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# Synthesis and Characterization of Hyperbranched Polyesters Based on Isophthalic Acid and Trimethylolpropane

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# Synthesis and Characterization of Hyperbranched Polyesters Based on Isophthalic Acid and Trimethylolpropane

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Hydroxyl-terminated hyperbranched polyesters (HBPEs) with aromatic/aliphatic structure were synthesized at three different monomer mole ratios ($A_2/B_3 = 1$, 0.9, and 0.6, respectively) by melt polycondensation of isophthalic acid and trimethylolpropane via $A_2$+ $B_3$ approach. Fourier transform infrared (FTIR) spectroscopy indicated that the expected HBPEs, which showed excellent solubility in a variety of polar solvents such as *N*, *N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and terahydrofuran (THF), were produced without gelation during the polymerization. The weight-average molecular weight of HBPEs ranged from 7014 to 8306 and their inherent viscosities were varied from 0.17 to 0.34 dL/g. The degree of branching of the HBPEs was estimated to be 0.39–0.49 by $^1$H-NMR and $^{13}$C-NMR measurement. Their glass transition temperature measured by differential scanning calorimetry (DSC) was between 64 and 86°C. The thermogravimetric analysis (TGA) measurement revealed that HBPEs had *ca* 8.5% weight-loss at 300°C in $N_2$.

**Keywords:** Hyperbranched polyester, polycondensation, $A_2+B_3$ approach

## 1 Introduction

During the past two decades, hyperbranched polymers have attracted considerable attention due to their unique chemical and physical properties. They are usually prepared from the self-condensation of $AB_2$-type monomers. However, most of the $AB_2$-type monomers are unavailable commercially; they are either expensive or have to be synthesized prior to polymerization. Recently, the $A_2+B_3$ type of polymerization has been demonstrated to be an alternative route to fabricate hyperbranched polymers, which provides a more facile approach to several families of hyperbranched polymers. In addition, $A_2$ and $B_3$ monomers are more readily obtained than $AB_2$-type monomers.

Preparation of hyperbranched polymers through the step-growth polymerization reactions of $A_2$ and $B_3$ type monomers has received widespread attention. Research has involved the synthesis of hyperbranched polymers from the reaction of $A_2+B_3$ and their potential applications, the notable examples were reported by Kakimoto (1–4), Fréchet (5–7), Voit (8,9), Long (10,11), Kricheldorf (12,13), and Okamoto (14).

Several hyperbranched polyesters (HBPEs) based on the $A_2+B_3$ synthetic strategy have already been reported. All-aliphatic HBPEs have been synthesized by an $A_2+B_3$ approach using fumaric acid and trimethylolpropane (15), adipic acid and glycerol (16), adipic acid and trimethylolpropane (17). Recently, all-aromatic HBPEs have been reported by Long (18), Samui (19), and Voit (20). However, until now, very little work has really been released on treating of hyperbranched aromatic/aliphatic polyesters prepared according to the $A_2+B_3$ strategy, although similar compositions are claimed in some patents (21–23).

In this work, hydroxyl-terminated HBPEs with aromatic/aliphatic structure were synthesized by melt polymerization of isophthalic acid (IPA) and trimethylolpropane (TMP) at 150°C in the presence of *p*-toluenesulfonic acid (*p*-TSA). The hyperbranched aromatic/aliphatic polyesters have moderate molecular weight and glass transition temperature, whose performance neither look like all-aromatic HBPEs to be too brittle, nor look like all-aliphatic HBPEs to be too soft, especially suited for using as polyols or reactive multifunctional components in coatings and resin formulations. No gelation was observed during the polymerization. The structure of the resulting HBPEs and their properties were investigated.

## 2 Experimental

### 2.1 Materials

All the chemical reagents were analytical grade. IPA was purchased from Chengdu Kelong Chemical Reagent

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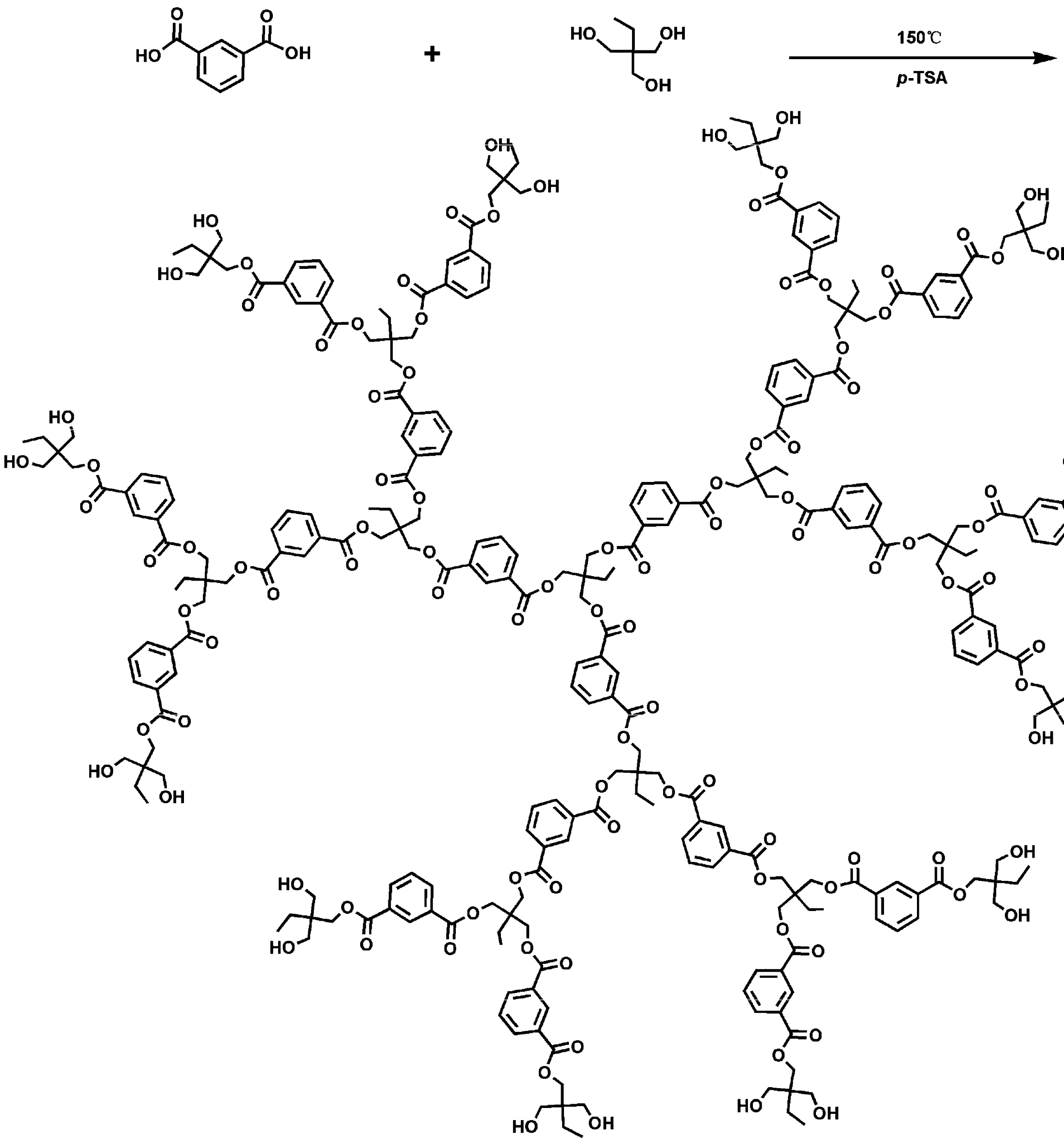

**Sch. 1.** Synthesis route and possible structure of HBPEs.

Factory (China). TMP was provided commercially by Tianjin Bodi Chemical Co., Ltd. (China). *p*-TSA was obtained from Shanghai Chemical Reagent Co., Ltd. (China). Acetone and ethyl ether were obtained from Tianjin Fuyu Fine Chemical Co., Ltd. (China) and used as received.

## 2.2 Synthesis of HBPEs

Different HBPEs were synthesized in a 250 ml four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and reflux condenser. The molar ratios of IPA and TMP were 1:1, 0.9:1, and 0.6:1, respectively. The reactant mixture was slowly heated and after melting of the reactants, the temperature was maintained at 150°C for 5–6 h to carry out the esterification reaction. The water formed during the polycondensation reaction was taken out by evaporation under reduced pressure (water pump). The reaction was monitored periodically by checking the acid value of the sample using the titration method and stopped when the acid value was not varied. The crude product was collected as pale yellow, clear brittle resins and was precipitated from acetone in ethyl ether, then was dried at 40°C under vacuum. The synthesis route was shown in Scheme 1.

## 2.3 Characterization

FTIR spectra were obtained using a Nexus-8700 spectrometer with samples in KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300-MHz NMR spectrometer operating at 300 MHz for $^{1}$H-NMR and 75 MHz for $^{13}$C-NMR, with teramethylsillane as the internal standard and

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dimethylsulfoxide-$d_6$ (DMSO-$d_6$) as the solvent, respectively. The degree of branching (DB) of the HBPEs can be determined both from $^1$H-NMR and $^{13}$C-NMR spectra signals according to the methods introduced in literature (24–26) by using the Frey equation (Eq. 1) (27):

$$DB_{Frey} = \frac{2D}{2D + L} \tag{1}$$

D indicates dendritic unit and L represents a linear unit. It is worth noting that the Frey equation, which has been established for hyperbranched polymers prepared from $AB_2$-type monomers, does not really apply for $A_2+B_3$ type hyperbranched polymers. Since there is no ready way to determine the DB of $A_2+B_3$ type hyperbranched polymers, a number of authors still use it.

Gel permeation chromatography (GPC, Waters Breeze, USA) with polystyrene as a standard, and the eluent was DMF containing 0.01 mol/L lithium bromide at a flow rate of 1.0 mL/min at 40°C. Differential scanning calorimetry (DSC) was conducted on a Q1000DSC+LNCS+FACS under $N_2$, with a heating rate of 10°C/min from 25 to 250°C, and the results were obtained in the second scan. The thermogravimetric analysis (TGA) was performed with a SDT-Q600 system at a scan rate of 10°C/min to 600°C under Nitrogen atmosphere. Viscosities of the polymer solutions (with a concentration of 0.2 g/dL) were measured with a capillary Ubbelohde viscometer in DMF at 25°C.

## 3 Results and Discussion

### 3.1 Molecular Design and Synthesis of HBPEs

In this work, HBPEs were synthesized by step-growth polycondensation of IPA (as $A_2$monomer) and TMP (as $B_3$ monomer) via $A_2+B_3$ approach. Both of the two monomers are commercially available and their properties are very suitable for preparing polyester resins used in coatings. As an ordinary dibasic acid, the esterification difficulty degree of IPA is situated between terephthalic acid and phthalic acid, but polyesters formed from IPA have good chemical stability, mechanical properties, and thermal deformation. TMP is a polyol which has three high reactive hydroxyl groups with the structure-like neopentane, the unique structure endows its excellent stability, and polyesters prepared from TMP have good chemical stability, gloss, and weather resisting property. Therefore, IPA and TMP were selected as materials to synthesize the HBPEs for coatings.

The synthesis was carried out using different monomers ratios ($A_2$:$B_3$ =1:1, 0.9:1 and 0.6:1, respectively). These three monomer ratios result in an excess of B functionalities without exception, because one molecule may bear one or more A functional groups in theory, when the monomer ratio of $A_2$ to $B_3$ is larger than 1:1. However, when the ratio of $A_2$ to $B_3$ is 1:1 or less than 1:1, in theory, the terminal groups will be exclusive B groups (28). According to Flory-Stockmayer's approach, the theoretical gel point for the 1:1 ratio can be calculated to 86.6% conversion of A-functionalities and a 0.9:1 mixture of $A_2$:$B_3$ will reach the gel point at a critical conversion of A-groups of 94.9%. However, the ratio of 0.6:1 will give gelation theoretically at 100% conversion of A-groups, which means that this system cannot form gels since one cannot reach complete conversion (29). Furthermore, the apparent viscosity and molecular weight of the reactants increase gradually with the progress of polymerization, so the synthetic process of $A_2+B_3$ system has to be controlled carefully to obtain the desired product, and usually one has to stop the reaction before completion to avoid gelation except the 0.6:1 mixture.

The reaction was maintained at a relatively low temperature, 150°C, to minimize the volatilization of monomers and unwanted side reactions. The reaction was driven toward high conversion as the water formed was removed continuously under reduced pressure with an optimized reaction time to avoid gelation. All the synthesized HBPEs exhibited low inherent viscosity (Table 1) and good solubility in typical polar solvents, such as *N*,*N*-dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and terahydrofuran (THF).

### 3.2 FTIR Analysis

Figure 1 shows the FTIR spectra of HBPE-1, HBPE-2, and HBPE-3, respectively. A strong and broad peak around 3200–3600 cm$^{-1}$ confirmed a high concentration of hydroxyl groups in HBPEs molecules. The peaks at 2983 cm$^{-1}$ and 2884 cm$^{-1}$ were the characteristic absorption of methyl, and the peaks at 1464 cm$^{-1}$ and 1385 cm$^{-1}$ could be attributed to the absorptions from methylene groups, as well as a peak at 727 cm$^{-1}$ which is due to the presence of the aromatic group originated from IPA, the peaks at

**Table 1.** Feed ratios and polymerization results of HBPEs

| *Polymer* | $A_2/B_3$ | *Yield (%)* | *Acid value (mgKOH/g)* | *Percent conversion of A groups (%)* | $\eta_{inh}$ *(dL/g)* |
|---|---|---|---|---|---|
| HBPE-1 | 1 | 79.5 | 47.58 | 85.1 | 0.34 |
| HBPE-2 | 0.9 | 77.3 | 19.46 | 94.1 | 0.25 |
| HBPE-3 | 0.6 | 63.2 | 2.33 | 99.1 | 0.17 |

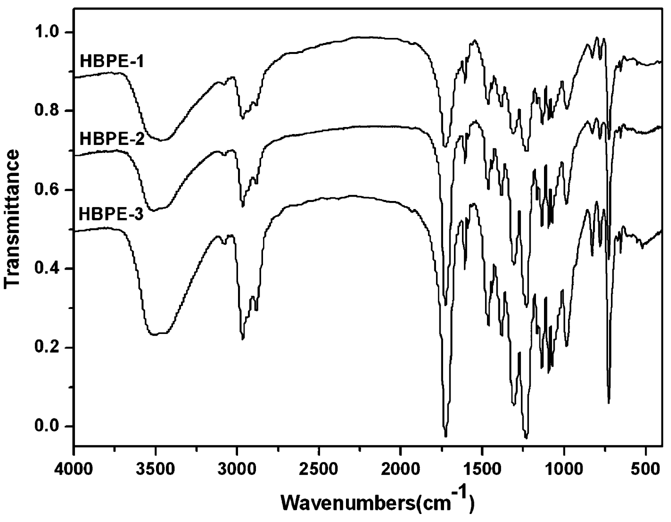

**Fig. 1.** FTIR spectra of HBPEs.

1734 cm$^{-1}$($\upsilon_{C=O}$ in ester bond), 1128 cm$^{-1}$ (C-O symmetric stretching) and 1046 cm$^{-1}$(asymmetric stretching), these being the characteristic absorption bands of polyesters. These data indicated that the polymers contained hydroxy groups, ester bonds, benzene ring, methyl and methylene groups, which were in agreement with our objective polymers.

### 3.3 NMR Analysis

In order to further confirm the chemistry structure and calculate the DB values of HBPEs, the $^1$H-NMR and $^{13}$C-NMR measurements were performed. The data of $^1$H-NMR confirmed the structure of the HBPEs. In the $^1$H-NMR spectrum of HBPE-1 in Figure 2, proton signals for aromatic rings at 7.56–8.38 ppm, $CH_2OC(O)$ at 4.14–4.31 ppm, $CH_2OH$ at 4.51–4.88 ppm and 3.38–3.54 ppm, DMSO-$d_6$ at 2.53 ppm, and $CH_3$ of TMP at 1.35–1.57 ppm, were observed. The other polymers (HBPE-2 and HBPE-3) show analogous $^1$H-NMR spectra as that for HBPE-1. These spectral data support production of the expected HBPEs.

DB is the most important parameter for hyperbranched polymers in the description of structural perfection. To calculate DB, the assignment of all three possible repeating units [terminal (T), linear (L) and dendritic (D) groups] in hyperbranched polymers is required. Unlike the well investigated classical hyperbranched polymers prepared from $AB_2$-type monomers, it is still difficult to define and understand well the structure of $A_2$+$B_3$ type hyperbranched polymer system precisely. Several concepts, such as the definition of repeat units and DB, were borrowed from the traditional hyperbranched polymers prepared from $AB_2$-type monomers.

The numbering of atoms and the assignments of the NMR signals from different units (T, L and D) of the

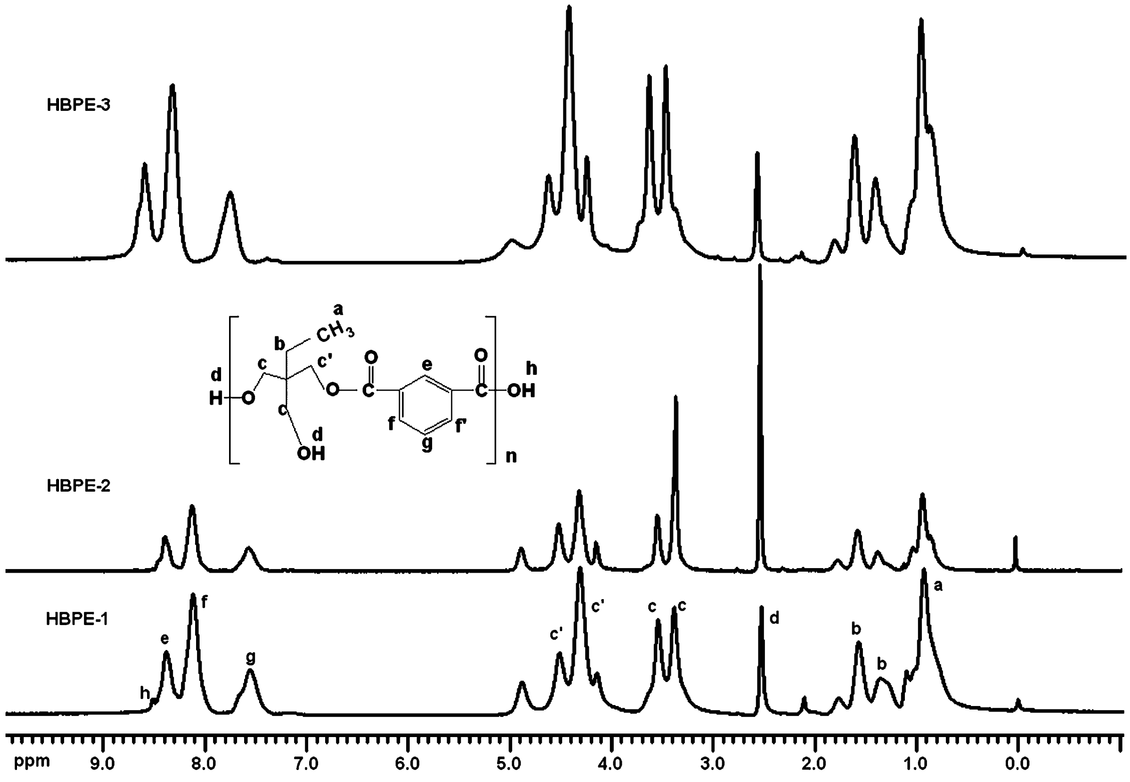

**Fig. 2.** $^1$H-NMR spectra of HBPEs.

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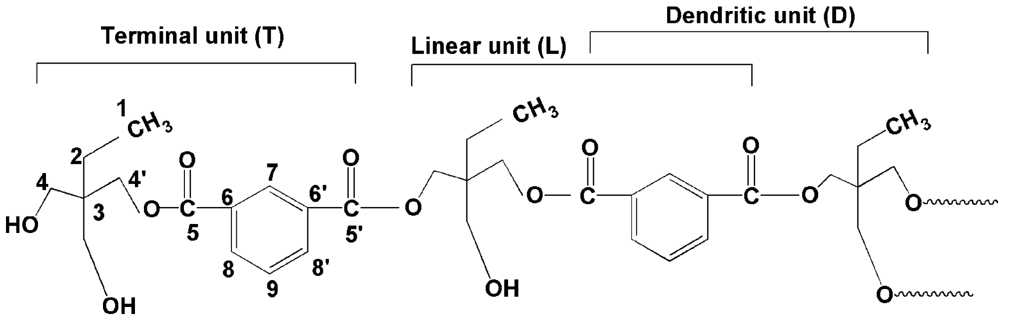

**Sch. 2.** Schematic sketch of the different structure units of HBPEs.

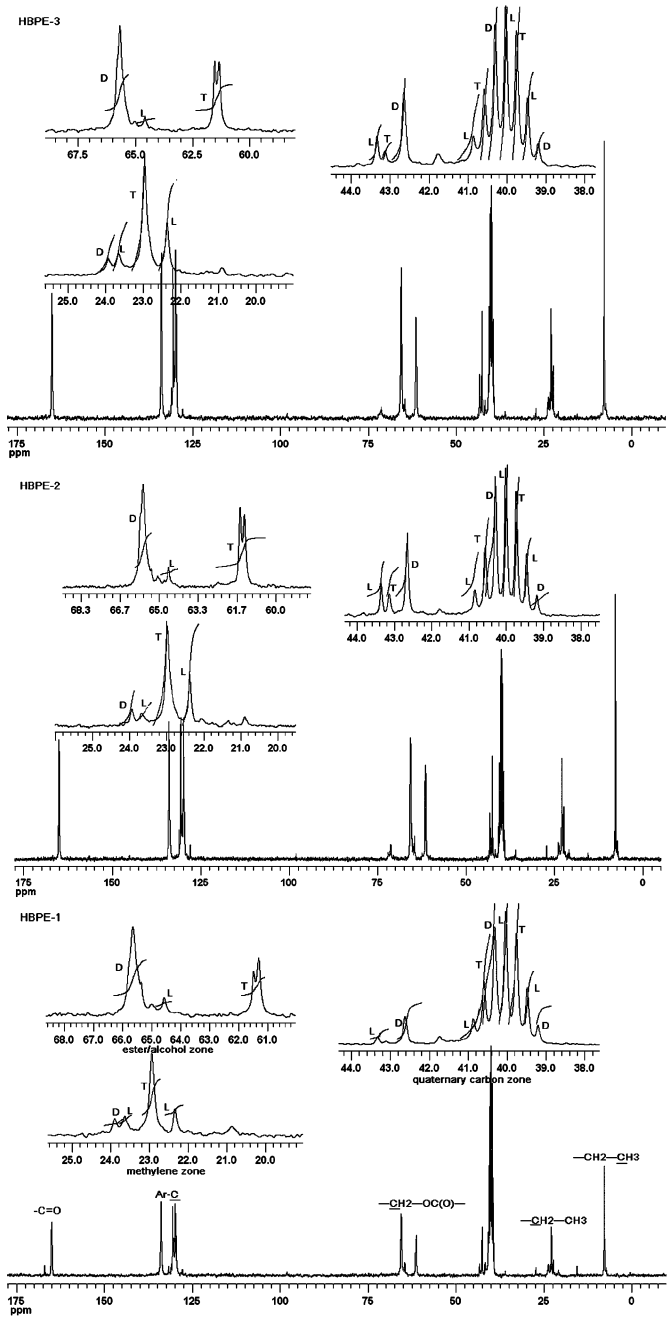

**Fig. 3.** $^{13}$C-NMR spectra of HBPEs.

HBPEs were done according to the reported method (30, 31). The different structure units of HBPEs are shown in Scheme 2, and the atoms of carbon are signed by 1, 2, 3, 4, 4′, 5, 5′, 6, 6′, 7, 8, 8′ and 9.

The $^{13}$C-NMR spectra of HBPEs (Fig. 3) showed that the resonances from the carbons in the T, L, and D units had different shifts due to the difference in their chemical environments. In Figure 3, the peaks at 165–167 ppm could be attributed to the carbonyl carbon of acid or ester, the peaks at 125–135 ppm are due to the aromatic carbons on the benzene ring, and the peaks at 60–67 ppm are due to the methylene carbon of ester and alcohol unit. The peaks between 39 and 44 ppm arise from quaternary carbons of TMP. The peak at 21–25 ppm is due to the methylene carbon, and the peak at 6–8 ppm is due to methyl carbon of $CH_3$ groups.

According to the good identification of different atoms and the well-separated signals corresponding to the different subunits from T, L and D parts, quantitative structural analysis of substructures from the $^{13}$C-NMR spectra was possible, resulting in the ratios of functional groups belonging to adequate structural units in the polymers. Therefore, the ratios of those subunits in the HBPEs can be estimated easily according to the intensity of the corresponding signals and the calculation of the values of DB was also possible.

The percentage of T, L and D units present in HBPEs, are calculated from the integral area ratios of methylene and quaternary carbon zone of $^{13}$C-NMR spectra, as a result, DB can be determined by using Equation 1 and the values of DB are shown in Table 2.

### 3.4 Molecular Weight and Polydispersity

The molecular weights of HBPEs have been determined by GPC using THF as solvent on the basis of linear

**Table 2.** Molecular weight and DB of HBPEs

| *Polymer* | $M_w$ | $M_n$ | $M_w/M_n$ | $DB_{Frey}$ |
|---|---|---|---|---|
| HBPE-1 | 8088 | 5833 | 1.39 | 0.49 |
| HBPE-2 | 8306 | 5956 | 1.39 | 0.48 |
| HBPE-3 | 7014 | 4377 | 1.60 | 0.39 |

**Table 3.** Thermal properties of HBPEs

| *Polymer* | $T_g(^\circ C)$ | $T_5(^\circ C)^a$ | $T_{10}(^\circ C)^a$ | *Weight residue at 600 °C (%)* |
|---|---|---|---|---|
| HBPE-1 | 85 | 242 | 321 | 6.58 |
| HBPE-2 | 86 | 344 | 372 | 8.76 |
| HBPE-3 | 64 | 309 | 340 | 5.50 |

[a] At this temperature the weight loss was 5% or 10%.

polystyrene standards. The weight-average molecular weight ($M_w$), number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$) are listed in Table 2. These data show that using the present synthetic strategy can obtain HBPEs with moderate molecular weights and narrow molecular weight distributions. It is well known that molecular weight determined by GPC measurements for a hyperbranched polymer is expected to be lower because of the smaller radius of chain gyration in comparison with linear counterparts (32). As a consequence, in this case, the actual molecular weight may have been higher than the experimental value.

### 3.5 Thermal Properties of HBPEs

Thermal stability of a polymer can provide an important guidance for its application. The studies of thermal behavior not only can explain the behavior of a polymer at high temperature, but also provide assistance for the establishment of selection criteria for specific applications of polymer materials (33).

The thermal properties of HBPEs determined by TGA and DSC are summarized in Table 3. All these HBPEs show similar decomposition behavior and good thermal stability in $N_2$ because they have same structures. TGA curves of HBPEs are shown in Figure 4. The sharp weight loss above 400°C is due to the heat decomposition of the polyester backbone. The glass transition temperatures ($T_g$) of the three HBPEs are 85°C, 86°C and 64°C, respectively. It also can be found that $T_g$ increases with increasing molecular weight.

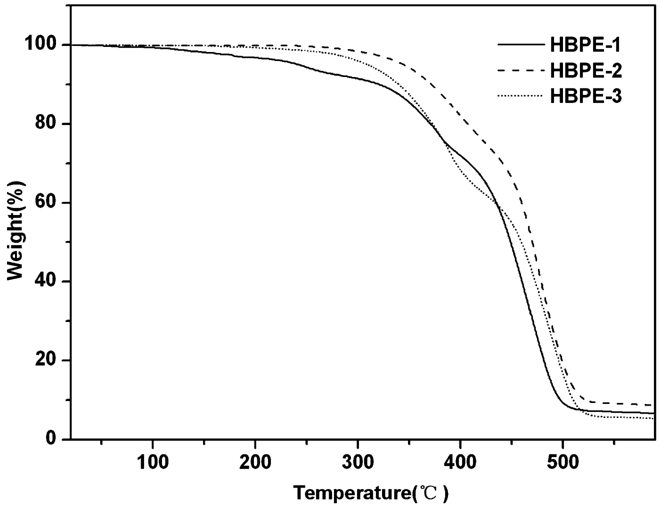

**Fig. 4.** TGA curves of HBPEs.

## 4 Conclusions

New HBPEs with good solubility and thermal stability were successfully synthesized by the readily available reagents of IPA and TMP via the $A_2+B_3$ approach. DB of HBPE-1, HBPE-2 and HBPE-3 were 0.49, 0.48, and 0.39, respectively. These HBPEs had moderate molecular weights and narrow polydispersities from 1.39 to 1.60, and had *ca* 8.5% weight-loss at 300°C in nitrogen, which render them particularly attractive in industrial applications. The application of HBPEs in coatings is under investigation and will be reported in a later study.

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