Hyperbranched Poly(ether ketone) with Carboxylic Acid Terminal Groups: Synthesis, Characterization, and Derivatization

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ABSTRACT: A new procedure is described for the formation of a hyperbranched poly(ether ketone) with carboxylic acid terminal groups. This preparation was based on the one-step synthesis of an AB_2-type monomer 5-phenoxyisophthalic acid using phosphorus pentoxide/methanesulfonic acid as the condensing agent and solvent. The electrophilic aromatic substitution reaction led to the formation of the aryl ketone linkage. With the help of model compounds, ^1H NMR studies revealed that the degree of branching of the poly(ether ketone) was about 55%. The terminated carboxylic acid groups were readily functionalized, yielding hyperbranched polymers with a variety of different functional chain ends. The nature of the chain ends was shown to dramatically affect physical properties of the hyperbranched macromolecules. The ammonium derivative was soluble in water and behaved as a unimolecular micelle.

Introduction

Recently, hyperbranched macromolecules have received considerable attention due to the expectation that their unique highly branched structure will impart unusual properties.[1a] Hyperbranched polymers may be considered as irregular analogues of the dendritic macromolecules that have a well-defined and perfectly branched structure.[1b] Although dendrimers are built up by step-by-step sequences,[1b] requiring isolation and purification after each step, hyperbranched polymers are prepared by direct one-step polymerization of AB_2 monomers.[2,3] The AB_2-type monomer is unique because there is double the amount of B functionality compared with the A functionality in the polymerization mixture. Despite this stoichiometric imbalance, a high molecular weight polymer is achieved because both functionalities are located on the same molecule. For each A functionality reacted, a new A functionality is connected to the polymer chain. As predicted theoretically by Flory,[4] direct polymerization of this type of monomer would produce polymers with a highly branched, irregular structure possessing one unreacted A functional group and $n + 1$ number of unreacted B functional groups at the chain ends of the polymers, where n is the degree of the polymerization. In pronounced contrast to linear polymers, these hyperbranched polymers possess numerous branching points and end groups. The chain-end functional groups have been shown to dramatically affect the physical properties of the hyperbranched polymers.[3,5]

Intense research efforts have been devoted to the development of novel synthetic routes to hyperbranched polymers as well as the investigation of the physical properties of these polymers. Aromatic poly(ether ketone)s are a class of polymer that gained technical interest because they have outstanding thermal and mechanical properties.[6] The preparation of traditional linear poly(ether ketone)s has been carried out by two methods,[7] the first of which 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 has been applied to the synthesis of hyperbranched/dendritic poly(ether ketone)s using AB_2 monomers containing a phenolic group and two aryl fluorides which were activated toward nucleophilic displacement by carbonyl moieties.[2i,3f,8]

This report describes another synthetic approach for the preparation of hyperbranched poly(ether ketone)s. The synthetic procedure used here is derived from the linear aromatic poly(ether ketone)s.[9] In this procedure the polymeric linkages are formed via direct self-polycondensation of the substituted isophthalic acid containing phenyl ether structures using phosphorus pentoxide/methanesulfonic acid in a weight ratio of 1:12 (PPMA) as condensing agent and solvent.[9,10] This one-step synthesis led to the formation of a hyperbranched poly(ether ketone) possessing numerous terminal carboxylic acid groups. By chemical modification reactions of the carboxylic chain ends, a variety of different functional groups were introduced into the hyperbranched poly(ether ketone). The effect of the chain-end functional group on the physical properties of these hyperbranched poly(ether ketone)s was investigated.

Experimental Section

General Directions. Tetrahydrofuran (THF) was distilled from a sodium diphenyl ketyl solution just before use. 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. 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 dimethylformamide (DMF) as the solvent. UV−vis absorption spectra were taken on a HP 8453 UV/vis spectrometer. Mass spectra were obtained on a JEOL JMS−HX 110 with EI ionization. Analytical TLC was performed on commercial Merck plated coated with silica gel GF254. Silica gel for column chromatography was Merck kieselgel 60 (70−230 mesh).

1,3-Dimethyl-5-phenoxybenzene, 1. A mixture of phenol (6.1 g, 64.8 mmol), toluene (6 mL), and KOH (3.03 g, 54 mmol)

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was heated at 145 °C for 2.5 h with the water collected in a Dean−Stark trap. Then, excess phenol and water were removed under reduced pressure at 160 °C for 3 h. Copper powder (0.1 g), 5-bromo-*m*-xylene (2 g, 10.8 mmol), and phenol (3 mL) were added to the dry salt. The mixture was stirred under nitrogen at 220 °C for 3 h. The reaction mixture was poured slowly into water (150 mL), and aqueous 5 wt % NaOH solution was added to dissolve the excess phenol. The mixture was extracted with ethyl acetate (3 × 70 mL). The combined extract was dried and evaporated to dryness. The crude product was purified by column chromatography, eluting with CH_2Cl_2/hexane 1:7 to give **1** (1.99 g, 93%) as a colorless liquid. ^1H NMR (acetone-d_6) δ 2.25 (s, 6 H), 6.61 (s, 2 H), 6.77 (s, 1 H), 6.97 (d, 2 H, $J = 8.7$ Hz), 7.10 (t, 1 H, $J = 7.4$ Hz), 7.35 (dd, 2 H, $J = 8.7, 7.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 21.3, 116.6, 118.8, 122.9, 125.0, 129.6, 139.5, 157.1, 157.4; MS (*m*/*e*) 198.1062, Calcd 198.1045 for $C_{14}H_{14}O$.

5-Phenoxyisophthalic Acid, 2. $KMnO_4$ (80 g, 0.51 mol) was added in small portions to a mixture of **1** (10 g, 50.4 mmol), water (70 mL), and pyridine (185 mL) heated at 100 °C during 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. The product was collected by filtration (11.2 g, 86%). ^1H NMR (DMSO-d_6) δ 7.13 (d, 2 H, $J = 8.1$ Hz), 7.24 (t, 1 H, $J = 7.2$ Hz), 7.46 (dd, 2 H, $J = 8.1, 7.2$ Hz), 7.64 (d, 2 H, $J = 0.9$ Hz), 8.19 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 119.9, 122.1, 124.5, 124.8, 130.5, 133.2, 155.5, 157.7, 166.1; MS (*m*/*e*) 258. 0522, Calcd 258.0528 for $C_{14}H_{10}O_5$.

Dimethyl 5-Phenoxyisophthalate, 3. A mixture of **2** (2 g, 7.75 mmol), methanol (20 mL), and concentrated H_2SO_4 (4 mL) was heated at reflux for 4 h. The reaction mixture was poured into water (300 mL) and extracted with ethyl acetate (3 × 70 mL). The combined extract was washed with aqueous sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was evaporated to give **3** (2.17 g, 98%). ^1H NMR ($CDCl_3$) δ 3.90(s, 6 H), 7.00(d, 2 H, $J = 8.4$ Hz), 7.16 (t, 1 H, $J = 7.2$ Hz), 7.36 (dd, 2 H, $J = 8.4, 7.2$ Hz), 7.82 (d, 2 H, $J = 1.5$ Hz), 8.39 (t, 1 H, $J = 1.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.4, 119.2, 123.5, 124.2, 125.1, 130.1, 132.2, 156.1, 157.8, 165.6; MS (*m*/*e*) 286.0839, Calcd 286.0841 for $C_{16}H_{14}O_5$.

Dimethyl 5-(4-Benzoylphenoxy)isophthalate, 4. A mixture of **3** (2 g, 6.99 mmol), benzoic acid (1.71 g, 14 mmol), and PPMA (20 mL) was stirred under nitrogen at 60 °C for 2 h. The reaction mixture was poured into water (500 mL), neutralized with sodium bicarbonate, and extracted with ethyl acetate (3 × 70 mL). The combined extract was dried, and the solvent was evaporated to give **4** (2.65 g, 97%). ^1H NMR ($CDCl_3$) 3.93 (s, 6 H), 7.04 (d, 2 H, $J = 9.3$ Hz), 7,47 (dd, 2 H, $J = 7.5, 7.2$ Hz), 7.57 (t, 1 H, $J = 7.2$ Hz), 7.78 (d, 2 H, $J = 7.5$ Hz), 7.84 (d, 2 H, $J = 9.3$ Hz), 7.91 (d, 2 H, $J = 1.5$ Hz), 8.49 (d, 1 H, $J = 1.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.5, 117.7, 124.8, 126.3, 128.2, 129.8, 132.2, 132.6, 132.9, 137.6, 156.1, 160.2, 165.4, 195.3; MS (*m*/*e*) 390.1112, Calcd 390.1103 for $C_{23}H_{18}O_6$.

5-(4-Benzoylphenoxy)isophthalic Acid, 5. A mixture of **4** (2.5 g, 6.4 mmol), methanol (25 mL), and 40 wt % NaOH (aq) (3 mL) was heated at reflux for 2 h. The solvent was removed by evaporation and poured into water (40 mL). The solution was acidified with 4 N HCl. The precipitated solid was isolated by filtration and recrystallized from ethyl acetate/methanol to give **5** (2.15 g, 93%). ^1H NMR (DMSO-d_6) 7.21 (d, 2 H, $J = 8.1$ Hz), 7.55 (dd, 2 H, $J = 8.1, 7.5$ Hz), 7.66 (t, 1 H, $J = 7.5$ Hz), 7.73 (d, 2 H, $J = 8.1$ Hz), 7.79 (d, 2 H, $J = 1.5$ Hz), 7.82 (d, 2 H, $J = 8.1$ Hz), 8.30 (s, 1 H); ^{13}C NMR (DMSO-d_6) 118.2, 123.6, 125.8, 128.6, 129.5, 132.4, 132.5, 134.2, 137.3, 155.8, 160.0, 166.1, 194.5; MS (*m*/*e*) 362.0792, Calcd 362.0790 for $C_{21}H_{14}O_6$.

3,5-Bis-(4-phenoxybenzoyl)-(4-benzoylphenoxy)benzene, 6, and 3-(4-Benzoylphenoxy)-5-(4-phenoxybenzoyl)benzoic acid, 7. A mixture of **5** (2.1 g, 5.8 mmol), diphenyl ether (1.48 g, 8.7 mmol), and PPMA (20 mL) was stirred under nitrogen at 60 °C for 4 h. The reaction mixture was poured into water (500 mL), and sodium bicarbonate was added to the solution to adjust pH ∼5. The solution was then extracted with ethyl acetate (3 × 80 mL). The combined extract was dried and evaporated to dryness. The crude product was purified by column chromatography, eluting with ethyl acetate/hexane 1:3 to give **6** (1.8 g, 47%). ^1H NMR ($CDCl_3$) δ 7.01 (d, 4 H, $J = 8.7$ Hz), 7.07 (d, 4 H, $J = 8.4$ Hz), 7.10 (d, 2 H, $J = 8.4$ Hz), 7.19 (t, 2 H, $J = 7.2$ Hz), 7.39 (dd, 4 H, $J = 8.7, 7.2$ Hz), 7.46 (dd, 2 H, $J = 7.5, 7.2$ Hz), 7.57 (t, 1 H, $J = 7.5$ Hz), 7.67 (d, 2 H, $J = 0.9$ Hz), 7.77 (d, 2 H, $J = 7.2$ Hz), 7.81 (d, 4 H, $J = 8.4$ Hz), 7.83 (s, 1 H), 7.87 (d, 2 H, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 117.1, 117.9, 120.2, 123.5, 124.8, 126.3, 128.2, 129.8, 130.1, 130.7, 132.2, 132.4, 132.5, 133.0, 137.5, 140.0, 155.1, 156.0, 160.0, 162.2, 193.4, 195.2; MS (*m*/*e*) 666.2040, Calcd 666.2042 for $C_{45}H_{30}O_6$. Further elution with ethyl acetate gave **7** (0.75 g, 25%). ^1H NMR ($CDCl_3$) δ 7.02 (d, 2 H, $J = 8.7$ Hz), 7.09 (d, 4 H, $J = 8.4$ Hz), 7.20 (t, 1 H, $J = 7.5$ Hz), 7.40 (dd, 2 H, $J = 8.7, 7.5$ Hz), 7.47 (dd, 2 H, $J = 7.8, 7.2$ Hz), 7.57 (t, 1 H, $J = 7.2$ Hz), 7.73 (s, 1 H), 7.78 (d, 2 H, $J = 7.8$ Hz), 7.81 (d, 2 H, $J = 8.4$ Hz), 7.85 (d, 2 H, $J = 8.4$ Hz), 7.97 (s, 1 H), 8.24 (s, 1 H); ^{13}C NMR($CDCl_3$) δ 117.1, 117.9, 120.3, 124.1, 124.8, 125.3, 126.8, 128.3, 129.9, 130.1, 130.6, 131.6, 132.4, 132.5, 132.7, 133.0, 137.5, 140.3, 155.1, 156.3, 160.6, 162.3, 169.9, 193.3, 195.5; MS (*m*/*e*) 514.1409, Calcd 514. 1416 for $C_{33}H_{22}O_6$.

Methyl 3-(4-benzoylphenoxy)-5-(4-phenoxybenzoyl)benzoate, 8. A mixture of **7** (0.35 g, 0.68 mmol), methanol (10 mL), and concentrated H_2SO_4 (0.5 mL) was heated at reflux for 4 h. The reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (3 × 30 mL). The combined extract was washed with aqueous sodium bicarbonate solution, dried, and evaporated to dryness. The crude product was purified by column chromatography, eluting with ethyl acetate/hexane 1:3 to give **8** (0.288 g, 80%). ^1H NMR ($CDCl_3$) δ 3.91 (s, 3 H), 7.02 (d, 2 H, $J = 8.7$ Hz), 7.07 (d, 2 H, $J = 8.7$ Hz), 7.09 (d, 2 H, $J = 8.7$ Hz), 7.20 (t, 1 H, $J = 7.5$ Hz), 7.40 (dd, 2 H, $J = 8.7, 7.5$ Hz), 7.47 (dd, 2 H, $J = 7.2, 6.9$ Hz), 7.57 (t, 1 H, $J = 7.2$ Hz), 7.68 (m, 1 H), 7.78 (d, 2 H, $J = 6.9$ Hz), 7.80 (d, 2 H, $J = 8.7$ Hz), 7.84 (d, 2 H, $J = 8.7$ Hz), 7.92 (m, 1 H), 8.18 (t, 1 H, $J = 1.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.5, 117.1, 117.8, 120.3, 123.6, 124.6, 124.8, 126.2, 128.2, 130.0, 130.7, 132.2, 132.4, 132.5, 133.0, 137.5, 140.2, 155.1, 156.1, 160.1, 162.2, 165.4, 193.3, 195.2; MS (*m*/*e*) 528.1580, Calcd 528.1573 for $C_{34}H_{24}O_6$.

Preparation of Hyperpranched Poly(ether ketone), P1. A solution of **2** (0.6 g) in PPMA (3.6 mL) was stirred under nitrogen at 110 °C for 10 h. The resulting solution 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 DMF into methanol to give **P1** (0.48 g, 86%).

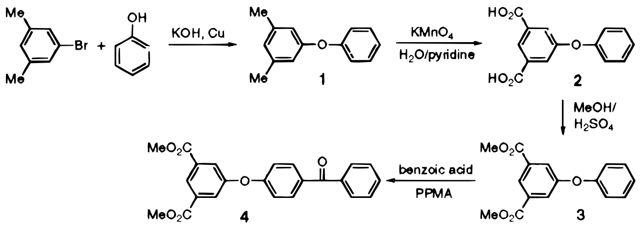
Preparation of Hyperbranched Poly(ether ketone), P2. A solution of **P1** (0.2 g) and thionyl chloride (0.18 mL) in anhydrous THF (3 mL) was heated at reflux for 4 h. The excess thionyl chloride and solvent were removed under reduced pressure. Anhydrous THF (4 mL), methanol (0.1 mL), and triethylamine (0.25 mL) were added to the polymeric acid chloride. The mixture was stirred at 25 °C for 12 h. The precipitate was filtered off and washed with THF. The filtrate was concentrated to 2 mL and precipitated into water (200 mL). The precipitate was collected by filtration and dried to give **P2** (0.2 g, 92%).

Preparation of Hyperbranched Poly(ether ketone), P3. A solution of **P1** (0.2 g) and diphenyl ether (0.66 g) in PPMA (5 mL) was heated at 50 °C for 24 h. The resulting solution was poured into water (400 mL) and neutralized with sodium bicarbonate. The precipitate was filtered, washed with water and methanol, and reprecipitated from DMF into methanol to give **P3** (0.24 g, 73%).

Preparation of Hyperbranched Poly(ether ketone), P4. P4 was prepared from **P1** and toluene using the same procedure as for **P3**, except that the reaction temperature was 110 °C (86%).

Preparation of Hyperbranched Poly(ether ketone), P5. A slow stream of anhydrous ammonia was bubbled through a solution of **P1** (0.35 g) in anhydrous THF (30 mL)

Scheme 1



for 25 min. The precipitate was collected by filtration, washed with THF, and dried (0.33 g, 88%).

Results and Discussion

Polymer Synthesis. The synthesis of the AB_2 monomer 5-phenoxyisophthalic acid, **2**, was performed by the Ullmann reaction of potassium phenate with 5-bromo-*m*-xylene to form compound **1**,[11] followed by oxidation of the methyl groups of **1** with $KMnO_4$,[12] as outlined in Scheme 1. The general procedure developed by Ueda and Sato[9] for the preparation of linear aromatic poly(ether ketone)s was applied to the AB_2 monomer, using PPMA as a condensing agent and solvent. 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 to enable condensation to proceed under rather mild reaction conditions. We first studied the reaction of the phenoxy group of monomer **2** with benzoic acid in PPMA to demonstrate the feasibility of using the reaction for the formation of hyperbranched poly(ether ketone). The carboxylic groups of **2** were converted to ester groups, and then the reaction of the methyl ester **3** with benzoic acid in PPMA proceeded at 60 °C and yielded **4** quantitatively after 2 h. NMR spectrum of the acylated product **4** revealed that the benzoyl group was exclusively at the *para*-position of the phenoxy group. The model reaction demonstrated that the acylation had taken place clearly at the *para*-position and that it is suitable as a polymer-forming reaction.

Polymerization of **2** in PPMA at 110 °C for 24 h gave the corresponding carboxylic acid-terminated hyperbranched poly(ether ketone), **P1**, in 86% yield. The structure of P1 and general reaction are shown in Scheme 2. The hyperbranched poly(ether ketone), **P1**, which had a high number of terminal carboxylic groups, could not be analyzed directly by SEC, because the polymer adsorbed to the column, resulting in incomplete elution. This problem was overcome by esterification of the carboxylic acids groups with methanol. By reacting with thionyl chloride, **P1** was readily converted to the polymeric acid chloride, which was then reacted with methanol to form the methyl ester-terminated polymer **P2**. ^{1}H NMR analysis confirmed that at least 95% of the carboxylic acids were esterified.

SEC analysis of a sample of **P2** gave M_n of 4200 and M_w of 14 300 ($M_w/M_n = 3.40$). The molecular weight of the polymer was calibrated against poly(ethylene glycol) standards. Because of the highly branched nature of hyperbranched macromolecules, SEC measurements tended to underestimate the true molecular weight.[13] The polymerization was sensitive to reaction time and reaction temperature. The molecular weight distributions of these poly(ether ketones) are broad, and broaden with increasing conversion. This observation is similar to previous reports of hyperbranched polymers and agrees with Flory's predications on molecular weight distribution behavior for highly branched systems.[4] Because monomer **2** is only partially soluble in PPMA at 100 °C, polymerization below that temperature gave low conversion. Polymerization carried out at temperatures greater than 120 °C also resulted in low molecular weight polymers. This might be caused by the decarboxylation of aromatic carboxylic acids in strong acids.[9]

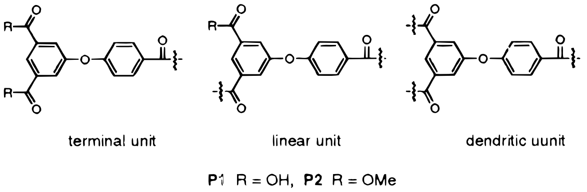
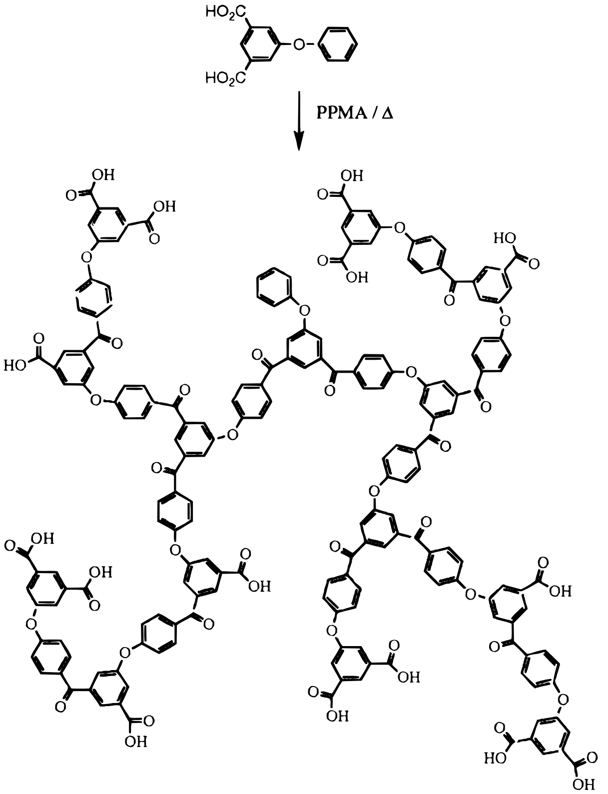


Figure 1. Structure of repeat units in the hyperbranched poly(ether ketone)s.

Scheme 2



Degree of Branching. Hyperbranched polymer **P1** was formed by a sequence of condensation of AB_2 monomer resulting in an irregular dendritic structure in which three different types of subunits may be present as shown in Figure 1. These include the terminal units, which have two carboxylic acid groups, the linear units, which have one carboxylic group and one benzoyl group, and the dendritic units, which have no free carboxylic acid group and two benzoyl groups. The degree of branching of hyperbranched polymers is given by

$$\mathrm{DB} = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{\text{total no. of units}}$$

A hyperbranched polymer takes DB values between 0 and 1. The extent of branching will have a profound influence on the physical properties of the polymeric

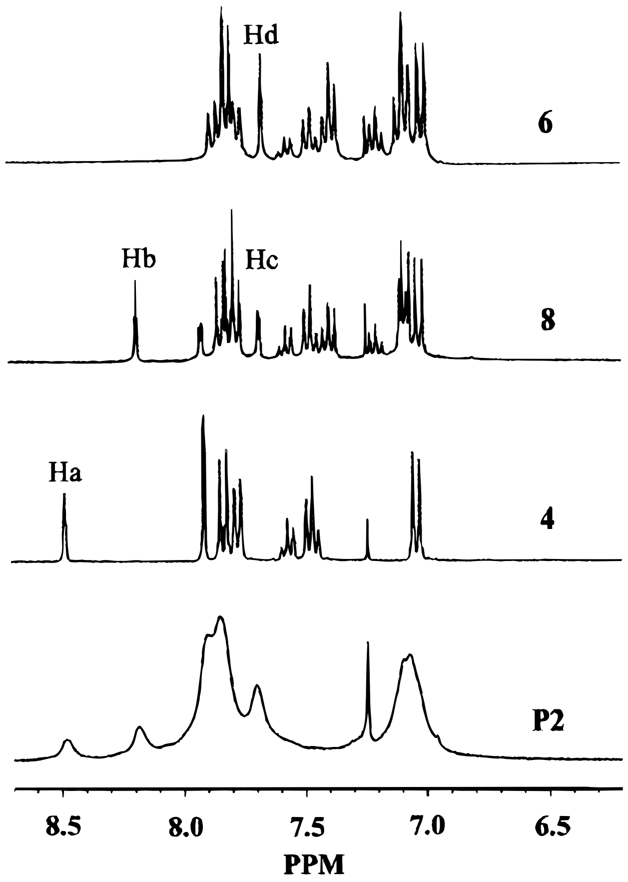
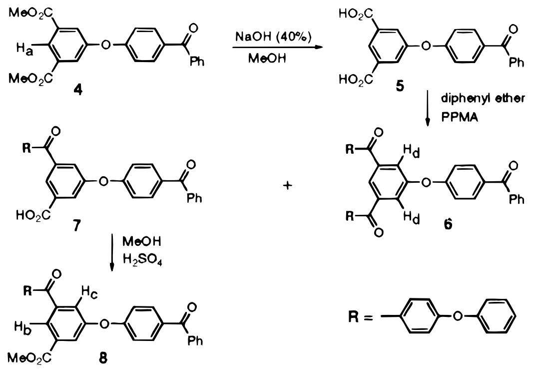


Figure 2. The 300-MHz ^{1}H NMR spectra in $CDCl_3$ of model compounds **4**, **6**, and **8** compared with the hyperbranched poly(ether ketone) **P2**.

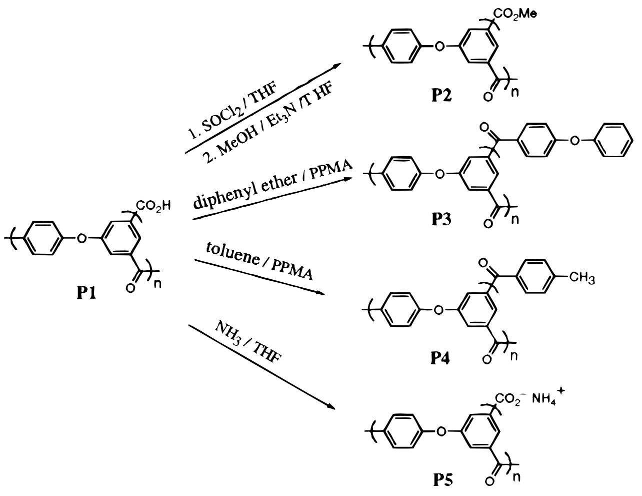
Scheme 3



material. Hawker et al.[2b] used NMR spectroscopy and model compounds to quantify the different subunits appearing in their hyperbranched materials, and the same methodology was applicable to the hyperbranched poly(ether ketone) described here.

For the acid-terminated **P1**, the degree of branching could not be determined directly from its ^{1}H NMR spectrum obtained in DMSO because the chemical shifts of the aromatic protons were not well enough resolved for this determination. However, the ^{1}H NMR spectrum of the methyl ester derivative **P2** showed sufficient differences in the chemical shifts of the aromatic protons to allow the degree of branching to be determined. The preparation of the model compounds useful for NMR characterization is detailed in Scheme 3. Figure 2 shows the ^{1}H NMR spectra for the model compounds **4**, **6**, and **8**.

Scheme 4



Distinct resonance for the terminal model compound, **4**, appears at 8.49 ppm (H_a), whereas the corresponding proton for the linear model compound, **8** (H_b), is observed at 8.19 ppm. The other resonances due to proton H_c of the linear, **8**, and protons H_d of the dendritric, **6**, are observed at 7.68 and 7.67 ppm, respectively. Good correlation is observed in the comparison of the ^{1}H NMR spectra of these model compounds with that of the methyl ester-terminated **P2**. The resonances at 8.48 and 8.14 ppm are attributed to protons H_a of the terminal subunit and H_b of the linear subunit, whereas the resonance at 7.70 ppm is due to protons H_c of the linear subunit and protons H_d of the dendritic subunit. Integration of these well-resolved resonances allows the relative percentage of each subunit to be determined. The percentage estimated for the terminal subunit is approximately equal to that for the dendritic subunit. The result is consistent with the theoretical prediction that the number of dendritic units is equal to the number of terminal units for an AB_2-type hyperbranched polymer possessing high molecular weight.[4] This consistency provides additional support for the assignments of the ^{1}H NMR spectra. With these formulas, the degree of branching for the hyperbranched poly(ether ketone) calculated was approximately 55%, independent of molecular weight. This indicates that branching does not change as a function of conversion.

Chemical Modification of Hyperbranched Poly(ether ketone) 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. As shown in Scheme 4, a variety of different functional groups could be introduced into **P1** by reactions of the terminated carboxylic acid groups. ^{1}H NMR integration was used to estimate the degree of functionalization in examples where the derivatives contain a functional group that exhibits a ^{1}H NMR peak well separated from the aromatic peaks. In another case, elemental analysis was used to determine the conversion yields. For all the modification reactions above, the use of excess reagents resulted in complete (95%) functionalization, indicating that the carboxylic acid groups at the chain ends are readily accessible to reagents in solution. By reacting with thionyl chloride, the carboxylic acid group of **P1** was readily converted to acid chloride, which was then reacted with methanol to give the ester derivative **P2**. In PPMA the carboxylic acid groups of **P1** reacted

Table 1. Effect of the Functionality of the Chain Ends on the Thermal and Solution Properties of the Hyperbranched Poly(ether ketone)s

		solubility[a] in						
polymer	T_g (°C)	CH_2Cl_2	$CHCl_3$	THF	DMF	NMP	DMSO	H_2O
P1	226	−	−	+	+	+	+−	−
P2	113	+	+	+	+	+	−	−
P3	135	+	+	+	+	+	−	−
P4	140	+	+	+	+	+	−	−
P5	236	−	−	−	+−[b]	+−[b]	+−[b]	+

[a] Solubility: +, soluble; +−, partially soluble; −, insoluble. [b] In hot solvent.

smoothly with aromatic electrophilics such as diphenyl ether and toluene to give the corresponding polymers with ketone chain ends **P3** and **P4**, respectively.

Properties such as the glass transition temperature (T_g) and the solubility of hyperbranched polymer are dramatically affected by the functionality of the terminal groups.[3] The T_g values determined by differential scanning calorimetry (DSC) of these poly(ether ketone)s are also very dependent on the nature of chain ends, with increases in T_g following increases in chain-end polarities (Table 1). The T_g of **P1**, which has polar carboxylic acid terminal groups, is 226 °C. The T_g values of **P2**, **P3**, and **P4**, which have less polar terminal groups such as ester and ketone groups, are 113, 135, and 140 °C, respectively.

The thermal stability of the hyperbranched poly(ether ketone)s was examined by thermogravimetric analysis (TGA). **P1** lost about 5 wt % at 170 °C and an additional 5 wt % at 324 °C, and **P2** lost 5 wt % at 246 °C and an additional 5 wt % at 278 °C. Weight losses observed for **P1** and **P2** may be caused by the thermal decomposition of the carboxylic groups and the methyl ester groups. When the functionality of the chain ends was changed to the ketone, the thermal stability increased. For example, **P3** was stable to 420 °C, with a 10 wt % loss occurring over 470 °C.

Because of their highly branched structures, these hyperbranched poly(ether ketone)s have enhanced solubility in organic solvents and are highly soluble in typical solvents such as THF, DMF, and *N*-methylpyrrolidone (NMP) (Table 1). However, the different chain ends resulted in differences of solubility in very polar and in relatively nonpolar solvents. **P1** was sparingly soluble in DMSO, whereas **P2**, **P3**, and **P4** were totally insoluble. Conversely, in solvents such as chloroform and dichloromethane **P1** was totally insoluble, whereas **P2**, **P3**, and **P4** were extremely soluble.

P1 was insoluble in water, but its ammonium derivative **P5** was water-soluble. Hyperbranched/dendritic macromolecules possessing terminate carboxylate groups resemble the environment of a micellar structure and are capable of enhancing the solubility of hydrophobic compounds in water.[14] Those macromolecules behaved as unimolecular micelles that do not suffer from the critical micelle concentration, and an increased solubilization of hydrophobic molecules in aqueous solutions was observed even at extremely low concentrations.[14] The micellar behavior of the carboxylate-terminated hyperbranched poly(ether ketone), **P5**, was studied using the same methodology reported previously by Hawker et al.[14d] The hydrophobic compound 1,4-diaminoanthraquinone, which has an strong absorption at 585 nm, was used as a probe to exam the solubilizing ability of **P5**. As it has been shown that within experimental error there is no change in the absorption coefficient with changes in solvent,[15] the value of ϵ_{max} (1.28×10^4 M^{-1} cm^{-1}) obtained in a mixture of methanol/water 9:1 was used to give a saturated concentration of 1,4-diaminoanthraquinone in pure water of 1.92×10^{-6} M, which agrees with values in the literature.[3f] Under the same conditions, the saturation concentrations of the hydrophobic compound in a series of aqueous solutions with changes in the concentration of **P5** were determined. In an aqueous solution of **P5** (3.37×10^{-4} M), the saturation concentration of 1,4-diaminoanthraquinone determined was 3.72×10^{-5} M, approximately a 20-fold increase when compared with pure water. On the average a single **P5** molecule with molecular weight M_w of 15 200 dissolves 0.11 molecule of 1,4-diaminoanthraquinone. As shown in Figure 3, increasing the concentration of **P5** resulted in a linear increase in saturation concentration of 1,4-diaminoanthraquinone. The solubility enhancement of 1,4-diaminoanthraquinone in P5 solutions was even observed at the concentrations of **P5** in the micromolar range, which is below the critical micelle concentration of the traditional micelle. This result demonstrates unimolecular micelle behavior of the hyperbranched polymer **P5**, which contrasts with traditional micelle behavior where essentially no solubility enhancement occurs below the critical micelle concentration.

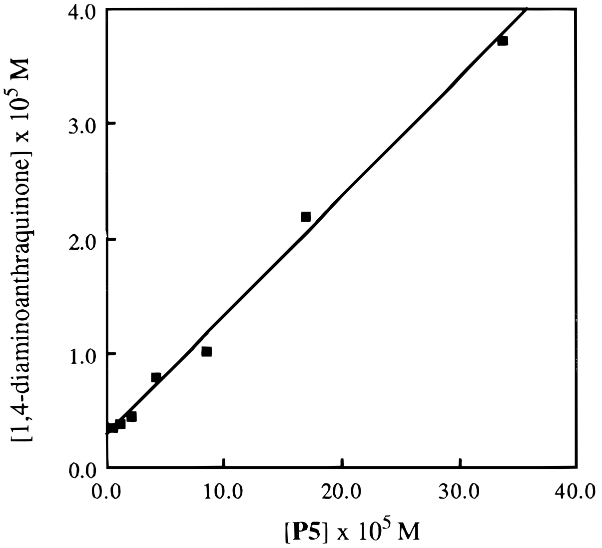


Figure 3. Saturation concentration of 1,4-diaminoanthraquinone as a function of the concentration of the carboxylate-terminated hyperbranched poly(ether ketone), **P5**, in water. The concentration of **P5** was estimated based on a molecular weight, M_w, of 15 200.

Summary

A hyperbranched poly(ether ketone) with terminal carboxylic acid groups was prepared by the one-step synthesis of an AB_2 monomer 5-phenoxyisophthalic acid using PPMA as condensing agent and solvent. This synthesis involved electrophilic aromatic substitution, resulting in the formation of the aryl ketone linkage. The degree of branching characterized by ^1H NMR was about 55%. The carboxylic acid groups at the chain ends were readily accessible to reagent in solution and were converted to a variety of functional groups. Physical properties, such as the glass transition temperature and the solubility of the hyperbranched poly(ether ketone)s depended heavily on the nature of the chain ends. The hyperbranched poly(ether ketone) with ammonium carboxylate terminal groups was soluble in water, and its unimolecular micellar behavior was demonstrated.

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