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Ionic conductivity of electrolytes formed from PEO–$LiCF_3SO_3$ complex with low molecular weight poly(ethylene glycol)

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Films of poly(ethylene oxide)–$LiCF_3SO_3$-based complexes containing different amounts of poly(ethylene glycol) (PEG) with molecular weights ranging from 400 to 2000 were prepared by solution casting. The ionic conductivity is presented as a function of temperature, molecular weight and the PEG content used. The conductivity increases with decreasing molecular weight of PEG and with increasing PEG content. The incorporation of PEG with a molecular weight of 600 or less gives rise to a maximum conductivity value of $3 \times 10^{-3}\,S\,m^{-1}$ at 25° C. The conductivity enhancement at room temperature can be attributed to the increase in the amorphous regions responsible for the ionic conduction.

1. Introduction

Polymer electrolytes based on alkali metal salt complexes of polyethers, such as poly(ethylene oxide) (PEO), exhibit conducting properties that have recently received a great deal of attention due to their potential application in solid-state batteries [1–4]. The intense interest in these materials has also arisen because of their advantageous mechanical properties, ease of fabrications as thin films, and good contact with electrode materials.

In particular, a number of PEO–lithium salt complexes have been shown to have ionic conductivities suitable for electrolyte use at temperatures around 100° C [5, 6]. However, at temperatures below 60° C, the conductivity is too poor to be acceptable for room-temperature devices. Several researchers have suggested methods for improving the conductivity of polymer electrolytes at low temperatures. We have previously demonstrated that thin films prepared by evaporating a suitable mixture of PEO and $LiCF_3SO_3$ or LiI exhibit a considerably high ionic conductivity of about $10^{-2}\,S\,m^{-1}$ at 25° C [7–9]. Recently, Kelly *et al.* [10] have shown that the room-temperature conductivity of a PEO–$LiCF_3SO_3$ system can be greatly increased through the addition of dimethoxy poly(ethylene glycol). The enhancement of conductivity in each material can probably be attributed to the presence of structural regions low in molecular weight.

In the present work, samples of PEO–$LiCF_3SO_3$ complexes with different amounts of PEG at differing low molecular weights were prepared by conventional solution casting. The ionic conductivity was studied as a function of temperature, the molecular weight of the PEG used and the amount of PEG. In addition, differential scanning calorimetry (DSC) work was carried out.

2. Experimental procedure

PEO with an average molecular weight of 600 000, obtained from Seitetsu Kagaku Ltd (Higashi-ku, Osaka, Japan) was used to prepare the polymer films. The lithium salt used for all the preparations was $LiCF_3SO_3$ (ICN Biomedicals Inc, Plainview, New York). The five kinds of PEG used, i.e. with molecular weights of 2000, 1500, 1000, 600 or 400 were supplied by Kanto Chemical Inc. (Chuo-ku, Tokyo, Japan).

The films were prepared using a solution-casting technique similar to that described by Weston and Steele [11]. The required amounts of PEO, PEG and $LiCF_3SO_3$ were weighed and dissolved in anhydrous acetonitrile (Kanto Chemical Inc.) to provide a 4 wt % solution. The sample compositions prepared were $[(1-x)\mathrm{PEO}\text{–}x\mathrm{PEG}(M)]\text{–}LiCF_3SO_3$, where $x = 0$ to 0.75 and M refers to molecular weight. The $LiCF_3SO_3$ concentration was fixed at 10 mol %, corresponding to a mole ratio of 9 : 1 for the polymer repeat unit and salt. After a homogeneous solution was obtained by stirring for 24 h at room temperature, it was cast on to a silica glass substrate. The residual solvent was allowed to slowly evaporate in a steady-flow nitrogen atmosphere for 12 h. It was then completely eliminated by heating under high vacuum ($\sim 10^{-4}$ Pa) for 24 h at 150° C.

Thermal analysis of the polymer films was carried out using a Rigaku DSC 8240 differential scanning calorimeter on the 1 mcal sec^{-1} scale with a heating rate of 5° C min^{-1}. The samples were typically 1 to 2 mg and were put in an aluminium pan in a steady-flow nitrogen atmosphere. Indium metal was used as the standard to calibrate the DSC temperature scale.

Sample conductivities parallel to the film surfaces were measured with interdigital gold blocking electrodes. These electrodes were fabricated on the sample surfaces using the same procedures described previously [12]. A.c. conductivity measurements were then performed using a Hewlett–Packard 4192A impedance analyser over the frequency range 5 Hz to

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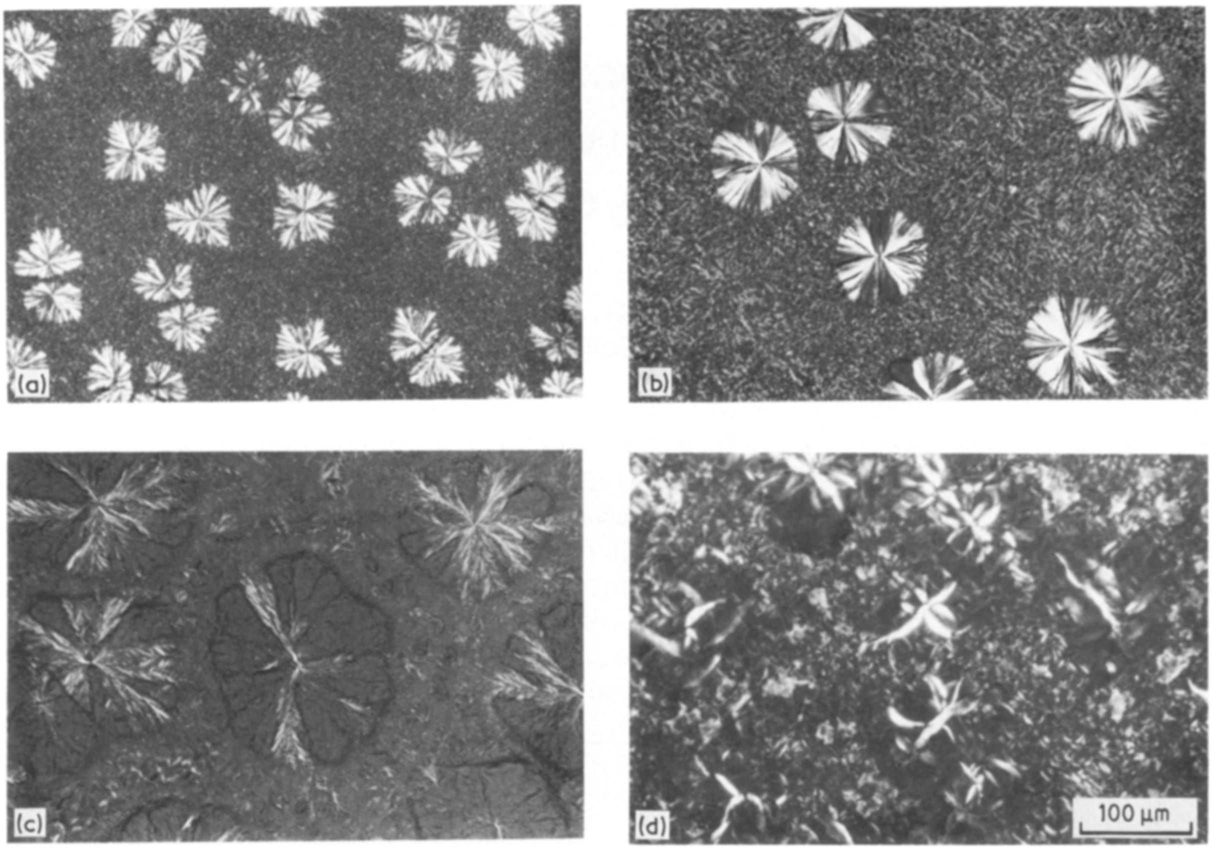

Figure 1 Typical micrographs of $[(1 - x)\mathrm{PEO}{-}x\mathrm{PEG}(600)]{-}\mathrm{LiCF_3SO_3}$ films with various values of x, as viewed between crossed polarizers. (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$ and (d) $x = 0.75$.

13 MHz. The measurements were made under steady-flow argon atmospheric conditions over a temperature range of −10 to 100° C.

3. Results and discussion

3.1. Structure

The electrolyte samples were prepared to be $\sim 5\,\mu\mathrm{m}$ thick using the technique mentioned above. All the thin films obtained were colourless and transparent and could be easily peeled off the casting substrates. Typical micrographs of films with various x values for PEG are shown in Fig. 1, as viewed between crossed polarizers. In all these films, spherulites were found to be present. Recently, it has been reported that PEO–$\mathrm{LiCF_3SO_3}$ films are spherulitic and contain more than one type of spherulite at room temperature [13]. An X-ray diffraction study of the present samples indicated the existence of a PEO crystalline phase and a crystalline complex salt phase. This suggested that there were two types of spherulites in the samples. As PEG content was increased, the spherulites decreased in number, while each spherulite increased in size. For the sample with $x = 0.75$, the crystalline form could not be clearly observed. In any event, the samples discussed here contained both crystalline and amorphous regions at room temperature.

Typical DSC traces of $[(1 - x)\mathrm{PEO}{-}x\mathrm{PEG}(600)]{-}\mathrm{LiCF_3SO_3}$ films with various x values are shown in Fig. 2. These traces were obtained when the films were initially heated at $5^\circ\mathrm{C\,min^{-1}}$. The DSC results are summarized in Table I. The melting temperature, T_m, here refers to the peak temperature of the main endothermic peak. The DSC trace for a PEO–$\mathrm{LiCF_3SO_3}$ film with no PEG shows endothermic peaks close to those found by other researchers [14–17] for a complex with the same composition. There were two endothermic peaks observed on heating. The main endothermic peak at 62.5° C corresponds to the melting of pure PEO crystalline phase. On the other hand, the diffuse high-temperature endothermic peak at about 140° C corresponds to the gradual dissolution of the fully complexed materials.

When PEG was incorporated, the DSC traces exhibited behaviour similar to that of the film with no PEG. However, increasing the x value to 0.50 caused the PEO melting peak temperature to decrease to 41.4° C. The high-temperature endothermic peak had a tendency to shift towards lower temperatures and to become more diffuse with increasing x. In the case of the sample with $x = 0.75$, the main endothermic peak and a sub-peak occurred at 46.8 and −6.2° C, respectively. The sub-peak at the lower temperature was probably caused by the melting of nearly pure PEG with a molecular weight of 600. In this sample, the

TABLE I Summary of DSC results for $[(1 - x)\mathrm{PEO}{-}x\mathrm{PEG}(600)]{-}\mathrm{LiCF_3SO_3}$ films with various x values.

x	T_m (° C)	Enthalpy ($\mathrm{cal\,g^{-1}}$)	Crystallinity (%)	T_g (° C)
0	62.5	26.3	58	−51.1
0.25	56.5	20.6	46	−57.0
0.50	41.4	13.0	29	−61.0
0.75	46.8	7.2	16	−55.0

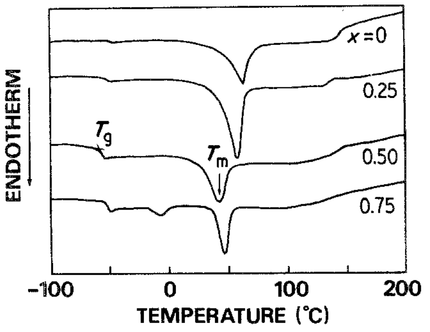

Figure 2 DSC traces for $[(1-x)\text{PEO}-x\text{PEG}(600)]-\text{LiCF}_3\text{SO}_3$ films with various values of x. Heated at $5°\text{C min}^{-1}$.

high-temperature endothermic peak was too diffuse to be clearly detected.

The melting enthalpy of the PEO phase was obtained from the endothermic-peak area using indium metal as the standard. The samples with no PEG exhibited a melting enthalpy of $26.3\,\text{cal g}^{-1}$. As PEG was increased, the melting enthalpy continuously decreased, reaching $7.2\,\text{cal g}^{-1}$ (with $x = 0.75$). The degree of crystallinity in the samples was roughly estimated by evaluating the enthalpy of the melting. Here, a value of $45\,\text{cal g}^{-1}$ was taken from the literature [18] as the melting enthalpy for 100% crystalline PEO. As a result, the crystallinity was found to go down from 58 to 16% with an increasing PEG content (see Table I).

A glass transition was also detected in the DSC trace for every sample. The glass transition temperature, T_g, of these samples decreased from -51.1 to $-61.0°$ C as the x value was increased up to 0.50. With $x = 0.75$, T_g was $-55.0°$ C.

From the above DSC analysis, it was also confirmed that these samples were composed of two crystalline phases and an amorphous phase at room temperature.

3.2. Conductivity

Conductivity measurements were carried out on these samples using ion-blocking gold electrodes and an a.c. technique over a wide frequency range. The impedance diagrams for all the samples were found to show a high-frequency well-defined semicircle and a low-frequency spike inclined at a certain angle to the real axis. Sample conductivity, σ, was calculated from the intersection of the low-frequency spike and the high-frequency semicircle.

A pronounced hysteresis in conductivity between heating and cooling was observed for all the samples. Conductivity data obtained upon cooling $[(1-x)\text{PEO}-x\text{PEG}(600)]-\text{LiCF}_3\text{SO}_3$ films with various x values are plotted as log σ against $1/T$ in Fig. 3. The LiCF_3SO_3 concentration was fixed at 10 mol %. Ionic conductivities at 25° C and activation energies for conduction in these samples are listed in Table II. In the case of a $\text{PEO}-\text{LiCF}_3\text{SO}_3$ complex with no PEG ($x = 0$), the conductivity decreased smoothly with decreasing temperature until about 48° C. There, it suddenly decreased over a narrow temperature range and then exhibited a smooth decrease again with a higher activation energy than at the higher temperatures. This abrupt decrease in conductivity coincided with the crystallization of PEO phase. Furthermore, the hysteresis phenomenon was observed in this region of melting and crystallization.

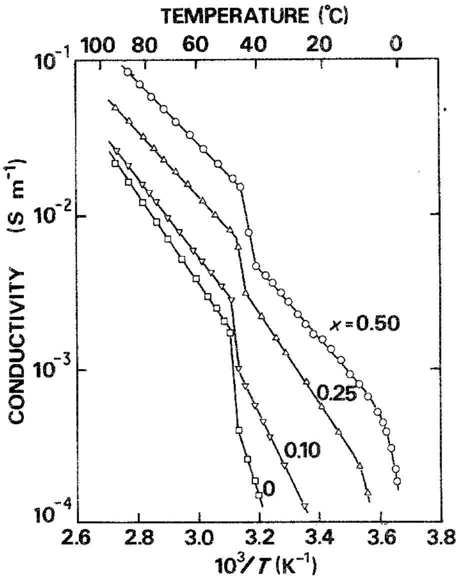

Figure 3 Dependence of conductivity on temperature in $[(1-x)\text{PEO}-x\text{PEG}(600)]-\text{LiCF}_3\text{SO}_3$ films with various values of x.

The ionic conductivity at high temperatures was considerably high, while it decreased to a very low value at low temperatures ($1.3 \times 10^{-5}\,\text{S m}^{-1}$ at 25° C). The apparent activation energy for conduction above 48° C was $55.3\,\text{kJ mol}^{-1}$, but increased to $124.7\,\text{kJ mol}^{-1}$ for temperatures below 48°C. These values are in good agreement with those obtained by Weston and Steele [11].

When PEG was incorporated, the temperature dependence for conductivity exhibited a behaviour similar to that of the film with no PEG. However, for the sample with $x = 0.25$ or 0.50, another steep decrease in conductivity was observed below about 10° C. ($x = 0.75$ is not discussed here as the results for $x = 0.50$ were virtually identical.) Overall, however, the conductivity increased across the whole temperature range with increasing PEG content. For instance, it was $1.7 \times 10^{-3}\,\text{S m}^{-1}$ at 25° C for the sample with $x = 0.50$, very much higher than in the case of $x = 0$. Increasing PEG content caused the E_1 and E_2 values for activation energies above and below the crystallization region to decrease. With $x = 0.50$, their values were 39.2 and $44.2\,\text{kJ mol}^{-1}$, respectively.

TABLE II Ionic conductivity at 25° C and activation energy for conduction in $[(1-x)\text{PEO}-x\text{PEG}(M)]-\text{LiCF}_3\text{SO}_3$ films. E_1 and E_2 are activation energies above and below the crystallization region, respectively.

PEG		Conductivity (S m^{-1}) at 25° C	Activation energy (kJ mol^{-1})	
M	x		E_1	E_2
600	0	1.3×10^{-5}	55.3	124.7
	0.10	1.6×10^{-4}	47.6	75.9
	0.25	7.8×10^{-4}	40.8	55.6
	0.50	1.7×10^{-3}	39.2	44.2
400	0.50	2.8×10^{-3}	38.9	47.9
1000	0.50	3.6×10^{-4}	40.1	170.0
1500	0.50	4.2×10^{-5}	43.2	165.2

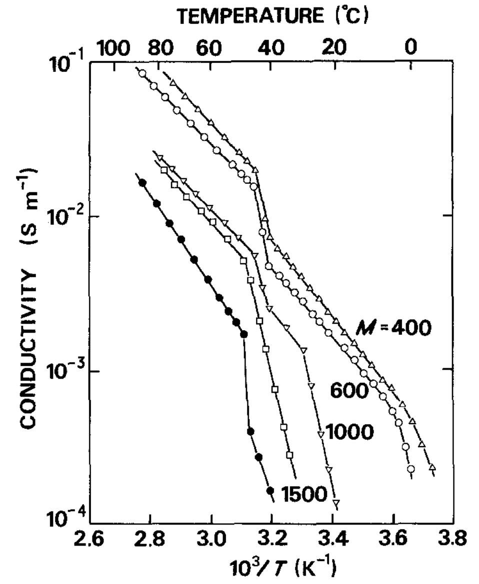

Figure 4 Dependence of conductivity on temperature in [0.50PEO–0.50PEG(M)]–$LiCF_3SO_3$ films prepared using PEG with various molecular weights.

The temperatures at which the abrupt change in conductivity occurred upon cooling changed from 48° C (with $x = 0$) to 42° C (with $x = 0.50$). These temperatures were considered to correspond to the melting and crystallization points of the PEO crystal phase. However, the change was much smaller than the melting point change (62 to 41° C) with PEG content found using the DSC when the samples were heated. This implies that the degree of supercooling was larger in the sampes with lower PEG content.

The reasons for enhanced conductivity due to the incorporation of PEG are considered as follows. It is found from the above DSC analysis that the degree of crystallinity in the sample is reduced with increasing PEG. This shows the increase in amorphous regions responsible for the ionic conduction. In addition, the incorporation of PEG causes a decrease in the glass transition temperature of the amorphous phase and thus enhances the mobility of the ions in the region.

Conductivity results obtained upon cooling for [0.50PEO–0.50PEG(M)]–$LiCF_3SO_3$ films prepared using PEG with various molecular weights are shown as a function of $1/T$ in Fig. 4. It can be seen that the conductivity increased with the decreasing molecular weight of the PEG used. Also, the activation energy for conduction at temperatures above the crystallization region decreased with decreasing M. In the case of the samples containing PEG with a molecular weight of 1000 or 1500, the activation energy at temperatures below the crystallization region exhibited values of 165 to 170 kJ mol^{-1}. The reason for this very large increase in activation energy has not been determined.

The conductivity values at 25 and 75° C for the samples with PEG of various molecular weights are plotted against x in Fig. 5. It is clear that the conductivity for these samples increased with increasing x and had a tendency to reach a certain saturation value above $x = 0.50$, no matter what molecular weight of PEG was used. When the molecular weight of PEG used was 600 or less, the conductivity showed a tendency to be almost the same.

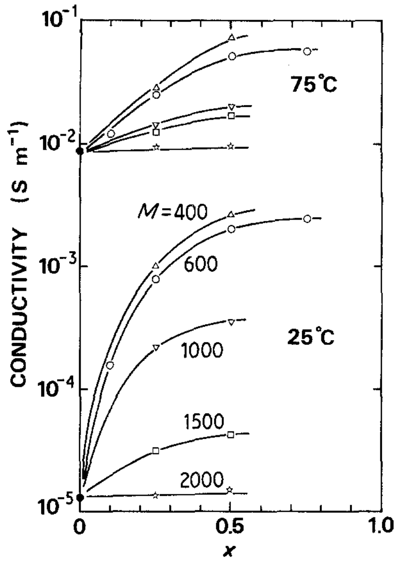

Figure 5 Values of isothermal conductivity at 25 and 75° C for [(1 − x)PEO–xPEO(M)]–$LiCF_3SO_3$ films plotted against x.

4. Conclusions

Electrolytes formed from PEO–$LiCF_3SO_3$ complexes containing different amounts of PEG at differing low molecular weights were prepared by conventional solution casting. Their ionic conductivity was studied as a function of temperature, molecular weight and the content of the PEG used. Results show that the conductivity values increase with decreasing PEG molecular weight and with increasing PEG content. This is attributed to the increase in the amorphous regions responsible for the ionic conduction. This conclusion is supported by the reduction in the degree of crystallinity with increasing PEG, which was found from the DSC analysis presented above. A maximum conductivity value of 3×10^{-3} S m^{-1} at 25° C can be obtained by the incorporation of PEG with a molecular weight of 600 or less.

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