

STRUCTURE-CONDUCTIVITY RELATIONSHIP IN POLYMER ELECTROLYTES FORMED BY NETWORK POLYMERS FROM POLY[DIMETHYLSILOXANE-g-POLY(ETHYLENE OXIDE)] AND LITHIUM PERCHLORATE

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Summary

The combination of LiClO_4 and network polymers from poly[dimethylsiloxane-g-poly(ethylene oxide)] has been applied to polymer electrolytes as an Li^+ ion conductor, and the structure/conductivity relationship has been investigated. The ionic conductivity is about $10^{-6} \text{ S cm}^{-1}$ at room temperature. The polymer electrolytes form a micro-heterogeneous structure from the constituent segments, and the incorporated LiClO_4 preferentially interacts with the poly(ethylene oxide) segments. The segmental motion of poly(ethylene oxide) appears to contribute to the ionic migration, while that of poly(dimethylsiloxane) does not. Not all of the incorporated LiClO_4 functions as carrier ions.

Introduction

Considerable interest has been focused on the high ionic conductivity of certain kinds of solvent-free, ion-containing polymers (*i.e.*, polymer electrolytes), particularly in terms of understanding the fundamental aspects of fast ion-transport in the substances and in their potential application as solid electrolytes. Polymer electrolytes are solid solutions in which polymers behave like solvents toward salts, and can conduct Li^+ ions when lithium salts are used. Since the Li^+ ion conductive polymer electrolytes are chemically stable, have a wide potential window [1, 2], and exhibit good compatibility with both the negative electrode (lithium) and the positive electrode (*e.g.*, V_6O_{13} , TiS_2) [3, 4], it is expected that polymer electrolytes will find use in rechargeable lithium batteries.

The ionic conductivity of a polymer electrolyte is determined by the product of the density and the mobility of the carrier ion. Thus, a high ionic conductivity is obtained in systems where both these factors have high values. It has been shown [5 - 15] that the structures of polymers greatly affect the ionic conductivity of their electrolytes. This indicates that both carrier gen-

eration and migration processes are influenced by the polymer structure. It has been proposed [11, 12] that the co-operative interaction of neighbouring polar groups with an ion is essential for the generation of carriers. As for carrier migration, a co-operative motion between carrier ions and polymer segments has been identified [9, 13, 14, 16]. Glass transition temperatures (T_g) of polymers are a measure of the rate of segmental mobility at a given temperature above T_g . Thus, reduction in T_g of polymer electrolytes is expected to lead to high ionic mobility, resulting in high ionic conductivity.

From this point of view, polymers containing siloxane units have been synthesized and the ionic conductivity of resulting polymer electrolytes has been investigated [8, 17, 18]. In this study, poly[dimethylsiloxane-g-poly(ethylene oxide)] has been used and the structure/conductivity relationship has been investigated. Similar types of polymer electrolytes have been examined recently by other authors [17, 18]. The work reported here discusses further aspects of this type of electrolyte.

Experimental

Poly[dimethylsiloxane-g-poly(ethylene oxide)], which was prepared by the hydrosilylation reaction of poly(ethylene glycol mono allyl ether) with poly(dimethylsiloxane-co-methylhydrosiloxane), was supplied by the Toshiba Silicone Co. The average molecular weight was 6×10^3 . The absence of hydrosilyl and allyl groups was confirmed by infrared spectra. Prior to use, the comb-type pre-polymer was dried under reduced pressure for 7 h at 43 °C. Hydroxyl groups of the pre-polymer were allowed to react with a given amount of freshly distilled 4-methyl-1,3-phenylene diisocyanate under dry nitrogen atmosphere at room temperature for 72 h to give the network polymers (1 - 4), as given in Fig. 1. Unreacted precursors were extracted from the networks by repeated treatment with distilled acetone. LiClO_4 was dissolved in the networks by immersion in acetone solutions of LiClO_4 , followed by complete evaporation of the solvent, as described elsewhere [7]. The polymer electrolytes were transparent elastomers, and had completely amorphous structures.

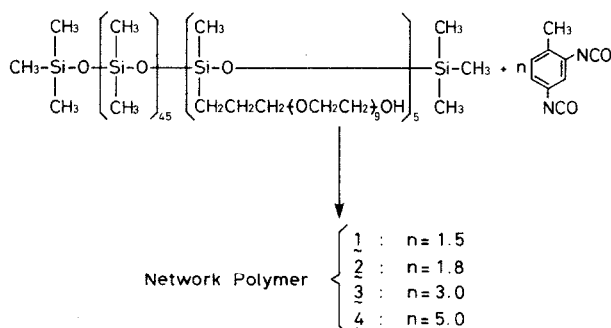


Fig. 1. Preparation of network polymers from poly[dimethylsiloxane-g-poly(ethylene oxide)].

The ionic conductivity of the polymer electrolytes was measured by the complex impedance method using platinum electrodes [5]. Differential scanning calorimetry (DSC) was conducted at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. The glass transition zone was determined as the temperature range between the two intersecting points of the base lines with the extrapolated sloping portion of the thermograms, which resulted from a heat capacity change. T_g was defined as the mid-point of the heat capacity change.

Results and discussion

Figure 2 shows the temperature dependence of the ionic conductivity of the polymer electrolytes (1 - 4) at an LiClO_4 concentration of 5 wt.%. The data showed the Williams-Landel-Ferry (WLF) type profile, as expected by virtue of the amorphous structure of the polymers. The ionic conductivity

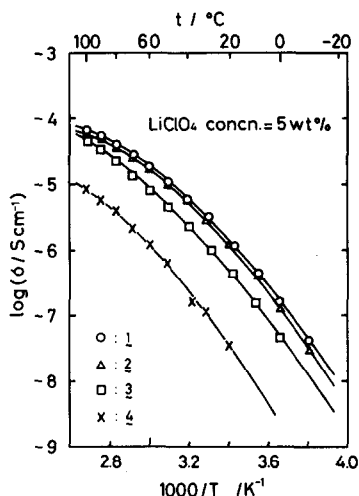


Fig. 2. Temperature dependence of ionic conductivity of polymer electrolytes (1 - 4).

decreased with increase in the cross-linking density. The room-temperature conductivities of the polymer electrolytes (1 - 3) were about 10^{-6} S cm^{-1} . The ionic conductivity of the poly(ethylene oxide) (PEO) networks with dissolved LiClO_4 reached 10^{-5} S cm^{-1} at $30\text{ }^{\circ}\text{C}$ [12, 15]. In spite of the introduction of highly flexible dimethylsiloxane units, these conductivity values are relatively low.

Figure 3 gives DSC traces of the polymer electrolytes (2) at various LiClO_4 concentrations. Each trace exhibits two base-line shifts; the shifts occurring at high- and low-temperatures are defined here as T_{g1} and T_{g2} , respectively. Figure 4 shows the changes in both T_{g1} and T_{g2} with LiClO_4 concentration; the glass transition zones are indicated by the bars. It can be seen that T_{g1} increases from -69 to $-31\text{ }^{\circ}\text{C}$ with increase in LiClO_4 concen-

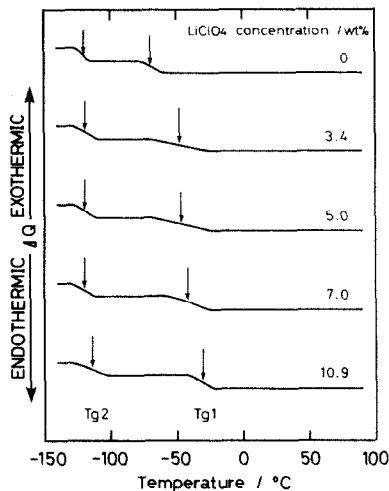


Fig. 3. DSC traces of polymer electrolytes (2) at various LiClO_4 concentrations.

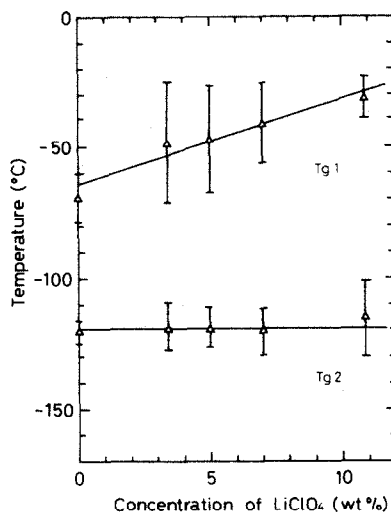


Fig. 4. Changes in T_{g1} and T_{g2} with LiClO_4 concentration for polymer electrolytes (2).

tration from 0 to 10.9 wt.%, whereas T_{g2} remained unchanged at -120°C . The PEO and poly(dimethylsiloxane) (PDMS) homopolymers have T_g values of -66 and -123°C , respectively. Thus, we have assigned T_{g1} and T_{g2} to the T_g of the PEO and PDMS segments in the polymer electrolytes, respectively. The appearance of each T_g of the constituent segments is caused by the micro-heterogeneous structure of the PEO and PDMS segments in the polymer electrolytes. Selective increase in T_{g1} with the LiClO_4 concentration implies that the incorporated LiClO_4 preferentially interacts with the PEO segments. It has been reported that the T_g of the PEO- LiClO_4 electrolytes increases with the salt concentration [12, 15].

The micro-heterogeneous structure and the preferential interaction of LiClO_4 with PEO segments were also confirmed by the fitting of the conductivity data to the following WLF type equation:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

Reasonable C_1 and C_2 values were obtained when T_{g1} , but not T_{g2} , was substituted for T_g in the equation, as shown in Table 1. The temperature dependence of the ionic conductivity could be reproduced exactly by the WLF equation with the parameters given in Table 1. This fact indicates that the incorporated LiClO_4 interacts with the PEO segments and its segmental motion mediates the ionic migration in the polymer electrolytes. The somewhat lower conductivity of the present polymer electrolytes, compared with the PEO- LiClO_4 electrolytes [12, 15], may be due to the fact that the high segmental mobility of the PDMS segments does not contribute to the ionic migration because of the micro-heterogeneous structure.

TABLE 1
WLF parameters for ionic conductivity

Electrolyte	LiClO ₄ concentration (wt.%)	T _g (°C)	C ₁	C ₂ (°C)	σ(T _g) (S cm ⁻¹)
1	4.7	-49	10.9	43.1	2.9 × 10 ⁻¹³
2	3.4	-48	13.6	24.6	1.3 × 10 ⁻¹⁶
2	5.0	-47	10.3	49.1	1.3 × 10 ⁻¹²
2	7.0	-42	10.0	46.9	2.2 × 10 ⁻¹²
2	10.9	-31	9.7	65.8	2.8 × 10 ⁻¹¹
3	5.0	-28	8.4	76.8	2.7 × 10 ⁻¹⁰
4	5.1	-20	9.3	62.3	7.2 × 10 ⁻¹²

Ion dissociation in the polymer electrolytes was investigated in the iso-free-volume states. Since the temperature dependence of ionic conductivity obeyed the WLF equation, it was assumed that the ionic mobility changed with temperature according to the free-volume mechanism [19]. This mechanism proposes a near equality of mobility in the iso-free-volume states. Figure 5 shows the ionic conductivity as a function of the LiClO₄ concentration in the electrolytes (2) at various $T - T_g$, that is, at various iso-free-volume states. The slope of the dotted line in the Figure represents the conductivity increase expected for the complete dissociation of the incorporated LiClO₄. The slopes of the conductivity increases were smaller than that of the dotted line. This indicates that all of the incorporated LiClO₄ does not function as carrier ions. It appears that ion pairing occurs with increasing LiClO₄ concentration.

Figure 6 presents data obtained from electrolytic experiments for an electrolyte (2) containing 5.0 wt.% LiClO₄ under an applied potential of

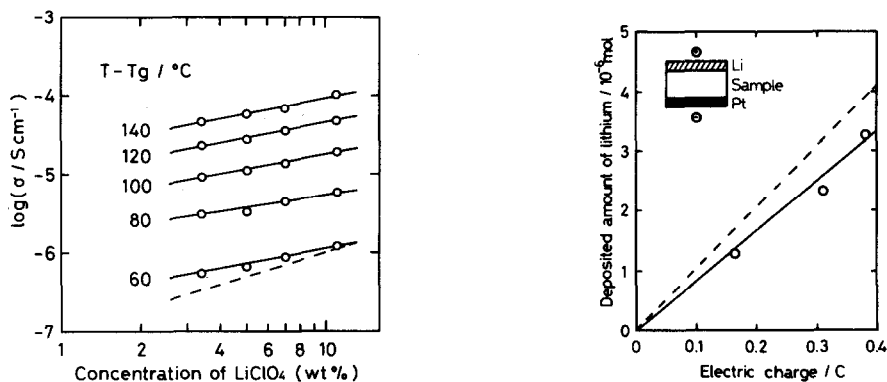


Fig. 5. Ionic conductivity as a function of LiClO₄ concentration for polymer electrolytes (2) at various reduced temperatures ($T - T_g$).

Fig. 6. Relation between amount of lithium deposited on a platinum cathode and electric charge through cells.

3.0 V. The cells shown in the Figure were electrolyzed for a given period, and the platinum cathodes were peeled off and then immersed in 0.1 M HCl solutions. The deposited amount of lithium was measured by analyzing these solutions with a flame emission spectrophotometer. The dotted line in Fig. 6 represents the calculated amount of lithium according to Faraday's law. The data show that the amount of the deposited lithium increases with the amount of electric charge through the cells. Thus, it can be concluded that the present polymer electrolyte is indeed an Li^+ ion conductor.

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