

# Synthesis and Conductivity Performance of Hyperbranched Polymer Electrolytes with Terminal Ionic Groups

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**ABSTRACT:** Hyperbranched polymer was synthesized from pentaerythritol (as the central core), 1,2,4-trimellitic anhydride, and epichlorohydrin, and then hyperbranched polymer electrolytes with terminal ionic groups were prepared by the reaction of hyperbranched polymer with *N*-methyl imidazole. The chemical structure, thermal behavior, and ionic conductive property of the hyperbranched polymer electrolytes were investigated by <sup>1</sup>H-NMR, FTIR,

differential scanning calorimetry, thermogravimetric analyzer, and complex impedance analysis, respectively. The ionic conductivity of hyperbranched polymer electrolyte was up to  $2.4 \times 10^{-4} \text{ S cm}^{-1}$  at 30°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3539–3544, 2010

**Key words:** hyperbranched; electrochemistry; polyelectrolyte; solid-state polymerization; synthesis

## INTRODUCTION

Ionic liquids (ILs) have attracted much attention because of their potential application for various electrochemical devices, such as lithium ion battery, dye-sensitized solar cell, electric double layer capacitors, polymer electrolyte fuel cells, and so forth.<sup>1–3</sup> This versatility is due to their quite unique characteristics, such as nonvolatility, nonflammability, high ion density, high thermal stability, extremely high ionic conductivity, and so on. However, when ILs are used as electrolyte materials, they have a disadvantage that both anions and cations are mobile in these bi-ionic systems.<sup>4</sup> During discharge, anions and cations migrate toward the oppositely charged electrodes, thereby polarize the electrolyte and increase its resistivity.<sup>5</sup> In addition, there is a fear of leakage of liquid ILs in battery technology as well as other organic electrolyte solutions.<sup>6</sup> To overcome this drawback, Ohno et al. prepared polymerizable ILs and their polymers as stable polymer electrolytes.<sup>7</sup> Vinylimidazole was quaternized with alkyl halide, obtained polymerizable ILs were polymerized to obtain ion conductive films. They also

designed various systems, such as polycation-type ILs, polyanion-type ILs, copolymer, poly(zwitterion)s, and so on. Polymerization of ILs itself is very effective not only to transport target ion but also to improve mechanical property. However, the polymerization of IL itself leads to decrease the ionic conductivity in spite of excellent ionic conductivity before polymerization. This conductivity drop is explained by the decrease in the segmental motion of ion. Binding of ions through covalent bonds (polymerization) reduced thermal motion of the ion unit and accordingly increased the glass transition temperature ( $T_g$ ). As the ionic conductivity is the function of  $T_g$ , it is essentially important to lower  $T_g$  for the improvement of ionic conductivity in the polymerized ILs.<sup>8–10</sup>

Hyperbranched polymers are interesting materials as a polymer electrolyte because they are completely amorphous, lower  $T_g$ , highly soluble, and highly processable, and have many branch ends, which could greatly contribute to ionic conduction.<sup>11,12</sup> Itoh and coworkers have investigated the polymer electrolytes based on hyperbranched polymer poly[bis(triethylene glycol)benzoate] and so on, and have found that the composite polymer electrolytes of PEO, BaTiO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N with the hyperbranched polymer show a high electrical conductivity at room temperature.<sup>13,14</sup>

Combined the advantage of IL with hyperbranched polymer, hyperbranched polymer with terminal ionic groups has drawn great interests in polymer electrolytes study.

In this work, we synthesized hyperbranched polymer with terminal IL groups (HBP-IL) in which PF<sub>6</sub><sup>-</sup>

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ion can migrate, whereas imidazolium cation is immobilized. At first, hyperbranched polymer was synthesized from pentaerythritol (as the central core), 1,2,4-trimellitic anhydride and epichlorohydrin, and then HBP-IL was prepared by reaction of hyperbranched polymer with *N*-methyl imidazole. The chemical structure, thermal behavior, and ionic conductive property of HBP-IL were investigated by  $^1\text{H-NMR}$ , FTIR, differential scanning calorimetry (DSC), thermogravimetric analyzer (TG), and complex impedance analysis, respectively. The ionic conductivity of HBP-IL was up to  $2.4 \times 10^{-4} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ .

## EXPERIMENTAL

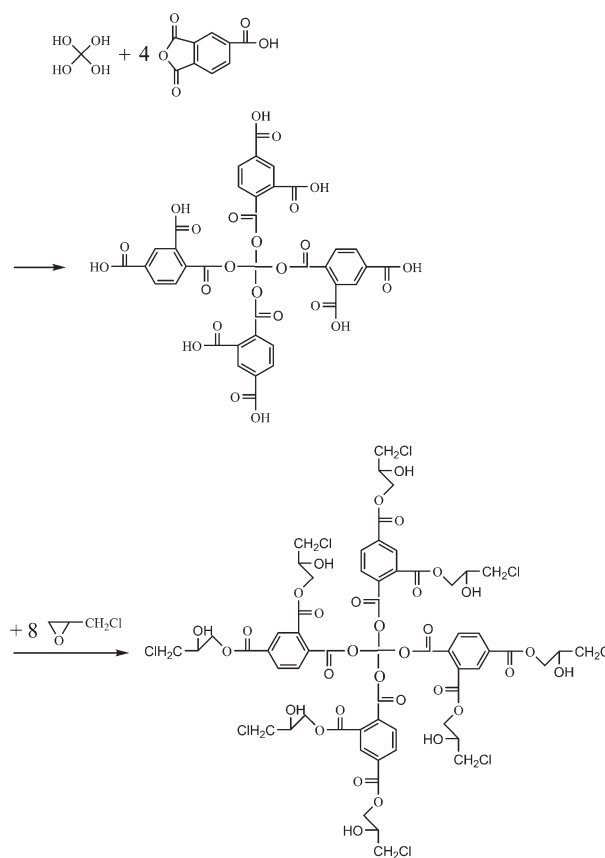
### Materials

*N*-methyl imidazole (>99.5%) was purchased from Taizhou Chem. Pentaerythritol, 1,2,4-trimellitic anhydride, epichlorohydrin, lithium hexafluorophosphate, and potassium hexafluorophosphate were purchased from Shanghai Chemical Reagent Company, China. These materials were dried under reduced pressure before use. *N,N*-dimethylformamide and acetone were purchased from Tianjing Chemical Reagent Company, China, was used as received.

### Synthesis of hyperbranched polymer

0.02 mol pentaerythritol, 0.08 mol 1,2,4-trimellitic anhydride, and 100 mL *N,N*-dimethylformamide, was placed in a flask equipped with a reflux condenser and a dropping funnel.<sup>15</sup> Under vigorous stirring with a magnetic stirring bar, the mixture was heated under  $\text{N}_2$  atmosphere at  $110^\circ\text{C}$  for 3 h, up to acid value of reaction system was invariable. 0.16 mol epichlorohydrin was slowly dropped into the above solution under agitation. After all epichlorohydrin was dropped, the reaction time was maintained for 3 h. The reaction mixture was precipitated with alcohol and then filtered. The product was purified by Soxhlet extraction with alcohol for 24 h, then dried under reduced pressure at  $70^\circ\text{C}$ . The hyperbranched polymer with eight hydroxy groups and eight chlorine groups (HBP-A) was obtained (see Scheme 1).  $^1\text{H-NMR}$  of HBP-A ( $\text{CDCl}_3$ ,  $\delta$ ): 8.87 (d, 1H), 4.40 (d, 2H), 4.14 (s, 1H), 3.53 (d, 2H), 2.01 (s, 1H).

The hyperbranched polymer with 16 hydroxy groups and 24 chlorine groups (HBP-B), was prepared as follows: HBP-A (0.01 mol) was dissolved in 100 mL *N,N*-dimethylformamide, and 0.08 mol 1,2,4-trimellitic anhydride was placed in a flask equipped with a reflux condenser and then the mixture was heated under  $\text{N}_2$  atmosphere at  $110^\circ\text{C}$  for 3 h, up to acid value of reaction system was invariable. 0.16 mol epichlorohydrin was then dropped slowly into the above solution under agitation. After all epi-



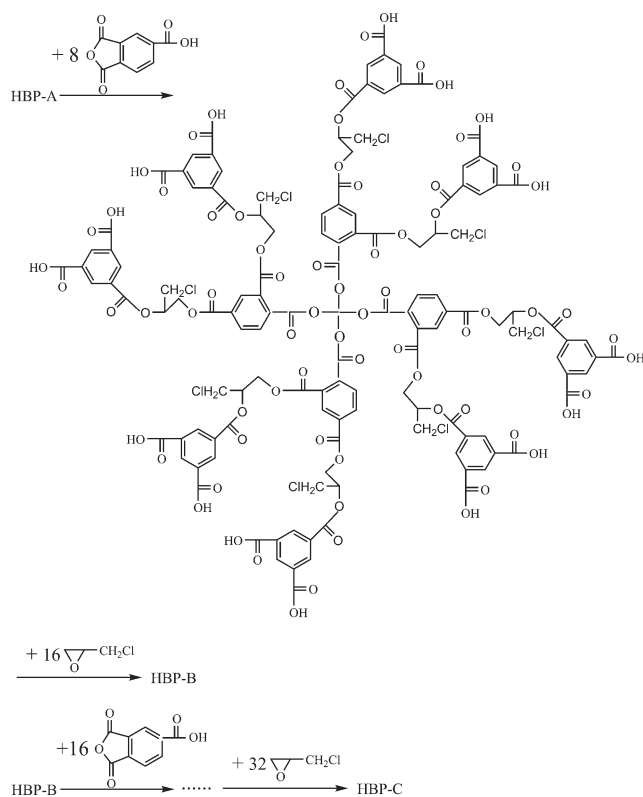
**Scheme 1** Synthesis of hyperbranched polymer, HBP-A with eight hydroxy groups and eight chlorine groups.

chlorohydrin was dropped, the reaction time was maintained for 3 h. The reaction mixture was precipitated with alcohol and then filtered. The product was purified by Soxhlet extraction with alcohol for 24 h, then was dried under reduced pressure at  $70^\circ\text{C}$ . The hyperbranched polymer with 16 hydroxy groups and 24 chlorine groups (HBP-B) was obtained (see Scheme 2).  $^1\text{H-NMR}$  of HBP-B ( $\text{CDCl}_3$ ,  $\delta$ ): 8.89 (t, 1H), 4.87 (d, 1H), 4.67 (d, 2H), 4.40 (d, 2H), 4.13 (s, 1H), 3.80 (d, 2H), 3.53 (d, 2H), 2.01 (s, 1H).

The hyperbranched polymer with 32 hydroxy groups and 56 chlorine groups (HBP-C), was prepared with 0.005 mol HBP-B, 0.08 mol 1,2,4-trimellitic anhydride, and 0.16 mol epichlorohydrin. The preparation procedure same as HBP-B.  $^1\text{H-NMR}$  of HBP-C ( $\text{CDCl}_3$ ,  $\delta$ ): 8.89 (t, 1H), 4.87 (d, 1H), 4.67 (d, 2H), 4.40 (d, 2H), 4.14 (s, 1H), 3.90 (d, 1H), 3.80 (d, 2H), 3.53 (d, 2H), 2.01 (s, 1H).

### Synthesis of hyperbranched polymer electrolytes with terminal ionic groups

0.01 mol HBP-A was dissolved in 100 mL *N,N*-dimethylformamide, and mixed with 0.08 mol *N*-methyl imidazole. After the mixture was stirred at  $90^\circ\text{C}$  for 48 h under  $\text{N}_2$  atmosphere to form hyperbranched polymer chlorides, and then ion exchange reaction



**Scheme 2** Synthesis of hyperbranched polymer, HBP-B with 16 hydroxy groups and 24 chlorine groups, and HBP-C with 32 hydroxy groups and 56 chlorine groups.

of the chloride with  $\text{K-PF}_6$  at ambient temperature to give hyperbranched polymer hexafluorophosphate ( $\text{PF}_6^-$ ) salts. The resulting crude ILs were purified by washing with pure water several times until no residual chloride anion was detected with the use of  $\text{AgNO}_3$ . All ILs were dried under high vacuum for at least 8 h at  $120^\circ\text{C}$  and were stored in an argon atmosphere glove box. The water content of the dried ILs, measured by using a Karl Fischer moisture titrator, was less than 50 ppm. The hyperbranched polymer with terminal eight  $\text{PF}_6^-$  anions (HBP-IL-A) was obtained (see Scheme 3). The  $^1\text{H-NMR}$  of HBP-IL-A ( $\text{CDCl}_3$ ,  $\delta$ ): 8.89 (d, 1H), 7.29 (d, 1H), 6.84 (d, 1H), 6.76 (d, 1H), 4.40 (d, 2H), 3.88 (s, 2H), 3.80 (s, 1H), 3.63 (s, 3H), 2.01 (s, 1H).

The preparation of hyperbranched polymer with terminal 24  $\text{PF}_6^-$  anions (HBP-IL-B) was the same means as HBP-IL-A, and a recipe as follows: 0.01 mol HBP-B, 0.24 mol *N*-methyl imidazole, and 0.24 mol potassium hexafluorophosphate ( $\text{KPF}_6$ ). The  $^1\text{H-NMR}$  of HBP-IL-B ( $\text{CDCl}_3$ ,  $\delta$ ): 8.89 (d, 1H), 7.29 (d, 1H), 6.84 (d, 1H), 6.76 (d, 1H), 4.87 (d, 1H), 4.67 (d, 2H), 4.40 (d, 2H), 3.88 (s, 2H), 3.80 (s, 1H), 3.63 (s, 3H), 2.01 (s, 1H).

The preparation of hyperbranched polymer with terminal 56  $\text{PF}_6^-$  anions (HBP-IL-C) was the same means as HBP-IL-A, and a recipe as follows: 0.01 mol

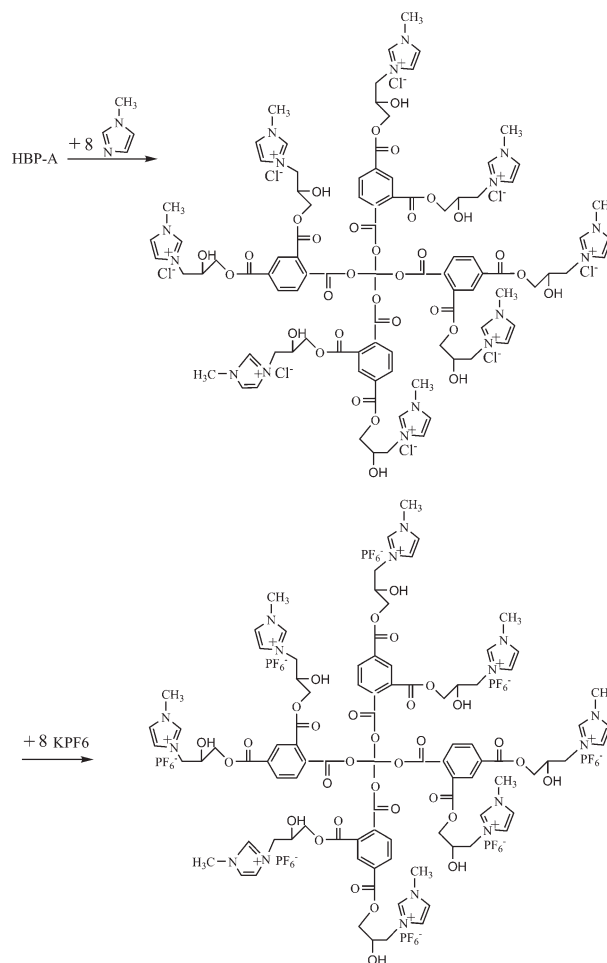
HBP-B, 0.56 mol *N*-methyl imidazole, and 0.56 mol potassium hexafluorophosphate ( $\text{KPF}_6$ ). The  $^1\text{H-NMR}$  of HBP-IL-C ( $\text{CDCl}_3$ ,  $\delta$ ): 8.89 (d, 1H), 7.29 (d, 1H), 6.84 (d, 1H), 6.76 (d, 1H), 4.88 (d, 1H), 4.67 (d, 2H), 4.41 (d, 2H), 3.88 (s, 2H), 3.80 (s, 1H), 3.63 (s, 3H), 2.01 (s, 1H).

## Characterization

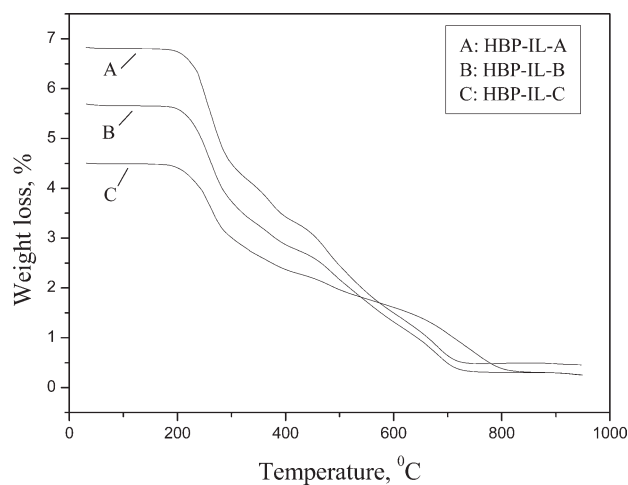
The IR spectra of the sample were recorded with a Fourier transform IR spectrometer (FTIR PE-2000). The test specimen was prepared by the KBr-disk method.

Thermal stability was determined with a TG (NETZSCHSTA 449C). The programmed heating range was from room temperature to  $1000^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

The thermal behavior of the samples was studied by means of DSC, a Dupont 2910 TA Instrument. DSC samples were encapsulated in aluminum pans and scanned under nitrogen gas. The experiments were performed from  $-100$  to  $50^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .



**Scheme 3** Synthesis of hyperbranched polymer with terminal hexafluorophosphate ions, HBP-IL-A.



**Figure 1** Thermal stability of HBP-IL-A, HBP-IL-B, and HBP-IL-C under  $N_2$  atmosphere.

The ionic conductivity of HBP-IL was measured by the complex impedance method using CHI660C electrochemical workstation (Chenhua Corp., Shanghai, China). The electrolytes were sandwiched between two stainless steel (SS) plates controlled by a teflon spacer. The data were collected over a frequency range  $10\text{--}10^5$  Hz and a temperature range from 30 to  $80^\circ\text{C}$  with the amplitude of 5 mV for an open circuit potential. All samples were first kept at  $80^\circ\text{C}$  for at least 2 h and then cooled to room temperature for the measurements. The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibration. The bulk resistance ( $R$ ) of the polymer electrolyte was found from impedance spectrum, where the intercept on the real axis gave the value. The ionic conductivity ( $\sigma$ ) was calculated by the following equation:  $\sigma = L/R \cdot S$ , where  $L$  is the thickness of the polymer electrolyte film and  $S$  is the area of the polymer electrolyte film.<sup>5</sup>

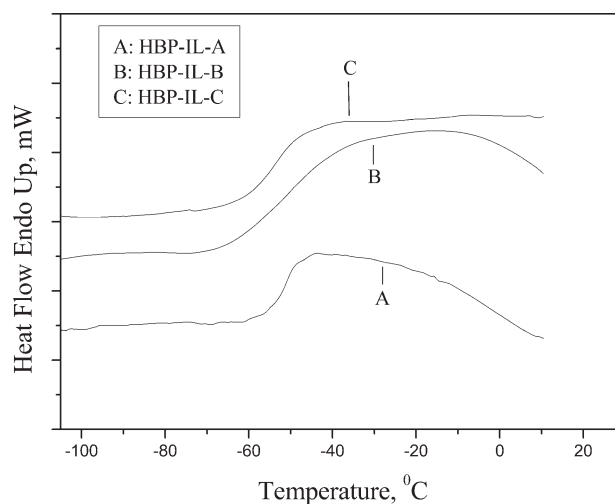
## RESULTS AND DISCUSSION

### Thermogravimetric analysis

Thermogravimetry curves of HBP-IL-A, HBP-IL-B, and HBP-IL-C were shown in Figure 1. It was clearly seen that rapid thermal degradation of HBP-IL-A, HBP-IL-B, and HBP-IL-C, respectively, occurred up to 280, 271, and  $270^\circ\text{C}$  under  $N_2$  atmosphere, which illustrated that the hyperbranched polymer electrolytes possessed excellent thermal stability, there was slight weight loss of around 2% before thermal decomposition because of the absorbing water from air.

### DSC measurement

The DSC measurements were carried out to analyze the glass transition temperature and phase behavior

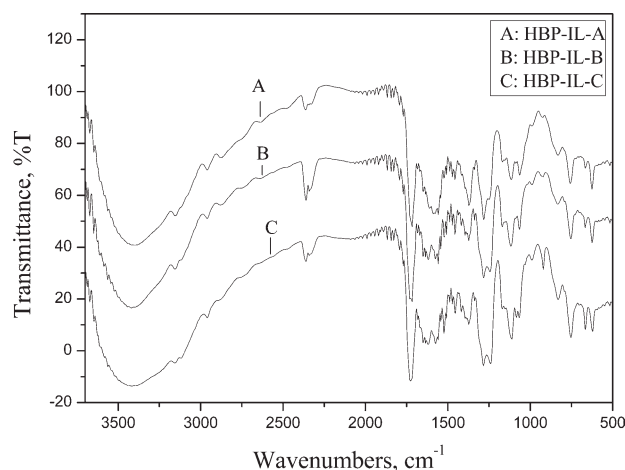


**Figure 2** DSC curves of hyperbranched polymer electrolytes, HBP-IL-A, HBP-IL-B, and HBP-IL-C.

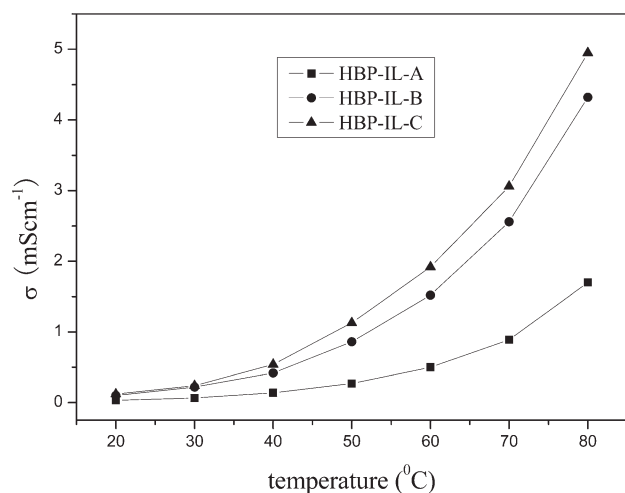
of the samples. DSC traces of the HBP-IL-A, HBP-IL-B, and HBP-IL-C were shown in Figure 2. The glass transition temperature ( $T_g$ ) were found to be  $-53^\circ\text{C}$ ,  $-57^\circ\text{C}$ , and  $-58^\circ\text{C}$  for the HBP-IL-A, HBP-IL-B, and HBP-IL-C, respectively. No crystalline melting peak was found in all the thermograms because of the amorphous state of the hyperbranched polymer electrolytes. Additionally, only one  $T_g$  was observed in each curve, indicated that the product prepared was the copolymer rather than their mixture. Furthermore, the  $T_g$  decreased with an increase in the content of 1,2,4-trimellitic anhydride, and epichlorohydrin in the polymer electrolytes.

### FTIR analysis

The FTIR spectra of the hyperbranched polymer electrolytes were illustrated in Figure 3. Compared with the monomers, the disappearing of the absorbance



**Figure 3** FTIR spectra of the hyperbranched polymer electrolytes, HBP-IL-A, HBP-IL-B, and HBP-IL-C.



**Figure 4** Temperature dependence of the hyperbranched polymer electrolytes, HBP-IL-A, HBP-IL-B, and HBP-IL-C,  $\sigma$  versus  $1/T$  plot.

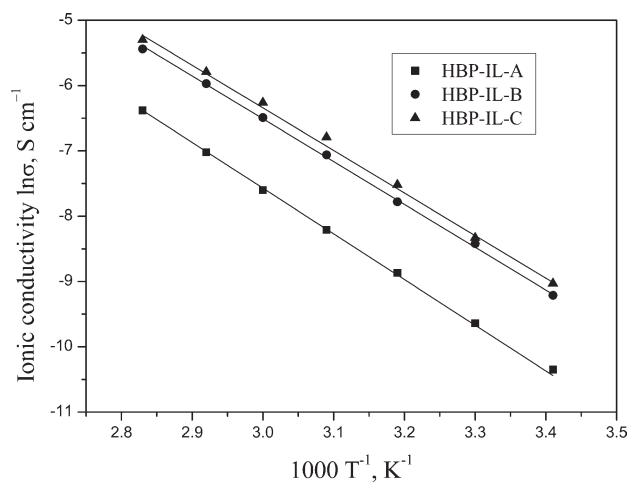
peak at  $1760\text{ cm}^{-1}$  and  $1850\text{ cm}^{-1}$  for corresponding anhydride group and  $905\text{ cm}^{-1}$  for corresponding epoxy groups, indicated that the hyperbranched reaction had occurred. The other peaks of the resulting hyperbranched polymer electrolytes were assigned as follows:  $3480$  ( $-\text{OH}$ ),  $3417$  ( $-\text{NH}-$ ),  $2960$  ( $-\text{CH}_3$ ,  $-\text{CH}_2$ ),  $1720$  ( $\text{C}=\text{O}$  stretching in carboxylic ether),  $1284$ ,  $1242$  ( $-\text{OH}$  stretching),  $1111$ ,  $1065$  ( $\text{C}-\text{O}$  stretching), and  $752\text{ cm}^{-1}$  (phenyl absorbance peak). It was observed that the OH and NH absorbance peak increased with the increasing of reactants content in the feeding composition.

### Ionic conductivity measurement

The ionic conductivity of all hyperbranched polymer electrolytes was determined by means of impedance spectroscopy. From the  $Z''$  versus  $Z'$  plot, the ionic conductivity values were calculated at each temperature from the intercept of the curve with real axis. As their cations were immobilized on polymer chains, the migration of them could be negligible and only the anions remain high mobility, HBP-IL-A, HBP-IL-B, and HBP-IL-C exhibited single anionic conduction. Temperature dependence of the ionic conductivity of three samples was shown in Figure

**TABLE I**  
Ionic Conductivity of Hyperbranched Polymer Electrolytes at 30 and 80°C and Their Glass Transition Temperatures

Polymer	$T_g$ (°C)	Conductivity ( $\text{S cm}^{-1}$ )	
		at 30°C	at 80°C
HBP-IL-A	-53	$6.5 \times 10^{-5}$	$1.7 \times 10^{-3}$
HBP-IL-B	-57	$2.2 \times 10^{-4}$	$4.3 \times 10^{-3}$
HBP-IL-C	-58	$2.4 \times 10^{-4}$	$4.9 \times 10^{-3}$



**Figure 5** Temperature dependence of conductivity of the hyperbranched polymer electrolytes, HBP-IL-A, HBP-IL-B, and HBP-IL-C,  $\ln \sigma$  versus  $1/T$  plot.

4. HBP-IL-C showed the highest ionic conductivity among three hyperbranched polymer electrolytes. The ionic conductivity values at 30 and 80°C were summarized in Table I along with the glass transition temperatures. A linear relationship found in the figure clearly indicated that the hyperbranched polymer electrolytes having lower  $T_g$  showed higher ionic conductivity. The ionic conductivity of hyperbranched polymer electrolytes at the contact temperature was closely related to their  $T_g$ , it is consistent with the results of Dalakoglou et al.<sup>16,17</sup> On the other hand, HBP-IL-C showed the highest ionic conductivity indicating that further branched polymers could provide a better charge carriers medium.

The ionic conductivity,  $\sigma$ , depends largely on temperature and rises exponentially as the temperature increases, because of the exponentially increase of ion mobility at increasing temperatures. The corresponding  $\ln \sigma$  versus  $1/T$  plot was almost linear in a wide temperature range (20–80°C) (Fig. 5). The conductivity relationship can be expressed by Arrhenius equation:  $\sigma = A_{\text{exp}} (-E_a/RT)$ , where  $E_a$  is the activation energy,  $A$  is a constant and  $T$  is the absolute temperature. From the slope of the curves activation energy of the ionic conductivity,  $E_a$  is estimated as,  $E_a = \text{slope} \times R$ , where  $R$  is gas constant. The activation energy of three samples (HBP-IL-A, HBP-IL-B, and HBP-IL-C) was 56.97, 55.73, and 53.27 kJ/mol, respectively.

### CONCLUSIONS

Hyperbranched polymers with terminal IL groups were synthesized and their ionic conductivity was investigated. The higher conductivity in these polymers could be attributed to the higher amorphicity, as confirmed by DSC analysis, providing more free

volume. The obtained hyperbranched polymers exhibited the highest ionic conductivity of  $2.4 \times 10^{-4} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ . Thermogravimetric result revealed that they have good thermal stability up to about  $270^\circ\text{C}$ .

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