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Poly(phosphazene−ethylene oxide) Di- and Triblock Copolymers as Solid Polymer Electrolytes

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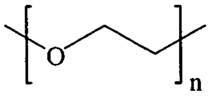
ABSTRACT: The synthesis of polyphosphazene-*co*-poly(ethylene oxide) block copolymers with well-defined molecular weights has been accomplished via end-functionalized polymer intermediates. Mono- and diamine-terminated poly(ethylene oxides) (PEO = $(CH_2CH_2O)_n-CH_2CH_2-$) were used to produce polymer-based phosphoranimines, $CH_3O-(CH_2CH_2O)_n-CH_2CH_2-NH(CF_3CH_2O)_2P{=}NSiMe_3$ and $Me_3SiN{=}P(OCH_2CF_3)NH-(CH_2CH_2O)_n-CH_2CH_2-NH(CF_3CH_2O)_2P{=}NSiMe_3$. These were then converted to macroinitiators via reaction with PCl_5 to produce $CH_3O-PEO-NH[(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ and $[Cl_3PN{=}P(OCH_2CF_3)NH-PEO-NH[(CF_3CH_2O)_2P{=}NPCl_3]^{2+}[PCl_6]_2^-$, respectively. These macroinitiators were used to polymerize $Cl_3P{=}NSiMe_3$ in a living manner to produce diblock copolymers of polyphosphazenes with poly(ethylene oxide) or triblock copolymers with poly(ethylene oxide) blocks flanked by polyphosphazene components. In addition, the monophosphoranimine-terminated PEO was employed as a terminator in the living, cationic polymerization of $Cl_3P{=}NSiMe_3$ to produce triblock copolymers with a polyphosphazene block flanked by two poly(ethylene oxide) blocks. Polymers for use as solid−ionic conduction media or hydrogels were produced by nucleophilic replacement of the chlorine atoms along the polyphosphazene segments by methoxyethoxyethoxy units. The ionic conductivities of these materials, after complexation with varying ratios of lithium triflate, ranged from 7.6×10^{-6} to 1.0×10^{-4} S cm^{-1} for a temperature range of 20−80 °C.

Introduction

One objective of this work was the synthesis of polyphosphazene systems that could be used in solid polymer electrolyte complexes. The first reports of complexes between poly(ethylene oxide) (PEO, **1**) and potassium thiocyanate salts appeared in the 1970s.[1−3] This was followed by the recognition that PEO salt complexes could be used as the ion-conducting medium in portable energy storage device.[4,5] Since then, there have been numerous studies and reviews on both the fundamental aspects of this subject and the use of polymer salt complexes in electrochemical devices.[6−9]



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Although progress has been made in enhancing the conductivity of solid polymer electrolytes, the most widely used systems are still based on salt solutions in liquids or gels. The current limited use of solid systems results from the strict requirements needed for a polymer to be suitable as a solid electrolyte material.[6,7] The macromolecule must solvate salts through the presence of cation or anion coordination sites throughout the polymer system. Oxygen atoms often serve this purpose. The polymer should also be amorphous over a wide temperature range, since crystalline domains impede the migration of ions across the matrix. Finally, an effective solid polymer electrolyte should allow the facile diffusion of ions by means of polymer molecular motion. Thus, a low glass transition temperature is desirable. Polymers that meet these three requirements are attractive candidates for solid polymer electrolytes in numerous fields including energy storage devices such as batteries.

Several reasons exist for the use of solid polymer electrolytes rather than liquids in batteries. Most polymers have good dimensional stability and are readily fabricated into a wide variety of shapes and sizes. Another advantage of polymers is their low density, which leads to increased energy densities. However, the main drawback of polymeric systems is the low ionic conductivity compared to liquid media. One way to overcome this shortcoming is through the production of a gel electrolyte via the addition of small molecule plasticizers. However, these additives are generally volatile, flammable species that create hazards in the final energy storage device. Thus, a major challenge exists to prepare a *solid* electrolyte system with room-temperature conductivities of 10^{-3} S/cm or higher.

The polymer that historically has received the most attention as a solid polymer electrolyte is poly(ethylene oxide).[6−9] A major disadvantage of PEO is its crystallinity, which limits the room-temperature ionic conductivity to 10^{-7} S/cm. A number of attempts to decrease the crystallinity of PEO have been based on PEO-containing copolymers. For example, several research groups have examined copolymers of PEO and poly(epichlorohydrin),[10−12] while others have used copolymers of PEO with polysiloxanes[13] or polyurethanes.[14] Another polymer system that has been developed in an

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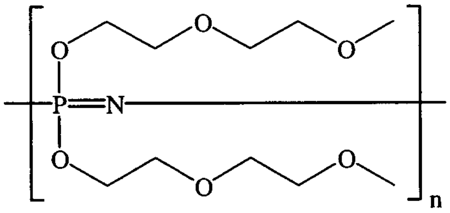
attempt to overcome the limitations of PEO is poly[bis(2-(2′-methoxyethoxy)ethoxy)phosphazene], MEEP (**2**), first reported by Shriver, Allcock, and their co-workers in 1984.[15−18] MEEP has six electron-donating oxygen atoms per polymer repeat unit that provide multiple cation coordination sites along the polymer chain. Also, the relatively short and flexible side groups prevent crystallization in the polymer. In addition to the side chains, the inherent flexibility of the polyphosphazene backbone gives MEEP a low T_g of −84 °C. Thus, MEEP is completely amorphous and, when treated with lithium triflate, gives significantly enhanced room-temperature ionic conductivity in the range of 10^{-5} S/cm. Furthermore, the conductivity of MEEP can be increased by 2 orders of magnitude by the addition of small quantities of organic molecules to generate a gel electrolyte.[19]



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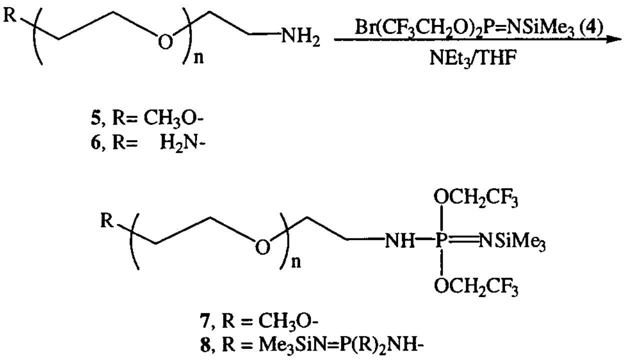
The amorphous morphology of MEEP is one of its primary advantages. However, it leads to poor dimensional stability and materials that flow under minimal stress. MEEP is, in fact, a gum rather than a solid polymer. Several research efforts have been directed toward improving the dimensional stability of MEEP. One approach involved γ- or ultraviolet-irradiation to yield dimensionally stable, cross-linked films that have similar ionic conductivities to that of the un-cross-linked polymer.[20−22] Blends of PEO and MEEP also showed improved mechanical properties, with ionic conductivities comparable to that of MEEP.[23−25] Other research aimed at improving the conductivity and dimensional stability of MEEP includes the synthesis of polyphosphazenes that possess branched oligo(oxyethylene) or crown ether side groups.[26,27]Hybrid phosphazene−organic copolymers may provide another option to overcome the low dimensional stability of MEEP. Several research groups have examined copolymers containing polyphosphazenes.[28−30] However, to our knowledge the work reported here is the first synthesis of well-defined, linear phosphazene−organic ionically conducting block copolymers.

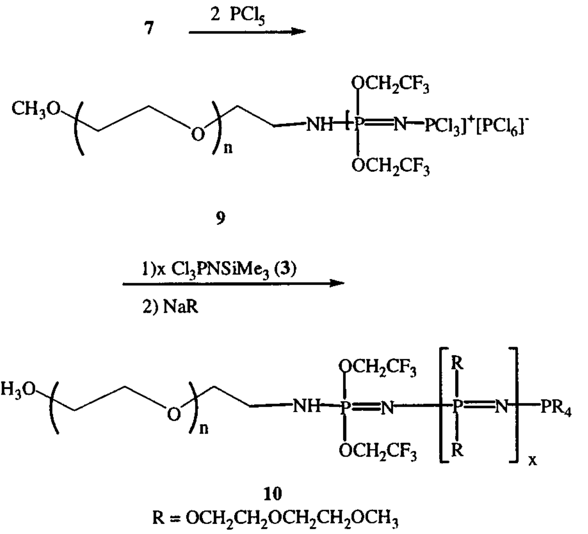
The development of an ambient temperature route for the synthesis of polyphosphazenes via the living, cationic polymerization of trichlorophosphoranimine ($Cl_3P{=}NSiMe_3$, **3**) provides a method for the synthesis of polymers with well-defined molecular weights, narrow polydispersities, and controlled architectures.[31−34] Previous studies, involving the polymerization behavior of $Cl_3P{=}NSiMe_3$, have shown that this monomer is readily initiated by short chain ionic species, such as $[Cl_3P{=}N{-}PCl_3]^+[PCl_6]^-$, to form linear poly(dichlorophosphazene) $[Cl_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$. Extensions of this methodology have yielded telechelic polyphosphazenes, triarmed star-branched polyphosphazenes, linear block copolymers, and graft copolymers.[35−40]

Recent advances have illustrated the feasibility of employing phosphoranimine-terminated *organic* polymers as initiators and/or terminators in the living, cationic polymerization of polyphosphazenes.[37−39] Thus, the utilization of preformed polymers in conjunction with the living cationic polymerization of **3** provides a method for the controlled synthesis of linear block copolymers that contain segments of polyphosphazenes and organic polymers. The objective of this present work was to expand the living, cationic polymerization of $Cl_3P{=}NSiMe_3$ and to produce materials that can be utilized as solid polymeric electrolytes. In this paper we report the synthesis of a variety of di- and triblock phosphazene−ethylene oxide copolymers produced from mono- and diphosphoranimine-terminated poly(ethylene oxides). We also report the ionic conductivities of complexes of these polymers with lithium triflate.

Scheme 1



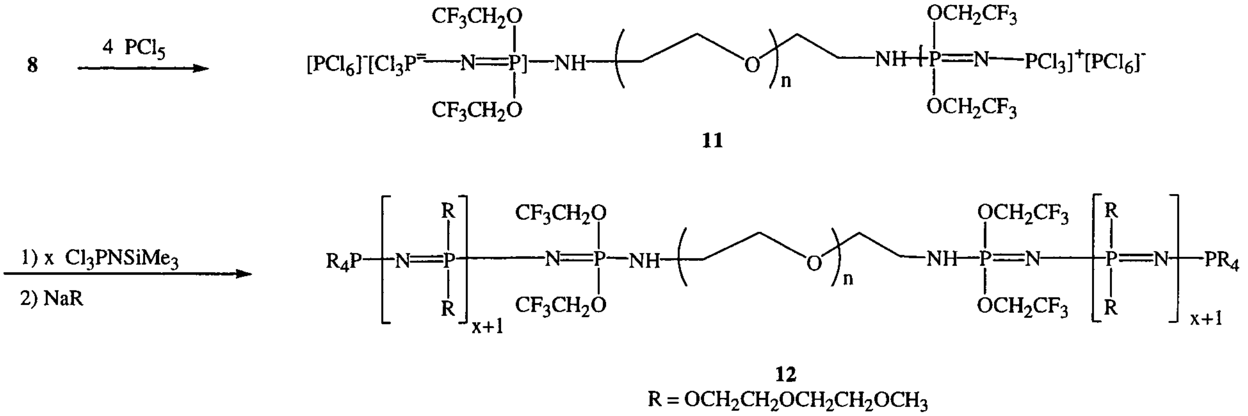
Scheme 2



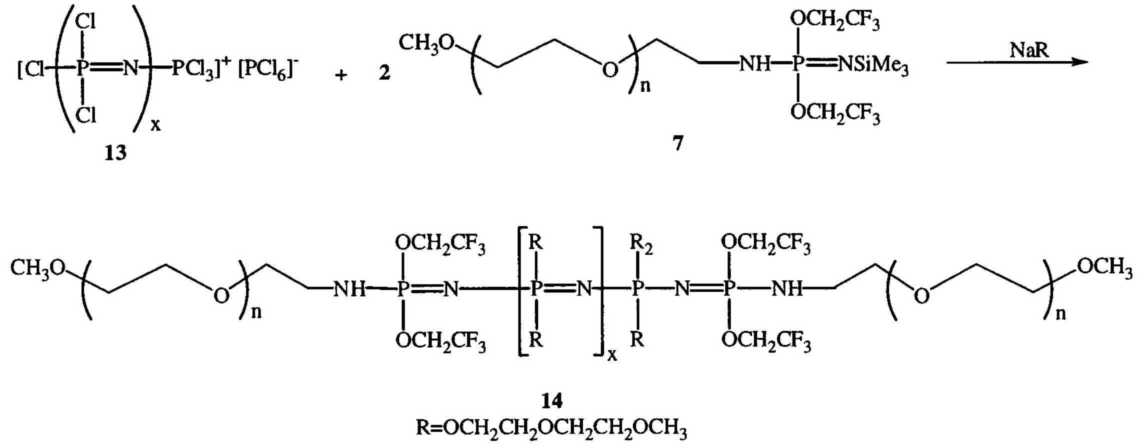
Results and Discussion

Synthesis of Phosphoranimine-Terminated Poly(ethylene oxide) (7 and 8). Phosphoranimines such as $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**4**) are known to readily undergo bromine replacement reactions in the presence of amines to produce phosphoranimines such as $R{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$. These species can then be utilized as initiators and/or terminators in the living polymerization of $Cl_3P{=}NSiMe_3$.[35] With this in mind, stoichiometric amounts of amine-terminated poly(ethylene oxide), such as $CH_3O{-}PEO{-}NH_2$ (**5**) and $H_2N{-}PEO{-}NH_2$ (**6**), were allowed to react with **4** in THF and in the presence of triethylamine. This process produced the phosphoranimine-terminated poly(ethylene oxide)s, $CH_3O{-}PEO{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (**7**) and $Me_3SiN{=}P(OCH_2CF_3)NH{-}PEO{-}NH(CF_3CH_2O)_2P{=}$

Scheme 3



Scheme 4



NSiMe$_3$ (**8**) (Scheme 1). The formation of **7** and **8** was evident from the characteristic peak near −1 ppm in the ^{31}P NMR spectra. Both products were obtained as white powders and were subsequently used as initiators in the living polymerization of **3**. The monofunctionalized poly(ethylene oxide) (**7**) was also used as a terminator for the living, cationic polymerization of phosphoranimines.

Synthesis of Poly(ethylene oxide)-*block*-polyphosphazene Diblock Copolymers (10). Scheme 2 outlines the strategy used for the production of poly(ethylene oxide)-*block*-polyphosphazene materials. The monophosphoranimine-terminated PEO (**7**) was first initiated with 2 mol equiv of PCl$_5$ at −78 °C in CH$_2$Cl$_2$ to generate the cationic initiator PEO−NH[(CF$_3$CH$_2$O)$_2$P=N−PCl$_3$]$^+$[PCl$_6$]$^-$ (**9**). The formation of this species was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum at 12 ppm and −5 ppm for the N−PCl$_3^+$ and (CF$_3$CH$_2$O)$_2$$P$=N units. Subsequent treatment of this initiator with a given amount of Cl$_3$P=NSiMe$_3$ provided diblock copolymers with specific chain lengths. Variations in the molecular weight of **10** were obtained by controlling the ratio of **9** to **3**. The progress of the reactions was monitored by ^{31}P NMR spectroscopy, which indicated the conversion of monomer at −54 ppm to polymer at −17 ppm. The chlorine atoms were then replaced by reaction with sodium methoxyethoxyethoxide to yield the chlorine-free block copolymer **10**.

Polyphosphazene-*block*-poly(ethylene oxide)-*block*-polyphosphazene Triblock Copolymers (12). Triblock copolymers **12** were synthesized using a similar procedure described for the synthesis of the diblock copolymers. As shown in Scheme 3, subsequent reaction of the difunctional PEO−phosphoranimine, **8**, with 4 mol equiv of PCl$_5$ in CH$_2$Cl$_2$ resulted in the formation of the initiator **11**. This ionic species was capable of inducing the polymerization of **3** to form triblock copolymers. The triblock copolymers were subsequently treated with sodium methoxyethoxyethoxide to produce the MEEP−PEO−MEEP triblock copolymer **12**.

Poly(ethylene oxide)-*block*-polyphosphazene-*block*-poly(ethylene oxide) Triblock Copolymers (14). Recent work in our group has shown that living polyphosphazene (**13**) can be terminated with triorganophosphoranimines, which allows the controlled introduction of two functional units at the termini of the polyphosphazene chain.[35,38] Thus, compound **7** was employed as a PEO macromolecular terminator for the living polymerization of polyphosphazenes. As illustrated in Scheme 4, triblock copolymers **14** were prepared by the addition of **7** to **13**. The termination process was monitored by ^{31}P NMR spectroscopy, which showed the disappearance of the PCl$_3^+$ terminal units at −8 ppm and the appearance of the new end groups at 5 ppm. Following complete termination, the chlorine atoms were replaced with methoxyethoxyethoxide via nucleophilic substitution to give PEO−MEEP−PEO triblock copolymer **14**.

Gel Permeation Chromatography Analysis. Molecular weight data were estimated using gel permeation chromatography (GPC) and are summarized in Table 1. As shown, the molecular weights obtained for these polymeric systems do not follow a consistent trend.

Table 1. Molecular Weight Data

polymer	PEO r.u.[a]/block	PN r.u.[a]/block	calcd wt % PN[b]	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ exptl[c]	PDI
10a	110	70	80	24.6	17.8	1.7
10b	110	140	89	44.4	17.8	1.6
10c	135	140	87	45.5	23.2	1.5
12a	80	50	88	31.9	21.0	2.7
12b	80	100	94	60.1	23.5	2.5
12c	80	120	95	71.5	36.8	2.0
14a	110	50	59	23.9	18.4	1.4
14b	110	100	75	38.2	20.9	1.9
14c	110	150	81	52.4	21.3	1.7

[a] Repeat units per block based on the starting PEO polymer and the initial ratio of monomer to PCl_5 initiator for 100% conversion. [b] Calculated from the initial ratio of monomer to PCl_5 initiator for 100% conversion. [c] Obtained by GPC vs polystyrene standards.

Table 2. Ionic Conductivity Data

polymer	ionic conductivity[a] ~20 °C	ionic conductivity[a] ~80 °C	wt % Li triflate[b]	[Li]/[−O−][c]
14c	4.6×10^{-5}	1.6×10^{-4}	5.0	0.015
14b	2.9×10^{-5}	1.9×10^{-4}	7.5	0.022
14a	3.4×10^{-5}	1.8×10^{-4}	5.0	0.015
12c	2.1×10^{-5}	1.8×10^{-4}	7.5	0.023
12b	1.0×10^{-5}	1.8×10^{-4}	7.5	0.023
12a	7.6×10^{-6}	2.2×10^{-4}	5.0	0.015
10c	1.2×10^{-5}	1.0×10^{-4}	5.0	0.015
10b	6.3×10^{-6}	1.7×10^{-4}	7.5	0.023
10a	1.2×10^{-5}	1.4×10^{-4}	5.0	0.015

[a] Ionic conductivities were measured within 3 deg of 20 and 80 °C. [b] The conductivities are reported for the samples with the weight percent lithium triflate that gave maximum conductivity at room temperature. [c] The number of lithium ions per ether oxygen.

However, the data obtained from elemental analysis and ^{1}H NMR do agree with theoretical values. Thus, we concluded that the variation of the molecular weights obtained from GPC was due to changes in the dynamic volumes of our block copolymers vs linear polystyrene and not a result of incomplete initiation or propagation during the polymerization process.

GPC analysis was also used to verify that the products obtained in this work were copolymers and not mixtures of PEO and MEEP homopolymers. It is well-known that the homopolymer of $[(CF_3CH_2O)_2P{=}N]_n$ has a negative polarity refractive index while block copolymers containing segments of $[(CF_3CH_2O)_2P{=}N]_n$ show a positive polarity refractive index. This change of polarity of the refractive index of the GPC peak is consistent with the GPC behavior of all-phosphazene block copolymers such as $[N{=}P(OCH_2CF_3)_2]_n{-}[N{=}PR_2]_m$ ($R_2 = Ph(OCH_2CF_3)$, Me(Et), Me_2) and is reliable evidence that block copolymers have been formed.[33,34] To illustrate the formation of block copolymers via GPC, analogous copolymers of **10**, **12**, and **14** with trifluoroethoxide side groups (i.e., $[(CF_3CH_2O)_2P{=}N]_n$) instead of methoxyethoxyethoxide were prepared. The synthesis of the trifluoroethoxide-derivatized polymers was carried out using the same methods as **10**, **12**, and **14**; however, the chloro derivative polymers were treated with sodium trifluoroethoxide rather than sodium methoxyethoxyethoxide. The analogous trifluoroethoxide-substituted polymers of **10**, **12**, and **14** gave refractive indices that had positive polarity, confirming, together with ^{1}H NMR spectroscopy, that these materials were block copolymers.

$LiSO_3CF_3$ Complexation and Ionic Conductivity. Polymer−salt complexes were formed by dissolving both the lithium triflate and the polymer in THF. The solvent was then allowed to evaporate in air to produce a homogeneous mixture as a film. Residual solvent and traces of water (from atmospheric moisture) were removed by heating under vacuum at 40 °C for 48 h, followed by an additional period of 48 h under vacuum at 25 °C. Data to determine ionic conductivity of the solid electrolytes were then gathered over a temperature range spanning 20−80 °C using an inert argon atmosphere. A summary of the ionic conductivity data collected is given in Table 2.

The room temperature ionic conductivities were slightly lower than those of MEEP systems (2.7×10^{-5} S/cm) but 2 orders of magnitude higher than that of PEO homopolymer-based electrolytes. Maximum conductivities were achieved with 5.0−7.5 wt % lithium triflate. The ionic conductivities of various di- and

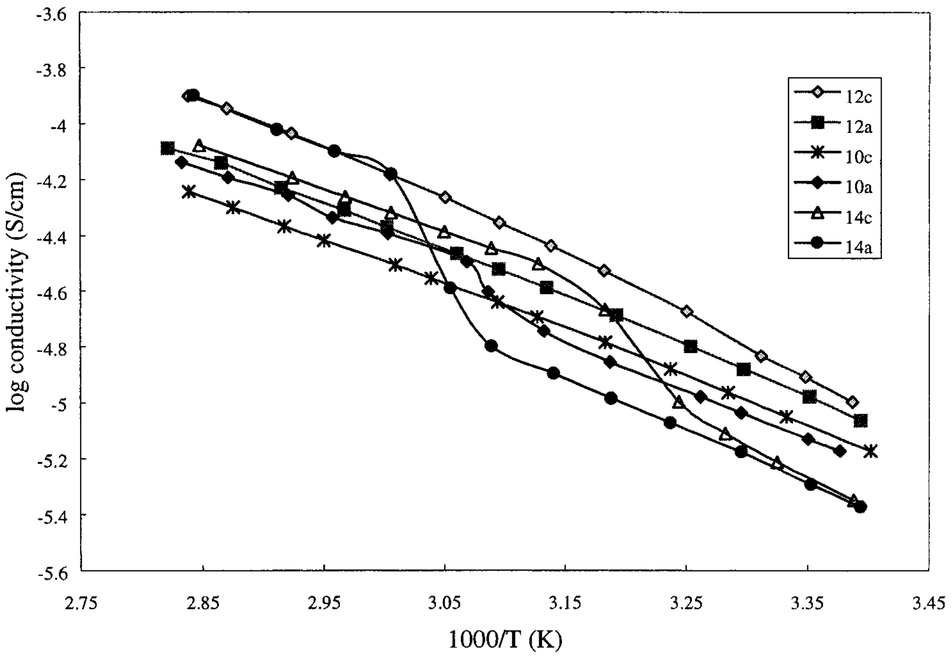


Figure 1. Variable temperature ionic conductivity of 7.5 wt % lithium triflate/block copolymer solid complex.

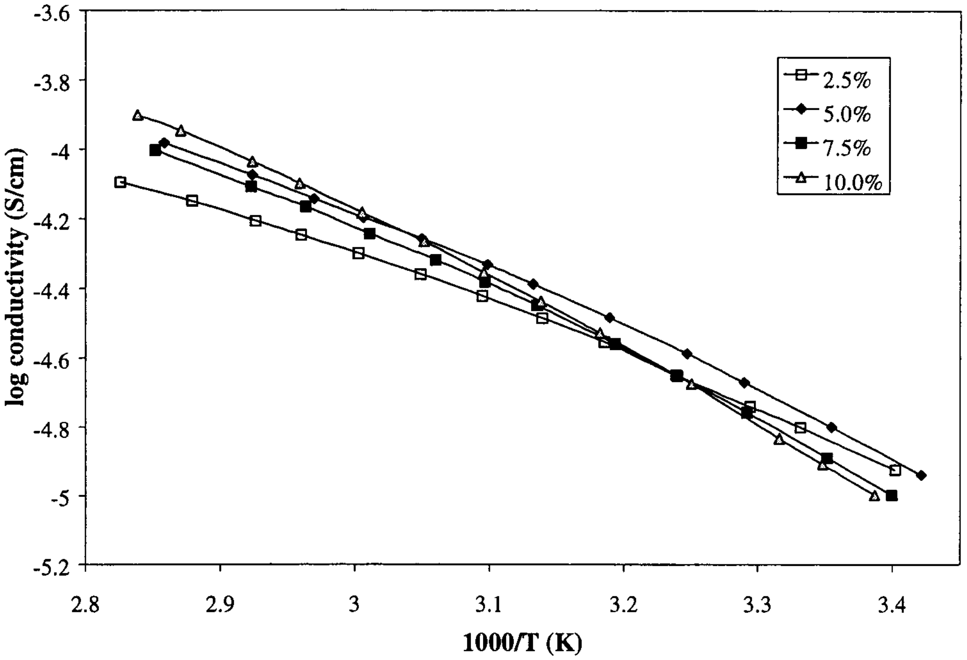


Figure 2. Variable temperature ionic conductivity of lithium triflate/block copolymer (**12b**) solid complex.

Table 3. DSC Data

polymer	wt % Li triflate	[Li]/[−O−]	DSC data (°C)[a] T_g (PN)	T_g (PEO)	T_m(PEO)
14c	0	0	−87	−53	47
	10	0.030	−70	*b*	*b*
14b	0	0	−84	−54	43
	10	0.030	−65	*b*	*b*
14a	0	0	−85	−52	45
	10	0.030	−66	*b*	34
12c	0	0	−84	*b*	30
	10	0.030	−62	*b*	*b*
12b	0	0	−84	*b*	*b*
	10	0.030	−64	*b*	*b*
12a	0	0	−82	−51	37
	10	0.030	−61	*b*	*b*
10c	0	0	−84	*b*	40
	10	0.030	−64	*b*	*b*
10b	0	0	−84	*b*	48
	10	0.030	−67	*b*	*b*
10a	0	0	−84	−54	45
	10	0.030	−68	*b*	43

[a] DSC data were collected on complexed samples of the copolymers. [b] Thermal transition not detectable.

triblock copolymer systems complexed with 7.5 wt % lithium triflate are shown in Figure 1. As seen, the lowest maximum conductivity achieved was for the di- or triblock copolymers that contained the highest percentage of PEO. This reflects the primary limitation of this classical polymer system. Figure 2 shows the change in ionic conductivity of polymer **12b** at different loadings of lithium triflate. The conductivity of all of the di- and triblock copolymer systems, upon complexation with lithium triflate, were similar to **12b** with conductivities in the range 10^{-7}−10^{-4} S cm^{-1}.

Materials Properties. Differential scanning calorimetry (DSC) was used to analyze the thermal properties of each copolymer both before and after complexation with lithium triflate. Table 3 summarizes the thermal analysis data for the polyphosphazene and poly(ethylene oxide) copolymer systems. A melting transition (T_m) for all but one pure copolymer was detected from the DSC spectra. The melting transitions were considerably lower than that of the PEO homopolymer. However, they were still above room temperature. It appears that, although the MEEP segments help to disrupt the poly(ethylene oxide) crystalline domains, the effect is not strong enough to remove all crystallinity. However, as the concentration of lithium triflate was increased, the melting transitions became more difficult to detect. In several samples, melting transitions were undetectable at higher loadings of lithium triflate. This is due to interactions between the lithium ions and the coordination sites on the polymer which disrupt the molecular order and break up the microcrystalline domains.

A strong correlation was found between the variable temperature conductivity plots and the T_m of the block copolymers. The data in Table 3 illustrate that the T_m's of the copolymers are greatly affected by the incorporation of lithium triflate. As examined by DSC, the T_m corresponding to the PEO segments became more difficult to detect as the concentration of lithium triflate was increased until, at a 10.0 wt % loading of lithium triflate, the T_m of several of the copolymers could no longer be detected. Figure 3 illustrates the interdependence of ionic conductivity, lithium triflate concentration, and the T_m of the copolymer system **14b**. The 2.5 wt % curve shows a dramatic increase in conductivity very near the poly(ethylene oxide) melting transition as detected by DSC, which correlates well with the melting of the crystalline domains. This sharp increase in ionic conductivity is again seen for the 5.0 wt % incorporation of lithium triflate. The 7.5 wt % curve shows a much less dramatic increase in the ionic conductivity, probably because the interactions between the polymer and the cation have already begun to disrupt the packing of the polymer chains and therefore decrease the degree of crystallinity. The 10.0 wt % lithium triflate curve is virtually linear and shows no evidence of a melting transition.

The glass transition temperature of the MEEP blocks was easily detected in all DSC analyses. Uncomplexed samples of the MEEP−PEO copolymers had T_g's near −84 °C, which increased as the percent of lithium triflate incorporated into the material was increased.

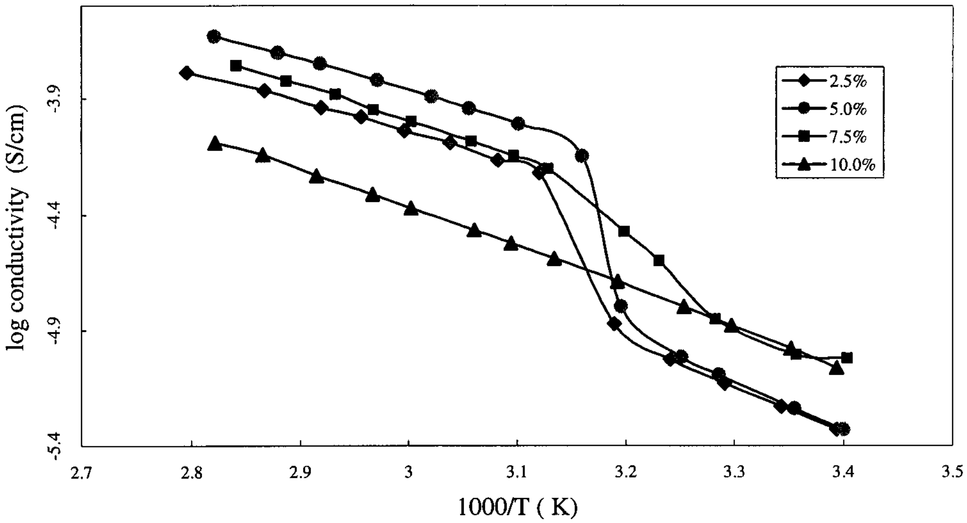


Figure 3. Variable temperature ionic conductivity of lithium triflate/block copolymer (**14b**) solid complex.

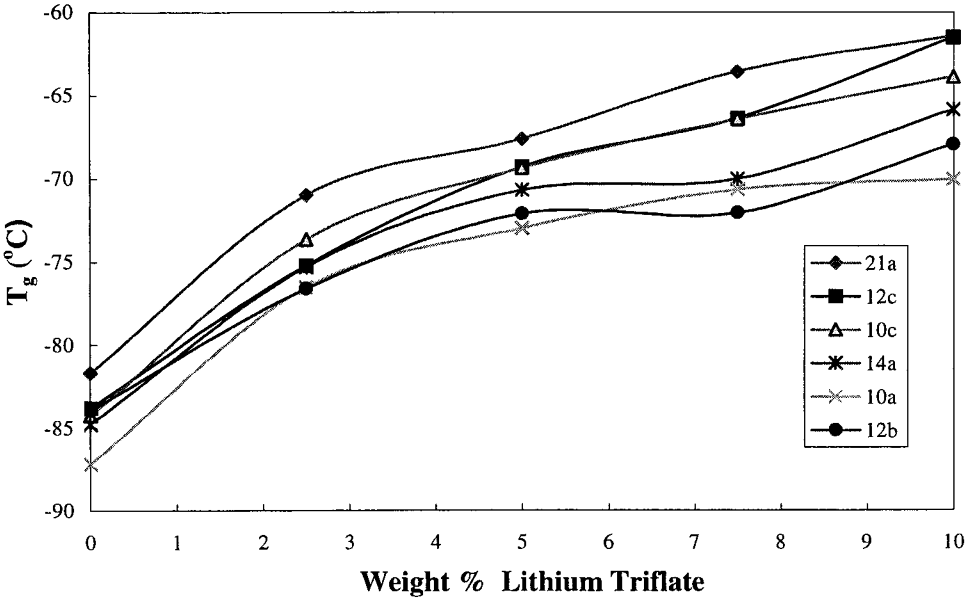


Figure 4. T_g vs weight percent lithium triflate of triblock and diblock copolymers.

This is due to the formation of ionic cross-links between the oxygen atoms on the polymers and the lithium cations. The T_g's corresponding to the MEEP blocks of both the uncomplexed copolymers and the copolymers complexed with 10.0 wt % lithium triflate are shown in Table 3. Figure 4 also illustrates the T_g of various copolymers as a function of the weight percent incorporation of lithium triflate. The T_g corresponding to the PEO block was very difficult to detect and was seen in only five of the nine uncomplexed copolymers studied. Furthermore, this T_g could no longer be detected after complexation with lithium triflate, due to the disordered state of the material. The addition of lithium triflate to the copolymer allows the lithium cations to form ionic cross-links between oxygen atoms in both the PEO and the MEEP blocks, thus reducing the microphase separation of the blocks. This is supported by the loss of crystallinity and only a single T_g present in DSC analysis. This is further confirmed by the increased linearity of the ionic conductivity plots as the percent of lithium triflate is increased.

The copolymer–salt adducts were soft semisolid materials. The film-forming properties and resistance to viscous flow of the copolymers are slightly better than those of high molecular weight MEEP homopolymers. A higher incorporation of PEO repeat units relative to the number of MEEP repeat units would presumably improve the mechanical properties further.

Summary

Hybrid phosphazene–organic-based block copolymers should combine the best properties of polyphosphazenes with those of traditional organic polymers. The preparation of a number of di- and triblock copolymers containing both polyphosphazene and poly(ethylene oxide) segments is described in this paper. The synthetic methodology provides access to phosphazene block copolymers with controlled molecular weights and narrow polydispersities. These results suggest that the living, cationic polymerization of phosphoranimines, combined with the use of macromolecular initiators or terminators, may be useful for the synthesis of a wide variety of other phosphazene–organic block copolymers. Work aimed at the further development of this area through the use of other organic polymeric systems is currently underway in our laboratory.

The copolymers synthesized here show only limited promise as *solid* polymer electrolytes after complexation with lithium triflate. Room temperature ionic conductivities were found to be similar to those of high molecular weight MEEP homopolymers and roughly 2 orders of magnitude higher than those of PEO homopolymers. However, the mechanical properties were slightly better than those of MEEP homopolymer systems. Nonetheless, the conclusion from this and our earlier work, based on more than 30 different polyphosphazenes with etheric side groups, is that solid polymer electrolytes are unlikely to show room-temperature conductivities in excess of 10^{-4} S/cm irrespective of the molecular engineering used to optimize the polymer flexibility and/or the coordination behavior. Thus, we conclude that technologically useful conductivities can only be achieved by the incorporation of smaller, conductivity-enhancing, oligomeric molecules. We have already demonstrated this principle,[19,41] and our future work will focus on this area of research.

Apart from the use of these copolymers in electrochemical devices, their properties as water-soluble macromolecules and precursors to biomedical hydrogels are of considerable interest. This too will be the subject of future studies.

Experimental Section

Materials. 2,2,2-Trifluoroethanol (98%), lithium bis(trimethylsilyl)amide (97%), 2,2,2-trifluoroethanol (99+%), sodium metal, CaH_2 (90−95%), benzophenone (99%), bromine (99.5%), lithium triflate (99.995%), and sodium metal were obtained from Aldrich and were used without further purification**.** Phosphorus pentachloride (Aldrich, 95%) was sublimed under vacuum. 2-(2-Methoxyethoxy)ethanol (Aldrich, 99%) was distilled from CaH_2 before use. Chromatographically pure samples of bis(2-aminoethyl)poly(ethylene glycol) (Shearwaterwater Polymers Inc.) and methoxy poly(ethylene glycol) amine (Fluka) were used as received. Sodium trifluoroethoxide, $Cl_3P{=}NSiMe_3$, and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ were synthesized and purified by literature procedures.[26] Dichloromethane (Aldrich) was dried and distilled from CaH_2. Tetrahydrofuran and hexane (EM Science) were distilled into the reaction flask from sodium benzophenone ketyl under an atmosphere of dry argon.

All glassware was dried overnight in an oven or 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. ^1H, ^{13}C, and ^{31}P spectra were recorded with a Bruker WM-360 NMR operated at 360, 146, and 27 MHz, respectively. ^1H and ^{13}C NMR spectra were referenced to an internal $CDCl_3$ sample. ^{31}P NMR chemical shifts were 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 and American Polymer Standards AM gel 10 mm and AM gel 10 mm 104 Å column. The system was calibrated vs polystyrene standards (Polysciences). The samples were eluted at 1 μm/min with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). 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 −120 to 100 °C under an atmosphere of dry nitrogen. The heating rates used were 20 and 40 °C/min. The thermal transitions were determined at 20 °C/min. For conductivity measurements, 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−13 MHz.

Preparation of Poly(ethylene oxide) Phosphoranimines (7 and 8). The poly(ethylene oxide) phosphoranimines, $CH_3O{-}PEO{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (**7**) and $Me_3SiN{=}P(OCH_2CF_3)_2NH{-}PEO{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (**8**), were prepared from monoamine-terminated PEO, $CH_3O{-}PEO{-}NH_2$ (**5**), and from bis-amino-terminated PEO, $H_2N{-}PEO{-}NH_2$ (**6**), respectively. A general procedure for the preparation of **8** is given. A mixture of **6** (M_n ca. 3480, 1.00 g, 0.29 mmol) and triethyleamine (0.06 g, 0.6 mmol), a halohalid acceptor, in THF (200 mL) was cooled to −78 °C. To this solution, $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**4**) (0.23 g, 0.60 mmol) was added dropwise over a 20 min period. The reaction mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The reaction mixture was filtered under vacuum through a glass frit, packed with Celite, to remove salts. The salts were washed three times with 40 mL of THF. All volatiles were removed in vacuo to produce a clear oil which was dried under vacuum and used without further purification. The phosphoranimine **5** was used to prepare **7**.

For **7**: ^1H NMR ($CDCl_3$): 4.18 (q, 4H, $CF_3\mathit{CH_2}O$), 3.41 (s, 3H, $\mathit{CH_3}O$), 3.55 (br s, ca. 260H, $\mathit{CH_2CH_2}O$), 2.48 (br s, 2H, $NH\mathit{CH_2}CH_2O$), 1.36 (br s, 2H, $NHCH_2\mathit{CH_2}O$), − 0.00 ppm (d, 18H, $SiMe_3$). ^{31}P NMR ($CDCl_3$): −0.78 ppm. ^{13}C NMR ($CDCl_3$): 124.6 (d of q, CF_3), 61.8 (d of q, CH_2O), 30.2 (br s, CH_2O) 2.5 ppm (d, $Si{-}CH_3$). Yield: 0.94 g, 87%.

For **8**: ^1H NMR ($CDCl_3$): 4.23 (q, 8H, $CF_3\mathit{CH_2}O$), 3.51 (br s, ca. 260H, $\mathit{CH_2CH_2}O$), 2.51 (br s, 4H, $NH\mathit{CH_2}CH_2O$), 1.40 (br s, 4H, $NHCH_2\mathit{CH_2}O$), −0.03 ppm (d, 18H, $SiMe_3$). ^{31}P NMR ($CDCl_3$): − 0.63 ppm. ^{13}C NMR ($CDCl_3$): 124.6 (d of q, CF_3), 61.8 (d of q, CH_2O), 30.2 (br s, CH_2O) 2.5 ppm (d, $Si{-}CH_3$). Yield: 0.97 g, 80%.

Synthesis of Poly(ethylene oxide)-*block*-polyphosphazene Copolymers (10). The macromolecular PEO initiator, $CH_3O{-}PEO{-}NH[(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ (**9**), was first prepared by the dropwise addition of a solution of **7** (2.76 g, 0.57 mol in 25 mL of CH_2Cl_2) to a stirred solution of PCl_5 (0.24 g, 1.14 mmol) in CH_2Cl_2 (200 mL) at −78 °C over a period of 20 min. The reaction mixture was then stirred at −78 °C for 1 h and then allowed to warm to room temperature. The formation of species **9** was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N{-}\mathit{P}Cl_3^+$ (ppm) and $(CF_3CH_2O)_2\mathit{P}{=}N$ (ppm) units. Subsequent reaction of this initiator with a given amount of $Cl_3P{=}NSiMe_3$ allowed the preparation of poly(ethylene oxide)-*block*-poly(dichlorophosphazenes) with specific chain lengths. The reaction mixture was stirred for 8 h, and then all volatiles were removed under reduced pressure. The block copolymer was then redissolved in 20 mL of THF and treated at 25 °C with a 2-fold molar excess 1.5 M sodium methoxyethoxyethoxide, per chlorine atom, in THF (1 mL). Polymer **10** was purified using dialysis.

For **9**: ^1H NMR (CD_2Cl_2): 5.74 (br m, 4H $CF_3C\mathit{H_2}O$), 3.51 (s, ca. 360H, $\mathit{CH_2CH_2}O$), 3.35 (s, $\mathit{CH_3}O$), 3.04 (br s,4H, $NH\mathit{CH_2}$-CH_2), 1.29 ppm (br s,4H, $NHCH_2\mathit{CH_2}$). ^{31}P NMR (CD_2Cl_2): 4.3 (d, $[(CF_3CH_2O)_2P{=}N]$), −6.8 (d, Hz, $N{-}PCl_3^+$). ^{13}C NMR (CD_2Cl_2): 130.3 (q of br m, $\mathit{C}F_3$), 70.1 (s, $\mathit{C}H_2\mathit{C}H_2O$), 64.3 (br m, $CF_3\mathit{CH_2}O$), 55.1 (s, $\mathit{CH_3}OPEG$), 35.1 (s, $NH\mathit{CH_2}CH_2O$), 29.1 ppm (s, $NHCH_2\mathit{CH2}O$). Yield: 88%.

For **10**: ^1H NMR (CD_2Cl_2): 4.35 (q, $CF_3\mathit{CH_2}O$), 4.05 (s, 4H), 3.6−3.7 (m, 8H), 3.45−3.55 (t, 4H), 3.3−3.4 (s, 6H), 3.35 (s, $\mathit{CH_3}O$), 2.20 (br s, $NH\mathit{CH_2}CH_2$) 1.41 (br s, $NHCH_2\mathit{CH_2}$). ^{31}P NMR (CD_2Cl_2): −6.93 (d, $[(CH_3OCH_2CH_2OCH_2CH_2OCH_2O)_2P{=}N]_n$), −6.81 (s, $[(CH_3OCH_2CH_2OCH_2CH_2OCH_2O)_2P{=}N]$). ^{13}C NMR (CD_2Cl_2): 124.6 (d of q, $\mathit{CF_3}$), 71.0 (s, $\mathit{CH2C}H_2O$), 63.8 (d of q, $CF_3\mathit{C}H_2O$), 58.3 (s,$\mathit{CH_3}O$), 35.0 (s, $NH\mathit{CH_2}CH_2$), 30.5 ppm (s, $NHCH_2\mathit{CH_2}$). Yield: 91%.

Synthesis of Polyphosphazene-*block*-poly(ethylene oxide)-*block*-polyphosphazene Copolymers (12). General procedure for the preparation of $R_4P[N{=}P(R)_2]_nN{=}P(OCH_2CF_3)_2{-}NH{-}(PEO)_m{-}NH{-}[(CF_3CH_2O)P{=}N]_nPR_4$ (**12** = $OCH_2CH_2OCH_2CH_2OCH_3$): The macromolecular PEO diinitiator, $[PCl_6]^-[PCl_3{}^+N{=}P{-}NH{-}PEO{-}NH{-}(CF_3CH_2O)_2P{=}NPCl_3]^+[PCl_6]^-$ (**9**), was first prepared by the dropwise addition of a solution of **8** (2.41 g, 0.63 mmol in 25 mL of CH_2Cl_2) to a stirred solution of PCl_5 (0.53 g, 2.54 mmol) in CH_2Cl_2 (200 mL) at −78 °C over a period of 20 min. The reaction mixture was then stirred at −78 °C for 1 h and then allowed to warm to room temperature. To a stirred solution of **11** (0.051 g, 0.19 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added $Cl_3P{=}NSiMe_3$ (4.4 g, 0.019 mol). After 3 h all of the monomer had reacted to produce the chloro derivative of **12** as evidenced by the disappearance of the ^{31}P NMR resonance for $Cl_3P{=}NSiMe_3$ at −54 ppm and the presence of a new resonance at −17.6 ppm for $[Cl_2P{=}N]_n$. All volatile species were removed under reduced pressure. The polymer was then dissolved in 10 mL of THF and treated with an excess 1.5 M sodium methoxyethyoxyethoxy. The mixture was then refluxed for 1 h and stirred at 25 °C for 24 h to produce the desired macromolecule. Polymer **12** was placed purified via dialysis in H_2O and then dried under vacuum.

For **12**: ^1H NMR (CD_2Cl_2): 4.23 (q, H, $CF_3\mathit{CH}_2O$), 3.06 (br m, H, $\mathit{CH}_2\mathit{CH}_2O$), 2.20 (br s, 2H, $NH\mathit{CH}_2CH_2$) 1.41 (br s, 2H, $NHCH_2\mathit{CH}_2$). ^{31}P NMR (CD_2Cl_2): −6.97 (d, $[(CH_3OCH_2CH_2OCH_2CH_2OCH_2O)_2P{=}N]$), −6.82 (s, $[(CH_3OCH_2CH_2OCH_2CH_2OCH_2O)_2\ P{=}N]_n$). ^{13}C NMR (CD_2Cl_2): 124.6 (d of q, CF_3), 71.0 (s, $\mathit{CH}_2\mathit{CH}_2O$), 63.8 (d of q, CH_2O), 35.0 (s, $NH\mathit{CH}_2CH2$), 30.5 ppm (s, $NHCH_2\mathit{CH}_2$). GPC: $M_\mathrm{n} = 1.5 \times 10^4$ and PDI = 1.16. Elemental analysis: Calcd: C, 31.43; H, 4.14; N, 3.83: Found: C, 31.62; H, 4.70; N, 3.82. Yield: 83%.

Synthesis of Poly(ethylene oxide)-*block*-polyphosphazene-*block*-poly(ethylene oxide) Copolymers (14). A PEO with a terminal phosphoranimine unit (**7**) was prepared as described earlier. Thus, living poly(dichlorophosphazene) (**13**) was terminated with a slight excess of **7**, followed by subsequent reaction with sodium trifluoroethoxide to yield the hydrolytically stable, trifluoroethoxy-substituted poly(ethylene oxide)-*block*-polyphosphazene-*block*-poly(ethylene oxide) copolymers (**14**). In all instances, ^{31}P NMR spectroscopy was used to monitor the termination of the living polymerization process. This was indicated by the disappearance of the PCl_3^+ resonance at +8 ppm and the subsequent appearance of a new resonance at −12 ppm following the addition of **7**. Replacement of the chlorine atoms with sodium trifluoroethoxide was also confirmed by ^{31}P NMR spectroscopy which revealed a resonance near −6 ppm for the substituted $[(CF_3CH_2O)_2P{=}N]_n$ polymer with no trace of $[Cl_2P{=}N]_n$ at −17 ppm. Excess PEO present in the product was removed via dialysis to yield well-defined polymers with narrow polydispersities.

For **14**: ^1H NMR (CD_2Cl_2): 4.23 (q, $CF_3\mathit{CH}_2O$), 3.61 (br m, $\mathit{CH}_2\mathit{CH}_2O$), 3.47 (s, CH_3O), 2.20 (br s, $NH\mathit{CH}_2CH_2$) 1.41 (br s, $NHCH_2\mathit{CH}_2$). ^{31}P NMR (CD_2Cl_2): −7.31 (d, $[(CF_3CH_2O)_2P{=}N]$), −7.22 (s, $[(CF_3CH_2O)_2P{=}N]_n$). ^{13}C NMR (CD_2Cl_2): 124.6 (d of q, CF_3), 71.0 (s, $\mathit{CH2C}H_2O$), 63.8 (d of q, $CF_3\mathit{C}H_2O$), 58.3 (s,CH_3O), 35.0 (s, $NH\mathit{CH}_2CH_2$), 30.5 ppm (s, $NHCH_2\mathit{CH}_2$). GPC: $M_\mathrm{n} = 2.9 \times 10^4$ and PDI = 1.4.

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