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SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF THE NOVEL POLYMER ELECTROLYTES BASED ON POLYESTERS CONTAINING ETHYLENE OXIDE MOIETY

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Abstract—The relationship between the structure and ionic conductivities of the polymer electrolytes formed with the aliphatic polyesters containing a different number of ethylene oxide (EO) units and lithium perchlorate has been investigated. These complexes were observed to be completely amorphous and showed the ionic conductivities up to $10^{-5} \sim 10^{-4}$ S/cm at 25°C. The main factor that affects the ionic conductivity in these systems was proved to be a solvating capacity of the matrix polymer caused by the difference in the density of polar groups.

Key words: aliphatic polyester, ethylene oxide, ionic conductivity, lithium perchlorate, polymer electrolyte.

INTRODUCTION

The great deal of studies have been made to enhance the room temperature conductivities of poly(ethylene oxide) (PEO) based polymer electrolytes by modifying the structure of polymer matrix[1–9]. To achieve this goal, the polymer must be capable of dissolving the alkali metal salt and ionizing it to produce sufficient number of the charge carriers. Also it must be amorphous and have a flexible chain to assist the ion transport.

In our work, we tried to obtain the polyesters containing a variable number of EO units in the polyester backbone for forming complexes with lithium perchlorate, having reduced crystallinity and low T_g value. These polymer electrolytes have been investigated in terms of a chemical structure. In order to elucidate the contribution of the number of carrier ions and their mobility to the ionic conductivity, we have also tried to analyze the ^{7}Li NMR spin–spin relaxation in these polymer electrolytes.

EXPERIMENTAL

Synthesis and characterization

A series of polyesters based on poly(ethylene glycol) (PEG) (MW = 200 ~ 3400) and sebacoyl chloride was synthesized in benzene with a small

amount of triethylamine as a catalyst *via* solution polycondensation route, as shown in Fig. 1. The triethylamine salt (TEA · HCl) was then filtered off, and the product was obtained by freeze drying of the filtrate under reduced pressure. ^{1}H NMR spectra were obtained in CDCl$_3$ solvent on a Bruker-AMX-500 NMR spectrometer with tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) was carried out using a Waters CV-150 instrument equipped with four μ-Styragel columns (500, 10^3, 10^4, 10^5 Å) and the system was calibrated with the monodisperse PEO standards in DMF (0.05 M LiBr) at 80°C. DSC thermal analysis was carried out to measure the T_g, T_m, ΔH_m values with a heating rate of 20°C/min in a temperature range from −100 to 100°C. The ^{7}Li NMR experiments were performed on 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, polyesters synthesized will be designated as

HO[CH₂CH₂O]ₘH + ClOC(CH₂)₈COCl
PEG   sebacoyl chloride

TEA, Benzene, 6 h
———————————————→ [(OCH₂CH₂)ₘOOC(CH₂)₈CO]ₙ + TEA · HCl

Fig. 1. The reaction scheme for synthesis of polyester containing EO moiety.

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PES (m, 8), where m indicates the number of EO units in the repeating unit.

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 left to evaporate the solvent 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 Solatron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range of 10 Hz ~ 10 MHz. Each sample was allowed to equilibrate for 1 h at any temperature before measurement.

RESULTS AND DISCUSSION

In order to determine the length of aliphatic methylene spacer on the polymer backbone in our system, we synthesized the polyesters containing a different number of methylene unit (2 ~ 10) in the polyester backbone, while the EO length was fixed to be 6. From the DSC studies of these materials, the glass transition temperature of PES was found to decrease with increasing the number of methylene spacer, which was probably due to an increase in flexibility caused by incorporation of the flexible methylene uint. However, the crystalline melting transition was observed when the length of methylene unit was 10. This is undesirable property as base material for polymer electrolyte, since it is generally known that high conductivity is necessarily associated with an amorphous phase of matrix polymer. Thus, we chose the sebacoyl chain as the methylene spacer to obtain the polyester having reduced crystallinity and low T_g value.

The structure of polyesters was characterized by ^{1}H NMR spectroscopy, an example of which is shown in Fig. 2. The methylene protons in the octamethylene unit adjacent to the carbonyl groups
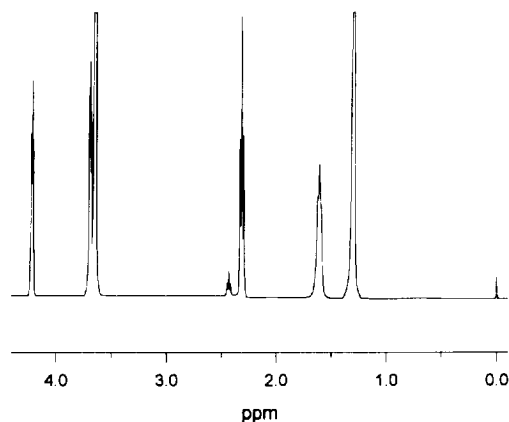
appeared as a triplet at $\delta = 2.32$, the β-methylene protons appeared at $\delta = 1.61$, while the remainder of methylenes observed at $\delta = 1.30$. The ended-methylene protons in the EO units adjacent to the ester units resonated further downfield as a triplet at $\delta = 4.22$, whereas the remainder methylene protons in internal EO units appeared at $\delta = 3.65$. The ratios were approximately $1.0 : 1.1 : 2.1 : 1.0 : 8.0$, which was consistent with the expected PES (9, 8) structure. All the other spectra were also confirmed to be consistent with the expected structures. The number average molecular weight of each polyester measured by GPC was estimated as about 20 500 ~ 29 800 and the polydispersity indexes ranged from 2.0 to 2.4.

The DSC thermograms of PESs as a change of EO length are shown in Fig. 3. The DSC thermogram of PEO(MW: 5 000 000) is also shown for comparative purpose in the same Figure. Most of the polyesters were observed to have relatively low T_g ($-53 \sim -44°$C). When the EO length was greater than 9, a melting peak appeared, and the increase in the length of EO segment was accompanied by an increase both in T_m and ΔH_m, indicating the tendency of the longer EO units to give the ordered structures. However the degree of crystallinity was significantly reduced by alternating introduction of octamethylene units as compared with that of PEO homopolymer.

The DSC results of PES (m, 8)/LiClO$_4$ complexes ([LiClO$_4$]/[EO] = 0.125) are summarized in Table 1. All the samples exhibit only the glass transition, which indicates that these complexes become completely amorphous by incorporating LiClO$_4$. The data in Table 1 also exhibit a larger value of ΔT_g with increasing the number of EO units up to about $m = 22$. This may be due to the high density of polar groups which solvate the lithium perchlorate in polyesters containing the longer EO units, since the intermolecular crosslinking mainly occured between the oxygen atoms on the EO units and the alkali metal cation. Thus, the segmental motion of the polymer chains decreases with increasing EO length. However, the value of ΔT_g is nearly constant above $m = 22$. When m is larger than 22, the polyesters
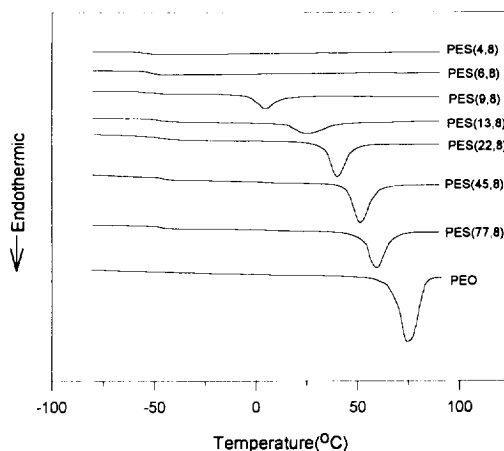

Fig. 2. ^{1}H NMR spectrum of PES (9, 8) in CDCl$_3$ at 25°C.

Fig. 3. DSC thermograms of PES (m, 8) as a function of EO length.

Table I. DSC results of PES (m, 8)/LiClO$_4$ ([LiClO$_4$]/[EO] = 0.125) complexes

Polymer electrolytes	T_g (°C)	ΔT_g (°C)*
PES(4, 8)/LiClO$_4$	−35.1	17.9
PES(6, 8)/LiClO$_4$	−33.1	20.2
PES(9, 8)/LiClO$_4$	−22.6	21.8
PES(13, 8)/LiClO$_4$	−22.9	22.5
PES(22, 8)/LiClO$_4$	−22.2	23.2
PES(45, 8)/LiClO$_4$	−20.7	23.3
PES(77, 8)/LiClO$_4$	−20.2	23.6

* The ΔT_g means the difference in the value of T_g between PES and PES/LiClO$_4$ complex.
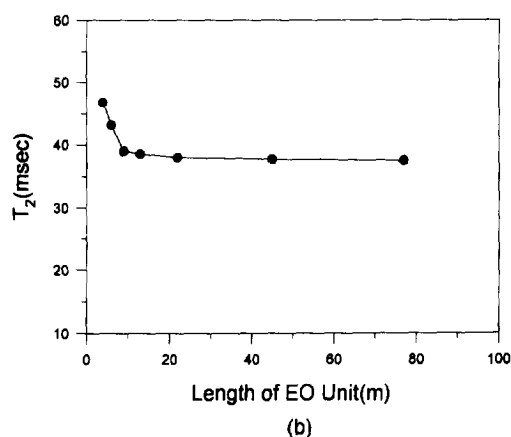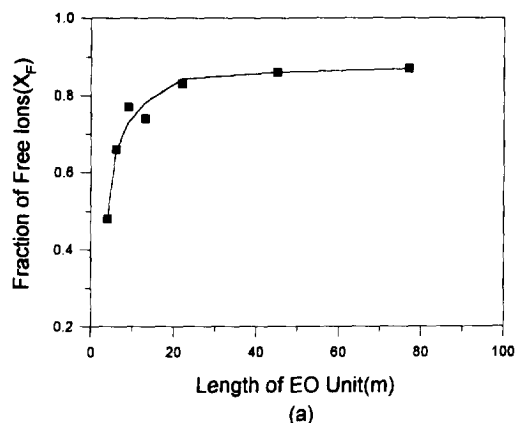

(a)

(b)

Fig. 5. The spin–spin relaxation time (T_2) and relative fraction of free mobile lithium ions as a function of EO length at 25°C: (a) T_2 vs. length of EO unit, (b) X_F vs. length of EO unit.

behave similar to pure PEO, since the EO groups as compared to octamethylene units are much more abundant in the backbone of PES. Therefore, the ion-polymer interactions may saturate irrespective of the value of m in this region.

Figure 4 shows the conductivity variation of the PES (m, 8)/LiClO$_4$ complexes prepared with the same LiClO$_4$ concentration as a function of EO length. It is apparent in this Figure that the number of EO unit in the repeating unit has a strong influence on the ionic conductivity. In case of smaller m, the ionic conductivity increases with increasing the number of EO unit. And there appears a critical length of EO unit above which the introduction of longer EO segments is useless or even negative for ionic conductivity. While the salt concentration added is the same in the polymer electrolytes studied, the PES containing more EO units would be more solvation active because of the higher density of polar groups, and thus favors the dissociation of the salt, giving somewhat more effective ionic carriers. As a result, the longer the EO segment in the repeating unit, the more the charge carriers. However in the case of PES containing the longer

Fig. 4. Ionic conductivities of PES (m, 8)/LiClO$_4$ ([LiClO$_4$]/[EO] = 0.125) as a function of a length of EO unit at a given temperature.

EO segments, the content of polar ether groups are so high that the effect of the number of EO unit to affect the solvating capacity is thought to be negligible. The ionic conductivity, therefore, was observed to be approximately constant over m = 22. It is also found that the ionic conductivities of these complexes range from 8 × 10^{-6} to 7 × 10^{-6} S/cm at room temperature, which are much higher than that (5 × 10^{-8} S/cm) 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. The degree of crystallinity of the linear PEO/LiClO$_4$ complex was found to be 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).

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 the previous

works[9–11], the spin–spin relaxation time (T_2) and the fraction of free lithium ions contributing to the ionic conductivity could be estimated from ^7Li NMR spin-spin relaxation experiment. It was found that ^7Li FID traces obtained by 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 $M_2(t)$ stand for the nuclear magnetization of the mobile lithium nucleus and the tightly bound lithium nucleus, respectively. The atom portions of ^7Li belonging to free mobile ions could be calculated by the equation of $X_F = M_1(0)/[M_1(0) + M_2(0)]$, where $M_1(0)$ and $M_2(0)$ were initial magnetization intensities of the corresponding lithium nucleus, respectively. The T_2 values and relative intensities (X_F) of free mobile lithium ions estimated from the two resolved components at 25°C are depicted in Fig. 5. It is clearly shown that X_F increases with EO length up to $m = 22$, and it is then nearly constant with further increasing EO length. The increase in the number of charge carriers with EO length up to $m = 22$ is attributed to the better solvating property of the PES containing longer EO unit. The T_2 value proportional to the mobility of the free mobile lithium ion is found to be slightly decreased with increasing EO length. The decline in T_2 is probably associated with the reduction of mobilities of free mobile cations due to the strong ion–polymer interaction promoting the salt solvation. From the above ^7Li NMR relaxation results, it is concluded that the variation in conductivity as a function of EO length shown in Fig. 4 is related to the number of charge carriers rather than ionic mobility.

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