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Conductivity and thermal studies of polymer electrolytes based on polyetheresters

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Abstract

A series of aliphatic polyetheresters of poly(ethylene glycol) and diacyl chloride containing a different number of methylene units was synthesized. The polyetheresters synthesized were complexed with lithium perchlorate to obtain a polymer electrolyte with high ionic conductivity and reduced crystallinity. The effect of polymer structure on the ionic conductivity and thermal properties of the polymer electrolytes was investigated. The ionic conductivity behavior of these samples was analyzed in terms of their thermal properties. ^{7}Li NMR spin–spin relaxation studies were also carried out in order to investigate the local environments and dynamics of ions in the polymer electrolytes.

Keywords: Ionic conductivity; Polyetherester; Polymer electrolyte; Thermal property

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1. Introduction

Polymer electrolytes have received considerable attention as solid electrolyte materials in advanced applications such as high energy-density batteries [1–3]. Much of the effort to date has focused on poly(ethylene oxide) (PEO) as the host material. These polymer electrolyte systems, however, exhibit poor ambient temperature conductivity and mechanical stability, which poses a serious threat to ambient temperature electrochemical applications. The observation of enhanced conductivity in amorphous phases prompted the synthesis of polymeric systems which incorporate the PEO segments in such a way as to inhibit the crystallization of PEO [4–12].

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In our work, we have tried to obtain polyetheresters containing a different number of methylene units in the polymer backbone for forming complexes with lithium perchlorate that have reduced crystallinity and low T_g values. The effect of polymer structure on the ionic conductivity and thermal properties of polymer electrolytes prepared with polyetheresters and lithium perchlorate has been investigated.

2. Experimental

2.1. *Materials*

Poly(ethylene glycol) (PEG)(MW: 300,1000) purchased from Aldrich was freeze-dried using freeze-pump-thaw cycles under reduced pressure (1.3×10^{-3} Pa). Benzene (HPLC grade), methanol (HPLC grade), triethylamine and diacyl chlorides were also supplied by Aldrich and used without any purification. Lithium perchlorate (Aldrich) was dried in a vacuum oven for 24 h at 120°C prior to use.

2.2. *Synthesis and characterization*

A series of polyetheresters based on PEG and diacyl chloride ($ClOC[CH_2]_nCOCl$, $n = 3$–8, 10) was synthesized in benzene with a small amount of triethylamine as catalyst, via the solution polycondensation route, as previously described [13]. The triethylamine salt (TEA·HCl) was then filtered off, and the product was obtained by freeze-drying the filtrate under reduced pressure. DSC thermal analysis was carried out to measure the T_g, T_{fus} and $\Delta_{fus}H$ values with a heating rate of 20°C min^{-1} in a temperature range from -100 to 100°C, using the DuPont 2000 Thermal Analyzer equipped with a 910 Differential Scanning Calorimeter. Samples were loaded in hermetically sealed aluminum pans and measurements were always taken under dry nitrogen atmosphere during the thermal scans. The recorded T_g was taken as the inflection point and T_{fus} was given as the peak of the melting endotherm. The crystallinity was estimated from the ratio of the experimentally determined $\Delta_{fus}H$ to the value of 203 J g^{-1} reported in the literature for the enthalpy of melting of 100% crystalline PEO [14]. The ^7Li NMR experiments were performed on a Bruker MSL-200 NMR spectrometer with a magnetic field of 4.7 T. The spin–spin relaxation time (T_2) was determined using the spin–echo technique by applying $90°$-τ-$90°$ pulse sequences and observing an echo at time 2τ. In this paper, the polyetheresters synthesized will be designated as PES(m, n), where m indicates the number of EO units, and n the number of methylenes in the repeating unit. For example, the chemical structure of PES(6,8) is given as $[-(OCH_2CH_2)_6OOC(CH_2)_8CO-]_p$.

2.3. *Conductivity measurements*

Appropriate amounts of polymer and $LiClO_4$ were dissolved in anhydrous methanol. The resulting solution was stirred and cast on a Teflon plate, then the solvent was left to evaporate slowly at room temperature. The sample formed was again dried in a vacuum oven at 60°C for 24 h in order to remove completely any trace of solvent present. These samples were sandwiched between the two stainless steel electrodes. The ionic conductivity of the polymer electrolyte was then measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range from 10 Hz to 10 MHz. Each sample was allowed to equilibrate for 1 h at any temperature before measurement.

3. Results and discussion

In order to investigate the effect of the length of the aliphatic methylene spacer in the repeating unit on the thermal properties and the ionic conductivities, we synthesized polyetheresters containing a different number of methylene units (3–8, 10), while the EO length was fixed at 6. The DSC results of PES(6, *n*) are summarized in Table 1. From the DSC results of these materials, the glass transition temperature of PES was found to decrease with increasing number of methylene spacers, which was probably due to the increase in flexibility caused by incorporation of the flexible methylene unit. All the PES samples except for PES(6, 10) exhibit only the glass transition, in spite of the presence of crystallinity in the precursor polymer, PEG 300, which indicates that the crystallinity is completely eliminated by the alternative introduction of the methylene unit. The DSC results of PES(6, *n*)/$LiClO_4$ complexes ($[LiClO_4]/[EO] = 0.125$) are summarized in Table 2. The data in Table 2 exhibit a lower value of ΔT_g on increasing the number of methylene units. This may be due to the relatively lower density of polar EO groups which solvate the lithium perchlorate in polyetheresters containing the longer methylene unit, since the intermolecular crosslinking mainly occurred between the oxygen atoms on the EO units and the alkali metal cation. Thus, the segmental motion of the polymer chains increases with increasing methylene length. The effect of the length of the methylene unit on the ionic conductivity is represented in Fig. 1, which shows the conductivity variation of the PES(6, *n*)/$LiClO_4$ complexes prepared with the same $LiClO_4$ concentration as a function of methylene length. It is apparent that the number of methylene units has a strong influence on the ionic conductivity. The ionic conductivity is observed to decrease as the number of methylene units increases. While

Table 1
DSC results of PEG 300 and PES (6, *n*)

Polymer	T_g/°C	T_{fus}/°C	$\Delta_{fus}H$/J g^{-1}
PEG 300	−67.9	−1.4	82.2
PES(6, 3)	−46.5		
PES (6, 4)	−47.6		
PES (6, 5)	−47.5		
PES (6, 6)	−48.9		
PES (6, 7)	−50.4		
PES (6, 8)	−50.7		
PES (6, 10)	−51.0	−7.3	29.5

Table 2
DSC results of PES (6, *n*)/$LiClO_4$ ($[LiClO_4]/[EO] = 0.125$) complexes

Polymer electrolyte	T_g/°C	T_{fus}/°C	$\Delta_{fus}H$/J g^{-1}	ΔT_g/°C [a]
PES(6, 3)/$LiClO_4$	−20.8			25.7
PES(6, 4)/$LiClO_4$	−22.1			25.5
PES(6, 5)/$LiClO_4$	−22.4			25.1
PES(6, 6)/$LiClO_4$	−24.5			24.4
PES(6, 7)/$LiClO_4$	−26.9			23.5
PES(6,8)/$LiClO_4$	−31.1			19.6
PES(6, 10)/$LiClO_4$	−33.4	−3.0	1.1	17.2

[a] ΔT_g is the difference in the T_g values of PES and PES/$LiClO_4$ complex.

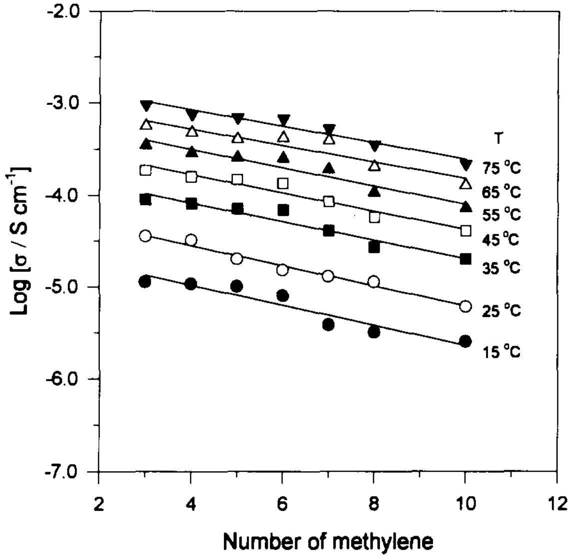

Fig. 1. Ionic conductivities of PES(6, *n*)/$LiClO_4$ ($[LiClO_4]/[EO] = 0.125$) as a function of length of methylene unit at a given temperature.

the salt concentration is the same in the polymer electrolytes studied, the PES containing fewer methylene units would be more solvation-active because of the higher density of polar groups. This favors the dissociation of the salt. As a result, there are more charge carriers for the polyetheresters with smaller methylene units. At room temperature, the maximum conductivity (3.5×10^{-5} S cm^{-1}) was observed at $n = 3$.

One of the most useful approaches to analyze the ionic conduction behavior in polymer electrolytes is to use the concept of free volume. The free volume is the space in a solid or liquid sample which is not occupied by polymer molecules. The ion transport depends on the formation of a free volume large enough for diffusive displacement. To compare the ionic conductivity based on the same free volume, we plotted the ionic conductivity against the reduced temperature $T - T_g$, since it has been reported that it gives a good approximation of the iso-free-volume condition [15–17]. This comparison is made in Fig. 2. The solvation by ether oxygen atoms is clearly shown in this figure at constant chain flexibility. There is a linear decrease in ionic conductivity as a result of decreasing the number of charge carrier ions with the number of methylene units, because the difference in segmental mobilities between these samples can be assumed to be negligible at the same value of $T - T_g$.

As the ionic conductivity is determined by the product of the number of carrier ions and their mobility, it is important that the contribution to ionic conductivity is resolved into these two factors, and that the effects of these factors on the ionic conductivity are investigated. According to previous studies [11, 12, 18], the spin–spin relaxation time (T_2) and the fraction of free lithium ions contributing to the ionic conductivity could be estimated from the ^{7}Li NMR spin–spin relaxation experiment. It was found that ^{7}Li FID traces obtained by the spin–echo technique in PES/LiClO$_4$ complexes were resolved into two components. The traces, therefore, could be fitted to the sum of the two components, $M(t) = M_1(t) + M_2(t)$, where $M_1(t)$ and $M_2(t)$ represent the nuclear magnetization of the mobile lithium nucleus and the tightly bound lithium nucleus, respectively. The atom portions of ^{7}Li belonging to free mobile ions could be calculated by the equation: $X_F = M_1(0)/[M_1(0) + M_2(0)]$, where $M_1(0)$ and $M_2(0)$ are the initial magnetization intensities of the corresponding lithium nucleus, respectively. The T_2 values and the relative intensities (X_F) of free mobile lithium ions estimated from the two resolved components at 25°C are depicted in Fig. 3. It is clearly shown that X_F

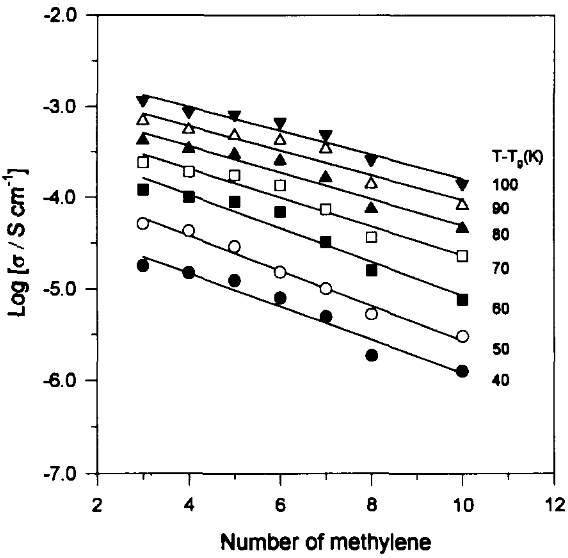

Fig. 2. Reduced isotherms of ionic conductivities for PES(6, n)/LiClO$_4$ ([LiClO$_4$]/[EO] = 0.125) as a function of length of methylene unit.

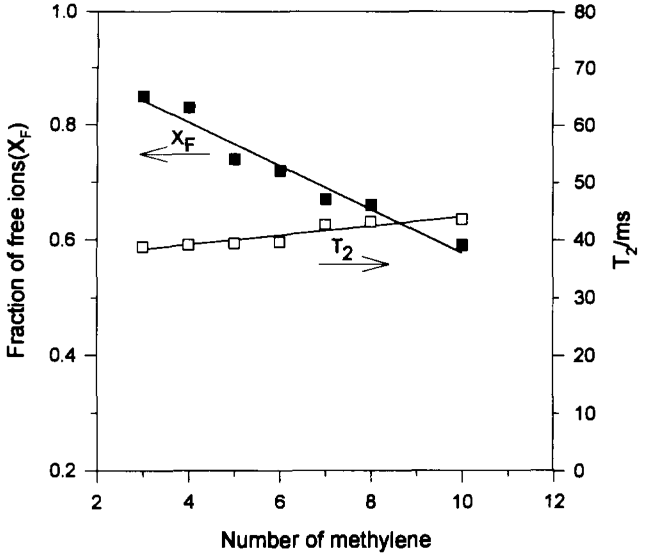

Fig. 3. The relative fraction of free mobile lithium ions (X_F) and their spin–spin relaxation time (T_2) as a function of methylene length at 25°C.

decreases with the methylene units, which may be attributed to the poor solvating capacity of the PES containing longer methylene units. This result is consistent with the previous assertion that the solvating capacity of the PES(6, *n*) examined decreases with methylene units, as explained in Fig. 2. The T_2 value proportional to the mobility of the free mobile lithium ion is found to be increased with increasing methylene units. The decline in T_2 with decreasing methylene length is probably associated with the reduction in mobilities of the free mobile cations due to the strong ion–polymer interaction promoting salt solvation. From the above ^{7}Li NMR relaxation results, it is concluded that the variation in conductivity as a function of methylene length shown in Fig. 1 is related to the number of charge carriers rather than to the ionic mobility.

In order to investigate the effect of the length of the aliphatic methylene spacer on the different length of EO, polyetheresters (PES(22, *n*)) containing a constant EO length of 22 and a different number of methylene units were synthesized. The DSC thermograms of PES(22, *n*) with changing methylene length are shown in Fig. 4. All of the polyetheresters were observed to have a crystalline melting transition irrespective of the number of methylenes. However, the degree of crystallinity was also found to be significantly reduced as compared with that of the precursor polymer, PEG 1000. The DSC results of PES(22, *n*)/$LiClO_4$ complexes ($[LiClO_4]/[EO] = 0.125$) are summarized in Table 3. All the samples exhibit only the glass transition, which indicates that these complexes become completely amorphous by incorporating $LiClO_4$. The value of ΔT_g is found to be nearly constant. When the length of the EO group is 22, the polyetheresters behave similarly to pure PEO, because the EO groups are more abundant than methylene units in the backbone of PES. Therefore, ion–polymer

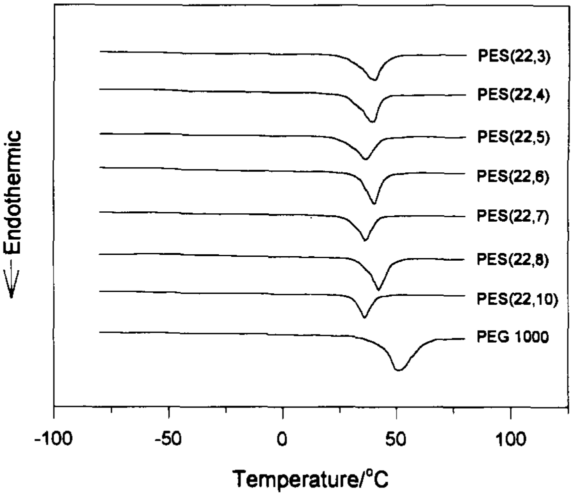

Fig. 4. DSC thermograms of PES(22, *n*) as a function of methylene length.

Table 3
DSC results of PES (22, *n*)/$LiClO_4$($[LiClO_4]/[EO] = 0.125$) complexes

Polymer electrolyte	$T_g/°C$	$\Delta T_g/°C$ [a]
PES(22, 3)/$LiClO_4$	−25.6	18.1
PES(22, 4)/$LiClO_4$	−26.3	14.7
PES(22, 5)/$LiClO_4$	−28.7	17.0
PES(22, 6)/$LiClO_4$	−28.3	14.7
PES(22, 7)/$LiClO_4$	−30.1	16.0
PES(22, 8)/$LiClO_4$	−26.5	18.9
PES(22, 10)/$LiClO_4$	−25.5	20.5

[a] ΔT_g is the difference in the T_g values of PES and PES/$LiClO_4$ complex

interaction may dominate irrespective of the value of *n* in the PES containing the longer EO groups. Fig. 5 shows the conductivity variation of the PES(22, *n*)/$LiClO_4$ complexes as a function of methylene length. It is apparent that the number of methylene units has little influence on the ionic conductivity. As mentioned earlier, the number of polar ether groups is so high that the effect of the number of methylene units on the solvating capacity is thought to be negligible. The ionic conductivities of these complexes range from 2.5×10^{-5} to 4.1×10^{-5} S cm^{-1} at room temperature, which are much higher than that of PEO/$LiClO_4$ complex. The significant increase in the ionic conductivities of the PES/$LiClO_4$ complexes as compared to that of PEO/$LiClO_4$ at ambient temperature may be due to the high degree of amorphicity of the PES/$LiClO_4$ complexes, since it is generally known that high conductivity is necessarily associated with an amorphous phase of a matrix polymer. The degree of crystallinity of the linear

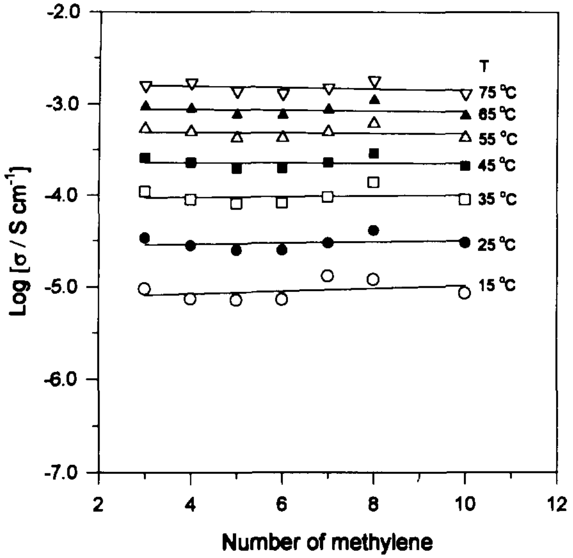

Fig. 5. Ionic conductivities of PES(22, *n*)/$LiClO_4$ ($[LiClO_4]/[EO] = 0.125$) as a function of length of methylene unit at a given temperature.

PEO/$LiClO_4$ complex was found to be 0.40 from the DSC thermogram, whereas the PES/$LiClO_4$ complexes were completely amorphous at the same $LiClO_4$ concentration ($[LiClO_4]/[EO] = 0.125$).

4. Conclusion

The effect of polymer structure on the ionic conductivity and thermal properties of polymer electrolytes containing lithium perchlorate was investigated. From the combination of the ionic conductivity and thermal properties of the polyetherester containing fewer ethylene oxide groups, as a function of methylene length (PES(6, *n*)/$LiClO_4$), the controlling factor for ionic conductivity and thermal property was shown to be a solvating capacity caused by the difference in the density of the polar ethylene oxide groups. In the case of polyetheresters containing a larger ethylene oxide group (PES(22, *n*)/$LiClO_4$), the number of methylene units had little influence on the ionic conductivity and thermal property, due to the saturated ion–polymer interaction.

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