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High-Conductivity Electrolytes Composed of Polystyrene Carrying Pendant Oligo(oxyethylene)cyclotriphosphazenes and $LiClO_4$

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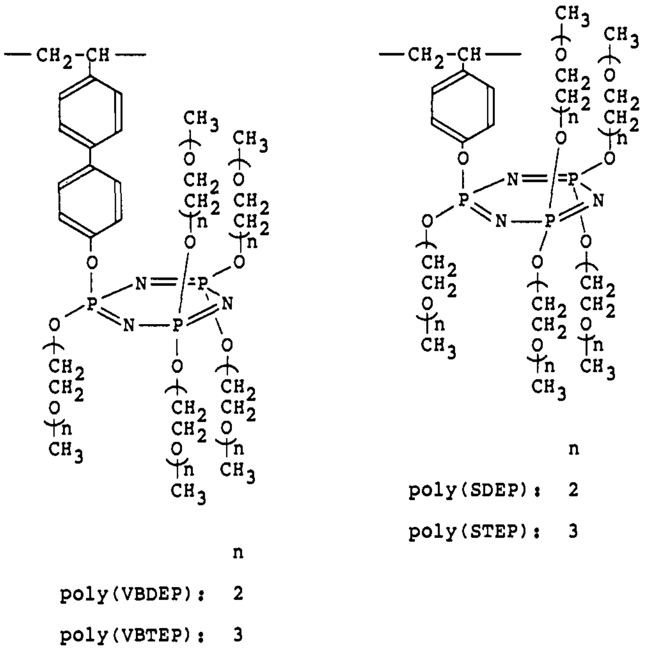
Abstract: Ionic conductivities of the complexes of polystyrene with pendant penta[oligo(oxyethylene)]cyclotriphosphazenes (poly(SDEP), $(-OCH_2CH_2)_nOCH_3$, $n = 2$; poly(STEP), $n = 3$) with $LiClO_4$ were investigated as a function of temperature and salt concentration. The glass transition temperatures (T_g) of side chains of poly(SDEP) and poly(STEP) were observed at −62 and −67 °C, respectively. Interestingly, the T_g values of the poly(STEP)-Li salt complexes of $[Li^+]/O > 0.5$ become higher than those of the poly(SDEP)-Li salt system. The conductivities of the complexes exhibit a non-Arrhenius temperature dependence, indicating an ion transport in the amorphous phase. In spite of the low segmental mobility of poly(STEP)-Li salt complexes, their conductivities are higher than those of the poly(SDEP) system and the maximum conductivities of 1.1×10^{-4} S/cm at 60 °C and 5.1×10^{-4} S/cm at 100 °C have been achieved at $[Li^+]/O = 0.05$. The high conductivities might be explained by an ion transport through a continuous conducting phase consisting of a number of oxyethylene chains without being affected by the mobility of the backbone. This implies that the flexibility of backbone is not an important factor to achieve a high conductivity. From the correlation between the polymer characteristics and the conductivity, the conduction appears to occur at a rate governed by both the mobility of side chains and the stability of the complex, which relates with ion-dipole interactions.

Introduction

Various comb-shaped polymer-alkaline-metal salt complexes have been prepared with the goal of preparing materials with ionically high conductive and mechanically good properties.[1-3] All of them have been prepared taking into account the flexibility of backbone and the length of side chain capable of complexing alkaline-metal salts. For example, the complexes of alkaline-metal salts with flexible polyacrylates,[4-11] poly(phosphazenes),[12-15] and poly(siloxane)[16] attached with oligo(oxyethylene) chains have been reported to have high conductivities of 10^{-3}-10^{-5} S/cm. On the other hand, when the rigid backbone such as polystyrene, which is desirable for electrochemical applications, was used, a high conductivity could not be achieved due to the low segmental mobility of the backbone.[17] These indicate that one criteria to attain a high ionic conductivity is a system with as low a glass transition temperature as possible.[1-3]

Chart I. Polycascade Polymer



Recently, we found that the complexes composed of poly{2-[(4′-vinyl-4-biphenylyl)oxy]penta[[(methoxyethoxy)ethoxy]ethoxy]cyclotriphosphazene}(poly(VBTEP)) (Chart I) and $LiClO_4$ have high conductivities of 10^{-4} S/cm at 60 °C, in spite of a rigid polymer backbone and demonstrated that the formation of a continuous conducting phase consisting of oxyethylene chains plays an important role for the conduction.[18] The results also suggest that the density of oxygen atoms around the backbone is one of the important factors to attain a fast ion transport. The polymer used is considered to be a "polycascade polymer", which has various features as a polymeric electrolyte host: (i) the introduction of many short oxyethylene chains into a phosphazene ring brings about a low glass transition temperature of the polymer, (ii) the density of oxygen atoms around the backbone is high even though short oxyethylene chains are used, (iii) the cooperative interaction of oxyethylene chains in neighboring monomer units is possible, (iv) the rigid and sterically large group such as benzene and phosphazene rings would be expected to yield an additional free volume around oxyethylene chains, and (v) the formation of complex with a small solvated ion radius is possible, which has been proposed by Watanabe et al.[2] All of them could contribute to an increase in conductivity. For the purpose of further de-

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velopment of polycascade polymer electrolyte host, we prepared new host polymers, poly{2-(4-vinylphenoxy)penta[oligo(oxyethylene)]cyclotriphosphazenes} (poly(SDEP) and poly(STEP)). For these polymers, it would be expected that the T_g lowers and the relative density of oxygen atoms around the backbone increases, compared to the poly(vinylbiphenyl) analogue. In this paper, the correlation between polymer characteristics and the temperature dependence of conductivity is described.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by Nihon Soda Co. *p*-Hydroxystyrene was prepared by decarboxylation of *p*-hydroxycinnamic acid.[19] $LiClO_4$ was dried under reduced pressure at 150 °C for 24 h. Methanol, THF, and benzene were dried by boiling at reflux over magnesium, $LiAlH_4$, and calcium hydride, respectively, and distilled.

Preparation of Monomer. A solution of *p*-hydroxystyrene (2.6 g, 22 mmol) and triethylamine (3.3 g, 33 mmol) in dry THF was added to a solution of $(NPCl_2)_3$ (9.0 g, 2.6 mmol) in THF at room temperature. The mixture was stirred for 5 h, and the resulting amine hydrochloride was removed by filtration. After removal of the solvent, 2-(4-vinylphenoxy)pentachlorocyclotriphosphazene (VPCP) was separated by a silica gel column (hexane, R_f = 0.36). Then, to a stirred solution of VPCP (4.0 g, 9.3 mmol) in dry THF was added a suspension of sodium (methoxyethoxy)ethoxide, prepared from diethylene glycol monomethyl ether (8.9 g, 74 mmol) and NaH (1.8 g, 74 mmol) in dry THF. The reaction mixture was stirred for 10 h at room temperature. The precipitate was filtered off, and the filtrate was concentrated by evaporation. The residue was purified on a silica gel column with ethyl acetate (R_f = 0.15) to give 2-(4-vinylphenoxy)penta[(methoxyethoxy)ethoxy]cyclotriphosphazene (SDEP) as a viscous liquid. VPCP: yield 4.5 g (48%); IR (neat) 1600, 1240–1150 cm^{-1}; ^1H NMR $CDCl_3$) δ 7.1–7.5 (m, 4 H, $-C_6H_4$), 6.9–5.1 (m, 3 H, $CH_2{=}CH-$). Anal. Calcd for $C_8H_7Cl_5N_3O_1P_3$: C, 22.28; H, 1.64; N, 9.74. Found: C, 21.78; H, 1.64; N, 9.49. SDEP: yield 3.8 g (48%); IR (neat) 1600, 1200, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (s, 4 H, $-C_6H_4-$), 6.9–5.0 (m, 3 H, $CH_2{=}CH-$), 4.3–3.3 (m, 55 H, $CH_3O(CH_2CH_2)_2-$). Anal. Calcd for $C_{33}H_{62}N_3O_{16}P_3$: C, 46.64; H, 7.35; N, 4.94. Found: C, 46.32; H, 7.10; N, 4.94.

Similarly, STEP was prepared from the reaction of VPCP with the sodium salt of triethylene glycol monomethyl ether. STEP was separated by using a silica gel column with ethyl acetate (yield 21%). STEP: IR (neat) 1600, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (s, 4 H, $-C_6H_4-$), 6.8–4.9 (m, 3 H, $CH_2{=}CH-$), 4.1–3.2 (m, 75 H, $(-OCH_2CH_2)_3OCH_3$). Anal. Calcd for $C_{43}H_{82}N_3O_{21}P_3$: C, 48.27; H, 7.72; N, 3.93. Found: C, 47.95; H, 7.58; N, 3.91.

Polymerization. A typical procedure was as follows. A solution of SDEP (3.5 g, 0.75 mol/L) and AIBN (2.4 × 10^{-2} mol/L) in ethanol was placed in a glass tube. The sample was degassed by a freeze–thaw procedure and sealed off. The polymerization was carried out in a bath maintained at 70 °C. The polymer was obtained by pouring the mixture into large amounts of hexane. The polymer was purified by pouring the polymer solution in THF into *n*-hexane. Poly(STEP) was prepared by the similar procedure.

Measurements. The measurement of ionic conductivity was carried out as follows. The polymer complexes were prepared by dissolving polymers and $LiClO_4$ in dry THF followed by casting on a Pt disk by centrifugation. The sample was dried at room temperature for 1 day under a nitrogen flow in a drybox and then under vacuum at 50 °C for 2 days (thickness, 50–100 μm). Ionic conductivity measurements were made over a frequency range of 100 Hz to 100 kHz with a Yokogawa-Hewlett-Packard 4274A LCR meter, and the conductivity was calculated from a complex impedance plot with computer curve fitting.

^1H NMR spectra were obtained from a JEOL PMX60SI spectrometer. Infrared spectra were recorded on a Shimadzu IR 420 spectrometer. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-6A instrument, equipped with Shimadzu HSG60/30, using THF as the eluent. The columns were calibrated with polystyrene standards. Glass transition temperatures were recorded on a Shimadzu DSC-50 differential scanning calorimeter at a heating rate of 10 °C/min.

Results and Discussion

Preparation of Poly(SDEP) and Poly(STEP). New host polymers, SDEP and STEP, were prepared as shown in Scheme I. The polymerizations of SDEP and STEP with AIBN initiator in ethanol at 70 °C gave highly sticky polycascade polymers with conversions of 57% (12 h) and 88% (17 h), respectively. The polymers are soluble in water and in a number of organic solvents. Spectral data and elemental analysis support poly(SDEP) and poly(STEP). The number average molecular weight of poly(SDEP), determined by GPC, was 22 000 with a polydispersity of M_w/M_n = 3.3. However, the GPC trace of poly(STEP) showed no significant peak and observed only a shift of the base line. Details of the polymerization of SDEP and STEP will be reported elsewhere.

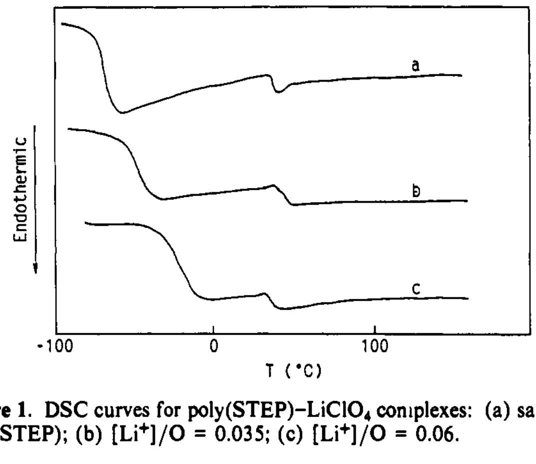
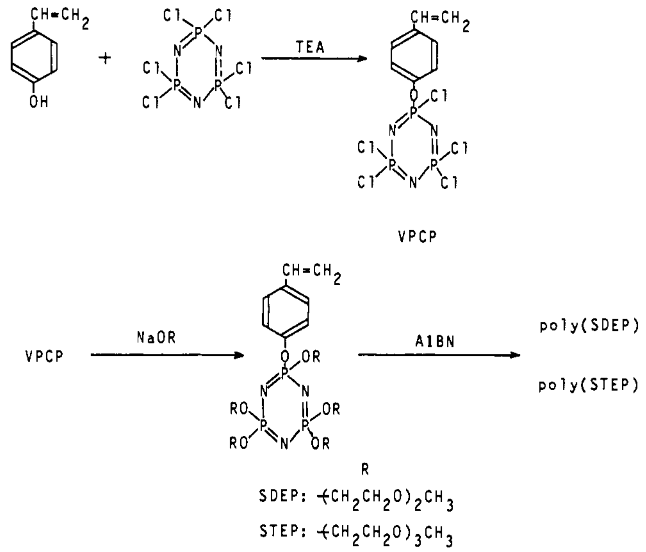


Figure 1. DSC curves for poly(STEP)–$LiClO_4$ complexes: (a) salt-free poly(STEP); (b) $[Li^+]/O$ = 0.035; (c) $[Li^+]/O$ = 0.06.

Scheme I. Preparation of Poly(SDEP) and Poly(STEP)



Thermal Properties of Poly(SDEP) and Poly(STEP). DSC measurement of poly(SDEP) and poly(STEP) showed the shifts from base lines around −62 and −67 °C, respectively. These low transition temperatures are considered to be the glass transition temperatures (T_g) of side oxyethylene chains.[21] When $LiClO_4$ was added to the polymers, the range of transition temperature was broadened as shown in Figure 1. The T_g values are lower by 5–10 °C than those of the poly(biphenyl) analogue.[18] In addition to the glass transition temperature, the weak peaks corresponding to crystallization (T_c) and melting transitions (T_m) were observed only when the polymers were cooled at −100 °C. Figure 2 shows the variation of glass transition temperatures of complexed polymers. The T_g values increased when the salt was added, but a significant change of T_c and T_m was not observed. Interestingly, the T_g values of poly(STEP)–salt complexes above $[Li^+]/O$ = 0.05 become higher than those of the complexes based on poly(SDEP).

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(21) The T_g was taken as the midpoint temperature of the base line shift observed during transition.

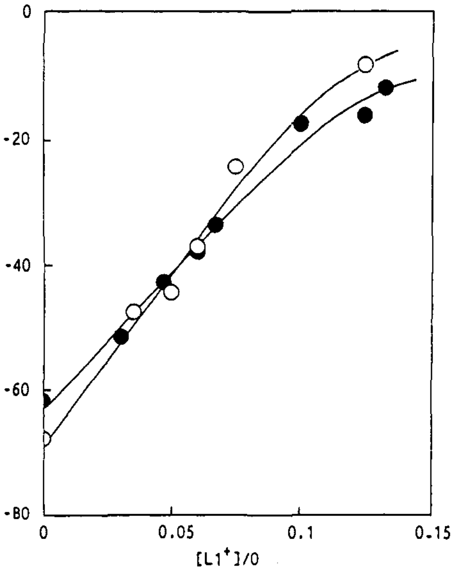
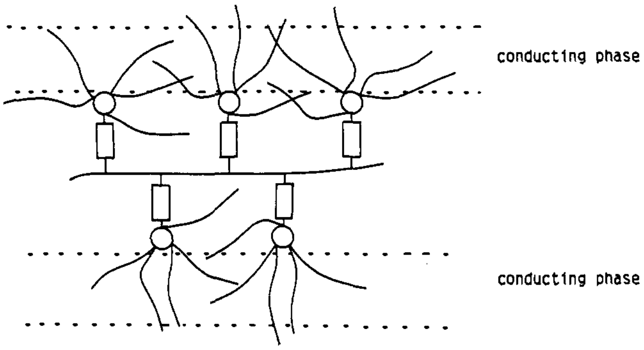


Figure 2. Variation of T_g for poly(SDEP)- (●) and poly(STEP)-LiClO$_4$ complexes (○).

Chart II. Schematic Representation of Continuous Conducting Phase[a]



[a] Key: oxystyrene, □; phosphazene ring, ○; oxyethylene chain, ~.

The increases in T_g can be attributed to the restriction of segmental motion caused by the interaction of cation with oxyethylene chains. In poly(SDEP) and poly(STEP) matrices, various complexes can be formed, e.g., the complexes formed between two oxyethylene chains on a phosphazene ring and Li$^+$ ion and three chains and Li$^+$ ion and by binding intermolecularly, etc. (Chart III). Among them it is reasonable to assume that the influence of intermolecular salt interaction, i.e., cross-linking of the chains, on T_g is larger than that of intrachain salt interaction, and the cross-linking is liable to occur for relatively long oxyethylene chains. The rapid increase in T_g for the complex of the poly(STEP) system might be attributed to the existence of the interchain salt complex with relatively high concentrations in its polymer matrix.

Ionic Conductivity. In the previous paper,[18] we demonstrated that ions can transport in the conducting phase consisting of oxyethylene chains, irrespective of the mobility of the backbone (Chart II). The formation of the conducting phase seems to be favorable for poly(SDEP) and poly(STEP), compared to the poly(vinylbiphenyl) analogue since the latter contains a sterically large biphenyl moiety. In Figure 3 is shown the temperature dependence of the ionic conductivity of poly(SDEP)- and poly(STEP)-LiClO$_4$ complexes. For all of the complexes, the plots of log σ vs $1/T$ are curved, indicating an ion transport in the amorphous phase. Such a type of ion transport has been described by the WLF equation or the VTF equation.[1-3] The VTF plots of conductivity data show good linearity when the standard temperature is taken as $T_g - 50$, as shown in Figure 4.

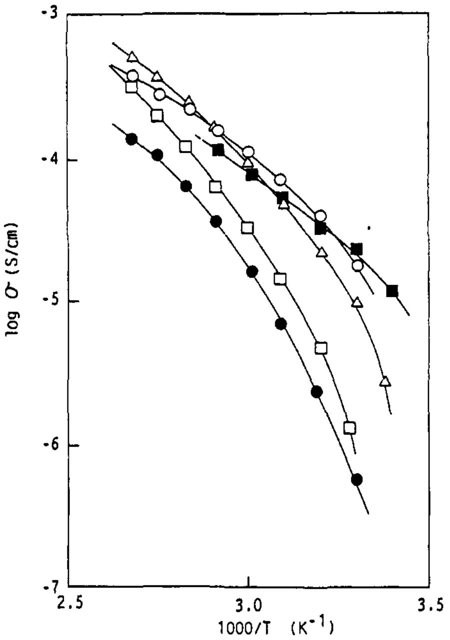


Figure 3. Temperature dependence of ionic conductivity for poly(SDEP)- (■, ●) and poly(STEP)-LiClO$_4$ complexes (○, △, □). [Li$^+$]/O = 0.03 (■), 0.10 (●), 0.050 (○), 0.075 (△), and 0.10 (□).

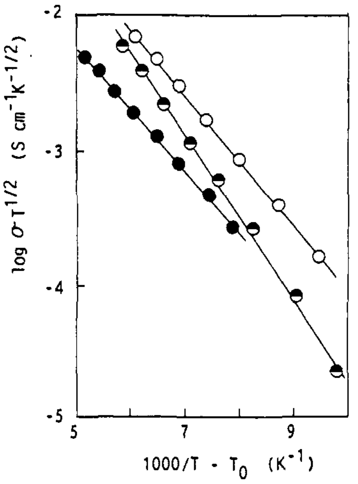


Figure 4. VTF plots of conduction data for poly(STEP)-LiClO$_4$ complexes. [Li$^+$]/O = 0.035 (●), 0.075 (◓), and 0.1 (○).

Table I. Ionic Conductivities of Poly(SDEP)- and Poly(STEP)-LiClO$_4$ Complexes

		10^5 S/cm		
polymer	[Li$^+$]/O	30 °C	60 °C	100 °C
poly(SDEP)	0.047	1.8	8.3	25.7
	0.060	0.7	5.6	34.7
	0.100	0.06	1.6	13.9
poly(STEP)	0.035	1.5	6.9	25.9
	0.050	1.8	11.1	37.8
	0.075	0.9	9.5	51.2
	0.100	0.1	3.3	30.9

The conductivities of the complexes are summarized in Table I. The conductivities of poly(STEP)-Li salt complexes are higher than those of complexes of poly(SDEP), although the former has higher T_g values than the latter above [Li$^+$]/O = 0.05. The maximum conductivities of 1.8×10^{-5} S/cm at 30 °C and 1.1×10^{-4} S/cm at 60 °C have been achieved for the poly(STEP)-Li salt complex of [Li$^+$]/O = 0.05. As expected, the conductivities are improved when poly(SDEP) is used in place of poly(VBDEP) as shown in Figure 5. Contrary to this, the poly(STEP) system has conductivities essentially similar to those of the poly(VBTEP) system. The T_g values of complexes based on poly(SDEP) are lower by 5-8 °C, ranging in concentration from [Li$^+$]/O = 0.03

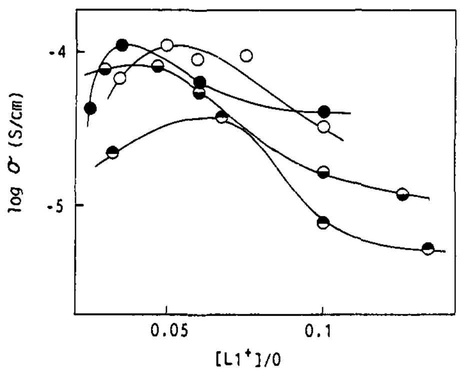


Figure 5. Comparison of conductivity of the complexes of polycascade polymers with $LiClO_4$ at 60 °C: poly(SDEP) (◒), poly(STEP) (○), poly(VBDEP) (◓), poly(VBTEP) (●).

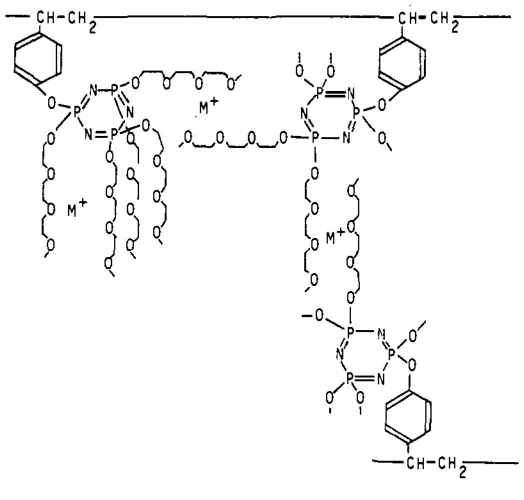
to 0.12, compared with the values of poly(VBDEP)–Li salt complexes. Similar temperature differences (5–10 °C) between the poly(SDEP) and the poly(VBTEP) systems are observed. From these results, the improvement of the conductivity observed for the poly(SDEP) system seems to be due to the relative increment of density of oxygen atoms around the backbone caused by changing from a structurally large biphenyl to a small phenyl moiety, rather than the mobility of chains. In other words, the polymers with long oxyethylene chains ($n = 3$) have almost sufficient oxygen atoms to form the conducting phase.

The maximum conductivities observed for poly(STEP)–Li salt complexes are 10^1–10^4 times higher than those of most of the complexes based on acrylates[4-11] and styrene–maleic anhydride.[17] It is interesting to compare the conductivities with those of highly flexible polyphosphazene–alkaline-metal salt complexes, which have the highest value in the comb-shaped polymer system. The conductivities are somewhat lower than those of the poly(phosphazene)–$AgSO_3CF_3$ system ($\sigma = 6.8 \times 10^{-4}$ S/cm at 55 °C) but higher than those of complexes of $LiSO_3CF_3$ ($\sigma = 7.5 \times 10^{-5}$ S/cm at 55 °C).[13] The fact that the complexes based on polystyrene have high conductivities indicates that the flexibility of the backbone is not the critical factor required to achieve high conductivities and an ion transport is mediated by the segmental motion of side oxyethylene chains without being affected by the mobility of the main chain.[18] For such an ion transport process, a complex with a small solvated ion radius can be formed and the conductivity temperature dependence would be expected to be small, as proposed by Watanabe et al.[2] In fact, the ratio of conductivity at 30 °C to one at 100 °C is 14 for the poly(SDEP)–Li salt complex of $[Li^+]/O = 0.047$. A similar small value was obtained for the poly(SDEP) system ($\sigma_{100}/\sigma_{30} = 18$, $[Li^+]/O = 0.037$). Thus, the small conductivity temperature dependence is one of the characteristics of the polycascade electrolytes.

The morphology of cast polymer is well-known to be influenced by the properties of solvent, especially for block and graft copolymers with hydrophobic and hydrophilic characters. It is likely that the morphological change of polymers affects the conductivity. In fact, Gray et al.[22,23] have demonstrated that the conductivities vary by a factor of 100 for the complexes based on styrene–butadiene–styrene. The conductivities of the poly(SDEP)–Li salt complex ($[Li^+]/O = 0.03$) casting from methanol, THF, and THF–benzene (5:1) are 1.1×10^{-4}, 7.9×10^{-5}, and 3.9×10^{-5} S/cm at 60 °C, respectively. The results suggest that the morphological change of the polymer also affects the conduction, although the direct information concerning the morphology is lacking.

Conduction Mechanism. It has been believed that the conduction occurs through an exchange of solvating ethylene oxide units at a rate governed by the segmental motion of ethylene oxide chains and the ion–dipole interactions, in addition to ion–ion interactions.[1] As described earlier, the T_g values of poly(SDEP)–Li salt complexes are lower than those of poly(STEP)–Li salt complexes ($[Li^+]/O > 0.05$), suggesting that the complex of poly(SDEP)Li system has higher local movement of side chains. If the conductivity is predominantly governed by the segmental motion of side chains, the poly(SDEP)–Li salt complex should show a high conductivity, compared with the complex of poly(STEP) (Chart III). However, this is not true. Some speculations are needed to explain the results. It has been accepted that the Li^+ ion coordinates oxygen atoms and the complex formed is related structurally to Li^+–crown ether complex. Such complexes are probably formed by two ways, intrachain and interchain salt interactions. Vögtle and Weber[24] have demonstrated that the complexing of octopus molecules having many donor atoms in the arms with alkali-metal picrates occurs faster and more completely than that of crown ethers and the complexing ability falls either by shortening of the chains or by diminution of their number. So, it is likely that the Li^+ ion coordinated with oxygen atoms in the three or more oxyethylene chains on a phosphazene ring forms a "tight complex" and moves with difficulty, whereas the complex formed by the interchain salt and the side chains on neighboring monomer units salt interactions is relatively loose and the Li^+ ion moves with ease. The polymer with long oxyethylene chains ($n = 3$) appears to facilitate the formation of loose complex since the chains can easily proximate one another. However, this interchain salt interaction brings about rapid increase in T_g. The high conductivities of poly(STEP)–Li^+ complexes with low segmental mobility might be interpreted by the structural parameter of the complex, which relates with ion–dipole interactions.

Chart III. Schematic Representation of the Complex Formation of Poly(STEP) with Li^+ Ion



Recently, it has been demonstrated that anions rather than cations contribute to the conduction on the basis of the results of transfer numbers of charged species.[1,25,26] The anions are considered to be loosely associated to the dipoles of the polymer and moved in tune with the segmental motion. The contribution of anions to the conduction becomes the more important when the complex between cations and oxygen atoms is tightly formed.[15] If the conduction occurs mainly by the migration of the anion, the poly(SDEP) system should exhibit higher conductivities than the poly(STEP) system since the former prefers to form the tight complex. However, the poly(SDEP) system has lower conductivities. This result suggests that the migration of the anion is not predominant over the conduction, although the relative contributions of the ions to the conduction will be drawn from the measurement of transport numbers of charged species.

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Thus, the conduction seems to occur at a rate governed by both the segmental mobility of side chains and the ion–dipole interactions, although ion–ion interactions will become important at higher concentrations of salt.[1,6-8]

Conclusions

The complexes of new polyelectrolytes carrying a pendant oligo(oxyethylene)cyclotriphosphazene and $LiClO_4$ have high ionic conductivities at ambient temperatures. The conductivities of the complexes are predominantly governed by the ion–dipole interactions and the segmental mobility of side chains without receiving any restriction of the mobility of backbone. In addition, it is suggested that the morphology of host polymer also influences conductivity. The effectiveness of the mobility of the backbone on the conductivity has been discussed previously.[1] This paper, however, offers the evidence that other structural factors rather than the mobility of the main chain is a key for a successful polymeric solid-state ionic conductor. The polycascade electrolyte has many advantages, i.e., a fast ion transport, a small conductivity temperature dependence, and a electrochemically stable polystyrene backbone, and is a good candidate for practical devices. Further study based on the concept described above is now in progress.

Acknowledgment. We thank Nihon Soda Co. for a generous gift of hexachlorocyclotriphosphazene.

Synthetic Studies in the Lysocellin Family of Polyether Antibiotics. The Total Synthesis of Ferensimycin B

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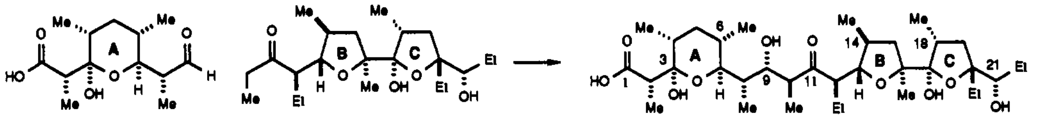
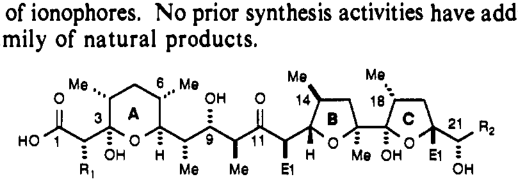
Abstract: A convergent asymmetric synthesis of the polyether antibiotic ferensimycin B has been completed. Chiral enolate bond constructions were employed to establish seven of the 16 stereocenters of the subunits **35** and **52**, which comprise the C_1–C_9 and C_{10}–C_{23} portions of ferensimycin B. The stereogenic centers at C_3, C_4, C_9, C_{10}, C_{16}, C_{17}, and C_{18} were incorporated through internal asymmetric induction, while those at C_{20} and C_{21} were established by using asymmetric epoxidation methodology. In this transformation, a vanadium-catalyzed internal epoxidation of a bis-homoallylic alcohol was employed to relay chirality from the C_{13} to the C_{16} oxygen-bearing stereocenter. A final aldol addition reaction on intermediates devoid of protecting groups united the fragments **52** and **35** to provide synthetic ferensimycin B, whose absolute configuration was found to be the same as that of the closely related ionophore lysocellin. This synthesis thus establishes the absolute configuration of ferensimycin B.



52 **35**

Ferensimycin B

Recent studies from this laboratory have described asymmetric syntheses of some of the principal representatives of the ionophore class of polyether antibiotics.[3] The present investigation describes the synthesis of ferensimycin B (**1a**), a member of the lysocellin family of ionophores. No prior synthesis activities have addressed this family of natural products.



Ferensimycin B **1a**: R_1 = Me; R_2 = Et
Ferensimycin A **1b**: R_1 = Me; R_2 = Me
Lysocellin **1c**: R_1 = H; R_2 = Et

In the construction of complex organic molecules, the synthesis plan frequently evolves from advances made in the synthesis of related structures that share some common architectural element. In this regard, ferensimycin shares common structural features with both lonomycin C (**2b**),[4] a target of current interest, and X-206 (**3b**),[5] a molecule whose synthesis has recently been realized.[3b] To illustrate this point, the insight gained in the construction of the γ- and δ-lactols found in X-206[3b] has proven to be instrumental in the design of the present ferensimycin synthesis. Similarly, in our ongoing efforts to develop a synthesis of lonomycin C,[6] the experience gained in the construction of the sensitive ring A, the carboxyl terminus, and, in particular, the potentially labile stereogenic center at C_2 of ferensimycin has proven to be invaluable in the ongoing development of a route to this latter

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