Synthesis and Characterization of Hyperbranched Aromatic Poly(ether imide)s

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ABSTRACT: The four AB$_2$ monomers, *N*-[3- or 4-bis(4-hydroxyphenyl)toluoyl]-4-chlorophthalimide and *N*-{3- or 4-[1,1-bis(4-hydroxyphenyl)]ethylphenyl}-4-chlorophthalimides, were prepared and used for synthesis of hyperbranched poly(ether imide)s bearing hydroxyl end groups. These hyperbranched poly-(ether imide)s had moderate molecular weights with broad distributions and showed glass-transition temperatures (*T*$_g$s) between 177 and 230 °C. The thermogravimetric analytic measurement revealed the decomposition temperature at 5% weight-loss temperatures (*T*$_d$$^{5\%}$) ranging from 240 to 281 °C. Analysis using ^{1}H NMR spectroscopy revealed the four types of hyperbranched poly(ether imide)s to have similar degrees of branching (ca. 60%). These polymers were modified by acylation or nucleophilic substitution reaction at the hydroxyl end groups. The conversion effectiveness depended on the type of modification reaction, modifier, and reaction conditions. The thermal stability and solubility of hyperbranched poly-(ether imide)s were improved by the modification of the end groups.

Introduction

Dendritic macromolecules such as dendrimers, dendrons, and hyperbranched polymers have received considerable attention due to their unique structure and properties.[1−4] Dendrimers are synthesized by controlling repetitive reaction sequences;[5−8] by contrast, hyperbranched polymers are generally prepared by a one-step polymerization. Therefore, they may be suitable for a large-scale production. Although hyperbranched polymers do not have perfectly defined structures, they retain many of the important features of dendritic macromolecules such as higher solubility, lower viscosity, and multiple end groups offering the possibility for further modification and special applications compared to their linear analogues.[8,9] In 1952, Flory published the statistical calculation methods for the one-step polymerization of AB$_2$-type monomers and copolymerization of AB and AB$_2$ monomers.[10] Thirty years later, Kricheldorf synthesized the aromatic polyester copolymers from AB and AB$_2$ monomers.[11] Kim and Webster reported the synthesis of hyperbranched polyphenylenes by the one-step polycondensation of AB$_2$ monomers in 1990.[12] Since then, a large number of hyperbranched polymers have been prepared.[4,13−20]

Aromatic polyimides are well-known for their excellent thermal stability, chemical resistance, and mechanical properties and have been applied widely in modern industries. However, aromatic polyimides are only soluble in highly polar solvents such as concentrated sulfuric acid. Moore's group synthesized a hyperbranched poly(ether imide) by self-condensation of 3,5-[di(-*tert*-butyldimethylsiyloxy)phenyl]-4-fluorphthalimide and modifying end group and revealed that hyperbranched aromatic poly(ether imide)s had better solubility than their linear analogues. They are soluble in amide type solvents, even in tetrahydrofuran, and can be used as specialty additives for other high-performance polymer materials.[21−24] Hyperbranched aromatic polyimides exhibiting good solubility or gas separation property were successfully prepared via polyamic acid methyl ester precursors[19,20] or from dianhydrides (A$_2$) and triamine monomers (B$_3$) by controlling the concentration and molar ratio of monomers.[25,26] Recently, Kakimoto's group[27] prepared new aromatic hyperbranched polyimides from 1,4-phenylenediamine (A$_2$) and tri(phthalic acid methyl ester) (B$_3$) in the presence of condensation agent. Shu et al.[28−30] reported the synthesis of dendritic poly(ether imide)s from the building block 1-(4-aminophenyl)-1,1-bis(4-hydroxyphenyl)-ethane and hyperbranched poly(ether imide)s from AB$_2$ monomer containing a fluoro-substituted phthalimide. In this paper, we report synthesis and characterization of various aromatic hyperbranched poly(ether imide)s with hydroxy, cyanophenyl, aromatic imide, aryl ester, and alkyl ester end groups from AB$_2$ monomers containing a chloro-substituted phthalimide. The degree of branching (DB) of the polymers can be easily determined without model compounds. The influence of the chain-end groups on the solubility and glass-transition temperature of the hyperbranched polymers was investigated.

Experimental Section

Chemicals. *N,N*-Dimethylacetamide (DMAc), *N*-methyl-2-pryolidinone (NMP), and pyridine were distilled from calcium hydride under reduced pressure. Acetic anhydride was used after distillation from magnesium. Benzoyl chloride and

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4-chlorobenzonitrile were distilled under reduced pressure before use. Other solvents and reagents were used as received.

Measurements. ^{1}H NMR spectra (DMSO-d_6) were recorded using a Varian Unity 400 MHz spectrometer using the residual ^{1}H solvent peak as reference. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. DSC and TG measurements were conducted with Perkin-Elmer Pyris 1 differential scanning calorimeter and Pyris 1 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen, respectively. Gel permeation chromatography (GPC) was performed with a Waters 410 fitted with polystyrene−divinylbenzene columns (two Shodex KD 806 M and 802) and a Waters 410 refractive index detector in tetrahydrofuran (THF) or was carried out using a Waters 410 fitted with Styragel HMW6E column with dimethylformamide (DMF) containing 0.05 M LiCl as mobile phase. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C.

4,4′-Dihydroxy-4″-nitrotriphenylmethane, 1A. A solution of *p*-nitrobenzaldehyde (30.40 g, 0.20 mol) and phenol (37.6 g, 0.40 mol) in acetic acid (100 mL) was stirred and cooled slowly to 11−12 °C. A cool mixture of sulfuric acid (40 mL) and acetic acid (60 mL) was added dropwise. The reaction mixture was kept at 11−12 °C for 18 h and then was poured into water. The material precipitated was washed with water. The crude product was purified by recrystallization from benzene. The product separated from benzene partly as resin and partly as large, pale yellow prisms of the benzene adduct (29.5 g, 30%), which melted at 52−57 °C, solidified with a continued slow rise in temperature, and melted again at 212−214 °C. IR (KBr): 3373 (O−H); 3089 (Ar$_3$C−H); 3034 (Ar−H); 1611, 1510, 1477, 1438 (C=C); 1595, 1344 (NO$_2$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.67 (s, 1H), 6.81 (d, 4H), 6.99 (d, 4H), 7.48 (d, 2H), 8.26 (d, 2H), 9.49 (s, 2H).

1,1-Bis(4-hydroxyphenyl)-1-(4-nitrophenyl)ethane, 1B. Zinc chloride (13.6 g, 0.10 mol) was added to a mixture of *p*-nitroacetophenone (82.6 g, 0.50 mol) and phenol (188.0 g, 2.0 mol), the apparatus was purged with dry hydrogen chloride to remove the air, and then the solution was stirred at 81−82 °C under hydrogen chloride for 20 h. The reaction mixture was poured into 1 L of hot water, and the precipitated product was recovered by filtration and washed with hot water several times. The yellow crude product was dissolved in a solution of sodium hydrogen carbonate (5%, 2.1 L) and then filtered. The filtrate was acidified with hydrochloric acid, and then the precipitate was recovered by filtration and washed with water to give light-yellow product **1B** (148 g, 88%). IR (KBr): 3400 (O−H); 3068, 3036 (Ar−H); 1594, 1510, 1479, (C=C); 1595, 1344 (NO$_2$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.17 (s, 3H), 6.79 (d, 4H), 6.93 (d, 4H), 7.40 (d, 2H), 8.24 (d, 2H), 9.47 (s, 2H).

4,4′-Dihydroxy-3″-nitrotriphenylmethene, 1C. A solution of *m*-nitrobenzaldehyde (15.2 g, 0.10 mol) and phenol (18.8 g, 0.20 mol) in acetic acid (70 mL) was stirred and cooled to 3−4 °C. A cool mixture of sulfuric acid (6 mL) and acetic acid (30 mL) was added dropwise. The mixture, which turned orange, was kept at 3−4 °C for 48 h and then poured into crushed ice and stirred. The resin separated was washed until free from acid and freed from adhering water. A solution of the resin in hot benzene deposited some red resin on cooling, followed by yellow crystals of the benzene adduct (17.9 g, 37%) which melted at 72 °C, solidified on slowly raising the temperature, and melted again at 156−157 °C. IR (KBr): 3371 (O−H); 3089 (Ar3C−H); 3034 (Ar−H); 1611, 1509, 1477, (C=C); 1595, 1529, 1344 (NO$_2$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.70 (s, 1H), 6.82 (d, 4H), 7.01 (d, 4H), 7.65 (m, 2H), 7.99 (s, 1H), 8.18 (d, 1H), 9.48 (s, 2H).

1,1-Bis(4-hydroxyphenyl)-1-(3-nitrophenyl)ethane, 1D. Compound **1D** was synthesized by condensation of *m*-nitroacetophenone and phenol. The synthesis procedure was similar to that for **1B**, as shown in Scheme 1. Yield: 90%. IR (KBr): 3373 (O−H); 1611, 1510, 1477, (C=C); 1594, 1525, 1352 (NO$_2$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.22 (s, 3H), 6.80 (d, 4H), 6.94 (d, 4H), 7.67 (m, 2H), 7.89 (s, 1H), 8.18 (d, 1H), 9.48 (s, 2H).

4-Amino-4′,4″-dihydroxytriphenylmethane, 2A. 5% Pd/C (1.60 g) was added to a solution of 4,4′-dihydroxy-4″-nitro-triphenylmethane (13.76 g) in 80 mL of ethanol. The resulting mixture was purged with nitrogen and then with hydrogen three times to remove oxygen and stirred vigorously at 35 °C under hydrogen for 1 week. The reaction mixture was then filtered, and the filtrate was evaporated to give 4-amino-4′,4″-dihydroxytriphenyl methane (8.18 g, 93%). IR (KBr): 3388, 3321 (N−H, O−H); 1596 (N−H), 1612, 1512, 1364 (C=C); 1252 (C−N); 1172 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.00 (s, 2H), 5.24 (s, 1H), 6.58 (d, 2H), 6.76 (d, 4H), 6.82 (d, 2H), 6.96 (d, 4H), 9.29 (s, 2H). Anal. Calcd for C$_{19}$H$_{17}$NO$_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.83; H, 5.79; N, 4.76.

1-(4-Aminophenyl)-1,1-bis(4-dihydroxyphenyl)ethane, 2B. Compound **2B** was synthesized by reduction of **1B**. The procedure was similar to that for **2A**, as shown in Scheme 1. Yield: 88%. IR (KBr): 3387, 3317 (N−H, O−H); 1587 (N−H), 1608, 1505, 1365 (C=C); 1237 (C−N); 1182 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.05 (s, 3H), 5.00 (s, 2H), 6.56 (d, 2H), 6.75 (m, 6H), 6.91 (d, 4H), 9.29 (s, 2H). Anal. Calcd for C$_{20}$H$_{19}$-NO$_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.05; H, 6.17; N, 4.55.

3-Amino-4′,4″-dihydroxytriphenylmethane, 2C. Compound **2C** was synthesized by reduction of **1C**. The synthesis procedure was similar to that for **2A**, as shown in Scheme 1. Yield: 93%. IR (KBr): 3373, 3313 (N−H, O−H); 3018 (Ar$_3$C−H); 1596 (N−H), 1610, 1510, 1456 (C=C); 1235 (C−N); 1171 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): 5.05 (s, 2H), 5.23 (s, 1H), 6.31 (d, 1H), 6.40 (s, 1H), 6.47 (d, 1H), 6.77 (d, 4H), 6.98 (d, 4H), 7.01 (d, 1H), 9.32 (s, 2H). Calcd for C$_{19}$H$_{17}$NO$_2$: C, 78.33; H, 5.88, N, 4.81. Found: C, 78.83; H, 5.79; N, 4.76.

1-(3-Aminophenyl)-1,1-bis(4-dihydroxyphenyl)ethane, 2D. Compound **2D** was synthesized by reduction of **1D**. The synthesis procedure was similar to that for **2A**, as shown in Scheme 1. Yield: 93%. IR (KBr): 3372, 3311 (N−H, O−H), 1593 (N−H), 1609, 1510, 1446 (C=C); 1243 (C−N); 1177 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.05 (s, 1H), 6.24 (s, 1H), 6.39 (s, 1H), 6.47 (d, 1H), 6.74 (d 4H), 6.94 (d, 4H), 6.98 (m, 1H), 9.37 (s 2H). Calcd for C$_{20}$H$_{19}$NO$_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.12; H, 6.49; N, 4.59.

***N*-[4-Bis(4-hydroxyphenyl)toluoyl]-4-chlorophthalimide, Monomer 3A.** A solution of 4-amino-4′,4″-dihydroxy-triphenylmethane (4.78 g, 16 mmol) and 4-chlorophthalic anhydride (3.10 g, 16.98 mmol) was dissolved in dry, deoxygenated dimethylacetamide (40 mL), stirred for 24 h at room temperature under a slow stream of nitrogen, and then was added xylene (20 mL); the mixture was refluxed to dehydrate for 10 h. After cooling the reaction mixture was poured into ethanol (100 mL). The precipitate was isolated by filtration, washed with *n*-hexane/ethanol (6/4), and dried in a vacuum to give **3A** (7.49 g, 95%). IR (KBr): 3477, 3231 (O−H), 1778, 1710 (C=O); 1611, 1511 (Ar−H); 1392 (C−N); 1096 (C−Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.55 (s, 1H), 6. 82 (d, 4H), 7.04 (d, 4H), 7.34 (d, 4H), 7.47 (m, 1 H), 8.07 (m, 2H), 9.39 (s, 2H). Calcd for C$_{27}$H$_{18}$ClNO$_2$: C, 71.13; H, 3.98; N, 3.07. Found: C, 71.25; H, 4.04; N, 3.17.

***N*-{4-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-4-chlorophthalimide, Monomer 3B.** Monomer **3B** was synthesized by condensation of **2B** and 4-chlorophthalic anhydride. The synthesis procedure was similar to that for monomer **3A**, as shown in Scheme 1. Yield: 90%. IR (KBr): 3046 (O−H), 1775, 1708 (C=O); 1609, 1507 (Ar−H); 1376 (C−N); 1091 (C−Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.18 (s, 3H), 6.80 (d, 4H), 6.98 (d, 4H), 7.28 (d, 2H), 7.44 (d, 2H), 8.07 (m, 2H), 8.16 (s, 1H), 9.42 (s, 2H). Calcd for C$_{28}$H$_{20}$ClNO$_2$: C, 71.57; H, 4.29; N, 2.98. Found: C, 71.59; H, 4.30; N, 2.85.

***N*-[3-Bis(4-hydroxyphenyl)toluoyl]-4-chlorophthalimide, Monomer 3C.** Monomer **3C** was synthesized by condensation of **2C** and 4-chlorophthalic anhydride. The synthesis procedure was similar to that for monomer **3A**, as shown in Scheme 1. Yield: 90%. IR (KBr): 3460 (O−H), 1772, 1713 (C=O); 1612, 1512 (Ar−H); 1383 (C−N); 1100 (C−Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.55 (s, 1H), 6.82 (d, 4H), 7.04 (d, 4H), 7.34 (d, 4H), 7.47 (m, 1H), 8.07 (m, 2H), 8.16 (s, 2H), 9.39 (s, 2H). Calcd for C$_{27}$H$_{18}$ClNO$_2$: C, 71.13; H, 3.98; N, 3.07. Found: C, 71.35; H, 3.95; N, 3.20.

***N*-{3-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-4-chlorophthalimide, Monomer 3D.** Monomer **3D** was synthesized

Scheme 1. Synthesis of Monomers
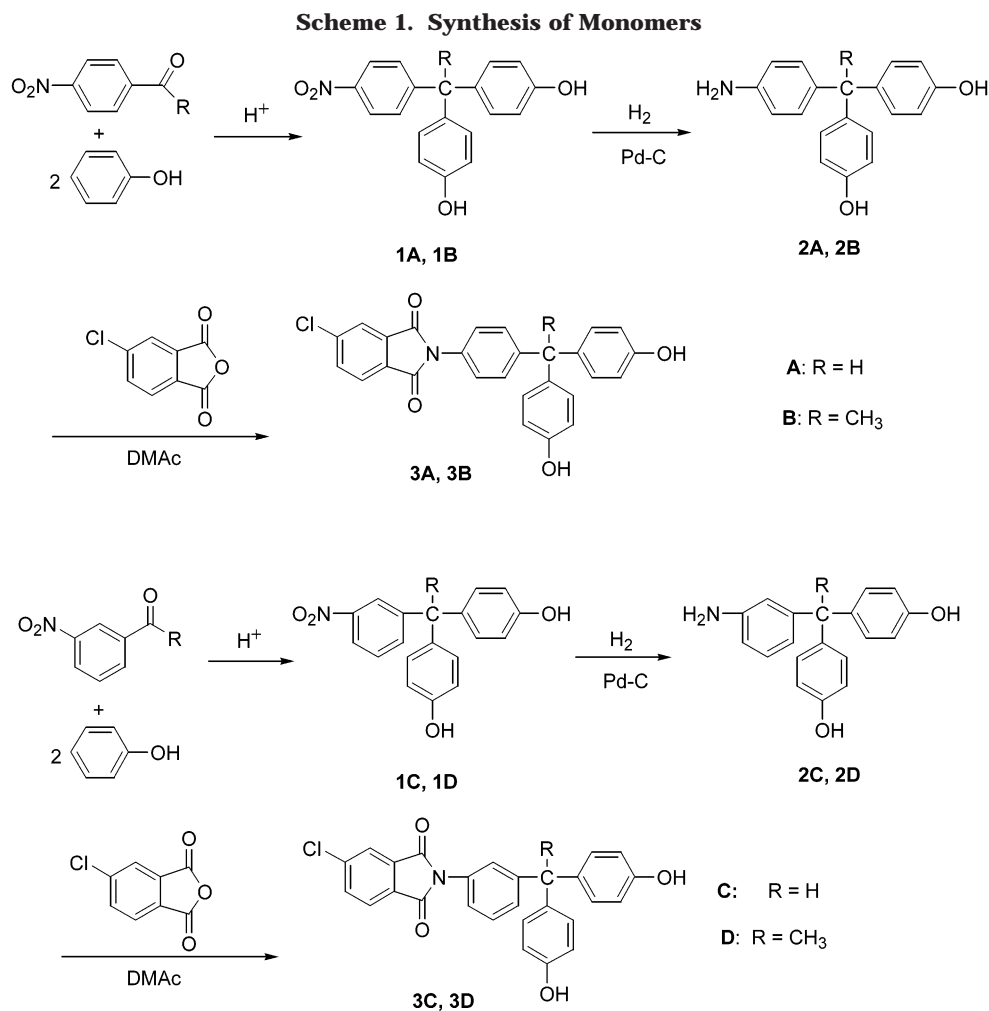
by condensation of **2D** and 4-chlorophthalic anhydride. The synthesis procedure was similar to that for monomer **3A**, as shown in Scheme 1. Yield: 97%. IR (KBr): 3421 (O−H), 1776, 1716 (C=O); 1610, 1511 (Ar−H); 1375 (C−N); 1102 (C−Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.03 (s,3H), 6.65 (d, 4H), 6.84 (d, 4H), 7.06 (d, 1H), 7.17 (s, 1H), 7.20 (d, 1H), 7.40 (m, 1H), 7.92 (s, 2H), 7.99 (s, 1H), 9.29 (s, 2H). Calcd for $C_{28}H_{20}ClNO_2$: C, 71.57; H, 4.29; N, 2.98. Found: C, 71.59; H, 4.03; N, 2.96.

General Procedure for the Synthesis of Hyperbranched Poly(ether imide)s, **4A−D**. Dry NMP (20 mL) and dry toluene (15 mL) were added to a mixture of AB$_2$ monomer (13 mmol) and potassium carbonate (2.90 g). The reaction mixture was then heated at reflux in nitrogen for 10 h, with the water being collected in a Dean−Stark trap. The distillate was collected and removed when the temperature of the reaction mixture had reached ca. 180 °C. After stirring and heating for 3 h, the reaction mixture was poured into water (1.6 L), and the precipitate was collected and reprecipitated twice from THF into methanol to give a white solid hyperbranched poly(ether imide).

General Procedure for Acylation of Hyperbranched Poly(ether imide)s. Acetic anhydride (in excess) and pyridine were added to a solution of hyperbranched poly(ether imide) in dry DMAc. The reaction mixture was then refluxed under an atmosphere of nitrogen for 30 h. After cooling, the reaction mixture was poured into water, and the precipitate was collected and reprecipitated twice from THF into methanol to give the ester-terminated hyperbranched poly(ether imide).

One-Pot Procedure for Synthesis of Imide-Terminated Hyperbranched Poly(ether imide)s. Dry DMAc or NMP (15 mL) and dry toluene (15 mL) were added to a mixture of AB$_2$ monomer (5 mmol) and potassium carbonate (0.6 g). The mixture was then refluxed in nitrogen for 10 h, with the water being collected in a Dean−Stark trap. The toluene was distilled

and removed. Stirring and heating were then continued for 11 h. After cooling, *N*-phenyl-4-chlorophthalimide (0.85 g) and potassium carbonate (0.26 g) were added. The procedure was carried out as described above. After cooling, the reaction mixture was poured into water (1 L). The precipitated polymer was dried and heated at ca. 240 °C under vacuum to remove excess *N*-phenyl-3-chlorophthalimide to afford the imide-terminated polymers.

Results and Discussion

Monomer Synthesis. The synthesis of monomers **3A−D** was accomplished in three steps from nitrobenzaldehyde or nitroacetophenone (Scheme 1). The synthesis of **2A** or **2C** was performed by the sulfuric acid-catalyzed condensation reaction of *p*- or *m*-nitrobenzaldehyde with phenol in cold acetic to give compound **1A** or **1C**,[31] followed by the reaction of the nitro group of **1A** or **1C** with H$_2$ catalyzed by Pd/C. Condensation of *p*- or *m*-nitroacetophenone and excess phenol in the presence of a mixture of zinc chloride and hydrogen chloride at 60−70 °C afforded 1,1-bis(4-dihydroxyphenyl)-1-(4-nitrophenyl)ethane or 1,1-bis(4-dihydroxyphenyl)-1-(3-nitrophenyl)ethane (**1B** or **1D**) in good yields. Compounds **2B−D** were easily prepared by hydrogenation of corresponding compounds **1B−D** in the presence of Pd/C catalyst. Reactions of **2A−D** with 4-chlorophthalic anhydride followed by imidizations in refluxing xylene afforded the corresponding monomers **3A−D**. The yields of these reactions were above 95%. The structure of **3A−D** was characterized by ^{1}H NMR and IR spectra and confirmed by elemental analysis.

Scheme 2. Synthesis of Hyperbranched Poly(ether imide)s

R = H: A, C
Me: B, D

$R_1 =$

a   b   c   d
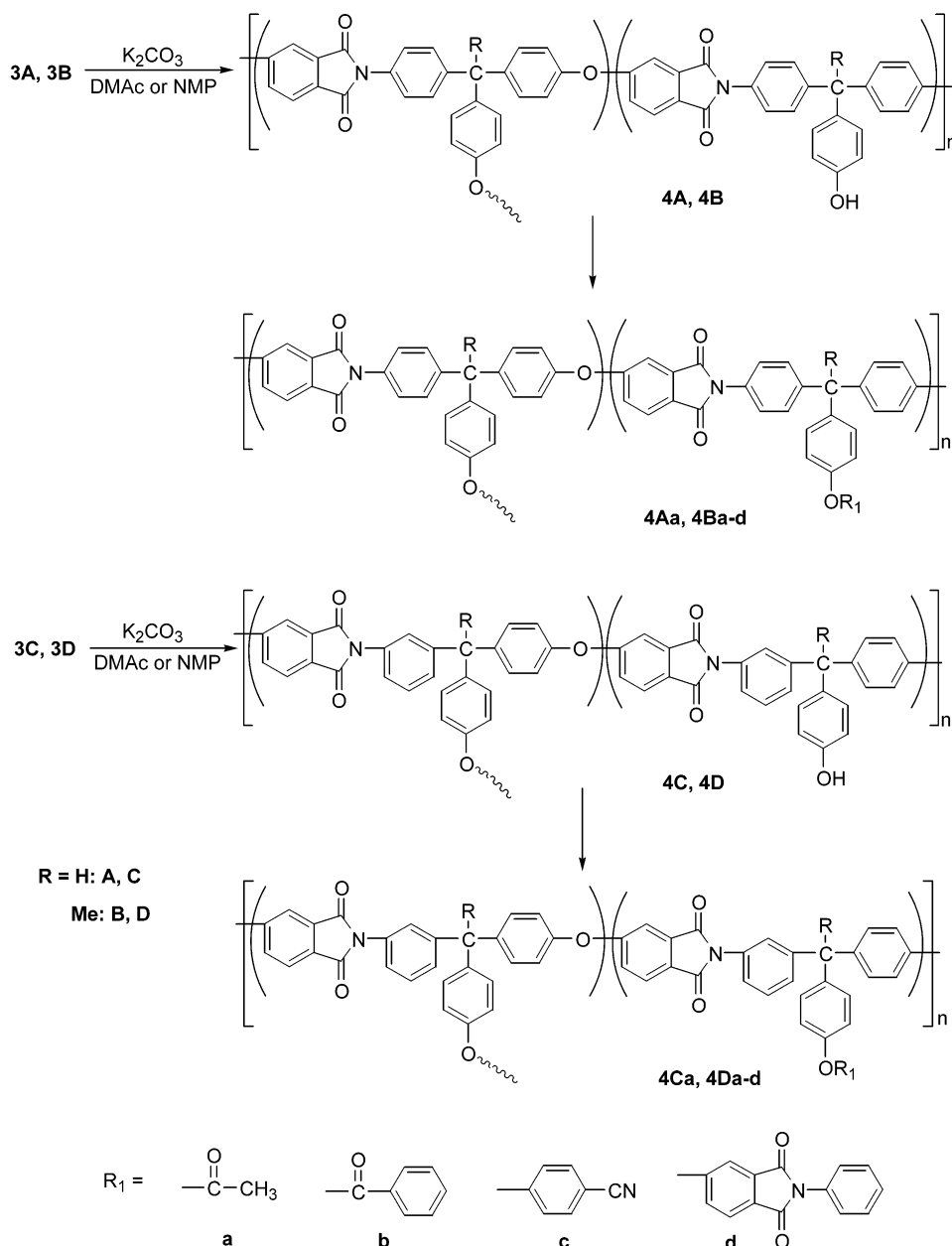
Synthesis and Properties of Hyperbranched Poly(ether imide)s with Hydroxy End Groups. Dendritic poly(ether imide)s can be prepared from **2B** and 3-nitro-*N*-phenylphthalimide having high reactivity at room temperature.[28] Preliminary experiments, however, suggested that hyperbranched poly(ether imide)s cannot be obtained under the same condition from corresponding monomers, **3A**−**D**, due to low reactivity. Poly(ether imide)s, **4A**−**D**, were prepared by self-condensation of corresponding monomers, **3A**−**D**, at high temperature and in the presence of potassium carbonate, as shown in Scheme 2.

As Scheme 3 shows, poly(ether imide) **4A** possesses three constructional units, linear units with H_{al} and H_{bl}, dendritic units with H_{ad}, and terminal units with H_{at} and H_{bt}. Obviously, the number of H_{al} equals that of H_{bl}, and the number of H_{at} equals half of that of H_{bt} in **4A**. It is expected that the proton NMR signal of H_a or H_b in each type unit is different from that of others. Thus, the NMR signal intensity of H_{al} equals that of

H_{bl}, and that of H_{at} equals half of that of H_{bt}. The monomer **3A** shows a single peak of Ar_3C-H (H_a) at 5.50 ppm and a single peak of OH (H_b) at 9.30 ppm, as shown in Figure 1. Polymer **4A** shows three peaks of H_a at 5.30 (a_1, H integration, $H_i = 0.74$), 5.50 (a_2, $H_i = 0.60$), and 5.70 ppm (a_3, $H_i = 0.57$) and two peaks of H_b at 9.30 ppm (b_1, $H_i = 1.20$) and 10.30 ppm (b_2, $H_i = 0.75$). According to the chemical environment of **3A** and **4A**, H_{at} of **4A** is similar to H_a of **3A**, and H_{bt} of **4A** is similar to H_b of **3A**. Hence, the chemical shift of NMR of these protons should be similar, too. Thus, as Figure 1 shows, a_2 must be at, and b_1 must be bt, so the other (b_2) must be bl. On the other hand, the integration of Ha_2 (Hat) almost equals half Hb_1 (Hbt); this is just agrees with theoretic analysis as mentioned above. Hence, it can be deduced that a_1 must be al due to the integration of Ha_1 almost equal to Hb_2 (Hbl), and another peak (a_3) must be ad.

DB of hyperbranched polymer was defined as the ratio of the sum of dendritic and terminal units vs total units
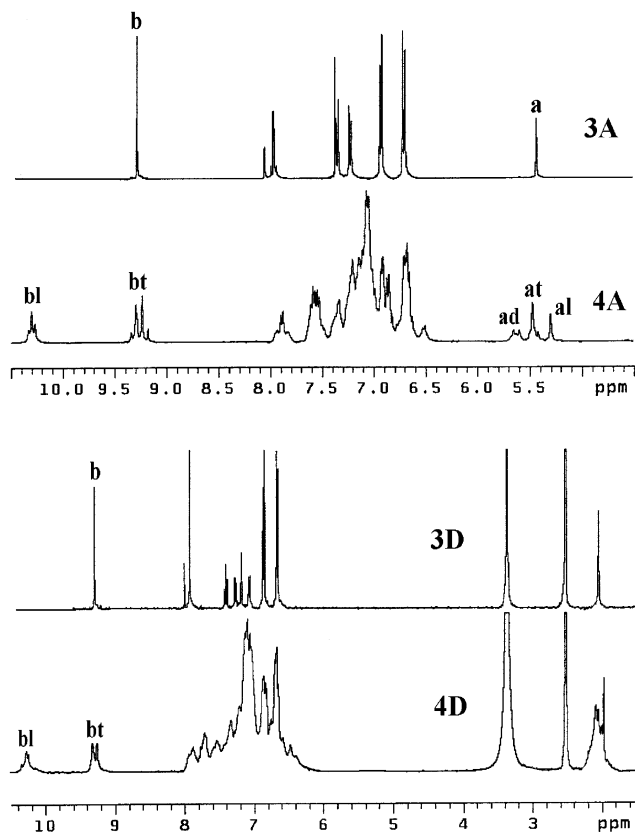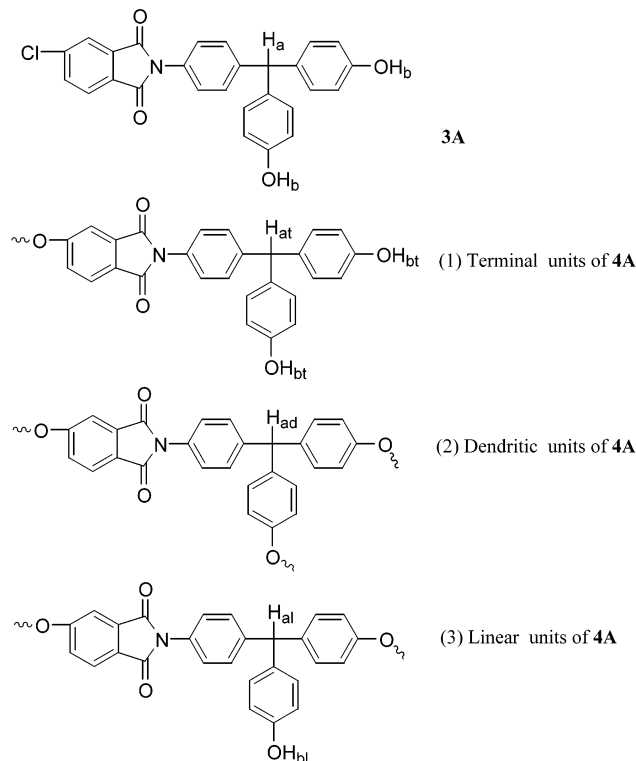
Figure 1. 400 MHz ^{1}H NMR spectra (d_6-DMSO, TMS, 20 °C) of **3A**, **4A**, **3D**, and **4D**.

Scheme 3. Structure of Monomer 3A and Three Constructional Units in Polymer 4A

(linear, dendritic, and terminal units) by Fréchet.[33] As described before, the three peaks of methine of **4A**, Had, Hat, and Hal (Figure 1), can be assigned to the dendritic units, terminal units, and linear units of **4A**, respectively. Therefore, DB of **4A** was determined to be 0.61
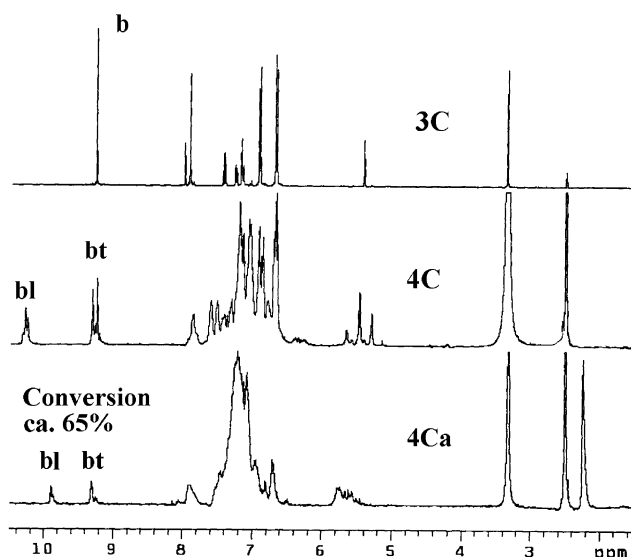

Figure 2. 400 MHz ^{1}H NMR spectra (d_6-DMSO, TMS, 20 °C) of monomer **3C**, polymer **4C**, and modified polymer **4Ca** by acylation for 10 h.

by calculating the integration ratio of these three peaks. The methine of **4C** also shows triplet at 5.30, 5.50, and 5.70 ppm (Figure 2) assigned to the dendritic units, terminal units, and linear units, respectively. Hence, the DB of **4C** was calculated to be 0.68 from integrated intensities of the distinct proton resonance of the methane similar to the case of **4A.** The DB of **4B** was determined to be 0.64 from integrated intensities of the distinct proton resonance of the methyl (triplet at D 2.18, T 2.08, L 2.00 ppm), as shown in Figure 3. Unfortunately, it was unsuccessful to determine the DB of **4D** using this method because of the overlapping of the ^{1}H NMR signals of methyl (1.96−2.09 ppm), as shown in Figure 1.

On the other hand, the degree of branching (DB) of one hyperbranched polymer based on AB$_2$ monomer can be estimated by another equation according to Frey's definition,[32] when the molecular weight of the hyperbranched polymer is high enough.

$$DB = 2T/(2T + L) \qquad (1)$$

where T and L are the fractions of terminal and linear incorporated monomers in a hyperbranched polymer based on AB$_2$ monomer. As shown in Scheme 3, one linear unit has one H$_{al}$ and one H$_{bl}$; one terminal unit possesses two H$_{bt}$. Hence, the DB can be calculated by the following equation:

$$DB = I_{Tb}/(I_{Tb} + I_{Lb}) \qquad (2)$$

where I_{Tb} and I_{Lb} are the signal intensity of H$_{bt}$ and H$_{bl}$, respectively. The DB of hyperbranched poly(ether imide) **4A** using the integration of terminal H$_{bt}$ (1.20) and linear proton H$_{bl}$ (0.75) gives a value of 0.62, according to eq 2. Similar to **4A**, the DB of **4B**, **4C**, and **4D** are estimated to be 0.63, 0.61, and 0.60, respectively. Comparing these results with those (0.61, 0.64, and 0.68) calculated from ^{1}H NMR of the methane or methyl of the polymers, it can be found that the difference between the two values of DB of the same hyperbranched polymer calculated from two distinct methods increase with the decrease of the molecular weight of polymers (see Table 1), indicating the DB calculated by
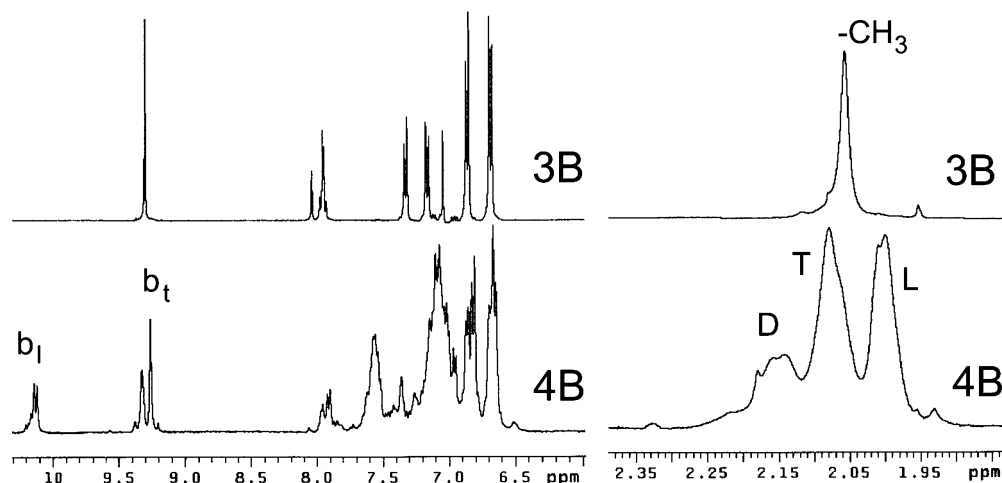
Figure 3. 400 MHz ^{1}H NMR spectra (d_6-DMSO, TMS, 20 °C) of **3B** and **4B**.

Table 1. Properties of Hyperbranched Poly(ether imide)s with Hydroxyl End Groups

polymer	react temp (°C)	react time (h)	yeild (%)	η_{inh}^a (dL/g)	$\bar{M}_w^b$ (kDa)	PDI^b	DB$_{Frey}$ 2T/ (2T + L)	DB$_{Fréchet}$ (D + T)/ (D + L + T)	T_g^c (°C)	$T_d^{5\% \, d}$ (°C)	EtOAc	CHCl$_3$	THF	DMAc	NMP
4A	180	12	85	0.16	8.03	3.95	0.62	0.61	230	281	− −	− −	+ +	+ +	+ +
4B	170	11	92	0.12	7.87	3.81	0.63	0.64	190	245	− −	+ −	+ +	+ +	+ +
4C	162	24	82	0.14	6.93	3.21	0.61	0.68	202	275	− −	− −	+ −	+ +	+ +
4D	175	10	88	0.15	5.69	2.69	0.60		177	240	− −	− −	+ +	+ +	+ +

^{a} Measured at 25 °C with c = 0.5 g/dL in DMAc. ^{b} The molecular weight was measured by GPC with DMF containing 0.05 M LiCl as eluent solvent. ^{c} DSC measurements with a heating rate of 10 °C/min in nitrogen. ^{d} TGA measurements with a heating rate of 10 °C/min in nitrogen. ^{e} Solubility studies were performed by adding 20 mg of polymer to 5 mL of the corresponding solvent: + + = soluble; − − = insoluble; + - = partially soluble.

the former method is more accurate than that calculated by the latter.

The properties of hyperbranched poly(ether imide)s with hydroxyl end groups are summarized in Table 1. In general, the polyimides from meta-oriented diamines have denser polymer chain packing and lower chain-segment mobility than those from the corresponding para-oriented diamines because of the larger conformational entropy of the meta-oriented chain. Furthermore, the former (meta-oriented) has lower glass transition temperature (T_g) than the latter.[34] Consequently, **4C** and **4D** possessing a meta-oriented chain have lower T_g than the corresponding polymers **4A** and **4B** possessing para-oriented chain, respectively. The polymers containing triphenylmethane units, **4A** and **4C**, have much higher T_g than the corresponding polymers containing triphenylethane units, **4B** and **4D**, respectively, as a consequence of the same packing density effect. The same trend was observed in the thermal decomposition temperature of these hyperbranched poly(ether imide)s (see Table 1).

Modification of Hyperbranched Poly(ether imide)s. Although all the hyperbranched poly(ether imide)s with hydroxyl end group, **4A**−**D**, have high T_gs, their thermal decomposition temperatures are very low because hydroxyl is not a thermally stable group. To improve their thermal stability, the hydroxyl end groups of the polymers were modified by acylation or nucleophilic substitution reaction.

The hyperbranched poly(ether imide) with hydroxyl end groups was dissolved in NMP. An acylation agent (in excess) and pyridine as a catalyst were added and heated at different temperatures according to the boiling point of acylation agent. The first acylation experiment was conducted with acetic anhydride. A 20% excess of

acetic anhydride was used for the acetylation of polymer **4C**, and the reaction temperature was limited to 140 °C. After 10 h, a product with conversion of phenolic hydroxyl to acetate of ca. 65% was obtained according to the analysis of the ^{1}H NMR spectra (Figure 2). The second acetylation experiment was conducted using a 50% excess of acetic anhydride for 24 h and gave a conversion around 85%. An attempt to further increase the conversion of acetylation by increasing the amount of acetylation agent and extending the reaction time was not successful. The higher boiling point of benzoyl chloride allowed a higher reaction temperature of 190 °C. Using an excess of 50% benzoyl chloride in combination with a reaction time of 24 h gave more than 90% acylation.

The nucleophilic substitution reactions of hyperbranched poly(ether imide)s with electrophiles were conduced by a "one-pot" procedure. The poly(ether imide) with hydroxyl end groups was prepared by self-condensation of corresponding AB$_2$ monomers. After cooling, an excess of 20% electrophilic agent and potassium carbonate (excess) were added and then were heated for several hours. A high conversion could be obtained easily in the case of 4-chlorophthaliimide. Nearly 100% conversion was achieved when polymer **4D** was reacted with *N*-phenyl-4-chlorophthaliimide at 200 °C for 10 h. However, only a low conversion was obtained when 4-chlorobenzonitrile was used as a modifying agent, although forcing conditions were utilized. The *N*-phenyl-4-chlorophthaliimide molecule is much bulkier than 4-chlorophthaliimide, but the conversion, using chlorobenzonitrile, was lower than that using *N*-phenyl-4-chlorophthaliimide. This fact is consistent with the proposal that the main factor affecting

Table 2. Properties of Modified Hyperbranched Poly(ether imide)s

polymer	react temp (°C)	react time (h)	conv[a] (%)	η_{inh}[b] (dL/g)	$\bar{M}_w$[c] (kDa)	PDI[c]	T_g[d] (°C)	T_d5%[e] (°C)	solubility[f] EtOAc	CHCl$_3$	THF	DMAc	NMP
4Aa	140	29	87	0.11	7.61	3.92	196	301	+ +	+ +	+ +	+ +	+ +
4Ba	140	24	85	0.08	4.23	2.53	165	251	+ +	+ +	+ +	+ +	+ +
4Bb	190	24	94	0.08	4.68	2.65	185	256	+ −	+ +	+ +	+ +	+ +
4Bc	170	11/21	63	0.11	5.42	2.61	178	257	+ −	+ −	+ −	+ +	+ +
4Bd	170	11/12	96	0.14			207	408	− −	− −	− −	+ +	+ +
4Ca	140	24	86	0.09	7.10	3.79	168	286	+ +	+ +	+ +	+ +	+ +
4Da	140	24	86	0.08	4.45	2.56	163	257	+ +	+ +	+ +	+ +	+ +
4Db	190	18	92	0.08	4.80	2.62	172	295	+ −	+ +	+ +	+ +	+ +
4Dc	200	10/18	76	0.10	5.34	2.58		297	− −	+ −	+ +	+ +	+ +
4Dd	200	10/10	98	0.15			214	315	− −	− −	− −	+ +	+ +

[a] Transform yield of end group was measured by ^{1}H NMR. [b] Measured at 25 °C with $c = 0.5$ g/dL in DMAc. [c] The molecular weight was measured by GPC with THF as eluent solvent. [d] DSC measurements with a heating rate of 10 °C/min in nitrogen. [e] TGA measurements with a heating rate of 10 °C/min in nitrogen. [f] + + = soluble; − − = insoluble; + − = partially soluble.

the conversion of end groups is the reactivity of the electrophile but not its steric bulk.

The modified polymers **4Bd** and **4Dd** were purified by sublimation of the excess 4-chlorophthaliimide, and the other modified polymers were purified by reprecipitation several times from THF into methanol. In all these experiments the conversion was checked by ^{1}H NMR spectroscopy of modified hyperbranched poly-(ether imide)s. The signal intensity ratios of the protons in residual hydroxyl to aromatic protons were used to calculate conversion.

The solubility of hyperbranched poly(ether imide)s, except for **4Bd** and **4Dd**, were improved by end-group modification, as shown in Tables 1 and 2. Among the modified polymers, those with ester end groups show the lowest weight-average molecular weight ($\bar{M}_w$) and the narrowest PDI, while those with cyanophenyl, which were prepared by one-pot procedure at higher temperature, exhibit the highest $\bar{M}_w$ and the broadest PDI in the polymers possessing same chain backbone. **4Ba−c** and **4Da−c** have a PDI of about 2.60, and **4Aa** and **4Ca** possess a broader PDI of above 3.70 (Table 2). This agreed with Flory's prediction of very large PDIs for AB$_2$ polymers.[10] The $\bar{M}_w$ and PDI of the hyperbranched poly-(ether imide)s, **4Bd** and **4Dd**, were not obtained because they are not soluble in THF. They have higher inherent viscosities than the other polymers. This indicates that they probably possess higher molecular weight than the others.

The two hyperbranched poly(ether imide)s with imide end groups (**4Bd** and **4Dd**) show higher T_gs than the parent polymers, and the other modified polymers exhibit much lower T_gs than the parent polymers due to both loss of H-bonding and the plasticization of the more flexible end groups. All of the modified hyperbranhced poly(ether imide)s exhibit much higher thermal decomposition temperature than the parent polymers. In other words, the thermal stability of hyperbranched poly(ether imide)s was improved by the modification of end groups. The two imide modification products, **4Bd** and **4Dd,** have the highest thermal stability among the polymers studied.

Conclusion

Hyperbranched aromatic poly(ether imide)s having various end groups were successfully prepared by the self-condensation of AB$_2$ monomers, *N*-[3- or 4-di(4-hydroxyphenyl)toluoyl-4-chlorophthalimide or *N*-{3- or 4-[1,1-di(4-hydroxyphenyl) ethylphenyl-4-chlorophthal-imides. The resulting hyperbranched poly(ether imide)s had lower inherent viscosity (0.12−0.16 dL/g) with DB

values of ca. 0.6 and exhibited good solubility in NMP, DMAc, THF, and CHCl$_3$. The T_gs and thermal stability of these hyperbranched poly(ether imide)s depend on the chain structure and the nature of the end groups. The polymers from *N*-[3- or 4-di(4-hydroxyphenyl)-toluoyl-4-chlorophthalimide possess higher T_gs and thermal decomposition temperatures than those from *N*-{3- or 4-[1,1-di(4-hydroxyphenyl)ethylphenyl-4-chlo-rophthalimides. Furthermore, the polymers based on monomers derived from para-isomers have higher T_gs and thermal decomposition temperatures than those based on corresponding meta-isomers. The thermal stability of hyperbranched poly(ether imide)s could be improved through acylation of their hydroxyl end groups. The maximum conversion of acetylation and benozyla-tion of the hydroxyl end groups was greater than 85 and 90%, respectively. The hyperbranched poly(ether imi-de)s can also be modified by nucleophilic substitution reaction. The main factor affecting conversion of hy-droxyl end groups is the reactivity of the electrophile, not its steric bulk. When *N*-phenyl-4-chlorophthalimide with high reactivity is used as the electrophile, more than 98% conversion was achieved. Among the hyper-branched poly(ether imide)s studied, the polymers modified by *N*-phenyl-4-chlorophthalimide possess the highest inherent viscosity and the best thermal stabili-ties.

References and Notes

(1) Uhrich, K. *Trends Polym. Sci.* **1997**, *5*, 388.
(2) Frey, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2193.
(3) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.
(4) Voit, B. I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.
(5) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(6) Malmstrom, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555.
(7) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.
(8) Wooley, K. L.; Hawker, C. J.; Pochan, J. *Polymer* **1994**, *35*, 4489.
(9) Hawker, C. J.; Frechet, J. M. *J. Chem. Soc., Perkin Trans.* **1992**, 2459.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(11) Kricheldorf, H. R.; Zang, Q. Z.; Schwarz, G. *Polymer* **1982**, *23*, 1821.
(12) Kim, Y. H.; Wester, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.
(13) Jikei, M.; Fujii, K.; Gang, Y.; Kakimoto, M. *Macromolecules* **2000**, *33*, 6228.
(14) Ishida, Y.; Andrew, C.; Sun, F.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 2832.
(15) Sunder, A.; Bauer, T.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33,* 1330.

(16) Sunder, A.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 309.

(17) Sunder, A.; Türk, H.; Haag, R.; Frey, H. *Macromolecules* **2000**, *33,* 7682.

(18) Gong, C. G.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2970.

(19) Yamanaka, K.; Jikei, M.; Kakimoto, M.-A. *Macromolecules* **2000**, *33*, 6937.

(20) Yamanaka, K.; Jikei, M.; Kakimoto, M.-A. *Macromolecules* **2000**, *33*, 1111.

(21) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1999**, *32*, 4764.

(22) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **2000**, *33*, 5315.

(23) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **2000**, *33*, 6412.

(24) Orlicki, J. A.; Thompson, J. L.; Markoski, L. J.; Still, K. N.; Moore, J. S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 936.

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

(26) Chen, H.; Yin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3804.

(27) Hao, J.-j; Jikei, M.; Kakimoto, M.-a. *Macromolecules* **2002**, *35*, 5372.

(28) Leu, C.-M.; Chang, Y.-T.; Shu, C.-F. *Macromolecules* **2000**, *33*, 2855.

(29) Leu, C.-M.; Shu, C.-F.; Teng, C.-F.; Shiea, J. *Polymer* **2001**, *42*, 2339.

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

(31) Driver, J. E.; Mok, S. F. *J. Chem. Soc.* **1955**, 3914.

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

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

(34) (a) Mi, Y.; Stern, S. A.; Trohalaki, S. *J. Membr. Sci.* **1993**, *77*, 41. (b) Kawakami, H.; Anzai, J.; Nagaoka, S. *J. Appl. Polym. Sci.* **1995**, *57*, 789. (c) Tamai, S.; Yamaguchi, A.; Ohta, M. *Polymer* **1996**, *37*, 3683. (d) Li, Y.-S.; Ding, M.-X.; Xu, J.-P. *Polymer* **1996**, *37*, 3451.