3464 *Macromolecules* 1991, *24*, 3464-3465

Ionic Conductivity of Polymer Complexes Formed by Polystyrene Derivatives with a Pendant Oligo(oxyethylene)cyclotriphosphazene and $LiClO_4$

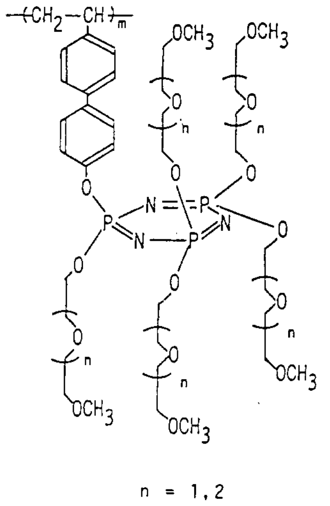
Much attention has been paid to polymeric solid electrolytes in view of the scientific interest and applications in solid-state batteries.[1] In particular, poly(ethylene oxides) and polymers with oxyethylene chains as a pendant group have been widely investigated. For comblike polymers, it has been pointed out that the flexibility of the polymer backbone, judged by the glass transition temperature, is especially important. The polymer most widely investigated in comblike polymers is the acrylic one with a pendant oligo(oxyethylene) chain.[2-8] Recently, the polymers with more flexible backbones, such as polyphosphazene and polysiloxane, which have short polyether chains as pendant side groups, also have been reported.[9-11] For electrochemical applications, the polystyrene backbone would be more desirable than the polyacrylate one. However, the fast alkali ion conductivity in polystyrene derivative–salt complexes has not been achieved due to the low mobility of the backbone.[12]

In a previous paper,[13] we reported the polymerization of multiarmed monomers, 2-[(4′-vinyl-4-biphenylyl)oxy]-2,4,4,6,6-pentakis[(methoxyethoxy)ethoxy]cyclotriphosphazene (PDEP) and -pentakis[[(methoxyethoxy)ethoxy]ethoxy]cyclotriphosphazene (PTEP), and the binding of organic salt by these polymers. The salt-solubilizing property of poly(PDEP) and poly(PTEP) attracted our attention as potential hosts for the formation of polymeric solid electrolytes. If the oxyethylene chains form a continuous conducting phase around the rigid backbone, carrier ions could move in the phase, irrespective of the rigidity of the backbone, and a high conductivity would be expected. In this paper, we report the ionic conductivity of the complexes between $LiClO_4$ and new host polymers, poly(PDEP) and poly(PTEP).

Poly(PDEP) and poly(PTEP) were prepared as described in the previous paper.[13] The number-average molecular weights of poly(PDEP) and poly(PTEP) are 32 000 and 20 000, respectively. 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, 20–40 μm). Ionic conductivity measurements (ac) were made over a frequency range of 100 Hz to 100 kHz, and the conductivity was calculated from a complex impedance plot with computer curve fitting.

DSC scans of poly(PDEP) and poly(PTEP) showed shifts from the base lines around −62 and −65 °C, respectively. Since the reorientational freedom of the polymer backbone is restricted by the steric hindrance of the biphenyl moiety, these low values are assumed to be for the glass transition of oxyethylene side chains, T_g. In addition to the glass transition, crystallization (T_c) and melting (T_m) transitions were observed only when the polymers were cooled to about −60 °C; T_c = 28 °C and T_m = 32 °C for poly(PDEP) and T_c = 36 °C and T_m = 41 °C for poly(PTEP). The presence of $LiClO_4$ influenced T_g, but no significant changes of the crystallization and the melting temperatures were observed. The T_g values of poly(PTEP) increase with an increase in the concentration of the lithium salt; T_g = −53 °C ($[Li^+]/O$ = 0.025), −48 (0.035), −42 (0.06), and −38 (0.075). Similar behavior in T_g was observed for poly(PDEP)–Li salt complexes. The increase in T_g values can be attributed to the restriction of segmental motion caused by the polymer–salt interaction.

Chart I



The temperature dependence of the ionic conductivity for polymer–lithium salt complexes was determined over the range 30–100 °C.[14] As shown in Figure 1, plots of log σ vs $1/T$ for poly(PDEP)- and poly(PTEP)–$LiClO_4$ complexes are curved, indicating a typical ion transport in amorphous polymers. The conductivity is affected by the length of oxyethylene chain. For example, the poly(PDEP)–Li salt complex of $[Li^+]/O$ = 0.033 has $\sigma = 7.6 \times 10^{-6}$ S cm^{-1} at 40 °C and 6.5×10^{-5} S cm^{-1} at 90 °C, and for the poly(PTEP)–Li salt complex, high values of $\sigma = 3.6 \times 10^{-5}$ at 40 °C and 2.9×10^{-4} S cm^{-1} at 90 °C were obtained at the salt concentration of $[Li^+]/O$ = 0.035. As shown in Figure 2, the conductivity is also affected by the salt concentration and the maximum conductivity of 1.1×10^{-4} S cm^{-1} at 60 °C has been achieved for the poly(PTEP)–$LiClO_4$ complex of $[Li^+]/O$ = 0.035. For poly(PDEP)–Li salt complexes, the maximum value of $\sigma = 1.2 \times 10^{-4}$ S cm^{-1} is reached at 90 °C ($[Li^+]/O$ = 0.067). As the temperature increases, the maximum conductivity shifts to higher salt concentrations. Qualitatively, the maximum in the conductivity and the changes in this maximum may be explained as follows; as the salt is added, the number of carriers increases but this is offset by the decrease of segmental motion, shown by the increase in T_g value. As the temperature increases, the chain mobility becomes high and consequently the maximum moves to a higher concentration of salt.

The conductivities observed for poly(PTEP)–Li salt complexes are 10^4 times higher than those of the comblike polymer based on styrene–maleic anhydride.[12] Furthermore, the values are comparable to or 1–2 orders of magnitude better than those of the complexes of flexible polyacrylates having one or two oxyethylene chains per monomer units.[2-8] It is interesting that such conductivities are compared to those of highly flexible polyphosphazene–alkaline metal salt complexes which have the highest value in comblike polymer systems. The conductivities observed are somewhat lower than those of the polyphosphazene–$AgSO_3CF_3$ system ($\sigma = 6.8 \times 10^{-4}$ S cm^{-1} at 55 °C) but higher than those of complexes of $LiSO_3CF_3$ ($\sigma = 7.5 \times 10^{-5}$ S cm^{-1} at 55 °C).[9b] These indicate that the flexibility of the backbone is not necessarily the important factor to achieve a high conductivity, if many short and flexible oxyethylene chains are introduced into the backbone. Although further information is needed to clarify the

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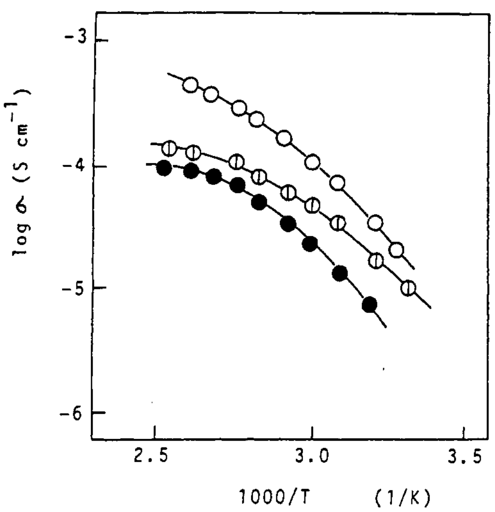

Figure 1. Temperature dependence of the ionic conductivity of poly(PDEP)-$LiClO_4$ (●) and poly(PTEP)-$LiClO_4$ (○, ⦶) complexes. $[Li^+]/O$ = (⦶) 0.025, (○) 0.035, (●) 0.067.

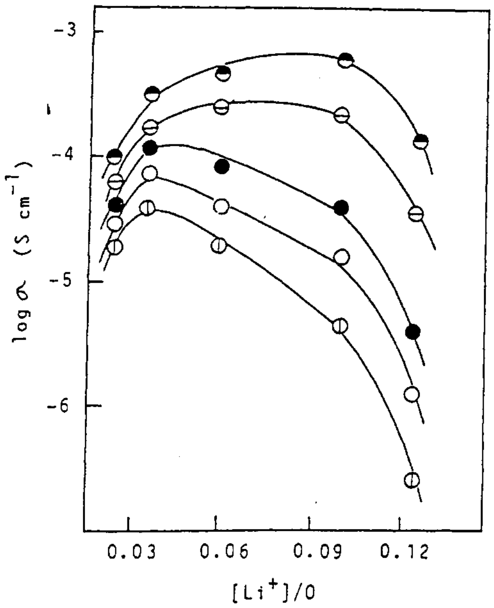

Figure 2. Variation of log σ with salt concentration for poly(PTEP)-$LiClO_4$ complexes, measured at 40 °C (⦶), 50 °C (○), 60 °C (●), 80 °C (⊖), and 100 °C (◓).

relationship between the polymer structure and the conductivity, the high conductivities of the complexes suggest that a number of oxyethylene chains form a conducting phase around rigid backbone and carrier ion transports in this phase almost without affecting the segmental motion of the backbone.

Poly(PDEP) and poly(PTEP) form amorphous complexes with $LiClO_4$, which exhibit good ionic conductivity at ambient temperatures. In addition, the complexes are soluble and can be cast, suggesting that they are viable alternatives for low-temperature thin-film battery applications. A detailed study is under way and will be reported in the near future.

Acknowledgment. We thank the Nihon Soda Co. for generous gifts of hexachlorocyclotriphosphazene. This work was partially supported by the Nagase Science and Technology Foundation.

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(14) When the DSC measurement of the polymer complexes with Li salt was carried out in the temperature range 0–120 °C, exothermic and endothermic peaks corresponding to T_c and T_m were not observed.

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Received January 2, 1991
Revised Manuscript Received March 21, 1991

Registry No. PDEP (homopolymer), 125357-31-5; PTEP (homopolymer), 125330-30-5; lithium perchlorate, 7791-03-9.