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Polymer 47 (2006) 1511–1518

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Novel hyperbranched poly(phenylene oxide)s with phenolic terminal groups: synthesis, characterization, and modification

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Received 15 September 2005; received in revised form 7 January 2006; accepted 10 January 2006

Abstract

Novel hyperbranched poly(phenylene oxide)s (HPPOs) with phenolic terminal groups were prepared from 4-bromo-4′,4″-dihydroxytriphenylmethane via a modified Ullmann reaction. This monomer was treated with potassium carbonate or sodium hydroxide as a base and copper chloride as a catalyst in an aprotogenic solvent, either dimethylsulphoxide (DMSO) or sulfolane. The sulfolane/NaOH system at higher temperature led to more rapid polymerization, and a relative high molecular weight. The degrees of branching of these HPPOs from the DMSO/K_2CO_3 and sulfolane/NaOH systems were 71 and 48%, respectively, as determined by ^1H NMR integration experiments. The phenolic terminal groups underwent facile modification, furnishing hyperbranched polymers with a variety of functional chain ends. The nature of the chain-end groups had a significant influence on the solubility of the hyperbranched poly(phenylene oxide)s. The resulting polymers were characterized by NMR, Fourier transform infrared, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Keywords: Hyperbranched poly(phenylene oxide); Synthesis; Modification

1. Introduction

The field of dendritic polymers is now established and a series of highly branched materials characterized in terms of both structure and physical properties have been reported [1–8]. In spite of the uncontrolled and irregular structure, hyperbranched polymers present one major advantage over their structurally perfect cousins (dendrimers), namely the easy of synthesis, which is most often a one-pot self-condensation of an AB_x type monomer. Now hyperbranched polymers find a role not only as bulk materials in rheology modifiers, processing additives, and coating applications, but also as functional materials in catalysts, sensors, and nanotemplating material applications [9–12]. Modification of the peripheral groups on hyperbranched polymers significantly influences their physical properties [13,14], which provides a possibility toward larger scale potential applications.

Now many hyperbranched poly(arylene ether)s have been reported, such as poly(ether sulfone) [15], poly(ether ketone) [16,17], poly(ether oxazole) [18], and poly(ether phenyl quinoxaline) [19–21]. However, the reactive monomers for these hyperbranched polymers contain electron-withdrawing groups, which facilitate aromatic nucleophilic substitution reactions. The linear poly(phenylene oxide)s (PPOs) are well-known and useful engineering plastics (as constructional materials and electric components) and also high-performance membrane materials for gas separation and pervaporation [22], but only a few studies on hyperbranched variants of these polymers have been reported due to the inherent difficulties in the synthesis and purification. 2,4,6-Tribromophenol is an example of an AB_3 type of monomer with unactivated halides, which can be polymerized with 1 equiv. of KOH and a catalytic amount of $K_3Fe(CN)_6$ [23]. Kim et al. reported recently a hyperbranched PPO derived from 3,5-dibromophenol with unactivated halides [24]. However, these hyperbranched PPOs lack adaptability toward structural variation, because they always give terminal aryl halides, which limit their chemical modification for larger scale potential applications. In this article, we report the first example of the synthesis and characterization of a novel hyperbranched poly(phenylene

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doi:10.1016/j.polymer.2006.01.018

oxide) with phenolic terminal groups, which can be readily modified by reaction for various potential applications.

2. Experimental

2.1. Materials and apparatus

Diisopropyl azodicarboxylate (DIAD) was supplied friendly by JinXiang Chemical Factory in Danyang city of China. *p*-Bromobenzaldehyde was purchased from Beijing Colory Chemicals (China) Co., Ltd. Other starting materials and reagents were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. All chemicals were used without further purification.

Reactions for HPPOs were first run in round-bottom flasks with Dean–Stark trap, efficient magnetic stirrer, and N_2 line. After the azeotropic distillation for removing water finished, the Dean–Stark trap was replaced with a condenser, and reactions proceeded at higher temperature. For the sulfolane/NaOH system, an efficient mechanical stirrer was introduced due to high solution viscosity. Reaction temperatures were controlled by a Thermo-watch WMZK-01. Air was excluded from the reaction vessels by a positive pressure of dry N_2 before reactions. Modifications of the resulting HPPOs were carried out in three-necked round-bottom flasks with condenser, efficient magnetic stirrer and N_2 line at room temperature.

2.2. Measurements

IR spectra of the compounds were obtained with a Thermo Nicolet Impact 210 FT-IR spectrophotometer using KBr pellet. NMR spectra of the synthesized compounds were recorded on Bruker Fourier Transform AVANCE 600 spectrometers. The ^{13}C NMR spectra used for integration were carefully recorded by using a longer pulse delay time (8 s) in order to account for the nuclei's different relaxation times. Gel permeation chromatography (GPC) diagrams were obtained with a Waters GPC 515-2410 system equipped with a RI detector and packing column (Waters Styragel HT3-5-6E) using tetrahydrofuran as an eluent at 30 °C. Number and weight average molecular weights of the samples were calculated on the basis of polystyrene standards. Differential scanning calorimetry (DSC) was performed with a Pyris 1 DSC instrument under nitrogen at a heating rate of 20 °C/min with a gas flow 20 mL/min. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGS-2 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen and air, respectively.

2.3. Synthesis and modification

2.3.1. 4-Bromo-4′,4″-dihydroxytriphenylmethane (3)

A solution of *p*-bromobenzaldehyde (6.01 g, 32.5 mmol) and phenol (6.33 g, 67.3 mmol) in acetic acid (12 mL) was cooled to 0 °C and a mixture of sulfuric acid (12 mL) and acetic acid (40 mL) was added dropwise with stirring. The mixture was kept at 0 °C for 72 h, and then stirred into crushed ice. The orange solid was separated by filtration, washed with water, and vacuum-dried overnight, and then recrystallized from benzene as the benzene compound in pale yellow crystals, which melted at 79–81 °C with loss of solvent. The unsolvated compound melted at 128–131 °C. Yield: 5.19 g, 45%. IR (KBr): ν (OH) = 3332 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 5.43 (s, 1H, CH), 6.78 (d, 4H, C_6H_4O), 6.94 (d, 4H, C_6H_4O), 7.07 (d, 2H, C_6H_4Br), 7.46 (d, 2H, C_6H_4Br), 8.25 (s, 2H, OH). ^{13}C NMR (DMSO-d_6): δ 54.9 (s, CH), 116.3 (s, C_6H_4O), 120.2 (s, C_6H_4Br), 131.0 (s, C_6H_4O), 132.2 (d, C_6H_4Br), 135.2 (s, C_6H_4O), 145.7 (s, C_6H_4Br), 156.8 (s, C_6H_4O).

2.3.2. Polymerization in DMSO/K_2CO_3

Under stirring and nitrogen atmosphere, the compound 3 (0.8070 g, 2.272 mmol) and anhydrous K_2CO_3 (0.3602 g, 2.606 mmol) were added to the mixture of DMSO (32 mL) and anhydrous toluene (8.0 mL). The reaction mixture was kept circumfluent for several hours, and the water in the reaction mixture was removed by azeotropic distillation of toluene. After cooling to 40 °C, catalyst CuCl (4.5 mg, 0.0455 mmol) was added to this reaction mixture. The reaction mixture was heated to the desired temperature (170 °C) and maintained for 32 h. The polymerization mixture was then cooled to room temperature, acidified with diluted aqueous HCl, and precipitated into the mixture of MeOH and H_2O (MeOH vs H_2O equals 4:6 (v/v)). After dried at 60 °C in vacuo, the crude product was dissolved in THF, and filtered to remove any unwanted insoluble material. The THF solution was added dropwise into hexamethylene with vigorous stirring over a period of several hours. The precipitate was then isolated, washed with hexamethylene, and dried thoroughly under vacuum to give the brick red hyperbranched polymer (0.4215 g, 68%). IR (KBr): 3410 cm^{-1} (ν OH), 1261 cm^{-1} (ν Ph-O-Ph), 821 cm^{-1} (γ Ph-H). ^{1}H NMR (CD_3CN): δ 5.29–5.34 (t, –(Ph)$_3$C*H*), 6.43–7.63 (br, Ph-*H*), 9.84 (s, –Ph-O*H*). ^{13}C NMR (DMSO-d_6): δ 54.3, 54.5, 55.0, 115.0, 115.5, 119.4, 126.5, 127.6, 129.3, 130.2, 131.4, 134.8, 145.1, 153.7, 156.3.

2.3.3. Polymerization in sulfolane/NaOH

This was prepared from the compound 3 (1.3404 g, 3.774 mmol), NaOH (0.3050 g, 7.32 mmol), sulfolane (41 mL) and catalyst CuCl (7.8 mg, 0.0788 mmol) using the similar procedure described for the polymerization in DMSO/K_2CO_3. Note that after adding catalyst CuCl to the reaction system, the reaction mixture was heated to 200 °C for 4 h and then up to 210 °C for 2 h. Yield: 0.4045 g, 39%. IR (KBr): 3404 cm^{-1} (ν OH), 1238 cm^{-1} (ν Ph-O-Ph), 826 cm^{-1} (γ Ph-H). ^{1}H NMR (CD_3CN): δ 5.41–5.51 (t, –(Ph)$_3$C*H*), 6.49–7.60 (br, Ph-*H*), 9.85 (s, –Ph-O*H*). ^{13}C NMR (DMSO-d_6): δ 51.0, 54.1, 54.8, 115.5, 118.8, 119.7, 126.5, 128.7, 129.3, 130.3, 130.8, 131.6, 134.0, 134.6, 135.2, 139.3, 139.9, 144.5, 153.5, 155.4, 156.2.

2.3.4. Methoxy-terminated hyperbranched poly(phenylene oxide) (MHPPO)

To a solution of HPPO (0.4512 g, 1.57 mmol hydroxyl groups), anhydrous methanol (0.34 mL, 8.40 mmol), and triphenylphosphine (2.0980 g, 8.0 mmol) in THF (14 mL) under nitrogen, diisopropyl azodicarboxylate (1.30 mL) was added dropwise. The mixture was stirred at room temperature (25 °C) for 24 h and then added to methanol. The collected polymer was purified by repeated precipitation from $CHCl_3$ into methanol. Yield: 0.3393 g. IR (KBr): 2934 cm^{-1} (ν_{as} CH_3), 2833 cm^{-1} (ν_s CH_3), 1464 cm^{-1} (δ_{as} CH_3), 1395 cm^{-1} (δ_s CH_3), 1251 cm^{-1} (ν Ph-O-Ph), 1033 cm^{-1} (ν_s Ph-O-CH_3), 810 cm^{-1} (γ Ph-H). ^{1}H NMR ($CDCl_3$): δ 3.75 (CH_3O–), 5.34 (–$(Ph)_3$C*H*), 6.44–7.53 (Ph-*H*).

2.3.5. 1-Butoxy-terminated hyperbranched poly(phenylene oxide) (BHPPO)

To a solution of HPPO (0.2669 g, 0.93 mmol hydroxyl groups), 1-butanol (0.85 mL, 9.28 mmol), and triphenylphosphine (2.4376 g, 9.29 mmol) in THF (14 mL) under nitrogen, diisopropyl azodicarboxylate (2.00 mL) was added dropwise. The mixture was stirred at room temperature (25 °C) for 24 h and then added to a solution of methanol and water (MeOH vs H_2O equals 2:1 (v/v)). The collected polymer was purified by repeated precipitation from $CHCl_3$ into methanol. Yield: 0.2409 g. IR (KBr): 2958 cm^{-1} (ν_{as} CH_3), 2932 cm^{-1} (ν_{as} CH_2), 2870 cm^{-1} (ν_s CH_3), 1469 cm^{-1} (δ_{as} CH_3 and δ_s CH_2), 1382 cm^{-1} (δ_s CH_3), 1247 cm^{-1} (ν Ph-O-Ph), 1028 cm^{-1} (ν_s Ph-O–CH_2), 809 cm^{-1} (γ Ph-H). ^{1}H NMR ($CDCl_3$): δ 0.90 (CH_3), 1.07–1.95 ($CH_3(CH_2)_2CH_2O$–), 3.88 (–CH_2CH_2O-Ph–), 5.31 (–$(Ph)_3$C*H*), 6.46–7.55 (Ph-*H*).

2.3.6. 2-Methoxyethoxy-terminated hyperbranched poly(phenylene oxide) (MEHPPO)

To a solution of HPPO (0.3497 g, 1.21 mmol hydroxyl groups), ethylene glycol monomethylether (0.96 mL, 12.16 mmol), and triphenylphosphine (3.1825 g, 12.13 mmol) in THF (14 mL) under nitrogen, diisopropyl azodicarboxylate (2.61 mL) was added dropwise. The mixture was stirred at room temperature (25 °C) for 24 h and then added to a solution of methanol and water (MeOH vs H_2O equals 2:1 (v/v)). The collected polymer was purified by repeated precipitation from THF into hexamethylene. Yield: 0.2505 g. IR (KBr): 2978 cm^{-1} (ν_{as} CH_3), 2925 cm^{-1} (ν_{as} CH_2), 2877 cm^{-1} (ν_s CH_3), 2819 cm^{-1} (ν_s CH_2), 1463 cm^{-1} (δ_s CH_2), 1453 cm^{-1} (δ_{as} CH_3), 1373 cm^{-1} (δ_s CH_3), 1249 cm^{-1} (ν Ph-O-Ph), 1124 cm^{-1} (ν_{as} CH_2–O–CH_2), 1034 cm^{-1} (ν_s Ph-O–CH_2), 811 cm^{-1} (γ Ph-H). ^{1}H NMR ($CDCl_3$): δ 3.41 (CH_3O–), 3.87 ($CH_3OCH_2CH_2O$-Ph–), 4.04 (–Ph-$OCH_2CH_2OCH_3$), 5.27 (–$(Ph)_3$C*H*), 6.50–7.56 (Ph-*H*).

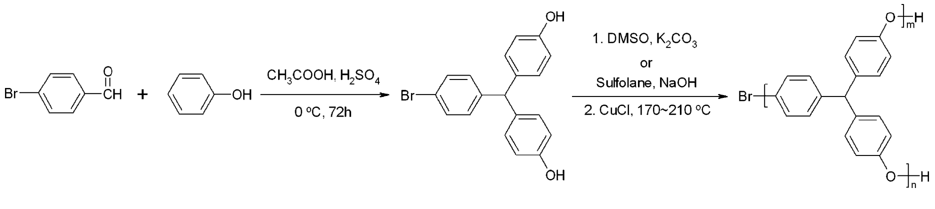
2.3.7. 2-(2-Methoxyethoxy)ethoxy-terminated hyperbranched poly(phenylene oxide) (MEEHPPO)

To a solution of HPPO (0.3189 g, 1.10 mmol hydroxyl groups), diethylene glycol monomethylether (1.30 mL, 11.04 mmol), and triphenylphosphine (2.8995 g, 11.05 mmol) in THF (14 mL) under nitrogen, diisopropyl azodicarboxylate (2.40 mL) was added dropwise. The mixture was stirred at room temperature (25 °C) for 24 h and then added to a solution of methanol and water (MeOH vs H_2O equals 2:1 (v/v)). The collected polymer was purified by repeated precipitation from THF into hexamethylene. Yield: 0.2366 g. IR (KBr): 2977 cm^{-1} (ν_{as} CH_3), 2924 cm^{-1} (ν_{as} CH_2), 2874 cm^{-1} (ν_s CH_3), 2822 cm^{-1} (ν_s CH_2), 1465 cm^{-1}(δ_s CH_2), 1453 cm^{-1} (δ_{as} CH_3), 1374 cm^{-1} (δ_s CH_3), 1249 cm^{-1} (ν Ph-O-Ph), 1109 cm^{-1} (ν_{as} CH_2–O–CH_2), 1031 cm^{-1} (ν_s Ph-O–CH_2), 819 cm^{-1} (γ Ph-H). ^{1}H NMR ($CDCl_3$): δ 3.36 (CH_3O–), 3.55 (–CH_2OCH_3), 3.69 (CH_3-OCH_2CH_2–), 3.82 (–Ph-OCH_2CH_2–), 4.06 (–Ph-OCH_2CH_2–), 5.31 (–$(Ph)_3$C*H*), 6.45–7.56 (Ph-*H*).

3. Results and discussion

3.1. Synthesis of the AB_2-type monomer 3

It is well known that phenolic and methylidyne groups have the capability of ‘catching’ free radicals and could inhibit oxidation of polymer materials. In addition, phenolic groups could be readily modified via William son reaction, Mitsunobu reaction etc. for various potential applications. For the preparation of an AB_2-type monomer in which the methylidyne group could be incorporated and the B part carried phenolic groups, commercially available *p*-bromobenzaldehyde and phenol were employed. AB_2-type monomer 3 (4-bromo-4′,4″-dihydroxytriphenylmethane) was synthesized (Scheme 1) according to Ref. [25], and treated by vacuumdrying at 70 °C for several days, but in its ^{1}H NMR spectrum in acetone-d_6, the peak belonging to the protons of compound benzene was found at 7.36 ppm (Fig. 1(a)). After again dried at 90 °C in vacuo for 2 days, the product had approximately 18% weight loss, and the peak corresponding to benzene protons disappeared in the spectrum (Fig. 1(b)). It implied that the solvation of compound 3 occurred while it was recrystallized from benzene. It could be seen that in the TGA thermogram of compound 3 dried at 70 °C in vacuo, a 17.8% weight loss within a temperature range of 79–118 °C occurred (Fig. 2), which is consistent with the calculated value by vacuumdrying experiment mentioned above. It



Scheme 1. Synthesis of HPPO from phenol and *p*-bromobenzaldehyde.

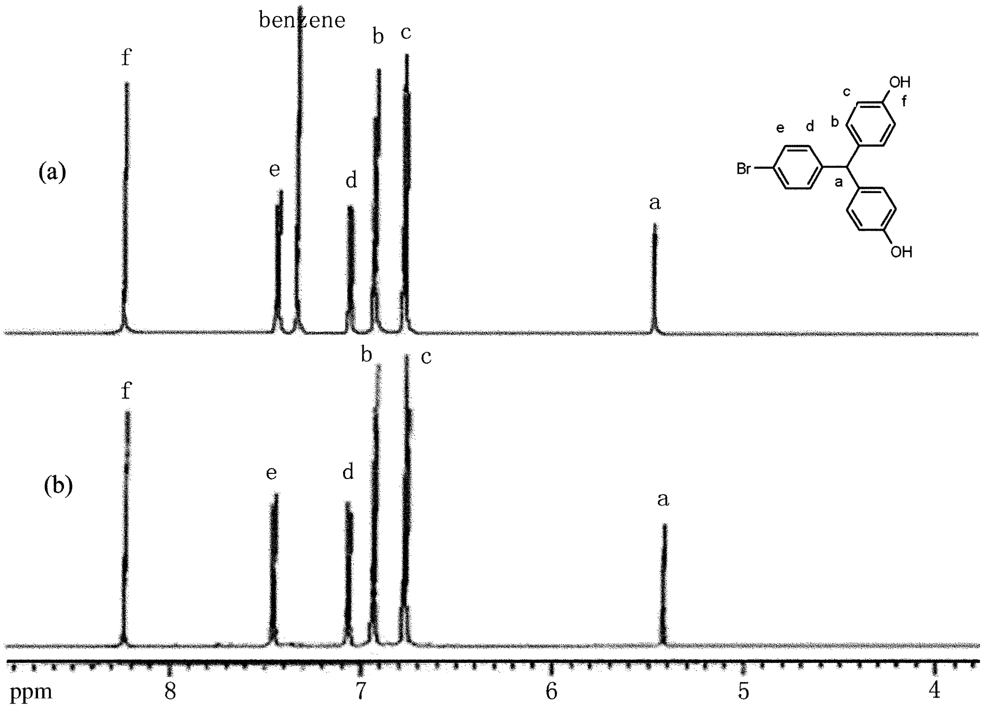


Fig. 1. ^{1}H NMR spectra of AB_2 monomer 3 dried in vacuo at 70 °C (a) and 90 °C (b) (in acetone-d_6).

further proved that the solvation behavior of compound 3 existed while the crude product was recrystallized from benzene. Compound 3 was well characterized by ^{1}H NMR, ^{13}C NMR, and IR.

3.2. Preparation of hyperbranched poly(phenylene oxide)

Hyperbranched poly(phenylene oxide) has been prepared using a modified Ullmann reaction (nucleophilic aromatic substitution reaction) similar to that used to prepare commercial linear poly(arylene ether)s, with 4-bromo-4′,4″-dihydroxytriphenylmethane as the branching AB_2 monomer, as shown in Scheme 1. For the sake of simplicity, Scheme 1 only shows the overall compositional repeat units, even though the hyperbranched polymers contain a combination of dendritic, linear, and terminal units. Ullmann reaction is a well-studied reaction; these reactions generally require relatively high temperatures (e.g. 210–230 °C) [26] or long reaction time (e.g. 5 days) [27] for low reactive monomers, and benzophenone is used as a typical solvent. Because the sodium (or potassium) salt of the monomer 3 was entirely insoluble in benzophenone, DMSO or sulfolane was used as a polymerization medium. In these reactions, CuCl acted as a catalyst, and Cu^+ could coordinate with the π system of the aromatic bromide, thus facilitating carbon–bromine cleavage. After polymerizations were accomplished, diluted aqueous HCl was added to quench any remaining phenolate anions, and then the crude polymers were isolated by precipitation into the mixture of MeOH and H_2O (MeOH vs H_2O equals 4:6 (v/v)). The resulting precipitates were thoroughly dried under vacuum at 60 °C, and then dissolved in certain amount of THF at room temperature. The THF solutions were filtered to remove the unwanted insoluble materials, and then reprecipitated with hexamethylene, followed by a filtration and dried thoroughly under vacuum, at last, the brick red powders could be obtained.

The resulting polymers were soluble in several organic solvents such as THF, DMF, DMAc or DMSO, but insoluble in various apolar and weak polar organic solvents such as benzene, toluene, ethanol, CH_2Cl_2, $CHCl_3$ and so on. These solubility results indicate that the highly branched structure and many phenolic terminal groups significantly affected the solubility. The linear poly(phenylene oxide) synthesized from 4-bromophenol is hardly soluble in any organic solvents [28].

The FT-IR spectrum of the resulting HPPO showed characteristic absorptions at about 1260 and 821 cm^{-1} corresponding to the Ph-O-Ph stretching and the Ph-H distorting, respectively (Fig. 3(a)), which indicate that the poly(phenylene oxide) prepared maintained the phenylene

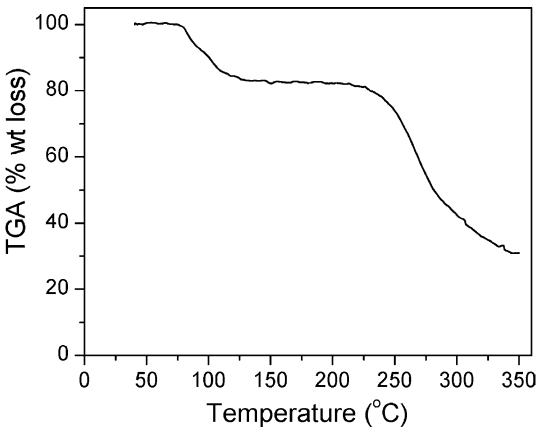


Fig. 2. TGA thermogram of AB_2 monomer dried at 70 °C in vacuo.

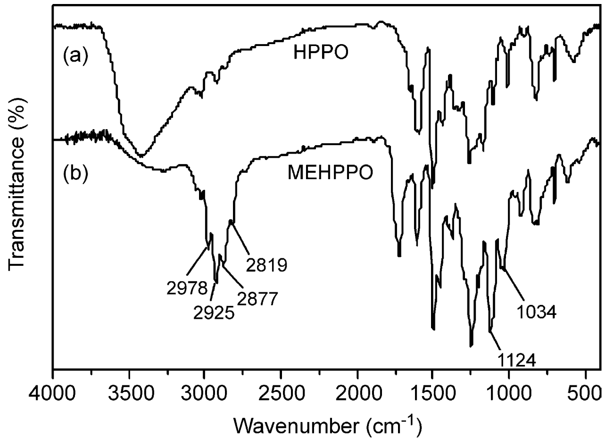


Fig. 3. The FT-IR spectra of HPPO (a) and MEHPPO (b).

structure with two *p*-substitution groups. In the ^{13}C NMR spectrum in DMSO-d_6 (Fig. 4), due to the presence of the phenyl ether bonds, a new peak at about 153.7 ppm of chemical shift appeared. The signal of the methylidyne carbons was still observed at about 54.5 ppm but split into several peaks, which may be attributed to its different chemical circumstances.

The average molecular weights (M_w and M_n) of the samples were determined by GPC using THF as solvent and polystyrene as standard, and the molecular weight distributions were unimodal. GPC curves from the DMSO/K_2CO_3 and sulfolane/NaOH systems are displayed graphically in Fig. 5 and polymerization results are summarized in Table 1. It was observed that the sulfolane/NaOH system led to more rapid polymerization, and the polymerization for this system gave a higher average molecular weight than that for the DMSO/K_2CO_3 system. The polydispersity of the resulting HPPOs increased with the increase of their molecular weights.

3.3. Degree of branching

The degree of branching (DB) is a typical characteristic frequently used to evaluate the irregularity of the structure of hyperbranched polymers. In principle, an AB_2 condensation polymerization can give rise to dendritic (*D*), linear (*L*) or terminal (*T*) units. According to the definition given by Fréchet [29], the degree of branching (DB) is calculated by the following equation:

$$DB = (D + T)/(D + T + L)$$

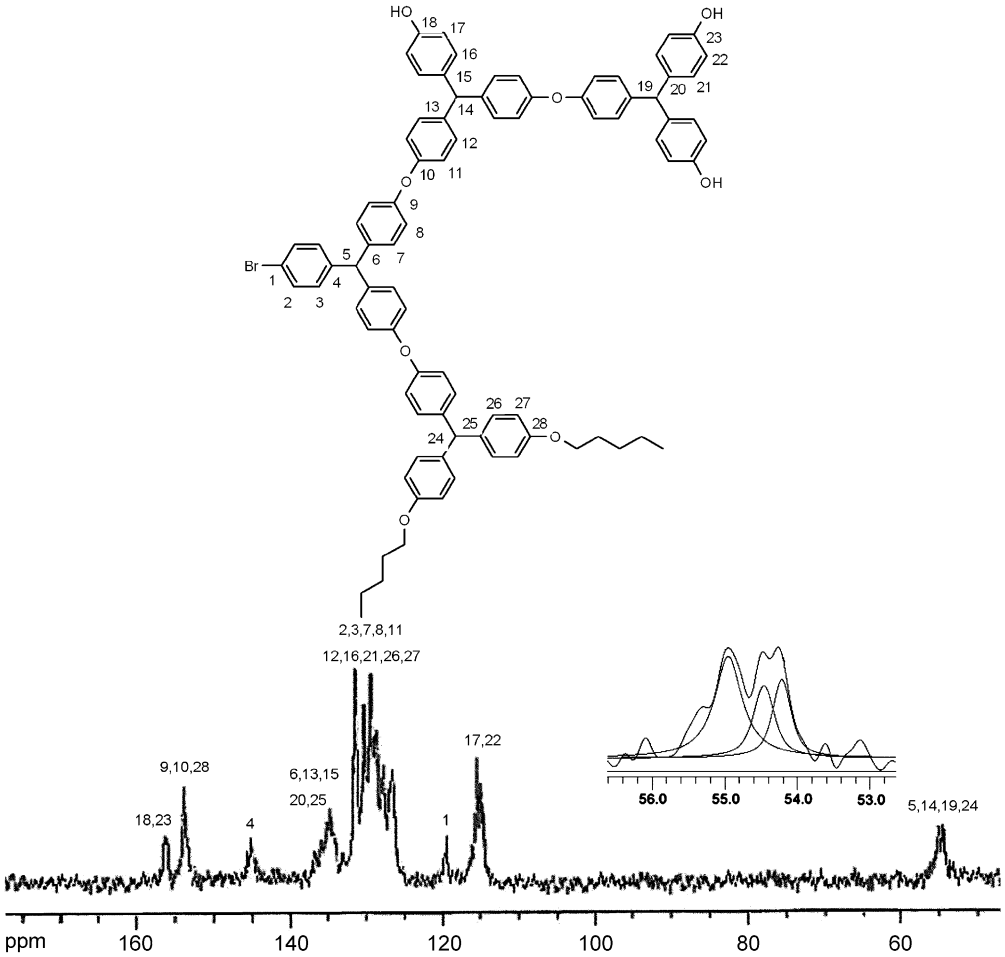


Fig. 4. ^{13}C NMR spectrum of HPPO (in DMSO-d_6).

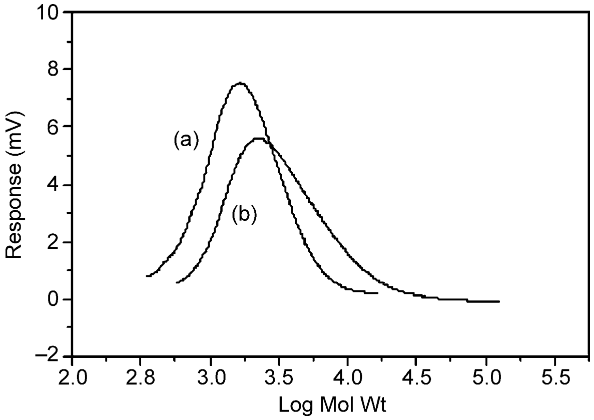


Fig. 5. GPC curves of HPPOs (a) for the DMSO/K_2CO_3 system and (b) for the sulfolane/NaOH system.

Table 1
Polymerization of AB_2-type monomer 3

Sample (solvent/base)	M_w (Da)	PD	DB (%)	T_g (°C)
DMSO/K_2CO_3[a]	2230	1.39	71	153
Sulfolane/NaOH[b]	5530	2.04	48	130

[a] Reaction condition: 170 °C for 32 h.
[b] Reaction condition: 200–210 °C for 6 h.

The ^1H NMR spectra in CD_3CN revealed fine structure attributable to the different types of repeat units (Fig. 6(a) and (b)). The DBs for the samples from the DMSO/K_2CO_3 and sulfolane/NaOH systems were 71 and 48% (Table 1), respectively. In addition, the sample from the DMSO/K_2CO_3 system was also characterized by the quantitative ^{13}C NMR spectrum in DMSO-d_6. It was observed that the signal of the methylidyne carbons at about 54.5 ppm split into three peaks attributable to the different types of repeat units in the polymer (Fig. 6(c)), but the peaks could not be used directly for integration due to overlapping. Adopting a curve-fitting procedure, the information of each individual peak was extracted, and the DB value of the resulting polymer could be calculated and was 74%, which accords with the calculated value from the ^1H NMR spectrum.

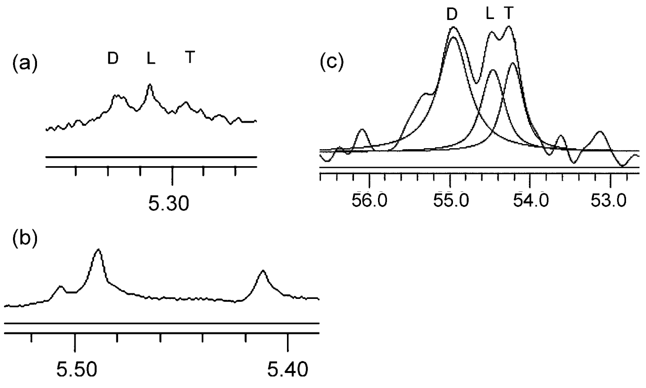


Fig. 6. ^1H NMR (a) and (b) and quantitative ^{13}C NMR (c) peak assignments for methylidyne carbons of HPPOs. (a) and (c) for the DMSO/K_2CO_3 system and (b) for the sulfolane/NaOH system.

The DB of the sample from the sulfolane/NaOH system had a distinct decrease compared with that from the DMSO/K_2CO_3 system. We think that higher temperature led to more rapid polymerization, and subsequently branched molecular architecture tended to linear. As we know, the entropy (S) increases while the temperature (T) increases. Therefore, the value of $T\Delta S$ would increase, and subsequently the change of free energy (ΔG) would decrease, which would lead to more rapid polymerization. However, for a given polymer chain, owing to the increase of entropy, the screening effect toward the B groups at linear units may enhance, which would decrease the reaction rate of these B groups. In addition, these groups were tied to the polymer backbone, which may also give rise to the decrease of their reaction rate. On the contrary, the reaction rate of the B groups at terminal units would greatly increase as the temperature increased. Thus, the higher temperature would enlarge the reactivity difference between the two types of B groups, i.e. enlarge the first shell substitution effect (In AB_2 molecules both B groups have the same reactivity, but as the first B group reacts, the second B group may have different one, which is the so-called first shell substitution effect [30]), and the polymerization in the sulfolane/NaOH system at higher temperature gave the branched product with more linear molecular architecture, i.e. with a lower DB.

3.4. Thermal properties

The thermal properties of the resulting HPPOs were studied with DSC and TGA. DSC analysis showed a clear T_g between 130 and 153 °C (Table 1), and no endothermic melting peak was observed up to 240 °C. The increase of T_g relative to that of linear poly(phenylene oxide) ($T_g \approx 95$ °C) may be a result of the highly branched molecular architecture reducing the mobility of the chain segments [24], or a result of the large number of phenolic terminal groups changing the nature of the intermolecular interactions. It is known that the increase in the polarity of the terminal groups can result in the enhancement in the extent of the intermolecular interactions, and subsequently increase the T_g values of the hyperbranched polymers [10]. Since our HPPOs had many polar phenolic terminal groups, they may have a tendency to increase T_g. Many hyperbranched polymers with higher T_g values relative to linear analogues have been reported [10,24,31,32]. The polymer prepared in the sulfolane/NaOH system had a lower observed T_g value (130 °C) compared with that in the DMSO/K_2CO_3 system (153 °C). This observation can be explained that the branched molecular architecture tended to linear with the decrease of degree of branching, and the mobility of the chain segments would increase. In addition, the intermolecular interactions may reduce with the decrease of degree of branching, which would also give rise to the reduction of the T_g value. The DSC curves showing the T_gs of polymers prepared from the DMSO/K_2CO_3 and sulfolane/NaOH systems are shown in Fig. 7.

The TGA experiments revealed that the HPPOs had thermal stability, with 5% weight loss temperature between 258 and 292 °C in nitrogen. In air, the 5% weight loss temperature of the polymers was between 280 and 330 °C, and slight higher

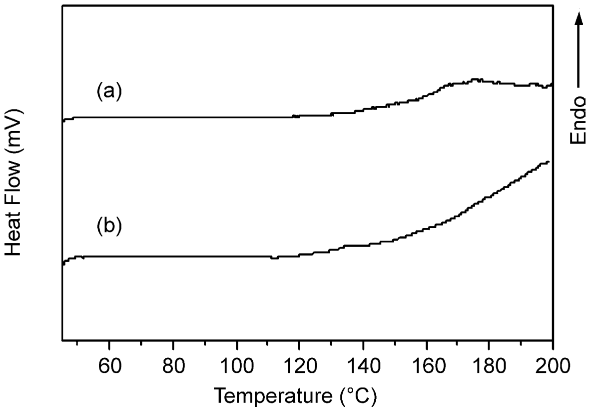


Fig. 7. DSC thermograms of HPPOs (scan rate 20 °C/min) (a) for the DMSO/K_2CO_3 system and (b) for the sulfolane/NaOH system.

than that in nitrogen. Under a nitrogen atmosphere, the HPPOs had a low rate of decomposition all along up to 700 °C with about 60% of the polymer residue. Under an air atmosphere, it was found that the HPPOs had two decomposition events. For the polymer from the DMSO/K_2CO_3 system, it had a low rate of decomposition up to 521 °C, with about 19% weight loss, and then a second T'_d of 521 °C with a T'_{max} of 600 °C appeared. The 700 °C residue was $<5\%$. The HPPO from the sulfolane/NaOH system had a similar result. The TGA values for all samples under both N_2 and air atmospheres are listed in Table 2, and Fig. 8 shows typical TGA curves for the HPPO (sulfolane/NaOH). In this figure, it was also found that the rate of weight loss in air was lower than that in nitrogen before the second T'_d. This phenomenon can be interpreted that some groups in HPPO may firstly be oxidized during decomposition process in air.

Table 2
Thermogravimetric analysis of HPPOs

Sample (atmosphere)	T_{d5} (°C)	T'_d (°C)	T'_{max} (°C)	Residue (%)
DMSO/K_2CO_3 (N_2)	258			62
Sulfolane/NaOH (N_2)	292			56
DMSO/K_2CO_3 (air)	280	521	600	4
Sulfolane/NaOH (air)[a]	330	489	567	8

[a] The sample was characterized on Netzsch STA 449 C simultaneous thermal analyzer.

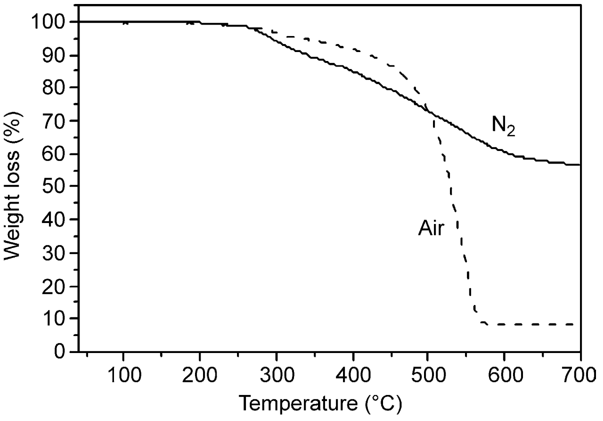
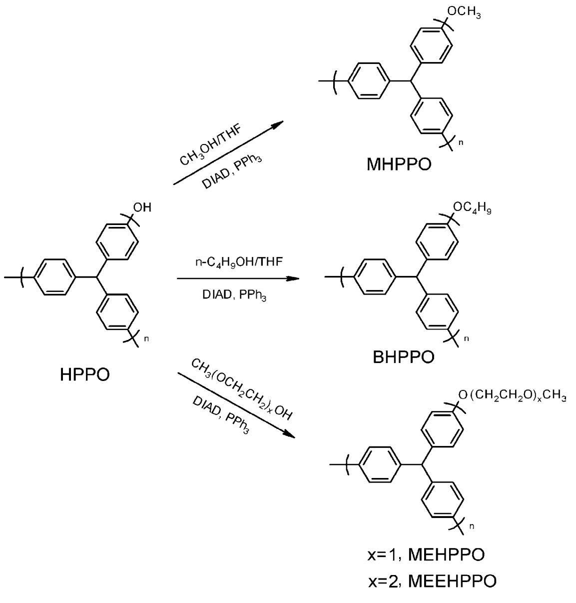


Fig. 8. TGA thermograms of HPPO from the sulfolane/NaOH system under N_2 atmosphere (solid line) and under air atmosphere (dashed line) (scan rate 10 °C/min).

3.5. Chemical modification of end groups

Hyperbranched polymers are characterized by their large number of chain-end groups. The modification of these peripheral branch-end groups gives rise to the great change of the material properties of hyperbranched polymers. For the HPPOs reported, they always give terminal aryl halides, which limit their chemical modification for larger scale potential applications. As shown in Scheme 2, different functional groups could be facilely introduced into the HPPOs prepared in this work via reactions of the terminal phenolic groups. A Mitsunobu reaction was employed for the preparation of modified HPPOs, in which methoxy, 1-butoxy, ethyleneoxy or diethyleneoxy units were coupled with the aryl hydroxyl branch-end. These modified HPPOs were well characterized by ^{1}H NMR and IR. In their ^{1}H NMR spectra in $CDCl_3$, a new peak appeared at 3.75–4.06 ppm corresponding to the proton absorption of the methylene (or methyl for MHPPO) which connected directly to oxygen in –O-Ph– group, which indicate the formation of aliphatic–aromatic ether bonds. In their IR spectra, the absorption bands appeared at about 1030 cm^{-1}, which were attributed to the Ph-O-CH_x ($x=2$ or 3) stretching. In addition, the characteristic absorption bands attributed to methyl, methylene, and/or aliphatic ether groups were also found at the corresponding wavenumber. A representative IR spectrum for MEHPPO is shown in Fig. 3(b).

The modification of the branch-end groups of the HPPO resulted in a remarkable change in its solubility. The HPPO was insoluble in chloroform, while modified HPPOs were soluble in chloroform. During the Mitsunobu reaction of HPPO



Scheme 2. Modification of HPPO.

Table 3
Solution properties of the HPPO and the modified HPPOs

Sample	Toluene	CH_2Cl_2	$CHCl_3$	THF	Ethyl acetate	DMF	DMSO
HPPO	−	−	−	+	±	+	+
MHPPO	±	+	+	+	±	±	±
BHPPO	+	+	+	+	±	±	−
MEHPPO	+	+	+	+	±	+	+
MEEHPPO	±	+	+	+	±	±	±

+, soluble; ±, partially soluble; −, insoluble.

with 1-butanol in THF to yield BHPPO, the precipitation occurred from reaction medium. However, when the product was dried after purification, it became soluble in THF. Solubility results of all polymers, including HPPO and modified HPPOs, are summarized Table 3.

4. Conclusions

Hyperbranched PPOs with terminal phenolic groups can be readily prepared by the one-pot polymerization of an AB_2 monomer, 4-bromo-4′,4″-dihydroxytriphenylmethane, using the modified Ullmann reaction methodology. The sulfolane/NaOH system at higher temperature led to more rapid polymerization. DB (or T_g) of the resulting samples was a function of the polymerization conditions: the polymer prepared in sulfolane/NaOH had a lower DB, and subsequently gave rise to a lower T_g value. Due to the presence of the branched structure and the large number of polar phenolic terminal groups, the resulting samples exhibited higher T_g values between 130 and 153 °C relative to linear PPOs ($T_g \approx 95$ °C), and no endothermic melting peak was observed up to 240 °C. The resulting polymers showed thermal stability, with 5% weight loss temperature of above 258 °C. The modification of the peripheral hydroxyl groups in the HPPOs can be facilely curried out by the Mitsunobu reaction, yielding hyperbranched polymers with a variety of functional chain ends, and brought about a significant change in their solubility. The simple, one-pot approach to HPPOs with phenolic terminal groups provides an entry to many further studies and applications for these new materials.

Acknowledgements

Financial support from National Natural Science Foundation of China (50473042) and Beijing Natural Science Foundation (2042017) is acknowledged with thanks.

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