 3200, which corresponds to about 72 polymer repeat units.

In higher molecular weight MEEP, a high degree of chain entanglement exists. The DeGennes model can be used to describe ion transport in this case, by means of the process of reptation or segmental motion.[36] The higher conductivities found in this study for low molecular weight MEEP (Figure 1) can be explained by the Rouse model.[37] In this, the entanglements encountered in the DeGennes model are not considered to be significant and it is thought that chain segments should not significantly impede the motion of other chain segments. Thus, the higher conductivities observed for MEEP with lower molecular weights can be explained by the migration of cations while they remain coordinated to the polymer chain.

In view of these facts, the following comparisons are interesting for the MEEP polymers synthesized: (1) low molecular weight versus high molecular weight, (2) star versus linear polymers of equal molecular weight, and (3) molecular weight of one individual star branch versus a linear polymer of comparable molecular weight as the branch (i.e., comparing a 180 repeat unit per arm (540 total) star polymer with a 180 repeat unit linear polymer).

The star-branched polymers **2b**−**c** have similar conductivities to the corresponding linear polymers **1c**−**d** with similar molecular weights (Table 2). Linear polymer **1c** ($M_n = 1.7 \times 10^4$, ca. 180 repeat units) has a higher conductivity than that of star-branched polymer **2c** ($M_n = 3.0 \times 10^4$, ca. 180 repeat units per arm). In the case of the star-branched polymer, the segmental density is greater than in the linear polymer. Hence it fits the DeGennes model, while the linear analogue fits the Rouse model. Viscosity measurements of the linear and star-branched polymers could offer more insight and are being investigated in addition to absolute molecular weight determination by light scattering.

Table 2. Maximum Conductivity Data for Star and Linear MEEP at 25 °C

polymer	max conductivity ($\times 10^5$ S cm^{-1})	mol % $LiSO_3CF_3$ added	mole ratio polymer:salt
1c	3.58	5	19:1
1d	2.38	5	19:1
2b	3.70	5	19:1
2c	2.70	10	9:1

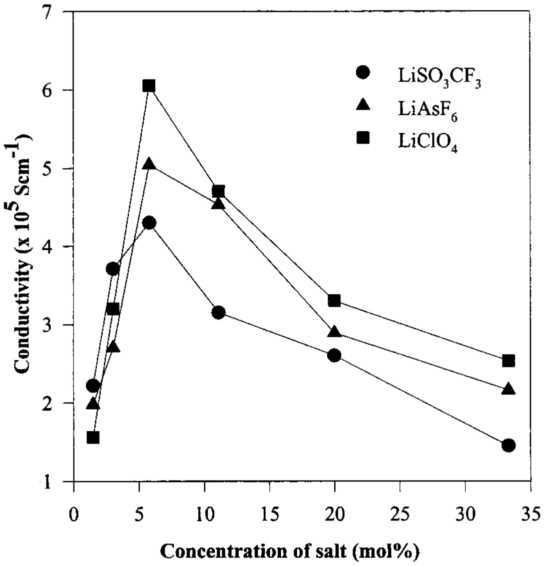


Figure 2. Variation of conductivity of polymer **3** with salt concentration.

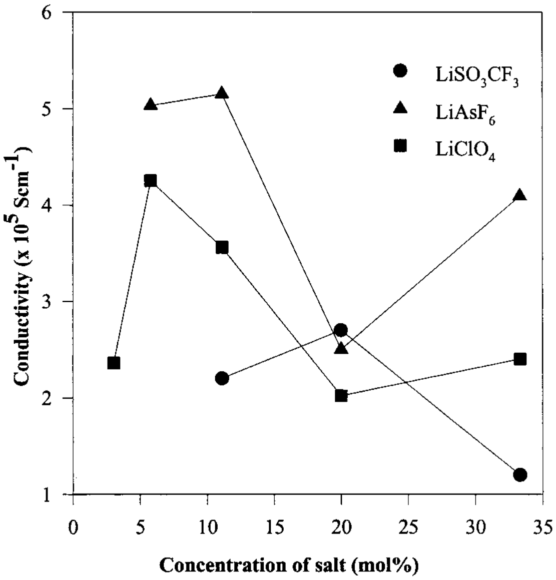


Figure 3. Variation of conductivity of high molecular weight MEEP with salt concentration.

The ionic conductivity data for polymer **3** were obtained with three different lithium salts ($LiSO_3CF_3$, $LiAsF_6$, and $LiClO_4$) (Figure 2). These results were compared with those for MEEP with a similar molecular weight (Figure 3). The maximum ionic conductivity for polymer **3** was obtained at a salt concentration of 5.8 mol %, which is similar to the amount required for maximum conductivity in the linear and triarm polymers. This similarity is probably due to the low molecular weights of the linear and triarm species despite the different polymer architectures. As mentioned above, fewer lithium ions are required for a higher ionic conductivity due to their migration while still coordinated to the polymer chain. The triarm polymers should have an increased segmental density compared to the linear polymers, but at the molecular weights reported, this difference is not significant. Polymer **3** has a large free volume and a greater number of ethyleneoxy units in a repeat unit. Thus, it requires a lower concentration of lithium ions to generate high ionic conductivities. With all three salts, polymer **3** gave higher conductivities than did the corresponding linear or star-branched MEEP systems. This is possibly due to (i) the larger number of coordination sites per repeat unit available in **3** and (ii) the lability of the ethyleneoxy side groups on the cyclotriphosphazene units, in addition to the oligoethyleneoxy unit that links the cyclotriphosphazene components to the backbone. The large number of ethyleneoxy units (26 per repeat unit) gives rise to more degrees of freedom, hence making this system an excellent solvent for the lithium ions.

Inoue et al. have described the synthesis and characterization of a related polymer. These "polycascade polymers" contain an oligoethylenoxy-bearing cyclotriphosphazene linked to polystyrene and poly(vinylbiphenyl).[40,41] These polymers were found to have low T_g values and to give conductivities in the range of 10^{-5} S cm^{-1} at 30 °C. These relatively high conductivities were thought to be due to the formation of a conducting phase associated with the ethyleneoxy units on the cyclotriphosphazene units attached to a nonconducting phase, namely, the polystyrene backbone. In the case of polymer **3**, both the ethyleneoxy side groups on the cyclotriphosphazene and the ethyleneoxy spacer that links it to the polymer are conducting, and hence it has a much higher conductivity than MEEP.

Also, in a previous study, which involved the use of small molecule additives in MEEP−lithium triflate systems, the maximum ionic conductivity obtained was 4.8×10^{-5} S cm^{-1} for a system that contained about 30 mol % of tetraglyme. The MEEP/lithium triflate complexes when mixed with **8b** showed a maximum ionic conductivity of about 3.5×10^{-5} S cm^{-1} at a concentration of about 30 mol % of **8b**. Polymer **3** can be compared directly with the above system: it gave a maximum ionic conductivity of 4.3×10^{-5} S cm^{-1} with lithium triflate. The difference is not of great significance, but polymer **3** offers the advantage of dimensional stability over the MEEP/salt systems as described in later sections.

Thermal Properties. All the polymers prepared in this work were examined by differential scanning calorimetry (DSC). In the absence of lithium triflate, all the polymers produced by the cationic polymerization method had similar T_g values (near −80 °C). The linear MEEP (**1d**) obtained by the living cationic method ($M_n = 1.2 \times 10^5$) consistently showed a slightly higher T_g (2−5 °C increase) than MEEP synthesized by the ring opening polymerization method ($M_n > 1 \times 10^6$). Because the star polymers **2a**−**c** contain three times the number of chain termini, compared to linear polymer of molecular weight equal to one of the arms, it might have been expected that the star polymers would have lower T_g values than their linear counterparts. This was not found for the MEEP used in this study.

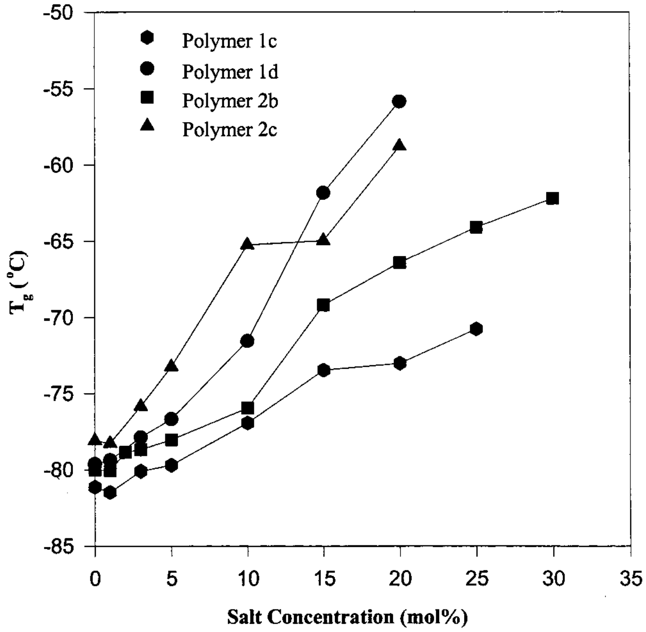


Figure 4. Variation of T_g with salt concentration.

Polymer **3** had considerably more dimensional stability than linear MEEP with a similar molecular weight, or the star polymers. It was completely amorphous over the temperature range of −100 to +100 °C. In the absence of salt, the polymer had a glass transition temperature at −74 °C, only a 10 °C increase over that of linear MEEP (**1**) with a similar chain length. This is surprising considering the bulky nature of the cyclotriphosphazene side units linked to the phosphazene backbone. But similar results have been seen in earlier work with polyphosphazenes that contain branched etheric side groups.[19] Increases in the number of side group termini from two (in the case of MEEP) to four in the branched side chain bearing polyphosphazenes do not increase the glass transition temperature (T_g) significantly. The T_g increased only from −84 °C for MEEP to −80 °C for its branched isomer. Increases in the number of free chain ends might be expected to increase the polymer free volume and hence lower the T_g. This effect appears to be offset by the decreased polymer flexibility caused by side group steric hindrance. Another factor that has to be considered in **3** is the length and labile nature of the triethyleneoxy spacer between the cyclotriphosphazene side group and the phosphazene backbone. It is well-known that the use of such etheric spacer units in polyphosphazenes that bear bulky side groups decreases the T_g compared with counterparts in which the bulky side groups are linked closely to the backbone. For example, poly[bis(4-phenylphenoxy)phosphazene] has a T_g of +93 °C, while poly[bis(2-(4-phenylphenoxy)ethoxy)phosphazene] has a T_g of +56 °C.[42,43] Despite the bulky nature of a side group, a spacer unit allows significant backbone relaxations and presumably preserves the flexibility of the skeleton.

The addition of salt increased the T_g in all cases (see Figures 4−6) and resulted in increased dimensional stability. Increasing salt concentration presumably increases the number of ionic cross-links, and this could decrease the side chain motion and polymer flexibility. As seen in Figure 4, the salt concentration has a greater effect on T_g for polymers **1d** and **2c** (540 repeat units) than for the lower molecular weight polymers **1c** and

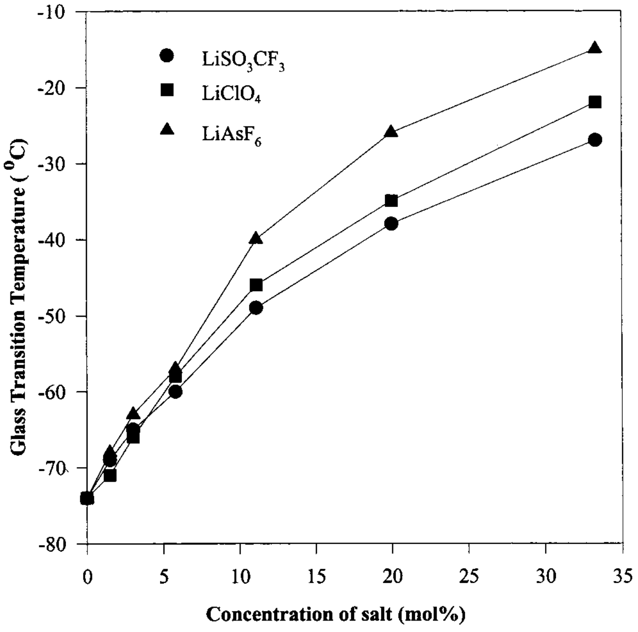


Figure 5. Variation of T_g of polymer **3** with salt concentration.

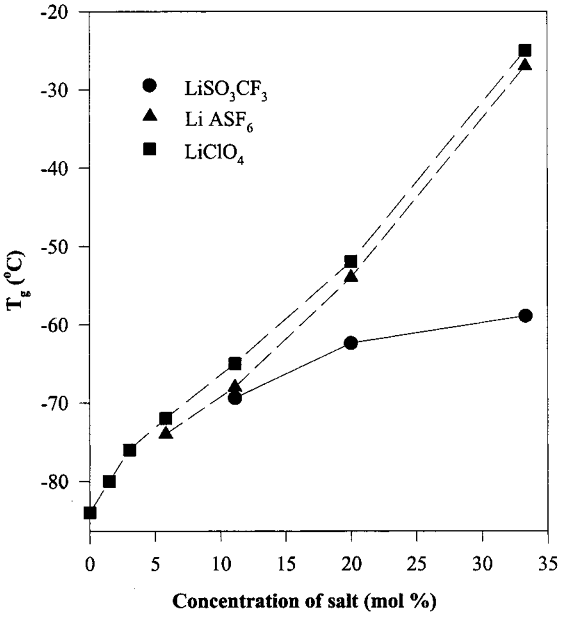


Figure 6. Variation of T_g of MEEP with salt concentration.

2b (180 repeat units). These values indicate more restricted polymer chain motion in the higher molecular weight polymers, since fewer ionic cross-links per chain are required to restrict motion in the longer chains than in the shorter chains. The T_g values of polymer **3** were higher than those of the MEEP complexes with the corresponding salts. This could be due to the extensive cross-linking that can occur at both the ethyleneoxy spacer unit and the methoxyethoxy ethoxy side groups on the cyclotriphosphazene units. As the concentration of the salt is increased to about 20%, the polymer−salt complex developed a tough morphology.

Physical Properties. At room temperature, high molecular weight MEEP ($M_n > 10^6$), synthesized via the ring opening polymerization method, is an adhesive semisolid that undergoes viscous flow under pressure.[21] This behavior is characteristic of a high molecular weight amorphous polymer well above its T_g.

For the triarm MEEP polymers **2a**−**c**, the low molecular weight star polymer **2b** ($M_n = 2.3 \times 10^4$, ca. 180 repeat units) was more viscous than the corresponding linear polymer of the same molecular weight **1c** ($M_n = 1.7 \times 10^4$, ca. 180 repeat units).[45] This can be explained by the lower ability of the star polymer to undergo reorientation and slippage than the linear polymer, due to the different orientations of the arms from the center. Also, at low molecular weights, the properties of the core may have a significant influence on the physical properties of the star polymer. However, at higher molecular weights the properties of the core are probably less significant; hence there was no noticeable difference in flow behavior between the long-chain star and linear polymers of similar molecular weights. This could be due to an increase in entanglements in the linear polymers. Increased resistance to flow occurred as $LiSO_3CF_3$ was added to polymers **1c**−**d** and **2b**−**c**, and this was attributed to the transient ionic cross-links formed as the lithium ions coordinate to the oxygen atoms of the etheric side groups. Thus, as salt concentration increases, so does the resistance to flow.

A high molecular weight star polymer with a narrow polydispersity was not synthesized because of the problems associated with multimodal distribution of molecular weight. Thus, no direct comparison could be made with high molecular weight MEEP ($M_n \sim 10^6$). Of all the polymers synthesized, polymer **3** was the most dimensionally stable and formed stable, free-standing films. This is probably due to extensive chain entanglements that result from the highly branched nature of the polymer. In practical applications this is a major advantage, because the polymer does not need to be cross-linked after fabrication into various shapes. When exposed to light for prolonged periods of time, polymer **3** becomes cross-linked, presumably through free radical C−H and C−C bond cleavage and cross-combination.

Differentiating between Linear and Star Polymers. The MEEP-type polymers **1a**−**d** and **2a**−**c** were all analyzed by GPC−light scattering experiments. However, problems arose due to polymer aggregation and interactions of the polymers with the GPC column, and no useful information could be obtained from the light scattering data that might distinguish between the linear and triarm star MEEP polymers of similar molecular weight. However, the intrinsic viscosities, determined at 40 °C in THF, showed that the star polymers have a lower viscosity in solution than their linear counterparts with a similar molecular weight, presumably because of their smaller hydrodynamic volume in solution. This is illustrated in Figure 7.

Conclusions

The synthesis and characterization of seven MEEP-type polymers prepared via the cationic "living" polymerization at ambient temperatures, and one highly branched side-group-containing polyphosphazene, are reported. Poly(dichlorophosphazenes) with controlled molecular weights and low polydispersity indices were synthesized by the cationic polymerization of a phosphoranimine $Cl_3P{=}NSiMe_3$ (**4**) using linear and triarmed initiators. Although none of the lower molecular weight polymers ($M_n < 10^5$) have a higher dimensional stability than the classical high molecular weight MEEP ($M_n > 10^6$), the star polymers impart more rigidity at low molecular weights ($M_n < 1 \times 10^3$) than do their linear counterparts with similar molecular weights. The

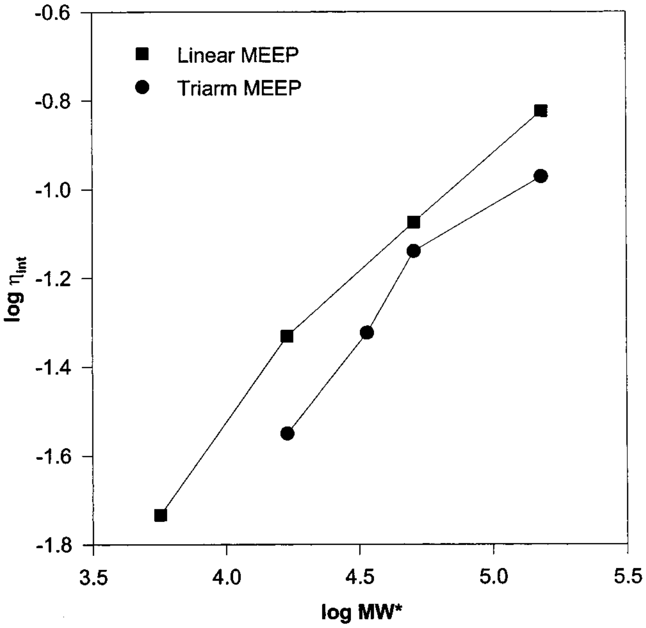


Figure 7. Variation of molecular weight with intrinsic viscosity. Molecular weight was calculated from monomer: initiator ratio.

highly branched, complex-architecture polymer **3**, synthesized by the ring opening polymerization method, is more rigid than MEEP with a comparable molecular weight. All the polymers studied followed a trend in conductivity that was similar to that of high molecular weight MEEP, where the addition of more salt increased the conductivity up to a maximum. The lower molecular weight polymers **1c** and **2b** and highly branched polymer **3** displayed higher maximum conductivities than MEEP. In future work, high molecular weight star polymers with narrow polydisperties need to be synthesized in order to compare them to MEEP synthesized by conventional methods. Another area being investigated in our program is the effect on the dimensional stability and ionic conductivity of increasing the number of arms of the star polymer.

Experimental Section

Materials. 2-(2-Methoxyethoxy)ethanol (Aldrich) was purified by vacuum distillation from $\mathrm{CaH_2}$. $\mathrm{N[CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+]_3[PCl_6^-]_3}$,[34] $\mathrm{Cl_3P{=}NSiMe_3}$,[29,30] $\mathrm{[-CH_2NH[(CF_3CH_2O)_2P{=}N-PCl_3^+]_2[PCl_6^-]_2}$,[44] and $\mathrm{NaOCH_2CH_2OCH_2CH_2OCH_3}$ were synthesized and purified by literature procedures. Phosphorus pentachloride (Aldrich) was sublimed under vacuum. Sodium metal and sodium hydride (60% suspension in mineral oil) were obtained from Aldrich and were used without further purification. Lithium triflate (Aldrich) was dried under vacuum (60 °C, 1 mmHg) for 2 days. Tetrahydrofuran (THF) and hexane (Aldrich) were distilled into the reaction flask from sodium-benzophenone ketyl in an atmosphere of dry argon. Dichloromethane (Aldrich) was dried and distilled from $\mathrm{CaH_2}$ and then from $\mathrm{P_2O_5}$ into the reaction flask.

All glassware was dried overnight in an oven or was flame-dried under vacuum before use. The reactions were carried out using standard Schlenk techniques or in an inert atmosphere glovebox (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

Equipment. ^{31}P, ^{13}C, and ^{1}H spectra were recorded with a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to an internal $\mathrm{CDCl_3}$ reference. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 mm guard, AM gel 10 mm linear and AM gel 10 mm 10^4 Å column, with the system calibrated versus polystyrene standards (Polysciences). The samples were eluted with a 0.01 M solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). GPC–light scattering experiments were performed with the use of a Wyatt Dawn DSP laser photometer operating at the 4880 Å argon ion laser line, coupled to a Wyatt Optilab DSP interferometric refractometer. Dilute solutions of **1a**–**d** and **2a**–**c** in a 0.01 M solution of tetra-*n*-butylammonium nitrate in THF gave a refractive index increment (d*n*/d*c*) of 0.054 mL/g, which was independent of the molecular weight of the sample. Dilute solution viscosity measurements were made at 40 °C with a Cannon Ubbelohde viscometer immersed in a water bath controlled to within 0.1 °C. Samples were diluted with THF containing 0.1% tetra-*n*-butylammonium bromide; and filtered. Glass transition temperatures were determined by DSC using a Perkin-Elmer-7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Polymer samples were heated from −100 to +75 °C under an atmosphere of dry nitrogen. The heating rates used were 10, 20 and 40 °C/min. The glass transition temperatures were determined at 20 °C/min.

Impedance Analysis. Solutions of polymer and salt were prepared with the use of freshly distilled THF. The THF was removed by evaporation and the polymer–salt complexes were placed in a vacuum oven (60 °C, 10 mmHg) for 2 days. The samples were allowed to cool under vacuum before 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. The polymers were then placed in a fixture to which leads were attached and complex impedance analyses performed using a Hewlett-Packard 4192A LF impedance analyzer with an ac frequency range of 5 Hz to 13 MHz.

Polymerization of $\mathrm{Cl_3P{=}NSiMe_3}$ (4) by $\mathrm{PCl_5}$ in Solution. General Procedure. Polymers **1a**–**c** were all prepared in a similar manner. $\mathrm{Cl_3P{=}NSiMe_3}$ (**4**) (2.81 g, 13 mmol) was added quickly to $\mathrm{PCl_5}$ (0.26 g, 1.3 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ at 25 °C to form $\mathrm{[Cl_3P{=}N(Cl_2P{=}N)_{\mathit{n}}PCl_3]^+[PCl_6]^-}$ (**5**) as determined by ^{31}P NMR spectroscopic analysis ($\delta = -17.1$ ppm). All volatiles were removed in vacuo. This product was dissolved in THF (250 mL), and a solution of the sodium salt of 2-(2-methoxyethoxy)ethanol (50 mL, 1.0 M) in THF (300 mL) was added dropwise, and the mixture was stirred overnight at 40 °C. The solvent was removed by rotary evaporation to leave a viscous solution which was dialyzed against water (5 days) and then methanol (2 days). For polymer **1a**: ^{31}P NMR ($\mathrm{CDCl_3}$), δ (ppm): −0.37 to −0.74 (d, $\mathrm{-N{=}\mathit{P}(OR_3)_3}$), −4.06 (t, $\mathrm{(RO)_3P-N{=}\mathit{P}(OR)_2-N{=}P(OR)_2-}$), −6.40 (d, $\mathrm{-(N{=}\mathit{P}(OR)_2)_{\mathit{n}}-N{=}P(OR)_3}$). ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 4.08 (br, 2H, $\mathrm{-POC\mathit{H}_2CH_2O-}$), 3.60–3.64 (m, 4H, $\mathrm{-POCH_2C\mathit{H}_2OC\mathit{H}_2CH_2O-}$), 3.49 (t, 2H, $\mathrm{-POCH_2CH_2OCH_2C\mathit{H}_2O-}$), 3.33 (s, 3H, $\mathrm{-OCH_2CH_2OCH_2CH_2OC\mathit{H}_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$), δ (ppm): 71.84 ($\mathrm{-POCH_2CH_2OCH_2\mathit{C}H_2O-}$), 70.51 ($\mathrm{-POCH_2\mathit{C}H_2O-}$), 70.24 ($\mathrm{POCH_2CH_2O\mathit{C}H_2-}$), 65.22 ($\mathrm{PO\mathit{C}H_2-}$), 58.81 ($\mathrm{-OCH_2CH_2OCH_2CH_2O\mathit{C}H_3}$). Anal. Calcd: C, 42.83; H, 7.91; N, 4.56. Found: C, 40.75; H, 7.17; N, 4.35; Cl, 0.54.

The molecular weights of **1** were controlled by variations in the phosphoranimine **4**:$\mathrm{PCl_5}$ ratios. These reactions were carried out with the following: (i) a 30:1 ratio of **4** (2.81 g, 13 mmol) with $\mathrm{PCl_5}$ (0.086 g, 0.41 mmol) to yield **1b**. For **1b**: ^{31}P NMR ($\mathrm{CDCl_3}$), δ (ppm): −7.67. Anal. Calcd: C, 42.58; H, 7.85; N, 4.81. Found: C, 41.62; H, 7.36; N, 4.68; Cl, 0.40.

(ii) a 90:1 ratio of **4** (2.81 g, 13 mmol) with $\mathrm{PCl_5}$ (0.029 g, 0.14 mmol) to yield **1c**. For **1c**: ^{31}P NMR ($\mathrm{CDCl_3}$), δ (ppm): −7.57. Anal. Calcd: C, 42.49; H, 7.84; N, 4.90. Found: C, 42.44; H, 7.38; N, 4.75; Cl, 0.18.

Polymerization of $\mathrm{Cl_3P{=}NSiMe_3}$ (4) by $\mathrm{N[CH_2CH_2NH(CF_3CH_2O)_2P{=}N-PCl_3^+]_3\ [PCl_6^-]_3}$ (7) in Solution. General Procedure. Polymers **2a**–**c** were all prepared in a similar manner. The following preparation of **2a** is typical. To a stirred solution of **7** (0.45 g, 0.21 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added **4** (2.80 g, 12 mmol). After 3 h all of the initial monomer **4** had reacted, as evidenced by the disappearance of the ^{31}P NMR resonance for **4** at −54 ppm and the presence of a new resonance at −17.6 ppm for $[N{=}PCl_2]_n$. For $N\{CH_2CH_2NH(CF_3CH_2O)_2P{-}N{=}PCl_2{-}N{=}PCl_2{-}[N{=}PCl_2]_n\}_3$: ^{31}P NMR (CH_2Cl_2): $\delta = 8.2$ (d, 1P, $^2J_{pp} = 29$ Hz, $(CF_3CH_2O)_2\mathit{P}{-}N{=}$), −14.5, −15.5 (t, 2P, $^2J_{pp} = 40$ Hz, $(CF_3CH_2O)_2P{-}N{=}\mathit{P}Cl_2{-}N{=}\mathit{P}Cl_2(N{=}PCl_2)_n]$), −17.6 ppm (br s, 18P, $[N{=}PCl_2]_n$). All volatile species were removed at reduced pressure. A solution of sodium 2-(2-methoxyethoxy)ethanol (50 mL, 1.0 M) was added to the poly(dichlorophosphazene) in THF (250 mL), and the mixture was refluxed overnight. The solvent was removed by rotary evaporation to leave a viscous solution which was dialyzed against water (5 days) and then methanol (2 days). Polymer **2a** was then washed with hexane. Polymer **2a**: ^{31}P NMR ($CDCl_3$), δ (ppm): 0.05 (br, m, 1P, $-N{=}\mathit{P}(OR_3)_3$), −3.41 (br, m, 2P, $-N{=}\mathit{P}(OR)_2{-}N{=}P(OR_3)_3$), −7.10 (s, 22P, $-(N{=}P(OR)_2)_n-$). ^1H NMR ($CDCl_3$), δ (ppm): 4.05 (br, 2H, $-POC\mathit{H}_2CH_2O-$), 3.63 (m, 4H, $-POCH_2C\mathit{H}_2OC\mathit{H}_2CH_2O-$), 3.49 (t, 2H, $-POCH_2CH_2OCH_2C\mathit{H}_2O-$), 3.35 (s, 3H, $-OCH_2CH_2OCH_2CH_2OC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 71.94 ($-POCH_2CH_2OCH_2\mathit{C}H_2O$), 70.38 ($-POCH_2\mathit{C}H_2O-$), 70.24 ($POCH_2CH_2O\mathit{C}H_2-$), 64.99 ($PO\mathit{C}H_2-$), 58.79 ($-OCH_2CH_2OCH_2CH_2O\mathit{C}H_3$). Anal. Calcd: C, 41.87; H, 7.65; N, 4.93. Found: C, 40.30; H, 7.17; N, 4.94; Cl, 0.44.

The molecular weights of **2** were controlled by variation of the **4**:initiator **7** ratios. These reactions were carried out with the following: (i) a 180:1 ratio of **4** (2.83 g, 12 mmol) with **7** (0.15 g, 0.067 mmol) to yield **2b**. For **2b**: ^{31}P NMR ($CDCl_3$), δ (ppm): −7.71. Anal. Calcd: C, 42.24; H, 7.76; N, 4.94. Found: C, 41.43; H, 7.33; N, 4.93; Cl, 0.38. (ii) A 540:1 ratio of **4** (2.80 g, 12 mmol) with **7** (0.048 g, 0.022 mmol) to yield **2c**. For **2c**: ^{31}P NMR ($CDCl_3$), δ (ppm): −7.71. Anal. Calcd: C, 42.36; H, 7.81; N, 4.95. Found: C, 41.51; H, 7.36; N, 4.80; Cl, 0.60.

Polymerization of $Cl_3P{=}NSiMe_3$ (4) by $[-CH_2NH[(CF_3CH_2O)_2P{=}N{-}PCl_3^+]_2[PCl_6^-]_2$ in Solution. The procedure for the synthesis of the difunctional initiator was similar to that followed for **7**, with the starting material being ethylenediamine.[44] The synthesis of the polymer was carried as follows: $Cl_3P{=}NSiMe_3$ (**4**) (3.17 g, 14 mmol) was added to the difunctional initiator $[-CH_2NH[(CF_3CH_2O)_2P{=}N{-}PCl_3^+]_2[PCl_6^-]_2$ (0.034 g, 0.026 mmol) to form the poly(dichlorophosphazene). This was dissolved in THF (250 mL) and a solution of the sodium salt of 2-(2-methoxyethoxy)ethanol (56 mL, 1.0 M) in THF (300 mL) was added dropwise and stirred overnight under warm conditions (40 °C). The solvent was removed by rotary evaporation to leave a dark viscous solution which was dialyzed against water (5 days) and then methanol (2 days). After purification a beige viscous oil was obtained. For polymer **1d**: ^{31}P NMR ($CDCl_3$), δ (ppm): −7.21 ($N{=}\mathit{P}(OR)_2$). ^1H NMR ($CDCl_3$), δ (ppm): 4.05 (br, s, 2H, $-POC\mathit{H}_2CH_2O-$), 3.59−3.63 (br, m, 4H, $-POCH_2C\mathit{H}_2OC\mathit{H}_2CH_2O-$), 3.49 (br, m, 2H, $-POCH_2CH_2OCH_2C\mathit{H}_2O-$), 3.34 (s, 3H, $-OCH_2CH_2OCH_2CH_2OC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 71.93 ($-POCH_2CH_2OCH_2\mathit{C}H_2O$), 70.37 ($-POCH_2\mathit{C}H_2O-$), 70.23 ($POCH_2CH_2O\mathit{C}H_2-$), 65.01 ($PO\mathit{C}H_2-$), 58.77 ($-OCH_2CH_2OCH_2CH_2O\mathit{C}H_3$). Anal. Calcd: C, 42.39; H, 7.86; N, 4.94. Found: C, 43.83; H, 7.43; N, 4.26; Cl, 0.37.

Synthesis of Mono(tetrahydropyranyl)triethylene Glycol ($THPO{-}CH_2CH_2(OCH_2CH_2)_2{-}OH$). To a solution of triethylene glycol (35.0 g, 0.23 mol) and pyridinium *p*-toluene sulfonate (PPTS) (0.57 g, 2.3 mmol.) in 500 mL of dichloromethane was added a mixture of 2,3-dihydropyran (17.64 g, 0.21 mol) in 200 mL of dichloromethane dropwise over a period of 3 h. The mixture was stirred for an additional 3 h at room temperature. The solution was then washed with small amounts of water and crude product was isolated by removal of solvent under vacuum. The crude material contained three different products, which were separated by column chromatography using a THF/hexane mixture (3:7) as the eluent. The required product, a colorless oil (10.8 g, 20% yield), was isolated as the second fraction. ^1H NMR: ($CDCl_3$), δ (ppm): 4.50 (q, 1H), 3.75 (m, 2H), 3.60 (m, 8H), 3.40 (m, 4H), 1.63 (m, 2H), 1.46 (m, 4H). ^{13}C NMR: ($CDCl_3$), δ (ppm) 98.9, 70.6, 70.5, 66.6, 62.2, 30.5, 25.4, 19.4. MS (*m*/*e*): calcd, 233; found, 233.

Synthesis of Penta(methoxyethoxyethoxy)monochlorocyclotriphosphazene (8a). (2-(2-Methoxyethoxy))ethanol (17.9 g, 0.15 mol.) was allowed to react overnight with sodium metal (3.50 g, 0.16 mol.) in THF (300 mL) in a three-neck flask. This solution was then cannulated into an additional funnel connected to a three-neck flask containing a solution of hexachlorocyclotriphosphazene (10 g, 0.029 mol) in THF (500 mL). The sodium alkoxide solution was added dropwise over a period of 3 h at room temperature. The ^{31}P NMR spectrum of the product solution indicated that only two compounds (63% of pentasubstituted compound (**8a**) and 37% hexasubstituted compound (**8b**)) were formed. The mixture of products was isolated by filtering off the salts and vacuum evaporation of the solvent. The product was stored under vacuum. ^{31}P NMR: ($CDCl_3$), δ 27.3 (t), 18.5 (s), 16.0 (d).

Synthesis of Compound 10. To a solution of the sodium salt of the monoprotected triethylene glycol (obtained by reaction of the alcohol (2.3 g, 9.8 mmol) with 60% sodium hydride (0.39 g, 9.8 mmol) in THF (100 mL)) was added a mixture of hexasubstituted and pentasubstituted compounds (10 g, which contains 6.3 g of pentasubstituted product). The mixture was stirred at room temperature and was complete in a period of 2 h as detected by ^{31}P NMR (singlet at +18.5 ppm). The product was isolated by removal of salt by centrifugation and evaporation of solvent. Deprotection of this compound (7.92 g, 8.22 mmol) was achieved by reaction with PPTS (0.21 g, 0.82 mmol) in 95% ethanol (200 mL) at 55 °C for 4 h. Compound **10** was separated from the hexasubstituted, by column chromatography using a mixture of THF/hexane (1:1) as the eluent. ^1H NMR: ($CDCl_3$), δ 4.05 (m, 12H), 3.70 (t, 2H), 3.65 (m, 28H), 3.58 (m, 6H), 3.47 (m, 4H), 3.32 (s, 15H). ^{13}C NMR: ($CDCl_3$), δ 71.8, 70.6, 70.5, 66.6, 66.5, 65.0, 58.9. MS (*m*/*e*) calcd 879; found 879.

Synthesis of Polymer 3. Poly(dichlorophosphazene) (0.27 g, 2.3 mmol) was dissolved in 100 mL of THF. Compound **10** (5 g, 5.7 mmol) was allowed to react with 60% sodium hydride (0.23 g, 5.7 mmol) in THF (100 mL). Once all the sodium hydride had reacted, the solution was transferred using a cannula into an addition funnel attached to the flask containing the solution of poly(dichlorophosphazene). The sodium salt was added dropwise to a warm solution of the polymer. The reaction was complete in a period of 12 h as observed by ^{31}P NMR. The polymer was purified by dialysis against water for 4 days and then against methanol for 3 days. Evaporation of solvent yielded an off-white polymer (3.60 g). ^{31}P NMR: ($CDCl_3$), δ −8.0, +18.5. ^1H NMR: ($CDCl_3$), δ (ppm) 4.05 (br, 24H), 4.01 (br, 4H), 3.59−3.40 (m, 76H), 3.29 (s, 30H). ^{13}C NMR: ($CDCl_3$), δ 72.0, 71.3, 69.8, 66.2, 65.5, 60.2, 58.7. Anal. Calcd: C, 41.31; H, 7.44; N, 5.44. Found: C, 40.62; H, 7.24; N, 5.49.

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