

## Comb polymer electrolytes

### Ionic conductivity and cation-polymer interaction

Liming Ding

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,  
Changchun 130022, People's Republic of China

Received: 8 April 1996/Revised version: 29 June 1996/Accepted: 2 July 1996

### Summary

Three comb polymers (CP) with oligo-oxyethylene side chains of the type  $-O(CH_2CH_2O)_nCH_3$  were prepared from methyl vinyl ether/maleic anhydride alternating copolymer. Homogeneous amorphous polymer electrolytes were made from CP and  $LiCF_3SO_3$  or  $LiClO_4$  by solvent-casting method, and their conductivities were measured as a function of temperature and salt concentration. The conductivity which displayed non-Arrhenius behaviour was analyzed using the Vogel-Tammann-Fulcher equation. The conductivity maximum appears at lower salt concentration when CP has longer side chains. XPS was used to study the cation-polymer interaction.

### Introduction

The potential application of solid polymer electrolytes in high energy density batteries and electrochromic windows has stimulated considerable investigation of the fundamental factors governing the ion-transport behaviour of these materials. Most attention has been paid to polymer electrolytes formed by dissolving alkali metal salts in PEO or PPO (PEO = poly(ethylene oxide), PPO = poly(propylene oxide)). PEO is undoubtedly the best solvating medium for a variety of metal salts. However, this material suffers from the drawback of forming a partially crystalline complex at room temperature. The low conductivities and poor mechanical properties preclude their room temperature application. 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 poly(methacrylic acid) (1-4), poly(itaconic acid) (5-6), polysiloxane (7-10), polyphosphazene (11-13) and polyglutamates (14-16) as the polymer backbone. These systems all show higher room temperature conductivities, when complexed with alkali metal salts, than those

corresponding PEO/salt electrolytes. We have prepared three comb polymers(CP) based on methyl vinyl ether/maleic anhydride alternating copolymer. The polymers are capable of dissolving many salts. In this paper the preliminary studies on the ionic conductivity of CP/salt electrolytes and cation-polymer interaction are reported.

## Experimental

### *Materials*

Poly(methyl vinyl ether-alt-maleic anhydride)(MA) and monomethylether of polyethylene glycols(PEGME)(MW350, 550 and 750) were supplied by Aldrich Chemical Co. Ltd., which were used without further purification. P-toluenesulfonic acid(PTSA, C.P. grade) was supplied by Shanghai 1st Chemical Reagent Factory, which was dried at 70°C under vacuum for 24h prior to use. Butanone(MEK) was refluxed in the presence of C.P. grade P<sub>2</sub>O<sub>5</sub> for 4h; methanol was dried over molecule sieve, type 4A, and then refluxed with metallic magnesium for 1h; acetone and hexane were both refluxed with CaH<sub>2</sub> for 4h. 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 N<sub>2</sub>. The mixture was stirred continuously for 24h 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 24h at 60°C. Then the reaction mixture was transferred to rotary evaporator for removal of the excess methanol. Thereafter, the product was purified by reprecipitation by using distilled acetone as solvent, and n-hexane as precipitant. Generally, four times of reprecipitation were necessary.

### *FTIR, NMR and Elemental Analysis*

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 <sup>13</sup>C NMR spectra of CP. Elemental analysis was performed with a Model 1106 Elemental Analyzer provided by Carlo Erba Strumentazione Co..

### *Film preparation*

Anhydrous LiCF<sub>3</sub>SO<sub>3</sub> and LiClO<sub>4</sub> (Aldrich) were dried under reduced pressure(10<sup>-3</sup> torr) at 130°C for 24h 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 acetone was allowed to evaporate at room temperature under a N<sub>2</sub> 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 dc conductivity measurements.

#### *Dc conductivity measurements*

The dc 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 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 -70~135°C. The glass transition temperatures( $T_g$ ) were determined as the midpoints of the heat capacity change during the relaxation temperature.

#### *X-ray photoelectron spectroscopy*

XPS spectra were obtained on a VG Scientific ESCALAB MKII Spectrometer with a Al-K $_{\alpha}$  x-ray source. Power: 14KV/20mA; Crevice: 5×6mm; Vacuum pressure: 5×10<sup>-8</sup> mbar.

## **Results and Discussion**

Scheme 1 summarizes the synthetic route for the comblike polymer host based on alternating maleic anhydride copolymer backbone. During the synthesis process, 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 a completely soluble product CP could be acquired. The IR spectrum of the purified final product CP350(n=7) is shown in Fig.1, both the absorption peaks at 1857.8 and 1779.2 cm<sup>-1</sup> are absent, indicating that the anhydride has been converted completely. The strong absorptions at 1732.4 and 1101.8 cm<sup>-1</sup> show that the product is a polyester of poly(ethylene glycol). The <sup>13</sup>C NMR spectrum of CP750(n=17) is shown in Fig.2. The assignment of the signals in the 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 and g, 32.1ppm. Table 1 shows the results of elemental analysis. All of the above characterization results confirmed the structures of the three products CP350, CP550 and CP750.

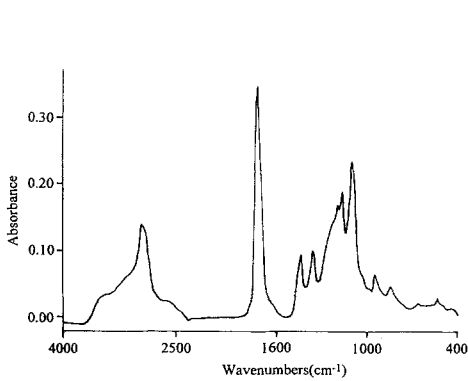


Fig.1 IR spectrum of CP350

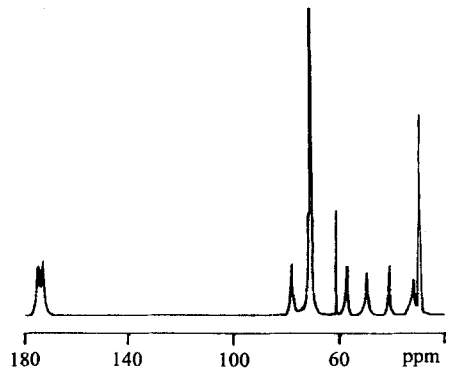
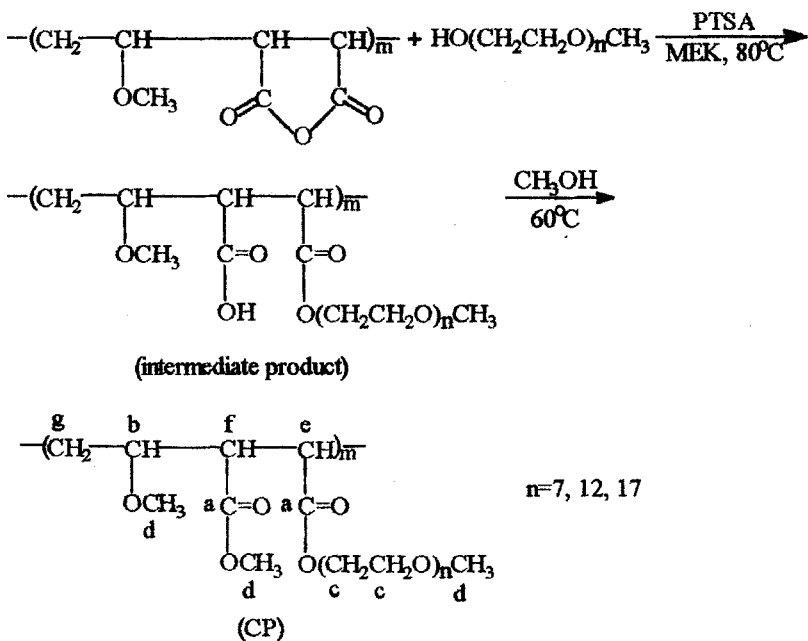
Fig.2 <sup>13</sup>C NMR spectrum of CP750

Table 1 Elemental analysis

	Calculated		Found	
	C	H	C	H
CP350(C <sub>23</sub> H <sub>42</sub> O <sub>12</sub> )	54.11	8.29	54.14	8.32
CP550(C <sub>33</sub> H <sub>62</sub> O <sub>17</sub> )	54.23	8.55	54.28	8.49
CP750(C <sub>43</sub> H <sub>82</sub> O <sub>22</sub> )	54.30	8.69	54.39	8.73



(Scheme 1)

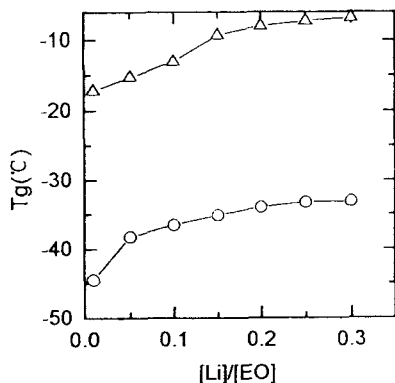


Fig.3 Variation of glass transition temperature with salt concentration for CP350/LiCF<sub>3</sub>SO<sub>3</sub> complexes. T<sub>g1</sub>(○), T<sub>g2</sub>(△).

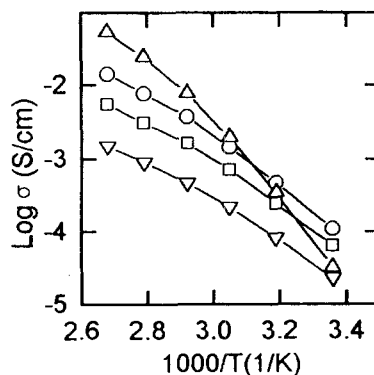


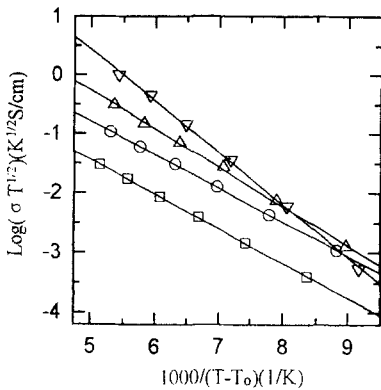
Fig.4 Plots of  $\log \sigma$  versus  $1000/T$  for CP350/LiCF<sub>3</sub>SO<sub>3</sub> complexes. [Li]/[EO]= 0.01(▽); 0.05(□); 0.10(○); 0.20(△).

CP350/LiCF<sub>3</sub>SO<sub>3</sub> 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, and the two T<sub>g</sub>s increase with increasing [Li]/[EO] ratio (as shown in Fig.3). The side chains are more flexible than -C-C-C-C- backbone, so T<sub>g1</sub> and T<sub>g2</sub> can be attributed to the glass transition temperature of oligo-oxyethylene side chains and polymer backbone respectively. The increase of T<sub>g</sub> reflects the effective coordination of cation to polymer, which reduces the side chain mobility either by restricting the motion of the coordinated side chain or by forming physical crosslinks through the cations(17). If the -COO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>CH<sub>3</sub> groups in CP are defined as the side chains, the remaining backbone still consists of polar groups, i.e., -OCH<sub>3</sub>, -COOCH<sub>3</sub>, which can also interact with Li<sup>+</sup> effectively as suggested by XPS studies, thus T<sub>g2</sub> increases with the increase of salt content. This contrasts finely with Watanabe's work(8) in which the T<sub>g</sub> of the siloxane backbone remained unchanged owing to the absence of polar groups attaching to the remaining backbone. The preliminary DSC studies on CP550/salt complexes gave the similar results except for the lower T<sub>g1</sub>.

The temperature dependence of the ionic conductivity of CP350/LiCF<sub>3</sub>SO<sub>3</sub> complex films over range 25-100°C is shown in Fig.4. The curvature of the plots suggests non-Arrhenius behaviour which was first observed for PEO/salt and PPO/salt complexes and described by the Vogel-Tammann-Fulcher(VTF) equation(18-20):

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

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<sub>0</sub> 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 CP350/LiCF<sub>3</sub>SO<sub>3</sub> complexes show excellent linearity(Fig.5) when taking T<sub>0</sub> as T<sub>g1</sub>-50K. The values of A and B listed in Table 2 are determined using a computer-fitting technique. A<sub>4</sub> >> A<sub>3</sub>, so the free



**Fig.5** Plots according to VTF equation.  
 $[\text{Li}]/[\text{EO}] = 0.01 (\square)$ ;  $0.05 (\circ)$ ;  $0.10 (\triangle)$ ;  
 $0.20 (\nabla)$ .

**Table 2** Parameters for the CP350/LiCF<sub>3</sub>SO<sub>3</sub> complexes derived from the VTF equation

No.	$[\text{Li}]/[\text{EO}]$	A	B
1	0.01	28	1331
2	0.05	110	1303
3	0.10	1023	1506
4	0.20	64565	2017

charge carrier concentration of sample No.4 is much higher than that of sample No.3, however, the pseudo-activation energy of the former is also higher, and the influence of parameter B on conductivity might be stronger than that of parameter A at lower temperatures, thus sample No.4 is less conductive than sample No.3 (see Fig.4).

The salt concentration dependence of ionic conductivity can be easily illustrated by examining isothermal plots of the  $\log(\text{conductivity})$  versus  $[\text{Li}]/[\text{EO}]$  ratios as shown in Fig.6. At 25°C, 55°C and 85°C, three pronounced conductivity maxima, i.e.,  $5.50 \times 10^{-6}$ ,  $2.63 \times 10^{-4}$  and  $2.51 \times 10^{-3}$  S/cm at  $[\text{Li}]/[\text{EO}]$  ratios of 0.07, 0.10 and 0.14 respectively can be observed. The showing of the conductivity maxima is due to two opposite effects. 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 microviscosity(1) which indicates the stiffening of the coordinated side chains. The free volume model is very useful for discussion of 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(21). 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 maximum moves to a higher salt concentration as the temperature increases.

Fig.7 shows the effect of length of side chains on ionic conductivity. The conductivity maximum appears at lower salt concentrations when CP has longer side chains. This might be due to the stronger interaction between the longer side chains and  $\text{Li}^+$ . The increase of

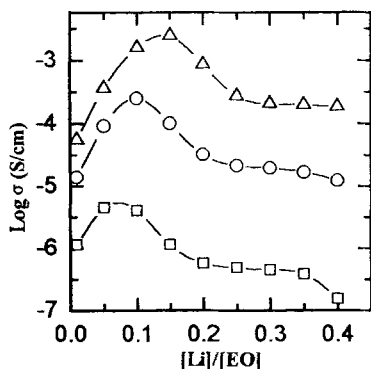


Fig.6 Variation of  $\log \sigma$  with salt content for CP550/LiClO<sub>4</sub> complexes. 298K( $\square$ ), 328K( $\circ$ ) and 358K( $\Delta$ ).

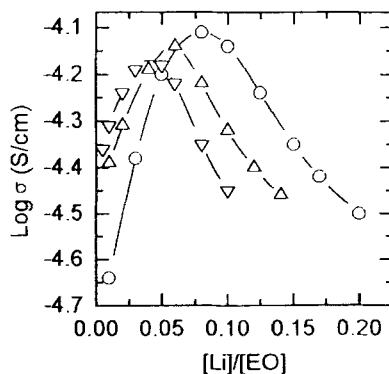


Fig.7 LiCF<sub>3</sub>SO<sub>3</sub> salt content dependence of ionic conductivity for CP350( $\circ$ ), CP550( $\Delta$ ), and CP750( $\nabla$ ) complexes.

microviscosity with salt content would be more extensive in CP/salt complexes with longer side chain, while the local viscosity has the greatest effect on the ionic mobility. Fig.7 also shows that CP/LiCF<sub>3</sub>SO<sub>3</sub> complex with longer side chains exhibits a higher ionic conductivity at low salt concentrations. It suggests that the stronger interaction between the longer side chains and Li<sup>+</sup> promote the dissociation of LiCF<sub>3</sub>SO<sub>3</sub>. This is in good agreement with the findings reported by Tsuchida et al.(1).

The ionic conductivity of solid polymer electrolytes is controlled by the mobility of side chains, ion-dipole interaction and the structure of complexes. So it is very important to study the cation-polymer interaction and get enough structural information for us to study the ion transport mechanism. The cation-polymer interactions have been studied extensively by IR and Raman techniques. Here, the preliminary results of XPS study is presented(as shown in Table 3). When LiClO<sub>4</sub> is added to CP350, the binding energies of

Table 3 XPS binding energies(eV) of various core level electrons in CP350, CP350/LiClO<sub>4</sub> complexes and LiClO<sub>4</sub>.

[Li]/[EO]	C <sub>1s</sub>			O <sub>1s</sub>		Cl <sub>2p</sub>
	C-H	C-O	C=O	C-O	C=O	
0	284.6	286.1	288.1	531.3	532.7	
0.01	284.6	286.1	288.1	530.5	531.9	206.6
0.1	284.6	286.1	288.1	530.7	532.1	207.3
0.5	284.6	286.1	288.1	530.8	532.3	207.5
1.0	284.6	286.1	288.1	530.9	532.4	207.7
LiClO <sub>4</sub>				532.5		208.2

\* Take the binding energy of C<sub>1s</sub>(283.7eV) resulting from trace impurity on the sample surface as the reference.

$O_{1s}$  and  $Cl_{2p}$  decrease, while there is no change in binding energy of  $C_{1s}$ . The coordination between the ether oxygen and  $Li^+$  makes the electron cloud of the C-H bond shift toward oxygen, and this increases the electron cloud density of oxygen, thus decreases the binding energy of  $O_{1s}$ . This result suggests that the oxygen atoms of two situations (C-O, C=O) might coordinate with  $Li^+$ . The solvation of CP350 makes  $LiClO_4$  ionize to ions and ion pairs, so the interaction between  $Li^+$  and  $ClO_4^-$  becomes weaker and the binding energy of  $Cl_{2p}$  becomes lower. But when salt content gets to a certain value, the contents of salt molecules and salt aggregates begin to increase, this would lead to the increasing of binding energy of  $Cl_{2p}$ .

## References

1. N. Kobayashi, M. Uchiyama, K. Shigehara, and E. Tsuchida (1985) *J. Phys. Chem.* 89: 987
2. N. Kobayashi, T. Hamada, H. Ohno, and E. Tsuchida (1986) *Polym. J.* 18: 661
3. E. Tsuchida, H. Ohno, N. Kobayashi, and H. Ishizaka (1989) *Macromolecules* 22: 1771
4. H. Nagasaka and M. Watanabe (1995) *Synth. Met.* 69: 557
5. J. M. G. Cowie and A. C. S. Martin (1985) *Polym. Commun.* 26: 298
6. J. M. G. Cowie, R. Ferguson, and A. C. S. Martin (1987) *Polym. Commun.* 28: 130
7. P. G. Hall, G. R. Davies, J. E. McIntyre, I. M. Ward, D. J. Bannister, and K. M. F. Le Brocq (1986) *Polym. Commun.* 27: 98
8. M. Watanabe, S. Nagano, K. Sanui, and N. Ogata (1987) *J. Power Sources* 20: 327
9. I. M. Khan, Y. Yuan, D. Fish, E. Wu, and J. Smid (1988) *Macromolecules* 21: 2684
10. R. Spindler and D. F. Shriver (1988) *Macromolecules* 21: 648
11. K. Inoue, Y. Nishikawa, and T. Tanigaki (1991) *Macromolecules* 24: 3464
12. Y. Tada, M. Sato, N. Takeno, Y. Nakacho, and K. Shigehara (1993) *Macromol. Chem.* 194: 2163
13. Y. Tada, M. Sato, N. Takeno, Y. Nakacho, and K. Shigehara (1994) *Chem. Mater.* 6: 27
14. M. Watanabe and N. Ogata (1988) *Br. Polym. J.* 20: 181
15. Y. Yamaguchi, S. Aoki, M. Watanabe, K. Sanui, and N. Ogata (1990) *Solid State Ionics* 40/41: 628
16. M. Watanabe, S. Aoki, K. Sanui, and N. Ogata (1993) *Polym. Adv. Techn.* 4: 179
17. J. M. G. Cowie, R. Ferguson, and S. Billotte (1993) *Polym. Adv. Techn.* 4: 139
18. H. Vogel (1921) *Phys. Z.* 22: 645
19. V. G. Tammann and W. Hesse (1926) *Z. Anorg. Allg. Chem.* 156: 245
20. G. S. Fulcher (1925) *J. Am. Ceram. Soc.* 8: 339
21. M. A. Ratner and D. F. Shriver (1988) *Chem. Rev.* 88: 109