Synthesis of Hyperbranched Aromatic Poly(amide−imide): Copolymerization of B′B$_2$ Monomer with A$_2$ Monomer

Yao-Te Chang and Ching-Fong Shu*

Department of Applied Chemistry, National Chiao Tung University, Hsin-Chu, Taiwan 30035, Republic of China

ABSTRACT: A hyperbranched aromatic poly(amide−imide) was prepared by the copolymerization of 4-(3,5-dicarboxyphenoxy)phthalic anhydride, a B′B$_2$ type monomer, and 1,4-phenylenediamine, an A$_2$ type monomer. The rapid reaction between the anhydride and amino group led to the formation of the dominant imide intermediate which can be regarded as a new AB$_2$ type of monomer. The intermediate, without isolation, was subjected to further polymerization in the presence of TPP/pyridine, as condensing agents, to give the hyperbranched poly(amide−imide), containing carboxylic acid chain ends. In comparison, the AB$_2$ monomer was prepared separately, and the conventional self-polymerization of this monomer was also studied. The structures of the obtained polymers were characterized by FTIR and ^{1}H NMR spectroscopy. The spectral data showed that these two polymers, prepared from two different synthetic approaches, have nearly identical structures. The degree of branching of the hyperbranched poly(amide−imide)s was estimated to be 60−61%. The terminal carboxylic acid groups were modified by reaction with a variety of aromatic amines to give the corresponding amide derivatives. The nature of the chain ends was shown to have a significant effect on the solubility and T_g of the hyperbranched poly(amide−imide)s.

Introduction

Hyperbranched macromolecules have received considerable attention since their unique, highly branched structure is expected to exhibit some unusual physical and chemical properties.[1−4] These polymers can be conveniently synthesized in a single step via a one-pot polymerization,[5] yet they maintain many of the architectural features and properties found in their well-defined dendrimer counterparts,[6−8] which are built up by tedious stepwise synthetic sequences.[9−12] The one-step synthesis allows hyperbranched polymers to be more readily available and prepared on a large scale for potential applications. These attractive features have led to the development of novel synthetic routes for the preparation of such polymers. Most hyperbranched polymers that have been developed were synthesized by the one-step self-polycondensation of AB$_n$ type monomers. Only a few studies have concerned the preparation of hyperbranched polymers through the copolymerization method, even if that route has more flexibility in generating diverse, hyperbranched materials. Fréchet et al. have reported the synthesis of hyperbranched aliphatic polyethers by the copolymerization of A$_2$ and B$_3$ type monomers.[13] Using this A$_2$ + B$_3$ strategy, hyperbranched aromatic polyamides and polyimides have been prepared by Kakimoto's and Okamoto's groups.[14−16] Recently, Yan et al. have reported a new A$_2$ + BB′$_2$ approach for the synthesis of hyperbranched copoly(sulfone−amine)s.[17]

Linear polyamides and polyimides are well-known as high-performance polymeric materials.[18,19] Their hyperbranched analogues have been prepared by the self-polymerization of AB$_2$ type monomers[20−25] or more recently by copolymerization methods.[14−16] Aromatic poly(amide−imide)s are a class of high-performance polymers which may combine the advantages of polyamides and polyimides; the resulting polymers should possess high thermal stabilities, coupled with good mechanical and chemical properties.[26,27] To the best of our knowledge, there has been no report regarding the preparation of hyperbranched aromatic poly(amide−imide)s. In this paper, we report the synthesis of a new hyperbranched poly(amide−imide) by copolymerization of an unsymmetrical B′B$_2$ type monomer with an A$_2$ type monomer. In the B′B$_2$ monomer, there are one anhydride and two carboxylic groups, while in the A$_2$ monomer, there are two amino functionalities. The anhydride (B′) is much more reactive than the carboxylic group (B) toward the amino group in the A$_2$ monomer. At the initial stage of the polycondensation, the rapid reaction between B′ and A groups results in the formation of the dominant imide intermediate. The intermediate can be regarded as a new AB$_2$ type of monomer, which contains one aminophenyl and two carboxyl functionalities. Without isolation, the AB$_2$ intermediate was subjected to further polymerization in the presence of TPP/pyridine, as condensing agents, to give the hyperbranched poly(amide−imide).[28,29] For comparison, the AB$_2$ intermediate was prepared separately and characterized; the conventional one-step self-polymerization of this AB$_2$ monomer was also studied.

Experimental Section

General Directions. *N*-Methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylformamide (DMF) were distilled over CaH$_2$ under reduced pressure. Pyridine was dried by distillation after being refluxed with KOH. 1,4-Phenylenediamine was recrystallized from MeOH. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. (2,3-Dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) was used as received. All other reagents and solvents were used as received from commercial sources unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer. IR spectra were obtained on a Nicolet 360 FT-IR spectrometer. Mass spectra were obtained on a JEOL JMS-SX 102A mass spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit, interfaced with a Waters 410 differential refractometer. Three 5 μm Waters styragel columns (300 × 7.8 mm), connected in series of decreasing order of pore size (10^5, 10^4, and 10^3 Å), were used with DMF as the eluent. Standard samples of PMMA were

used for calibration. Differential scanning calorimetry (DSC) was performed using a Du Pont TA 2000 instrument, with a heating/cooling rate of 20 °C min^{-1}. Samples were scanned from 30 to 400 °C and then cooled to 30 °C and scanned a second time from 30 to 400 °C. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analyses (TGA) were made on a Du Pont TGA 2950 instrument. The thermal stability of the samples was determined in nitrogen by measuring weight loss while heating at a rate of 20 °C min^{-1}.

Dimethyl 5-(3,4-Dicyanophenoxy)isophthalate (1). A mixture of dimethyl 5-hydroxyisophthalate (5.00 g, 26.9 mmol), 4-nitrophthalonitrile (4.65 g, 26.9 mmol), K$_2$CO$_3$ (5.00 g, 36.2 mmol), and DMF (20 mL) was heated at 130 °C for 4 h. After this period, the reaction mixture was cooled and poured into 200 mL of water. The precipitated crude product was collected by filtration, dried under vacuum, and purified by recrystallization from ethyl acetate to afford **1** (8.20 g, 91.4%). ^{1}H NMR (DMSO-d_6): δ 3.89 (s, 6H), 7.53 (dd, 1H, $J = 8.7, 2.7$ Hz), 7.89 (d, 1H, $J = 2.7$ Hz), 7.93 (d, 2H, $J = 1.5$ Hz), 8.14 (d, 1H, $J = 8.7$ Hz), 8.36 (t, 1H, $J = 1.5$ Hz). ^{13}C NMR (DMSO-d_6): δ 52.7, 109.2, 115.2, 115.7, 116.9, 122.8, 123.1, 125.2, 126.4, 132.5, 136.3, 154.4, 160.2, 164.5. HRMS [M$^+$]: 336.0745. Calcd 336.0746 for C$_{18}$H$_{12}$N$_2$O$_5$.

4-(3,5-Dicarboxyphenoxy)phthalic Acid (2). To a solution of KOH (14.0 g, 0.25 mol) in a mixture of water−ethanol (100 mL/80 mL) was added compound **1** (7.00 g, 28.3 mmol). The mixture was then refluxed for 24 h. The resulting solution was diluted with water (250 mL) and acidified with 6 N HCl-(aq) to pH ∼1. The precipitated product was filtered, washed thoroughly with water, and dried to give **2** (7.00 g, 97.1%). ^{1}H NMR (DMSO-d_6): δ 7.24 (dd, 1H, $J = 8.7, 2.7$ Hz), 7.71 (d, 1H, $J = 2.7$ Hz), 7.73 (d, 2H, $J = 1.5$ Hz), 8.23 (d, 1H, $J = 8.7$ Hz), 8.28 (t, 1H, $J = 1.5$ Hz). ^{13}C NMR (DMSO-d_6): δ 120.6, 121.5, 123.4, 125.6, 130.1, 133.9, 135.4, 137.8, 156.4, 157.8, 166.2, 167.4. HRMS [M$^+$ − H]: 345.0236. Calcd 345.0247 for C$_{16}$H$_9$O$_9$.

4-(3,5-Dicarboxyphenoxy)phthalic Anhydride (3). A mixture of compound **2** (6.00 g, 17.3 mmol), acetic anhydride (6.0 mL), and acetic acid (6.0 mL) was stirred under reflux for 12 h. After cooling, the precipitate was collected by filtration, washed with a small amount of glacial acetic acid, and then dried under vacuum at 140 °C for 12 h to yield **3** (4.85 g, 85. %). ^{1}H NMR (DMSO-d_6): δ 7.63 (dd, 1H, $J = 8.1, 2.1$ Hz), 7.68 (d, 1H, $J = 2.1$ Hz), 7.84 (d, 2H, $J = 1.2$ Hz), 8.10 (d, 1H, $J = 8.1$ Hz), 8.34 (t, 1H, $J = 1.5$ Hz), 13.55 (br, 2H). ^{13}C NMR (DMSO-d_6): δ 114.2, 124.2, 125.7, 126.0, 126.6, 127.9, 134.1, 134.3, 155.2, 162.5, 162.6, 162.9, 165.9. HRMS [M$^+$]: 328.0209. Calcd 328.0219 for C$_{16}$H$_8$O$_8$.

N-(4-Aminophenyl)-4-(3,5-dicarboxyphenoxy)phthalimide (4). To a solution of compound **3** (400 mg, 1.22 mmol) in NMP (4.0 mL) was added 1,4-phenylenediamine (132 mg, 1.22 mmol). The mixture was stirred at 25 °C under nitrogen for 2 h and then heated at 150 °C for 12 h. The resulting solution was cooled and then poured into dilute HCl(aq) (60 mL). The precipitated product was filtered, washed with water, and dried to give **4** (421 mg, 82.6%). ^{1}H NMR (DMSO-d_6): δ 6.67 (d, 2H, $J = 8.4$ Hz), 7.03 (d, 2H, $J = 8.4$ Hz), 7.40−7.54 (m, 2H), 7.81 (d, 2H, $J = 1.2$ Hz), 7.96 (d, 1H, $J = 8.9$ Hz), 8.31 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 113.2, 114.3, 120.5, 123.9, 124.2, 125.8, 126.1, 126.8, 128.3, 133.6, 134.5, 147.7, 156.0, 161.4, 165.8, 166.7, 166.9. HRMS [M$^+$]: 418.0785. Calcd 418.0801 for C$_{22}$H$_{14}$N$_2$O$_7$.

N-(4-Aminophenyl)phthalimide (5). A solution of 1,4-phenylenediamine (3.00 g, 27.8 mmol) and phthalic anhydride (4.11 g, 27.8 mmol) in DMF (6.0 mL) was heated at 150 °C for 4 h. The solution was poured into water (200 mL). The precipitated product was filtered and dried to give **5** (5.95 g, 90.0%). ^{1}H NMR (DMSO-d_6): δ 5.33 (s, 2H), 6.62 (d, 2H, $J = 8.4$ Hz), 7.00 (d, 2H, $J = 8.4$ Hz), 7.81−7.95 (m, 4H). ^{13}C NMR (DMSO-d_6): δ 113.6, 119.6, 123.2, 128.2, 131.6, 134.5, 148.8, 167.6. HRMS [M$^+$]: 238.0737. Calcd 238.0742 for C$_{14}$H$_{10}$N$_2$O$_2$.

Synthesis of Model Compound 6. A solution of compound **3** (1.00 g, 3.05 mmol) and aniline (284 mg, 3.05 mmol) in NMP (6.0 mL) was heated at 150 °C under nitrogen for 12 h. The

solution was then added dropwise to water (200 mL). The precipitated product was collected by filtration and purified by recrystallization from acetic acid to afford **6** (1.01 g, 82.2%). ^{1}H NMR (DMSO-d_6): δ 7.38−7.58 (m, 7H), 7.82 (d, 2H, $J = 1.2$ Hz), 8.01 (d, 1H, $J = 8.1$ Hz), 8.32 (t, 1H, $J = 1.2$ Hz), 13.51 (br, 2H). ^{13}C NMR (DMSO-d_6): δ 113.3, 124.0, 124.3, 126.0, 126.2, 126.7, 127.4, 128.2, 129.0, 132.0, 133.7, 134.4, 155.9, 161.6, 165.9, 166.2, 166.4. HRMS [M$^+$]: 403.0694. Calcd 403.0692 for C$_{22}$H$_{13}$NO$_7$.
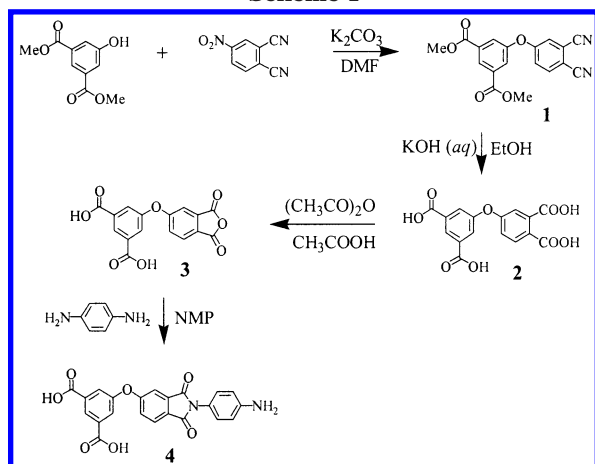
Synthesis of Model Compounds 7 and 8. A solution of **5** (531 mg, 2.24 mmol), **6** (600 mg, 1.49 mmol), DBOP (570 mg, 1.49 mmol), and 3 drops of triethylamine in NMP (6.0 mL) was stirred at 25 °C under nitrogen for 12 h. The resulting solution was added dropwise to a mixture of methanol (50 mL) and water (50 mL). The precipitated product was collected by filtration and purified by column chromatography, eluting with CHCl$_3$/ethyl acetate (4:1) to give **8** (0.44 g, 35%). Further elution with CHCl$_3$/CH$_3$OH (3:1) and recrystallization from acetic acid afforded **7** (0.31 g, 33%). Compound **7**: ^{1}H NMR (DMSO-d_6): δ 7.37−7.61 (m, 9H), 7.80 (br, 1H), 7.88−8.10 (m, 8H), 8.47 (br, 1H), 10.69 (s, 1H), 12.68 (br, 1H). ^{13}C NMR (DMSO-d_6): δ 113.1, 120.9, 122.8, 123.3, 123.4, 124.1, 124.9, 126.0, 126.6, 127.4, 127.5, 127.7, 128.1, 128.9, 131.6, 131.9, 133.5, 134.5, 134.7, 137.3, 138.5, 155.6, 161.7, 163.8, 166.1, 166.2, 166.4, 167.1. HRMS [M$^+$ + H]: 624.1415. Calcd 624.1407 for C$_{36}$H$_{22}$N$_3$O$_8$. Compound **8**: ^{1}H NMR (DMSO-d_6): δ 7.40−7.63 (m, 9H), 7.82−8.10 (m, 9H), 8.55 (br, 1H), 10.59 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 113.4, 121.5, 122.7, 124.1, 124.4, 124.6, 126.7, 127.1, 127.9, 128.3, 128.7, 129.5, 132.3, 132.7, 135.1, 135.4, 138.1, 139.2, 156.0, 162.7, 164.8, 166.8, 166.9, 167.7. HRMS [M$^+$ + H]: 844.2046. Calcd 844.2044 for C$_{50}$H$_{30}$N$_5$O$_9$.

Preparation of Polymer PAI-1. (A) Direct polymerization of monomer **3** with 1,4-phenylenediamine: The monomer **3** (200 mg, 610 μmol) was added in one portion to a stirred solution of 1,4-phenylenediamine (65.9 mg, 610 μmol) in NMP (2.0 mL) under nitrogen at 25 °C. Stirring was continued at 25 °C for 2 h and at 150 °C for 12 h. The solution was cooled, added pyridine (0.50 mL) and TPP (0.32 mL, 1.22 mmol), and then heated at 120 °C for 12 h. After cooling, the resulting polymer was precipitated into methanol. The polymer was collected, washed with hot water, purified by reprecipitation from DMF into methanol twice, and dried under vacuum to give **PAI-1** (202 mg, 83.2%). (B) Self-polycondensation of monomer **4**: A solution of compound **4** (800 mg, 1.61 mmol), TPP (1.0 mL, 3.2 mmol), and LiCl (160 mg, 3.77 mmol) in NMP/pyridine (10.0 mL, 4:1 v/v) was heated at 120 °C under nitrogen for 12 h. After cooling, the resulting polymer was precipitated into methanol. The polymer was collected, washed with hot water, purified by reprecipitation from DMF into methanol twice, and dried under vacuum to give **PAI-1** (732 mg, 95.6%). ^{1}H NMR (DMSO-d_6): δ 7.30−7.68 (m, 4H), 7.75−8.08 (m, 5H), 8.28−8.56 (m, 1H), 10.69 (s, 1H), 13.51 (br, 1H). IR (KBr): 2500−3500 (broad, O−H and N−H), 1772, 1716 (C=O, imide ring), 1665 (C=O, amide), 1373 cm^{-1} (C−N, imide).

Preparation of Polymer PAI-2. A solution of **PAI-1** (100 mg, 250 μmol), aniline (85 mg, 0.91 mmol), DBOP (383 mg, 1.00 mmol), and 3 drops of triethylamine in NMP (2.0 mL) was stirred at 25 °C under nitrogen for 12 h. The resulting solution was added dropwise to methanol (100 mL) with agitation. The polymer was collected by filtration, washed with warm water, and purified by reprecipitation from DMF into methanol twice to give **PAI-2** (114 mg, 96.0%). ^{1}H NMR (DMSO-d_6): δ 6.80−7.65 (m, 8H), 7.70−8.10 (m, 6H), 8.42−8.58 (m, 1H), 10.48 (br, 1H), 10.68 (br, 1H). IR (KBr): 1772, 1716 (C=O, imide ring), 1665 (C=O, amide), 1373 cm^{-1} (C−N, imide).

Preparation of Polymer PAI-3. PAI-3 was prepared from **PAI-1** (100 mg, 250 μmol) and 4-n-decylaniline (233 mg, 1.00 mmol) following the same procedure as described for the preparation of **PAI-2**. Yield: 138 mg, 89.8%. ^{1}H NMR (DMSO-d_6): δ 0.55−1.62 (m, 21H), 6.80−7.80 (m, 9H), 7.82−8.20 (m, 4H), 8.40−8.56 (m, 1H), 10.39 (br, 1H), 10.69 (br, 1H). IR (KBr): 1772, 1716 (C=O, imide ring), 1665 (C=O, amide), 1373 cm^{-1} (C−N, imide).

<div style="text-align:center">**Scheme 1**</div>
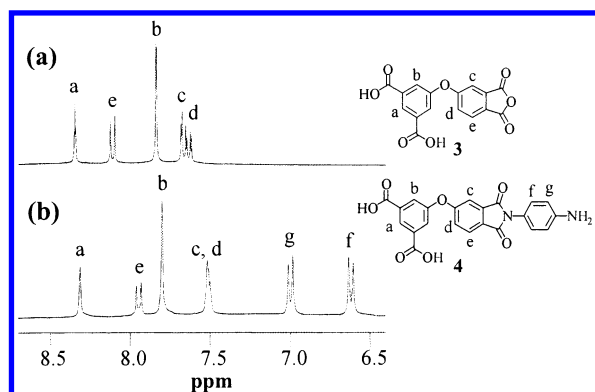

<div style="text-align:center">**Scheme 2**</div>

mixture of the monomer **3** and 1,4-phenylenediamine was reacted in NMP to form the amic acid, which was then thermally cyclized to give the AB$_2$-type intermediate in situ, with an imide linkage. It should be noted that the amino group in the AB$_2$ molecule is deactivated in comparison with the original amino groups in the A$_2$ monomer, due to the formation of the imide (amide) group in the para position of the benzene ring system.[14] Therefore, the possibility of reaction of the former with the phthalic anhydride (B′) of a second B′B$_2$ molecule is diminished and can be neglected under the reaction conditions; the formation of the AB$_2$ intermediate is the predominate reaction at the initial stage of the copolymerization. This is supported by the fact that the AB$_2$ intermediate, which is identical to the AB$_2$ type monomer **4**, can be isolated with an almost quantitative yield in the first stage of the polymerization. Without isolation, the AB$_2$ type intermediate was polymerized at 120 °C for 12 h in the presence of TPP/pyridine, as condensing agents, to yield **PAI-1**. No gelation occurred during this polymerization. This polymer could also be synthesized by the self-polycondensation of the AB$_2$ type monomer **4**. The one-step polymerization of **4** was carried out in NMP at 120 °C for 12 h using TPP/pyridine as condensing agents. The structure of **PAI-1** was characterized by FTIR and ^{1}H NMR spectroscopy. It was found that the two different synthetic approaches led to hyperbranched poly(amide−imide)s with almost identical structures. In the IR spectra, the polymers exhibit characteristic carbonyl absorptions corresponding to an imide ring at 1772 (C=O asymmetric stretching) and 1716 cm^{-1} (C=O symmetric stretching), in addition to the typical aromatic−imide C−N stretching at 1373 cm^{-1}. The carbonyl absorptions of the cyclic anhydride unit at 1849 and 1783 cm^{-1} in monomer **3** have disappeared. In addition, the C=O stretching of the amide group appears at 1665 cm^{-1}. The carbonyl stretching of the terminal carboxylic acid group at ~1700 cm^{-1} is obscured by the absorption of the imide ring. The broad bands between 2500 and 3500 cm^{-1} are attributed to amide N−H and acid O−H stretches. In the ^{1}H NMR spectrum of **PAI-1**s, the resonance of the proton of the amide group appears at 10.69 ppm, and a broad peak at 13.51 ppm from the proton of the terminal carboxylic acid group is also observed.

The hyperbranched poly(amide−imide), **PAI-1**, which has a high number of terminal carboxyl groups, could not be analyzed directly by gel permeation chromatography (GPC) because the polymer adsorbed to the column, resulting in incomplete elution.[30] This problem was overcome by the transformation of the carboxylic acids groups into amide groups. By reacting with excess aniline, **PAI-1** was readily converted to the amide-terminated polymer **PAI-2** (vide post). GPC analyses showed that the weight-average molecular weights (M_w) and polydispersities (M_w/M_n) were approximately 4.4 ×

Preparation of Polymer PAI-4. **PAI-4** was prepared from **PAI-1** (100 mg, 250 μmol) and compound **5** (238 mg, 1.00 mmol) following the same procedure as described for the preparation of **PAI-2**. Yield: 146 mg, 94.2%. ^{1}H NMR (DMSO-d_6): δ 7.30−7.68 (m, 6H), 7.80−8.08 (m, 11H), 8.54 (br, 1H), 10.69 (br, 2H). IR (KBr): 1772, 1716 (C=O, imide ring), 1665 (C=O, amide), 1378 cm^{-1} (C−N, imide).
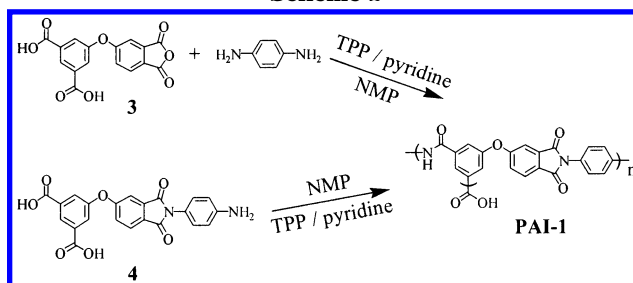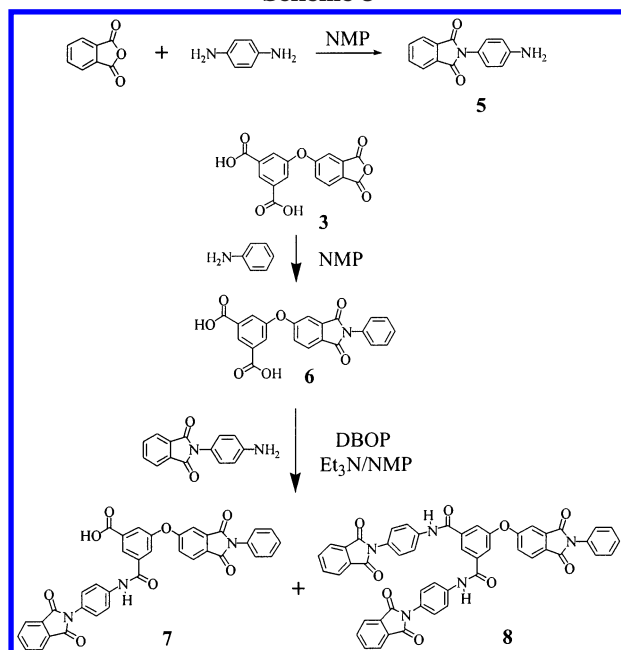
Results and Discussion

Monomer Synthesis. Two kinds of monomers, **3** and **4**, were prepared as shown in Scheme 1. Nucleophilic substitution of the nitro function of 4-nitropthalonitrile with the phenoxide of dimethyl 5-hydroxyisophthalate in a K$_2$CO$_3$/DMF medium yielded dimethyl 5-(3,4-dicyanophenoxy)isophthalate (**1**). Alkaline hydrolysis of compound **1** in KOH(aq)/ethanol gave 4-(3,5-dicarboxyphenoxy)phthalic acid (**2**), which was subsequently dehydrated with acetic anhydride to form the B′B$_2$ type monomer **3**. The condensation of **3** with 1,4-phenylenediamine followed by cyclodehydration afforded the AB$_2$ type monomer **4**. Monomer **3** has one phthalic anhydride and two carboxylic acid groups, while monomer **4** contains one aminophenyl and two carboxyl functionalities joined with an ether−imide linkage. The structures of the synthesized compounds were verified by ^{1}H NMR and ^{13}C NMR spectroscopy as well as by mass spectroscopy. Figure 1 shows the ^{1}H NMR spectra of monomers **3** and **4**, which are consistent with the assigned structures.

Polymer Synthesis. As shown in Scheme 2, the hyperbranched poly(amide−imide) **PAI-1** was prepared by the direct polymerization of the B′B$_2$ monomer **3** with the A$_2$ monomer 1,4-phenylenediamine. An equimolar

Figure 1. ^{1}H NMR spectra of compounds (a) **3** and (b) **4** in DMSO-d_6.

Scheme 3

Figure 2. ^{1}H NMR spectra in DMSO-d_6 of model compounds (a) **6**, (b) **7**, and (c) **8** compared with the hyperbranched poly-(amide−imide)s **PAI-1**s prepared by either the (d) self-polymerization of monomer **4** or (e) the copolymerization method.

10^4 g/mol and 2.7, respectively, for the amide-terminated polymer of **PAI-1** prepared from the direct polymerization of the B′B$_2$ with the A$_2$ monomers,. The amide derivative of **PAI-1**, prepared by the self-polycondensation of the AB$_2$ type monomer **4** under the same conditions, has similar M_w and M_w/M_n values: 4.1×10^4 g/mol and 2.5. These values, however, are only indicative, since the highly branched nature of **PAI-1** deviates strongly from that of linear, coillike poly-(methyl methacrylate) standards. The solution viscosity of **PAI-1**s was also evaluated in DMAc at a concentration of 0.5 g/dL at 30 °C. The inherent viscosity (η_{inh}) was 0.29 and 0.28 g/dL respectively for the hyperbranched polymers **PAI-1**s prepared by the copolymerization method and by the self-polymerization of monomer **4**. The comparison of the solution viscosity reveals that there is no cross-linking taken place in the direct copolymerization. This is consistent with the observation that no gelation occurred during the copolymerization.

Degree of Branching. Hyperbranched polymers, which were formed by a sequence of condensation of AB$_2$ monomers, have an irregular dendritic structure in which three different types of subunits may be present. In this work, the hyperbranched poly(amide−imide) **PAI-1** is composed of three kinds of repeating units: the terminal units, which have two carboxylic acid groups, the linear units, which have one amide group and one carboxylic acid group, and the dendritic units, which have two amide groups and no free carboxylic acid group. The degree of branching (DB), a typical property often used to evaluate the structural irregularity of hyperbranched polymers, was defined as the sum of dendritic and terminal units vs the total number of units.[31,32] A combination of NMR spectroscopy and comparative studies on a model compound was used to quantify the different subunits present in the hyperbranched polymer and, subsequently, to determine its DB.[31]

The preparation of the model compounds useful for NMR characterization is illustrated in Scheme 3. Model compounds **6**, **7**, and **8** resemble the terminal unit, the linear unit, and the dendritic unit, respectively. Their
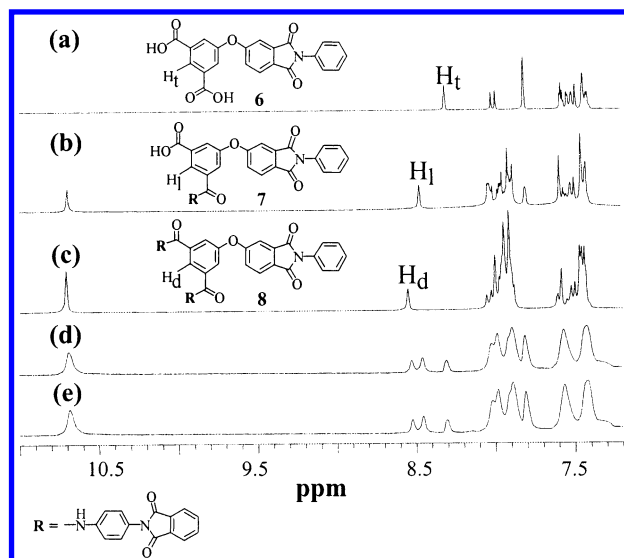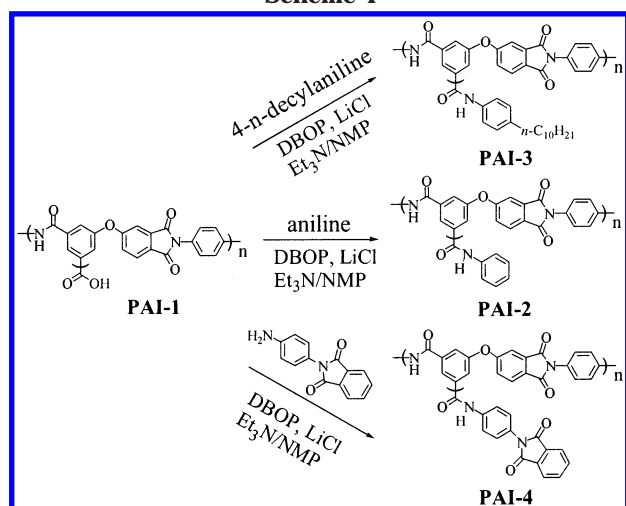
^{1}H NMR spectra are depicted in Figure 2. A distinct resonance for the terminal model compound, **6**, appears at 8.32 ppm (H$_t$), whereas resonances of the corresponding protons for the linear and dendritic model compounds, **7** (H$_l$), and **8** (H$_d$), are observed at 8.47 and 8.55 ppm, respectively. Figure 2 also shows the ^{1}H NMR spectra of the hyperbranched poly(amide−imide)s. In comparing the ^{1}H NMR spectra of **PAI-1**s with those of the model compounds, one can clearly assign the resonances at 8.32, 8.47, and 8.55 ppm to the proton of the terminal, linear, and dendritic subunits in the hyperbranched polymer, respectively. On the basis of the integration of these well-resolved resonances, the relative percentages of each subunit in **PAI-1**s can be determined. It was noted that the percentage estimated for the terminal subunit is approximately equal to that for the dendritic subunit. This 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.[5] With these formulas, the DB of the poly-(amide−imide) **PAI-1**, prepared by the direct polymerization of monomer **3** with 1,4-phenylenediamine, is estimated to be 61%. This value is nearly the same as the DB calculated for the **PAI-1** synthesized by the self-polycondensation of the AB$_2$ type monomer **4**, which is 60%.
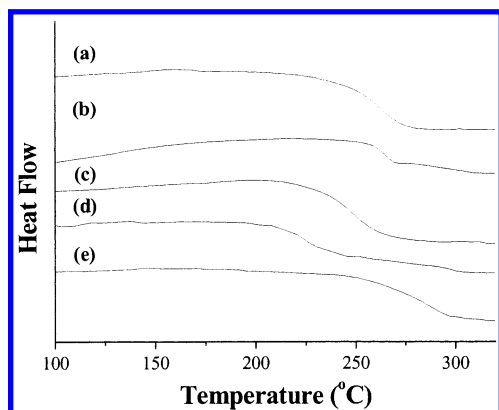
Chemical Modification. As predicted theoretically by Flory,[5] the direct polymerization of AB$_n$ type monomers is expected to produce a highly branched, irregular structure that contains a large number of end groups. In this study, the end groups in the resulting hyperbranched poly(amide−imide) **PAI-1** are carboxylic acids, which could be readily functionalized to yield hyperbranched polymers with a variety of functional chain ends. As shown in Scheme 4, the modification of the carboxylic end groups of **PAI-1** was carried out with different kinds of aromatic amines, in the presence of DBOP as the condensation agent, to give the corresponding amide derivatives. We chose DBOP as the activator[33] and ran the condensation reaction at room temperature to prevent transamination, which is a side reaction occurring at high temperatures. In the modi-

Scheme 4

polymer	T_g (°C)	solubility[c] in				
		THF	DMF	DMAc	DMSO	pyridine
PAI-1[a]	262	−	+	+	+	+
PAI-1[b]	263	−	+	+	+	+
PAI-2	248	−	+	+	+	+
PAI-3	223	+	+	+	+ −	+
PAI-4	283	−	+	+	+	+

[a] Prepared by the copolymerization approach. [b] Prepared by self-polymerization of monomer **4**. [c] Solubility: +, soluble; −, insoluble; + −, soluble on heating.

fication reaction, the use of excess amino reagents resulted in almost complete (>95%) functionalization, as confirmed by the ¹H NMR spectra of the derivative. After end-capping, the broad peak at 13.51 ppm, associated with the proton of the terminal carboxylic acid group, disappeared. For **PAI-2-3**, an additional resonance due to the proton of the terminal amide group appears in the region of 10.4−10.5 ppm. It is interesting to note that for **PAI-4** the signals corresponding to the proton of the terminal (H_t), linear (H_l), and dendritic (H_d) subunits shown in Figure 2 coalesce at 8.54 ppm. This is attributed to the similarity of the chemical environments for the three different subunits in **PAI-4**. This result is consistent with the observation that, in **PAI-4**, the chemical shift of the proton of the terminal amide group is the same as that of the interior amide group. Thus, there is only one resonance with an integration of 2 H for the protons of the two different kinds of amides. The integration analyses of ¹H NMR spectra of the derivatives indicate that the modification reactions proceeded almost quantitatively.

The nature of the end groups influences the physical and chemical properties of hyperbranched polymers.[34] The glass transition temperatures (T_g's) of poly(amide−imide)s **PAI-1-4** were investigated by differential scanning calorimetry (DSC), and the results are presented in Figure 3 and Table 1. As reported, the transition from the polar function to nonpolar end groups results in a decrease in T_g due to the reduction in the extent of

intermolecular interactions in the polymeric molecules.[35] The T_g of **PAI-1**, which has polar carboxylic terminal groups, is 262 °C, while the T_g value of **PAI-2**, which has less polar amide terminal groups, is 248 °C. A further decrease in T_g to 223 °C was observed for **PAI-3**, due to the introduction of long, flexible *n*-decyl chain ends. **PAI-4**, which has rigid, imide chain ends, has a T_g of 283 °C. Because of their highly branched structures, these poly(amide−imide)s have enhanced solubility in organic solvents and are highly soluble in polar solvents such as DMAc, NMP, and pyridine (Table 1). However, the different chain ends led to solubility differences in very polar and in relatively nonpolar solvents. **PAI-1-2** and **PAI-4** are soluble in DMSO and insoluble in THF, whereas **PAI-3,** which possesses long *n*-decyl chain ends**,** is soluble in hot DMSO as well as in THF.

Summary

We have synthesized a hyperbranched poly(amide−imide) via the A_2 + B′B_2 approach. The copolymerization of 4-(3,5-dicarboxyphenoxy)phthalic anhydride (**3**), a B′B_2 type monomer, and 1,4-phenylenediamine, an A_2 type monomer, resulted in a hyperbranched poly-(amide−imide) containing terminal carboxylic acid groups. No gelation occurred during the polymerization. For comparison, we also carried out the synthesis of this hyperbranched polymer via the conventional self-polymerization of *N*-(4-aminophenyl)-4-(3,5-dicarboxyphenoxy)phthalimide (**4**), an AB$_2$ monomer. Both approaches led to hyperbranched poly(amide−imide)s with almost identical structures. The degree of branching of the polymers was approximately 60%, as determined by a combination of model compound studies and ¹H NMR integration data. End-capping of the terminal carboxylic acid groups was accomplished by reacting with different kinds of aromatic amines. Thermal and solubility properties of the resulting polymers depend on the nature of the chain-end groups.

References and Notes

(1) Malmström, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555.
(2) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.
(3) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.
(4) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233 and references cited in the reviews.
(5) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(6) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(7) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives;* VCH: Weinheim, FRG, 1996.

Figure 3. DSC thermograms of hyperbranched poly(amide−imide)s (a) **PAI-1** prepared by self-polymerization of monomer **4**, (b) **PAI-1** prepared by the copolymeriztion method, (c) **PAI-2**, (d) **PAI-3**, and (e) **PAI-4**.

(8) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74.

(9) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117.

(10) Newkome, G. R.; Yao, Z.-Q.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003.

(11) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(12) Xu, Z. F.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354.

(13) Emrick, T.; Chang, H.-T.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 6380.

(14) Jikei, M.; Chon, S.-H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061.

(15) Fang, J.; Kita, H.; Okamoto, K. *Macromolecules* **2000**, *33*, 4639.

(16) Hao, J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2002**, *35*, 5372.

(17) (a) Yan, D.; Gao, C. *Macromolecules* **2000**, *33*, 7693. (b) Gao, C.; Yan, D. *Macromolecules* **2001**, *34*, 156. (c) Gao, C.; Yan, D. *Chem. Commun.* **2001**, 107. (d) Gao, C.; Yan, D.; Zhu, X.; Huang, W. *Polymer* **2001**, *42*, 7603. (e) Gao, C.; Yan, D.; Tang, W. *Macromol. Chem. Phys.* **2001**, *202*, 3035.

(18) Cassidy, P. E. *Thermally Stable Polymer*; Marcel Dekker: New York, 1980.

(19) *Polymides*; Wilson, D., Stenzenberger, H. D., Hergenrother, P. M., Eds.; Blackie: New York, 1990.

(20) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.

(21) (a) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1998**, *31*, 5964. (b) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215. (c) Jikei, M.; Fujii, K.; Yang, G.; Kakimoto, M. *Macromolecules* **2000**, *33*, 6228. (d) Jikei, M.; Fujii, K.; Yang, G.; Kakimoto, M. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2001**, *39*, 3304.

(22) Monticilli, O.; Mendichi, R.; Bisbano, S.; Mariani, A.; Russo, S. *Macromol. Chem. Phys.* **2000**, *201*, 2123.

(23) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 1111. (b) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 6937. (c) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2001**, *34*, 3910.

(24) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1999**, *32*, 4764. (b) Markoski, L. J.; Thompson, J. L.; Moore, J. S. *Macromolecules* **2000**, *33*, 5315.

(25) Wu, F.-I.; Shu, C.-F. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2001**, *39*, 2536.

(26) Liaw, D.-J.; Hsu, P.-N.; Chen, W.-H.; Liaw, B.-Y. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2001**, *39*, 3498.

(27) Yang, C.-P.; Chen, R.-S.; Wang, M.-J. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2002**, *40*, 1092.

(28) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci.*, *Polym. Chem. Ed.* **1975**, *13*, 1373.

(29) Tullos, G. L.; Mathias, L. J.; Langsam, M. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **1999**, *37*, 1183.

(30) Shu, C.-F.; Leu, C.-M. *Macromolecules* **1999**, *32*, 100.

(31) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(32) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.

(33) Ueda, M.; Maneyama, A.; Hashimoto, K. *Macromolecules* **1988**, *21*, 18.

(34) Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370.

(35) Schmaljohann, D.; Häussler, L.; Pötschke, P.; Voit, B. I.; Loontjens, T. J. A. *Macromol. Chem. Phys.* **2000**, *201*, 49.