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Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters for **1–3** (7 pages); listings of observed and calculated structure factors for **1–3** (78 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Electrical Response of Phosphazene Polyelectrolytes

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Abstract: New phosphazene-based polymers have been synthesized, which function as single-ion conductors of either sodium or halide ions. As a prelude to the synthesis of these polymers, similar substitution reactions were carried out on hexchlorocyclotriphosphazene and the products were well characterized. The polyelectrolytes were characterized by ^{1}H NMR, ^{31}P NMR, IR, DSC, and ac complex impedance studies. The temperature dependence of the conductivity of these polyelectrolytes follows the VTF equation, indicating that, as with polymer–salt complexes, ion transport is promoted by polymer-segment motion. The ionic conductivity of the polyelectrolytes containing bromide and iodide is 2 orders of magnitude higher than that of the sodium polyelectrolytes at 30–80 °C.

There has been considerable interest in the mechanism of charge transport in polymer and polyelectrolytes and in the potential applications of these materials in solid-state devices.[1-4] Phosphazene- and siloxane-based comb polymers have been reported to exhibit high conductivity with alkali metal salts of trifluoromethanesulfonates, thiocyanates, and iodides.[5-7] The drawback with these polymer–salt complexes as polymer electrolytes is that both cations and anions are mobile, and as a result, fundamental studies of single-ion transport are difficult. In addition, most applications of these materials are based on the transport of only one ion, such as Li$^+$ in a lithium battery. In these applications the mobility of the anion leads to unwanted gradients in electrolyte concentration. A solution to this problem is to covalently attach the counterion to the polymer backbone. In the absence of solvent, conventional polyelectrolytes are rigid solids, which show poor conductivity. The introduction of plasticizers into polyelectrolytes greatly increases their conductivity, but plasticized systems are inherently less stable than pure polymers.[8] Recently, polyelectrolytes of crosslinked phosphates[9] and poly[(oligo(oxyethylene)methacrylate)-*co*-(alkali-metal methacrylates)][10] have been shown to be sodium ion conductors but show poor conductivity at room temperature.

We report the synthesis of elastomeric phosphazene polyelectrolytes in which the side groups are short chain oligo ether alkoxy and alkoxy sulfonate, quaternary or trialkylammonium salts. These new polyelectrolytes exhibit good ionic conductivity without added plasticizers or inorganic salts. A preliminary communication has appeared.[11]

Experimental Section

Materials. All the experimental manipulations were carried out under an inert atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl. Acetonitrile (MeCN) was distilled from calcium hydride. The sodium salt of 2-hydroxyethanesulfonic acid, 15-crown-5, and sodium spheres (Aldrich) were used as received; 2-(2-methoxyethoxy)ethanol (MeeOH) (Aldrich) was dried over molecular sieves (4A) and distilled before used. Poly(ethylene glycol methyl ether) (PEGOH) of average molecular weight 350, *N*,*N*-dimethylethanolamine and *N*,*N*-diethylethanolamine (Aldrich) were dried over molecular sieves (4A) before used. All haloalkanes were distilled prior to use, and other chemicals were reagent-grade purity.

Dialysis tubes (American Scientific Products) used in the purification of the polymer normally had a cutoff molecular weight of 1000, but a molecular weight cutoff of 3500 was used for polymers synthesized with the sodium salt of PEGOH.

Sodium ethane sulfonate was prepared by the neutralization of ethanesulfonic acid with sodium hydroxide in an aqueous solution and was recrystallized from methanol. Reactions involving iodoalkanes were carried out in the dark. Poly(dichlorophosphazene), (NPCl$_2$)$_n$ (**1**) was prepared by the thermal polymerization of hexachlorocyclo-

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(1) Tonge, J. S.; Shriver, D. F. *Polymers for Electronic Applications*; Lai, J., Ed.; CRC: Boca Raton, FL, in press.

(2) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.

(3) See for example: *Polymer Electrolyte Reveiws*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: New York, 1987; Chapters 1–3.

(4) Armand, M. B. *Annu. Rev. Mater. Sci.* **1986**, *16*, 245.

(5) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

(6) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *Solid State Ionics* **1986**, *18/19*, 258.

(7) Spindler, R.; Shriver, D. F. *Macromolecules* **1988**, *21*, 648.

(8) Hardy, L. C.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823.

(9) LeNest, J. F.; Gandini, A.; Cheradame, H.; Cohen-Addad, J. P. *Polym. Commun.* **1987**, *28*, 302.

(10) (a) Tsuchida, E.; Kobayashi, N.; Ohno, H. *Macromolecules* **1988**, *21*, 96. (b) Kobayashi, N.; Hamada, T.; Ohno, H.; Tsuchida, E. *Polym. J.* **1986**, *18*, 661.

(11) Ganapathiappan, S.; Chen, K.; Shriver, D. F. *Macromolecules* **1988**, *21*, 2299.

0002-7863/89/1511-4091$01.50/0

Table 1. Experimental Details[a] for the Synthesis of Poly(phosphazene sulfonates) **6–15**

$NaOC_2H_4SO_3Na$		15-crown-5		alcohol[b]		sodium[c]		x (polymer obtained)[d]
g	mmol	g	mmol	g	mmol	g	mmol	
				ROH				
6.88	40.5	24.0	109.1	7.3	60.8	1.3	56.5	1.54 (**6**)
2.92	17.2	11.4	51.8	11.2	93.3	4.0	173.9	1.75 (**7**)
2.04	12.0	8.4	38.2	12.0	100.0	4.0	173.9	1.80 (**8**)
1.63	9.6	6.3	28.6	12.2	101.7	4.0	173.9	1.86 (**9**)[f]
1.17	6.9	4.5	20.5	12.7	105.8	2.5	108.7	1.90 (**10**)
0.59	3.5	2.3	10.5	13.2	110.0	2.6	113.0	1.96 (**11**)
				R′OH				
2.04	12.0	8.4	38.2	35.0	100.0	4.0	173.9	1.80 (**12**)
1.63	9.6	13.6[e]	37.8	35.9	102.6	4.0	173.9	1.86 (**13**)
1.17	6.9	4.5	28.6	36.9	105.4	4.0	173.9	1.90 (**14**)
0.59	3.5	2.3	10.5	37.0	105.7	4.0	173.9	1.96 (**15**)

[a] In all the reactions linear $(NPCl_2)_n$ (**1**) (4g, 34.5 mmol) in THF (350 mL) was used. [b] R = $C_2H_4OC_2H_4OCH_3$ and R′ = $(C_2H_4O)_{7.22}CH_3$. In the alkoxide preparation, THF(200 mL) was used. [c] Unreacted sodium was removed wherever excess was used. [d] Where the polymers are of the formula $[NP(OR)_x(OC_2H_4SO_3Na)_{2-x}]$. Yield of the polymers was 60–70%. [e] Dibenzo-18-crown-6 was used. [f] Anal.[14] Calcd: C, 40.07; H, 7.38; N, 4.88; P, 10.78. Found: C, 41.75; H, 8.19; N, 5.12; P, 8.01.

triphosphazene, $N_3P_3Cl_6$ (**2**), at 250 °C in vacuum[12] and stored under a dry nitrogen atmosphere. Poly[bis[(methoxyethoxy)ethoxy]phosphazene] (MEEP) was prepared by the method described previously.[13] Polymer–salt complexes of MEEP with sodium ethane sulfonate were prepared from weighed amounts of dried $NaC_2H_5SO_3$ and MEEP in deionized water. After 24 h, the water was removed and the salt complex was dired under vacuum at 60 °C for 40 h. The concentration of salt in the complex is expressed as a molar ratio.

Instrumental Methods. Proton and ^{31}P NMR spectra were recorded on a JEOL FX 90 spectrometer operating at 90 MHz. Proton NMR spectra for all the samples were recorded in either $CDCl_3$ or D_2O containing TMS or DSS as an internal standard. Chemical shifts (δ/ppm) are referenced to internal TMS or DSS for ^1H NMR and to external 85% H_3PO_4 for ^{31}P NMR; upfield shifts are negative. Conductivity values were obtained by complex impedance spectra[1] with a Hewlett-Packard 4192A in the frequency range 10 Hz to 3 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer; IR spectra for all polymers show a strong band in the range 1220–1260 cm^{-1} attributable to $\nu(P{=}N)$. DSC measurements were performed on a Perkin-Elmer DSC-2 with liquid-N_2 cooling. Glass-transition temperatures were measured at four heating rates (5, 10, 20, 40 K/min), and the Tg for the sample was determined by extrapolating to a zero heating rate.

Preparation of $NaOC_2H_4SO_3Na$ (3). The sodium salt of 2-hydroxyethanesulfonic acid (50 g, 0.34 mol) was mixed with sodium hydride (8.2 g, 0.34 mol) in THF (300 mL). This mixture was heated under reflux for 120 h and cooled. Methanol (100 mL) was slowly added to the above mixture and then warmed. The mixture was filtered and the precipitate was extracted with hot methanol (4 × 200 mL). The precipitate, $Na_2OC_2H_4SO_3$ (**3**), was obtained in 58.3% yield: ^1H NMR 3.16 (t, 2 H), 3.95 (t, 2 H) and $^3J(HH)$ = 6.6 Hz.

Reaction of $N_3P_3Cl_6$ (2) with $NaOC_2H_4SO_3Na$ (3). Compound **3** (0.34 g, 2 mmol) and 15-crown-5 (2.64 g, 12 mmol) were stirred in THF (50 mL). Compound **2** (0.7 g, 2 mmol) in THF (50 mL) was added over a period of 30 min and then heated to a reflux for 36 h. The reaction mixture was filtered and the filtrate was evaporated in vacuum to obtain an oil consisting of $N_3P_3Cl_5(OC_2H_4SO_3Na)$ (**4**) and $N_3P_3Cl_5(OSO_2C_2H_4ONa)$ (**5**) in a 3:2 molar ratio.

Reaction of $N_3P_3Cl_6$ (2) with $NaC_2H_5SO_3$. Compound **2** (0.7 g, 2 mmol) in THF (50 mL) was added to a slurry of $NaC_2H_5SO_3$ (0.26 g, 2 mmol) in THF containing 15-crown-5.(1.32 g, 6 mmol). The contents were heated under reflux for 24 h. The reaction mixture was filtered and the solvent from the filtrate was evaporated to obtain a hygroscopic oil, $N_3P_3Cl_5(OSO_2C_2H_5)$ in 15-crown-5. The chloro precursors were further characterized by converting them into their 2-(2-methoxyethoxy)ethoxy derivatives. This alkoxylation was carried out in refluxing THF with an excess of the sodium salt of MeeOH.

Table 11. NMR,[a] Conductivity, and Thermal Data for Sodium Poly(phosphazene sulfonates) **6–15**

polymer	^{31}P NMR (P¹)	^{31}P NMR (P²)	conductivity, Ω^{-1} cm^{-1} at 30 °C	conductivity, Ω^{-1} cm^{-1} at 80 °C	ratio of ether oxygen to sodium ion	Tg, K
6	4 to −6[c]		*d*	*d*	6.7	
7	4 to −6[c]		*d*	*d*	14.0	208
8	−6.0	−2 to −4	2.6×10^{-7}[e]	5.4×10^{-7}	18.0	204
9	−6.7	−1.4	4.2×10^{-7}	7.4×10^{-7}	26.6	194
10	−6.9	−1.5	4.6×10^{-7}	1.3×10^{-6}	38.0	197
11	−6.6	−1.3	2.3×10^{-7}	4.8×10^{-7}	98.0	195
12	0 to −6[c]		8.2×10^{-7}[e]	1.7×10^{-6}	65.0	206
13	−7.0	−5.1	4.9×10^{-7}	1.9×10^{-6}	96.0	205
14	−7.1	−5.0	7.2×10^{-7}	2.9×10^{-6}	137.0	206
15	−7.4	−5.7	2.4×10^{-7}	1.5×10^{-6}	354.0	206

[a] Solvent was D_2O. Proton NMR spectra show the following peaks for polymers **6–11**: 3.4 (s, OCH_3), 3.7 (b, OCH_2), 4.2 (b, $POCH_2$); in addition, a peak at δ 1.9 (b, CH_2S) are observed for polymers **6–9**. The ^1H NMR spectra for polymers **12–15** show peaks at δ 3.4 (G, OCH_3), 3.7 (b, OCH_2), and 4.1 (b, $POCH_2$). [b] P¹ = ($\equiv P(OR)_2$ and P² ; $\equiv P(OR)(OC_2H_4SO_3Na)$. [c] Broad signals. [d] Conductivity too low to measure. [e] At 50 °C.

Table III. Quantities of Reagents Used in the Synthesis of Poly((*N*,*N*-dialkylaminoethoxy)phosphazenes)[a] and Composition of the Product

step 1 ROH[b,c]		step 1 sodium[d]		step 2: $HOC_2H_4NR_2'$[c]			composition sodium[d]		composition x (polymer obtained)[e]
g	mmol	g	mmol	R′	g	mmol	g	mmol	
9.3	77.4	2.4	104.3	Me	8.5	94.8	2.5	108.7	1.92 (**16**)
8.3	69.1	2.2	95.7	Me	9.2	103.4	3.2	139.1	1.81 (**17**)
7.3	60.8	1.9	82.6	Me	10.0	112.1	3.5	152.2	1.66 (**18**)
8.2	69.1	2.2	95.7	Et	12.1	103.4	3.2	139.1	1.84 (**19**)
7.2	60.8	1.9	82.6	Et	13.1	112.1	3.5	152.2	1.66 (**20**)

[a] In all reactions the linear poly(dichlorophosphazene) **1** (5 g, 43.1 mmol) was used in THF (350 mL). [b] R = $C_2H_4OC_2H_4OCH_3$. [c] The alkoxide was prepared in 200 mL of THF. [d] Unreacted sodium was removed. [e] Where the polymers are of the formula $[NP(OR)_x(OC_2H_4NR_2')_{2-x}]$. Yield of the polymers was 60–70%. The deviation in the composition of the resulting polymers was due to the error involved in the NMR integration (±5%) and the small glass pieces present in the starting material **1**.

Reaction of $N_3P_3Cl_6$ (2) with $NaCF_3SO_3$. Compound **2** (1.72 g, 4.9 mmol) was dissolved in THF (50 mL). Sodium trifluoromethanesulfonate (0.86 g, 4.9 mmol) and 15-crown-5 (3.3 g, 15 mmol) were added, and the reaction mixture was heated to reflux for 72 h. Phosphorus-31 NMR spectra indicated that no reaction occurred.

Reaction of $(NPCl_2)_n$ (1) with $NaC_2H_5SO_3$. The linear polymer **1** (1 g, 8.6 mmol) was dissolved in THF (100 mL). Sodium enthanesulfonate (3.4 g, 25.8 mmol) and 15-crown-5 (11.4 g, 51.8 mmol) were added to the above solution and heated under reflux for 48 h. The solvent was evaporated; the product was dissolved in water and dialyzed against dionized water for 120 h. No product was obtained when the water was evaporated from the contents of the dialysis bag. Apparently the polymer hydrolyzed to yield low molecular weight products.

Synthesis of Poly(phosphazene sulfonates). A general procedure for the synthesis of polyphosphazene sulfonates is described below and details of the experiments and the polymers obtained are summarized in Table I. A slurry of the dinegative compound **3** in THF containing 15-crown-5 was prepared. The linear polymer **1** in THF was added to the above mixture over a period of 30 min. The contents were heated to reflux for 14 h. The sodium alkoxide was prepared by treating the alcohol, MeeOH, or PEGOH with sodium in refluxing THF for 12 h and was added to the above reaction mixture and refluxed further for 36 h. As indicated by NMR measurements, the alkoxide displaces both chloride and sulfonate attached to phosphorus. After removal of the solvent, the residue was dissolved in water and dialyzed against deionized water for about 120 h. The dialyzed material was filtered and water from the filtrate was distilled under reduced pressure to obtain polyphosphazene sulfonates. These polymers were then dried under vacuum (3 × 10^{-5} Torr) prior to the conductivity measurements. NMR and conductivity data are listed in Table II.

Synthesis of Poly((*N*,*N*-dialkylaminoethoxy)phosphazenes). The general synthetic method is described below, and the experimental details are summarized in Table III. In step 1, the sodium salt of MeeOH was prepared by the reaction of MeeOH with sodium in refluxing THF for

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(12) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972.

(13) Allcock, H. R.; austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

(14) Often the discrepancies involved in the elemental analysis for phosphazene salts has been attributed to incomplete combustion.[15]

(15) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.

Table IV. NMR and Conductivity Data for Polyelectrolytes, $[NP(OC_2H_4OC_2H_4OCH_3)_a(OC_2H_4N^+R_2R'X^-)_{2-a}]_n$, with Anion as Conducting Species

					NMR data		conductivity (Ω^{-1} cm^{-1})		ratio of ether oxygen to halide ion	
a	R	R′	X	compd	^{31}P	^{1}H	at 30 °C	at 80 °C		Tg, K
1.92	Me			**16**	−9.0	2.2 (s), 2.5 (b), 3.4 (s), 3.6 (b), 4.1 (b)	3.1×10^{-6}	9.7×10^{-6}		194
	Me	Me	I	**21**	−9.0	3.4 (s), 3.6 (b), 4.1 (b), 4.2 (b)	2.2×10^{-5}	1.2×10^{-4}	48	202
	Me	Et	Br	**22**	−9.0	3.4 (s), 3.6 (b), 4.1 (b)	1.3×10^{-5}	5.8×10^{-5}	48	200
	Me	H	Cl	**23**	−8.9	3.4 (s), 3.6 (b), 4.0 (b)	5.3×10^{-6}	1.6×10^{-5}	48	199
1.81	Me			**17**	−9.0	2.3 (s), 2.6 (t), 3.4 (s), 3.6 (b), 4.1 (b)	2.3×10^{-6}	6.8×10^{-6}		198
	Me	Me	I	**24**	−8.5	3.4 (s), 3.6 (b), 4.1 (b), 4.2 (b)	1.9×10^{-5}	1.9×10^{-4}	19	216
	Me	Et	Br	**25**	−8.8	1.4 (b), 3.4 (s), 3.6 (b), 4.1 (b), 4.4 (b)	1.5×10^{-5}	1.4×10^{-4}	19	212
	Me	H	Cl	**26**	−8.6	3.4 (s), 3.6 (b), 4.1 (b), 4.3 (b)	1.6×10^{-6}	9.1×10^{-6}	19	206
	Me	Et	I	**27**	−8.8	1.5 (b), 3.4 (s), 3.6 (b), 4.1 (b), 4.4 (b)	1.2×10^{-5}	2.1×10^{-4}	19	214
1.66	Me			**18**	−9.0	2.2 (s), 3.3 (s), 3.4 (s), 3.6 (b), 4.1 (b)	4.8×10^{-7}	5.0×10^{-6}		199
	Me	Me	I	28	−8.4	2.9 (b), 3.4 (s), 3.6 (b), 4.1 (b), 4.2 (b)	8.0×10^{-6}	8.1×10^{-5}	9.8	223
		Et	Br	**29**	−8.5	2.9 (b), 3.4 (s), 3.6 (b), 4.1 (b)	6.7×10^{-6}	6.6×10^{-5}	9.8	216
		H	Cl	**30**	−8.8	4.1 (b), 3.4 (s), 3.6 (b), 2.3 (s)	3.7×10^{-7}	2.5×10^{-6}	9.8	205
1.66	Et			**19**	−9.0	1.0 (t), 2.4–2.7 (m), 3.3 (s), 3.4 (s), 3.6 (b), 4.1 (b)	*b*	1.1×10^{-7}		195
		Me	I	**31**	*a*	1.4 (b), 3.4 (s), 3.6 (b), 4.1 (b)	1.0×10^{-5}	1.2×10^{-4}	9.8	221
		Et	I	**32**	−8.8	1.4 (b), 3.4 (s), 4.1 (b)	1.8×10^{-5}	1.7×10^{-4}	9.8	220
		Bu	I	**33**	−9.0	1.0 (t), 1.3–1.4 (m), 2.9 (b), 3.4 (s), 3.6 (b), 4.1 (b)	9.2×10^{-6}	4.7×10^{-5}	9.8	202
		Et	Br	**34**	−8.9	1.0 (t), 2.7 (m), 3.4 (s), 3.6 (b), 4.1 (b)	7.1×10^{-6}	4.9×10^{-5}	9.8	207
		Bu	Br	**35**	−9.0	1.0 (t), 1–3 (m), 2.7 (m), 3.4 (s), 3.6 (b), 4.1 (b)	2.1×10^{-6}	9.1×10^{-6}	9.8	199
		H	Cl	**36**	−8.9	1.3 (b), 2.9 (b), 3.4 (s), 3.6 (b), 4.1 (b)	1.4×10^{-7}	9.4×10^{-7}	9.8	202
1.84	Et			**20**	−9.0	1.0 (t), 2.6 (m), 3.4 (s), 3.6 (b), 4.1 (b)	7.2×10^{-7}	2.9×10^{-6}		197
		Et	I	**37**	*a*	1.4 (b), 3.4 (s), 4.1 (b), 3.6 (b)	1.4×10^{-5}	8.4×10^{-5}	23	210
		Et	Br	**38**	*a*	0.88 (b), 1.3 (b), 3.4 (s), 3.6 (b), 4.1 (b)	2.8×10^{-6}	1.5×10^{-5}	23	205

[a] Data not obtained. [b] Conductivity too low to measure.

12 h. This solution was then added to a solution of polymer **1** in THF over a period of 30 min and refluxed for 16 h. In step 2, a solution of the sodium salt of *N*,*N*-dialkylethanolamine was added and the reflux was continued for 24 h. After removal of the solvent, the nonvolatile product was dissolved in water and dialyzed against deionized water for 120 h. It was filtered and the water was removed under vacuum to obtain polymers **16–20**.

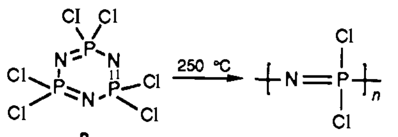
Quaternization Reactions. In a typical experiment the polymer **17** (1 g, 36 mmol) was dissolved in MeCN (50 mL), iodoethane (2.9 mL, 18.8 mmol) was added, and the mixture was stirred for 24 h at room temperature. Acetonitrile and unreacted iodoethane were removed in vacuo to obtain $[NP(OC_2H_4OC_2H_4OCH_3)_{1.81}(OC_2H_4N^+Me_2EtI^-)_{0.19}]_n$ (**27**) (1.0 g, 95% yield). The same procedure was adopted for the synthesis of polymers **21**, **22**, **24**, **25**, **28**, **29**, and **31–35** from polymers **16**, **18–20**, and appropriate haloalkanes. NMR and conductivity data are listed in Table IV. When 1-iodobutane and 1-bromobutane were the reactants, the reaction mixture was refluxed for 2 h followed by removal of solvent under vacuum.

Preparation of Chloride Ion Conducting Polymers. Typically, the polymer **17** (1 g, 3.6 mmol) was dissolved in water (20 mL). A 5% solution of hydrochloric acid (15 mL) was added and the mixture was stirred for 12 h at ampient temperature. The solution was dialyzed for 120 h and water was evaporated to obtain $[NP(OC_2H_4OC_2H_4OCH_3)_{1.81}(OC_2H_4N^+HMe_2Cl^-)_{0.19}]_n$ (**26**) (0.96 g, 85% yield). The same method was used for the preparation of polymers **23**, **30**, and **36**.

Results and Discussion

Cation Conductors. To establish reaction conditions and obtain spectroscopic data for the characterization of the polymer electrolytes, the reaction of $N_3P_3Cl_6$ (**2**) with the dinegative compound $NaOC_2H_4SO_3Na$ (**3**) has been investigated. The reaction of **2** with **3** gives the monosubstituted derivatives $Na[N_3P_3Cl_5(OC_2H_4SO_3)]$ (**4**) and $Na[N_3P_3Cl_5(OSO_2C_2H_4O)]$ (**5**) in the ratio 3:2.[11] Although a substantial amount of product **5** is formed in the above reaction, the initial product is compound **4**. It is also possible that the nucleophilic attack of the alkoxide end of compound **5** at the phosphorus center attached to the sulfonate group with another molecule may also produce **4** and the dianion **3**. Thus the ratio 3:2 represents an equilibrium value. The reactivity of sulfonate toward **2** is confirmed by the reaction of **2** with sodium ethanesulfonate. Sulfonate groups attached to phosphorus center can be readily displaced by alkoxides. Treatment of compounds **4** and **5** with excess sodium alkoxide produced $Na[N_3P_3(OR)_5(OC_2H_4SO_3)]$ and $N_3P_3(OR)_6$ ($R = C_2H_4OC_2H_4OCH_3$), respectively . Although compound **2** reacts with sodium ethanesulfonate, no reaction occurs with sodium trifluoromethanesulfonate; the starting material **2** is recovered unchanged. The presence of electronegative fluorine atoms reduces the nucleophilicity of the sulfonate ion.

The starting material for the synthesis of phosphazene polyelectrolytes is the linear polymer **1** which is in turn synthesized by the ring-opening thermal polymerization of compound **2** as show below.



2 **1**

The following poly(phosphazene sulfonates), $[NP(OR)_x(OC_2H_4SO_3Na)_{2-x}]_n$ [R = Mee, *x* = 1.54, 1.75, 1.80, 1.86, 1.90, and 1.96 (**6–11**); R = PEG, *x* = 1.80, 1.86, 1.90, and 1.96 (**12–15**)] have been prepared by varying the stoichiometry of the dinegative compound and the alkoxide with respect to the polymer **1**. The composition of each polymer has been determined from the integral intensities of appropriate peaks from either ^{1}H or ^{31}P NMR spectrum. Polymers **9–11** and **13–15** exhibit very weak signals for CH_2S protons in ^{1}H NMR spectra whereas ^{31}P NMR show two distinct peaks corresponding to $\equiv P(OR)_2$ and $\equiv P(OR)(OC_2H_4SO_3Na)$. The ^{31}P NMR spectrum for the polymer **11** is illustrated in Figure 1. No peaks corresponding to unreacted or partially reacted $\equiv PCl_2$ centers were seen. For polymers **6**, **7**, and **12**, broad signals have been observed since the units $\equiv P(OR)_2$, $\equiv P(OR)(OC_2H_4SO_3Na)$, and $\equiv P(OC_2H_4SO_3Na)_2$ may be present in a random manner. The polymers **6** and **7** are insoluble in common organic solvents whereas polymers **8–15** are soluble in acetone and methanol.

Since the sulfonate anion reacts with the $\equiv PCl_2$ center, attempts to prepare polymers $[NP(OSO_2R)_2]_n$ ($R = C_2H_5$) have been unsuccessful. The above polymer may have been formed, but it appears that water is sufficiently nucleophilic to displace sulfonate groups and the resulting hydrolysis product degrades to low molecular weight compounds.

Thermal data for sodium poly(phosphazene sulfonates) is shown in Table II. The glass-transition temperature is essentially constant within the concentration range studied for the same oligo ether side chain.

Conductivity data for the poly(phosphazene sulfonates) **6–15** at 30 and 80 °C is shown in Table II and the temperature de-

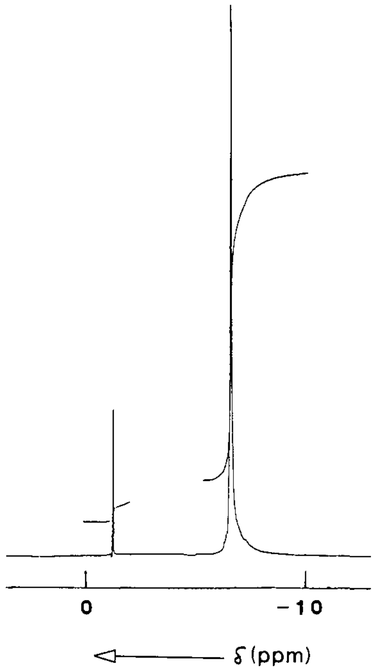


Figure 1. The $^{31}P\{^1H\}$ NMR spectrum (36.2 MHz, D_2O) of $[NP(OMee)_{1.96}(OC_2H_4SO_3Na)_{0.04}]_n$ (**11**).

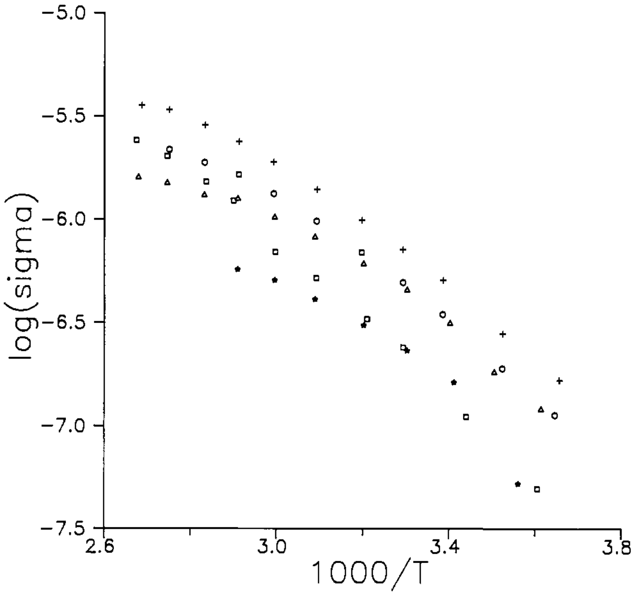


Figure 2. Arrhenius plot for the conductivity of typical poly(phosphazene sulfonates): △ (**10**), * (**11**), ○ (**13**), + (**14**), and □ (**15**).

Table V. Calculated Normalized Conductivity for Poly(phosphazene sulfonates) **8–15**

polymer	ratio of ether oxygen to sodium	normalized conductivity	cations per polymer unit $[NP(OR)_2]$
8	18.0	0.41	0.11
9	26.0	0.56	0.08
10	38.0	1.00	0.05
11	98.0	0.36	0.02
12	65.0	0.58	0.11
13	96.0	0.66	0.08
14	137.0	1.00	0.05
15	354.0	0.53	0.02

[a] Strictly it is difficult to say polymer unit as $[NP(OR)_2]$ for polyelectrolytes reported here.

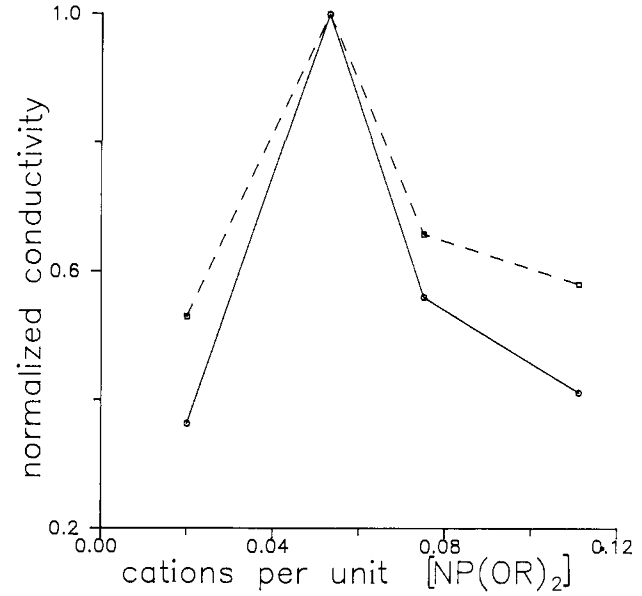


Figure 3. Plot of normalized conductivity at 80 °C vs cations per polymer unit, $[NP(OR)_2]$, for poly(phosphazene sulfonates).

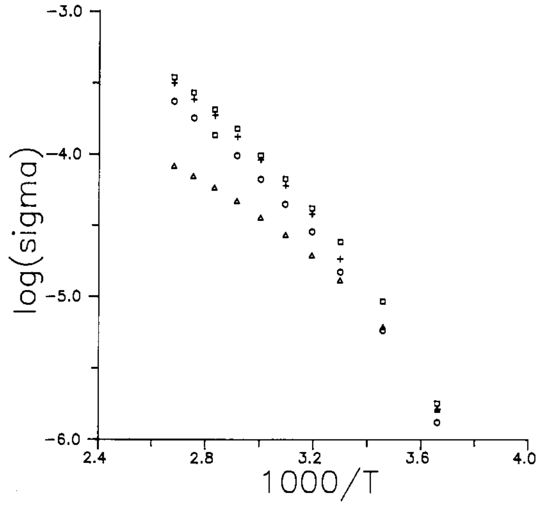


Figure 4. Temperature-dependent conductivity plotted as log σ vs 1000/T of typical halide ion conductors: (△) $[NP(OMee)_{1.92}(OC_2H_4N^+Me_2EtBr^-)_{0.08}]_n$ (**22**), (+) $[NP(OMee)_{1.81}(OC_2H_4N^+Me_3I^-)_{0.19}]_n$ (**24**), (○) $[NP(OMee)_{1.81}(OC_2H_4N^+Me_2EtBr^-)_{0.19}]_n$ (**25**), and (□) $[NP(OMee)_{1.81}(OC_2H_4N^+Me_2EtI^-)_{0.19}]_n$ (**27**).

pendent conductivity for the polyelectrolytes **10**, **11**, and **13–15** is illustrated in Figure 2. The curved log σ vs $1/T$ plots indicate VTF behavior similar to that seen for the phosphazene polymer electrolytes.[1,16] As the sulfonate concentration in the polymer is increased, the ionic conductivity generally undergoes an initial increase followed by a decrease. The conductivity increases slightly when the length of the oligo ether side chain is increased. Conductivity data (Table II) were normalized so that the most conducting complex of each polymer is equal to 1 (see Table V). The plot of normalized conductivity with the polymer repeat unit $[NP(OR)_2]$ is shown in Figure 3. In the polymer–salt complexes, a plot of conductivity versus the ratio of salt per ether oxygens generally goes through a maximum.[16] By contrast, the ionic conductivity of the polyelectrolytes depends on the ratio of the number of sulfonate groups to the oligo ether side chains. In other words, ether side chains of varying length have the same influence on the ionic conductivity. A plausible explanation for this phenomenon is that the attachment of negative charge to the polymer backbone by covalent bonds restricts the associated sodium ion to a small volume element that is not accessed by ether oxygens that are far removed from the backbone. Therefore, only the ether oxygens close to the sulfonate–Na^+ ion pair influence the sodium ion mobility.

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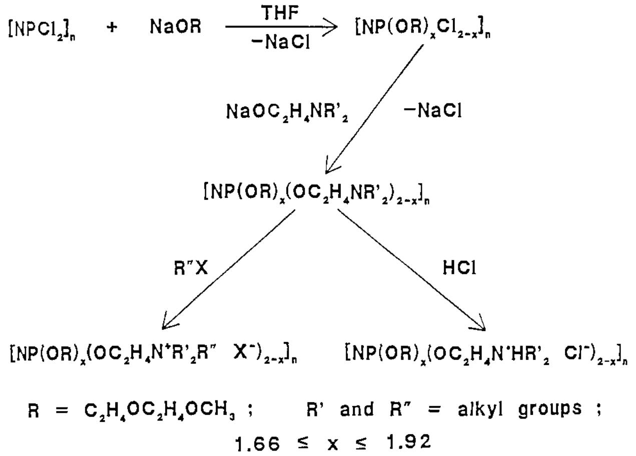
(16) Blonsky, P. M. Ph.D. dissertation, Northwestern University, 1985.

Table VI. Comparison of Ionic Conductivities of Alkanesulfonates and Fluoroalkanesulfonates

polymer	temp, °C	ratio of ether oxygen to sodium	ionic conductivity, Ω^{-1} cm^{-1}
$(MEEP)_4NaCF_3SO_3$[a]	30	16	7.8×10^{-5}
	80	16	2.3×10^{-3}
$(MEEP)_4NaC_2H_5SO_3$	30	16	2.0×10^{-6}
	80	16	9.5×10^{-6}
$(MEEP)_{9.5}NaC_2H_5SO_3$	30	38	2.0×10^{-6}
	80	38	8.2×10^{-6}
10	30	38	4.6×10^{-7}
	80	38	1.3×10^{-6}

[a] From ref 6.

Scheme I



The conductivity observed in the present study is 2 orders of magnitude less than that of the polymer electrolyte of MEEP complexes.[5,6] This low ionic conductivity may arise from ion pair formation between sulfonate and sodium ions because the alkane sulfonate groups in the polyelectrolytes are more basic than the $CF_3SO_3^-$ ion employed in the related polymer–salt complexes. This conclusion is strengthened by the observation that the conductivity of MEEP complexes with sodium ethanesulfonate (Table VI) is comparable to that of poly(phosphazene sulfonate) polyelectrolytes but approximately 2 orders of magnitude lower than that of trifluoromethanesulfonate complexes of MEEP.

Anion Conductors. The polyelectrolytes with mobile anions were prepared by the quaternization of amine groups on the polymer side chains with haloalkanes or hydrochloric acid. The following polymers $[NP(OR)_x(OC_2H_4NR'_2)_{2-x}]_n$ [R = Mee, R' = CH_3, x = 1.66, 1.81 and 1.92 (**16–18**); R = Mee, R' = C_2H_5, x = 1.66 and 1.84 (**19** and **20**)] have been prepared by the treatment of **1** with the stoichiometric amount of sodium salt of MeeOH followed by excess of sodium salt of *N,N*-dialkylethanolamine as shown in Scheme I. The above polymers are treated with excess haloalkanes, viz. iodomethane, iodoethane, 1-iodobutane, bromoethane, and 1-bromobutane, in MeCN to yield polymers, **21–36**. These polymers are soluble in chloroform, acetone, and methanol. Complete quaternization of the tertiary amino group was demonstrated by the disappearance of the ^{1}H NMR signal at 2.2–2.7 ppm due to NCH_3 or NCH_2 protons (see Table IV for the data). Earlier studies indicate that quaternization of the backbone nitrogen atoms does not occur for poly(alkoxy- or (aryloxy)phosphazenes).[17] Similarly, attempts to quaternize the polymers in the present study leads to a ^{31}P NMR signal around −9.0 ppm, which is unshifted from the parent polymer. A single ^{31}P NMR signal is observed for polymers with a range of side groups: $\equiv P(OR)_2$, $\equiv P(OR)(OC_2H_4NR'_2)$, $\equiv P(OC_2H_4NR'_2)_2$, and $\equiv P(OR)(OC_2H_4N^+R'_2R''X^-)$. Apparently the ^{31}P chemical shifts are insensitive to the various alkoxy side chains and as a consequence, it is not possible to determine the degree of disorder in placement of various alkoxy side chains along the PN backbone.

Thermal data for anion conductors is shown in Table IV. The glass-transition temperatures of quaternized polymers are higher than those of their unquaternized precursors. Apparently the coulomb interactions between charged groups reduce the segmental motion and therefore increase Tg. For both iodide and bromide conductors, Tg increases as the anion concentration increases. This trend is not very obvious in chloride conductors. Generally, Tg increase in the order $Cl^- < Br^- < I^-$ for the same anion concentration. This trend is more obvious when the anion concentration is high.

The order of increasing electrical conductivity of halide ion conductors is $Cl^- < Br^- < I^-$ (Figure 4); so, the largest halide, which sould be the most loosely ion paired is the most mobile. As the concentration of anion is increased with respect to the alkoxy side groups, the conductivity initially increases and then decreases. The optimum conductivity is found when the ether oxygen to anion ratio is 19. This behavior is similar to that of polymer electrolytes. The conductivity for these polyelectrolytes is comparable to that of MEEP salt complexes, where both ions are mobile, and approximately 2 orders of magnitude greater than that of sodium ion polyelectrolytes prepared in the present study. There is no significant change in the conductivity when the length of the alkyl group attached to the nitrogen atom of the quaternary ammonium salt is increased.

Conclusion

The single-ion conductors with new polyelectrolytes with pendant sulfonate side chains and sodium counterions display low ionic conductivity, which is attributed to strong ion pairing between Na^+ and the basic sulfonate anion. The bromide and iodide ion polyelectrolyte conductors show much higher electrical conductivity on the order of 10^{-4} Ω^{-1} cm^{-1} at 80 °C. Apparently, ion pairing is weaker in the anion conductors. These polyelectrolytes form an excellent testing ground for theories of ion transport in polymers because single ion diffusion coefficients can be deduced via the Stokes–Einstein equation directly from the conductivity data. The polyelectrolytes also may have advantages in practical devices since salt migration in a dc field is prevented.

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(17) Allcock, H. R.; Levin, M. L.; Austin, P. E. *Inorg. Chem.* **1986**, *25*, 2281.