Synthesis of Hyperbranched Aromatic Polyimides via Polyamic Acid Methyl Ester Precursor

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Introduction. Recently, dendritic macromolecules have attracted considerable attention due to new physical and chemical properties caused by their unique structures.[1−5] They are mainly classified into dendrimers with well-defined structures and hyperbranched polymers having statistically branched architecture. Although the synthesis of dendrimers requires many reaction steps, hyperbranched polymers are prepared by one-step polymerization of AB_x monomers and seem to be suitable for large scale production. As compared to their linear analogues, hyperbranched polymers possess good solubility in organic solvents, decreased viscosity and interchain entanglement. In addition, various functional groups can be introduced into their structures to create new functional polymeric materials. Hyperbranched polymers have been produced mainly by condensation method, i.e., hyperbranched polyphenylenes,[6] polyesters,[7] polyamides,[8] polyethers,[9] poly(ether−ketone)s,[10] and poly(siloxysilane)s.[11] In the case of hyperbranched polymers with heterocyclic structures, the syntheses of hyperbranched poly(phenylquinoxaline)s,[12] polycarbazoles,[13] poly(ester−imide)s,[14] and poly(ether−imide)s[15] have already been reported to date. These heterocyclic hyperbranched polymers have been prepared only by the one-step method from AB_2 type monomers including heterocyclic structures. The two-step preparation, in which a hyperbranched precursor was prepared from an AB_2 type monomer without a heterocyclic structure and subsequently converted to a heterocyclic hyperbranched polymer, has not been reported yet.

In this paper, we report the first successful synthesis of soluble hyperbranched aromatic polyimide via a polyamic acid methyl ester precursor. The precursor was prepared from self-polycondensation of an AB_2 type monomer, an isomeric mixture of 3,5-bis(4-aminophenoxy)diphenyl ether-3′,4′-dicarboxylic acid monomethyl ester **1**, in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP)[16] as a condensing agent.

Results and Discussion. Scheme 1 (eq 1) shows a synthetic route of AB_2 monomer **1** for hyperbranched polyimide starting from 3,5-dimethoxyphenol.[17] From the ^{1}H NMR analysis, the ratio of two isomers for *p*:*m*-methylester substitution was 1:3.8.

As shown in Scheme 2 (eq 2), the direct self-polycondensation of **1** was carried out in the presence of DBOP as a condensing agent in *N*-methyl-2-pyrrolidinone (NMP) at room temperature for 3 h. The polymerization reaction proceeded in homogeneous solution. After pouring the reaction solution into methanol containing 0.1 wt % lithium chloride (0.1 wt % LiCl/CH_3OH), a white powdery product was obtained in 86% yield (**2** in Table 1).[18] The molecular weight information on the resulting **2** was not obtained because it turned to gel in various polar aprotic solvents and was insoluble in other organic solvents such as tetrahydrofuran and chloroform. In the ^{1}H NMR spectrum of **2** in dimethyl sulfoxide-d_6 (DMSO-d_6) at 100 °C under a partially gel state, a singlet peak assigned to amide proton appeared at 10.10 ppm with a one-third integration value for that of methyl ester one at 3.75 ppm. The absorption of 1660 cm^{-1} attributed to the amide group was observed in the IR spectrum.

Table 1. Preparation and Properties of Hyperbranched Aromatic Polyamic Acid Methyl Ester Precursor and Polyimide

polymer	yield (%)	M_w (M_w/M_n)[a]	η_{inh}[b] (dL/g)	T_{10}[c]/T_g[d] (°C)	solubility[e] NMP	DMSO	THF
2	86				gel	gel	−
3	86	188 000 (3.0)	0.29	470/193	+	+	−

[a] Determined by GPC measurements with a laser light scattering detector in DMF containing LiBr (0.01 mol/L). [b] Measured in NMP at a concentration of 0.5 g/dL at 30 °C. [c] T_{10} was determined by TG at a heating rate of 10 °C/min in nitrogen. [d] Determined by DSC at a heating rate of 10 °C/min in nitrogen on second heating. [e] (+); soluble, (−); insoluble.

Imidization reactions of **2** were carried out by both thermal and chemical methods. After heat treatment of **2** at 300 °C for 1 h under vacuum, a yellow powdery product which was not soluble in organic solvents and concentrated sulfuric acid was obtained. In the IR spectrum of the resulting product, characteristic imide absorption appeared at 1721 and 1779 cm^{-1}, and a shoulder peak around 1650 cm^{-1} was also observed. No weight loss was shown below 350 °C in thermogravimetric analysis. These results indicated that this product had an imide structure including a small amount of amic acid methyl ester unit. On the other hand, the treatment of **2** in nitrobenzene at 180 °C for 5 h afforded a brown product which showed almost the same IR spectrum without the absorption around 1650 cm^{-1}. Unfortunately, this brown product was also insoluble in organic solvents.

The chemical imidization of **2** was carried out in the presence of acetic anhydride and pyridine in DMSO at 100 °C for 24 h, as shown in eq 2. After gelation was observed at the beginning of the treatment, the solution became homogeneous in 1 h. Pouring the resulting solution into 0.1 wt % LiCl/CH_3OH and reprecipitating from *N*,*N*-dimethylformamide (DMF) solution into 0.1 wt % LiCl/CH_3OH, one could obtain the light yellow powdery product **3** in 86% yield.[19] Cross-linking reactions did not seem to have occurred because **3** exhibited good solubility in NMP and DMSO. The polymer **3** had a weight-average molecular weight (M_w) of 188 000 and polydispersity index (M_w/M_n) of 3.0 determined by GPC measurement with a laser light scattering detector[20] and an inherent viscosity (η_{inh}) of 0.29 dL/g (Table 1). In the ^{1}H NMR spectrum of **3**, as compared with that of **2**, the amide (10.10 ppm) and methyl ester peaks (3.75 ppm) disappeared, and two peaks appeared at 9.60 and 2.00 ppm attributed to new amide and acetyl protons, respectively. In addition, the integration ratio of peaks for the amide proton, acetyl and all aromatic protons (6.40−7.88 ppm) was observed to be 1, 3, and 14, which was consistent with the calculated ratio. In the IR

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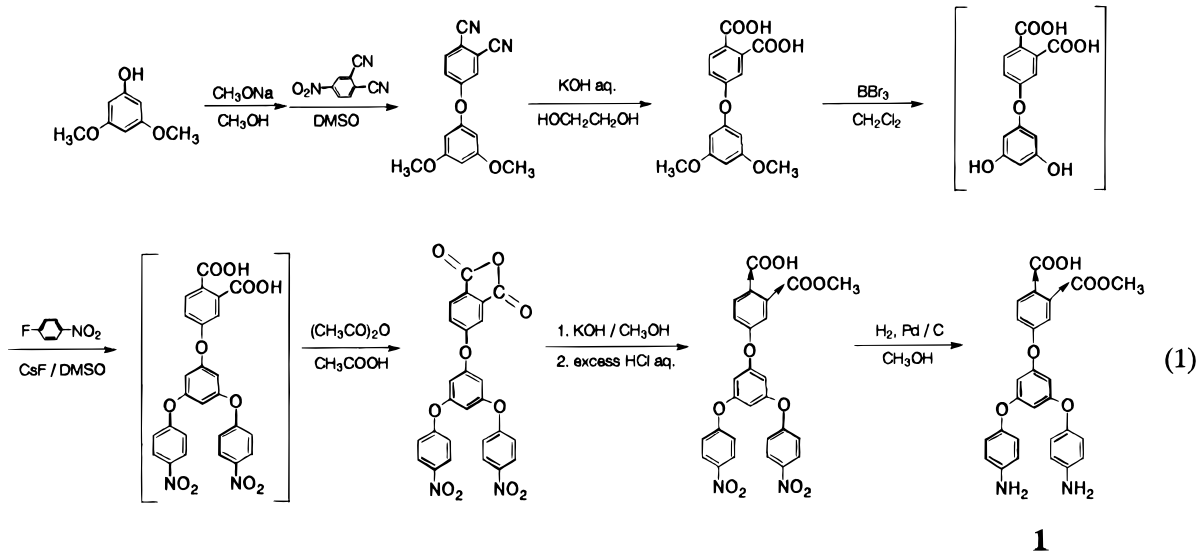
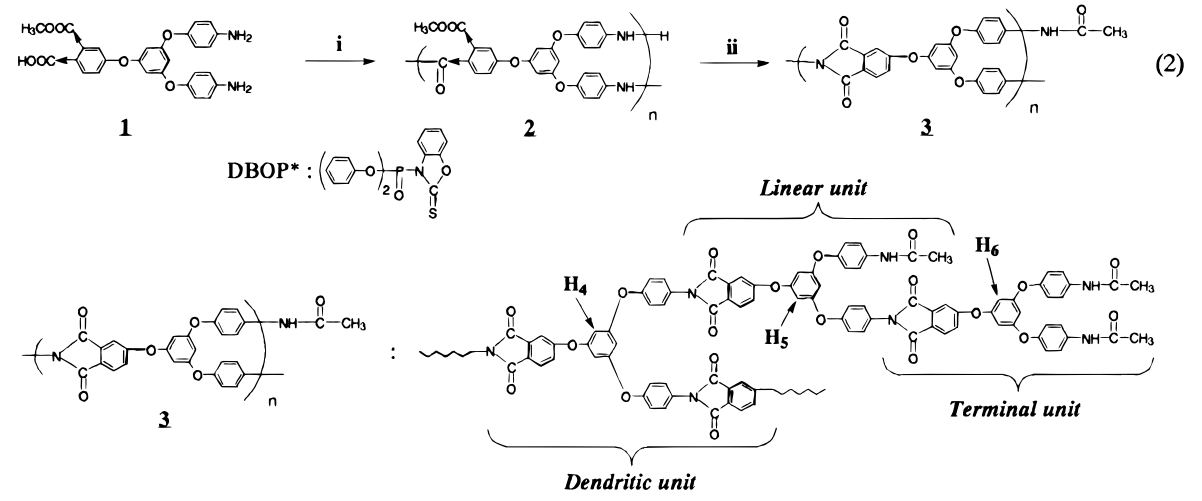
Scheme 1

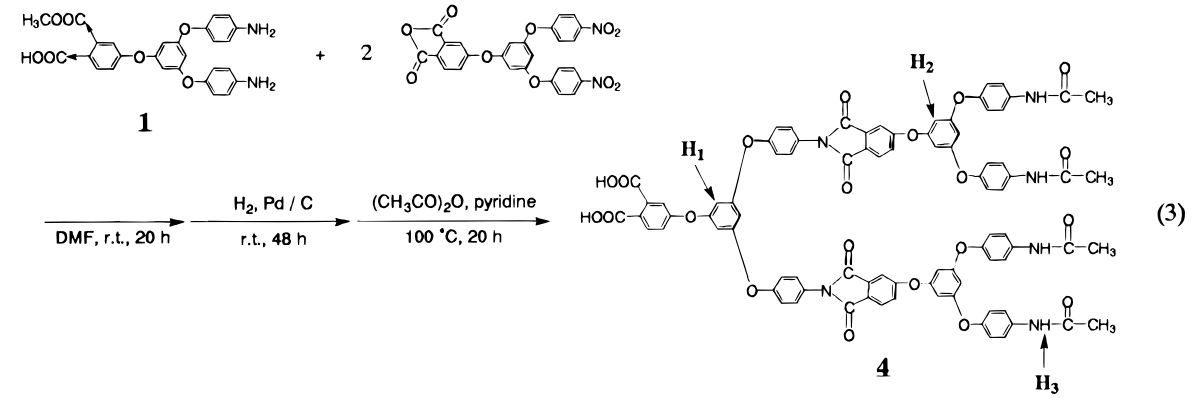


Scheme 2



i: DBOP*, $(CH_3CH_2)_3N$, NMP, r.t., 3 h; **ii**: $(CH_3CO)_2O$, pyridine, DMSO, 100 °C, 24 h

Scheme 3



spectrum, two peaks characteristic of imide groups were clearly detected at 1720 and 1780 cm^{-1}, and the absorption assigned to the amide group remained at 1669 cm^{-1}. From these results, it was concluded that treatment with acetic anhydride and pyridine could quantitatively convert the polyamic acid ester precursor **2** to the soluble hyperbranched aromatic polyimide **3** possessing acetamide end groups.

The degree of branching (DB) of hyperbranched polymers was defined as the ratio of the sum of dendritic and terminal units versus total units (linear, dendritic, and terminal units).[21] DB of the resulting hyperbranched aromatic polyimide **3** could be determined by ^1H NMR analysis as shown in Figure 1. A model compound **4**[22] was prepared as shown in Scheme 3 (eq 3). A characteristic amide peak (H_3) and two peaks

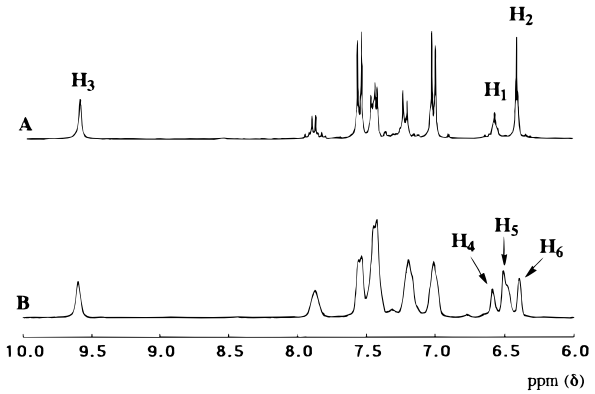


Figure 1. ^{1}H NMR spectra of (A) the model compound **4** and (B) polymer **3** in DMSO-d_6 at 100 °C.

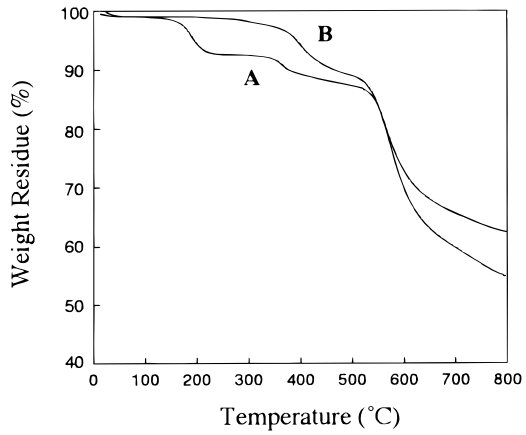


Figure 2. TG curves of (A) polymer **2** and (B) **3** at a heating rate of 10 °C/min in nitrogen.

attributed to triphenoxy-substituted aromatic group (H_1 and H_2) were detected at 9.60, 6.58, and 6.41 ppm with an integration ratio of 4, 3, and 6 (spectrum A in Figure 1). In spectrum B, three kinds of peaks, H_4, H_5, and H_6, were observed at 6.59, 6.51, and 6.40 ppm, respectively. As compared with the spectrum of the model compound, H_6 can be assigned to the terminal unit of **3**. Also it was confirmed that the integration of H_4 and H_6 was almost equal. Statistically, the number of dendritic units becomes the same as that of terminal units when the degree of polymerization is large enough. Therefore, peak H_4 was assigned to the dendritic unit, and H_5 was attributed to the linear unit. DB of **3** was determined to be 0.48 by calculating the integration ratio of these three peaks

Thermal properties of the resulting polymers were investigated by thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements. TG behavior of **2** and **3** was shown as curves A and B in Figure 2, respectively. In curve A, weight loss (6.7 wt %) caused by elimination of methanol was observed in the range of 180−230 °C, which was close to the calculated weight loss of 6.8 wt %. In curve B, no weight loss was observed below 250 °C, and 10 wt % loss temperature (T_{10}) was measured to be 470 °C in nitrogen (Table 1). From DSC analysis, the glass transition temperature (T_g) of **3** was detected at 193 °C in nitrogen.

In summary, we have successfully prepared hyperbranched aromatic polyimide via a polyamic acid methyl ester precursor, which was prepared by self-polycondensation of an AB_2 monomer **1**. The resulting hyperbranched aromatic polyimide had no cross-linked structure and exhibited good solubility in NMP, DMF, and DMSO, while retaining good thermal stability.

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(17) An isomeric mixture of 3,5-bis(4-aminophenoxy)diphenyl ether-3′,4′-dicarboxylic acid monomethyl ester (**1**) (AB_2 monomer) was obtained as a brown powdery product: 39% total yield starting from 3,5-dimethoxyphenol; IR (KBr) 1721 cm^{-1} (carboxyl, ester group); ^{1}H NMR (DMSO-d_6) δ 7.79−7.82 (d, 0.79H, Ar−H), 7.67−7.69 (d, 0.21H, Ar−H), 7.26−7.37 (m, 6H, Ar−H), 7.11−7.20 (m, 2H, Ar−H), 6.75−6.80 (m, 4H, Ar−H), 6.54−6.58 (m, 4H, Ar−H), 6.13−6.19 (m, 3H, Ar−H), 3.77 (br, 3H, methyl ester) ppm. Anal. Calcd for $C_{27}H_{22}N_2O_7$: C, 66.66; H, 4.56; N, 5.76. Found: C, 66.12; H, 4.56; N, 5.61.
(18) Polymer **2** was prepared as mentioned below. To a 50-mL three-necked flask fitted with nitrogen inlet and outlet tube were added through nitrogen 0.603 g (1.24 mmol) of **1**, 0.568 g (1.48 mmol) of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP), 0.17 mL (1.24 mmol) of triethylamine, and 3 mL of NMP. The reaction mixture was stirred for 3 h at room temperature. After addition of 6 mL of NMP, the mixture was poured into 350 mL of methanol containing 0.1 wt % lithium chloride (0.1 wt % LiCl/CH_3-OH), and the precipitated polymer was collected by filtration. The product was dried overnight at room temperature under vacuum: yield 0.504 g (86%); IR (KBr) 1663 (amide), 1725 cm^{-1} (ester group); ^{1}H NMR (DMSO-d_6, 100 °C) δ 10.10

(s, 1H, amide-H), 6.65−7.86 (m, 11H, Ar−H), 6.23−6.41 (m, 3H, Ar−H), 3.75 (br, 3H, methyl ester) ppm.

(19) Polymer **3** was prepared as mentioned below. To a 50-mL three-necked flask through nitrogen were added 0.453 g of **2**, 1.10 mL (11.7 mmol) of acetic anhydride, 0.70 mL (8.7 mmol) of pyridine, and 7 mL of DMSO. The reaction mixture was stirred for 24 h at 100 °C, and diluted with 20 mL of DMSO. The solution was poured into 1800 mL of 0.1 wt % $LiCl/CH_3OH$ to precipitate the polymer. The precipitated polymer was collected by filtration, and dissolved in DMF. After reprecipitation, the product was filtered, washed with hot 0.1 wt % $LiCl/CH_3OH$, and dried overnight at 120 °C under vacuum: yield 0.398 g (86%); IR (KBr) 1670 (amide), 1720, 1780 cm^{-1}(imide group); ^1H NMR (DMSO-d_6, 100 °C) δ 9.60 (s, 1H, amide-H), 7.00−7.88 (m, 11H, Ar−H), 6.40−6.60 (m, 3H, Ar−H), 2.00 (s, 3H, acetyl) ppm. Anal. Calcd for $C_{28}H_{18}N_2O_6$: C, 70.28; H, 3.79; N, 5.85) Found: C, 67.74; H, 3.53; N, 5.55.

(20) Gel permeation chromatography (GPC) was performed in DMF containing 0.01 mol/L of lithium bromide as an eluent. The absolute molecular weight was calculated by GPC with a laser light scattering detector. The specific refractive increment (d*n*/d*c*) at 690 nm was determined to be 0.168 mL/g.

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(22) Model compound **4** was obtained as a white powdery product: 70% total yield starting from **1**; IR (KBr) 1673 (amide), 1721, 1779 cm^{-1} (imide group); ^1H NMR (DMSO-d_6, 100 °C) δ 9.60 (s, 4H, amide-H), 7.81−7.96 (m, 3H, Ar−H), 7.55−7.62 (d, 9H, Ar−H), 7.43−7.48 (m, 9H, Ar−H), 7.21−7.24 (m, 5H, Ar−H), 7.01−7.04 (m, 9H, Ar−H), 6.57−6.58 (m, 3H, Ar−H), 6.41−6.42 (m, 6H, Ar−H), 2.00 (s, 12H, acetyl) ppm.

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