

Ionic Conductivity of Solid Polymer Electrolytes Based on Modified Alternating Maleic Anhydride Copolymer with Oligo(oxyethylene) Side Chains

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ABSTRACT: Comb-like polymers (CP) based on modified alternating methyl vinyl ether/maleic anhydride copolymer with oligo-oxyethylene side chains of the type $-O(CH_2CH_2O)_nCH_3$ have been synthesized and characterized, and complexed with lithium salts to form amorphous polymer electrolytes. CP/salt complexes showed conductivity up to $10^{-5} S cm^{-1}$ at room temperature. The temperature dependence of ionic conductivity suggests that the ion transport is controlled by segmental motion of the polymer, shown by linear curves obtained in Vogel–Tammann–Fulcher plots. The ionic conductivity maximum moves to a higher salt concentration as the temperature increases. IR results indicate that the ester in CP might decompose at 140°C and reproduce the maleic anhydride ring.

KEY WORDS Comb Polymers / Polymer Electrolytes / Glass Transition Temperature / Ionic Conductivity / Vogel–Tammann–Fulcher Equation /

The high ionic conductivities which have been observed in polymer/alkali metal salt complexes, particularly those involving poly(ethylene oxide) (PEO) and lithium salts, have stimulated great interest in these systems as electrolytes for all solid-state, high-energy-density batteries.^{1,2} The ion-conducting polymers can also be used as solvent-free electrolytes or electrode materials in sensors and electrochromic displays. During the past 20 years, the study of solid polymer electrolytes (SPE) has been very active.^{3–5} PEO, the most extensively studied polymer, can form complexes with a wide range of metal salts including alkali, alkaline earth, and transition metal salts. PEO/salt electrolytes suffer from one major drawback in that PEO is semicrystalline at ambient temperature. NMR studies indicate that ion transport occurs in the amorphous regions of the polymer and, taken together with temperature dependence measurements, implicate polymer segmental motion in the conduction mechanism.³ High and valuable ionic conductivities can only be obtained after the temperature of the system exceeds the melting point of PEO, which is about 338 K. In order to destroy the crystallinity of PEO and obtain totally amorphous electrolyte materials, many researchers choose the method to prepare comb polymers by attaching short ethylene oxide (EO) unit sequences to an existing polymer backbone. A lot of comb polymers with oligo-oxyethylene side chains have been prepared by using polymethacrylate,^{6–10} polyglutamates,^{11–13} polysiloxane,^{14–16} polyphosphazene,^{17–22} and poly(itaconic acid)^{23,24} as the polymer backbone. These systems all show higher room temperature conductivities, when complexed with alkali metal salts, than those corresponding PEO/salt electrolytes.

Alternating maleic anhydride copolymers are a group

of high reactive bifunctional polymeric materials and are commercially available. Recently, Rietman and coworkers²⁵ have synthesized single-ion (Li) conducting polymer by reacting monomethyl ether with either poly(styrene-*alt*-maleic anhydride) or poly(ethylene-*alt*-maleic anhydride) and then treating with LiOH solution to form lithium salt. Just like other single-ion polymeric electrolytes, their room temperature conductivities were very low (*ca.* $10^{-7} S cm^{-1}$), and such a low level of conductivity is of no practical significance. Besides, in Rietman's work the resulting rubbery product was usually insoluble and this hindered the addition of Li ions. The present work is an approach alternative to Rietman's study, *i.e.*, to prepare polymer host for bi-ionic conductors by reacting monomethyl ether of PEG with another maleic anhydride alternating copolymer, poly(methyl vinyl ether-*alt*-maleic anhydride) and endcapping the residual carboxylic acid group with methanol. In this study, we report the method of avoiding gel formation during preparation, the results of structural characterization by IR, ¹³C NMR and elemental analysis, the measurements of the glass transition temperatures and ionic conductivity. The ionic conductivity of CP/salt complexes was studied as a function of temperature and salt concentration. The effects of the side chain length and the ionic size of the complexed salt on ionic conductivity were also explored.

EXPERIMENTAL

Materials

Poly(methyl vinyl ether-*alt*-maleic anhydride) (MA) and monomethylether of polyethylene glycols (PEGME) (MW 350, 550 and 750) were supplied by Aldrich Chemical Co., Ltd., which were used without further purification. *p*-Toluenesulfonic acid (PTSA, C.P. grade)

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was supplied by Shanghai 1st Chemical Reagent Factory, which was dried at 70°C under vacuum for 24 h prior to use. Butanone (MEK) was refluxed in the presence of C.P. grade P₂O₅ for 4 h; methanol was dried over molecule sieve, type 4A, and then refluxed with metallic magnesium for 1 h; acetone and hexane were both refluxed with CaH₂ for 4 h. After refluxing all the solvents were distilled just before use.

Synthesis of the Comb Polymer

The esterification of MA with PEGME without gel formation was achieved at first by dissolving MA and PEGME (mole ratio 1:2) in freshly distilled MEK, then injecting a definite volume of MEK solution of PTSA to the mixture under a flow of N₂. The mixture was stirred continuously for 24 h at 80°C. After the reaction came to the end, the mixture was transferred to a rotary evaporator to remove MEK, then an excess amount of freshly distilled methanol (*ca.* 200-fold) was added to the residue so as to endcap the unreacted carboxyl group. The reaction proceeded with continuous stirring for 24 h at 60°C. The reaction mixture was then transferred to the rotary evaporator for removal of the excess methanol. Thereafter, the product (CP) was purified by reprecipitation by using distilled MEK as solvent, and *n*-hexane as precipitant. Generally, four times of reprecipitation were necessary. All the three polymers present themselves as white elastomeric solids.

General Methods

Absorbance IR spectra were obtained on a BIO-RAD FTS-7 spectrometer. Samples for IR spectroscopy were cast onto KBr plates. A Varian unity-400 spectrometer was used to obtain the ¹³C NMR spectra of CP. The number-average molecular weight (*M_n*) was obtained by a Waters 208 gel permeation chromatography (GPC) assembly. Elution counts were calibrated by well-defined polystyrene standards. THF solutions were used and the flow rate was 1 mL min⁻¹. The purified samples CP350, CP550, and CP750 have number-average molecular weights of 1.6 × 10⁵, 2.3 × 10⁵, and 3.0 × 10⁵, respectively. Elemental analysis was performed with a Model 1106 Elemental Analyzer provided by Carlo Erba Strumentazione Co. *Anal.* Calcd for C₂₃H₄₂O₁₂ per repeat unit of CP350: C, 54.11%; H, 8.29%. Found: C, 54.14%; H, 8.32%. *Anal.* Calcd for C₃₃H₆₂O₁₇ per repeat unit of CP550: C, 54.23%; H, 8.55%. Found: C, 54.28%; H, 8.49%. *Anal.* Calcd for C₄₃H₈₂O₂₂ per repeat unit of CP750: C, 54.30%; H, 8.69%. Found: C, 54.39%; H, 8.73%. DSC measurements were performed on a Perkin-Elmer DSC-7 instrument equipped with a liquid nitrogen cooling system and a heating/cooling rate of 20 K min⁻¹. Polymer complexes were hermetically sealed in Al pans. The samples were subjected to a heating-cooling-reheating cycle and the temperature range used was generally -70–135°C. The glass transition temperatures (*T_g*) were determined as the midpoints of the heat capacity change during the relaxation temperature.

Preparation of Solid Electrolyte Film

Anhydrous LiClO₄ and LiCF₃SO₃ (Aldrich) were dried under reduced pressure (10⁻³ Torr) at 130°C for 24 h, LiPF₆ (Aldrich) at 50°C for 24 h, and then were

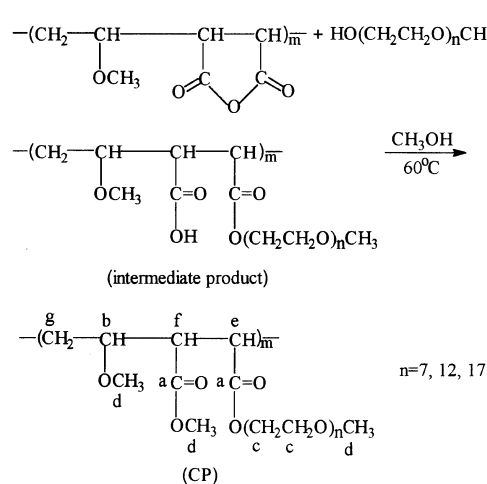
dissolved in dry acetone. CP/acetone and salt/acetone were mixed in appropriate proportions to obtain polymer/salt complexes of desired composition. The solutions were cast on Teflon dishes, and the solvent was allowed to evaporate at room temperature under a N₂ stream until the solutions did not flow. The samples obtained were dried thoroughly *in vacuo* at 70°C for 72 h until the water content determined by using Karl Fischer reagent was less than 0.01%. Dried samples were stored in sealed containers within an argon-filled dry box. All samples were dried again overnight in a vacuum at 70°C before conductivity measurements.

Conductivity Measurements

Polymer electrolyte samples of 1 cm diameter and approximately 0.025 cm thickness were placed between two spring loaded stainless steel electrodes. Conductivity measurements were carried out in a thermally insulated box with thermocouples positioned close to the samples to monitor and control the temperature of the electrolyte films to an accuracy of better than ±0.5 K. The complex impedance of the samples was measured in the 298–373 K temperature range, with a Solartron 1255 FRA connected to a Solartron 1287 electrochemical interface; applied signal amplitude was 1 V in the nominal frequency range of 0.1 Hz to 1 MHz. The conductivity was determined as a function of temperature while allowing an equilibration time of 1 h at each incremental rise in temperature.

RESULTS AND DISCUSSION

The three comb-like polymers based on alternating maleic anhydride copolymer was prepared according to Scheme 1. Under the catalysis of externally added acid, the esterification of the alternating maleic anhydride copolymer with low MW alcohol can only form a semi-ester, *i.e.*, only one of the two carboxylic acids can be converted into ester.²⁶ In our case of using PEGME as an esterification agent, similar result was obtained. The same result was also reported by Rietman.²⁵ However, in contrast with the low MW monofunctional alcohol, the use of PEGME often results in an insoluble product. The formation of the insoluble product would bring about many difficulties in the experimental work, *e.g.*,



Scheme 1. Synthesis of CP.

purification, characterization and film preparation. The gel formation might be caused by the presence of trace impurity of unmethylated PEG, which is very difficult to be removed from the bulk of PEGME completely. Then we tried to overcome this difficulty by allowing the esterification to proceed in solution, and have succeeded in obtaining completely soluble products. Several organic solvents such as DMF, cyclohexanone and MEK have been selected for the solution esterification. Among them, MEK seemed to be the most favorable. Although DMF is a good solvent for MA, it usually causes the product discolored; as for cyclohexanone, the solubility for the intermediary is rather poor. Besides, THF also manifests itself as a fairly good solvent for this esterification. During the synthesis operation, it was found that after the completion of the first step of the reaction, the intermediary was very difficult to be obtained since it readily became an insoluble gel even if it was dried in an oven at 50°C. Thus the second step of the reaction was started by adding an excess amount of dry methanol right after the removal of MEK. Only in this way could a completely soluble final product CP be obtained.

The IR spectrum of the purified final product CP550 is shown in Figure 1. Generally, pentagonal anhydride shows two absorbance peaks at 1870–1750 cm^{-1} , which can be assigned to the stretching mode of C=O²⁷. In the IR spectrum of MA,²⁸ the two characteristic absorption peaks of maleic anhydride group appear at 1857.8 and 1779.2 cm^{-1} , while in Figure 1, both the absorption peaks are absent, indicating that the anhydride has been converted completely. The strong absorptions at 1733.3 and 1103.2 cm^{-1} corresponding to C=O stretching mode and C–O–C asymmetric stretching mode, respectively²⁷ show that the product is a polyester of poly(ethylene glycol) (PEG).

The structure of CP was further examined by ¹³C NMR spectrum. According to the presumed formula of CP (see Scheme 1), there are four different carbons in the main chain, *i.e.*, one methylene carbon **g** and three tertiary carbons **b**, **e**, **f**. In the side chains, there are two carbonyl carbons **a**, three methyl carbons **d**, one of which belongs to the methoxyl group and the other two to the ester groups, and the methylene carbons **c** in the PEG group. The ¹³C NMR spectrum of CP750 is shown in Figure 2. Apparently the 72.8–69.9 ppm signal is the concentration of the secondary carbon **c** in the $-(\text{CH}_2\text{CH}_2\text{O})-$ group, while the 61.2 ppm signal is due to the carbon in the $-\text{CH}_2\text{OH}$ group, which arises from the unreacted end of PEG mixed with PEGME.²⁷ Therefore, the assignment of the signals in CP750 ¹³C NMR spectrum are: carbon **a**, 175.8–172.5; **b**, 78.2–77.2; **c**, 72.8–69.9; **d**, 57.5; **e**, 49.6; **f**, 41.1; **g**, 32.1 ppm. On the basis of the above characterization results, the presumed structure of CP shown in Scheme 1 is now well confirmed.

In order to clarify the relationship between ionic conductivity and segmental motion of the polymer matrix, the dependence of T_g on salt content should be determined. CP550/LiClO₄ complexes showed only glass transitions in DSC curves (see Figure 3), which indicated that these samples were completely amorphous at ambient temperatures. It is very interesting to note that there are two glass transitions, and the two T_g s increase

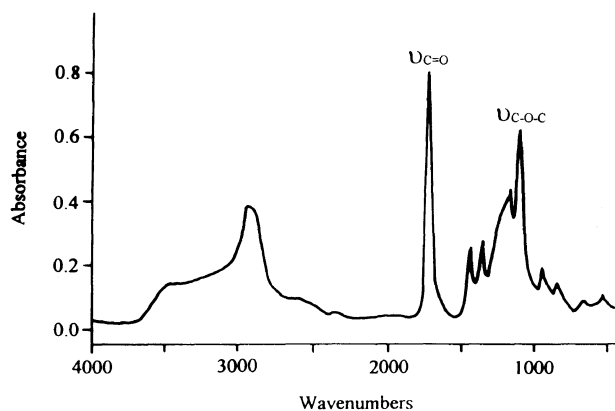


Figure 1. IR spectrum for CP550.

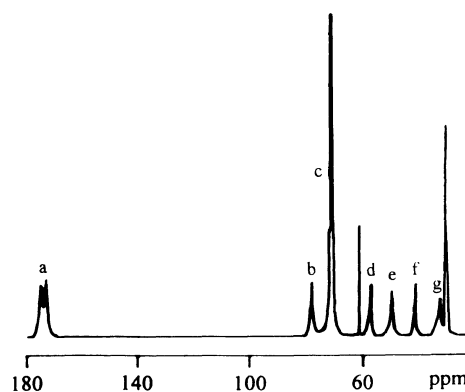
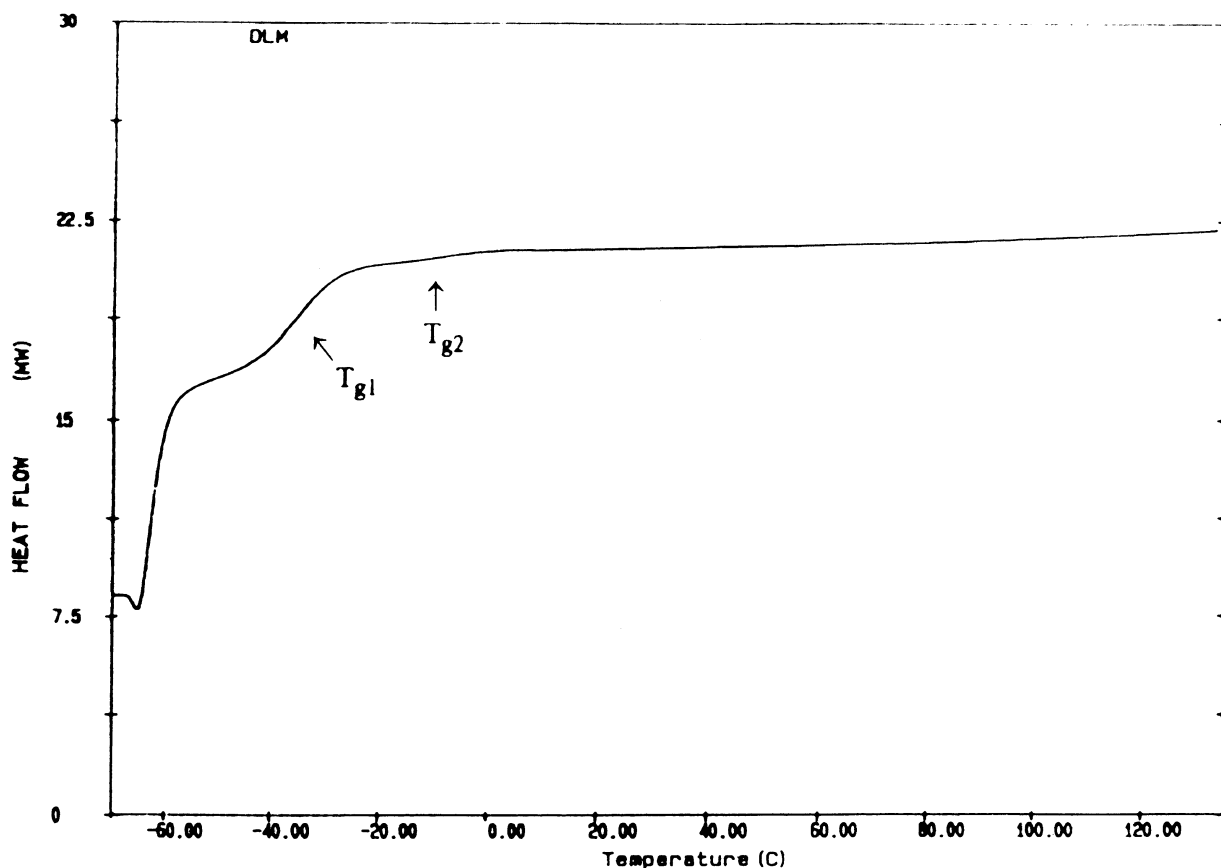


Figure 2. ¹³C NMR spectrum for CP750.

with increasing [Li]/[EO] ratio (as shown in Figure 4). T_{g1} and T_{g2} can be attributed to the glass transition temperature of oligo-oxyethylene side chains and polymer backbone respectively, since the side chains are more flexible than $-\text{C}-\text{C}-\text{C}-\text{C}-$ backbone. There are two factors involved in the increase of T_g with salt content: (1) interaction between ether oxygen atoms and Li^+ increases the microviscosity of the solid electrolyte film and (2) the polymer segment is expanded by the introduction of charges on the polymer chains because of the electrostatic repulsion.⁸ At low salt concentrations, the large value of ΔT_g (increase in T_g) indicates a substantial dissociation of the salt to form solvated cations leading to crosslinking or chain stiffening, whereas low ΔT_g values suggest that the dissociation is small and the salt exists predominantly as ion pairs.²⁹ If the $-\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ groups in CP are defined as the side chains, the remaining backbone still consists of polar groups, *i.e.*, $-\text{OCH}_3$, $-\text{COOCH}_3$, which can also interact with Li^+ effectively, thus T_{g2} increases with the increase of salt content. This contrasts finely with Watanabe's work¹⁵ in which the T_g of the siloxane backbone remained unchanged owing to the absence of polar groups attaching to the remaining backbone.

The temperature dependence of the ionic conductivity of CP550/LiClO₄ electrolyte films is shown in Figure 5 over a range of salt concentrations. These data were collected on heating, and the discrepancies with the corresponding cooling curves were generally less than 5%. The curvature of the plots is characteristics of amorphous polymer electrolytes, suggesting that the ion-transport mechanism follows the WLF mechanism.³⁰



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Figure 3. DSC trace for CP550/LiClO₄ complex with [Li]/[EO] ratio of 0.10.

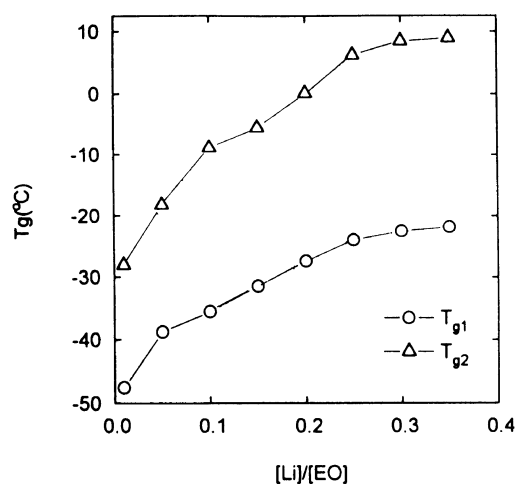


Figure 4. Variation of glass transition temperature with salt concentration for CP550/LiClO₄ complexes.

The data can be more adequately described by the Vogel–Tamman–Fulcher (VTF) equation^{31–33}:

$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)] \quad (1)$$

where A is a pre-exponential term which is related to the concentration of the free charge carriers, B is an apparent activation energy depending on the free energy barrier opposing configurational rearrangements, T_0 can be regarded as the temperature below which there is no further entropy loss due to configurational changes in

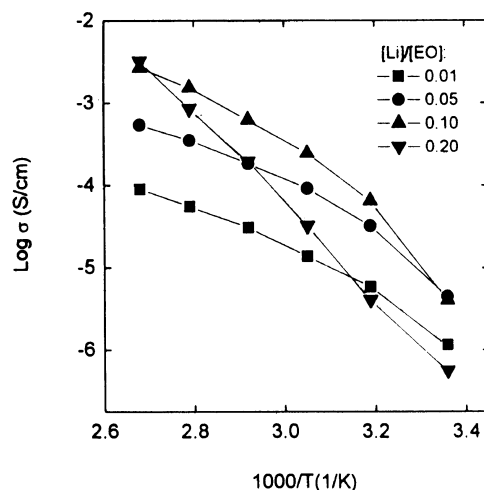


Figure 5. Temperature dependence of ionic conductivity for CP550/LiClO₄ complexes.

the polymer. Linear VTF plots of CP550/LiClO₄ complexes were obtained by treating the conductivity data according to eq 1 and taking T_0 as $T_{g1} - 50$ K or T_{g1} (see Figure 6). The corresponding parameters listed in Table I were determined by using a computer-fitting technique. Here, the slope B is converted to an activation energy, and this conversion may not be particularly meaningful as suggested by Cowie *et al.*³⁴ Table I shows that B is related to the salt concentration, so B must be associated with T_g in some way through the ability of the polymer

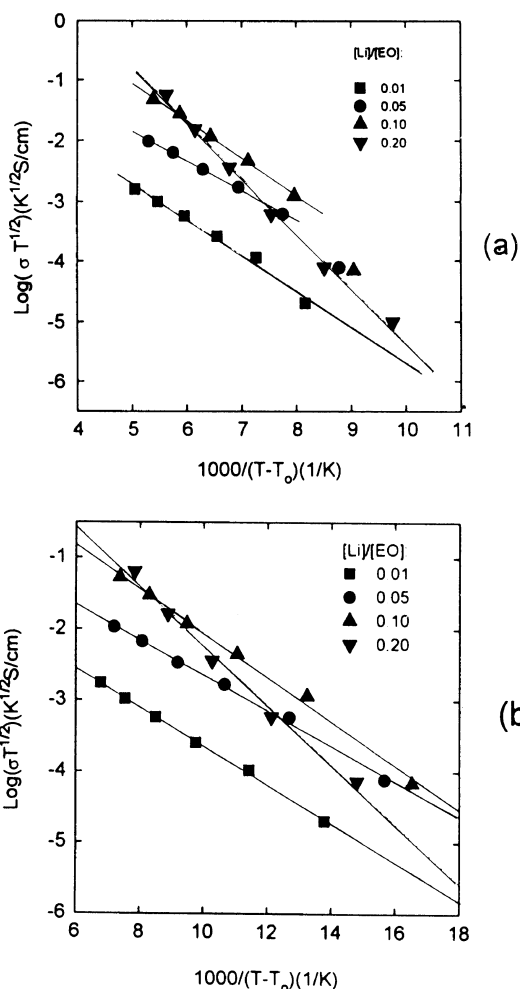


Figure 6. VTF behavior of ionic conduction for CP550/LiClO₄ complexes: (a) $T_0 = T_{g1} - 50$ K, (b) $T_0 = T_{g1}$.

Table I. Apparent activation energies derived from the slope of the VTF plots for CP550/LiClO₄ complexes

No.	[Li]/[EO]	Figure 6(a) $B'/J \text{ mol}^{-1}$	Figure 6(b) $B'/J \text{ mol}^{-1}$
1	0.01	1372	628.4
2	0.05	1115	573.0
3	0.10	1421	712.9
4	0.20	2113	964.4

to ionize the salt and thereby change the activation energy for chain rearrangement.³⁵

The salt concentration dependence of ionic conductivity can be easily illustrated by examining isothermal plots of the $\log(\text{conductivity})$ versus [Li]/[EO] ratios as shown in Figure 7. At 25°C, 55°C, and 85°C, three pronounced conductivity maxima *i.e.*, 7.76×10^{-5} , 2.45×10^{-3} , and $2.34 \times 10^{-2} \text{ S cm}^{-1}$ at [Li]/[EO] ratios of 0.077, 0.16, and 0.20, respectively, can be observed. The conductivity data pass through a maximum, indicating that the effects of increasing charge carrier density are overcome by the accompanying decrease in segmental mobility. This decrease in segmental mobility arises from virtual cross-linking and has an obvious signature in the increased glass transition temperature.³⁶ The free volume model is very useful for discussion of

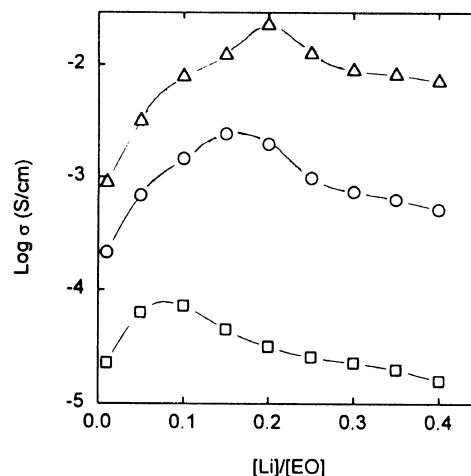


Figure 7. Salt concentration dependence of ionic conductivity for CP350/LiCF₃SO₃ complexes. 298 K (□), 328 K (○), and 358 K (△).

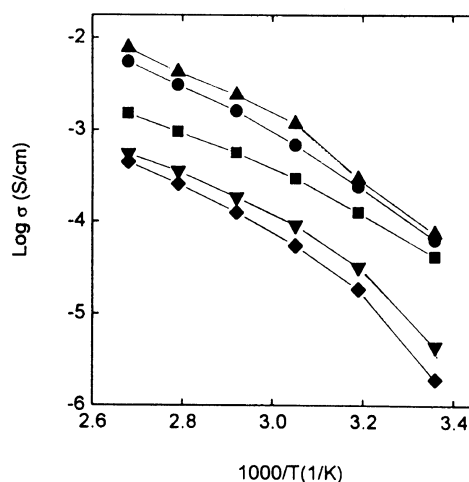
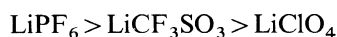


Figure 8. Temperature dependence of ionic conductivity for CP350/LiClO₄ (■), CP350/LiCF₃SO₃ (●), CP350/LiPF₆ (▲), CP550/LiClO₄ (▼), and CP750/LiClO₄ (◆) complexes with constant [Li]/[EO] ratio of 0.05.

ion-transport mechanism and for understanding of the polymer segment mobility. It states that as temperature increases, the expansivity of the material produces local empty space, free volume, into which ions, solvated molecules or polymer segments themselves can move.³ The overall mobility of the material is determined by the amount of free volume present in the material. As temperature increases, the amount of free volume increases, this leads to the increases of ion mobility and segment mobility. Only at higher salt concentrations can the minus effect on ionic conductivity resulting from stiffening of the coordinated side chains counteract the positive effect on conductivity resulting from the increase of the overall mobility of the electrolyte material. Therefore, the ionic conductivity maximum moves to a higher salt concentration as the temperature increases.

The log conductivities of five CP/salt electrolyte samples with a constant [Li]/[EO] ratio of 0.05 but containing varying Li salt species (different anions) or varying side chain length are shown in Figure 8 plotted against reciprocal temperature. When the Li⁺ cation is common to the systems and the anion is varied, the conductivity decreases in the order



which accords well with the decreasing order of anion radius.^{37,38} The ionic conductivity of the three salt complexes at 25°C are 7.41×10^{-5} , 6.31×10^{-5} , and $4.17 \times 10^{-5} \text{ S cm}^{-1}$ respectively. As suggested by Watanabe *et al.*,³⁷ ionic conduction in polymer electrolytes results from hopping of carrier ions. The most stable hopping sites are the anions. The energy necessary for ion separation is given by

$$\Delta E = [e^2 / (4\pi\epsilon_0\epsilon)] \times (r_c + r_a)^{-1} \quad (2)$$

where ϵ_0 is the vacuum dielectric constant, ϵ is the dielectric constant, r_c and r_a are the cation and anion radius respectively. As the ionic size of the salt increases, the energy required for ion separation decreases, resulting in an increase in ionic conductivity. Though the above conductivity order conforms well with the trends observed by other research groups,³⁷⁻³⁹ the explanation is empirical, there are still some other different reports and different explanation.^{6,40} So it seems imprudent to attempt to correlate the conductivity of polymer electrolytes to a particular property of the polymer or the Li salts. It appears that the mobility and concentration of the ions responsible for optimum ionic conductivity are determined by a careful balance among the lattice energy of the salt, the dielectric constant and basicity of the host polymer, polymer backbone flexibility and the degree of the amorphous character of the polymer/salt complex.³⁹ Figure 8 also shows that the CP/salt electrolyte with longer side chains exhibits lower ionic conductivity. As the side chain length increases, the microviscosity of the system increases, which results from entanglements among the longer oxyethylene side chains and decreases the mobility of carrier ions, thus decreases the ionic conductivity. But at lower salt concentrations, the trends will be different as reported in detail by Tsuchida *et al.*⁶

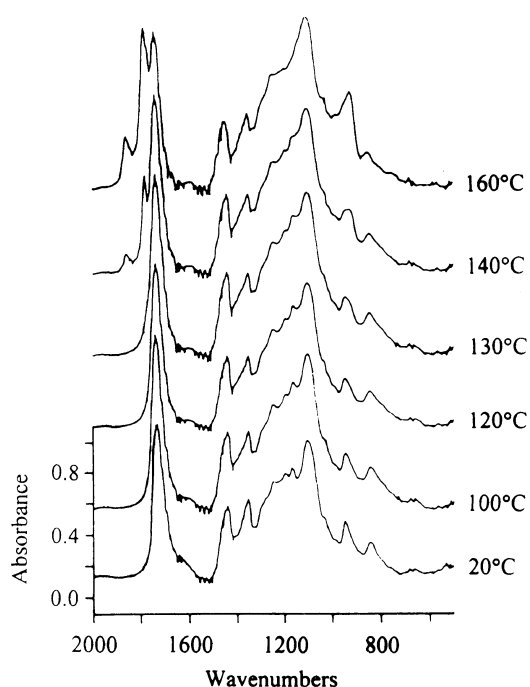
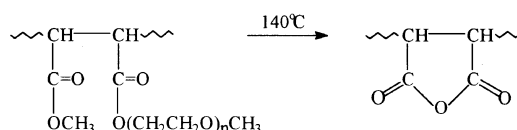


Figure 9. IR spectra for CP350 at various temperatures.

In order to understand the thermal stability of CP and ascertain the mechanism of thermal decomposition, we tried to inspect the molecule structure change of CP350 during the gradual temperature-raising process by using a temperature-changing IR technique with a heating rate of 2°C min^{-1} . Figure 9 shows that the structure of CP350 doesn't change until the temperature reaches 140°C when two new absorbance peaks appear at 1859.5 and 1781.2 cm^{-1} . The new bands are the very characteristics of maleic anhydride ring. This implies that the ester in CP350 might decompose at 140°C and reproduce maleic anhydride ring (as shown in Scheme 2). So the upper-limit-temperature of the CP/salt complexes as practical solid electrolyte materials might be 140°C.



Scheme 2. Thermal decomposition of CP.

CONCLUSIONS

Three new amorphous comb polymers with low T_g values have been synthesized based on alternating maleic anhydride copolymer. They can form amorphous complexes with alkali metal salts which display high ionic conductivities at ambient temperatures. The temperature dependence of the ionic conductivity suggests that the conduction follows the WLF mechanism, which is confirmed by Vogel–Tammann–Fulcher plots. Thus the ionic conductivity of these polymer electrolytes is strongly affected by segmental motion in the polymer matrix. Although there are a few similarities between our work and Rietman's, the synthesis method, the polymer structure, the SPE film preparation and the properties of the resulting SPE materials are quite different, the conductivities of our materials are much higher. The conductivity difference is due to three respects. First, the polymers we prepared have longer ether side chains which can interact with Li^+ more strongly to enhance the dissociation of salts. Second, the polar side groups such as $-\text{OCH}_3$, $-\text{COOCH}_3$ instead of benzene group may assist in the salt dissociation. Third, our materials are bi-ionic conductors which are generally more conductive than single-ion conductors. The polymer electrolyte materials reported here are soluble and can readily be cast into thin films suggesting that they are viable alternatives for low-temperature thin-film battery applications. Further electrochemical studies on these rubbery electrolytes are in progress.

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