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Synthesis, modification, and characterization of hyperbranched poly(ether ketones)

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Abstract

This report presents the synthesis and chemical modification of hyperbranched poly(ether ketones). The polymer was conveniently prepared by direct polycondensation of an AB_2 monomer, 3,5-diphenoxybenzoic acid, using phosphorus pentoxide/methanesulfonic acid (PPMA) as the condensing agent and solvent. The hyperbranched poly(ether ketone) could be modified via the electrophilic aromatic substitution of the active phenoxy groups at the chain ends with a variety of carboxylic acids. The thermal properties of the hyperbranched poly(ether ketones) depend heavily on the nature of the chain end, with glass transition temperature ranging from −24°C to 180°C. Moreover, the length of the terminal alkyl groups significantly influences the solubility of the hyperbranched poly(ether ketones). By varying the chain ends, hyperbranched poly(ether ketones) soluble in either a polar or nonpolar solvent could be obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrophilic aromatic substitution; Glass transition temperature; Hyperbranched poly(ether ketone)

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1. Introduction

In recent years, nonlinear polymers such as dendritic or hyperbranched macromolecules have attracted considerable attention owing to the potential new properties of their highly branched, highly functionalized, three-dimension globular structure [1,2]. Dendrimers which have a well-defined and perfectly branching structure are built up by either a stepwise divergent or a convergent approach [3–6]. The sequential synthetic scheme frequently involves isolating and purifying the product at every step of the growth process, thereby limiting the large scale preparation. As an alternative, hyperbranched polymers are prepared by a one-step polymerization process that yields a highly branched, irregular structure. Although having a less perfect structure than dendrimers, hyperbranched polymers still maintain many of the architectural features found in their more perfectly defined dendritic counterparts and are supposed to exhibit properties resembling those of dendritic ones [7].

The one-step synthesis allows hyperbranched polymers to be more readily available and prepared on a large scale for potential applications. This attractive feature has led to the development of novel synthetic routes for the preparation of hyperbranched polymers [8–36], especially the one-step synthesis based on AB_2 monomers which have A and 2B functional groups located at 1, 3, 5 positions of a benzene ring. This report concerns the use of an AB_2 monomer, 3,5-diphenyoxybenzoic acid, in the one-step preparation of a hyperbranched poly(ether ketone). Two methods were used to prepare traditional linear poly(ether ketones) [37, 38]. The first method is a synthesis involving nucleophilic aromatic substitution, resulting in the formation of an aryl ether linkage. The second method is a synthesis involving electrophilic aromatic substitution in which an aryl ketone linkage is obtained. The nucleophilic reaction was applied to synthesise hyperbranched/dendritic poly(ether ketones) using AB_2 monomers containing a phenolic group and two aryl fluorides which were activated toward nucleophilic displacement by carbonyl moieties [16,35,39]. The synthetic procedure used herein is derived from the electrophilic substitution reaction developed by Ueda to prepare linear aromatic poly(ether ketones) [40–42]. In this procedure, the polymeric aryl ketone linkages are formed via direct self-polycondensation of the substituted benzoic acid containing phenyl ether structures using a mixture of phosphorus pentoxide/methanesulfonic acid (PPMA) as the condensing agent and solvent [40–43]. This one-step synthesis leads to the formation of a hyperbranched poly(ether ketone). This polymer could be derivatized by reacting the

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terminal phenoxy groups with various carboxylic acids. The physical properties of these hyperbranched poly(ether ketones) are investigated, along with the effect of changes in the nature of the chain ends which are evaluated as well.

2. Experimental section

2.1. General directions

The reagent PPMA (Eaton's reagent) was obtained from Aldrich and used as received. Other starting materials and reagents were used as obtained from the suppliers. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity 300 MHz spectrometer. Differential scanning calorimetry (DSC) was performed on a SEIKO SSC 5200 DSC using a heating/cooling rate of 10°C min^{-1}. Thermogravimetric analysis (TGA) was made on a SEIKO TG/DTA 200 using a heating rate of 10°C min^{-1} in nitrogen. Size-exclusion chromatography (SEC) was carried out on a Waters chromatography connected to a waters 410 differential refractometer with DMF as the solvent. UV–VIS absorption spectra were taken on a HP 8453 UV/VIS spectrometer. Infrared spectra were recorded on a Nicolet 520 FTIR spectrometer. Mass spectra were obtained on a JEOL JMS-HX 110 with EI ionization. Analytical TLC was performed on commercial Merck plate coated with silica gel GF254. Silica gel for column chromatography was Merck kieselgel 60 (70–230 mesh).

2.2. 1-Methyl-3,5-diphenoxybenzene (**1**)

2.2.1. Method A

A mixture of phenol (9.04 g, 96.1 mmol), KOH (4.4 g, 80.0 mmol), and toluene (6 ml) was stirred at 145°C for 4 h with water being collected in a Dean–Stark trap. Excess phenol and water were then removed under reduced pressure at 160°C for 2 h. To the dry salt was added copper powder (0.1 g), 3,5-dibromotoluene (2.0 g, 8.0 mmol), and phenol (4 ml). The reaction mixture was stirred under nitrogen at 210°C for 3 h. The reaction mixture was poured into water (150 ml), and 5 wt.% NaOH aqueous solution was added to dissolve the excess phenol. The mixture was extracted with ethyl acetate (3 × 70 ml). The combined extracts were dried and evaporated to dryness. The crude product was purified by column chromatography, eluting with CH_2Cl_2/hexane 1 : 2 to give **1** (2.08 g, 94%) as a colorless liquid.

2.2.2. Method B

A mixture of 5-methylresorcinol (10 g, 80.6 mmol), KOH (9.04 g, 161.1 mmol), and toluene (150 ml) was stirred at 145°C for 4 h with water being collected in a Dean–Stark trap. The solvent and water were then removed under reduced pressure at 160°C for 2 h. To the dry salt was added bromobenzene (63 g, 400 mmol), CuCl (3 g), and pyridine (160 ml). The mixture was stirred under nitrogen at 140°C for 15 h. The reaction mixture was poured into water (500 ml), acidified with 4 N HCl_{aq}, and extracted with ethyl acetate (3 × 250 ml). The combined extracts were dried and evaporated to dryness. The crude product was purified by column chromatography, eluting with CH_2Cl_2/hexane 1 : 2 to give **1** (15.81 g, 71%). ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 6.48 (t, 1 H, $J = 2.4$ Hz), 6.53 (d, 2 H, $J = 2.4$ Hz), 7.01 (d, 4 H, $J = 8.4$ Hz), 7.09 (t, 2 H, $J = 7.2$ Hz), 7.32 (dd, 4 H, $J = 8.4, 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 106.5, 114.0, 119.1, 123.4, 129.7, 141.0, 156.8, 158.4; MS(*m*/*e*) 276.1150, calcd. 276.1150 for $C_{19}H_{16}O_2$.

2.3. 3,5-Diphenoxybenzoic acid (**2**)

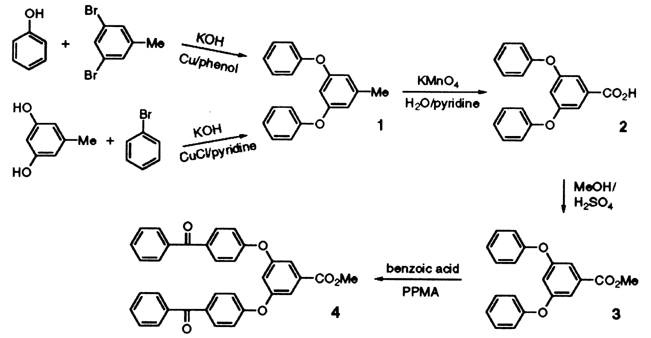
To a mixture of **1** (12.0 g, 43.4 mmol), water (6 ml), and pyridine (160 ml) heated at 100°C, $KMnO_4$ (68 g, 0.43 mmol) was added in small portions over 6 h. The reaction mixture was stirred at 120°C for 36 h. The manganese dioxide was filtered and extracted with hot water, and the filtrate was acidified with 4 N $HCl_{(aq)}$. The product was collected by filtration and purified by column chromatography, eluting with $CHCl_3$ and then ethyl acetate to give **2** (10.65 g, 80%). ^{1}H NMR (D6-DMSO) δ 6.90 (t, 1 H, $J =$ 2.4 Hz), 7.10 (d, 4 H, $J = 8.4$ Hz), 7.12 (d, 2 H, $J = 2.4$ Hz), 7.21 (t, 2 H, $J = 7.2$ Hz), 7.44 (dd, 4 H, $J = 8.4, 7.2$ Hz), 13.29 (br, 1 H); ^{13}C NMR (D6-DMSO) δ 112.1, 112.4, 119.7, 124.6, 130.3, 133.8, 155.4, 158.7, 166.1; MS (*m*/*e*) 306.0870, calcd. 306.0892 for $C_{19}H_{14}O_4$.

2.4. Methyl 3,5-diphenoxybenzoate (**3**)

A mixture of **2** (0.15 g, 0.49 mmol), methanol (4 ml) and concentrated H_2SO_4 (0.2 ml) was heated at reflux for 3 h. The reaction mixture was poured into water (150 ml), neutralized with aqueous sodium bicarbonate solution, and extracted with ethyl acetate (3 × 30 ml). The combined extracts were dried and evaporated to dryness to give **3** (0.152 g, 97%). ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 6.86 (t, 1 H, $J = 2.1$ Hz), 7.02 (d, 4 H, $J = 8.7$ Hz), 7.13 (t, 2 H, $J =$ 7.8 Hz), 7.34 (d, 2 H, $J = 2.1$ Hz), 7.35 (dd, 4 H, $J = 8.7$, 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 52.3, 113.3, 113.8, 119.3, 124.0, 129.9, 132.7, 156.1, 158.7, 166.0; MS (*m*/*e*) 320.1044, calcd. 320.1049 for $C_{20}H_{16}O_4$.

2.5. Methyl 3,5-di(4-benzoylphenoxy)benzoate (**4**)

A mixture of **3** (0.2 g, 0.624 mmol), benzoic acid (0.47 g, 3.85 mmol), and PPMA (3.5 ml) was stirred under nitrogen at 80°C for 4 h. The reaction mixture was poured into water (200 ml), neutralized with sodium bicarbonate, and extracted with ethyl acetate (3 × 50 ml). The combined extracts were dried over anhydrous sodium sulfate, and evaporated to dryness to give **4** (0.32 g, 97%). ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3 H), 7.02 (t, 1 H, $J = 2.4$ Hz), 7.08 (d, 4 H, $J = 8.7$ Hz), 7.47 (dd, 4 H, $J = 7.5, 7.2$ Hz), 7.53 (d, 2 H, $J = 2.4$ Hz), 7.57 (t, 2 H, $J = 7.2$ Hz), 7.77 (d, 4 H,

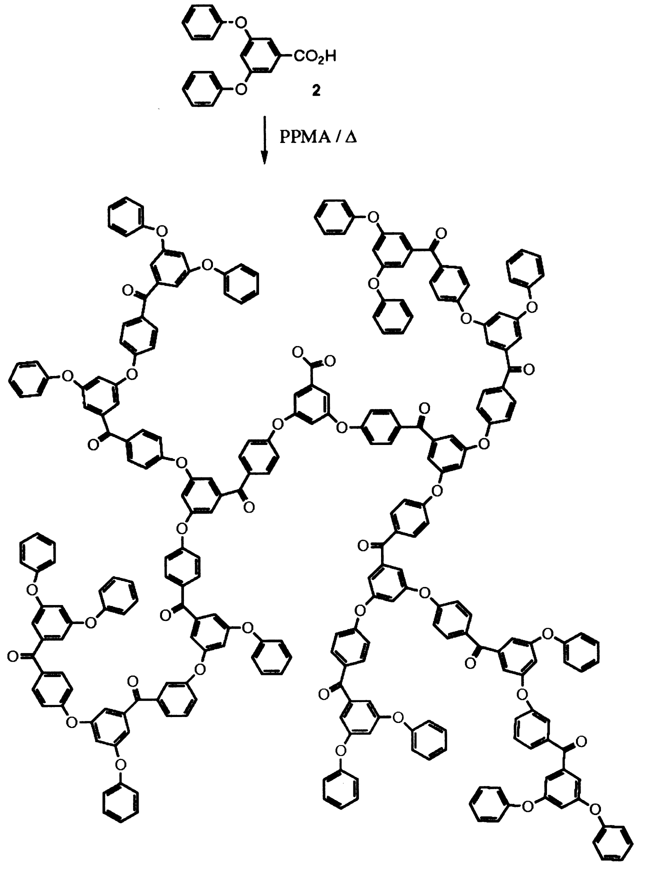


Scheme 1.

$J = 7.5$ Hz), 7.84 (d, 4 H, $J = 8.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.5, 115.5, 116.1, 117.9, 128.3, 129.8, 132.3, 132.6, 133.0, 133.4, 137.6, 157.3, 160.1, 165.5, 195.3; MS (*m*/*e*) 528.1539, calcd. 528.1573 for $C_{34}H_{24}O_6$.

2.6. Preparation of hyperbranched poly(ether ketone) (*P1*)

A solution of **2** (0.6 g) in PPMA (3.6 ml) was stirred under nitrogen at 90°C for 24 h. The reaction mixture was poured into water (200 ml). The polymer was collected, washed with water, and stirred again in water (200 ml) at 70°C for 12 h. The polymer was collected and dried in vacuo. The crude product was purified by precipitating from CH_2Cl_2 into methanol to give **P1** (0.5 g, 89%). Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.16; H, 4.20. Found: C, 77.70; H, 4.19.



Scheme 2.

2.7. Preparation of hyperbranched poly(ether ketone) (*P2*)

A solution of **P1** (0.1 g) and *p*-toluic acid (0.66 g) in PPMA (3 ml) was heated at 90°C for 6 h. The resulting solution was poured into water (300 ml). The precipitate was filtered, and washed with water and methanol, and reprecipitated from DMF into methanol to give **P2** (0.12 g, 87%).

2.8. Preparation of hyperbranched poly(ether ketone) (*P3*)

A solution of **P1** (0.1 g) and 4-*n*-octylbenzoic acid (0.32 g) in PPMA (3 ml) was heated at 90°C for 6 h. The resulting solution was poured into water (300 ml). The precipitate was filtered, and washed with water and methanol, and reprecipitated from THF into methanol to give **P3** (0.11 g, 62%).

2.9. Preparation of hyperbranched poly(ether ketone) (*P4*)

A solution of **P1** (0.1 g) and stearic acid (0.47 g) in PPMA (4 ml) was heated at 90°C for 6 h. The resulting solution was poured into water (300 ml). The precipitate was filtered and washed with water and acetone. The polymer was dissolved in hot toluene (100 ml). The solution was then concentrated to 2 ml, and precipitated into acetone to give **P4** (0.12 g, 64%).

3. Results and discussion

3.1. Synthesis and characterization of the hyperbranched poly(ether ketone) (*P1*)

The AB_2 monomer 3,5-diphenoxybenzoic acid, **2**, was prepared by either reacting phenol with 5-dibromotoluene or reacting 5-methylresorcinol with bromobenzene via the Ullmann reaction to form compound **1** [44, 45], followed by oxidation of the methyl group of **1** with $KMnO_4$ [46], as outlined in Scheme 1. The general procedure developed by Ueda for the preparation of linear aromatic poly(ether ketone)s [40–42] was applied to the one-step polymerization of the AB_2 monomer. The synthesis of poly(ether ketone) is based on the electrophilic aromatic substitution, in which an aryl ketone linkage is formed by condensing an carboxylic group with an activated phenyl group. In this synthetic procedure, PPMA was used as the condensing agent and solvent [43]. PPMA is expected to react with the carboxylic acid group to yield a highly activated mixed anhydride intermediate between the carboxylic acid and methanesulfonic acid and enable condensation to proceed under rather mild reaction conditions. To demonstrate the feasibility of using this reaction for the formation

Table 1
Polymerization of 3,5-diphenoxybenzoic acid in PPMA

Temperature (°C)	Time (h)	M_w [a]	M_n [a]	M_w/M_n	T_g (°C)
90	6	20 180	4890	4.12	150
90	12	31 990	5750	5.58	159
90	24	59 460	6740	8.82	168
110	6	98 500	7710	12.78	180

[a] SEC in DMF solutions calibrated against poly(ethylene glycol) standards.

of hyperbranched poly(ether ketones), the reaction of benzoic acid with the bis-phenoxy groups of monomer **2** in PPMA was chosen as the model reaction for the polymerization of **2**. The carboxylic group of **2** was initially protected as a methyl ester group to give compound **3**, which was then reacted with an excess of benzoic acid. The model reaction proceeded at 80°C in PPMA and yielded compound **4** quantitatively after 4 h. In the acylated product **4**, the two benzoyl groups were exclusively at the *para* position of the bis-phenoxy groups, as analyzed by NMR spectroscopy. The model reaction revealed that the acylation had taken place clearly at the *para* position. Based on the model study it seems apparent that the electrophilic aromatic substitution of **2** occurs in the yield and selectivity required for a polymer forming reaction.

The one-step polymerization of **2** was performed in PPMA to give the corresponding hyperbranched poly(ether ketone), **P1**. The structure of **P1** and the general reaction are shown in Scheme 2. The IR spectrum of **P1** exhibits characteristic absorptions at 1664 and 1212 cm^{-1} corresponding to the C=O and C–O–C stretching. As predicted theoretically by Flory [47], the direct polymerization of AB_2 type monomers would produce polymers with a highly branched, irregular structure, which prevents close packing and crystallization of various polymer segments. The hyperbranched **P1** was found to be highly soluble in a variety of solvents such as $CHCl_3$, CH_2Cl_2, THF, DMF, and NMP. The enhanced solubility of **P1** when compared to that of linear poly(ether ketone)s is consistent with the highly branched structure of **P1** and is in agreement with similar results obtained for other hyperbranched macromolecules [35]. Unlike dendritic macromolecules, which are essentially perfectly branched, hyperbranched macromolecules have a much more irregular structure. The concept of the degree of branching was introduced to better define the structure of the hyperbranched polymers [9]. In the AB_2 systems such as 1,3,5-substituted benzene, the degree of branching determined by NMR is usually about 50%–60% [8,17–19,24]. However, for the hyperbranched poly(ether ketone) **P1**, the degree of branching could not be determined from its ^1H NMR spectrum because the chemical shifts of the aromatic protons were not well resolved for this determination.

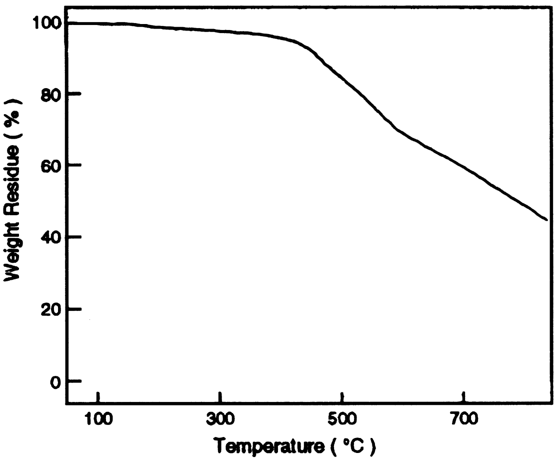
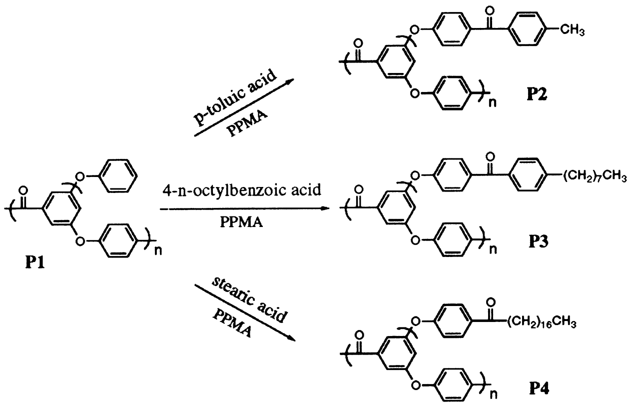


Fig. 1. TGA thermogram of hyperbranched poly(ether ketone) **P1**.



Scheme 3.

The molecular weight of the hyperbranched poly(ether ketone) was determined by SEC analysis in DMF solutions calibrated against poly(ethylene glycol) standards, and used only for a rough estimate. It was noted that SEC measurements, in which linear polymer standards were used to determine molecular masses for highly branched polymers, tended to underestimate the true molecular weight of the hyperbranched polymers [48]. The molecular weight of the resulting polymer was sensitive to the reaction time and the reaction temperature. As seen in Table 1, samples with a broad range of molecular weights were prepared. The molecular weight distribution of these poly(ether ketones) is broad, and broader than that of hyperbranched poly(ether ketones) prepared by nucleophilic substitution [35]. As the molecular weight increases, the molecular weight distribution becomes broader. This observation resembles previous reports of other hyperbranched polymers [18,24,32] and is consistent with the predictions of Flory [47].

The glass transition temperature (T_g) of the hyperbranched poly(ether ketone) was determined by DSC. T_g of **P1**, which was observed to increase modestly with molecular weight, ranged from 150°C to 180°C, as shown in Table 1. The thermal stability of **P1** was examined by TGA. A typical trace for polymer **P1** is shown in Fig. 1. The polymer is stable up to 400°C, with a 10% weight loss occurring over 460°C. This result indicates that the thermal

Table 2
Effect of the functionality of the chain ends on the thermal and solution properties of the hyperbranched poly(ether ketones)

Polymer	T_g(°C)	Solubility[a]						
		Octane	Toluene	CH_2Cl_2	$CHCl_3$	THF	DMF	NMP
P1	150	−	−	+	+	+	+	+
P2		−	−	+	+	+	+	+
P3	16	−	±	+	+	+	+	+
P4	− 24	±	±	±	±	±	−	−

[a] Solubility: +, soluble; ±, partially soluble; −, insoluble.

stability of the hyperbranched poly(ether ketone) **P1** is comparable to that of the linear analog [40–42].

3.2. Chemical modification of hyperbranched poly(ether ketones) (*P1*)

Hyperbranched polymers based on AB_2 monomers are characterized by a large number of chain end groups, the number of which is equal to the degree of polymerization plus one. The terminal phenoxy groups in **P1** are active toward electrophilic substitution and readily react with carboxylic acids to form aryl ketone linkages. As shown in Scheme 3, alkyl groups with different chain length could be introduced into the terminal positions of **P1** by reacting the terminated phenoxy groups with a variety of carboxylic acids using PPMA as the condensing agent and solvent. The degree of functionalization of the derivatized polymers was estimated by comparing ^1H NMR integration of the alkyl peaks with that of the aromatic peaks. For **P2** and **P3**, the ^1H NMR analysis showed that the functionalization was almost completed ($>$ 95%), indicating the phenoxy groups at the chain ends of **P1** are readily accessible to reagents in solution. For **P4**, ^1H NMR analysis in solvents such as $CDCl_3$ and THF(D_4) revealed an interesting solution state behavior. The aromatic peaks become obscure owing to the significant broadening of their ^1H NMR resonances and only the resonances associated with the heptadecyl group at the chain ends were observed. This spectroscopic observation may be attributed to the formation of aggregates in solution, with the more polar dendritric poly(ether ketone) block likely to be situated at the core and surrounded by the nonpolar, long linear alkyl chains. The aggregation might significantly increase the relaxation times for the aromatic protons of the confined aryl-ether–ketone blocks and lead to the broadening of their ^1H NMR resonances. Similarly spectroscopic phenomena was observed in dendritic–linear block copolymers [49]. Further, the ratio of the ^1H NMR integration of the alkyl peaks to that of the aromatic peaks is about twice larger than expected if the convertion of the formation of **P4** is 100%. This may result from the broadening of ^1H NMR resonances caused by the aggregation or from the contamination of unreacted stearic acid in **P4**. Nevertheless, the latter possibility can be easily ruled out by DSC experiments. For a sample of **P4** mixed with 0.1 equivalent of stearic acid, in addition to the endothermic curve corresponding to the glass transition of the polymer, an endothermic peak arising from the melt of stearic acid was also observed. A sample containing **P4** only, however, did not show any melting point in the DSC thermogram. Therefore, we conclude that the smaller than expected integration for the aromatic protons may also be attributed to the broadening of their ^1H NMR resonances resulting from the aggregation.

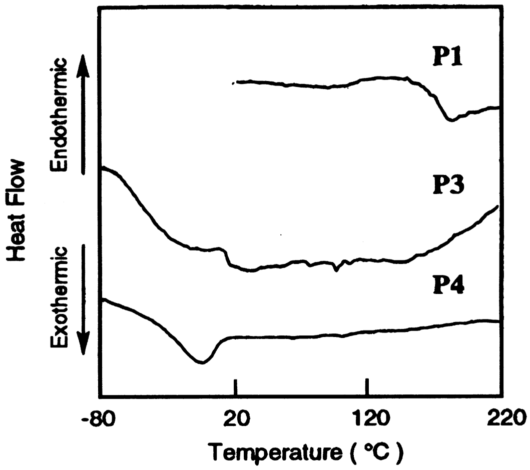


Fig. 2. DSC thermograms of hyperbranched poly(ether ketones) **P1**, **P3** and **P4**.

It was shown that the nature of the chain ends markedly affects properties such as the glass transition temperature (T_g) and the solubility of hyperbranched polymer (Table 2) [29–36, 50–52]. As shown in Fig. 2, the T_gs determined by DSC of these poly(ether ketones) heavily depend on the chain length of the terminal alkyl groups, with decreases in T_g following increases in alkyl chain length. On going from **P1**, to an octyl end group, **P3**, the glass transition temperature of the hyperbranched poly(ether ketones) drops from 150°C to 16°C. A further decrease in T_g to − 24°C is observed for the polymer **P4** with heptadecyl end groups. Attempts were made to measure the T_g of **P2**. However, between 0°C and 300°C, no reliable endotherm corresponding to the glass transition of **P2** was observed.

As a result of the lack of crystalline packing and complexation of the solvent in the cavities, the hyperbranched poly(ether ketone) has an enhanced solubility in organic solvents. **P1** and **P2** are highly soluble in typical solvents such as CH_2Cl_2, THF, DMF and NMP. However, the different chain ends led to differences in solubility in polar and nonpolar solvents. An increase in the chain length of the terminal alkyl groups implies a reduction in the solubility of the polymer in polar solvents, resulting in a situation in which **P4** is insoluble in DMF. Conversely, the linear alkyl chains help impart solubility in nonpolar solvents. Although **P1** and **P2** are totally insoluble in nonpolar solvents, **P3** and **P4** are soluble in toluene and **P4** is partially soluble in octane.

4. Summary

A hyperbranched poly(ether ketone) was conveniently prepared by the self-condensation of an AB_2 monomer, 3,5-diphenoxybenzoic acid, using PPMA as the condensing agent and solvent. This one-step synthesis involved electrophilic aromatic substitution, resulting in the formation of the ketone linkage. The phenoxy groups at the chain ends of the hyperbranched poly(ether ketone) are highly reactive for further electrophilic aromatic substitution and readily reacted with various carboxylic acids. In addition, the nature of the chain ends markedly affects the physical properties such as glass transition temperature and solubility of the modified hyperbranched poly(ether ketones). As the length of the terminal alkyl groups increase, the T_g of the polymer decreases, and the solubility of the polymer in polar solvents is reduced, becoming more soluble in nonpolar solvents.

Acknowledgements

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