

Composite Polymer Electrolytes Based on the Low Crosslinked Copolymer of Linear and Hyperbranched Polyurethanes

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Received 9 July 2006; accepted 5 December 2006

DOI 10.1002/app.26064

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Low crosslinked copolymer of linear and hyperbranched polyurethane (CHPU) was prepared, and the ionic conductivities and thermal properties of the composite polymer electrolytes composed of CHPU and LiClO_4 were investigated. The FTIR and Raman spectra analysis indicated that the polyurethane copolymer could dissolve more lithium salt than the corresponding polymer electrolytes of the non crosslinked hyperbranched polyurethane, and showed higher conductivities. At salt

concentration $\text{EO/Li} = 4$, the electrolyte CHPU30- LiClO_4 reached its maximum conductivity, $1.51 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C . DSC measurement was also used for the analysis of the thermal properties of polymer electrolytes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3607–3613, 2007

Key words: hyperbranched polymer; ionic conductivity; polymer electrolytes; polyurethane; crosslinked copolymer

INTRODUCTION

The ionic conductivity of polymers complexed with a variety of inorganic salts has been widely studied because these complexes as polymer electrolytes have potential applications such as all-solid-state batteries, electrochemical cells, and electrochromic devices. However, there are serious impediments to the commercialization of the above applications. The most significant drawback of the conventional polymer electrolytes is their low conductivity at ambient temperature. Large research efforts have been devoted to form networks, comb-like polymers with short ethylene glycol side chains, and copolymers with other units and adding plasticizers.^{1–2}

Hyperbranched polymers are interesting materials as a matrix polymer because they are completely amorphous, highly soluble, and highly processable, and have many branch-ends that could greatly contribute to ionic conduction.^{3–5} But the nonentangled state of hyperbranched macromolecules imposes rather poor mechanical properties and results in brittle polymer. This disadvantage could be avoided by copolymerized or mixed with linear polymer.

In our previous work,⁶ polymer electrolytes based on the hybrid of linear and hyperbranched polyurethane (MHPU) was investigated. It was found that the hyperbranched polymer could function as a

“solvent” for the lithium salt and was helpful to prevent the formation of ion-pair and aggregates. This performance was helpful to increase the conductivity in relation to the linear polyurethane electrolytes. We also compared the polymer electrolytes based on the linear polyurethane (LPU), hybrid of linear and hyperbranched polyurethane (MHPU), and copolymer of linear and hyperbranched polyurethane (CHPU) at an EO/Li ratio of 4.⁷ The copolymerization between hyperbranched and linear polyurethane in CHPU improved the coordination degree between Lithium ion and polymer and prevented the formation of ion-pair and aggregates further. In this work, composite polymer electrolytes composed of CHPU and LiClO_4 were investigated. The dependence of the ionic conductivity upon the lithium salt concentration, hyperbranched polymer concentration, and the correlation of these dependences upon the evolution of the microstructures were studied. The dependence of the ionic conductivity upon the lithium salt concentration, hyperbranched polymer concentration, and the correlation of these dependences upon the evolution of the microstructures were studied.

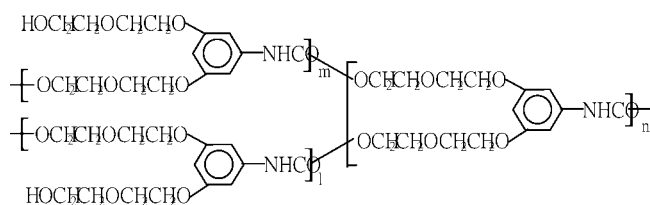
EXPERIMENTAL

Materials

LiClO_4 was dried under reduced pressure prior to use. The linear polyurethane (LPU) was synthesized from 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD), PEO ($M_n = 1000$). The molar ratio

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of MDI : BD : PEO was 3 : 2 : 1. The synthesis procedure of the hyperbranched polyurethane (HPU) has been described in detail in our previous report.⁸ The structural formula was showed as follows. The molecular structure in each pair of brackets is a defined repeat unit, containing four $\text{CH}_2\text{CH}_2\text{O}$ groups.



Low crosslinked copolymer of linear and hyperbranched polyurethane (CHPU) was synthesized using the synthesis procedure of LPU. Part of BD was replaced by HPU which had many hydroxyl groups in the terminal. Low crosslinked copolymer was acquired by controlling the ratio of NCO/OH. The weight percent of hyperbranched polyurethane in copolymer was to be 10%, 20%, and 30% (CHPU10–30). The hybrid of linear and hyperbranched polyurethane (MHPU30) contained 30% of HPU.

Preparation of polymer electrolyte film

The CHPU and LiClO_4 were solvated in THF; then the solution was cast into a Teflon plate. A film formed at ambient temperature, and it was dried in a vacuum oven for 48 h at 60°C . The salt concentration was from an EO/ Li^+ ratio of 2 to 30 (EO is the number of the ether oxygen).

Measurement

The IR spectra were recorded at ambient temperature on a Perkin–Elmer model 963 FTIR spectrophotometer

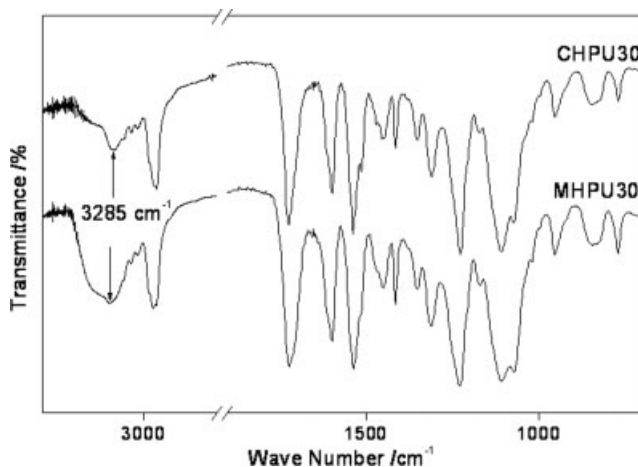


Figure 1 The FTIR spectra for the copolymer CHPU30 and the hybrid MHPU30.

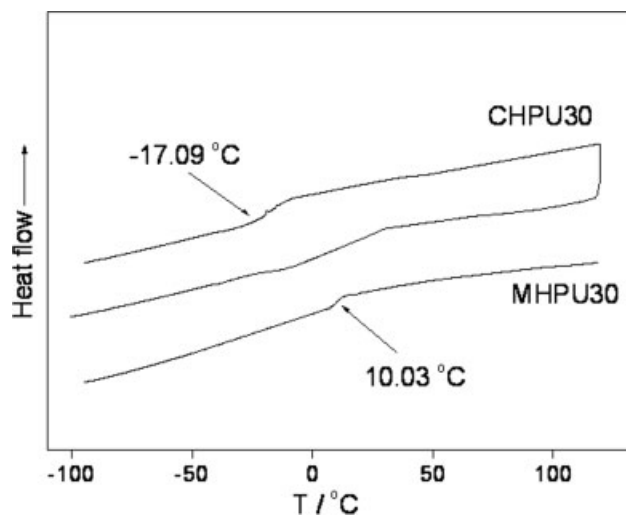


Figure 2 The DSC curve for the copolymer CHPU30 and the hybrid MHPU30.

in the range of $400\text{--}4000\text{ cm}^{-1}$ with a wave number resolution of 2 cm^{-1} . The Raman spectra were performed at room temperature in the range of $50\text{--}3500\text{ cm}^{-1}$ with a wave number resolution of 2 cm^{-1} . The spectra were recorded on a Bruker model EQUINOX-55 Infrared-Raman spectrophotometer with a Raman module FRA 106 and a near infrared YAG laser with wavelength 1064 nm . The electrolyte system with a HPU/CHPU ratio of 30% had good mechanical properties and was selected in the spectroscopic analysis. Band deconvolution of the FTIR and Raman spectra was obtained by using a Gaussian-Lorentzian sum. The maximum error associated with the fit was estimated to be 5%.

The thermal properties of the polymer matrix and the polymer electrolytes were studied by means of differential scanning calorimeter (DSC; Perkin–Elmer-Pyris-1) under a nitrogen atmosphere. The sample was cooled to -100°C and heated to 120°C at a rate of $10^\circ\text{C min}^{-1}$.

The complex impedance spectra were measured from 25°C to 100°C using a Hewlett–Packard 4192A LF impedance analyzer over a frequency range of 1 Hz to 1M Hz. The films were cut to a required size (10 mm in diameter and 0.2–0.3 mm thick) and were sandwiched between two copper electrodes.

RESULTS AND DISCUSSION

Characterization of the low crosslinked copolymer

Figure 1 shows the IR spectra of the copolymer CHPU30 and the hybrid of MHPU30. The band centered at about 3285 cm^{-1} was attributed to the stretching of hydroxyl groups. The band of MHPU30 was broader than that of CHPU30. HPU contained

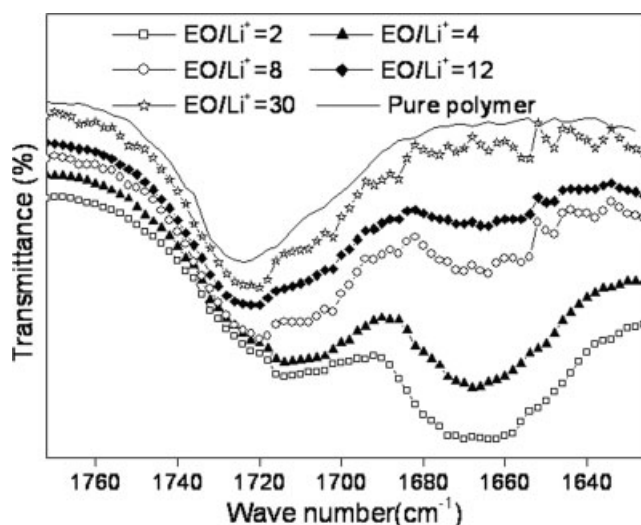


Figure 3 The FTIR spectrum (carbonyl) of CHPU30-LiClO₄ samples.

in the hybrid had many hydroxyl groups in the terminal. The association between the hydroxyl groups made this band obviously broader, while in the copolymer part of the terminal hydroxyl had taken part in the copolymer reactions.

DSC curves of the copolymer CHPU30 and the hybrid of MHPU30 are presented in Figure 2. From the curves, glass-transition temperature (T_g) for CHPU and MHPU was -17.09 and 10.34°C , respectively. The copolymer has the lower T_g than the hybrid. This result indicated that the mobility of segments in the copolymer is higher than that in the hybrid, and could enhance the ionic conductivity.

Characterization of the polymer electrolytes

FTIR spectra analysis

Figure 3 shows the carbonyl absorption peaks of the CHPU30-LiClO₄ samples with different salt concentration. All the carbonyl absorption curves were normalized to the free urethane carbonyl group region (around 1725 cm^{-1}) to compensate for differences in signal intensity due to varying sample thickness and the sample composition. The band centered at about 1726 cm^{-1} (peak I) was attributed to the stretching of free urethane carbonyl groups, whereas the band at about 1703 cm^{-1} (peak II) was assigned to the bonding degree of Li⁺ with carbonyl groups⁹⁻¹¹ (Fig. 4). A constant baseline had been subtracted in the deconvolution figures to do the analysis.

It was interesting to find that a third band centered at about 1668 cm^{-1} appeared in some curves. According to our research, this band was not observed at low salt concentration ($\text{EO/Li} \geq 30$). This band which was not observed in our previous hybrid system⁷ could be attributed to bonded carbonyl groups and might be related to the characteristics of carbonyl groups in the copolymer of linear and hyperbranched polyurethane. It was obviously that this low cross-linked structure improved the coordination degree of carbonyl groups with Lithium ion further.

The deconvolution of the carbonyl region by Gaussian function was performed and listed in Table I. The areas of the bonded urethane carbonyl groups (peak II + III) increased with increasing salt concentration. This was attributed to the fact that the ionic coordination between free urethane carbonyl and Li⁺ increased with increasing salt concentration.

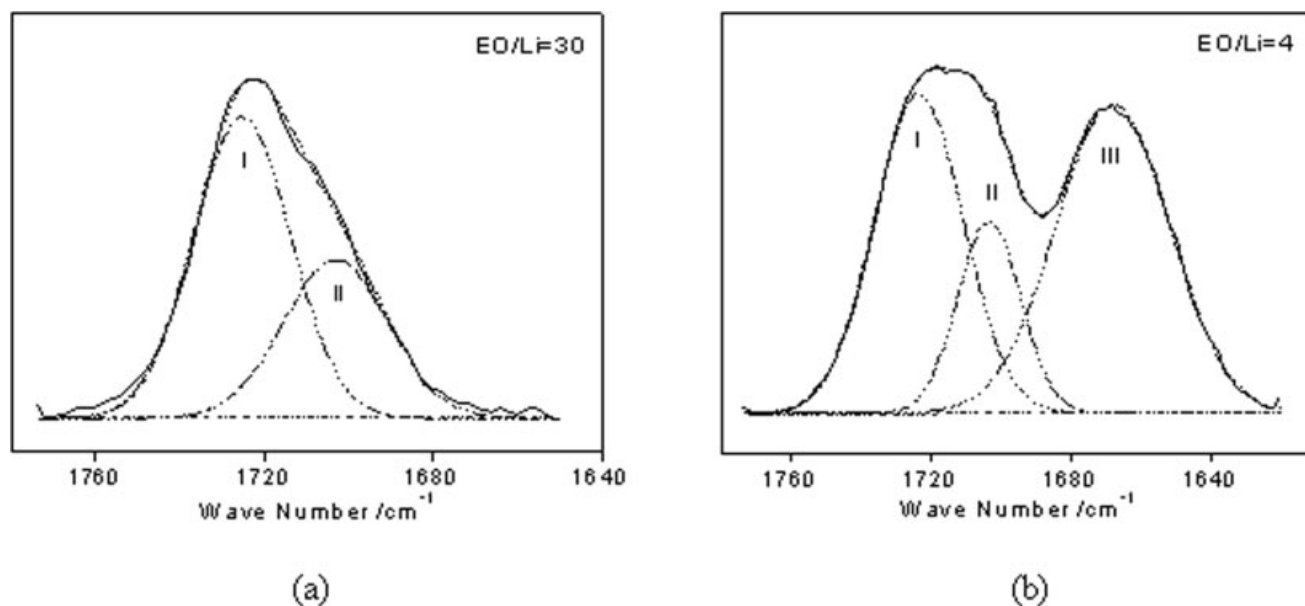


Figure 4 The decomposition curves of FTIR spectrum (carbonyl group).

TABLE I
Decomposition Results of CHPU30-LiClO₄ Samples
in the C=O and -O- Stretching Region

Stretching region	Film	EO/Li ⁺	Peak area (%)		
			I	II	III
C=O	CHPU30-2	2	23.38	16.56	60.06
	CHPU30-4	4	41.03	10.32	48.65
	CHPU30-8	8	60.09	11.99	27.92
	CHPU30-12	12	62.76	14.91	22.33
	CHPU30-20	20	68.50	18.19	13.31
	CHPU30-30	30	72.02	27.98	
-O-	CHPU30-2	2	46.24	49.15	4.61
	CHPU30-4	4	48.49	46.78	4.73
	CHPU30-8	8	56.92	38.59	4.94
	CHPU30-12	12	61.52	33.39	5.19
	CHPU30-20	20	63.33	31.45	5.22
	CHPU30-30	30	67.68	26.92	5.40

With increasing salt concentration (decreasing EO/Li⁺), the bonded area increased slightly first, then increased sharply at higher salt concentration.

Figure 5 shows the ether group absorption peaks of the MHPU30-LiClO₄ samples with different salt concentration. The band centered at around 1107 cm⁻¹ (peak I) was attributed to the stretching of free ether groups, whereas the band at about 1070 cm⁻¹ (peak II) was assigned to the bonding degree of Li⁺ with ether groups^{9,12} (Fig. 6). The little peak centered at around 1026 cm⁻¹ (peak III) might be related to the characteristics of ether groups in the copolymer which was not observed in our previous hybrid system.⁷ The position and the area of peak III kept almost unchanged during all the invested salt concentration. All the ether group absorption curves were normalized to the free ether group region (around 1107 cm⁻¹).

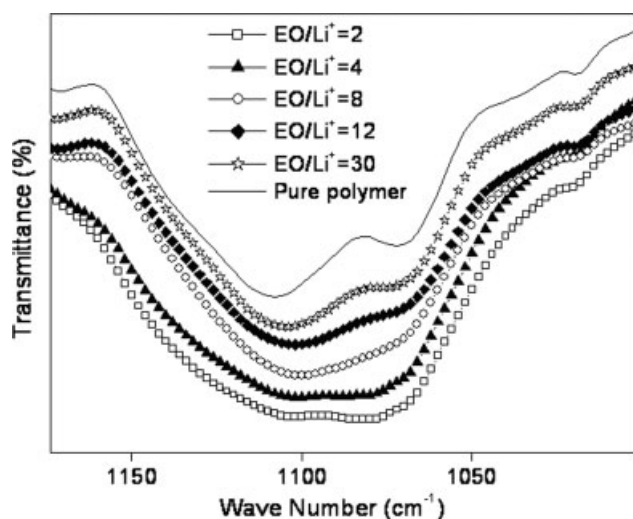


Figure 5 The FTIR spectrum (ether group) of CHPU30-LiClO₄ samples.

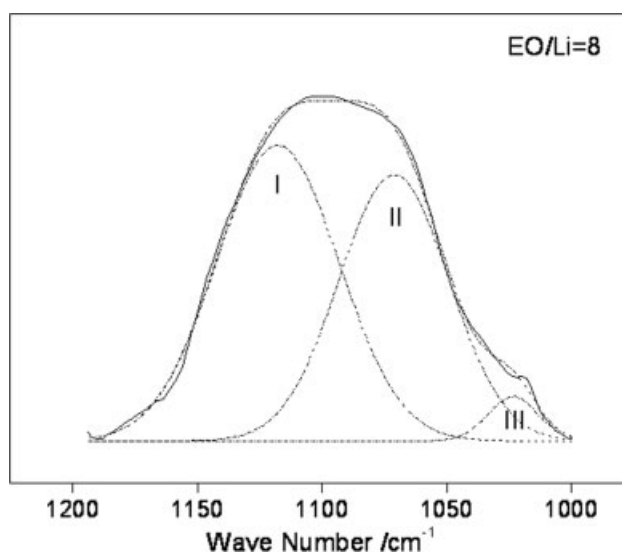


Figure 6 The decomposition curves of FTIR spectrum (ether group).

The deconvolution of the ether group region by Gaussian function was also performed and listed in Table I. The areas of the bonded ether groups (peak II) increased with increasing salt concentration. This was attributed to the fact that the ionic coordination between free ether groups and Li⁺ increased with increasing salt concentration.

From Table I, there was some interesting finding when the salt concentration increased from EO/Li⁺ = 30 to 2. The areas of the bonded ether groups increased gradually. The areas of the bonded urethane carbonyl groups first increased very small, then the increase became rapidly at higher salt content. It could be draw the following conclusions: Li⁺ preferred bonding with the ether group at first, and,

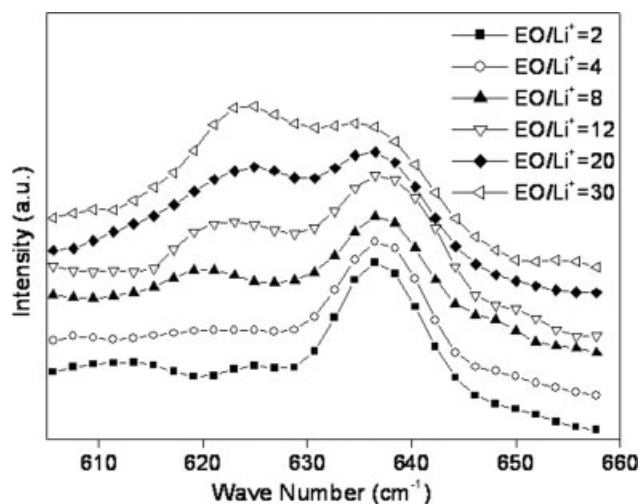


Figure 7 Raman band associated with ClO₄⁻ bending mode of CHPU30-LiClO₄ samples.

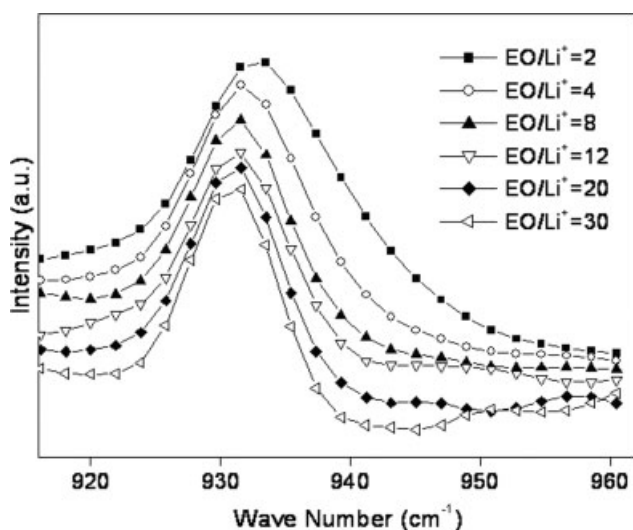


Figure 8 Raman band associated with $\text{ClO}_4^- \nu_1$ mode of CHPU30- LiClO_4 samples.

when the salt concentration reached a certain level, the Li^+ bonded with the carbonyl.

Raman spectra analysis

Figure 7 shows the Raman spectra band associated to the anion ClO_4^- bending mode. The band might be separated in to two contributions.¹³ The lower frequency component (622 cm^{-1}) was attributed to "free ions" ClO_4^- anions, whereas the higher frequency component (637 cm^{-1}) could be associated with the presence of contact-ion pairs. It could be found that the fraction of contact-ion pairs increased with the increasing salt concentration.

Figure 8 shows the Raman spectra between 920 and 970 cm^{-1} of the CHPU30- LiClO_4 samples with different salt concentration. This band was associated to the anion ClO_4^- symmetric stretching mode (ν_1). Figure 9 shows the three Lorentzian fittings of the ν_1 band.^{9,14} The first peak (peak I) around 931 cm^{-1} was assigned

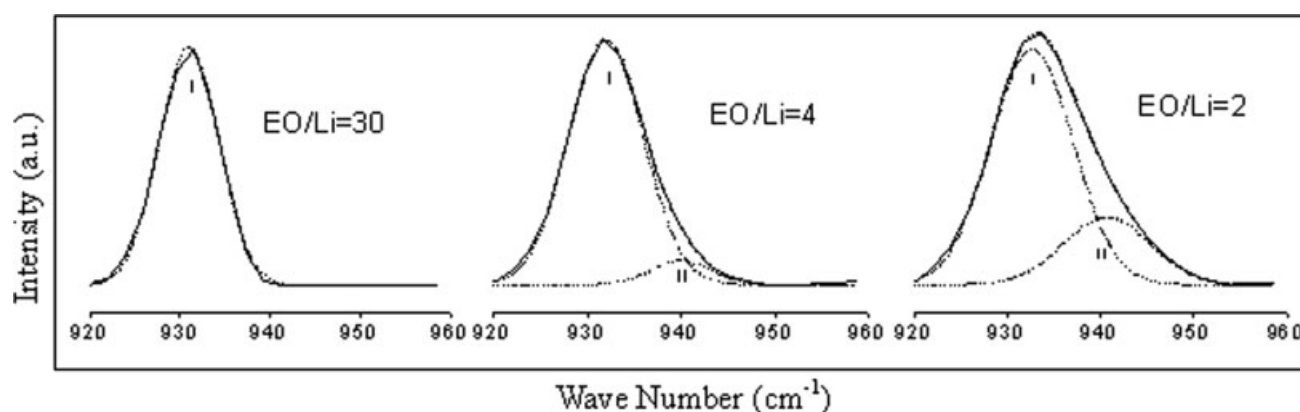


Figure 9 Raman band associated with $\text{ClO}_4^- \nu_1$ mode fitted by the sum of Lorentzian lines.

to free-ions. The ion pair $\text{Li}^+\text{-ClO}_4^-$ could be identified by the second peak (peak II), which appears around 938 cm^{-1} . The fraction of contact-ion pairs increased with the increasing salt concentration. But even when the salt concentration increased to $\text{EO/Li}^+ = 2$, the salt aggregates did not appear which would be indicated by the third peak around 945 cm^{-1} . Compared to the studies of our previous hybrid system,⁷ it could be concluded that the copolymerization between hyperbranched and linear polyurethane enhanced the function for dissolving more salt.

DSC analysis

It is well known that ion transference in SPEs greatly well depends on the mobility of the polymer chain, which can be characterized by the glass-transition temperature (T_g). In general, the polymer chain mobility was higher for the materials of lower T_g . The DSC curves for the CHPU- LiClO_4 samples are shown in Figure 10. The T_g of the polymer electrolytes first decreases with the increase in Li salt concentration since the interaction between the polymer and salt disrupt regular structure of the polymer, but further increase in the Li salt concentration above an EO/Li ratio of 4 cause a increase in T_g due to the strong interaction between the polymer and salt (Table II). The melting transition of the oligo(ethylene glycol) units is absent in the DSC traces. This essentially amorphous structure is due to the highly branched nature of the macromolecules and indicates the inclusion of branching units disrupts packing of the linear segments, which prevents crystallization and is helpful to enhance the ionic conductivity.

Ionic conductivity analysis

Figure 11 shows the salt concentration dependence of the conductivity, respectively, the lithium salt concentration from an EO/Li ratio of 2.0 to 30 for the

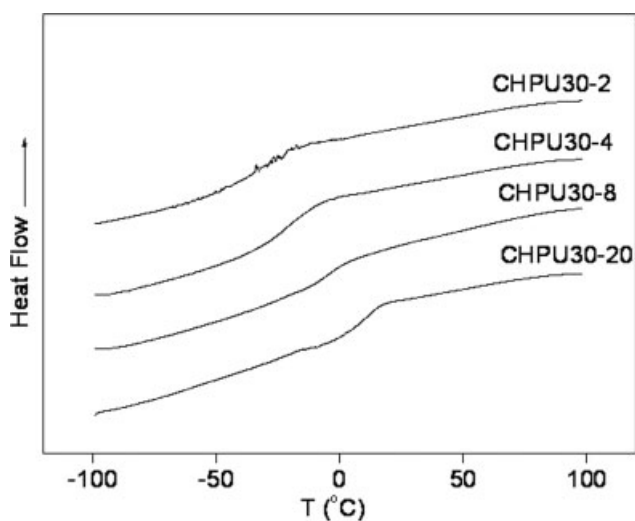


Figure 10 The DSC curves for the CHPU30-LiClO₄ samples.

polymer electrolytes based on CHPU10, CHPU20 and CHPU30. At about the EO/Li ratio of 4, the conductivity of CHPU30-LiClO₄ samples reaches its maximum, $1.51 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C. After the maximum value, the conductivity decreases with the increasing lithium salt concentration for all the three-polymer electrolyte samples. This behavior is similar to most of the salt concentration dependences of polymer electrolytes. It was also shown that the conductivity kept increasing with increasing concentration of HPU from 10% to 30%. This performance might be attributed to the spherical shape of the hyperbranched polymer. The fraction of free volume in these systems increased accordingly, which led to an increase in the ionic conductivity.¹⁵

The salt concentration had important effects on the ionic conductivity. The number of ionic particles increased with the increase of the salt concentration, which was good for the increase of the ionic conductivity. However, higher salt concentration made it easy to form ion pair and aggregates, which increased the interaction between ion-ion and ion-polymer, and limited the mobility of charge carriers in the polymer matrix. Thus there was a certain EO/Li⁺ ratio at which the complex had the highest ionic conductivity. It is well known that the conductivity maximum of a PEO-based polymer electrolyte usually appears around the EO/Li⁺ ratio of 8. The conductivity maximum of present system appeared at a higher salt concentration of EO/Li⁺ = 4. This could be attributed to the high

TABLE II
DSC Data of CHPU30-LiClO₄ Samples

Film	EO/Li ⁺	T_{gr} , °C (onset)
CHPU30-2	2	-28.65
CHPU30-4	4	-29.62
CHPU30-8	8	-9.28
CHPU30-20	20	-2.85

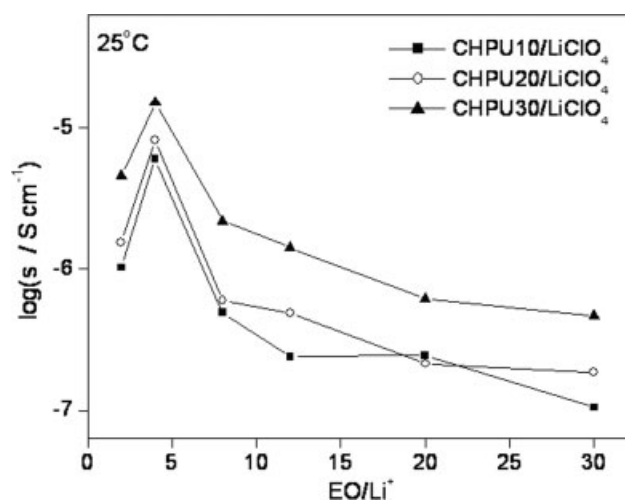


Figure 11 HPU concentration dependence of the conductivity for CHPU10-30/LiClO₄ series.

solvating capability of the hyperbranched polymer. This also could be confirmed by the result of FTIR and Raman spectra analysis.

Figure 12 illustrates the temperature dependence of ionic conductivity at different salt concentration. It indicated that the ionic conductivity of all samples apparently was enhanced with increasing temperature. This could be easily understood on the basis of the ionic transport mechanism of solid polymer electrolytes (SPEs).¹⁰ When the temperature was increased, the mobility of polymer chains was enhanced, and the fraction of free volume in these systems increased accordingly.

CONCLUSIONS

Low crosslinked copolymer of linear and hyperbranched polyurethane (CHPU) was prepared, and the ionic conductivities of the composite polymer

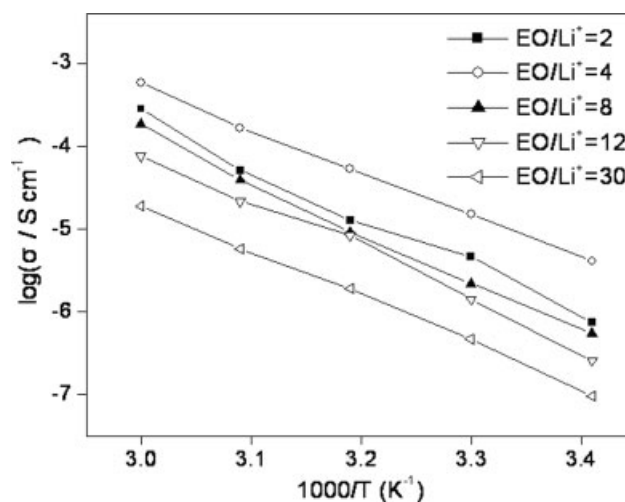


Figure 12 The effect of temperature on ionic conductivity of CHPU30-LiClO₄ samples.

electrolytes composed of CHPU and LiClO_4 were investigated. Comparing to our previous hybrid system, FTIR, Raman analysis showed that the copolymerization between hyperbranched and linear polyurethane in CHPU improved the coordination degree between Lithium ion and polymer further and prevented the formation of ion-pair and aggregates. So the copolymers could dissolve more salt and provide more ionic particles participating in conduction. This performance was consistent with the result of conductivity. The conductivity CHPU/ LiClO_4 samples reached its maximum, $1.51 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C , at a salt concentration about the EO/Li ratio of 4.

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