Synthesis and Properties of Hyperbranched Aromatic Polyamide Copolymers from AB and AB_2 Monomers by Direct Polycondensation

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ABSTRACT: Hyperbranched aromatic polyamide copolymers were prepared by direct polycondensation of 3-(4-aminophenoxy)benzoic acid (AB monomer) and 3,5-bis(4-aminophenoxy)benzoic acid (AB_2 monomer) in the presence of triphenyl phosphite and pyridine as condensation agents. The structure of resulting polymers was confirmed by IR, ^{1}H, and ^{13}C NMR measurements. The composition of monomers determined by ^{1}H NMR was almost identical to the feed ratio of monomers. ^{13}C NMR revealed that the copolymers were composed of five kinds of repeating units whose ratio was consistent with statistical distribution. The resulting copolymers were soluble in aprotic polar solvents such as DMF, NMP, and DMSO, and transparent yellow films were prepared from DMF solution of the copolymers. The temperature of a 5% weight loss determined by TGA was over 400 °C for all copolymers. The feed ratio of the monomers affected the glass transition temperatures (T_gs) and the softening points (T_ss). A minimum T_g was observed at a 50% of the AB_2 monomer whereas T_ss gradually decreased with increasing the AB_2 monomer and became constant over a 60%. Young's modulus determined by the tensile test decreased from 2.4 to 1.6 GPa with increasing amount of the AB_2 monomer in the range 0−60%.

Introduction

Dendritic macromolecules, such as dendrons, dendrimers, and hyperbranched polymers, have received considerable attention due to their unique shapes and properties.[1−5] Hyperbranched polymers are generally prepared by one-step polymerization of AB_x type monomers in contrast with dendrimers prepared by multistep reactions.[6,7] Therefore, hyperbranched polymers are suitable for a large-scale production and wide range of applications. From the structural viewpoint, hyperbranched polymers have linear units which have one unreacted B function in addition to dendritic and terminal units. In 1952, Flory reported statistical calculations for a one-step polymerization of AB_2 type monomers and copolymerization of AB and AB_2 monomers,[8] and then, Kricheldorf reported the synthesis of aromatic polyester copolymers from AB and AB_2 monomers in 1982.[9] Various hyperbranched polymers have been prepared since Kim and Webster reported the synthesis of hyperbranched polyphenylenes by the one-step polycondensation of AB_2 monomers in 1990.[10] Hyperbranched polymers commonly show good solubility in organic solvents and low solution viscosity, similar to dendrimers. The similarity suggests that hyperbranched polymers are less entangled in solution than conventional linear polymers. It is also well-known that dendrimers and hyperbranched polymers are generally amorphous, even if the linear analogues are known as crystalline polymers.

There are a few papers about copolymerization of AB and AB_x type monomers so far.[9,11−14] The introduction of AB monomers allows the control of the average distance between branching points. Branching density in main chains generally affect the properties of the resulting hyperbranched polymers, similar to low- and high-density polyethylenes.[15] Recently, our group and others have reported the synthesis of hyperbranched aromatic polyamides from AB_2 type monomers by direct polycondensation.[16−21] It was found that the hyperbranched polyamide was soluble in organic solvents due to consecutive branching structure, whereas the linear analogues, such as poly(phenylene terephthalamide)s, are insoluble after the isolation from production process.[22] In this paper, we describe the copolymerization of 3-(4-aminophenoxy)benzoic acid as an AB type monomer and 3,5-bis(4-aminophenoxy)benzoic acid as an AB_2 type monomer, by direct polymerization in the presence of triphenyl phosphite and pyridine as condensation agents.

Experimental Section

Measurements. Infrared (IR) spectra were recorded using a Shimadzu FTIR-8100 Fourier transform infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-AL 300 spectrometer. Thermo gravimetric analysis (TGA) was carried out with a Seiko TGA 6200 at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was carried out with a Seiko DSC 6200 at a heating rate of 10 °C/min in nitrogen. Thermal mechanical analysis (TMA) was carried out with a Seiko TMA/SS 6000 at a heating rate of 5 °C/min. Inherent viscosity was measured in NMP (0.5 g/dL) at 30 °C. Gel permeation chromatography (GPC) measurements were carried out with a JASCO HPLC 880PU, polystyrene−divinylbenzene column (two Shodex KD-806M and KD-802), and a Shodex RI-71 refractive index detector. DMF containing 0.01 mol/L of lithium bromide was used as an eluent. Tensile tests were carried out at room temperature with a Toyo Baldwin Tensilon UTM-II-20 using a crosshead speed of 4.0 mm/min. The width and thickness of film strips were 5.0 mm and about 40 μm, respectively, and the gauge length was 10 mm.

Materials. 3,5-Dihydroxybenzoic acid was purified by recrystallization from water and dried in a vacuum at 80 °C for 12 h. 3-Hydoroxybenzoic acid was purified by recrystallization from ethanol and dried in a vacuum at 80 °C for 12 h. *N*,*N*-Dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP) were used after distillation under reduce pressure from calcium hydride. Lithium chloride was dried at 230 °C overnight before use. Other solvents and reagents were used without further purification.

3,5-Bis(4-aminophenoxy)benzoic Acid (AB_2 Monomer). The AB_2 monomer was prepared from 3,5-dihydroxybenzoic

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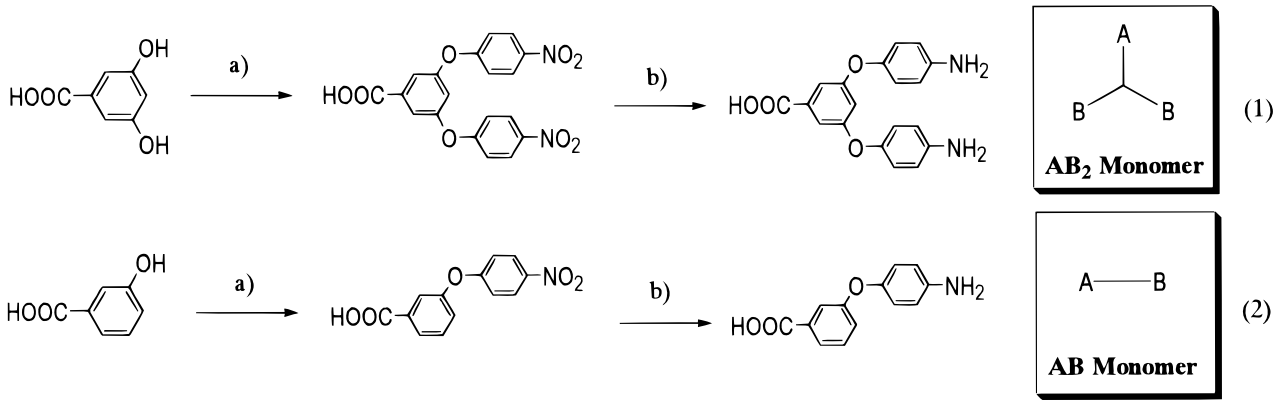
Scheme 1



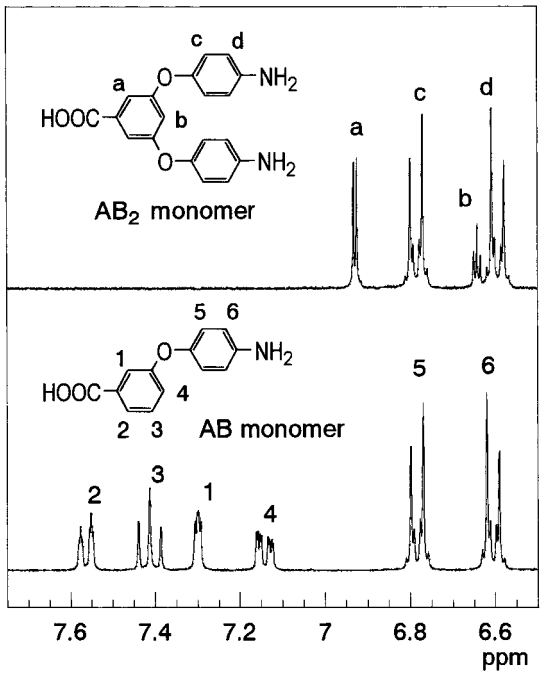


Figure 1. ^{1}H NMR spectra of AB_2 and AB monomers.

acid and 4-fluoronitrobenzene, as reported in our previous work (Scheme 1 (1)).[16−18] The reduction of the nitro intermediate was carried out in the mixture of tetrahydrofuran and ethanol (1:1 by volume) instead of DMF. Yield 76%. IR (KBr): 3378, 1682, 1622, 1592, 1509, 1441, 1213, 1127, 1003, 830 cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.78; H, 4.70; N, 8.20. The ^{1}H NMR spectrum of the AB_2 monomer and the assignment of peaks are described in Figure 1.

3-(4-Aminophenoxy)benzoic Acid (AB Monomer). The AB monomer was prepared from 3-hydroxybenzoic acid and 4-fluoronitorobenzene, as described in our previous work (Scheme 1 (2)).[16−18] The reduction of the nitro intermediate was carried out in the mixture of tetrahydrofuran and ethanol (1:1 by volume) instead of DMF. Yield: 75%. IR (KBr): 3401, 1690, 1505, 1453, 1308, 1231, 938, 843 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.43; H, 4.97; N, 6.01. The ^{1}H NMR spectrum of the AB monomer and the assignment of peaks are described in Figure 1.

Direct Polycondensation of the AB_2 Monomer (Entry 6 in Table 1). Direct polymerization of the AB_2 monomer was carried out in the presence of triphenyl phosphite, pyridine, and lithium chloride, as reported in the literature.[17,18] Yield 98%. IR (KBr): 1657, 1588, 1505, 1433, 1406, 1323, 1208, 1167, 1125, 1003, 833 cm^{-1}. ^{1}H NMR (DMSO-d_6, ppm): 10.23 (amide), 7.74, 7.32, 7.20, 7.08, 6.80, 6.60, 6.49, 4.96 (amine).

Table 1. Direct Polycondensation of the AB_2 Monomer[a]

entry	equiv to COOH[b]	LiCl (g)	temp (°C)	yield (%)	η_{inh}[c] (dL/g)
1	2.0	0.25	110	87	0.31
2	2.0		110	82	0.23
3	1.5	0.25	110	gel	
4	1.2	0.25	110	gel	
5	1.1	0.25	110	gel	
6	1.1	0.25	100	86	0.28

[a] The direct polycondensation was conducted in NMP in the presence of LiCl, pyridine, and TPP for 3 h. [b] Feed molar ratio of condensation agent, TPP, against carboxylic acid groups. [c] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

Anal. Calcd for $(C_{19}H_{14}N_2O_3)_n$: C, 71.69; H, 4.43; N, 8.80. Found: C, 70.47; H, 4.88; N, 8.49.

Copolymerization of AB_2 and AB Monomers (AB_2/AB = 50/50). In a three-necked flask, 0.84 g (2.5 mmol) of the AB_2 monomer and 0.57 g (2.5 mmol) of the AB monomer were dissolved in 10 mL of NMP, and then 0.5 g of lithium chloride, 2.5 mL of pyridine, and 1.43 mL (5.5 mmol) of TPP were charged into the flask. The solution was heated to 100 °C and stirred under nitrogen. After 3 h, the solution was poured into 900 mL of methanol to precipitate the polymer. The precipitate was collected by filtration and dried in a vacuum at room temperature. The crude product was purified by reprecipitation from NMP solution into methanol containing 0.1 wt % of lithium chloride. The product was finally filtered and washed in boiling mixture of methanol/ water (1:1) and dried in a vacuum at 100 °C. Yield 97%. IR (KBr): 1659, 1586, 1505, 1482, 1435, 1406, 1318, 1267, 1211, 1167, 1127, 1003, 835 cm^{-1}. ^{1}H NMR (DMSO-d_6, ppm): 10.03 (amide), 7.76, 7.61, 7.41, 7.36, 7.25, 7.15, 7.07, 6.79, 6.63, 6.55, 4.71 (amine). Anal. Found: C, 71.95; H, 4.64; N, 7.70.

Results and Discussion

Polymerization of AB and AB_2 Monomers. Homopolymers from the AB_2 and the AB monomers were prepared by direct polycondensation in the presence of triphenyl phosphite (TPP) and pyridine as condensation agents, as shown in Tables 1 and 2. We have recently reported that the hyperbranched aromatic polyamide with an inherent viscosity of 0.19 dL/g was prepared by the direct polycondensation at 100 °C in the absence of inorganic salts.[18] The inherent viscosity was improved to 0.31 dL/g by polymerizing at 110 °C in the presence of 2 equiv of TPP against carboxylic acid. In the absence of lithium chloride, the inherent viscosity decreased to 0.23 dL/g, but no precipitation was observed during the polymerization (entry 2 in Table 1). It seems that lithium chloride promote the direct polymerization to

Scheme 2

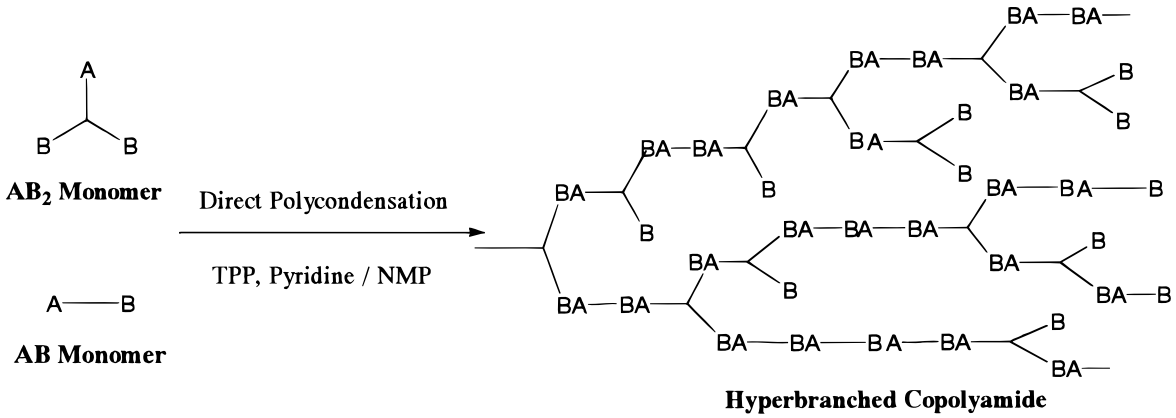


Table 2. Direct Polycondensation of the AB Monomer[a]

entry	equiv to COOH[b]	pyridine (mL)	yield (%)	η_{inh}[c] (dL/g)
7	1.0	0.92	85	0.48
8	1.2	1.11	103	0.45
9	1.5	1.38	93	0.74
10	2.0	1.84	93	0.53

[a] The direct polycondensation was conducted in NMP in the presence of LiCl, pyridine, and TPP at 110 °C for 3 h. [b] Feed molar ratio of condensation agent, TPP, against carboxylic acid groups. [c] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

give the polymer with a higher inherent viscosity.[23] Unfortunately, it was difficult to remove all of contaminated TPP in the resulting polymers prepared with 2 equiv of TPP. Theoretically, 1 equiv of TPP is enough to promote the polymerization since it activates carboxylic acid, and then the activated complex is attacked by nucleophiles. Therefore, the direct polymerization in the presence of small excess amount of TPP was carried out as shown in entries 3−6 in Table 1. Gelation was observed for the polymerization at 110 °C (entries 3−5 in Table 1). The polymerization at 100 °C with small excess amount of TPP proceeded without gelation (entry 6). After reprecipitating the polymer into methanol containing lithium chloride (0.1 wt %) from DMF solution twice, the hyperbranched polyamide was isolated as a white powder. Excess TPP might play an important role to reduce intermolecular interaction between propagating molecules in entries 1 and 2. The spectroscopic data of the resulting polymer were consistent with those reported in our previous work.[16,18]

Direct polymerization of the AB monomer was also carried out, as shown in Table 2. A small excess amount of TPP gave a linear polyamide in good yield. The inherent viscosity of the linear polyamide was relatively high in comparison with that of the hyperbranched polyamide. The structure of the polymer was confirmed by IR spectroscopy. The peak at 1690 cm^{-1} attributed to a carboxylic acid group and 3401 cm^{-1} attributed to an amino group disappeared, and a new absorption at 1653 cm^{-1} attributed to amide bonds was observed after the polymerization of the AB monomer. The linear polyamide was partially soluble in NMP and almost insoluble in other organic solvents, while no precipitation was observed during the polymerization.

Copolymerization of AB and AB_2 Monomers. Copolymerization of the AB and the AB_2 monomers in the presence of TPP was carried out, as shown in Scheme 2 and Table 3. Each copolymer was isolated in

Table 3. Preparation of Copolymers from AB and AB_2 Monomers[a]

polymer	AB_2:AB[b]	yield (%)	F_{AB_2}	η_{inh}[d] (dL/g)	M_w[e]	M_w/M_n
1	100:0	95	100	0.22	9.8×10^4	2.3
2	87.5:12.5	82	87	0.42	2.5×10^5	3.8
3	75:25	93	76	0.27	1.7×10^5	3.0
4	62.5:37.5	83[c]	63	0.41	3.3×10^5	4.1
5	50:50	93	50	0.40	1.5×10^5	2.4
6	37.5:62.5	82[c]	38	0.37	2.1×10^5	3.3
7	25:75	91	25	0.46	2.2×10^5	4.5
8	12.5:87.5	85[c]	13	0.68	2.8×10^5	4.1
9	5:95	83[c]		0.96		
10	0:100	88[c]		0.77[f]		

[a] The direct polycondensation was conducted in the presence of LiCl, pyridine, and TPP in NMP at 110 °C for 3 h. [b] Feed molar ratio of monomers. [c] After four times of reprecipitation. [d] Inherent viscosity measured in NMP at a concentration of 0.5 g/dL at 30 °C. [e] Determined by GPC in DMF solution containing LiCl (0.01 mol/L). M_w and M_n were calculated based on polystyrene standards. [f] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

good yield. Inherent viscosity of the copolymers increased with increasing feed ratio of the AB monomer. Molecular weight of the copolymers determined by GPC was more than 10^5, which implies that the resulting copolymers have enough high molecular weight. The polydispersity represented by M_w/M_n was fairly large and was dispersed randomly against the feed ratio of the monomers.

The structures of the polymers were confirmed by IR, ^1H, and ^{13}C NMR measurements. In IR spectra of all resulting polymers, a new absorption peak attributed to amide carbonyl groups was observed at 1659 cm^{-1}, while a peak attributed to carboxylic acid groups at 1682 cm^{-1} in monomers disappeared. Figure 2 shows the IR spectra of the copolymer (1:1) and the corresponding homopolymers. The shoulder peak at 1300 cm^{-1} for the AB_2 homopolymer and the peak at 1266 cm^{-1} for the AB homopolymer were attributed to asymmetric vibrations of aromatic ether bonds. The resulting copolymer possessed both peaks, and the relative intensity of the peaks became weak in comparison with the homopolymers. A peak at 1127 cm^{-1} and a shoulder peak at 1481 cm^{-1}, which might be assigned to ether bonds arising from the AB_2 monomer and C−C stretching vibration of the 1,3-substituted benzene ring, respectively, were also observed in the spectrum of the copolymer. It is clear that the resulting copolymer is composed of the both repeating units of the AB and the AB_2 monomers.

Figure 3 shows ^1H NMR spectra of the copolymer (1:1) and the AB_2 homopolymer. A multiple peak at 10.0

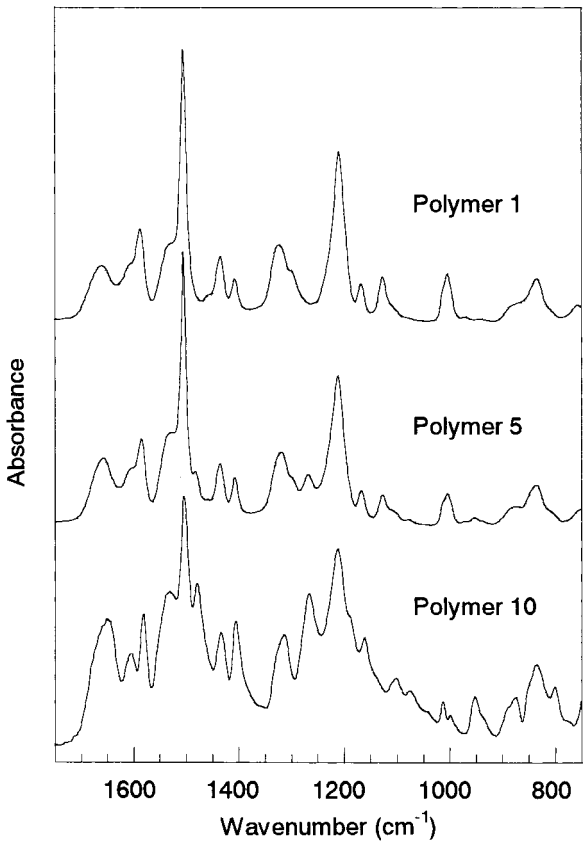


Figure 2. FT-IR spectra of polymers **1**, **5**, and **10**.

ppm assigned to amide protons and a broad peak at 4.7 ppm assigned to unreacted amino protons were observed for both the copolymer and the AB_2 homopolymer. The presence of unreacted amino groups in the copolymer was caused by the incorporation of the AB_2 unit in the resulting polymer. The peaks attributed to aromatic protons arisen from the AB unit were observed from 7.61 to 7.41 ppm in the spectrum of the copolymer. Aromatic protons arisen from 4-amino-substituted benzene rings could be distinguished at 6.6 and 6.8 ppm, which allows to determine the ratio of the AB and the AB_2 units in the copolymer. Generally, hyperbranched polymers prepared from AB_2 monomers have many unreacted B functions in contrast with conventional linear polymers. The number of unreacted B function (N_B) must depend on the composition of the monomers in the case of copolymerization of AB and AB_2 monomers since the N_B is equal to the number of the AB_2 unit (N_{AB_2}) plus 1 (eq 1). In this work, the total number of repeating units (N_{total}) is equal to the number of amide protons (N_{amide}) plus 1 (eq 2). Therefore, a fraction of the AB_2 monomer in the resulting copolymer (F_{AB_2}) can be calculated from N_B and N_{amide}, as described in eq 3. When the molecular weight of the polymer is high enough, F_{AB_2} can be represented by the ratio of N_B against N_{amide}. The N_B can be calculated from the integration of the peaks at 6.6 and 6.8 ppm for four aromatic protons, and the N_{amide} can be determined from the peak at 10.0 ppm. The calculated F_{AB_2} for each copolymer is listed in Table 3. It is obvious that the composition ratio of the copolymer was consistent well with the feed ratio of monomers.

$$N_B = N_{AB_2} + 1 \tag{1}$$

$$N_{total} = N_{amide} + 1 \tag{2}$$

$$F_{AB_2} = \frac{N_{AB_2}}{N_{total}} = \frac{N_B - 1}{N_{amide} + 1} \approx \frac{N_B}{N_{amide}} \tag{3}$$

Carbonyl peaks in ^{13}C NMR spectra of the AB_2 homopolymer and the copolymers are shown in Figure 4. A pulse delay of 15 s in ^{13}C NMR measurements allowed quantitative consideration, since T_1 of the peaks were shorter than 3 s. As reported previously, the AB_2 homopolymer showed three kinds of carbonyl peaks which can be attributed to dendritic (D), linear (L), and terminal (T) units. The integration ratio of T:L:D was 0.9:2.2:1.0, and the degree of branching calculated by Fréchet's equation[24] was determined to be 0.46. On the other hand, five kinds of carbonyl peaks were observed for the copolymer prepared from the AB and the AB_2 monomers. The possible five kinds of repeating units are described in Figure 5. L_l and T_l represent the linear and terminal units arisen from the AB monomer,

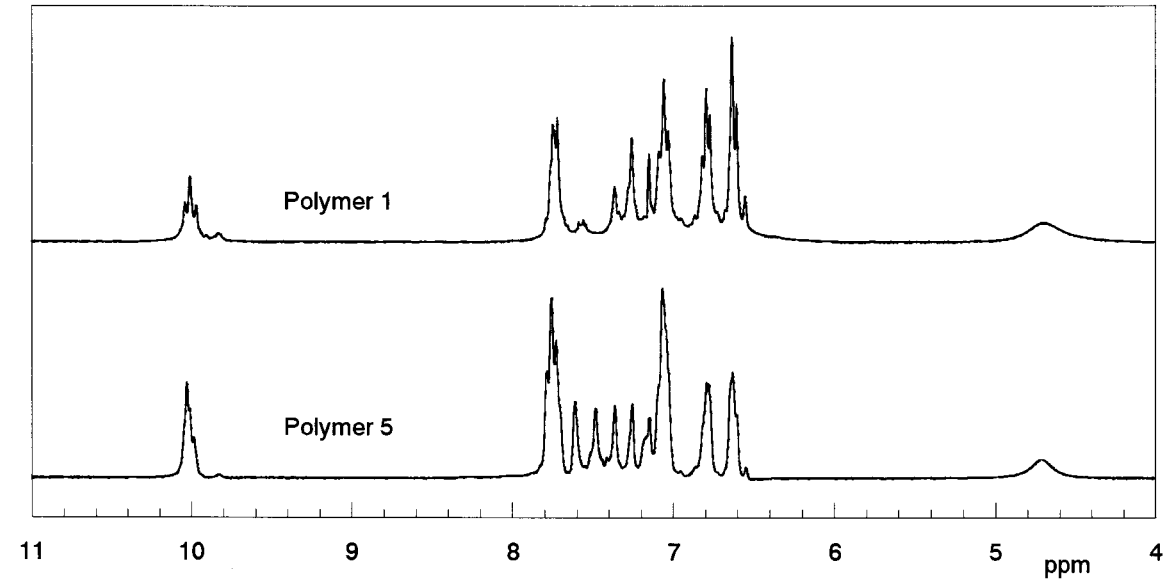


Figure 3. ^1H NMR spectra of polymers **1** and **5**.

Table 4. Solubility of Polyamides[a]

polymer	AB_2:AB	solubility					
		NMP	DMAc	DMSO	DMF	*m*-cresol	methoxyethanol
1	100:0	+	+	+	+	+	+
2	87.5:12.5	+	+	+	+	+	+
3	75:25	+	+	+	+	+	+
4	62.5:37.5	+	+	+	+	+	−
5	50:50	+	+	+	+	+	−
6	37.5:62.5	+	+	+	+	+	−
7	25:75	+	+	+	+	+	−
8	12.5:87.5	+	+	+	+	−	−
9	5:95	+	−	−	−	−	−
10	0:100	±	−	−	−	−	−

[a] Symbols: +, soluble; −, insoluble; ±, partially soluble.

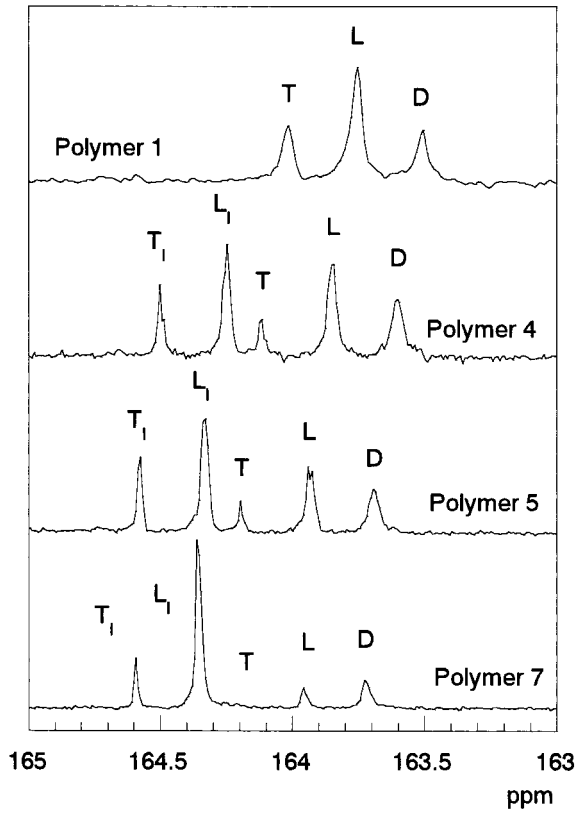


Figure 4. ^{13}C NMR spectra of polymers **1**, **4**, **5**, and **7**.

respectively. The assignment of the peaks was carried out based on the peak intensity change caused by the ratio of monomers. The integration ratio of the peaks (T_l:L_l:T:L:D) for the copolymer **5** (1:1) was calculated to be 2.9:6.8:1.0:4.3:3.8, which agreed with the ratio calculated by statistical consideration (3:6:1:4:4).[25]

Properties of Copolymers. The resulting copolymers had a good solubility in organic solvents, as shown in Table 4. As reported previously, the AB_2 homopolymer is soluble in polar solvents, such as DMF, *m*-cresol, and methoxyethanol, and the AB homopolymer is only partially soluble in NMP. The solubility of the resulting polymers was improved significantly by the introduction of the AB_2 monomer. For example, the copolymer composed of the AB unit (87.5 mol %) and the AB_2 unit (12.5 mol %) was soluble in aprotic polar solvents, such as NMP, DMF, and DMSO. Transparent yellow films of the copolymers were prepared by casting the DMF solution onto a glass plate and subsequent drying in a vacuum at 200 °C. Self-standing films could not be obtained from both homopolymers since the viscosity of the AB_2 homopolymer solution was low, caused by missing entanglements, and the solubility of the AB homopolymer was restricted.

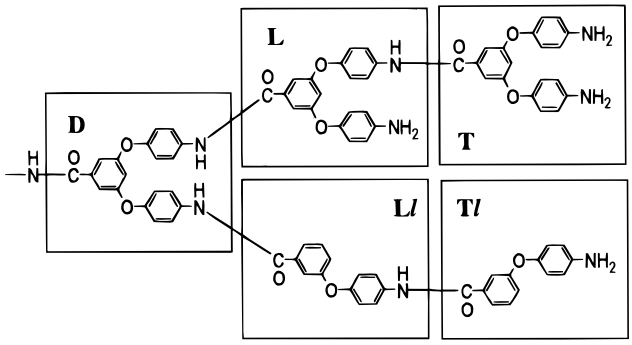


Figure 5. Possible repeating units of the hyperbranched copolyamide.

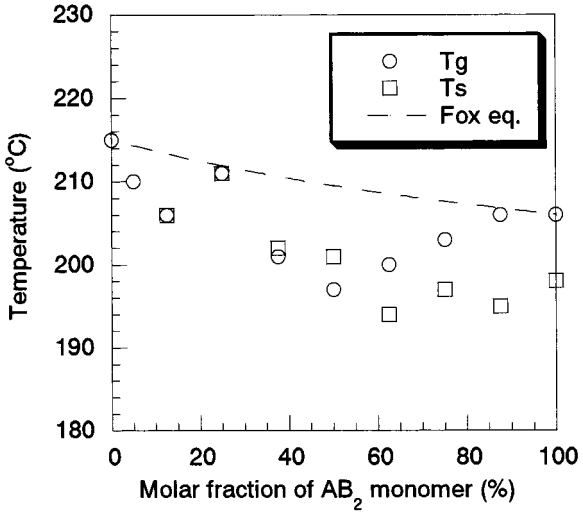


Figure 6. Dependence of T_g and T_s of the copolyamides on the fraction of the AB_2 monomer. The line corresponds to Fox's equation.

Thermal properties of the polymers were investigated by TGA, DSC, and TMA. TGA revealed that the temperatures of a 5% weight loss for all polymers were higher than 400 °C. The degradation behavior of the copolymers seemed to be similar and independent of the ratio of monomers. The ratio of monomers affected glass transition temperatures (T_gs) determined by DSC and softening points (T_ss) determined by TMA, as shown in Figure 6. The T_gs decreased from 215 °C by the introduction of the AB_2 monomer. A minimum at 196 °C was observed for a composition with a 50% of the AB_2 monomer, and then, the T_g increased slightly to 206 °C, which corresponds to the T_g of the hyperbranched

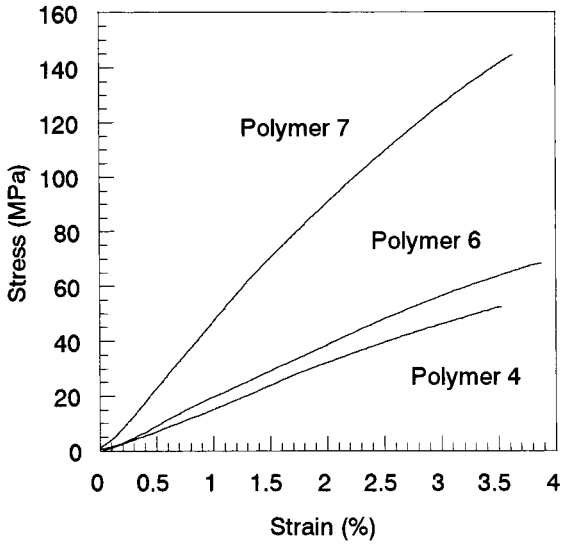


Figure 7. Stress−strain curves of casting films of polymers **4**, **6**, and **7**.

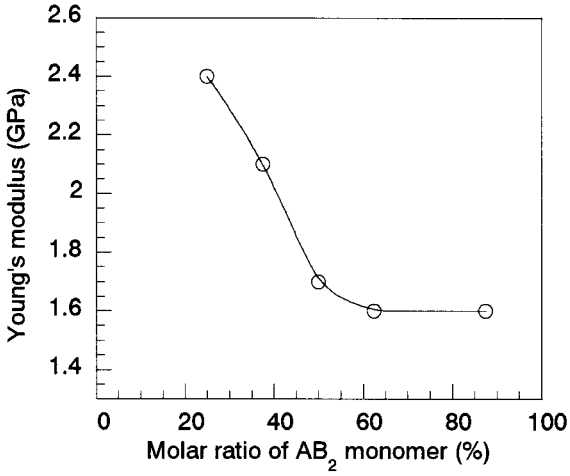


Figure 8. Dependence of Young's modulus determined by tensile tests on the fraction of the AB_2 monomer.

polymer prepared from the AB_2 monomer. Minimum peaks in DSC measurements were also observed for the aromatic polyester copolymers composed of linear and branching units.[12,13] It is clear that the T_g for each composition is lower than the value calculated by Fox's equation.[26] T_ss determined by TMA gradually decreased to 198 °C with increasing the molar ratio of the AB_2 monomer in the range 0−60%. The T_ss of the copolymers became constant over a 60% of the AB_2 monomer, and no clear minimum was observed. It seems that the relationship between the composition of monomers and the thermal properties of resulting copolymers is different from one reported for conventional linear copolymers. In the case of copolymerization of AB and AB_2 monomers, an intermolecular entanglement in the copolymers might be decreased with increasing the amount of the AB_2 monomer, which causes an increase in free volume of the copolymer with increasing the molar ratio of the AB_2 monomer. In addition, the number of unreacted B function (amino group) increases with increasing the molar ratio of the AB_2 monomer.

There are very few papers about mechanical properties of hyperbranched polymers.[27] It is known that dendritic macromolecules such as dendrimers and hyperbranched polymers are less entangled than conventional linear polymers, which might cause poor mechanical properties. A tensile test of the copolymers was carried out in order to investigate the influence of the branching units on mechanical properties. Figure 7 shows stress−strain curves for the copolymers prepared from the AB_2/AB monomers of 62.5/37.5 (polymer 4), 37.5/62.5 (polymer 6), and 25/75 (polymer 7). The stress at breaking point increased with decreasing the amount of the AB_2 monomer while the strain at breaking point for each copolymer was about 3.5% and independent of the feed ratio of monomers. Young's moduli calculated by the initial slope of the S−S curves are plotted against the feed ratio of monomers, as shown in Figure 8. The high modulus in the range 2.40−1.57 GPa was obtained, which are typical values for aromatic polyamides.[19] The modulus decreased with increasing the feed ratio of the AB_2 monomer and became almost constant over a 60% of the AB_2 monomer. The data suggest that the intermolecular entanglement of the copolymers decreases by the introduction of the AB_2 branching unit, which results in the decrease of the modulus in proportional to the feed ratio of the AB_2 monomer. It is interesting to note that the modulus extrapolated to 100% AB_2 was about 1.5 GPa.

Conclusions

The hyperbranched aromatic polyamide copolymers were prepared from the AB and the AB_2 monomers by direct polymerization in the presence of condensation agents. A slightly excess amount of triphenyl phosphite gave white powdery polymers in good yield. ^{1}H NMR of the copolymers revealed that the composition of the monomers was almost the same as the feed ratio of monomers. The resulting copolymers were composed of five kinds of repeating units, which was confirmed by ^{13}C NMR measurements. The integration ratio of the peaks was consistent with the ratio calculated by statistical consideration. Solubility of the resulting polymers in organic solvents was remarkably improved by the incorporation of the AB_2 monomer, and transparent yellow films were prepared from DMF solution of the copolymers. All resulting polymers were thermally stable owing to their aromatic amide structure. T_g and T_s decreased by the introduction of the AB_2 monomer, but the plots of the thermal properties against the composition of monomers seem to be different from one reported for conventional linear copolymers. The Young's modulus determined by tensile test decreased from 2.4 to 1.6 GPa with increasing the AB_2 monomer in the range 0−60% and then became constant over a 60% of the AB_2 monomer. The decrease might be caused by less entangled nature of hyperbranched polymers prepared from AB_2 monomers.

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