Phosphorus-containing polymers from THPS. II: synthesis and property of phosphorus-containing hyperbranched aromatic-aliphatic polyamides

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(Received 9 July 2014; accepted 6 November 2014)

Phosphorus-containing hyperbranched aromatic-aliphatic polyamides are prepared via direct polymerization of triacid (B\textsubscript{3}) with different diamines (A\textsubscript{2}), which for improving the processability of aromatic polyamides while keeping excellent thermal and mechanical property. The triacid (B\textsubscript{3}), tris(2-carboxyethyl)phosphine oxide (TCEPO), is synthesized from tetrakis(hydroxymethyl)phosphonium sulfate and its structure is verified by Fourier transform infrared, \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{31}P NMR spectroscopy. Then, the polycondensation reaction of TCEPO with \textit{p}-phenylene diamine, 4,4'-oxyphenylene diamine and 4,4'-methylenedianiline result in three phosphorus-containing hyperbranched aromatic-aliphatic polyamides, and the degree of branching is found between 0.66 and 0.71. Gel permeation chromatography measurement reveal that all hyperbranched aromatic-aliphatic polyamides have moderate number-averaged molecular weights and narrow molecular weight distribution. The Dynamic mechanical thermal analysis results show all polymers have two glass transition temperatures (\(T_g\)) in the temperature range 85.3–128.0 °C and have high storage modulus about 1.52–3.19 GPa at 50 °C. The TGA results reveal the initial degradation temperatures (\(T_d\)) and the temperatures for 10% gravimetric loss (\(T_{10}\)) for the hyperbranched aromatic-aliphatic polyamides are in the range of 214–250 and 256–333 °C, and the maximum decomposition temperatures (\(T_m\)) are about 500 °C, and also the char yields of polymers at 850 °C are about 39.4–48.4%, which indicate good thermal stability.

\textbf{Keywords:} phosphorus-containing polymer; hyperbranched aromatic-aliphatic polyamides; tris(2-carboxyethyl)phosphine oxide; tetrakis(hydroxymethyl)phosphonium sulfate; thermal stability

1. Introduction

Aromatic polyamides are acknowledged as one of the indispensable high-performance polymers, but all aromatic polyamides are generally characterized by poor processability arising from the rigid aromatic repeating units. Hyperbranched polymers usually have good solubility and low viscosity compared to the linear analogues.[1–12] Combining of chemically stable amide bonds with hyperbranched structures not only retained excellent thermal and flame-resistant properties of aromatic polyamides, but also decreased melt viscosity and excellent solubility which improved the processability.[13–20] Moreover, introduction of flexible aliphatic units into the main chain is another method to improve the processability of aromatic polyamides. This type of aromatic-aliphatic polyamides was known as glass-clear nyons with exceptional properties. Therefore, great efforts have been made to develop hyperbranched aromatic-aliphatic polyamides which included the introduction of flexible blocks as spacer units and the design of new aromatic-aliphatic \(AB_2\) building blocks.[21,22] The hyperbranched aromatic-aliphatic polyamides simultaneously possessed the advantages of hyperbranched polyamides and aromatic-aliphatic polyamides, which were expected to be high performance materials.

It is well known that phosphorus compounds are excellent candidates for thermally stable materials. Organophosphorus compounds have been used as flame retardants for decades.[23] The presence of the phosphorus compound plays an important role in the high performance of thermally stable materials due to its ability to inhibit ignition and promote char formation. The phosphorus-containing polymers, therefore, have been extensively synthesized and characterized to investigate the improvement of thermal properties.[24–28] Phosphorus-containing polyamides were for the first time provided by Joseph Pellon.[29] These phosphorus-containing polyamides generally were found to be amorphous—relatively low softening materials having an extended solubility range. Glass transition temperatures as a function of structure for phosphorus-containing polyamides were analyzed in terms of the effect of polarity, steric behavior, and bond flexibility differences.[30] Shalaby [31] had investigated the crystallizability and...
thermoplastic materials. Besides linear phosphorus-containing polyamides, several phosphorus-containing hyperbranched polymers, such as hyperbranched polyaspartimides,[32] hyperbranched polycarbonate esters,[33] hyperbranched polyphosphoester bisphenol-S ester,[34] were successfully prepared. And these polymers also showed good solubility in common solvents, high glass-transition temperatures, and excellent thermal stability. In this paper, three new phosphorus-containing hyperbranched aliphatic-aromatic polyamides were synthesized by direct polycondensation reaction of tris(2-carboxyethyl)phosphine oxide (TCEPO) with p-phenylene diamine (PD), 4,4’-oxyphenylene diamine (ODA) and 4,4’-methyleneedianiline (MDA), respectively (Scheme 1). TCEPO, the phosphorus-containing aliphatic triacid was synthesized from tetrakis(hydroxymethyl) phosphonium sulfate (THPS), which is a safe phosphorus-containing compound used as flame retardant and biocides. THPS is usually looked as a byproduct for consuming the PH3 which is a highly toxic and pyrophoric gas in phosphorous chemical industry. In order to consume THPS, the byproduct of phosphorous chemical industry, we have used THPS as a reactive intermediate to introduce expediently the phosphorus element into the main chain of polyureas, which is an isocyanate-free strategy.[35] The present work is the first attempt to synthesize phosphorus-containing hyperbranched aliphatic-aromatic polyamides using the environmentally-friendly THPS as a starting material.

2. Experimental

2.1. Materials

Tetrakis(hydroxymethyl)phosphonium sulfate (THPS) was purchased from Hubei Xingfa Chemical Company, China; methanol, 30% hydrogen peroxide, concentrated hydrochloric acid, glacial acetic acid, 4-methyl-2-pentanone, triphenyl phosphite (TPP), 1-methyl-2-pyrrolidone (NMP), pyridine, PD, 4,4’-oxyphenylene diamine and 4,4’-methylenedianiline were purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd. All chemicals were used as received without further purification.

2.2. Techniques

1H, 13C, and 31P NMR spectra of the monomers and polymers were recorded using 400 MHz Bruker NMR spectrometer in DMSO-d6, D2O, and CDCl3 containing small amount of TMS as internal standard.

Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex 70 FTIR spectrometer. Solid samples were prepared as KBr pellets and recorded at room temperature in the region of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

Thermal gravimetric analysis (TGA) data for polymers were taken on a PerkinElmer Thermal Analysis under N2 atmosphere at a rate of 10 °C·min⁻¹ from room temperature up to 850 °C. Dynamic mechanical thermal analysis (DMA) was performed on polymer films (with dimensions around 40 × 10 × 1.0 mm) with a PerkinElmer Instruments Diamond DMA analyzer, working in a tensile mode. The storage modulus, E’, and the loss tangent, tan δ, of each sample were obtained as function of temperature over the range from room temperature up to 200 °C, at frequency of 1 Hz, and at a heating rate of 5 °C·min⁻¹. The polymer films for DMA were prepared by compression molding at 140 °C for 5 min.

The molecular weight of polymer was determined by gel permeation chromatography (GPC) in N,N-Dimethylformamide (DMF) containing LiCl (0.5%, wt%) using polystyrene as standards. The flow rate of DMF (containing LiCl) was maintained as 1 mL/min. The polymer solution was prepared by dissolving 10 mg of the sample in 1 mL of DMF (containing LiCl), filtered and injected for recording the GPC chromatograms. The chromatograms were recorded using Waters 510 pump and Waters 410 differential RI detector.

2.3. Monomer synthesis

2.3.1. Synthesis of tris(2-cyanoethyl)phosphine [36]

While stirring to a solution of 180.3 g (0.33 mol) of 75% aqueous THPS in 75 mL of alcohol, a solution of 39.1 g (0.60 mol) of 85% potassium hydroxide was added in 40 mL of distilled water, below 30 °C by cooling outside. Next 116.4 g (2.20 mol) of acrylonitrile was added at such speed that the temperature of reaction mixture was 35–40 °C. After stirring overnight at room temperature, the reaction mixture was poured into ice water. The precipitate was collected, washed with cold water, and dried to obtain 98.3 g (77.2%) of tris(2-cyanoethyl)phosphine (TCP), m.p. 98–99 °C.

IR (KBr, cm⁻¹): 2920 (CH2), 2245 (CN). 1H NMR (DMSO-d6, ppm): 1.83 (t, 6H, P–CH2), 2.61–2.67 (m, 6H, CH2). 31P NMR (DMSO-d6, ppm): −25.15.

2.3.2 Synthesis of tris(2-cyanoethyl)phosphine oxide [37]

Ninety-seven grams (0.50 mol) of TCP was dissolved in 250 mL of glacial acetic acid by warming to 55 °C. A solution of 56.7 g (0.50 mol) of 30% aqueous hydrogen peroxide in 25 mL of glacial acetic acid was added dropwise with stirring while the temperature was maintained at 50–55 °C by means of an ice-bath. The mixture was stirred at 50 °C for an additional 30 min
and concentrated to about 100 mL by rotary evaporation under reduced pressure. Acetone (100 mL) was added, and the precipitated solid was collected by filtration and air-dried to obtain 90.0 g (86.0%) of the oxide, m.p. 172–173 °C. Recrystallization from aqueous isopropyl alcohol did not change the melting point.

IR (KBr, cm\(^{-1}\)): 2973, 2934 (CH\(_2\)), 2240 (CN), 1228, 1162 (P=O). \(^1\)H NMR (DMSO-\(d_6\), ppm): 2.17–2.23 (m, 6H, O=P–CH\(_2\)), 2.71–2.75 (m, 6H, CH\(_2\)). \(^{31}\)P NMR (DMSO-\(d_6\), ppm): 43.43.

### 2.3.2 Synthesis of TCEPO

A solution of 21.0 g (0.10 mol) of tris(2-cyanoethyl)phosphine oxide (TCPO) in 300 mL concentrated hydrochloric acid (35%) was refluxed for 6 h. The resulting solution was evaporated to dryness under reduced pressure. The residue was extracted with 50 mL of hot glacial acetic acid. Methyl isobutyl ketone (100 mL) was added to the extract and the precipitated solid was collected to obtain 25.1 g (94.5%) of the oxide, m.p. 152–153 °C. Recrystallization from isopropyl alcohol furnished the pure compound, m.p. 153–154 °C.

IR (KBr, cm\(^{-1}\)): 3300–2500, 955(OH); 2970, 2933 (CH\(_2\)); 1738, 1708 (carboxyl C=O), 1415, 1348 (C–O). \(^1\)HN M R(D\(_2\)O, ppm): 2.07 (q, 6H, P–CH\(_2\)), 2.53 (q, 6H, CH\(_2\)). \(^{13}\)C NMR (D\(_2\)O, ppm): 21.47 (P–CH\(_2\)), 25.74 (CH\(_2\)), 175.87 (COOH). \(^{31}\)P NMR (D\(_2\)O, ppm): 56.66.

### 2.4. Polymer synthesis

All of the polymers were prepared in the same manner.[16] The following describes the preparation of PD-01 as an example. A well-dried three-necked flask was charged with 1.08 g (10 mmol) of PD, 2.66 g (10 mmol) of TCEPO, 7.5 mL of pyridine, and 80 mL of NMP. Triphenyl phosphite (TPP) (7.82 mL, 30 mmol) was added to the solution after the monomers were dissolved completely. The mixture was heated at 80 °C for 3 h and then poured into 500 mL of methanol containing 10 mL of 12 N aqueous HCl. The precipitated products were collected by filtration and purified by reprecipitation from NMP solution into methanol. The products were washed with hot methanol and dried in vacuum at 100 °C overnight. The reaction conditions and results of the polymerization are summarized in Table 1.
TCP with hydrogen peroxide in acetic acid and obtained TCPO in 86.0% yield. The preparation of TCEPO from TCP has been investigated by Rauhut [37] who found that hydrolysis of the TCP in the presence of KOH and then acidi fi cation with concentrated hydrochloric acid could obtain tris(2-carboxyethyl)phosphine hydrochloride, and oxidation of tris(2-carboxyethyl)phosphine hydrochloride with hydrogen peroxide in aqueous sodium acetate gave TCEPO in 94.5% yield. However, in this paper, direct hydrolysis of the TCPO with concentrated hydrochloric acid could obtain TCEPO in the same yield.

The chemical structure of the TCEPO was verified by FTIR and NMR spectroscopy. As shown in supporting information Figure S7, FTIR spectra showed characteristic bands of carboxyl groups at 1738 and 1708 cm⁻¹. ¹H NMR spectra of TCEPO (see Figure 2(i)) showed the characteristic methylene C–H peaks at 2.05–2.12 ppm (connected with P atom) and 2.51–2.58 ppm (connected with carboxyl), and no significant signal of the carboxyl proton was observed. In ¹³C NMR spectrum (Figure 1(a)), the signals appeared at 175.87, 25.74, and 21.47 ppm confirming the formation of carboxyl and two kinds of methylene. As shown in Figure 1(b), ³¹P NMR spectrum of TCEPO showed a peak at 56.66 ppm. These results clearly confirmed that compound TCEPO synthesized herein was consistent with the proposed structure.

Table 1. Direct polycondensation of diamines and TCEPO in the presence of condensation agents.

| Code  | Diamine | NMP (mL) | TPP (mmol) | Pyridine (mL) | LiCl (g) | Mₚ, g mol⁻¹ | PDI | Yield (%) |
|-------|---------|----------|------------|---------------|----------|-------------|-----|----------|
| PD-01 | PD      | 80       | 30         | 7.5           | 0        | 1500        | 1.04| 66       |
| PD-02 | PD      | 80       | 30         | 7.5           | 0        | 1900        | 1.03| 75       |
| PD-03 | PD      | 80       | 20         | 5.0           | 0        | 65,600      | 1.23| 83       |
| PD-04 | PD      | 80       | 20         | 5.0           | 0        | 46,400      | 1.38| 92       |
| PD-05 | PD      | 65       | 30         | 7.5           | 0        | 1800        | 1.03| 82       |
| PD-06 | PD      | 50       | 20         | 5.0           | 0        | 1900        | 1.03| 86       |
| ODA-01| ODA     | 80       | 30         | 7.5           | 0        | 81,400      | 1.86| 73       |
| ODA-02| ODA     | 80       | 30         | 7.5           | 0        | 65,500      | 1.62| 81       |
| ODA-03| ODA     | 80       | 20         | 5.0           | 0        | 86,200      | 2.04| 71       |
| ODA-04| ODA     | 80       | 20         | 5.0           | 0        | 116,800     | 1.88| 64       |
| ODA-05| ODA     | 65       | 30         | 7.5           | 0        | 1300        | 1.02| 86       |
| ODA-06| ODA     | 65       | 20         | 5.0           | 0        | –           | –   | –        |
| ODA-07| ODA     | 65       | 20         | 5.0           | 1        | –           | –   | –        |
| MDA-01|MDA     | 80       | 30         | 7.5           | 0        | 38,600      | 1.28| 75       |
| MDA-02|MDA     | 80       | 30         | 7.5           | 0        | 27,300      | 1.16| 78       |
| MDA-03|MDA     | 80       | 20         | 5.0           | 0        | 46,500      | 1.37| 76       |
| MDA-04|MDA     | 80       | 20         | 5.0           | 0        | 58,000      | 1.72| 86       |
| MDA-05|MDA     | 65       | 30         | 7.5           | 0        | 45,100      | 1.51| 82       |
| MDA-06|MDA     | 65       | 20         | 5.0           | 0        | –           | –   | –        |
| MDA-07|MDA     | 65       | 20         | 5.0           | 1        | –           | –   | –        |

Figure 1. NMR of TEPCO, (a) ¹³C NMR, (b) ³¹P NMR.
3.2. Synthesis of hyperbranched polyamides

In this paper, we use commercially available diamine (PD, ODA, and MDA) as A₂ and a triacid, TCEPO, as B₃ to synthesize a series of phosphorus-containing hyperbranched aliphatic-aromatic polyamides in the presence of TPP and pyridine as condensing agents (as showed in Scheme 1). Hyperbranched systems were obtained through polycondensation of ABₙ (n ≥ 2) monomers in most of the early reports. In recent studies, however, there has been an increased interest in A₂ + B₃ systems because of the possibility that commercially available monomers may be important in industrial applications. Usually, this kind of reaction lead to networks, but soluble hyperbranched polymers can also be obtained by using optimum monomer concentration and stoichiometry and by stopping the reaction before it reached the gel point. The reaction of A₂ monomers with B₃ monomers may lead, to some extent, to the formation of AB₂ intermediates that undergo further polymerization reactions to give hyperbranched polymers, but many other structural units can be formed depending on reaction conditions. In this research, when PD reacted with TCEPO with a feed ratio of A₂-B₃ of 1:1 at 80 °C for 3 h with a total monomer concentration of 0.25–0.31 mol·L⁻¹ (4.35–6.78 wt %), and with three or two equivalents of TPP, no gelation was observed for the polymerization. If 4,4'-oxyphenylene diamine or 4,4'-methylenedianiline, instead of PD, was used to react with TCEPO, and with a total monomer concentration of 0.25–0.31 mol·L⁻¹, soluble hyperbranched polyamide was successfully achieved with three equivalents of TPP. If the amount of TPP was decreased to two equivalents, with a total monomer concentration of 0.31 mol·L⁻¹ gelation occurred in 2 h. So gelation occurred more easily for the polymerization of ODA or MDA and TCEPO than that of PA and TCEPO, which may be attributed to the higher degree of branching (DB) or the higher percentage of trisubstituted TCEPO units in the resulting polymer formed from ODA or MDA and TCEPO. While the reaction was performed with LiCl, gel formation was observed within 30 min and soluble hyperbranched polyamide was not obtained. Addition of LiCl can accelerate the polymerization.

The structure of the hyperbranched polyamides was confirmed by FTIR (Figure S8–S10 in supporting information) and ¹H NMR (Figure 2) measurements. Taking PD-03 as an example, the absorption peaks attributed to amide groups (–CONH–) were observed at 1666, 1570, and 3269 cm⁻¹, and that attributed to carboxylic groups was observed at 1737 cm⁻¹. The FTIR spectrum of ODA-04 and MDA-04 were almost identical to that of PD-03, all of the characteristic absorption bands were observed, however, with a small frequency shift. Moreover, an additional peak from the ether band (Ph–O–Ph) at about 1218 cm⁻¹ was observed with the

Figure 2. ¹H NMR of TEPCO and polymers, (i) TEPCO, (ii) PA-03, (iii) ODA-04, (iv) MDA-04.
ODA-04. ¹H NMR analysis results further supported the chemical structures of the polymers obtained. Figure 2(ii) showed the ¹H NMR spectra of PD-03. The peak at $\delta = 7.49$ was assigned to contributions from the aromatic protons in PD-03. The aromatic protons were assigned at 6.91 and 7.56 ppm in ¹H NMR spectrum of ODA-04 (Figure 2(iii)), and at 7.08 and 7.48 ppm in ¹H NMR spectrum of MDA-04 (Figure 2(iv)), respectively. All amide protons in the spectrum of three polymers could be found nearby 10.04 ppm. The peaks at $\delta = 2.04$ and 2.18 ppm were assigned to contributions from the methylene protons (a and a') close to P=O linkage in TCEPO unit. The methylene protons (b and b') close to C=O linkage in TCEPO unit appeared at higher ppm in the ¹H NMR spectrum (2.69 and 2.55 ppm). Moreover, an additional peak from the methylene protons (Ph–CH$_2$–Ph) at 3.78 ppm was observed in ¹H NMR spectrum of MDA-04.

The structural perfection of hyperbranched polymers is generally characterized by the DB, which is defined by Frechet [48] as follows:

$$\text{DB} = \frac{(D + T)}{(D + T + L)}$$  

(1)

where $D$, $T$, and $L$ refer to the numbers of dendritic, terminal, and linear units in the polymer, respectively. Experimentally, DB is usually determined from ¹H NMR spectroscopy by comparing the integration of the peaks for the respective units in the hyperbranched polymers. [49] For the PD-03, the peaks at $\delta = 2.04$ and 2.18 were assigned to contributions from the methylene protons (a and a') close to P=O linkage in TCEPO unit and the methylene protons (b and b') close to C=O linkage in TCEPO unit appeared at higher ppm in the ¹H NMR spectrum (2.69 and 2.55) which contain the information on DB. It is obvious that for the PD-03 the peaks around 2.04–2.18, and 2.55–2.69 ppm should be attributed to both dendritic, terminal, and linear units (peaks in the two regions are overlapped). The ¹H NMR spectra of ODA-04 and MDA-04 are similar to PD-03. Therefore, DB could not be determined from ¹H NMR spectroscopy by comparing the integration of the peaks for the respective units in the hyperbranched polyamides.

On the other hand, the DB of the phosphorus containing hyperbranched polyamides was determined from their $^{31}$P NMR spectra. As showed in Figure 3, the $T$, $L$, and $D$ units of PD-03 could be observed. As can be seen in Figure 4(a), the $T$, $L$, and $D$ units of PD-03 showed different absorption peaks at $\delta = 47.97$, 46.84, and 46.44 ppm, respectively. Although the peaks for the L and D units are partly overlapped, the DB of the TCEPO-based hyperbranched polyamides were roughly obtained from the peak area ratios from $^{31}$P MNR spectra. According to Equation (1), the DB of PD-03, ODA-04, and MDA-04 were thus estimated to be 0.66, 0.67, and 0.71, respectively. The calculated DB values of the polymers were listed in Table 2.

### 3.3. Molecular weight determination

The molecular weights of the hyperbranched polymers were estimated by GPC with linear polystyrene as standards. Although GPC calibrated with linear standards significantly underestimated the number-averaged molecular weights for branched systems, GPC analysis is still the commonly used means for measuring the molecular weights of hyperbranched polymers. The results from the GPC experiments of hyperbranched polyamides which were obtained in different monomer concentration and the amount of TPP/pyridine were presented in Table 1.
The $M_n$ of the PDs was about 65,600, while the polydispersity index (PDI = $M_w/M_n$) was 1.23, in the system of 80 mL NMP, 20 mmol TPP, and 5 mL pyridine. And $M_n$ of the others were under 2000, PDI were 1.03 or 1.04. The GPC of the ODAs showed the higher number-averaged molecular weights, while retaining a narrow molecular weight distribution ($M_n = 65,500–116,800$, PDI = 1.62–2.04), except as in the system of 65 mL NMP, 30 mmol triphenyl phosphite, and 7.5 mL pyridine ($M_n = 1300$, PDI = 1.02). The $M_n$ of MDAs were in the range of 27,300–58,000 and polydispersity were in range of 1.16–1.72. The real molecular weight of the polymer may be even larger than the value estimated from polystyrene standards because dendritic macromolecules generally have smaller size than linear polymers with the same molecular weight and can hardly be expanded in solution.

3.4. Thermal properties of hyperbranched polyamides

The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses ($T_5$ and $T_{10}$, respectively) of the polymers and the residue at 850 °C (char yield). The TGA at a rate of 10 °C min$^{-1}$ under nitrogen atmosphere was utilized to examine the thermal properties of the hyperbranched polyamides. The TGA curves

| Code   | $T_5$ (°C) | $T_{10}$ (°C) | $T_m$ (°C) | Char yield | $T_{g1}$ (°C)$^a$ | $T_{g2}$ (°C)$^a$ | $E'$ (GPa)$^a$ | DB |
|--------|------------|---------------|------------|------------|-------------------|-------------------|----------------|-----|
| PD-03  | 250        | 333           | 503        | 48.4       | 85.3              | 112.6             | 2.63           | 0.66|
| ODA-04 | 214        | 261           | 507        | 45.1       | 86.9              | 123.1             | 1.52           | 0.67|
| MDA-04 | 210        | 256           | 492        | 39.4       | 108.2             | 128.0             | 3.19           | 0.71|

$^a$Measured by DMA at a heating rate of 5 °C/min; Storage modulus ($E'$) is recorded at 50 °C.

Figure 5. Thermal analysis curves of polymers. (a) TGA curves of the polymers; (b) DMA curves of the polymer PD-03; (c) DMA curves of the polymer ODA-04; (d) DMA curves of the polymer MDA-04.
of polymers PD-03, ODA-04, and MDA-04 were showed in Figure 5(a) and the results were summarized in Table 2. As given in Table 2, the initial degradation temperatures \( (T_d) \) for PD-03, ODA-04, and MDA-04 were 250, 214, and 210 °C, respectively, and the maximum decomposition temperatures \( (T_m) \) were 503, 507, and 494 °C, respectively. The temperatures for 10% gravimetric loss \( (T_{10}) \) were in the range of 256–333 °C and also the char yields of polymers at 850 °C were about 39.4–48.4%, which was indicative of good thermal stability. Lin and co-workers [50,51] reported that the thermal stability of phosphorus containing thermosets was related to the electron density of the carbon adjacent to the phosphorus. The lower the electron density of the carbon, the lower its thermal stability. In this case, the electron-withdrawing P=O group reduced the electron density of the carbon, destabilizing the P–C bond. This may be the cause of that the \( T_d \) of the obtained hyperbranched polyamides were slightly lower than of the hyperbranched polyamides reported in the literature.[48] But the char yields of the obtained hyperbranched polyamides were far higher than that of the reported hyperbranched polyamides (the char yields of polymers at 600 °C were about 11–22%). The high thermal stability for the polymer was from the TCEPO groups. The phosphorus in the compound acted as a promoter of char formation, and the formed phosphorus-rich char was extremely thermally stable as compared with the pure carbonous char. The increased char formation indicates an enhanced flame retardancy.

The study on the dynamic mechanical properties of the hyperbranched polyamides can reveal the changes of the material structure in the process of the temperature increasing and the effect for the different diamine monomers. The dynamic mechanical behavior of the polymers was analyzed at a frequency of 1 Hz. The results for the storage modulus, \( E' \), and tan \( \delta \) are shown in Figure 5(b)–(d) and Table 2. In Table 2, PD-03, ODA-04, and MDA-04 showed a storage modulus about 2.63, 1.52, and 3.19 GPa at 50 °C, respectively, These results indicated that these hyperbranched polyamides had good mechanical properties at glassy state. In addition, \( E' \) of PD-03, ODA-04, and MDA-04 decreased sharply as temperature increased from 70 to 140 °C, from 60 to 150 °C, and from 90 to 140 °C, respectively (Figure 5(b)–(d)).

As seen in Figure 5(b)–(d), two tan \( \delta \) peaks of three samples were observed, these results indicated that these hyperbranched polyamides samples had two glass transition temperatures, the \( T_g \) values of the polymers were listed in Table 2. The first \( T_g \) of PD-03, ODA-04, and MDA-04 was 85.3, 86.9, and 108.2 °C, respectively. The second \( T_g \) of them was 112.6, 123.1, and 128.0 °C, respectively. Glass-transition temperature depends on the mobility of the polymer backbone, which in turn is sterically or chemically defined. In addition, the free volume of the molecules, which is reflected by the \( T_g \), depends on the end group interactions. From the topological point of view, \( T_g \) is increased with decreasing of branching degree and branching density, due to limitations in the molecular mobility.[49] Therefore, the most probable explanation for the two glass transition temperatures of our prepared hyperbranched polyamides, was the existence of two hyperbranched polyamides with different branching degree and branching density.

4. Conclusions
In this work, TCEPO, a phosphorus-containing aliphatic triacid, was first synthesized from tetrakis(hydroxy-methyl)phosphonium sulfate. Three new phosphorus-containing hyperbranched aromatic-aliphatic polyamides were successfully prepared by polycondensation reaction of TCEPO with PD, 4,4′-oxyphenylene diamine and 4,4′-methylenedianiline, respectively. GPC revealed that all hyperbranched aromatic-aliphatic polyamides had moderate number-averaged molecular weights, while retaining a narrow molecular weight distribution. The DMA results showed all polymers had two glass transition temperatures \( (T_g) \) in the temperature range 85.3–128.0 °C and had high storage modulus of about 1.52–3.19 GPa at 50 °C. These results indicated that the as-prepared hyperbranched polyamides had good mechanical properties at glassy state and better processability. The TGA showed that the initial degradation temperatures \( (T_d) \) and the temperatures for 10% gravimetric loss \( (T_{10}) \) for the hyperbranched aromatic-aliphatic polyamides were in the range of 214–250 °C and 256–333 °C, the maximum decomposition temperatures \( (T_m) \) were about 500 °C, and also the char yields of polymers at 850 °C were about 39.4–48.4%, which was indicative of good thermal stability.

Acknowledgments
The authors thank the NSF of China (No. 21274049), Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University (No. JDGD-2013-06) and the Fundamental Research Fund for Central Universities (2013QN159) for financial support. All authors give sincere thanks to Analysis and Testing Center of HUST for NMR, TGA, and DMA test.

Funding
Fundamental Research Fund for Central Universities (2013QN159).

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