

LITHIUM ION CONDUCTING POLYMER ELECTROLYTES BASED ON ALTERNATING MALEIC ANHYDRIDE COPOLYMER WITH OLIGO-OXYETHYLENE SIDE CHAINS

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ABSTRACT

A comb polymer with oligo-oxyethylene side chains of the type $-(CH_2CH_2O)_{12}CH_3$ was prepared from methyl vinyl ether/maleic anhydride copolymer and poly (ethylene glycol) methyl ether. The polymer can dissolve $LiClO_4$ salt to form homogeneous amorphous polymer electrolyte. The ac ion conduction was measured using the complex impedance method, and conductivities were investigated as functions of temperatures and salt concentration. The complexes were first found to have two classes of glass transition which increase with increasing salt content. The optimum conductivity attained at $25^\circ C$ is in the order of $5.50 \times 10^{-6} Scm^{-1}$. IR spectroscopy was used to study the cation-polymer interaction.

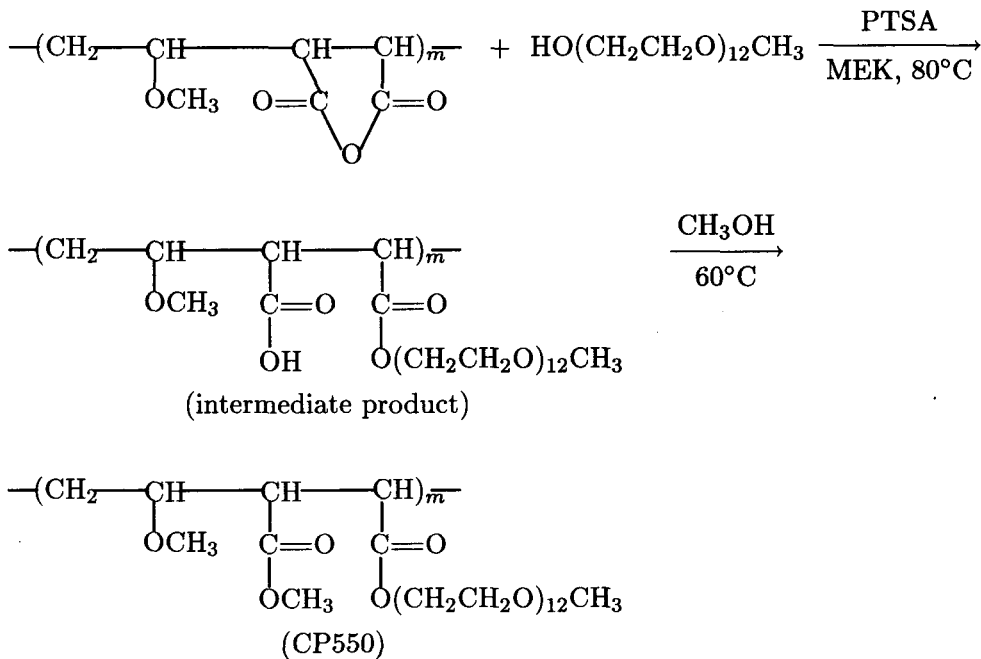
INTRODUCTION

During the past two decades, solid polymer electrolytes (SPE) have attracted considerable attention due to their potential application in primary or secondary high energy density batteries, smart windows and solid state transistors^[1,2]. PEO can dissolve a lot of alkali metal salts, but its semicrystalline regions reduce the free volume and impair the ion transport. One method to inhibit the crystallization is to synthesize comb polymers with oligo-oxyethylene side chains attached to a polymer backbone. If the length of side chains is kept short to prevent from crystallization, amorphous polymer will be obtained. Blonsky, Smid, Cowie, Spindler and Watanabe^[3-7] have developed respectively several systems which proved to be effective polymer hosts. We have prepared comb polymers based on methyl vinyl ether/maleic anhydride copolymer. The products are flexible and totally amorphous. These materials are capable of dissolving $LiClO_4$ and ion conduction was measured for the resulting mixtures. This paper reports a study on the ionic conductivity and cation-polymer interaction.

EXPERIMENTAL

Synthesis of the comb polymer

CP550 was synthesized by two-step esterification reaction between methyl vinyl ether/maleic anhydride copolymer (Aldrich), poly (ethylene glycol) methyl ether (Aldrich, M.W. 550) and methanol. The first esterification was carried out in freshly prepared butanone (MEK) using p-toluenesulfonic acid as a catalyst at 80°C, the anhydride ring opened, forming a carboxylic acid and an ester. Then the intermediate product was dissolved in 300-fold amount of methanol and the second esterification was performed (as shown in Scheme 1). The product was dissolved in acetone and precipitated in dried hexane. Purification was effected by further dissolution/precipitation procedures. The structure of CP550 was characterized by ¹³C NMR, IR, and elemental analysis. All the results are consistent with the expected formula^[8–11].



Scheme 1

Film preparation

Anhydrous LiClO_4 (Aldrich) was dried under reduced pressure (10^{-3}torr) at 150°C for 20h and then was dissolved in dry acetone. CP550/acetone and LiClO_4 /acetone were mixed in appropriate proportions to obtain polymer-salt complexes of desired composition. The solutions were cast on Teflon dishes, and acetone was

allowed to evaporate at room temperature under a N_2 stream until the solutions did not flow. The samples obtained were dried thoroughly in vacuo at 70°C for 72h 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 ac conductivity measurements.

AC conductivity measurements

The ac conductivity was measured in the 298-373K temperature range under dry nitrogen flow, with a Solartron 1255 FRA connected to a Solartron 1287 electrochemical interface; applied signal amplitude was 1V in the nominal frequency range of 0.1Hz to 1MHz. The real and imaginary parts of the complex impedance were plotted as shown in Fig.1, from which the conductivity can be derived. The conductivity was determined as a function of temperature while allowing an equilibration time of 1h at each incremental rise in temperature. Polymer electrolyte samples of 1cm diameter and approximately 0.025cm thickness were placed between two spring loaded stainless steel electrodes.

Differential scanning calorimetry

DSC measurements were performed on a Perkin-Elmer DSC-7 instrument equipped with a liquid nitrogen cooling system and a heating/cooling rate of 20K/min. 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 $-70 \sim 135^\circ\text{C}$. The glass transition temperatures (T_g) were determined as the mid-points of the heat capacity change during the relaxation temperature.

FTIR

Absorbance IR spectra were obtained on a BIO-RAD FTS-7 spectrometer. Samples for IR spectroscopy were cast onto KBr plates.

RESULTS AND DISCUSSION

Fig.1 shows the complex impedance plot of CP550/ LiClO_4 complex at 40°C . It is typical for those SPE films with ion-blocking electrodes. The spur appeared at low frequency was ascribed to double-layer capacitance in a cell with an ion blocking electrode. Deviation of the spur from ideal can be due to some physical properties such as surface roughness, large mobility ratios, and blocking incompleteness^[12,13].

CP550/ LiClO_4 complexes showed only glass transitions in the DSC curves, which indicated that these samples were completely amorphous at ambient temperatures. It is very interesting to note that there are two glass transitions (as shown in Fig. 2),

and the two T_g s increase with increasing $[\text{Li}]/[\text{EO}]$ ratio (see Table 1). 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. The increase of T_g reflects the effective coordination of cation to polymer, which reduce the side chain mobility either by restricting the motion of the coordinated side chain or by forming physical crosslinks through the cations. Our previous work^[11] shows that the oxygen atoms of two situations ($\text{C}=\text{O}$, $\text{C}-\text{O}$) might coordinate with Li^+ , so T_{g2} also increases with the incorporation of LiClO_4 .

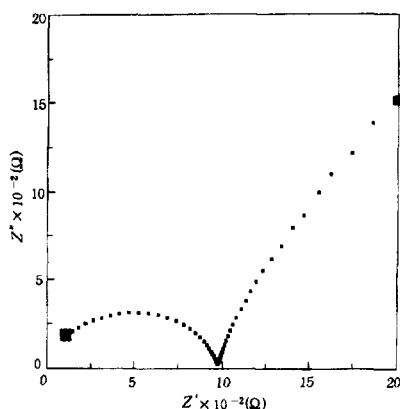


Fig. 1 Impedance plot at 40°C of a CP550/ LiClO_4 electrolyte ($[\text{Li}]/[\text{EO}]=0.05$) between two stainless steel electrodes. Frequency range: 1MHz—0.1Hz

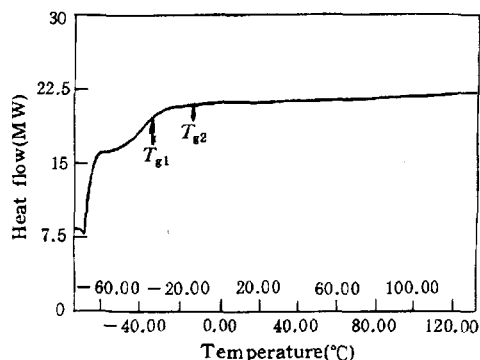


Fig.2 DSC trace of CP550/ LiClO_4 complex with $[\text{Li}]/[\text{EO}]$ ratio of 0.15

Table 1 Glass transition temperatures for CP550/ LiClO_4 complexes

$[\text{Li}]/[\text{EO}]$	$T_{g1} (^{\circ}\text{C})$	$T_{g2} (^{\circ}\text{C})$
0.01	-47.5	-28
0.05	-38.8	-18
0.10	-35.5	-9
0.15	-31.5	-5.5
0.20	-27.5	0
0.25	-24.0	6
0.30	-22.5	8.5
0.35	-19.0	10

The temperature dependence of the ionic conductivity of CP550/ LiClO_4 complex films over range 25—100°C is shown in Fig.3. The curvature in the plots indicates

that the ion transport obeys the WLF equation^[14]. Non-Arrhenius behaviour was first observed for PEO/salt and PPO/salt complexes and described by the Vogel-Tammann-Fulcher (VTF) equation^[15-17]:

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

where A is a pre-exponential term which is related to the concentration of the free charge carriers, B is pseudo-activation energy which is directly proportional to the free energy barrier. T_0 can be regarded as the temperature below which there is no further entropy loss due to configurational changes in the polymer. The VTF plots of CP550/LiClO₄ complexes show excellent linearity (Fig.4) when taking T_0 as $T_g - 50\text{K}$. The values of A and B listed in Table 2 are determined by using a computer-fitting technique. The free charge carrier concentration of sample No.4 is higher than that of sample No.3, however, the pseudo-activation energy of the former is higher, and the influence of parameter B to conductivity might be stronger than that of parameter A , thus sample No.4 is less conductive than sample No.3 (see Fig.3).

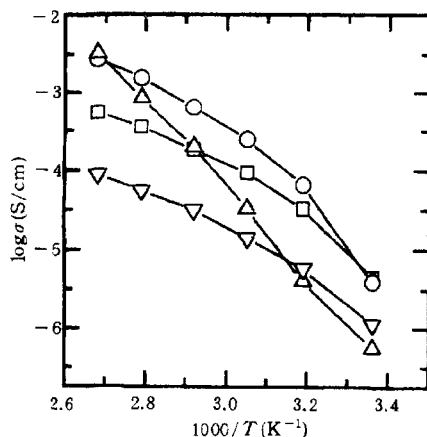


Fig.3 Variation of log (conductivity) with reciprocal temperature for CP550/LiClO₄ complexes with [Li]/[EO] ratios of (▽) 0.01; (□) 0.05; (○) 0.10; (△) 0.20

Table 2 Parameters for the CP550/LiClO₄ complexes derived from the VTF equation

No.	[Li]/[EO]	A	B
1	0.01	0.69	1200
2	0.05	3.7	1115
3	0.10	107	1421
4	0.20	19604	2282

The plots in Fig.3 show that the ionic conductivity varies with both temperature

and salt concentration. The latter dependence can be easily illustrated by examining isothermal plots of the log (conductivity) versus $[\text{Li}]/[\text{EO}]$ ratios as shown in Fig.5. At 25°C, 55°C and 85°C, three pronounced conductivity maxima i.e. 5.50×10^{-6} , 2.63×10^{-4} and 2.51×10^{-3} S/cm at $[\text{Li}]/[\text{EO}]$ ratios of 0.07, 0.10 and 0.14 respectively can be observed. These maxima move to higher salt concentrations as the temperature increases. Such a feature was also reported by Cowie et al.^[18] from their study of the $\text{PVMEO}_3/\text{LiClO}_4$ system. The showing of the maximum conductivity is due to two opposite effects^[19]. The charge carriers increase as more salt is added to the solid solutions of polymer but this increasing is finally offset by the increase of T_g which indicates the stiffening of the coordinated side chains. The coordinating ability of the side chains might increase with the increasing of temperature.

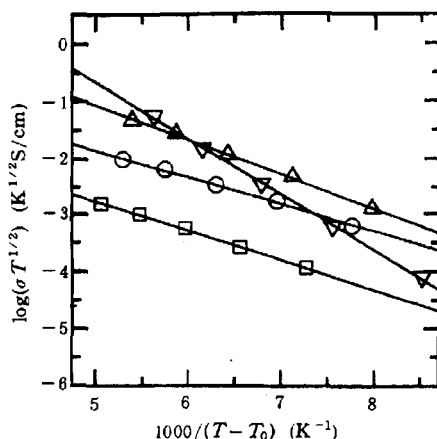


Fig.4 Data from Fig.3 plotted according to equation (1) with $[\text{Li}]/[\text{EO}]$ ratios of ($\square$) 0.01; ($\circ$) 0.05; ($\triangle$) 0.10; (∇) 0.20

The ionic conductivity of solid polymer electrolytes is governed by the mobility of side chains, ion-dipole interaction and the structure of complexes^[20]. So it is very important to study the cation-polymer interaction and get enough structural information for any detailed analysis of the ion transport mechanism. Papke^[21] and Torell^[22] have focused their attention on the structure of PEO/salt and PPO/salt complexes. They have studied the cation-polymer interactions extensively by both IR and Raman techniques and got satisfactory results. In our vibrational study of the $\text{CP550}/\text{LiClO}_4$ complexes, the main interest is focused on the changes of C—O—C vibrational modes. All $\text{CP550}/\text{LiClO}_4$ complexes have very similar IR spectra (as shown in Fig.6). Compared with pure CP550, some obvious differences can be found. Some slight shifting to lower wavenumber and broadening of the

1101.8cm^{-1} band does occur (see Table 3). This can be due to the coordination of Li^+ to ether oxygens. The new band at 624.8cm^{-1} of medium intensity in Fig.6(b) is characteristic of ClO_4^- . This band also shifts to lower wavenumber because of the coordination, but only slighter shifting in comparison with that of C—O—C .

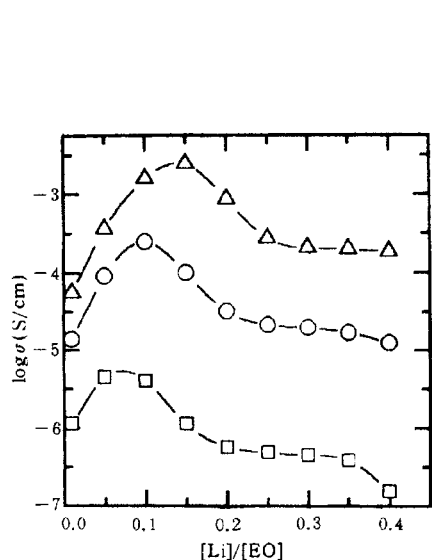


Fig.5 Variation of log (conductivity) with salt concentrations for CP550/ LiClO_4 complexes, measured at temperatures of 298K (□); 328K (○) and 358K (△)

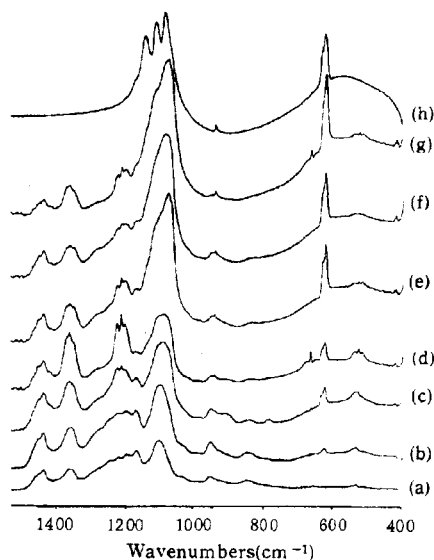


Fig.6 IR spectra for pure CP550 (a), LiClO_4 (h) and CP550/ LiClO_4 complexes with $[\text{Li}]/[\text{EO}]$ ratios of 0.01 (b); 0.1 (c); 0.2 (d); 0.3 (e); 0.4 (f) and 1.0 (g)

Table 3 The bands of C—O—C and ClO_4^- in the IR spectra (cm^{-1})

$[\text{Li}]/[\text{EO}]$	C—O—C	LiClO_4
0	1101.8	-
0.01	1100.0	624.8
0.1	1091.6	625.0
0.2	1090.8	625.7
0.3	1077.0	624.9
0.4	1080.9	625.5
1.0	1078.3	625.3
LiClO_4	-	627.3

Keywords:

Comb polymer; Lithium perchlorate; Ionic conductivity; Polymer electrolyte; Glass transition temperature

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