Preparation of Hyperbranched Aromatic Polyimide without Linear Units by End-Capping Reaction

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Received November 13, 2000; Revised Manuscript Received March 13, 2001

ABSTRACT: Direct self-polycondensation of an AB_2 type monomer (**1**) followed by chemical modification with a branched reagent (**2**) afforded a precursor. Chemical imidization of the precursor gave a hyperbranched aromatic polyimide (**12**) with a weight-average molecular weight of 98 000 and an inherent viscosity of 0.13 dL/g. The structures of polymers were successfully characterized by ^{1}H NMR and IR spectroscopy. Using a model compound, the degree of branching (DB) of the hyperbranched polyimide was determined to be 1.0 by ^{1}H NMR analysis. A significant difference in T_1 (^{1}H NMR pulse spin−lattice relaxation time) values between dendritic, linear, and terminal units was not observed. T_1 values were found to decrease with increasing the size of end groups. By thermal analyses, 5 wt % thermal loss and glass transition temperatures of polyimides were observed at above 365 °C and at around 170 °C, respectively. The precursor and polyimides exhibited good solubility in NMP, DMF, and THF.

Introduction

Recently, dendritic macromolecules have attracted considerable attention due to the new physical and chemical properties caused by their unique structures.[1] 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 can be 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 considerably better solubility in organic solvents, lower viscosity, and decreased interchain entanglement. In addition, various functional groups can be introduced into their structures to create new functional polymeric materials.

Hyperbranched polymers prepared from AB_x monomers are generally composed of dendritic, linear, and terminal units. These units are distinguished by the number of the reacted B group. The degree of branching (DB), which was defined as the ratio of the sum of dendritic and terminal units over the sum of units, has been widely used to assess hyperbranched polymer structure.[2] In the case of one-pot polymerization of AB_2 monomers, DB of resulting hyperbranched polymers was statistically close to 0.5 when the conversion of the A group was 100%. Control of DB might be important in affecting the properties of hyperbranched polymers. Recently, Moore reported an effect of DB for hyperbranched aromatic poly(ether imide)s on rheological properties.[3] In that report, onset of shear thinning appeared at lower shear rates as DB decreases in the range of 0.42−0.66. However, the hyperbranched aromatic poly(ether imide)s with varying DB had much differences in weight-average molecular weight (from 82.2 to 295.4 kDa). Therefore, observed rheological properties may not be caused by only the change in DB. Furthermore, the range of DB was relatively narrow to clarify the effect of DB. Up to now, it is still not clear whether tailored properties of hyperbranched polymers can be obtained by manipulating DB.

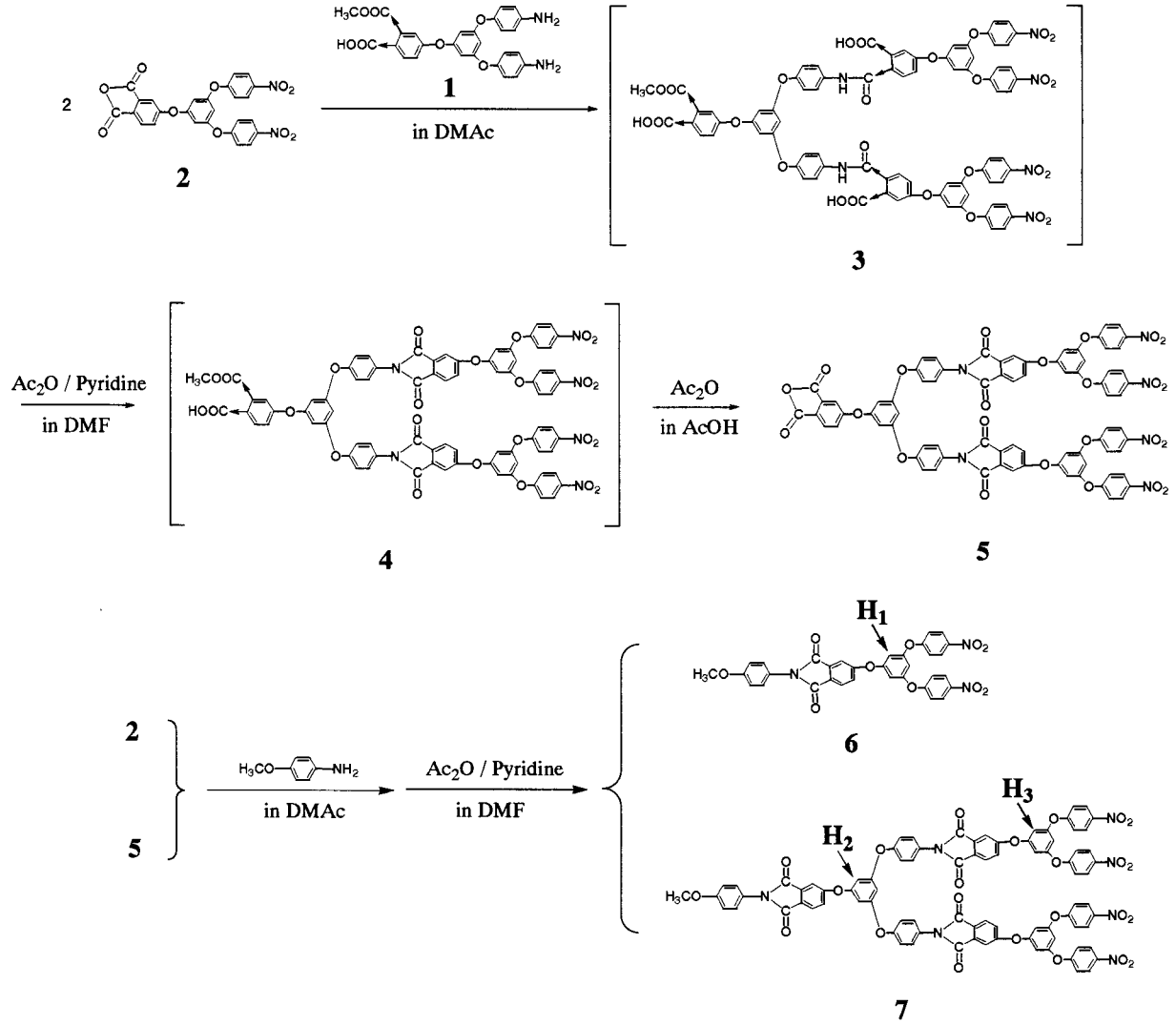
Frey suggested various possibilities for the control and enhancement of DB, i.e., enhanced reactivity of linear vs terminal units, polymerization of macromonomers including prefabricated dendritic units, and slow addition of AB_x monomers in the presence of core molecules.[4] Hyperbranched poly(amidoamine),[5] poly(ether ketone),[6] polyamide,[7] and poly(phenylacetylene)[8] with controlled and enhanced DB were already prepared to date. Frey also reported the synthesis of hyperbranched polycarbosilane with DB of 0.92 by the end-capping approach.[9] This DB-enhanced hyperbranched polycarbosilane was prepared from self-hydrosilylation of triallylsilane as an AB_3 monomer and subsequent end-capping reactions to convert linear and semidendritic units to dendritic and terminal units. The end-capping reactions were composed of two steps which included hydrosilylation with trichlorosilane and Grignard reaction with allylmagnesium bromide. However, this approach could not achieve DB of 1.0. Moreover, the core molecule, 2-(10-decen-1-yl)-1,3-oxazoline, was required in the polymerization mixture to control molecular weight, and the molecular weight of the resulting polymer was relatively low.

Recently, we reported details on the preparation and properties of hyperbranched aromatic polyimides with various end groups via polyamic acid methyl ester precursors.[10,11] The precursors were prepared from the self-polycondensation of an AB_2 type monomer, 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)[12] as a condensing agent and subsequent chemical modification of the free amine end groups. We also found that the resulting hyperbranched polyimides had unique dielectric and optical properties.

In this study, we have successfully prepared a hyperbranched aromatic polyimide without linear units by end-capping reactions. The precursor was produced by self-polycondensation of **1** in the presence of DBOP and continuous end-capping with 3,5-bis(4-nitrophenoxy)-diphenyl ether-3′,4′-dicarboxylic anhydride (**2**) possessing the branched structure. In addition, various func-

10.1021/ma001936v CCC: $20.00
Published on Web 05/11/2001

Scheme 1



tional end groups were successfully introduced into hyperbranched polyimides. T_1 (^{1}H NMR pulse spin−lattice relaxation time) values, which could determine the mobility of protons, were applied to estimate the steric environments of hyperbranched polyimides with various end groups.

Results and Discussion

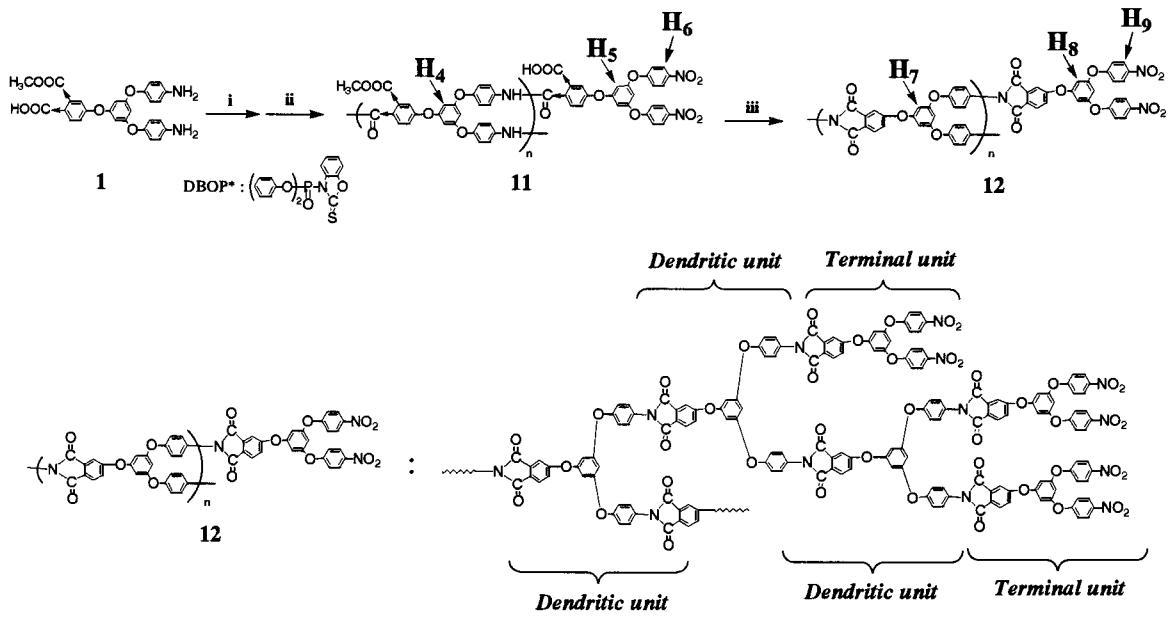
Preparation of Model Compounds 6 and 7. To assign the structure of resulting hyperbranched polymers and investigate the mobility of protons in polymers, model compounds **6** and **7** were prepared as described below.

As reported previously, the AB_2 type monomer **1** was prepared in a total of eight steps from 3,5-dimethoxyphenol as a starting material.[11] In the preparation process, an intermediate compound **2** could be obtained. The structures of **1** and **2** were confirmed by ^{1}H NMR, IR, and elemental analyses. From the ^{1}H NMR analysis of **1**, the ratio of two isomers for *p*:*m*-methyl ester substitution was found to be 1.0:3.8.

As shown in Scheme 1, the coupling reaction of **1** with 2 equiv of **2** afforded a compound **3**. By treatment of **3** with acetic anhydride and pyridine, an imidized compound **4** was obtained. Dehydration at the focal point of **4** in a mixture of acetic anhydride and acetic acid gave a pure compound **5**, which included one phthalic anhydride and two imide groups. In the ^{1}H NMR spectrum of **5**, the peak for methyl ester protons (3.75 ppm) had disappeared. Two peaks assigned to the anhydride group were clearly detected at 1780 and 1850 cm^{-1} in the IR spectrum. Also from 2D-NMR (^{1}H−^{13}C COSY) and MALDI-TOF mass spectroscopic methods, the structure of **5** was fully characterized. Treatment of **5** with *p*-anisidine and subsequent chemical imidization produced model compound **7**. The ^{1}H NMR spectrum of **7** showed methoxy protons at 3.81 ppm. IR and elemental analyses also confirmed the formation of **7**. With the same method, another model compound **6** was successfully prepared from **2**.

Polymer Syntheses. As reported previously,[11] direct self-polycondensation of **1** was carried out in the presence of DBOP[12] as a condensing agent (step i in Scheme 2). By subsequent chemical modification of free amine end groups with **2** (1.25 equiv, step ii), an end-capped precursor **11** was recovered as a white powdery product with 98% yield. Inherent viscosity (η_{inh}) of **11** was 0.13 dL/g (Table 1). The structure of **11** was characterized by ^{1}H NMR and IR analyses. In the ^{1}H NMR spectrum (spectrum B in Figure 1), two peaks for amide protons were clearly detected at 10.08 and 10.04 ppm, which were assigned to an amide proton arisen from self-

Scheme 2



Key; i: DBOP*, $(CH_3CH_2)_3N$, NMP, r.t., 3 h; ii: **2**, r.t., 3 h; iii: $(CH_3CO)_2O$, pyridine, DMF, 100 °C, 24 h.

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

polymer	yield (%)	M_w (M_w/M_n)[a]	η_{inh} (dL/g)[b]
11	98		0.13
12	93	98000 (2.6)	0.13

[a] Determined by GPC measurements in DMF containing lithium bromide (0.01 mol/L) based on polystyrene standards. [b] Measured in NMP at a concentration of 0.5 g/dL at 30 °C.

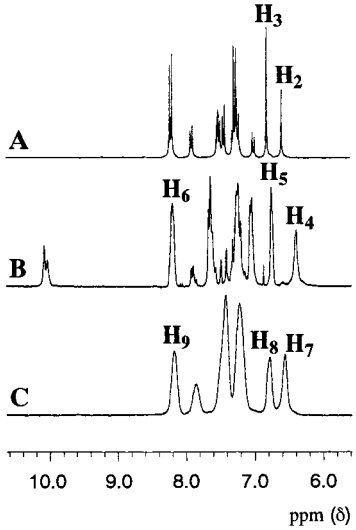


Figure 1. ^{1}H NMR spectra of (A) model compound **7**, (B) polymers **11**, and (C) **12** in DMSO-d_6 at 100 °C.

polycondensation and that from end-capping reaction, respectively. The integration ratio of peaks H_4 (triphenoxy-substituted aromatic protons in main chain) to H_5 (those in end groups) to H_6 (aromatic protons located in both ortho positions to the nitro groups) was calculated to be 3:3:4. This ratio was in good agreement with the ratio estimated from the quantitative end-capped product. From IR analyses, both the formation of amide linkages (1665 cm^{-1}) and the presence of nitro groups (1345 cm^{-1}) were confirmed.

Chemical imidization of **11** was carried out with acetic anhydride and pyridine. A light yellow powdery product **12** was obtained in 93% yield. From GPC measurement using polystyrene standards, a weight-average molecular weight (M_w) of **12** was 98 000 with a polydispersity index (M_w/M_n) of 2.6. The inherent viscosity value was 0.13 dL/g (Table 1). As compared with ^{1}H NMR spectrum of **11**, the disappearance of amide and methyl ester protons was observed in the spectrum of **12** (spectrum C in Figure 1). In the IR spectrum of **12**, two characteristic imide peaks appeared at 1723 and 1781 cm^{-1}, while the characteristic amide peak at 1665 cm^{-1} had disappeared. The spectroscopic data indicated that polymer **12** had been fully imidized.

The degree of branching (DB) of the resulting hyperbranched polyimide **12** could be determined by ^{1}H NMR analysis. The ^{1}H NMR spectrum of **12** (spectrum C in Figure 1) showed two kinds of peaks for triphenoxy-substituted aromatic protons, H_7 (6.56 ppm) and H_8 (6.78 ppm), with the integration ratio of 1:1. In spectrum A of **7**, peaks H_2 at 6.62 ppm and H_3 at 6.83 ppm can be models for dendritic and terminal units. By comparison between spectra A and C, peaks H_7 and H_8 can be assigned to the dendritic and terminal units in **12**, respectively. In addition, any peaks assigned to the linear unit were not observed in the spectrum of **12**. Therefore, the DB value of **12**, which was defined as the ratio of the sum of dendritic and terminal units vs total units, was determined to be 1.0. During the end-capping reaction, one linear unit should be converted to one dendritic plus one terminal unit and one terminal unit to one dendritic plus two terminal units. Since quantitative conversions of both end-capping and imidization reactions had been achieved, polyimide **12** must be comprised of only dendritic and terminal units with the ratio of 1:1, theoretically. This consideration also supported the formation of the hyperbranched aromatic polyimide with DB of 1.0. However, it must be noted that polyimide **12**, prepared from self-polycondensation

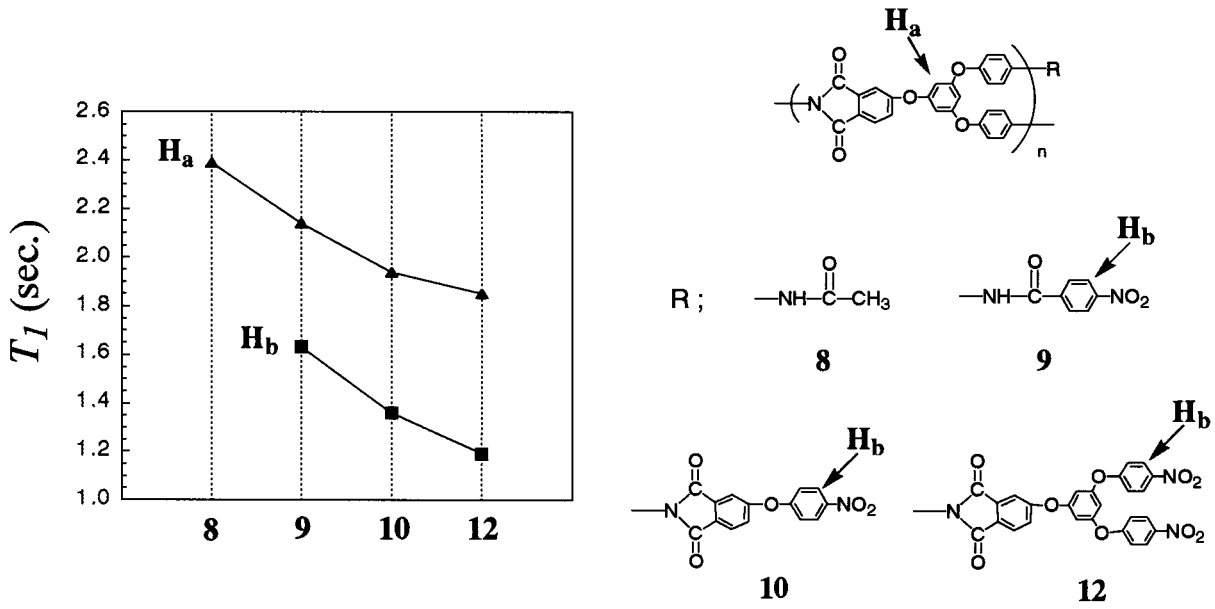


Figure 2. Dependence of end groups in hyperbranched polyimides on T_1 values.

Table 2. Results of T_1 Measurements[a]

	T_1 (s)			
	model compound		polymer	
H_a[b]	**6**	**7**	**8**	**12**
dendritic		2.39 (H_2)	2.46	1.85 (H_7)
linear			2.39	
terminal	2.43 (H_1)	2.51 (H_3)	2.34	1.61 (H_8)

[a] T_1 (300 MHz ^{1}H NMR pulse spin−lattice relaxation time) was measured by inversion recovery method in DMSO-d_6 at a concentration of 25 mg/mL at 30 °C with a pulse delay of 15 s. [b] H_a represents triphenoxy-substituted aromatic protons.

Table 3. Thermal Properties and Solubility of Resulting Polymers

		solubility[c]			
polymer	T_5[a]/T_g[b] (°C)	NMP	DMF	DMSO	THF
10	370/174	++	++	++	++
11		++	++	++	++
12	365/168	++	++	++	++

[a] T_5 (5 wt % loss temperature) was determined by TG at a heating rate of 10 °C/min in nitrogen. [b] Determined by DSC at a heating rate of 10 °C/min in nitrogen on second heating. [c] Key: (++) soluble at room temperature.

of **1**, did not have a regular architecture similar to that of dendrimers.

To evaluate the structure of hyperbranched polyimides, T_1 (^{1}H NMR pulse spin−lattice relaxation time) values, which allow to estimate the mobility of protons in polymers, were measured (Table 2). In Table 2, H_a represents triphenoxy-substituted aromatic protons. For **12**, the T_1 value of H_a attributed to dendritic units (H_7, 1.85 s) was found to be similar to that attributed to terminal units (H_8, 1.61 s). In the previous report, the ^{1}H NMR spectrum of a polyimide **8**[13] with acetoamide end groups (DB was 0.48, in Figure 2) showed distinguished H_a protons assigned to dendritic, linear, and terminal units.[10,11] For polyimide **8**, T_1 values of H_a protons for dendritic, linear, and terminal units were measured to be 2.46, 2.39, and 2.34 s, respectively. In both polyimides, a significant difference in T_1 values between each unit was not observed. This indicated that steric environments of these units were almost the same and was found to agree well with the distribution of each unit resulting from off-lattice Monte Carlo simulation.[14] From these results, we suggest that each unit in hyperbranched polymers has random location over the polymer structure, which is quite different from distinct location observed in azobenzene containing poly(benzyl ether) dendrimers.[15]

Furthermore, in comparison between **8** and **12**, polyimide **12** had much lower T_1 values than **8**. This result was caused by more restricted mobility of protons in **12**, which was arisen from introduction of larger end groups. From comparison with monomeric unit **6** or trimeric one **7**, it was also found that H_a protons in polyimide **8** had almost the same mobility as those in **6** or **7**. This suggests that H_a protons in **8** possess relatively free mobility even in the polymeric structures.

As shown in Figure 2, the dependence of size of end groups in hyperbranched polyimides on T_1 values was investigated in detail. In the similar fashion as that for polyimides **8** and **12**, polyimides **9** and **10** were successfully prepared by using 4-nitrobenzoyl chloride and 4-(4′-nitrophenoxy)phthalic anhydride[16] as end-capping agents, respectively (see Experimental Section). The T_1 value of H_a in the main chain decreased from 2.40 to 1.85 s on going from **8** to **12**. Also for that of H_b (peaks for aromatic protons located in both ortho positions to the nitro groups), a noticeable decrease from 1.63 to 1.19 s was observed on going from **9** to **12**. It was clear that both decrements were corresponding to growing restricted mobility of aromatic protons, which was caused by the introduction of larger end groups into the polymer structures.

Polymer Properties. Thermal properties and solubility of resulting polymers are summarized in Table 3. From thermogravimetric (TG) analyses, T_5 (5 wt % loss temperature) of polyimides **10** and **12** were observed at 370 and 365 °C, respectively. In both TG curves, the weight loss attributed to the removal of nitro groups was detected at above 250 °C. DSC thermograms on second heating showed glass transition temperature (T_g) for **10** at 174 °C and that for **12** at 165 °C. It was assumed that introduction of more ether linkages into end groups afforded the lower T_g value for **12**. The precursor **11** and polyimides **10** and **12** were soluble in

NMP, DMF, DMSO, and THF. Good solubility of polymers could be achieved by incorporating further ether bonds and/or branched units in the structures.

Conclusion

We successfully prepared a hyperbranched aromatic polyimide without linear units via an end-capped precursor. From the ^{1}H NMR analysis, DB of the resulting hyperbranched aromatic polyimide was estimated to be 1.0. Analyses of T_1 values of aromatic protons in hyperbranched polyimides suggested that all units (dendritic, linear, and terminal units) located randomly in the polymer structures. In addition, the values decreased with increasing the size of end groups. Resulting precursor and polyimides had excellent solubility in common organic solvents while retaining good thermal stability.

Experimental Section

Chemicals. *N*-Methyl-2-pyrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetoamide (DMAc), pyridine, and triethylamine were distilled from calcium hydride. Acetic anhydride was used after distillation in the presence of magnesium. Other solvents and reagents were used as received.

Measurements. ^{1}H, ^{13}C, and ^{1}H−^{13}C COSY NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer. IR spectra were recorded on a Shimadzu FT/IR-8100 spectrophotometer. T_1 (300 MHz ^{1}H NMR pulse spin−lattice relaxation time) was measured by inversion recovery method in DMSO-d_6 at a concentration of 25 mg/mL at 30 °C with a pulse delay of 15 s. Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements were performed with a Seiko DSC 6200 and TG/DTA 6200, respectively. Gel permeation chromatography (GPC) was performed with a JASCO HPLC 880 PU fitted with polystyrene−divinylbenzene columns (two Shodex KD 806 M and 802) and a Shodex RI-71 refractive index detector in DMF containing 0.01 mol/L of lithium bromide as an eluent. The MALDI-TOF mass spectrum was recorded on a Shimadzu Kratos Kompact MALDI IV tDE instrument operated in reflectron mode using 1,8-dihydroxy-9[10*H*]-anthracene (dithranol) as a matrix, THF as a solvent, and silver trifluoromethanesulfonate as an additive agent.

Model Compound Preparation. a. Synthesis of 5 Starting from a Coupling Reaction of 1 with 2. To a 50 mL round-bottomed flask fitted with gas inlet and outlet tubes in an ice−water bath (0−3 °C), 0.472 g (0.97 mmol) of **1** and 6 mL of DMAc were added through nitrogen. After dissolving completely, 1.047 g (2.03 mmol) of **2** and 2 mL of DMAc were added to the flask. The reaction mixture was stirred for 15 min at 0−3 °C and for 18 h at room temperature and then diluted with 6 mL of DMAc. The resulting solution was poured into 0.6 N hydrochloric acid aqueous (HCl(aq)) solution to precipitate. A 1.524 g sample of the white powdery product (**3**) was obtained after drying overnight at room temperature under vacuum (IR (KBr) 1650−1750 (amic acid + phthalic acid monoester), 1345 cm^{-1} (nitro group)). This product **3** was used in the next step without further purification.

To a 50 mL round-bottomed flask, 1.401 g of **3** and 20 mL of DMF were added at room temperature through nitrogen. After dissolving completely, 3.5 mL of acetic anhydride and 2.1 mL of pyridine were added to the flask. The reaction mixture was stirred for 26 h at room temperature. The resulting solution was poured into a mixture of methanol and water (1/1) containing 10 vol % of 12 N HCl(aq) solution to precipitate. A 1.524 g sample of the white powdery product (**4**) was obtained after drying overnight at room temperature under vacuum (IR (KBr) 1723, 1780 (imide), 1650−1723 (phthalic acid monoester), 1345 cm^{-1} (nitro group)). Also, product **4** was used in the next step without further purification.

To the 100 mL of round-bottomed flask fitted with a condenser and a gas inlet tube, 1.120 g of **4**, 3 mL of acetic anhydride, and 30 mL of glacial acetic acid were added under nitrogen. The reaction mixture was stirred for 10 h under reflux. During the reaction, a brown oil was observed in the reaction mixture. After cooling the mixture, the oil converted to a brown solid. After collection by filtration, the solid was retreated with acetic anhydride and glacial acetic acid. The brown powdery product (**5**) was obtained after drying overnight at 130 °C under vacuum, giving 0.543 g; 80% yield starting from **1**. ^{1}H NMR (DMF-d_7, at 100 °C): δ 8.24−8.27 (d, 8H, Ar−H), 8.06−8.09 (d, 1H, Ar−H), 7.92−7.95 (d, 2H, Ar−H), 7.52−7.70 (m, 10H, Ar−H), 7.28−7.36 (d+d, 13H, Ar−H), 6.92 (s, 6H, Ar−H), 6.72 (s, 3H, Ar−H) ppm. ^{13}C NMR (DMF-d_7, at 30 °C): δ 167.09, 166.96, 164.28, 163.37, 163.25, 162.92, 162.73, 162.29, 160.23, 158.85, 158.40, 157.76, 156.45, 143.98, 135.21, 134.93, 129.66, 128.83, 128.42, 127.26, 126.77, 126.39, 126.29, 126.07, 124.56, 119.95, 119.03, 114.34, 113.50, 109.61, 109.45, 107.34, 106.88 ppm. IR (KBr): 1780, 1851 (anhydride), 1722, 1780 (imide), 1345 cm^{-1} (nitro group). MALDI-TOF MS *m*/*z* calcd for 1555.08 (M + Ag$^+$), found 1556.11. Elemental analysis: Calcd for $C_{78}H_{42}N_6O_{24}$: C, 64.74; H, 2.93; N, 5.81). Found: C, 64.49; H, 3.05; N, 5.73.

b. Synthesis of 6. 6 was prepared from **2** and *p*-anisidine by the similar procedure used in the preparation of **7**. Yield 71%. ^{1}H NMR (DMSO-d_6, at 100 °C): δ 8.22−8.25 (d, 4H, Ar−H), 7.93−7.95 (d, 1H, Ar−H), 7.53−7.56 (m, 2H, Ar−H), 7.28−7.33 (d+d, 6H, Ar−H), 7.03−7.06 (d, 2H, Ar−H), 6.84 (br, 3H, Ar−H), 3.82 (s, 3H, methoxy) ppm. IR (KBr): 1717, 1777 (imide), 1345 cm^{-1} (nitro group). Elemental analysis: Calcd for $C_{33}H_{21}N_3O_{10}$: C, 63.98; H, 3.42; N, 6.78. Found: C, 64.04; H, 3.72; N, 6.74.

c. Synthesis of 7. To a 50 mL round-bottomed flask through nitrogen, 0.402 g of **5**, 0.175 g (1.42 mmol, 5 equiv) of sublimated *p*-anisidine, and 2.6 mL of DMAc were added at room temperature. The reaction mixture was maintained for 18 h at that temperature. The resulting solution was poured into a mixture of methanol and water (1/1) containing 3 vol % of 12 N HCl(aq) solution to precipitate. The white powder (0.443 g) was obtained after drying overnight at room temperature under vacuum.

To a 50 mL round-bottomed flask under nitrogen, the resulting powder, 1.0 mL of acetic anhydride, 0.6 mL of pyridine, and 6 mL of DMF were added. The reaction mixture was stirred for 24 h at 120 °C. The resulting solution was poured into methanol containing 4 vol % of 12 N HCl(aq) solution to precipitate. After collection by filtration and following washing with hot methanol, the brown powdery product was obtained after drying overnight at 100 °C under vacuum, giving 0.378 g. Yield 90%. ^{1}H NMR (DMSO-d_6, at 100 °C): δ 8.20−8.26 (d, 8H, Ar−H), 7.91−7.94 (d+d, 3H, Ar−H), 7.51−7.56 (m, 6H, Ar−H), 7.44−7.47 (d, 4H, Ar−H), 7.24−7.33 (m, 14H, Ar−H), 7.01−7.04 (d, 2H, Ar−H), 6.83 (s, 6H, Ar−H), 6.62 (s, 3H, Ar−H), 3.81 (s, 3H, methoxy) ppm. IR (KBr): 1721, 1779 (imide), 1345 cm^{-1} (nitro group). Elemental analysis. Calcd for $C_{85}H_{49}N_7O_{24}$: C, 65.77; H, 3.18; N, 6.32. Found: C, 65.77; H, 3.43; N, 6.35.

Polymer Preparation. a. Direct Self-Polycondensation of 1 and End-Capping Reaction with 2 (Preparation of Polymer 11). According to experimental details reported previously[10,11] (0.202 g (0.42 mmol) of **1**, 0.192 g (0.50 mmol) of DBOP, and 0.260 g (0.51 mmol) of **2**), the white powdery product **11** (0.401 g) was obtained with 98% yield; inherent viscosity η_{inh} = 0.13 dL/g. ^{1}H NMR (DMSO-d_6, 100 °C): δ 10.04−10.08 (s+s, 2H, amide-H), 8.21−8.25 (br, 4H, Ar−H), 7.04−7.65 (m, 14H, Ar−H), 6.76−6.87 (br, 3H, Ar−H), 6.39 (br, 3H, Ar−H), 3.74 (br, 3H, methyl ester) ppm. IR (KBr): 1725 (ester), 1665 (amide), 1345 cm^{-1} (nitro group).

b. Chemical Imidization (Preparation of Polymer 12). According to experimental details reported previously[10,11] (0.343 g of **11**, 0.80 mL of acetic anhydride, and 0.50 mL of pyridine), the light yellow powdery product **12** (0.304 g) was obtained with 93% yield; weight-average molecular weight: M_w = 98 000, polydispersity index: M_w/M_n = 2.6 (using polystyrene standards); η_{inh} = 0.13 dL/g; 5 wt % loss temperature: T_5 =

365 °C, glass transition temperature: T_g = 168 °C. ^{1}H NMR (DMSO-d_6, 100 °C): δ 8.18 (br, 4H, Ar−H), 7.86 (br, 2H, Ar−H), 7.22−7.43 (br+br, 16H, Ar−H), 6.78 (br, 3H, Ar−H), 6.58 (br, 3H, Ar−H) ppm. IR (KBr): 1723, 1781 (imide), 1346 cm^{-1} (nitro group). Elemental analysis. Calcd for $C_{52}H_{28}N_4O_{14}$: C, 66.96; H, 3.03; N, 6.01. Found: C, 65.54; H, 3.52; N, 6.09.

c. Preparation of Polymer 9. Polymer **9** was prepared from self-polycondensation of **1**, end-capping with 4-nitrobenzoyl chloride (3 equiv), and chemical imidization by the similar procedure used for the preparation of **11** and **12**; 88% yield; M_w = 94 000, M_w/M_n = 2.0 (using polystyrene standards). ^{1}H NMR (DMSO-d_6, 100 °C): δ 10.30 (s, 1H, amide-H), 8.27 (br, 2H, Ar−H), 8.15 (br, 2H, Ar−H), 7.12−7.87 (m, 11H, Ar−H), 6.48−6.57 (m, 3H, Ar−H) ppm. IR (KBr): 1721, 1777 (imide), 1680 (amide), 1348 cm^{-1}(nitro group).

d. Preparation of Polymer 10. Polymer **10** was prepared from self-polycondensation of **1**, end-capping with 4-(4′-nitrophenoxy)phthalic anhydride (3 equiv), and chemical imidization by the similar procedure used for the preparation of **11** and **12**; 83% yield; M_w = 49 000, M_w/M_n = 2.1 (using polystyrene standards); T_5 = 370 °C, T_g = 174 °C. ^{1}H NMR (DMSO-d_6, 100 °C): δ 8.27−8.30 (s+s, 2H, Ar−H), 7.24−7.97 (m, 20H, Ar−H), 6.61 (m, 3H, Ar−H) ppm. IR (KBr): 1721, 1779 (imide), 1345 cm^{-1} (nitro group).

Acknowledgment. The authors are grateful to Prof. Tsutomu Yokozawa and Dr. Shuichi Hiraoka of the Kanagawa University for the MALDI-TOF mass spectroscopy measurements.

References and Notes

(1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176. Tomallia, D. A. *Adv. Mater.* **1994**, *6*, 529. Voit, B. I. *Acta Polym.* **1995**, *46*, 87. Fréchet, J. M. J. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1399. Malmoström, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555. Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279. Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685. Hawker, C. J. *Adv. Polym. Sci.* **1999**, *147*, 114. Fisher, M.; Vögle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. Voit, B. I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505. Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453.

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

(3) Thompson, D. S.; Markoski, L. J.; Moore, J. S.; Sendijarevic, I.; Lee, A.; McHugh, A. J. *Macromolecules* **2000**, *33*, 6412.

(4) Hölter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298.

(5) Hobson, L. J.; Feast, W. J. *Polymer* **1999**, *40*, 1279.

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

(7) Ishida, Y.; Sun, A. C. F.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 2832.

(8) Moore, J. S.; Bharathi, P. *Macromolecules* **2000**, *33*, 3212.

(9) Lach, C.; Frey, H. *Macromolecules* **1998**, *31*, 2381.

(10) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 1111.

(11) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 6937.

(12) Ueda, M.; Kameyama, A.; Hashimoto, K. *Macromolecules* **1988**, *21*, 19.

(13) Polyimide **8** was prepared as described in ref 11. The absolute M_w was 50 000 with M_w/M_n of 1.6, determined 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.

(14) Lee, Y. U.; Jang, S. S.; Jo, W. H. *Macromol. Theory Simul.* **2000**, *9*, 188.

(15) Jiang, D. L.; Aida, T. *Nature* **1997**, *388*, 454.

(16) Experimental detail on the preparation of 4-(4′-nitrophenoxy)-phthalic anhydride is described in an article entitled "Semicrystalline Polyimides Starting from AB-type Monomers". Liu, X. Q.; Yamanaka, K.; Jikei, M.; Kakimoto, M. *Chem. Mater.* **2000**, *12*, 3885.

MA001936V