

# The effects of salt concentration on ion state and conductivity in comb cross-linked polymer electrolytes

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A new type of comb cross-linked polyurethane/acrylate polymer was designed. The polymer has sparse network structure with many long comb molecule chains. A new solid polymer electrolyte (SPE) was prepared based on the polymer. The salt in the solid polymer electrolytes has different existent states with different salt contents. With increase of salt concentration, the ion pairing gradually becomes important existent form of salt, and  $T_g$  value of the SPE increases. At the same time, ionic conductivity increases rapidly. It is possible to design novel solid polymer electrolytes with high ionic conductivity to meet practical application by comb cross-linked polymer with high salt content. © 2003 Kluwer Academic Publishers

## 1. Introduction

Solid polymer electrolytes are of great interest for the potential applications of flexible, plastic ion transporting medium in vital modern electrochemical device such as high energy density batteries and all-solid-state rechargeable lithium batteries [1]. Early in the history of the SPEs, ion transport inside crystalline PEO-helices was believed to be the prime contributor [2]. Since first shown by Berthier *et al.* [3], it becomes consensus now that ion conduction takes place mainly in the amorphous phase above the glass transition temperature. The conduction mechanism was focused on creation of free volume arising from the dynamics of the polymer chains in the amorphous phase, depending on free ions as charge carriers. So almost all new polymer electrolytes were designed by suppressing crystallinity of the polymer and increasing the concentration of free ions. However, it was found that the maximum conductivity of polymer electrolytes, resigned according to the conduction mechanism, was still insufficient for many lithium battery applications [4]. At the same time, as most studies about conduction mechanism were built on the PEO/salt system, some experimental results from other polymer electrolytes systems couldn't be explained by the conduction mechanism. In recent years, the conduction in the crystalline region was attached importance to over again, and some good studies were done [4, 5]. The latest studies by P.G. Bruce *et al.* showed that, in contrast to the prevailing view, ionic conductivity in the static, ordered environment of the crystalline phase can be greater than that in the equivalent amorphous material above  $T_g$  [6].

In this work, a kind of comb cross-linked polymer, with sparse network and long comb chains, was designed. Fig. 1 showed the structure schemes of different polymers. We prepared a type of comb cross-linked polymer electrolyte by polyurethane and polyacrylate complex. The interrelations among salt concentration, ion states and conductivity were mainly investigated.

## 2. Experimental

### 2.1. Material

2,4-toluene diisocyanate(TDI) (Aldrich Chemical Co.), poly(propylene glycol) (PPG  $M_n = 1000$ ) (Shandong Dahua Chemical plant), 2-hydroxyethyl methacrylate (2-HEMA) (C.R.grade Tianjing Chemical Reagent Experimental Factory), poly(ethylene glycol) (PEG) ( $M_n = 600$ , Aldrich Chemical Co.), dibutyltindilaurate were used. TDI was vacuum-distilled before used. The inhibitor in 2-HEMA was removed through a removing column. 2,2-Azobisisobutyronitrile (AIBN) (A.R. grade, Aldrich Chemical Co.) was dried at 30°C in a decompressed condition after recrystallized. Dioxane and formamide (Shanghai Solvent Factory) were used as received. Lithium perchlorate(LiClO<sub>4</sub>) (A.R. grade, Shanghai Chemical Reagent Factory) was dried at 120°C in a vacuum oven for 10 h before use.

### 2.2. Synthesis of PEG-modified urethane acrylate macromonomer (PEG-UA)

Three-step processes synthesized PEG-UA macromonomer. Firstly, TDI and PPG were poured

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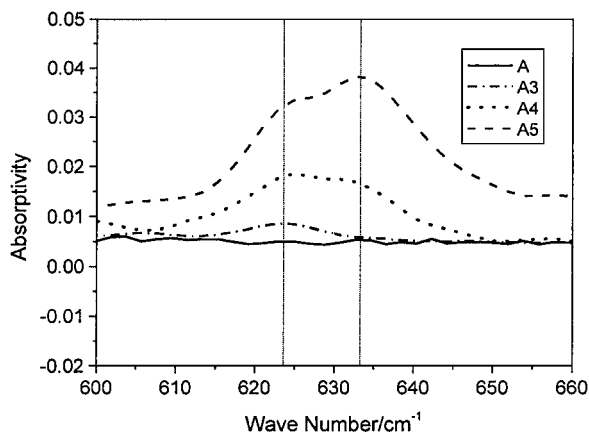


Figure 2 Raman band associated with  $\text{ClO}_4^-$  bending mode at 298 K.

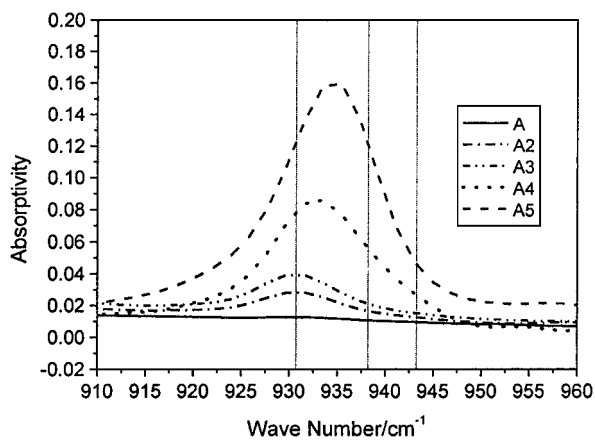


Figure 3 Raman band associated with  $\text{ClO}_4^-$   $\nu_1$  mode at 298 K.

### 3.2. The effects of salt concentration on ion states

In recent years, Raman spectroscopy studies were known to be very useful to analyze ion-ion interaction in polymer electrolytes [10, 11]. Figs 2 and 3 showed the change of position and shape of the characteristic bands of the perchlorate anion in electrolytes with increasing of salt concentrations. Fig. 2 shows the bending mode of  $\text{ClO}_4^-$  anion, which was separated into two contributions (Fig. 4). The lower frequency component (about  $623\text{ cm}^{-1}$ ) is attributed to “free”

perchlorate anions, whereas the higher frequency component (about  $633\text{ cm}^{-1}$ ) can be associated with the presence of ion pairings [10]. In the spectra of the polymer electrolytes, the most intense feature is the band around  $934\text{ cm}^{-1}$  (Fig. 3), which is responded to with the symmetric stretching mode of the anion ( $\nu_1$  mode). The band could be divided into three peaks, which correspond to each of the three kinds of perchlorate ion modes. The first peak, around  $931\text{--}934\text{ cm}^{-1}$ , responds to free-ions. The peak, around  $938\text{ cm}^{-1}$ , was used to identify the ion pair. The appearance of a sharp peak at  $953\text{ cm}^{-1}$  showed the form of ionic aggregates [11].

Shown in Figs 2–4, when the salt content was under 15 wt%, almost all salt existed as free ions. With increasing salt content, the ratio of free ions in the electrolytes decreases continually. The ratio of ion pairing greatly increased with increasing salt content from 21.4 wt% to 26 wt%, and the ion pairing was the main form for salt in the latter.

P.G. Bruce *et al.* have carefully studied the structural feature of some PEO/salt systems [4, 12]. They attained some important results about ion-polymer substructure (or ion states) with different salt contents. According to some former studies [13, 14], possible ion states in the comb cross-linked polymer electrolytes were shown in Fig. 5. In the electrolytes with low salt content, a free cation was coordinated only by several ether oxygens, without anions. For single ion pairing, the cation was coordinated by several ether oxygens and one anion. When salt content increased continually, several cations and anions coordinated each other with ether oxygens, which was multi-ion pairing. When some cations were surrounded by anions only, the ionic aggregates formed.

### 3.3. The effects of salt concentration on $T_g$

The thermal properties of the electrolytes with different salt concentration were studied by DSC. There is an obvious glass transition in the DSC trace, which corresponds to the transition of soft segment in the amorphous region. Both Fig. 6 and Table II showed changes of  $T_g$  and  $\Delta C_p$  corresponding to the soft segment with increasing  $\text{LiClO}_4$  content in the electrolytes. The  $T_g$  value increases from  $-36.9^\circ\text{C}$  to  $-15.4^\circ\text{C}$  with

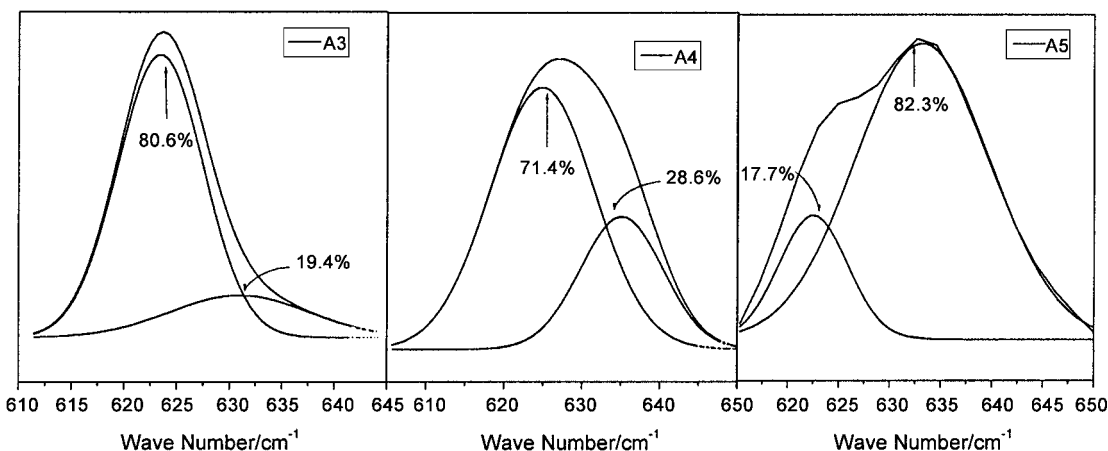


Figure 4 Raman band associated fitted by the sum of lorentzian lines.

TABLE II DSC data of the comb crosslinking polymer and electrolytes

Samples	$T_g/^\circ\text{C}$		$\Delta C_p/J/g \cdot ^\circ\text{C}$
	Onset	Midpoint	
A	-43.049	-36.901	0.815
A1	-37.449	-30.492	0.804
A2	-32.256	-23.688	0.608
A3	-28.055	-15.405	0.406
A4	-29.785	-26.488	0.225

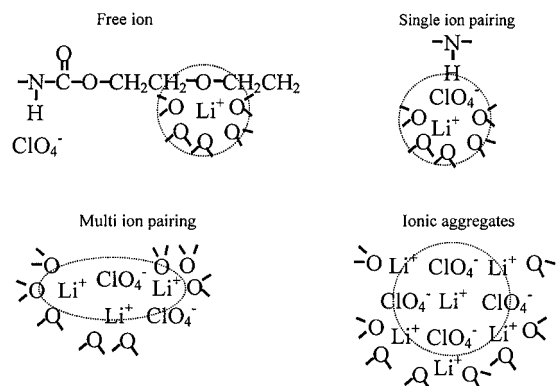


Figure 5 Schematics of possible ion states in polymer electrolytes.

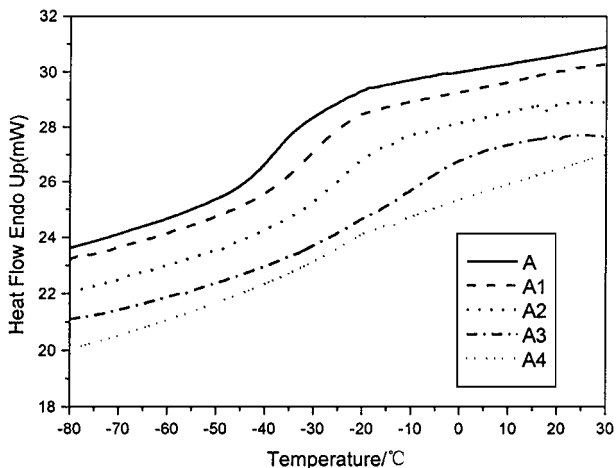


Figure 6 DSC cure of polymer electrolytes with different salt concentrations.

increasing  $\text{LiClO}_4$  content from 0 to 15 wt%. The cause is that the polyether chain stiffens due to the interactions between the salt ions and the polyether oxygens. The decrease of  $\Delta C_p$  also indicates the ability of chain movement was poorer with increasing salt content. This is consistent with the previous reports [15, 16].

From Fig. 6, we could also find an extraordinary result that the sample A4 only had a faintness  $T_g$  transition at a lower temperature than A3. The variation of soft segment  $T_g$  values with salt concentration can be explained on the basis of interactions between various types of ion states and the polyether chain mentioned above. When salt concentration was under 15 wt% (A3), almost all salt was transformed into free ions, which were coordinated by enough ether oxygens. When salt concentration was 21 wt% (A4), the ether oxygens, which could coordinate cations, were

exhausted. Some cations had to form ion pairings with far fewer oxygens. So the soft segment was very rigid. From the above, we could suggest that each free  $\text{Li}^+$  cation is most probably coordinated by six contiguous ether oxygens, which is consistent with some previous reports [4, 17].

### 3.4. The effects of salt concentration and temperature on the ionic conductivity

Fig. 7 shows the temperature dependence of ionic conductivities of the SPEs with different salt concentration. The conduction behavior could be divided into two types obviously. For the sample A1 and A2, the conduction behavior obeys Arrhenius equation:

$$\sigma = A \exp[-E_a/RT]$$

where  $A$  is pre-exponential factor,  $E_a$  the activation energy and  $T$  the temperature in Kelvin [18]. For samples A3, A4 and A5, the conductivity curve has a turning point at about 298 K. The conductivities increased slowly under 298 K, and the increase became faster above 298 K. The Fig. 8 shows the salt concentration dependence of conductivities of electrolytes with different temperature. The effect was slight when the salt concentration was low. The ion conductivities almost

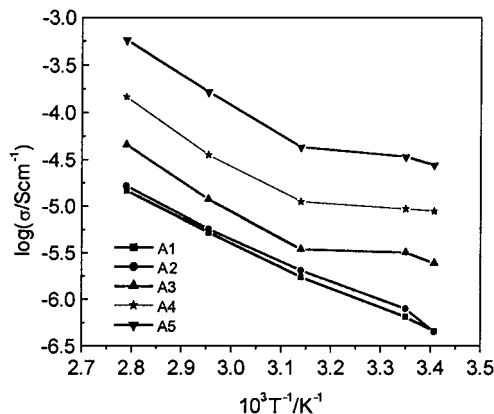


Figure 7 Temperature dependence of the conductivity for polymer electrolytes with different salt concentration.

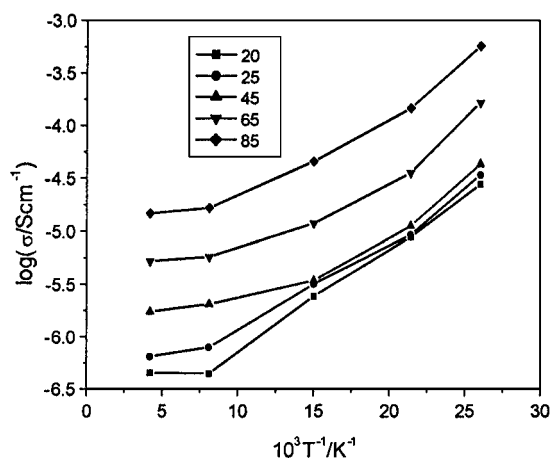


Figure 8 Salt concentration dependence of the conductivity for polymer electrolytes.

had no difference between the electrolytes containing 4 wt% and 8 wt% salt content. With increasing salt concentration, the increase in rate of ionic conductivity got progressively faster. The conductivity increased more than five times when salt increased from 21.4 wt% (A4) to 26 wt% (A5).

We had attained similar outcomes from several other systems before, such as hyperbranched polyurethane [19], which couldn't be explained by the prevalent conduction mechanism. Some researchers also gave accordant results, and then they hadn't given the reason for it [20].

Most of the studies indicated that the charge carriers mainly came from free ions, and ion pairing may effectively trap the mobile cations [21]. In fact, free ions are stable and not "free" due to strong lithium oxygen interactions. According to calculations, the energy of per Lithium-ether oxygen bond was above  $100 \text{ kJ} \cdot \text{mol}^{-1}$  [22]. The lithium transference number is too low.

As shown by Bruce PG etc, if the sites to which an ion migrates are already present in the polymer electrolyte owing to its structure, then as soon as the vibrating ion gains sufficient energy to hop, migration will take place [6]. The ion pairing also could gain sufficient energy to hop and allow migration to take place, due to a weaker ion pairing ( $\text{ClO}_4^-$ - $\text{Li}^+$ -5PEO) interaction [17].

#### 4. Conclusions

When salt content is low, the free ion is the main form of salt in the electrolyte. When the polymer-salt ratio ( $-\text{O}-:\text{Li}^+$ ) was less than 6:1, the ratio of ion pairing increased with increasing salt content. The ion pairing became the important existent form of salt in the electrolyte. Somewhat unexpectedly, the ionic conductivity increased greatly, the increase rate of conductivity got progressively faster during a definite range. In this condition, ion pairing conduction perhaps is a kind of conduction form to gain high ionic conductivity in SPE.

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