Polyphosphazenes Bearing Branched and Linear Oligoethyleneoxy Side Groups as Solid Solvents for Ionic Conduction

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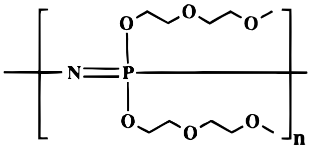
ABSTRACT: A new series of solid polymer electrolyte materials based on the poly(organophosphazene) system has been designed and synthesized. The new polymers contain linear or branched oligoethyleneoxy side chains. The polymers were characterized by ^{31}P, ^{13}C, and ^{1}H-NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and elemental analysis. The ambient temperature (25 °C) ionic conductivities of the polymers complexed with lithium triflate were measured by complex impedance analysis. The polymers that bear linear oligoethyleneoxy side chains [$NP\{O(CH_2CH_2O)_n CH_3\}_2$], have low glass transition temperatures that range from −84 to −75 °C. These polymers have properties that are similar to those of the classical counterpart poly[bis(2-(2-methoxyethoxy)ethoxy)-phosphazene. They have low dimensional stabilities and undergo viscous flow even at room temperature. The polymers with branched oligoethyleneoxy side chains (podands) have similar glass transition temperatures, in the range of −82 to −79 °C. However, the bulk dimensional stabilities of the branched polymers are significantly higher than those of the corresponding linear side chain series. The branched side chain polymers resist viscous flow and readily form thin, free-standing films. The podand polymers also dissolve lithium triflate to form ionically conducting materials with conductivity levels similar to those of the polymers bearing linear side chains.

Introduction

Solid solutions of salts such as lithium triflate ($LiSO_3CF_3$) in poly(ethylene oxide) (PEO) have been studied extensively as ionically conducting materials.[1−7] The oxygen atoms in the backbone of PEO can coordinate to metal cations and facilitate ion-pair separation. This separation can then favor electrical conduction through ion transport. However, the level of conductivity of PEO is limited by its high degree of crystallinity. An amorphous polymer will allow high ion mobility and hence promote high ionic conductivity. The presence of microcrystalline domains will impede ion mobility both by blocking the paths of ions and by reducing the overall polymer flexibility. The three basic property requirements for polymers to act as good solid polymer electrolytes are as follows: (a) it polymer should have a low glass transition temperature (T_g), which is an indicator of high macromolecular flexibility, (b) it should be amorphous, and (c) it should possess cation or anion coordination sites to assist in the process of salt solvation and ion-pair separation. In principle, the higher the number of coordination sites per polymer repeat unit, the more effective this process will be.

Poly(ethylene oxide) has a crystalline melting temperature of 65 °C and does not become wholly amorphous until heated above 100 °C. Hence, PEO is an effective ionic conductor only above 100 °C. At room temperature the conductivity is significantly reduced due to the presence of crystallinity. This has prompted many researchers to attempt to modify the properties of PEO.[8−19]

In the mid 1980s poly[bis(2-(2′-methoxyethoxy)ethoxy)-phosphazene], MEEP (**4**), was first synthesized and studied as a polymer electrolyte by Shriver, Allcock, and their co-workers.[20,21] This polymer is amorphous over a temperature range from at least −100 to 100 °C in the presence of dissolved $LiSO_3CF_3$ or $AgSO_3CF_3$ and was found to show room temperature conductivities of up to 3 orders of magnitude higher than PEO. This behavior is attributed to the high polymer backbone flexibility (T_g, −84 °C) and to the amorphous morphology of the polymer. Each repeating unit bears six oxygen atoms, of which at least four serve as coordination sites. The two oxygen atoms bonded to the phosphorus atom appear to play only a minor role in ion coordination.[6] Polymer **4** has since been studied extensively as a solid polymer electrolyte material by a number of different research groups and has been incorporated into experimental rechargeable lithium batteries.[22,23]



MEEP (4)

One disadvantage of MEEP for solid electrolyte applications is its poor dimensional stability and its tendency to undergo viscous flow under pressure. However, the dimensional stability for thin film battery applications can be markedly improved by cross-linking the chains using ultraviolet or γ-ray irradiation.[24,25] Only a small degree of cross-linking is required to render the polymer dimensionally stable. The resultant materials show no significant increase in the glass transition temperature and no decrease in the ionic conductivity of the salt-complexed polymer.

In this paper we discuss the synthesis, characterization, and physical properties, including ionic conductivity, of a new series of related poly(organophosphazenes) that bear linear or branched oligoethyleneoxy side chains. The objectives of this study were to examine

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Chart 1. Linear Side Group Polyphosphazenes

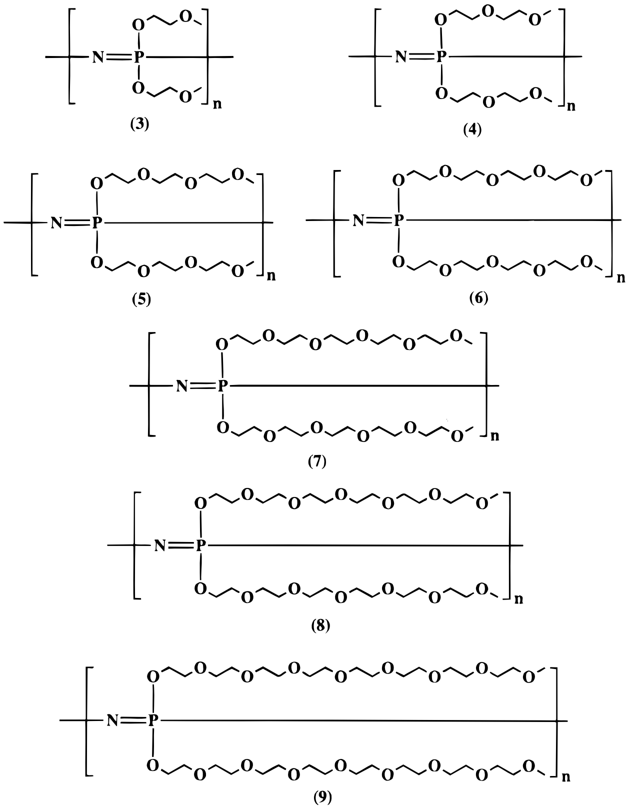
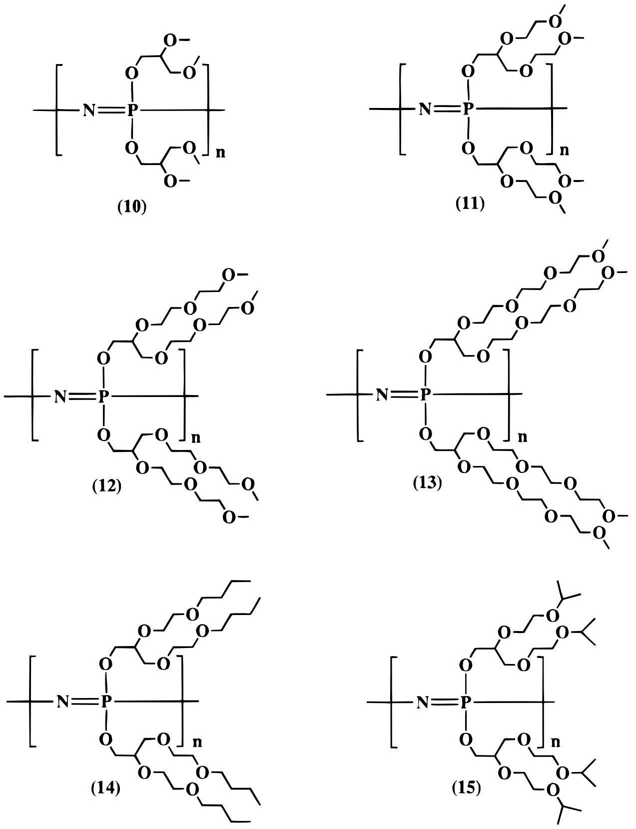
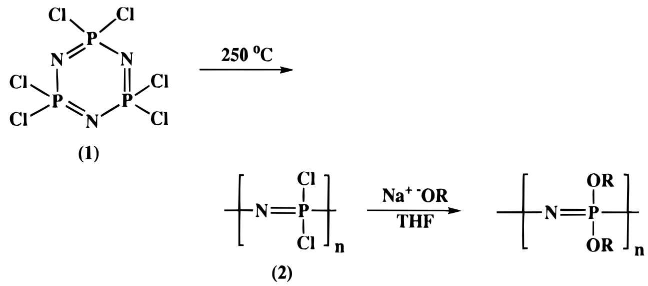


Chart 2. Branched Side Group Polyphosphazenes



the effects of polymer side chain structure on (a) ionic conduction following salt complexation and (b) physical properties such as glass transition temperature, crystallinity and dimensional stability. The structures of the new macromolecules are shown in Charts 1 and 2. These polymers are good candidate materials for uses such as solid polymer electrolyte hosts in rechargeable lithium batteries and membranes and in possible biomedical devices.

Scheme 1. General Synthesis of Polyphosphazenes



The first group, shown in Chart 1, consists of polymers with linear oligoethyleneoxy side chains with the general formula $[NP(OCH_2CH_2)_xOCH_3]_n$, where x ranges from 1 to 8. These polymers were synthesized in order to study the effect of increasing oligoethyleneoxy side chain length on the glass transition temperature, crystallinity, and ionic conductivity following the incorporation of lithium triflate.

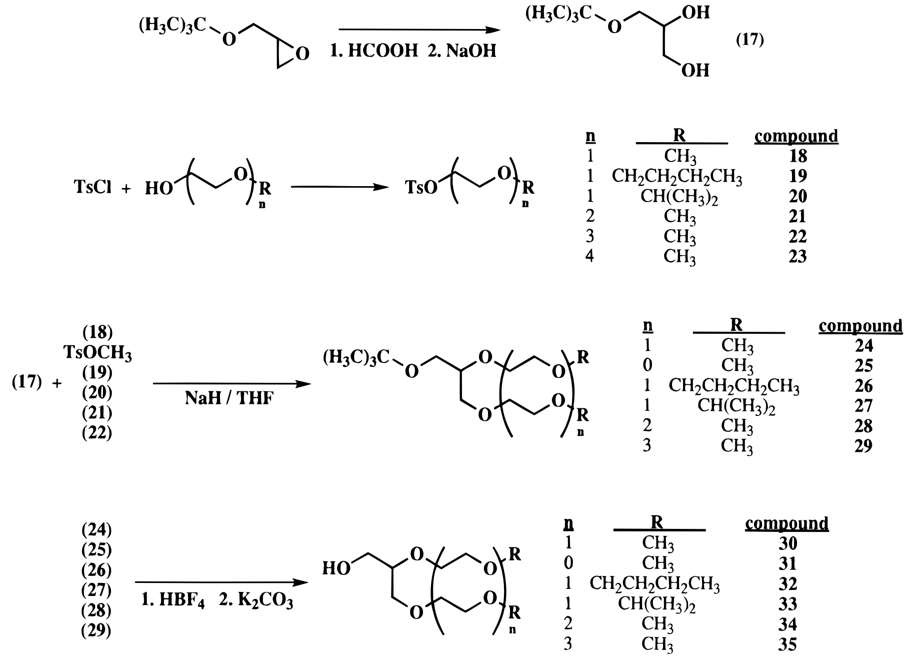
Earlier studies indicated that the ionic conductivity of salt-complexed polyphosphazenes with linear side chains increases with increasing side chain length.[26] It was our initial intention to further clarify and examine this trend. As discussed, ionic conductivity in salt-complexed polymers occurs via ion diffusion through the amorphous regions of the matrix. Thus, the effect of oligoethyleneoxy side chain length on the onset and degree of crystallinity will be discussed in this paper. Intuitively, it might be expected that the ionic conductivity of poly(organophosphazene) salt complexes should increase with increasing length of the oligoether side chains. Polymers with longer ethyleneoxy side chains should have a greater capacity for salt dissolution compared with shorter side chain polymers, due to the larger number of ion coordinating groups per repeat unit. However, longer side chains could also increase the opportunities for side group close packing and hence induce crystallinity. It was anticipated that the possibility for inducing crystallinity would increase as the length of the oligoethyleneoxy side chain increased. The physical properties of very long ethyleneoxy side chain polyphosphazenes would ultimately tend toward those of poly(ethylene oxide).

In an attempt to avoid crystallinity, we designed the second series of polymers shown in Chart 2. These materials contain branched oligoethyleneoxy side chains. Several of these branched side chain polymers are the structural isomers of one of the linear side chain polymers. The rationale used was that a branched side chain structure would increase the free volume and reduce the tendency for side chain crystallization while, at the same time, maintaining the same number of ion-coordinating sites per polymer repeat unit as in the linear analogues.

Results and Discussion

Polymers **3**–**15** were synthesized by treatment of the sodium salts of the appropriate alcohols with poly(dichlorophosphazene) in tetrahydrofuran using techniques that are similar to those reported previously for the synthesis of MEEP (see Scheme 1).[27] The alcohols used in these syntheses were prepared by the pathways shown in Schemes 2 and 3. All of the other alcohols were obtained commercially.

Scheme 2. Synthesis of Branched Side Groups

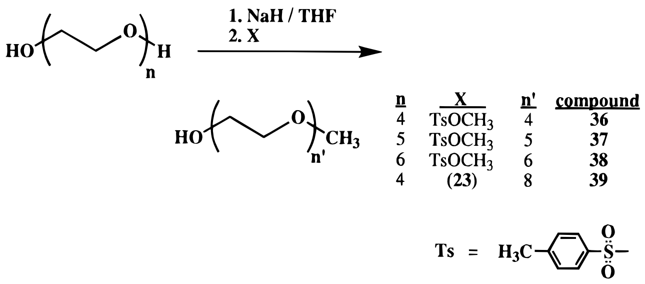


n	R	compound
1	CH_3	18
1	$CH_2CH_2CH_2CH_3$	19
1	$CH(CH_3)_2$	20
2	CH_3	21
3	CH_3	22
4	CH_3	23

n	R	compound
1	CH_3	24
0	CH_3	25
1	$CH_2CH_2CH_2CH_3$	26
1	$CH(CH_3)_2$	27
2	CH_3	28
3	CH_3	29

n	R	compound
1	CH_3	30
0	CH_3	31
1	$CH_2CH_2CH_2CH_3$	32
1	$CH(CH_3)_2$	33
2	CH_3	34
3	CH_3	35

Scheme 3. Synthesis of Longer Linear Side Groups



n	X	n'	compound
4	$TsOCH_3$	4	36
5	$TsOCH_3$	5	37
6	$TsOCH_3$	6	38
4	(23)	8	39

The molecular structures of polymers **3**–**15** were assessed by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, as well as by elemental microanalysis. The molecular weights were estimated by gel permeation chromatography. Glass transition temperatures were determined by differential scanning calorimetry (DSC). The characterization data are shown in Table 1. The polymers were found to be soluble in most organic solvents and in water, except for polymers **14** and **15**, which are water insoluble.

Ionic Conductivity. The polymers formed homogeneous amorphous salt complexes with lithium triflate. The ionic conductivities of the salt complexes were measured by complex impedance analysis. The lithium triflate salt-complexed polymers have maximum, ambient, ionic conductivities in the range from 6.4×10^{-7} to 4.8×10^{-5} S cm^{-1}, as shown in Table 2. The value found in this work for MEEP was similar to that previously reported, and this was used as a control.[20,21]

The ionic conductivity as a function of salt concentration for polymers **3**–**15** is shown in Figures 1 and 2. The maximum ionic conductivity was found to occur with polymers that contained the highest number of ethyleneoxy units per polymer repeat unit. This trend is particularly apparent in Figure 1. As shown, the maximum conductivity rose as the length of the oligoethyleneoxy side chain was increased. Polymers **8** and **9**, with six and eight ethyleneoxy groups per side chain, respectively, displayed the highest conductivities in this series. However, the maximum conductivity measured for **9** is similar to and in fact slightly lower than that of **8**. As discussed later in this paper, crystalline melting transitions were detected for both of these polymers. However, the T_m for polymer **9** (0 °C) is much closer to room temperature than is the value for polymer **8** (−25 °C). At room temperature, polymer **9** is not detectably crystalline, but it may not be wholly amorphous either. This may explain the observed plateauing out or slight decrease in room temperature ionic conductivity. In Figure 2 the polymers with the longer side chains (i.e. with a larger number of coordinating ethylene oxide groups) had the highest maximum conductivities. Polymers **14** and **15**, with non-ion-coordinating groups at the terminus of each side chain branch, displayed lower ionic conductivities. In all cases, polymers that contained linear side chains showed somewhat higher ionic conductivities than did the branched side chain structural isomers.

For all the polymer systems, the conductivity rose steeply as the salt concentration was increased, reached a maximum, and then declined. This increase in conductivity with salt concentration probably reflects a rise in the number of charge carriers. The conductivity decline at higher salt concentrations is attributed to (a) a decrease in the number of free polymer coordination sites (uncoordinated sites are needed to accept migrating lithium ions), (b) ionic crosslinking as coordination sites from different side chains become associated with the same cation, and possibly (c) ion-pair association effects. The effect of ionic crosslinking becomes manifest as an increase in the glass transition temperature, which was detected experimentally. An example of this effect is shown in Figure 3 for polymers **6** and **11**, which contain the same number of ethyleneoxy units per repeat unit. The glass transition temperature of polymer **11** rose from −81 to 4 °C with increasing salt complexation.

Thermal Properties. The glass transition temperatures of the salt-free and salt-complexed polymers were measured using differential scanning calorimetry.

(a) Linear Side Chains. Polymers **3**–**6** remained amorphous over a temperature range from −100 to 100 °C. However, crystallinity was detected when the side chain length reached five ethyleneoxy units (polymer

Table 1. Characterization Data for Polymers 3−15

	NMR data, δ, ppm vs $CDCl_3$				
polymer	^{1}H	^{31}P	^{13}C	T_g (°C)	M_w (PDI)
3	3.35 (s, 6H), 3.55 (m, 4H), 4.05 (s, 4H)	−7.5	58.6, 64.8, 71.6	−81	1.05×10^6 (1.52)
4	3.30−3.40 (s, 6H), 3.45−3.55 (t, 4H), 3.60−3.70 (m, 8H), 4.05 (s, 4H)	−7.7	58.8, 65.0, 70.3, 70.4, 72.0	−84	1.10×10^6 (1.61)
5	3.35 (s, 6H), 3.50−3.80 (m, 20H), 3.90−4.20 (m, 4H)	−8.0	58.9, 64.9, 70.3, 70.4, 70.5, 70.6, 71.9	−80	1.40×10^6 (1.98)
6	3.36 (s, 6H), 3.50−3.55 (t, 4H), 3.60−3.68 (m, 24H), 4.01 (s, 4H)	−8.0	58.9, 64.8, 70.3, 70.4, 70.5, 70.6, 71.9	−80	9.21×10^6 (2.12)
7	3.35 (s, 6H), 3.50−3.70 (m, 36H), 4.00 (s, 4H)	−8.0	59.0, 64.8, 70.3, 70.4, 70.5, 71.9	−79 (T_m = −30)	2.11×10^5 (2.43)
8	3.35 (s, 6H), 3.50−3.70 (m, 44H), 4.00 (s, 4H)	−8.2	59.0, 64.8, 70.3, 70.4, 70.5, 70.6, 71.9	−76 (T_m = −25)	8.63×10^5 (2.52)
9	3.35 (s, 6H), 3.50−3.70 (m, 60H), 4.00 (s, 4H)	−8.2	59.0, 64.8, 70.3, 70.4, 70.5, 71.9	−75 (T_m = 0)	5.77×10^5 (3.10)
10	3.35 (s, 6H), 3.45 (s, 6H), 3.50−3.60 (m, 6H), 3.95−4.00 (s, 4H)	−8.1	57.8, 59.1, 64.9, 72.4, 79.0	−79	1.02×10^6 (1.57)
11	3.30−3.40 (s, 12H), 3.50−3.55 (br), 3.60−3.70 (br), 3.70−3.85 (br), 3.85−3.95 (br)	−8.0	58.6, 58.7, 66.2, 69.6, 70.3, 70.6, 71.9, 72.1, 78.6	−81	1.06×10^6 (2.74)
12	3.30−3.35 (br), 3.50−3.55 (br), 3.55−3.65 (br), 3.70−3.80 (br), 3.85−3.90 (br)	−9.2	58.7, 58.8, 65.3, 69.8, 70.3, 70.4, 70.5, 70.6, 70.7, 71.7, 71.9, 78.4	−81	1.00×10^6 (1.50)
13	3.30−3.40 (br), 3.40−3.55 (br), 3.60−3.70 (br), 3.75−3.85 (br), 3.90−4.00 (br)	−9.2	58.8, 58.9, 65.6, 69.8, 70.3, 70.4, 70.5, 70.6, 70.7, 71.7, 71.9, 78.4	−82	1.20×10^6 (1.40)
14	0.90−1.00 (t, 12H), 1.30−1.40 (m, 8H), 1.50−1.65 (m, 8H), 3.40−3.95 (m, 34H)	−8.9	13.9, 14.0, 19.2, 19.3, 31.9, 32.0, 65.4, 69.8, 70.0, 70.2, 70.7, 70.9, 71.0, 71.8, 78.5	−86	1.10×10^6 (2.95)
15	1.10−1.20 (d, 24 H), 3.45−3.80 (m, 26H), 3.85−3.95 (s, 4 H)	−9.2	22.2, 22.3, 65.2, 67.3, 67.5, 70.1, 71.0, 71.4, 72.0, 78.5	−77	6.63×10^5 (3.81)

Table 2. Maximum Ionic Conductivities for Polymers 3−6 and 8−15 (25 °C), $(LiSO_3CF_3)_x$:$[NPR_2]_n$ Complexes

polymer	x	mol % Li^+	conductivity, σ S/cm
3	0.066	6.2	2.6×10^{-5}
4	0.250	20.0	2.7×10^{-5}
5	0.125	11.1	3.2×10^{-5}
6	0.327	24.6	3.7×10^{-5}
8	0.708	41.5	4.8×10^{-5}
9	0.680	40.5	4.5×10^{-5}
10	0.198	16.5	1.6×10^{-6}
11	0.170	14.5	1.2×10^{-5}
12	0.235	19.0	3.7×10^{-5}
13	0.274	21.5	3.9×10^{-5}
14	0.260	20.6	1.2×10^{-6}
15	0.092	8.4	6.4×10^{-7}

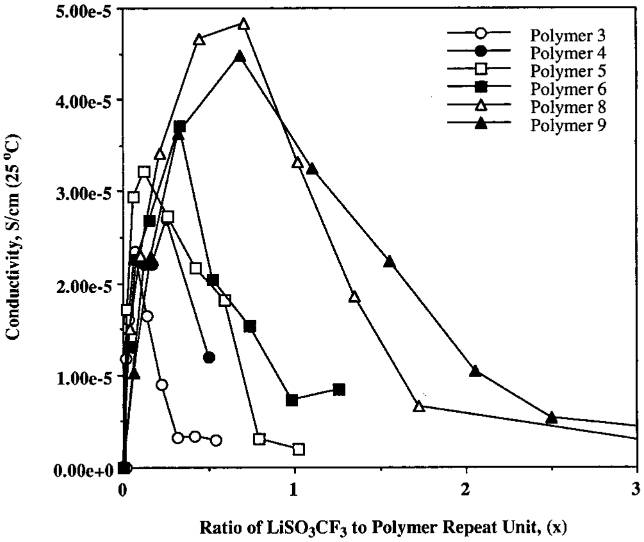


Figure 1. Ionic conductivities of $(LiSO_3CF_3)_x$:$[NPR_2]_n$ complexes for polymers **3**−**6**, **8**, and **9** (25 °C).

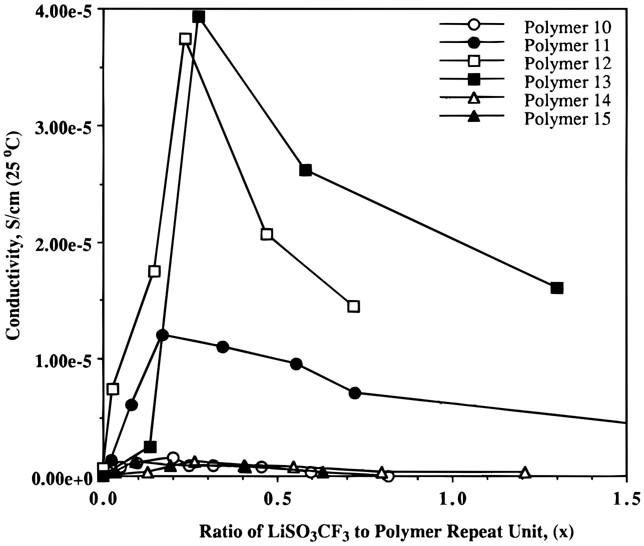


Figure 2. Ionic conductivities of $(LiSO_3CF_3)_x$:$[NPR_2]_n$ complexes for polymers **10**−**15** (25 °C).

7). Polymers **7**, **8**, and **9** had melting transitions at −30, −25, and 0 °C, respectively. The presence of a T_m marks the lower temperature limit for the use of a material as a solid polymer electrolyte in energy storage devices such as rechargeable batteries. However, room temperature applications are still possible since all the materials are amorphous at ambient temperatures.

(b) Branched Side Chains. All the branched side group polymers, **10**−**15**, shown in Chart 2, are amorphous over the temperature range from −100 to 100 °C. The glass transition temperatures of polymers **10**−**15** were similar to those of the linear side chain polymers **3**−**9**. This is perhaps surprising since it might be predicted that polymers such as **10** and **11** would suffer from increased side chain steric hindrance and might have higher T_g values than their corresponding linear analogues, **4** and **6**. However, the T_g's for polymers **10**, **11**, **4**, and **6** are almost identical and are near −80 °C. The unexpectedly low T_g's of these polymers may be due to large increases in polymer free volume following the introduction of four side chain termini per polymer repeat unit, compared to polymers **3**−**9**, which only have two side chain termini per repeat unit. Polymer free volume is known to increase as the number of free chain ends increases. Hence, an increase in branching may result in a significant increase in free volume and a corresponding lowering of the glass transition temperature. Thus, the effects of increased free volume in polymers **10**−**15** may offset the opposing effect of

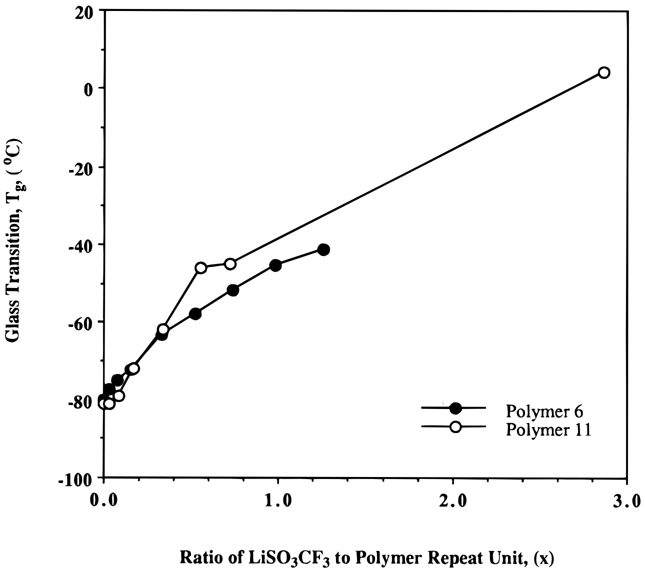


Figure 3. Glass transition temperatures of $(LiSO_3CF_3)_x$:$[NPR_2]_n$ complexes for polymers **6** and **11**.

increasing side chain steric hindrance, resulting in a constant low T_g. Also the similarity between the T_g's may indicate that the polymers have similar "local viscosities". Despite being sterically bulky compared to linear groups, the branched side groups are still sufficiently flexible to allow significant backbone relaxations and large scale motions, which also enhances ion motion and ionic conductivity.

The bulk macroscopic properties of polymers **10**−**15** are significantly different from those of the linear side chain polymers **3**−**9**. The branched side group polymers **10**−**15** have higher dimensional stabilities than do polymers **3**−**9**. For example, polymer **10**, which is the branched isomer of polymer **4**, readily forms free-standing, dimensionally stable thin films when cast from a suitable solvent. By contrast, polymer **4** is a viscous, liquid-like material which will flow under the influence of gravity, and will not form dimensionally stable films unless crosslinked by ultraviolet or γ-ray irradiation.[24,25]

Simple viscosity experiments were carried out to illustrate the differences in bulk dimensional stability between structural isomers **4** and **10**. When subjected to a downward load as applied by a quartz probe, a sample of polymer **4** deformed sufficiently within less than 20 min to allow the probe to completely penetrate the material. A sample of polymer **10** was slightly deformed initially by the experiment, but did not flow significantly thereafter. After 100 min, polymer **10** still retained 70% of its original thickness. This experiment demonstrates the important differences in materials morphology between these two closely related polymers. The increased dimensional stability of polymers **10** and **11** is of considerable practical value because it allows the fabrication of free-standing, nonflowing, thin polymer films without the need for chemical or radiation crosslinking.

Conclusions. Poly(organophosphazenes) with linear and branched oligoethyleneoxy side chains were synthesized. Some physical properties of these polymers were compared with those of the control polymer MEEP (**4**). The ambient temperature conductivities of many of these polymers complexed with lithium triflate were found to be very similar to that of polymer **4**. The polymers that bear linear oligoethyleneoxy side chains also had other similar characteristics to that of polymer **4**, such as low glass transition temperatures and low dimensional stabilities. The linear side chain polymers all formed amorphous polymer−salt complexes with lithium triflate. The optimum ionic conductivity of the linear polymer−salt complexes increased with increasing length of the side chain. Polymers with side chains that contain five or more ethyleneoxy units have crystalline melting transitions at low temperatures. The branched side-group (podand) polymers are amorphous over a wide temperature range and have significantly higher dimensional stabilities than polymer **4** and the related polymers **3** and **5**−**9**. The extra dimensional stability of the podand polymers **10**−**15** is probably a consequence of their increased capacity for side chain entanglement. Despite the high dimensional stability, the branched side-group polymers have low glass transition temperatures and form ionically conducting complexes with lithium triflate. Polymers **14** and **15**, which have *n*-butyl or *sec*-propyl side chain termini, had ionic conductivities that were lower than those of the other materials. All the polymers showed increasing conductivity with increasing salt concentration. In each system the conductivity reached a maximum at a certain salt concentration. Above this critical concentration the ionic conductivity decreased as the T_g of the system rose.

Experimental Section

Equipment. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^1H (360 MHz) NMR spectra were obtained by using a Brucker 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. ^1H and ^{13}C were referenced to external tetramethylsilane. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Chemical ionization (CI) mass spectra were measured using a Kratos MS-25 spectrometer. Molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1047A refractive index detector and a Polymer Laboratories PL gel 10 μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium nitrate in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluorethoxy)phosphazene] prepared by Drs. R. Singler and G. Hagnauer at the U.S. Army Materials Research Laboratories, Watertown, MA. 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 +165 °C under an atmosphere of dry nitrogen. The heating rates used were 10, 20, and 40 °C/min. The glass transition temperatures were determined by extrapolation to zero degrees heating rate. Sample sizes were between 10 and 30 mg. Dimensional stability experiments were conducted with the use of a thermal mechanical analyzer (TMA) using a Perkin-Elmer-7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. Polymer samples were subjected to a constant downward compressive load of 500 mN, applied by a 3.5 mm diameter circular tip quartz probe, for 100 min at 25 °C. Samples were 0.9−1.5 mm in thickness. Conductivity measurements were made using a Hewlett-Packard 4192A LF impedance analyzer at a potential of 1 V with an alternating current frequency range of 5 Hz to 13 MHz. The samples were sandwiched between platinum electrodes. The platinum electrode polymer electrolyte cell was compressed between aluminum blocks held in a polycarbonate fixture. Electrical leads were attached between the impedance analyzer and the aluminum blocks. All conductivity measurements were carried out under an atmosphere of argon at 25 °C.

Materials. Hexachlorocyclotriphosphazene, (**1**, $(NPCl_2)_3$) (Ethyl Corp/ Nippon Fine Chemical) was purified by recrystallization from heptane followed by sublimation at 40 °C (0.05 Torr). Poly(dichlorophosphazene) (**2**) was prepared by the ring-opening polymerization of **1** at 250 °C. This method has been reported previously.[28] Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was distilled in an atmosphere of dry nitrogen before use. All other reagents (Aldrich, Acros, and Fluka) were used as received or distilled prior to use. Reactions that involved the use of chlorophosphazenes were carried out in an atmosphere of dry nitrogen or argon. The water used for dialysis experiments was distilled and deionized.

3-*tert*-Butoxy-1,2-propanediol (17). Compound **17** was prepared by the method described by Montanari and Tundo.[29] *tert*-Butyl glycidyl ether (Aldrich) (141 mL, 1.0 mol) was added 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 further at room temperature for 12 h. A solution of sodium hydroxide (100 g, 2.5 mol) in 125 mL of water was added slowly, and the temperature was kept 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 **17** as a colorless oil (75 g, 54%) (bp 55−60 °C, 0.015 Torr): ^{1}H-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 and 27.2; mass spectroscopy, *m*/*e* 149 MH^+, 93 ($M - C(CH_3)_3)H^+$ base peak.

2-(2-Methoxyethoxy)ethyl *p*-Toluenesulfonate (18). Compound **18** was prepared according to the method described by Gokel et al.[30] A slurry of *p*-toluenesulfonyl chloride (189.8 g, 0.996 mol) and pyridine (200 mL) was mechanically stirred in a three-necked argon-filled flask. The temperature of the reaction mixture was maintained at approximately 5 °C (dry ice−ethanol bath), while 2-(2-methoxy ethoxy)ethanol (119.5 g, 0.996 mol) (Aldrich) was added slowly from an addition funnel. After the addition was complete, the mixture was stirred for 15 min. The mixture was then 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), dried ($MgSO_4$), and reduced to a minimum volume by evaporation to yield a colorless oil (168.0 g, 61%): ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.3−7.7 (m, 4H), 3.45−4.2 (m, 8H) 3.35 (s, 3H) 2.5 (s, 3H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 144.7, 132.9, 129.7, 127.9, 77.4, 77.0, 76.6, 71.7, 70.6, 69.1, 68.6, 58.9, and 21.5; mass spectroscopy, *m*/*e* 275 MH^+ base peak.

2-*n*-Butoxyethyl *p*-Toluenesulfonate (19). Compound **19** was prepared as described for **18**. The following reagents and quantities were used: *p*-toluenesulfonyl chloride (194 g, 1.019 mol), pyridine (200 mL), and 2-*n*-butoxyethanol (110 g, 0.932 mol) (Aldrich). The final product was a yellow oil (184 g, 68%): ^{1}H-NMR ($CDCl_3$), δ (ppm) 7.8 (d, 2H), 7.35 (d, 2H), 4.15 (t, 2H), 3.6 (t, 2H), 3.4 (t, 2H), 2.45 (s, 3H), 1.5 (m, 2H), 1.3 (m, 2H), 0.9 (t, 3H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 144.7, 133.0, 129.8, 127.9, 71.3, 69.3, 68.0, 31.6, 21.6, 19.1, and 13.9; mass spectroscopy, *m*/*e* 273 MH^+ base peak.

2-*sec*-Propoxyethyl *p*-Toluenesulfonate (20). Compound **20** was prepared as described for **18**. The following reagents and quantities were used: *p*-toluenesulfonyl chloride (190 g, 1.0 mol), pyridine (200 mL), and 2-*sec*-propoxyethanol (100 g, 0.962 mol) (Aldrich). The final product was a yellow oil (194 g, 82%): ^{1}H-NMR ($CDCl_3$), δ (ppm) 7.8 (d, 2H), 7.35 (d, 2H), 4.15 (t, 2H), 3.5−3.6 (m, 3 H), 2.40 (s, 3H), 1.1 (d, 6H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 144.7, 133.0, 129.8, 127.9, 72.2, 69.6, 65.4, 21.8, and 21.6; mass spectroscopy, *m*/*e* 258 MH^+ base peak.

2-Methoxyethyl *p*-Toluenesulfonate (21). Compound **21** was prepared as described for **18**. The following reagents and quantities were used: *p*-toluenesulfonyl chloride (210.65 g, 1.1 mol), pyridine (200 mL), and 2-methoxyethanol (76.0 g, 1.0 mol) (Aldrich). The final product was a colorless oily liquid (120 g, 52%) (bp 110−115 °C, 0.01 Torr): ^{1}H-NMR ($CDCl_3$), δ (ppm) 7.3−7.7 (m, 4H), 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, and 21.5; mass spectroscopy, *m*/*e* 231 MH^+ base peak.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl *p*-Toluenesulfonate (22). Compound **22** was prepared as described for **18**. The following reagents and quantities were used: *p*-toluenesulfonyl chloride (170.4 g, 0.894 mol), pyridine (400 mL), and 2-(2-(2-methoxyethoxy)ethoxy)ethanol (148.7 g, 0.907 mol) (Aldrich). The final product was a pale yellow liquid (122 g, 42%): ^{1}H-NMR ($CDCl_3$), δ (ppm) 7.3−7.7 (m, 4H), 3.3−4.2 (m, 12H) 3.35 (s, 3H), 2.4 (s, 3H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 144.7, 132.9, 129.7, 127.9, 77.3, 76.9, 76.6, 71.8, 70.6, 69.1, 68.6, 58.9, and 21.5; mass spectroscopy, *m*/*e* 319 MH^+ base peak.

2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethyl *p*-Toluenesulfonate (23). Compound **23** was prepared as described for **18**. The following reagents and quantities were used: *p*-toluenesulfonyl chloride (42.0 g, 0.22 mol), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethanol (44.2 g, 0.31 mol) (Acros), and pyridine (100 mL). The final product was a yellow oil (47.6 g, 61%): ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.75−7.8 (d, 2H), 7.35−7.4 (d, 2H), 4.15−4.2 (t, 2H), 3.55−3.75 (m, 14H), 3.4 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 144.8, 133.1, 129.8, 127.9, 71.9, 70.7, 70.6, 70.5, 69.2, 68.6, 58.9, and 21.6; mass spectroscopy, *m*/*e* 363 MH^+ base peak.

1-(*tert*-Butyloxy)-2,3-bis(2-methoxyethoxy)propane (24). Compound **21** (31.0 g, 0.135 mol) was added to a mixture of 3-*tert*-butoxy-1,2-propanediol (**17**), (9.18 g, 0.062 mol) and sodium hydride (7.44 g, 0.186 mol of a 60% by weight solution in mineral oil) in refluxing dry THF (500 mL). 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 removed by evaporation under vacuum. The residue was extracted with chloroform, dried ($MgSO_4$), and filtered, and solvent was 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, dried ($MgSO_4$), and filtered. The solvent was removed by rotary evaporation under vacuum to give a pale yellow oil. The crude product was distilled to give a colorless liquid (11.1 g, 67%) (bp 120−125 °C, 0.25 Torr): ^{1}H-NMR ($CDCl_3$), δ (ppm) 3.3−3.85 (m, 19H), 1.3 (s, 9H). ^{13}C-NMR ($CDCl_3$), δ (ppm) 79.0, 73.0, 72.2, 72.0, 71.7, 70.6, 69.7, 61.7, 59.0, 58.8, and 27.4; mass spectroscopy, *m*/*e* 265 MH^+, 209 ($M - C(CH_3)_3)H^+$ base peak. Elemental analysis found: C, 59.1; H, 10.5. $C_{13}H_{28}O_5$ requires: C, 59.1; H, 10.6.

1-(*tert*-Butyloxy)-2,3-dimethoxypropane (25). Compound **25** was prepared as described for **24**. The following reagents and quantities were used: compound **17** (50.0 g, 0.338 mol), methyl *p*-toluenesulfonate (129.0 g, 0.693 mol), sodium hydride (30.0 g, 0.750 mol of a 60% by weight solution in mineral oil), and THF (1750 mL). The final product was a colorless liquid (32.9 g, 55%) (bp 150−156 °C, 760 Torr): ^{1}H-NMR ($CDCl_3$), δ (ppm) 3.55−3.35 (m, 11H) and 1.20 (s 9H); ^{13}C-NMR ($CDCl_3$), δ, (ppm) 79.7, 72.9, 72.5, 61.0, 59.1, 57.9, and 27.4; mass spectroscopy, *m*/*e* 177 MH^+, 121 ($M - C(CH_3)_3)H^+$ base peak. Elemental analysis found: C, 61.5; H, 11.6. $C_9H_{20}O_3$ requires: C, 61.4; H, 11.4.

1-(*tert*-Butyloxy)-2,3-bis(2-*n*-butoxyethoxy)propane (26). Compound **26** was prepared as described for **24**. The following reagents and quantities were used: compound **17** (25.5 g, 0.172 mol), compound **19** (91.5 g, 0.336 mol), sodium hydride (14.0 g, 0.350 mol of a 60% by weight solution in mineral oil), and THF (1000 mL). The final product was a colorless liquid (30.0 g, 60%) (bp 105−116 °C, 0.05 Torr): ^{1}H-NMR ($CDCl_3$), δ (ppm) 3.8−3.4 (m, 17H), 1.55 (m, 4H), 1.35 (m, 4H), 1.2 (s, 9H), 0.9 (t, 6H); ^{13}C-NMR ($CDCl_3$), δ (ppm) 78.9, 72.9, 71.6, 71.1, 71.1, 70.8, 70.3, 70.1, 69.8, 61.7, 31.7, 27.4, 19.3, and 13.9; mass spectroscopy, *m*/*e* 349 MH^+, 293 ($M - C(CH_3)_3)H^+$ base peak. Elemental analysis found: C, 65.0; H, 11.3. $C_{19}H_{40}O_5$ requires: C, 65.5; H 11.5.

1-(*tert*-Butyloxy)-2,3-bis(2-*sec*-propoxyethoxy)propane (27). Compound **27** was prepared as described for **24**. The following reagents and quantities were used: compound **17** (18.5 g, 0.125 mol), compound **20** (65.0 g, 0.252 mol), sodium hydride (15.0 g, 0.375 mol of a 60% by weight solution in mineral oil), and THF (750 mL). The final product was a colorless liquid (19.6 g, 49%) (bp 78−83 °C, 0.004 Torr): ^{1}H-

NMR (CDCl$_3$), δ (ppm) 3.8−3.4 (m, 15H), 1.15 (s, 9H), 1.12 (d, 12H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.0, 77.4, 77.0, 76.7, 72.9, 71.8, 71.7, 71.6, 71.0, 70.1, 67.6, 67.4, 61.7, 27.5, and 22.1; mass spectroscopy, *m/e* 321 MH$^+$, 265 (M − C(CH$_3$)$_3$)H$^+$ base peak. Elemental analysis found: C, 63.4%; H, 11.3. C$_{17}$H$_{36}$O$_5$ requires: C, 63.8; H, 11.2.

1-(*tert*-Butyloxy)-2,3-bis(2-(2-methoxyethoxy)ethoxy)propane (28). Compound **28** was prepared as described for **24**. The following reagents and quantities were used: compound **17** (35.0 g, 0.236 mol), compound **18** (125.0 g, 0.456 mol), sodium hydride (25.0 g, 0.625 mol of a 60% by weight solution in mineral oil), and THF (1500 mL). The final product was a colorless liquid (bp 124−131 °C, 0.02 Torr) (29.11 g, 35%): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.3−3.8 (m, 27H), 1.25 (s, 9H). ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.0, 71.93, 71.91, 71.6, 70.7, 70.5, 70.48, 70.4, 69.8, 61.6, 59.0 and 27.4; mass spectroscopy, *m/e* 353 MH$^+$, 296 (M − C(CH$_3$)$_3$)H$^+$ base peak. Elemental analysis found: C, 58.6; H, 10.2. C$_{17}$H$_{36}$O$_7$ requires: C, 58.0; H, 10.2.

1-(*tert*-Butyloxy)-2,3-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propane (29). Compound **29** was prepared as described for **24**. The following reagents and quantities were used: compound **17** (25.0 g, 0.169 mol), compound **22** (122.0 g, 0.384 mol), sodium hydride (15.0 g, 0.375 mol of a 60% by weight solution in mineral oil), and THF (1500 mL). The final product was a colorless liquid (bp 209−211 °C, 0.05 Torr): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.75−3.8 (m, 4H), 3.4−3.7 (m, 25H), 3.36−3.4 (s, 6H), 1.19 (s, 9H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 78.7, 72.6, 71.7, 71.3, 70.5, 70.34, 70.33, 70.30, 70.27, 70.25, 69.5, 61.4, 58.7, and 27.2; mass spectroscopy, *m/e* 441 MH$^+$, 384 (M − C(CH$_3$)$_3$)H$^+$ base peak. Elemental analysis found: C, 57.2; H, 9.9. C$_{21}$H$_{44}$O$_9$ requires: C, 57.3; H, 10.0.

2,3-Bis(2-methoxyethoxy)propanol (30). Compound **30** was prepared by a method similar to that described by Montanari and Tundo for the synthesis of a 2-(hydroxymethyl)-1,4,7,10,13,16-hexaoxacyclooctadecane and KBF$_4$ complex.[29] To a solution of compound **24** (10.0 g, 0.038 mol) in dichloromethane (100 mL) was added tetrafluoroboric acid (Fluka) (13.7 mL of a 54% solution in diethyl ether). The mixture was stirred at room temperature for 20 min. The acid was neutralized with excess 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%): ^{1}H-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) 79.6, 72.1, 71.7, 71.2, 70.6, 69.4, 62.4, 58.8, and 58.75; mass spectroscopy, *m/e* 209 MH$^+$ base peak. Elemental analysis found: C, 52.1; H, 9.5. C$_9$H$_{20}$O$_5$ requires: C, 52.0; H, 9.6.

2,3-Dimethoxypropanol (31). Compound **31** was prepared as described for **30**. The following reagents and quantities were used: compound **25** (20.7 g, 0.118 mol), tetrafluoroboric acid (Fluka) (26 mL of a 54% solution in diethyl ether), dichloromethane (250 mL), and excess potassium carbonate. The final product was a colorless liquid (9.8 g, 68%) (bp 24−27 °C, 0.03 Torr): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.35−3.8 (m, 11H), 2.2 (t, 1H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.9, 72.4, 62.4, 59.3, and 57.7; mass spectroscopy, *m/e* 121 MH$^+$ base peak. Elemental analysis found: C, 50.5; H, 10.4. C$_5$H$_{12}$O$_3$ requires: C, 50.0; H, 10.0.

2,3-Bis(2-*n*-butoxyethoxy)propanol (32). Compound **32** was prepared as described for **30**. The following reagents and quantities were used: compound **26** (38.0 g, 0.109 mol), tetrafluoroboric acid (Fluka) (22 mL of a 54% solution in diethyl ether), dichloromethane (100 mL), and excess potassium carbonate. The final product was a colorless liquid (17.3 g, 59%) (bp 95−120 °C, 0.04 Torr): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.4−3.9 (m, 17H), 3.1−3.2 (m, 1H), 1.5−1.6 (m, 4H), 1.3−1.4 (m, 4H), 0.9−0.95 (t, 6H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.6, 71.3, 71.1, 70.8, 70.3, 69.9, 69.7, 62.8, 31.7, 19.3, and 13.9; mass spectroscopy, *m/e* 293 MH$^+$ base peak. Elemental analysis found: C, 62.2; H, 11.3. C$_{15}$H$_{32}$O$_5$ requires: C, 61.7; H, 11.0.

2,3-Bis(2-*sec*-propoxyethoxy)propanol (33). Compound **33** was prepared as described for **30**. The following reagents and quantities were used: compound **27** (25.0 g, 0.078 mol), tetrafluoroboric acid (Fluka) (14.3 mL of a 54% solution in diethyl ether), dichloromethane (100 mL), and excess potassium carbonate. The final product was a colorless liquid (8.45 g, 41%) (bp 86−90 °C, 0.01 Torr): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.9−3.5 (m, 15H), 3.3 (s, 1H), 1.2−1.1 (s, 12H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.0, 72.0, 71.9, 71.4, 71.1, 70.1, 67.7, 67.3, 62.9, and 22.0; mass spectroscopy, *m/e* 265 MH$^+$ base peak. Elemental analysis found: C, 59.1; H, 10.7. C$_{13}$H$_{28}$O$_5$ requires: C, 59.1, H, 10.6.

2,3-Bis(2-(2-methoxyethoxy)ethoxy)propanol (34). Compound **34** was prepared as described for **30**. The following reagents and quantities were used: compound **28** (23.5 g, 0.0668 mol), tetrafluoroboric acid (Fluka) (14.1 mL of a 54% solution in diethylether), dichloromethane (100 mL), and excess potassium carbonate. The final product was a colorless liquid (9.6 g, 49%) (bp 125−140 °C, 0.040 Torr): ^{1}H-NMR, δ (ppm) 3.5−3.9 (m, 21H), 3.35 (s, 6H), 2.9−2.95 (s, 1H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.5, 72.1, 71.7, 71.2, 70.7, 70.6, 70.5, 70.4, 70.3, 69.8, 62.5, 58.9, and 58.8; mass spectroscopy, *m/e* 297 MH$^+$ base peak. Elemental analysis found: C, 52.7; H, 9.5. C$_{13}$H$_{28}$O$_7$ requires: C, 52.7; H, 9.5.

2,3-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propanol (35). Compound **35** was prepared as described for **30**. The following reagents and quantities were used: compound **29** (27.5 g, 0.063 mol), tetrafluoroboric acid (Fluka) (13.5 mL of a 54% solution in diethyl ether), excess potassium carbonate, and dichloromethane (100 mL). The final product was a pale yellow oil (21.0 g, 88%) (bp 178 °C, 0.01 Torr): ^{1}H-NMR (CDCl$_3$), δ (ppm) 3.5−4.0 (m, 27H), 3.35−3.4 (s, 6H); ^{13}C-NMR (CDCl$_3$), δ (ppm) 79.6, 72.4, 71.7, 70.8, 70.6, 70.4, 70.3, 69.2, 62.1, and 58.9; mass spectroscopy, *m/e* 385 MH$^+$ base peak. Elemental analysis found: C, 52.2; H, 9.5. C$_{17}$H$_{36}$O$_9$ requires: C, 53.1; H, 9.4.

2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethanol (36). A suspension of sodium hydride (19.1 g, 0.502 mol of a 60% by weight solution in mineral oil) in THF (500 mL) was added to a solution of tetraethylene glycol (92.2 g, 0.475 mol) (Aldrich) in THF (800 mL) and the mixture was stirred at room temperature under an atmosphere of argon for approximately 1 h. Methyl *p*-tosylate (88.7 g, 0.477 mol) was added slowly to the mixture. The reaction mixture was stirred at room temperature for several hours, during which time a heavy white precipitate formed. The reaction mixture was then heated to reflux and maintained at that temperature for at least 2 h. The mixture was filtered to remove inorganic salts. The filtrate solution was concentrated by reduced pressure rotary evaporation to give a pale yellow oil. The crude product was distilled under reduced pressure to yield **36** as a colorless liquid (48.5 g, 49%) (bp 112 °C, 0.02 Torr): ^{1}H-NMR, (CDCl$_3$), δ (ppm) 3.5−3.75 (m, 16H), 3.3 (s, 3H), 2.69 (s, 1H); ^{13}C-NMR, (CDCl$_3$), δ (ppm) 72.8, 72.5, 71.9, 70.57, 70.52, 70.47, 70.3, 61.7, and 58.9; mass spectroscopy, *m/e* 209 MH$^+$ base peak. Elemental analysis found: C, 52.1; H, 9.5. C$_9$H$_{20}$O$_5$ requires: C, 52.0; H, 9.6.

2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethanol. (37). Compound **37** was prepared as described for **36**. The following reagents and quantities were used: sodium hydride (6.50 g, 0.163 mol of a 60% by weight solution in mineral oil), THF (200 mL), pentaethylene glycol (39.5 g, 0.166 mol) (Aldrich), THF (800 mL), and methyl *p*-tosylate (29.0 g, 0.156 mol). The crude product was purified by column chromatography using 70−230 mesh silica gel eluted with 90% chloroform/10% methanol. Fractions which contained the desired product were distilled under reduced pressure to yield **37** as a colorless oil (24.0 g, 61%) (bp 130−138 °C, 0.04 Torr): ^{1}H-NMR, (CDCl$_3$), δ (ppm) 3.5−3.75 (m, 20H), 3.35 (s, 3H), 2.60 (s, 1H); ^{13}C-NMR, (CDCl$_3$), δ (ppm) 72.4, 71.9, 70.6, 70.5, 70.4, 70.3, 61.7, and 59.0; mass spectroscopy *m/e* 252 MH$^+$. An elementally pure sample of this material was not obtained. However, mass spectroscopy indicated that the required compound **37** after vacuum distillation was contaminated with a slight impurity believed to be CH$_3$(OCH$_2$CH$_2$)$_5$OCH$_3$, *m/e* 267 MH$^+$. The slightly impure compound **37** was used without further purification.

2-(2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethanol. (38). Compound **38** was prepared as described for **36**. The following reagents and quantities were used: sodium hydride (14.0 g, 0.350 mol of a 60% by weight solution in mineral oil), THF (200 mL), hexaethylene glycol (100.0 g, 0.354 mol) (Aldrich), THF (1000 mL), and methyl *p*-tosylate (65.0 g, 0.349 mol). The crude product was purified by column chromatography using 70−230 mesh silica gel eluted with 90% chloroform/10% methanol. Fractions which contained the desired product were distilled under reduced pressure to yield **38** as a colorless liquid (103.4 g, 58%) (bp 159−160 °C, 0.007 Torr): ^{1}H-NMR, ($CDCl_3$) δ (ppm) 3.5−3.75 (m, 24H), 3.36 (s, 3H), 2.84 (s, 1H); ^{13}C-NMR, ($CDCl_3$) δ (ppm) 72.4, 71.9, 70.6, 70.5, 70.4, 70.3, 61.7, and 59.0; mass spectroscopy, *m/e* 297 MH^+. An elementally pure sample of this material was not obtained. However, mass spectroscopy indicated that the required compound **38** after vacuum distillation was contaminated with a slight impurity believed to be $CH_3(OCH_2CH_2)_6OCH_3$, *m/e* 311 MH^+. The slightly impure compound **38** was used without further purification.

2-(2-(2-(2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethanol. (39). Compound **39** was prepared as described for **36**. The following reagents and quantities were used: sodium hydride (5.4 g, 0.135 mol of a 60% by weight solution in mineral oil), THF (250 mL), tetraethylene glycol (28.3 g, 0.146 mol) (Aldrich), THF (500 mL), and **23** (45.8 g, 0.126 mol). The crude product was distilled under reduced pressure to yield **39** as a colorless liquid (32.7 g, 67.2%) (bp 195−207 °C, 0.02 Torr): ^{1}H-NMR, ($CDCl_3$) δ (ppm) 3.5−3.75 (m, 32H), 3.35 (s, 3H), 2.65 (s, 1H); ^{13}C-NMR, ($CDCl_3$) δ (ppm) 72.4, 71.9, 70.5, 70.4, 70.3, 61.7, and 59.0; mass spectroscopy, *m/e* 385 MH^+ base peak. Elemental analysis found: C, 52.9; H, 9.7. $C_{17}H_{36}O_9$ requires: C, 53.1; H, 9.4.

Poly[bis(2-methoxyethoxy)phosphazene] (3). Polymer **3** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (3.00 g, 0.0259 mol), 2-methoxyethanol (5.90 g, 0.0776 mol) (Aldrich), sodium (1.78 g, 0.0776 mol), and THF (750 mL). The polymer was purified by dialysis against water (2 weeks) and methanol (2 weeks). The final product, polymer **3**, was obtained as a soft, highly viscous material (3.28 g, 65%). Elemental analysis found: C, 36.7; H, 7.0; N, 6.8. Requires: C, 36.9; H, 7.2; N, 7.2.

Poly[bis(2-(2-methoxyethoxy)ethoxy)]phosphazene (4). 2-(2-Methoxyethoxy)ethanol (15.55 g, 0.129 mol) was added to sodium metal (3.0 g, 0.124 mol) in dry tetrahydrofuran (800 mL). Once the sodium salt was formed, to this was added a solution of poly(dichlorophosphazene) (**2**) (5.0 g, 0.043 mol) in THF (400 mL) under an atmosphere of argon. The reaction mixture was stirred and refluxed for 24 h under argon and allowed to cool to room temperature. The reaction mixture was concentrated by evaporation under vacuum. The concentrated residue was precipitated into hexane, and the recovered polymer further purified by dialysis first against water (2 weeks) and then methanol (1 week). The solvent was removed by reduced pressure rotary evaporation and the remaining polymer was redissolved in THF and precipitated into hexane. The recovered material was dried under vacuum at approximately 50 °C for 2 days. The final product, polymer **4**, was obtained as a soft, highly viscous material (7.3 g, 60%). Elemental analysis found: C, 41.6; H, 7.8; N, 4.8. Requires: C, 42.4; H, 7.8; N, 5.0.

Poly[bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)]phosphazene (5). Polymer **5** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (2.08 g, 0.0179 mol), 2-(2-(2-methoxyethoxy)ethoxy)ethanol (8.81 g, 0.0537 mol) (Aldrich), sodium (1.235 g, 0.0537 mol), and THF (750 mL). The polymer was purified by dialysis against water (2 weeks) and methanol (2 weeks). The final product, polymer **5**, was obtained as a soft, highly viscous material (4.45 g, 67%). Elemental analysis found: C, 44.2; H, 8.5; N, 3.8. Requires: C, 45.3; H, 8.1; N, 3.8.

Poly[bis(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)phosphazene] (6). Polymer **6** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (3.0 g, 0.026 mol), **36** (21.5 g, 0.103 mol), sodium hydride (4.14 g, 0.1035 mol of a 60% by weight solution in mineral oil), and THF (500 mL). The polymer was purified by dialysis against water (2 weeks) and methanol (2 weeks). The final product, polymer **6**, was obtained as a viscous material (8.9 g, 75%). Elemental analysis found: C, 46.9; H, 8.6; N, 3.6. Requires: C, 47.0; H, 8.3; N, 3.1.

Poly[bis(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethyoxy)ethoxy)ethoxy)phosphazene] (7). Polymer **7** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (2.0 g, 0.017 mol), **37** (15.7 g, 0.062 mol), sodium metal (1.2 g, 0.052 mol), and THF (700 mL). The polymer was purified by precipitation into hexane followed by dialysis in water (2 weeks) and methanol (1 week). The final product, polymer **7**, was obtained as a viscous material (6.1 g, 65%). Elemental analysis found: C, 47.4; H, 8.8; N, 2.6. Requires: C, 48.3; H, 8.5; N, 2.6.

Poly[bis(2-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)phosphazene] (8). Polymer **8** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.7 g, 0.015 mol), **38** (15.0 g, 0.051 mol), sodium metal (1.0 g, 0.043 mol), and THF (600 mL). The polymer was purified by precipitation into hexane followed by dialysis in water (2 weeks) and methanol (1 week). The final product, polymer **8**, was obtained as a viscous material (8.4 g, 78%). Elemental analysis found: C, 48.7; H, 8.9; N, 2.1. Requires: C, 49.1; H, 8.6; N, 2.2.

Poly[bis(2-(2-(2-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)phosphazene] (9). Polymer **9** was prepared as described for polymer **4**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.0 g, 0.0086 mol), **39** (10.7 g, 0.028 mol), sodium hydride (0.70 g, 0.029 mol), and THF (300 mL). The polymer was purified by dialysis in water (2 weeks) and methanol (1 week) followed by precipitation into hexane. The final product, polymer **9**,was obtained as a viscous material (5.0 g, 71%). Elemental analysis found: C, 49.4; H, 8.7; N, 1.7. Requires: C, 50.3; H, 8.6; N, 1.7.

Poly[bis(2,3-dimethoxypropoxy)phosphazene] (10). Polymer **10** was prepared as described for polymer **11**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.0 g, 0.0086 mol), **31** (3.5 g, 0.029 mol), sodium hydride (1.25 g, 0.031 mol of a 60% by weight solution in mineral oil), and THF (500 mL). The polymer was purified by dialysis in water (1 week) and methanol (1 week) followed by multiple precipitations into hexane. The final product, polymer **9**, was obtained as a white gum (1.65 g, 68%). Elemental analysis found: C, 41.7; H, 7.8; N 5.0. Requires: C, 42.4; H, 7.8; N, 5.0.

Poly[bis(2,3-bis(2-methoxyethoxy)propoxy)phosphazene] (11). Compound **30** (10.68 g, 0.052 mol) was added to sodium metal (1.20 g, 0.052 mol) in dry tetrahydrofuran (200 mL). Once the sodium salt was formed, to this was added a solution of poly(dichlorophosphazene) (**2**) (2.0 g, 0.017 mol) in THF (400 mL) under an atmosphere of argon. The reaction mixture was stirred and refluxed for 24 h under argon and allowed to cool to room temperature. The reaction mixture was concentrated by evaporation under vacuum. The concentrated residue was dialyzed first against water and then methanol for several days. The solvent was removed by reduced pressure rotary evaporation to yield polymer **11**, which was dried under vacuum at approximately 80 °C for 3 days. The final product, polymer **11**, was obtained as a white gum (6.3 g, 80%). Elemental analysis found: C, 46.1; H, 8.5, N, 3.0. Requires: C, 47.3; H, 7.9; N, 3.1.

Poly[bis(2,3-bis(2-(2-methoxyethoxy)ethoxy)propoxy)phosphazene (12). Polymer **12** was prepared as described for polymer **11**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.0 g, 0.009 mol), compound **34** (14.6 g, 0.049 mol), sodium hydride (1.9 g, 0.048 mol of a 60% by weight solution in mineral oil), and THF (500 mL). The polymer was purified by dialysis in water (2 weeks) and methanol (1 week). The final product, polymer **12**, was obtained as a pale brown material (4.1 g, 75%). Elemental analysis found: C, 48.2; H, 8.2; N, 2.2. Requires: C, 49.1; H, 8.6; N, 2.2.

Poly[bis(2,3-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propoxy)phosphazene] (13). Polymer **13** was prepared as described for polymer **11**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.6 g, 0.014 mol), compound **35** (27.0 g, 0.070 mol), sodium hydride (3.5 g, 0.088 mol of a 60% by weight solution in mineral oil) and THF (500 mL). The polymer was purified by dialysis in water (2 weeks) and methanol (1 week). The final product, polymer **13**, was obtained as a pale brown material (6.1 g, 55%). Elemental analysis found: C, 48.4; H, 8.5; N, 1.5. Requires: C, 50.3; H, 8.6; N, 1.7.

Poly[bis(2,3-bis(2-*n*-butoxyethoxy)propoxy)phosphazene] (14). Polymer **14** was prepared as described for polymer **11**. The following reagents and quantities were used: poly(dichlorphosphazene) (**2**) (1.0 g, 0.0086 mol), sodium hydride (0.65 g, 0.027 mol), **32** (8.0 g, 0.027 mol), and THF (600 mL). The polymer was purified by repeated precipitations into distilled/deionized water and ethanol from THF. The final product, polymer **14**, was obtained as a white solid (4.2 g, 78%). Elemental analysis found: C, 56.3; H, 10.4; N, 2.3. Requires: C, 57.4; H, 10.0; N, 2.2.

Poly[bis(2,3-bis(2-*sec*-propoxyethoxy)propoxy)phosphzene] (15). Polymer **15** was prepared as described for polymer **11**. The following reagents and quantities were used: poly(dichlorophosphazene) (**2**) (1.0 g, 0.0086 mol), sodium hydride (1.2 g, 0.030 mol of a 60% by weight solution in mineral oil), **33**, (7.8 g, 0.029 mol), and THF (800 mL). The polymer was purified by repeated precipitations into distilled/deionized water from THF. The final product, polymer **15**, was obtained as a white solid (3.4 g, 68%). Elemental analysis found: C, 53.5; H, 9.8; N, 2.7. Requires: C, 54.6; H, 9.5; N, 2.5.

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