Synthesis and Characterization of Hyperbranched Aromatic Polyamide Copolymers Prepared from AB_2 and AB Monomers

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Summary: A series of hyperbranched aromatic polyamide copolymers has been prepared and characterized from direct polycondensation of AB_2 and AB monomers. Structure of the monomers and the molar ratio of AB_2/AB showed strong influence on the properties of resulting copolymers. A small amount of AB_2 branching unit improved markedly the solubility of the resulting copolymer. Mark-Houwink parameters of the copolymers were essentially independent of the mole ratio of the monomers. The physical and mechanical properties of resulting copolymers were influenced not only by the mole ratio of monomers, but also by the structure of the monomers employed.

Keywords: copolymerization, hyperbranched polyamide, mechanical properties, solution properties, thermal properties

Introduction

It is well-known that architecture of polymers affects strongly polymer properties even if the polymers are composed of the same repeating units. Figure 1 shows that the architecture of branched macromolecules depends on the branching density. Random and irregular branching leads to a crosslinked material (**a** in Figure 1). On the other hand, regular and consecutive branching results in the formation of a highly branched material (**b** and **c** in Figure1), called dendritic macromolecules. It is known that properties of dendritic macromolecules are very different from those of crosslinked materials and linear polymers. Unique properties of dendritic macromolecules, which include good solubility, low viscosity, encapsulation effect, and multi-functionality, are attributed to globular shape of the molecules and the presence of many functional groups on the periphery. Dendritic macromolecules are usually classified into dendrimers and hyperbranched polymers. One of the advantages of hyperbranched polymers is that they can be prepared from one-step polymerization of AB_x type monomers. This is in sharp contrast to dendrimers which must be prepared by multi-step reactions. Although hyperbranched polymers usually contain insufficient branching units, which are called linear

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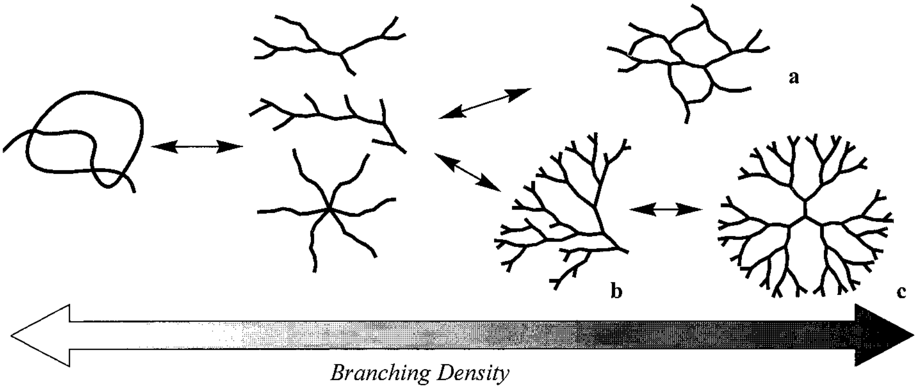
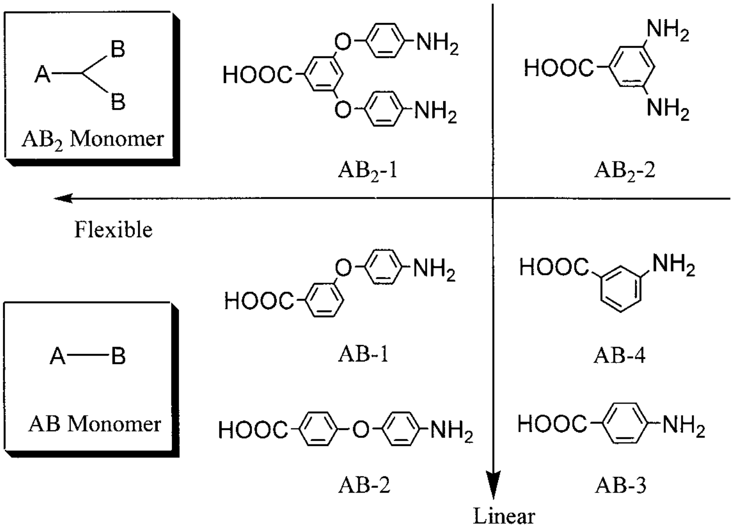


Fig. 1. Architecture of branched macromolecules.

units, the properties of hyperbranched polymers are often very similar to those of the corresponding dendrimers.[1-4] Therefore, hyperbranched polymers are attractive new materials for industrial applications because of their simple production process. Branching density of a hyperbranched polymer can be controlled by the mole ratio of AB_2 and AB monomers. The effect of branching point on polymer properties of resulting polymers can be quantitatively evaluated by the mole ratio of AB_2 and AB monomers. The concept of the copolymerization was first proposed by Flory about 50 years ago,[5] and then, Kricheldorf reported the first attempt to introduce AB_2 type branching unit for synthetic polymers in 1982.[6] We have recently reported the copolymerization of 3,5-bis(4-aminophenoxy)benzoic acid (AB_2) and 4-aminophenoxybenzoic acid (AB).[7,8] In this paper, we focus on the effects of the number of branching unit and the structure of branching component on the physical and mechanical properties of resulting copolymers prepared from direct copolycondensation of AB_2 and AB monomers.

Experimental Section

Materials. 3,5-Bis(4-aminophenoxy)benzoic acid (AB_2-1) was prepared from 4-fluoronitrobenzene and 3,5-dihydroxybenzoic acid, as described in the literature.[7] 3,5-Diaminobenzoic acid (AB_2-2) was purified by recrystallization in ethanol. 3-(4-Amino phenoxy)benzoic acid (AB-1) was prepared from 4-fluoronitrobenzene and 3-hydroxybenzoic acid, as described in the literature.[7] 4-(4-Aminophenoxy)benzoic acid (AB-2) was preparedfrom condensation reaction of 4-hydroxybenzoic acid and 4-fluoronitrobenzene and subsequent hydrogenation in the presence of palladium on acitivated carbon as a catalyst. 4-Aminobenzoic acid (AB-3) was purified by recrystallization in ethanol. 3-Aminobenzoic acid (AB-4) was purified by recrystallization in water. N-Methyl pyrrolidone (NMP) and pyridine 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.



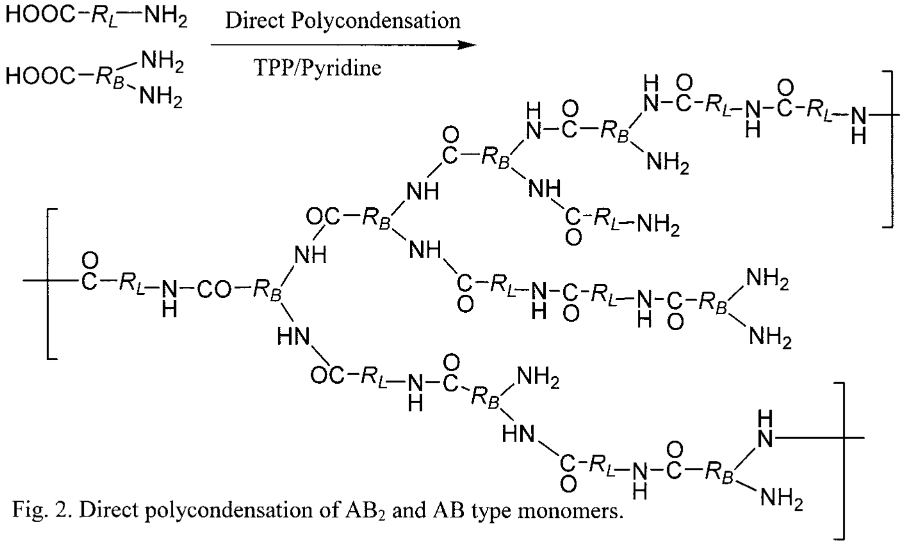


Fig. 2. Direct polycondensation of AB_2 and AB type monomers.

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. Gel permeation chromatography (GPC) measurements were carried out using a Viscotek TDA302 Triple Detector Array with polystyrene-divinylbenzene columns (two Shodex KD-806M and KD-802). 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.

Copolymerization of AB_2-1 and AB-1 (50/50). In a three-necked flask, 0.84 g (2.5 mmol) of AB_2-1 and 0.57 g (2.5 mmol) of AB-1 were dissolved in 10 mL of NMP, and then, 0.5g of lithium chloride, 2.5 mL of pyridine and 1.43 mL (5.5 mmol) of triphenylphosphite (TPP) were charged into the flask. The solution was heated to 100 °C and stirred under nitrogen. After 3h, the solution was poured into 1000 mL of methanol to precipitate the polymer. The precipitate was collected by filtration and dried in vacuum at room temperature. The crude product was purified by reprecipitation from DMF 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 vacuum at 100 °C. Yield 93 %. 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.

Copolymerization of AB_2-1 and AB-3 (50/50). AB_2-1 (1.261 g: 3.75 mmol) and AB-3 (0.514 g:3.75 mmol) were copolymerized in the same manner as that of AB_2-1 and AB-1. Benzoyl chloride (4 mL) was added to the reaction mixture before isolation of crude product in order to modify end amino groups. Yield 94 %. IR(KBr): 1657, 1601, 1505, 1435, 1406, 1318, 1267, 1208, 1167, 1127, 1003, 841 cm^{-1}. ^{1}H-NMR (DMSO-d_6, ppm): 10.07, 7.97, 7.80, 7.51, 7.39, 7.10, 6.79.

Spectorscopic data for other copolymers. AB$_2$-2-AB-1 (50/50): IR(KBr): 1657, 1601, 1539, 1447, 1273, 1225, 855 cm^{-1}. ^{1}H-NMR (DMSO-d_6, ppm): 10.22, 8.47, 8.10, 8.02, 7.80, 7.52, 7.19, 7.07. AB$_2$-2-AB-3 (50/50): IR(KBr): 1659, 1599, 1525, 1514, 1449, 1323, 1282, 1244, 1186, 850 cm^{-1}. ^{1}H-NMR (DMSO-d_6, ppm): 10.23, 7.97, 7.80, 7.51, 7.39, 7.10, 6.79. AB$_2$-2-AB-4 (50/50): IR(KBr): 1659, 1599, 1545, 1485, 1447, 1327, 1304, 880 cm^{-1}. ^{1}H-NMR (DMSO-d_6, ppm): 10.24, 8.49, 8.38, 8.11, 8.01, 7.75, 7.52.

Results and Discussion

Preparation of Copolymers. Hyperbranched aromatic polyamide copolymers were prepared by direct polycondensation of AB$_2$ and AB monomers in the presence of triphenylphosphite (TPP) and pyridine acting as condensation agents, as shown in Figure 2. Two AB$_2$ type monomers, 3,5-bis(4- aminophenoxy)benzoic acid (AB$_2$-1) and 3,5-diaminobenzoic acid (AB2-2), and four AB type monomers were examined for the copolymerization. Table 1 shows the results for copolymerization of AB2-1 and AB-1. The functional groups in AB-1 were designed to give equal reactivity with AB2-1. The direct polycondensation proceeded successfully and the resulting copolymers were isolated in good yield. The amount (mol%) of incorporated AB$_2$-1 in the copolymers, determined by ^{1}H NMR measurements, was almost consistent with the formulated mole ratio of monomers. Absolute molecular weight determined by a triple-online detector was in the range 10^4-10^5 with relatively large polydispersity.

Table 1. Preparation of hyperbranched polyamide copolymers from AB$_2$-1 and AB-1.

Initial mole ratio AB$_2$:AB	Yield (%)	r_{AB2} [a)]	η_{inh}(dL/g) [b)]	M_w [c)]	M_w/M_n [c)]
100 : 0	95	100	0.22	3.60×10^4	2.08
87.5 : 12.5	82	87	0.42	7.57×10^4	3.68
75 : 25	93	76	0.27	5.91×10^4	3.10
50 : 50	93	50	0.40	6.67×10^4	3.19
12.5 : 87.5	85	13	0.68	11.7×10^4	3.68
0 : 100	88	-	0.77	-	-

[a)] Incorporated mol% of AB$_2$-1 in the copolymer determined by integration ratio of ^{1}H NMR measurements.
[b)] Measured in NMP at a concentration of 0.5 g/dL at 30□C.
[c)] Absolute molecular weight determined by GPC equipped with a triple-online detector (refractive index, low-angle laser light scattering, and viscosity) in DMF containing lithium bromide of 0.01 mol/L.

Table 2. Preparation of hyperbranched polyamide copolymer from AB_2-1 and AB-3.

Initial mole ratio AB_2 : AB	r_{AB2} [a)]	Yield (%)	η_{inh}, [b)] (dL/g)	M_w [c)]	M_w/M_n [c)]
80:20	80	96	0.21	3.56×10^4	1.86
50:50	50	94	0.23	3.66×10^4	1.67
20:80	25	79	0.24	0.822×10^3	1.18
0 :100	-	96	1.05[d)]	-	-

[a)] Incorporated mol% of AB_2-1 in the copolymer determined by ^{1}H-NMR measurement.

[b)] Inherent viscosity measured in NMP at a concentration of 0.5 g/dL at 30 °C.

[c)] Absolute molecular weight determined by GPC equipped with a triple-online detector (refractive index, low-angle laser light scattering, and viscosity) in DMF containing lithium bromide of 0.01 mol/L.

[d)] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

A rigid AB type monomer, 4-aminobenzoic acid (AB-3), was also copolymerized with AB_2-1. The reactivity of functional groups may be different from that of AB_2-1. The copolymerization was carried out in the presence of TPP and pyridine in NMP. In order to improve the solubility of the resulting copolymers, amino end groups were reacted with benzoyl chloride before isolation. As shown in Table 2, the copolymers were isolated in good yield. When the mole ratio of AB_2-1 was 20 %, the resulting copolymer contained 25% AB_2-1 component, which is greater than the initial mole ratio (20%). The data suggested that AB-3 has lower reactivity than AB_2-1.

Table 3. Copolymerization of AB_2-2 and AB monomers to form hyperbranched polyamide copolymers.[a)]

Monomer [b)]		Yield (%)	η_{inh}, [c)] (dL/g)	M_w [d)]	M_w/M_n [d)]
AB_2-2	-	93	0.26	15.4×10^4	1.42
AB_2-2	AB-1	91	0.32	7.09×10^4	1.72
AB_2-2	AB-3	94	0.20	9.08×10^4	1.35
AB_2-2	AB-4	85	0.17	7.71×10^4	1.31

[a)] The direct polycondensation was carried out in the presence of triphenylphosphite and pyridine at 100□C for 3h. End amino groups were reacted with benzoyl chloride before isolation of the product.

[b)] Initial molar ratio of AB_2-2 and an AB monomer was 1:1.

[c)] Inherent viscosity measured in NMP at a concentration of 0.5 g/dL at 30 °C.

[d)] Absolute molecular weight determined by GPC equipped with a triple-online detector (refractive index, low-angle laser light scattering, and viscosity) in DMF containing lithium bromide of 0.01 mol/L.

Copolymerization of AB_2-2 and various AB monomers was carried out in the same manner. Resulting copolymers having amino end groups were insoluble or partially soluble in aprotic polar solvents after isolation. The lower solubility compared with the copolymers prepared from AB_2-1 most likely is caused by the more rigid structure of AB_2-2. Therefore, end amino groups were reacted with benzoyl chloride in order to improve the solubility. The results for the copolymerizations are summarized in Table 3. All copolymerizations proceeded successfully to form corresponding copolymers in high yield. Their molecular weights determined by GPC with the triple-online detector were reasonablly high.

Properties of Copolymers. The solubility of copolymers was markedly improved by incorporation of AB_2 type branching unit. In the case of AB_2-1 and AB-1, the addition of AB_2-1 in 5mol% affected the solubility of the resulting copolymer.[7] The solubility in m-cresol and methoxyethanol depended on the mole ratio of the monomers. As shown in Table 4, the copolymers from AB_2-1 and AB-3 having amino end groups were insoluble in most of organic solvents after isolation. However, the solubility was improved after the amino end groups were reacted with benzoyl chloride. It is clear that the end-capping reaction reduces solute-solute interaction.

Table 4. Solubility of hyperbranched polyamide copolymers from AB_2-1 and AB-3.

AB_2: AB	End group	Solubility					
		NMP	DMAc	DMSO	DMF	*m*-Cresol	Methoxy ethanol
20:80	$-NH_2$	–	–	–	–	–	–
50:50	$-NH_2$	–	–	–	–	–	–
100:0	-NHCOPh	+	+	+	+	+	+
80:20	-NHCOPh	+	+	+	+	+	–
50:50	-NHCOPh	+	+	+	+	+	–
20:80	-NHCOPh	–	+	+	+	–	–
0:100	-NHCOPh	–	–	–	–	–	–

+: Soluble
-: Insoluble

As shown in Table 1, inherent viscosity of the resulting copolymers increased with increasing the feed amount of AB-1. The relationship between weight average molecular weight and intrinsic viscosity of the copolymers from AB_2-1 and AB-1 was investigated by GPC with a triple-online detector: the triple-online detector is capable of monitoring low angle laser light scattering, viscosity, and reflactive index all at the same time. Figure 3 shows Mark-Houwink plots of the copolymers. A linear relationship was observed for each copolymer and the lines closely overlapped with each other. As shown in the inserted figure, all of the slopes observed were around 0.45 even if the mol% of AB_2-1 was 12.5%. It is well-known that most of linear polymers have a value of the slope between 0.5 to 0.8 and dendritic macromolecules often

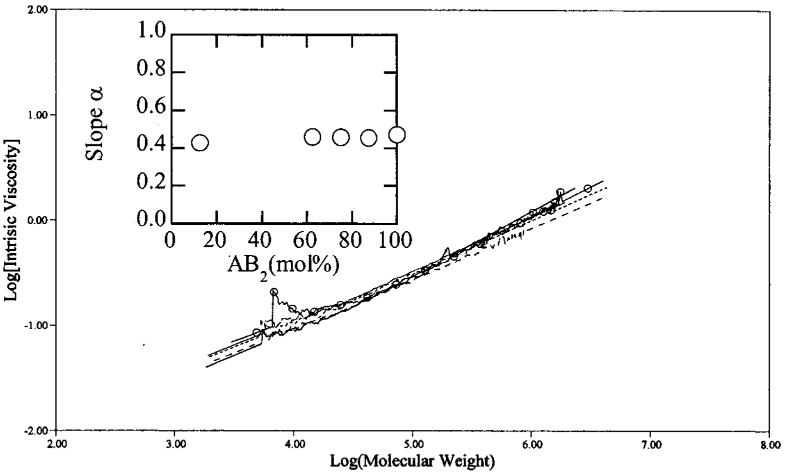


Fig. 3. Mark-Houwink plot of the hyperbranched aromatic polyamide copolymers.

show the slope smaller than 0.5. In this work, the slope was slightly lower than 0.5 and seemed to be independent on the initial molar ratio of the monomers in the range studied. The slope for the AB-1 homopolymer could not be determined because of their poor solubilitiy in the GPC solvent used.

Glass transition temperature (T_g) of the copolymer also varied showing a dependence on the structure and mole ratio of the monomers used, as shown in Figure 4. T_g of the copolymer decreased with increasing the feed ratio of AB_2-1, whereas the incorporation of AB_2-2 unit increased T_g of the copolymer. It is interesting to note that all of the relationship showed unique curvature shape. The T_gs of the copolymers were lower than the value expected by Fox's equation,[9] which is commonly applied for linear copolymers. In literatures, Kricheldorf observed unexpected minimum peaks of T_g for hyperbranched polyester copolymers.[10,11] There are two possible reasons. One is that the number of end functional groups is directly ralated to the mole ratio of monomers. The other is that the degree of intermolecular

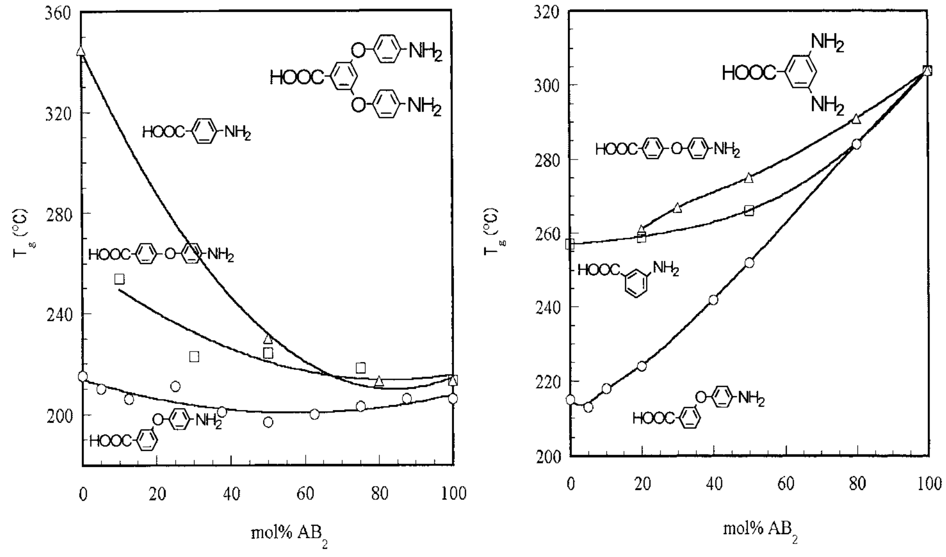


Fig. 4. Glass transition temperature (T_g) of hyprabranched polyamide copolymers prepared from AB_2-1 (a) and AB_2-2 (b).

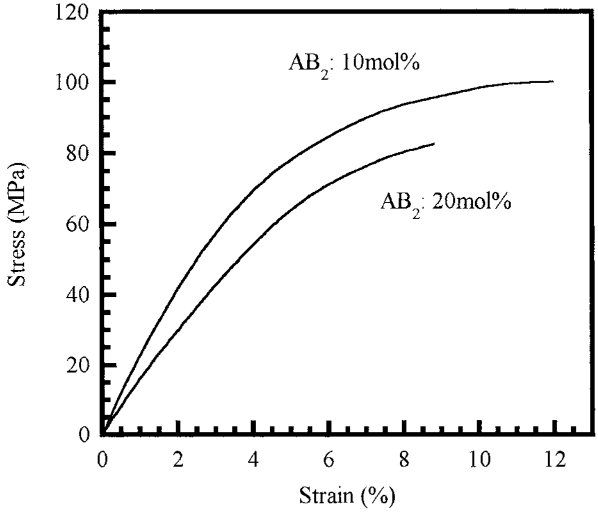


Fig. 5. Stress-strain curve of the hyperbranched polyamide copolymers prepared from AB_2-2 and AB-1.

entanglement is highly influenced by the ratio of monomers. We are unable to discern which of the two factors governs the Tg behavior, based on the results obtained. Further study is needed.

It was extremely difficult or impossible to cast films from the hyperbranched polyamide homopolymers due to low solution viscosity. The linear aromatic polyamides were practically insoluble in organic solvents after isolation. Only some of the copolymers gave flexible films by casting copolymer solution onto glass plates. Tensile tests were carried out to evaluate the effect of the branching units on the mechanical properties. The stress-strain (S-S) curve of the copolymer prepared from AB_2-2 and AB-1 is shown in Figure 5. As expected, Young's molulus determined by the initial slope of S-S curves decreased when the feed ratio of AB_2-2 was increased. The same trend was also observed for the copolymers from AB_2-1/AB-1[7] and AB_2-2/AB-2. This suggests that intermolecular entanglement decreases by the incorporation of the AB_2 branching units. The decrease in maximum strain or elongation may be caused by the incorporation of the rigid structure of AB_2-2 in the polymer backbone.

Conclusion

Hyprabranched aromatic polyamide copolymers were successfully prepared by direct polycondensation of AB_2 and AB monomers in the presence of TPP and pyridine as condensation agents. Properties of resulting copolymers, such as solubility, viscosity, glass transition temperature, and mechanical properties, were strongly dependent on the structure and the mole ratio of monomers. A small amount of AB_2 branching unit markedly affected solubility and viscosity of the copolymers. Flexible cast films could be prepared from the copolymers due to inreased intermolecular entanglement by the incorporation of AB unit.

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