Macromolecules 1988, *21*, 2299–2301 **2299**

When the aqueous bilayer solution of **2** (chloride form) and the aqueous poly(sodium styrene sulfonate)[10] separately prepared were mixed, the instantaneous precipitation due to formation of polyion complex of the polyanion and the cationic bilayer component was observed. Since no precipitate was observed during polymerization for the mixed bilayer systems (**1** and **2**) in spite of the formation of high molecular weight polymers, the resulting polymers would have a suitable conformation for maintaining an aqueous bilayer state.

In summary, extremely high molecular weight polymers can be produced under mild conditions in a bilayer state by taking advantage of the well-defined bilayer surface and fixation of the photoinitiator at the most effective position for initiation. Attempts to reveal the conformational structure of such polymers and the morphology of polymerized bilayer membranes are now in progress.

Registry No. 1, 114908-01-9; 2 (homopolymer), 114908-03-1.

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(6) The photoinitiator of **1** was prepared as follows.[7] Sodium *O*-ethyl xanthate (0.37 g, 2.6 mmol) and 1.1 g (1.7 mmol) of *N*-(chloroacetyl)-L-glutamic acid dihexadecyl ester[8] were dissolved in 100 mL of THF and refluxed for 4 h in the dark, and then NaCl formed was separated and THF was removed. The residues were recrystallized from methanol giving a pale yellow powder: yield 52%; mp 54 °C. The purity was confirmed by UV spectrum (λ_{max} = 278 nm: π–π^* transition of SC(=S)O; $\epsilon_{max} = 1.13 \times 10^4$ L mol^{-1} cm^{-1}). NMR spectrum was consistent with the structure: NMR ($CDCl_3$) δ 0.89 (t, 6, CH_3), 1.45 (s, 2, C(=S)OCH_2). Anal. Calcd for $C_{42}H_{79}O_6NS_2$: C, 66.53; H, 10.50; N, 1.85. Found: C, 66.39; H, 10.58; N, 1.78. The polymerizable amphiphile of **2** was prepared by anion-exchanging reaction of the corresponding double-chain ammonium chloride[8] with sodium styrene sulfonate. The chloroform solution (10 mL) of double-chain ammonium chloride (1 g, 1.4 mmol) and the methanol solution (30 mL) of sodium styrene sulfonate (0.44 g, 2.1 mmol) were mixed and stirred for 4 h at room temperature. After separation of NaCl formed and removal of solvent, the residues were extracted with chloroform giving a colorless powder: yield 72%; mp 81–82.5 °C; NMR ($CDCl_3$) δ 0.89 (t, 6, CH_3), 5.28, 5.76, 6.72 (d, 3, vinyl), 7.43, 7.80 (d, 4, phenyl). Anal. Calcd for $C_{50}H_{90}O_8N_2S$: C, 68.30; H, 10.32; N, 3.19. Found: C, 68.22; H, 10.40; N, 3.02.

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(10) Poly(sodium styrene sulfonate) was prepared by radical polymerization of sodium styrene sulfonate with sodium *O*-ethyl xanthate in aqueous solution upon UV irradiation and purified by reprecipitation from aqueous solution into methanol to remove unreacted monomer.

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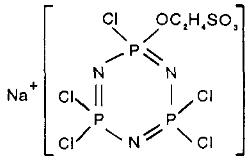
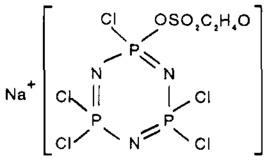
A New Class of Cation Conductors: Polyphosphazene Sulfonates

In recent years there has been considerable interest in the mechanism of charge transport in solvent-free polymer electrolytes and in the potential application of these electrolytes in electrochemical devices.[1-3] Most attention has been paid to polymer electrolytes formed from linear-chain polyethers, poly(ethylene oxide) or poly(propylene oxide) with alkali metal salts. Recently, polymer electrolytes based on phosphazene and siloxane comb polymers have been reported, which exhibit better conductivity at room temperature than for the linear-chain polyether electrolytes.[4-6] The high conductivity of these materials arises from their highly flexible polymer segments. A drawback for most polymer electrolytes is that the transference number for the cation lies in the range 0.3–0.5. In order to increase the fraction of the charge carried by the cation, we have experimented with polymers in which the anion is covalently attached to the polymer (polyelectrolytes). Conventional polyelectrolytes are rigid materials in the absence of solvent; however, we have shown that certain plasticizers greatly improve the conductivity of polymers such as sodium poly(styrenesulfonate), and we suggested that polyelectrolytes that incorporate flexible groups by covalent bonds would be a logical next step.[7,8] This more elegant approach was realized by LeNest and co-workers who synthesized a polyelectrolyte based on cross-linked ether networks containing phosphate charged groups.[9] Conference reports of other flexible polyelectrolytes also have appeared.[10] Also, the electrical properties of a polyether–polyelectrolyte blend have been investigated.[11] In this communication, we report the synthesis and conductivity of a new class of polyelectrolytes having phosphazene backbone and with sulfonate and oligoether side chains.

As a model system for the analogous reaction with linear poly(dichlorophosphazene), $[NPCl_2]_n$, we investigated the equimolar reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with the disodium salt of 2-hydroxyethanesulfonic acid, $NaOC_2H_4SO_3Na$, in THF in the presence of 15-crown-5. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two sets of an A_2B pattern [set i, 22.2 ppm (d), 0.5 ppm (t), ^2J(PP) = 45 Hz; set ii, 22.8 ppm (d), 3.9 ppm (t), ^2J(PP) = 66 Hz] in the intensity ratio 3:2. The chemical shift and intensity of the signals suggest that the products should be assigned as compounds **1** and **2**: The ^{31}P NMR assignments for **2** were confirmed by the $^{31}P\{^1H\}$ NMR spectrum of the product obtained from the equimolar reaction of $N_3P_3Cl_6$ with sodium ethanesulfonate, $NaC_2H_5SO_3$; A_2B pattern, 21.8 ppm (d), 3.4 ppm (t); ^2J(PP) = 64 Hz consistent with a monosubstituted derivative, $N_3P_3Cl_5(OSO_2C_2H_5)$. Thus, the alkoxysulfonate acts as a difunctional reagent toward $N_3P_3Cl_6$. ^{31}P NMR spectra gave no indication of the presence of spirocyclic or ansa products. Also, intensities in the ^{31}P NMR gave no evidence for intermolecular condensation products. Surprisingly, the sulfonate is sufficiently nucleophilic to displace chlorine atoms from the $\equiv PCl_2$ center.



1



2

In THF the dinegative compound, $NaOC_2H_4SO_3Na$, reacts with an excess of linear $[NPCl_2]_n$ in the presence

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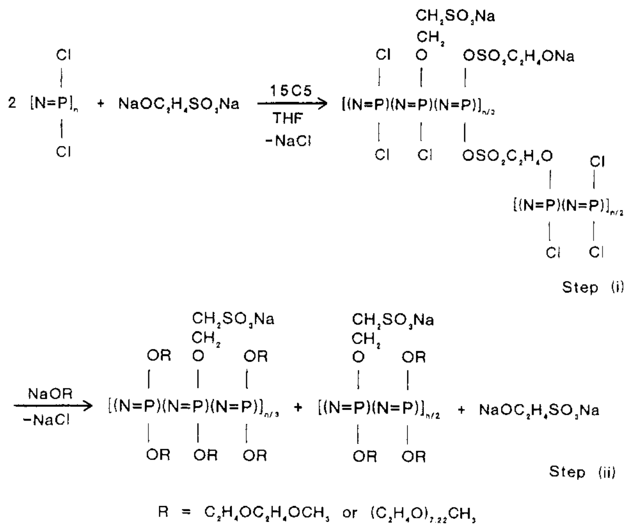
Table I
Comparison of Phosphazene Salt Complexes with a Phosphazene Polyelectrolyte

polymer	temp, °C	ratio of ether O to Na	ionic conductivity, s cm^{-1}
$[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.8}(OC_2H_4SO_3Na)_{0.20}]_n$ (**6**)	80	18:1	1.7×10^{-6}
$(MEEP)(Na[CH_2{=}CHCH_2SO_3])_{0.29}$ (**7**)	80	14:1	9.6×10^{-6}
$(MEEP)(NaCF_3SO_3)_{0.25}$[5]	80	16:1	4.5×10^{-4}

Scheme I



of 15-crown-5 to produce a partially substituted product (Scheme I). The reaction mixture was then treated with the sodium salt of 2-(2-methoxyethoxy)ethanol or poly(ethylene glycol methyl ether) of average molecular weight 350 to yield derivatives of polyphosphazene sulfonates. This reaction introduces neutral polyether side chains and, in the process, displaces the sulfonate groups and chlorine atoms attached to phosphorus atoms.[12] Also, any cross-linking by the alkoxysulfonate is removed in this process (Scheme I, step ii). Independent experiments confirmed that the alkoxide ion displaces sulfonate groups. For example, treatment of compounds 1 and 2 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.

The ^{31}P and ^1H NMR and IR spectra for the resulting polymers indicate total halogen replacement.[13] The ratio of the sulfonate group to the ether side groups is established by the ratio of the integral intensities of OCH_2 protons with CH_2S protons from ^1H NMR spectra. In addition, qualitative tests using Ag^+ demonstrated the lack of appreciable chloride in the product. The amount of sulfonate groups incorporated in the polymer backbone is generally 50% of that initially used in the reaction. The advantages of this synthetic procedure are that the length of the ether side groups and the ratio of the sulfonate groups to ether groups can be easily varied. Presumably the substitution reactions do not occur in a stereo regular manner.

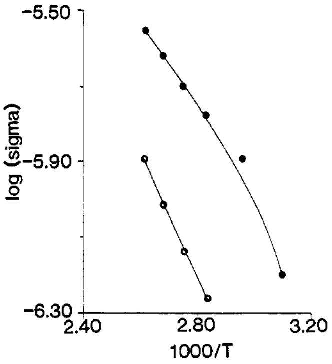


Figure 1. Arrhenius plot for the conductivity of polyphosphazene sulfonates: (●) $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.8}(OC_2H_4SO_3Na)_{0.2}]_n$ (**6**) and (○) $[NP(OC_2H_4OC_2H_4OCH_3)_{1.8}(OC_2H_4SO_3Na)_{0.2}]_n$ (**5**).

The following polymers $[NP(OR)_x(OC_2H_4SO_3Na)_{2-x}]_n$ [$R = C_2H_4OC_2H_4OCH_3$, x = 1.54, 1.75, and 1.80 (**3**–**5**); $R = (C_2H_4O)_{7.22}CH_3$, x = 1.80 (**6**)] were prepared to test the influence of charge concentration on ion transport. The value of 7.22 for the number of OC_2H_4 repeating units reflects the average molecular weight of the poly(ethylene glycol) starting material. The analysis for two typical polymers is as follows: Anal. Calcd[14] for **4**: C, 38.28; H, 7.03; N, 4.83. Found: C, 36.06; H, 6.61; N, 6.22. Anal. Calcd[15] for **6**: C, 48.18; H, 8.34; N, 1.99. Found: C, 46.13; H, 8.15; N, 2.78. The phosphazene polyelectrolytes with high sulfonate concentration, **3** and **4**, are rigid solids, whereas polymers **5** and **6** are elastomers at room temperature. Ionic conductivities were measured by complex impedance spectroscopy[1] in the frequency range 10–3 × 10^6 Hz, using stainless steel electrodes. Gentle curves were obtained when log σ is plotted aginst $1/T$ (Figure 1), as expected for ion transport in amorphous polymers.[3,16] The low conductivity observed for these polyelectrolytes may be attributed to the significant ion pair between sodium and sulfonate ions. In order to confirm this assumption, we prepared a polymer electrolyte formed by poly(bis(methoxyethoxyethoxyphosphazene)), $[NP(OC_2H_4OC_2H_4OCH_3)_2]_n$ (MEEP), with sodium allylsulfonate of composition $(MEEP)(Na[CH_2{=}CHCH_2SO_3])_{0.29}$ (**7**). The ionic conductivity of polymer **7** is given in Table I along with that of polymer electrolyte $(MEEP)(NaCF_3SO_3)_{0.25}$. The ionic conductivity of polymer electrolyte **7** is comparable to that of polyelectrolyte **6** but 2 orders of magnitude lower than that of $(MEEP)(NaCF_3SO_3)_{0.25}$, which suggests that there is extensive ion-pair formation between sodium cation and sulfonate anion. The general synthetic procedure employed here should permit the attachment of a wide variety of pendant charged groups to the phosphazene backbone. A detailed study is under way on other charged groups and on the dependence of conductivity on charge concentration.

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Registry No. $N_3P_3Cl_6$, 940-71-6; $N_3P_3Cl_5(OSO_2C_2H_5)$, 115077-19-5; $NaOC_2H_4SO_3Na$, 115077-18-4.

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(13) ^{31}P NMR: 4 to −6 ppm (br) (D_2O/H_3PO_4). Broadness decreases as the amount of sulfonate groups in the polymer backbone decreases. ^{1}H NMR: 3.7 and 4.2 ppm (br) for OCH_2 protons, 3.4 ppm (s) for OCH_3 protons, and 1.9 ppm (br) for SCH_2 protons [D_2O/TMS (ext.)]. IR: 1210–1280 cm^{-1} (b) for ν(P=N) and 1050–1100 cm^{-1} (b) for $\nu(SO_3Na)$.
(14) Stoichiometry of polyphosphazene sulfonate is taken from the integral intensity ratios of appropriate peaks from the ^{1}H NMR spectra.
(15) Stoichiometry is expected on the basis of the general trend observed for the preparation of polymers **3–5** under similar experimental conditions.
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Multinuclear Solid-State NMR Study of Phase Transitions in Poly[bis(4-ethylphenoxy)phosphazene]

Recently[1-16] much attention has been paid to the structural and thermal properties of poly(organophosphazenes) [—N=P(R_2)]— in view of the scientific interest and potential applications of these polymers. Polyphosphazenes are unusual polymers that, like silicones and silanes, have an inorganic backbone structure. It is well-known[17] that most polyphosphazenes undergo three transitions, the glass transition T_g, the thermotropic transition from crystal to mesophase, so-called $T(1)$, and the melting transition T_m. Among these transitions, the thermotropic phase transition in these polymers is most interesting and is responsible for drastic changes in their properties. Furthermore, recently it has been found that some polyphosphazenes have a number of different crystalline modifications or polymorphs below $T(1)$ and their occurrence strongly depends on the crystallization conditions.[18-20]

These crystalline modifications and mesophase have been studied mainly by X-ray diffraction, electron beam diffraction, and thermal analysis. Only a few studies have been done on the dynamic properties of polyphosphazenes.[21-24] Solid-state nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful methods for studying the local dynamics and conformations of polymers. To our knowledge, however, there has been no study of the mesomorphic phase transitions in polyphosphazenes by solid-state, high-resolution NMR. Poly(organophosphazenes) have two kinds of nuclei, ^{31}P and ^{13}C, which are easily accessible to study by solid-state, high-resolution NMR. ^{31}P NMR provides information on the conformation and mobility of the backbone, while ^{13}C NMR gives information on the conformation, packing, and mobility of the side groups.

In this paper, we report preliminary results from ^{13}P and ^{13}C NMR studies on the phase transitions of poly[bis(4-ethylphenoxy)phosphazene] (PBEPP)[25,26] along with the results of DSC thermal analysis and X-ray diffraction analysis.

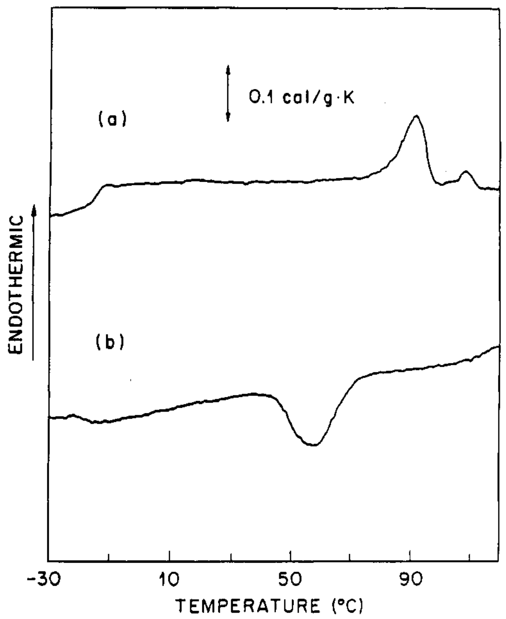
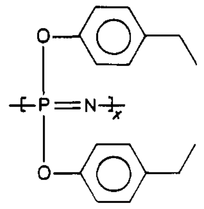


Figure 1. DSC scans of PBEBB in the heating (a) and cooling (b) process.



PBEPP

PBEPP was prepared from the Allcock procedure.[27] Polydichlorophosphazene was prepared by heating purified $(NPCl_2)_3$ in a sealed glass tube for 5 days at 250 °C with rigorous exclusion of moisture. Derivitization of $(NPCl_2)_x$ with the 4-ethylphenoxide residue was accomplished by a slight modification of the usual process.[27] Elemental analysis of the polymer showed <0.2% residual chlorine. Gel permeation chromatography indicated an average molecular weight of the order of 10^6. The polymer was soluble in tetrahydrofuran, chloroform, and benzene. A ^{31}P NMR (C_6H_6) spectrum of the sample consisted of a sharp singlet at −19.30 ppm (ext. H_3PO_4). The ^{31}P NMR (C_6H_6) spectrum of the corresponding cyclic trimer $[NP(OC_6H_4\text{-}4\text{-}C_2H_5)_2]_3$ exhibited a singlet at 8.80 ppm (ext. H_3PO_4). Full details of the sample preparation will be given elsewhere.[28]

^{31}P and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135 °C by use of heated flow. Temperature was controlled within ±1 °C. PBEPP in rubbery form was packed in an aluminum oxide rotor with Vespel or Kel-F caps. A 45-kHz radiofrequency field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimum cross-polarization (CP) time of ^{13}C from ^{1}H was found to be 2 ms at room temperature and we used this value at all the temperatures. The ^{13}C spectra were referenced to the resonance of POM (89.1 ppm from TMS) and the ^{31}P spectra to the resonance of H_3PO_4 (0 ppm).

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