

## Syntheses and Properties of Different Degree of Branching Polyamides Derived from an ABB' Type Monomer, 4-(2,4-Diaminophenoxy) Benzoic Acid

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**ABSTRACT:** Hyperbranched polyamides with different degree of branchings (DBs) were prepared by different polycondensation conditions from an ABB' type monomer, 4-(2,4-diaminophenoxy)benzoic acid. Polyamide (PA1) with multi-amino groups prepared in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonic acid diphenyl ester (DBOP) and triethylamine as condensing agents at room temperature had lower DB of 0.1. Polyamide (PA2) with multi-amino groups prepared in the presence of triphenylphosphite and pyridine as condensing agent at 100 °C had higher DB of 0.2. The free amino groups of both polyamides were modified by acetyl chloride, benzoyl chloride and phthalic anhydride, respectively, to give corresponding modified polyamides. The solubility and thermal properties were not influenced by the different DBs but were influenced by the end groups. Strong films were prepared from polyamides with lower DBs and polyamides with amino groups. [DOI 10.1295/polymj.36.804]

**KEY WORDS** Polyamide / Modification / Degree of Branching / Shape Factor / Tensile Strength / ABB' Monomer /

Hyperbranched polymers have been attracting considerable attention due to their unique characteristics: branched structure, which results in low viscosity and high solubility, and their large number of end groups, which can be modified for many applications.<sup>1,2</sup> However, most of hyperbranched polymers derived from AB<sub>2</sub> monomers do not afford strong films due to lack of chain entanglements, which is a necessity for the mechanical properties of engineering plastics. We have previously reported a new method for increasing chain entanglement by preparing low degree of branching hyperbranched polymers from an ABB' type monomer.<sup>3</sup>

On the other hand, Frey has pointed out that DB statically approached 0.5 in case of the polymerization of AB<sub>2</sub> monomers.<sup>4</sup> Most of the hyperbranched polymers reported in the literature have actually DBs close to 0.5. There have been several attempts to increase DBs: (1) polymerization of dendrons having prefabricated dendritic units;<sup>5</sup> (2) polymerization of AB<sub>x</sub> monomers in the presence of core molecules (Bf);<sup>6,7</sup> (3) enhancement of the reactivity of linear units formed during the polymerization.<sup>8–10</sup> Thompson *et al.* also prepared a series of hyperbranched poly(ether imide)s with different degrees of branching by changing the polymerization time from 2.5 to 20 min.<sup>11</sup> The changes in DB are a result of molecular rearrangements occurring *via* a transesterification mechanism.

Generally speaking, because reaction rate constants dependent on temperature and activation energy, for an ABB' monomer, the relative reactivity of the B and B' functional group may change as changing reaction conditions (temperature or condensing agent). That is, it is possible to vary the degree of branching of polymers derived from an ABB' type monomer by changing the reaction conditions.

In this paper, we focus on the synthesis of polyamides with different degree of branching derived from an ABB' type monomer by using different condensation agents. The properties and structure of the polyamides derived from different reaction conditions were investigated. The end modification and properties of the resulting polyamides are also described.

### EXPERIMENTAL

#### Materials

*N*-methyl pyrrolidone (NMP) was distilled under reduced pressure and stored over 4 Å molecular sieves. Pyridine was dried by distillation after refluxing with KOH. Triethylamine (TEA) was purified by general distillation. Phthalic anhydride was purified by sublimation. (2,3-Dihydro-2-thioxo-3-benzoxazolyl) phosphonic acid diphenyl ester (DBOP) (Tokyo Chemical Industry Co.) was used as received. Acetic anhydride was dried over magnesium, followed by

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distillation under an atmosphere of nitrogen before use. Other reagents and solvents were used as received from commercial sources.

#### Measurements

FT-IR spectra were recorded on a Shimadzu FTIR-8100 FT-IR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer. Differential thermal calorimeter (DSC), thermogravimetric analyses (TGA) were conducted with a Seiko DSC 6200 and TG/DTA 6200, respectively, at a heating rate of  $10^\circ\text{C}/\text{min}$  under the atmosphere of nitrogen. Gel permeation chromatography (GPC) measurements were performed in DMF with 0.01 M lithium bromide at  $35^\circ\text{C}$  with an ASAHI TECHNEION flow system AT-2002, and a Viscotek TDA302 refractive index detector and dual light scattering and differential pressure viscometer (triple array). Viscosity measurements were carried out at a concentration of  $0.5\text{ g/dL}$  in NMP at  $30^\circ\text{C}$  using an Ostwald viscometer. Tensile tests were carried out on a TENSILON/UTM-II-20 machine with a strain rate  $4\text{ mm/min}$  at room temperature. The specimens for the test are in the size of  $40 \times 5\text{ mm}$ , and the thickness of about  $0.05\text{ mm}$ .

#### Monomer Synthesis

**Synthesis of 4-(2,4-Dinitrophenoxy)benzoic Acid Methyl Ester (I).** To a mixture containing  $25.87\text{ g}$  ( $0.17\text{ mol}$ ) of 4-hydroxybenzoic acid methyl ester,  $23.50\text{ g}$  ( $0.17\text{ mol}$ ) of potassium carbonate and  $300\text{ mL}$  of DMSO, 2,4-dinitrofluorobenzene  $32.13\text{ g}$  ( $0.17\text{ mol}$ ) were added and stirred at room temperature for 24 h. Then, the reaction mixture was poured into 1 L of cold, dilute hydrochloric acid to precipitate the product. The crude product was filtered, washed with water, and dried under vacuum at  $50^\circ\text{C}$ . The reaction mixture after work up afforded  $54.09\text{ g}$  (yield 99%). IR (KBr,  $\text{cm}^{-1}$ ): 1714 (C=O), 1539 and 1345 ( $\text{NO}_2$ ), 1246 (C–O–C).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  8.90–8.92 (m, 1H), 8.47–8.51 (m, 1H), 8.04–8.08 (d, 2H), 7.33–7.40 (m, 3H), 3.86 (s, 3H). Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_7$ : C, 52.84%; H, 3.17%; N, 8.80%. Found: C, 52.87%; H, 3.34%; N, 8.76%.

**Synthesis of 4-(2,4-Diaminophenoxy)benzoic Acid Methyl Ester (II).** A mixture of  $15.91\text{ g}$  ( $0.05\text{ mol}$ ) of 4-(2,4-dinitrophenoxy)benzoic acid methyl ester (I),  $2.70\text{ g}$  of 10% palladium-charcoal catalyst in  $300\text{ mL}$  of acetic ethyl was stirred under an atmosphere of hydrogen at room temperature for 96 h. The reaction mixture was filtered with Celite to remove palladium-charcoal.  $12.80\text{ g}$  of the compound (II) with brown colored was obtained after evaporating the filtrate under reduced pressure and drying at room temperature under vacuum for 48 h (yield 99%). IR (KBr,

$\text{cm}^{-1}$ ): 3361, 3442 (N–H); 1711 (C=O),  $1237\text{ cm}^{-1}$  (C–O–C).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  7.85–7.90 (d, 2H), 6.88–6.92 (d, 2H), 6.53–6.56 (d, 1H), 6.03–6.04 (d, 1H), 5.81–5.85 (q, 1H), 4.75 (s, 2H), 4.58 (s, 2H), 3.79 (s, 3H). Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 65.11%; H, 5.46%; N, 10.85%. Found: C, 65.12%; H, 5.46%; N, 10.66%.

**Synthesis of 4-(2,4-Diaminophenoxy)benzoic Acid (III).** In a flask,  $11.62\text{ g}$  ( $45\text{ mmol}$ ) of 4-(2,4-diaminophenoxy)benzoic acid methyl ester (II),  $15\text{ g}$  of potassium carbonate and  $150\text{ mL}$  of water were heated at  $80^\circ\text{C}$  and stirred for 24 h. After cooling to room temperature, the mixture was poured into  $300\text{ mL}$  of water and added by 6N hydrochloric acid to pH 5. The crude product was collected by filtration, washed with cold water, and dried at  $50^\circ\text{C}$  in a vacuum, giving  $10.77\text{ g}$ , yield 98%. IR (KBr,  $\text{cm}^{-1}$ ): 3382, 3472 (N–H); 1688 (C=O),  $1234\text{ cm}^{-1}$  (C–O–C).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  7.83–7.86 (d, 2H), 6.84–6.87 (d, 2H), 6.52–6.55 (d, 1H), 6.02–6.03 (d, 1H), 5.81–5.84 (q, 1H), 4.60 (–NH $_2$ ).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  101.23, 103.14, 115.11, 121.90, 123.69, 131.22, 131.29, 140.86, 146.80, 162.67, 166.94. Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$ : C, 63.93%; H, 4.95%; N, 11.47%. Found: C, 63.55%; H, 5.01%; N, 11.53%.

**Synthesis of Model Compounds: 1,3-Diamino-4-phenoxybenzene (DAPB), 4-Phenoxyphenylamine (p-APB) and 2-Phenoxyphenylamine (o-APB).** To a mixture containing  $4.75\text{ g}$  ( $0.05\text{ mol}$ ) of phenol,  $6.91\text{ g}$  ( $0.05\text{ mol}$ ) of potassium carbonate and  $100\text{ mL}$  of DMSO, 2,4-dinitrofluorobenzene  $9.31\text{ g}$  ( $0.05\text{ mol}$ ) were added and stirred at room temperature for 24 h. Then, the reaction mixture was poured into 1 L of cold, dilute hydrochloric acid to precipitate the product. The product was filtered, washed with water, and dried under vacuum at  $50^\circ\text{C}$ . The product was stirred in  $300\text{ mL}$  of acetic ethyl with  $2.70\text{ g}$  of 10% palladium-charcoal catalyst under hydrogen atmosphere at room temperature for 24 h. The reaction mixture was filtered with Celite to remove palladium-charcoal. Then, DAPB was obtained after evaporating the solvent and vacuum drying in good yield.

4-Phenoxyphenylamine (p-APB) was synthesized in the same procedures from phenol and 4-fluoronitrobenzene except the temperature was  $50^\circ\text{C}$  in the nucleophilic substitution step. 2-Phenoxyphenylamine (o-APB) was prepared as p-APB did from phenol and 2-fluoronitrobenzene.

#### Polymer Preparations

**Polyamide (PAI).** To a  $100\text{-mL}$  three-necked flask fitted with nitrogen inlet and outlet tubes were added  $3.50\text{ g}$  ( $14.3\text{ mmol}$ ) of 4-(2,4-diaminophenoxy)benzoic acid (III),  $6.59\text{ g}$  ( $17.2\text{ mmol}$ ) of (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonic acid diphenyl ester

(**DBOP**), 1.74 g (17.2 mmol) of triethylamine, and 50 mL of NMP through nitrogen. The reaction mixture was stirred for 3 h at room temperature. The resulting solution was poured into 1000 mL of methanol containing 0.1 wt % lithium chloride (0.1 wt % LiCl/CH<sub>3</sub>OH), and precipitated polymer was washed by refluxing methanol and collected by filtration. The product (**PA1**) was dried overnight at room temperature under vacuum, giving 3.01 g: 93% yield. IR (KBr, cm<sup>-1</sup>): 1652 (C=O, amide).

**Polyamide (PA2).** In a flask, 7.00 g (28.6 mmol) of 4-(2,4-diaminophenoxy)benzoic acid was dissolved in 50 mL of NMP, then 2.3 mL (30 mmol) of pyridine and 7.8 mL (30 mmol) of triphenylphosphite were charged into the flask. The solution was heated to 100 °C and stirred under nitrogen for 3 h. After the temperature decreased to room temperature, the solution was slowly poured into 1000 mL of methanol containing 0.1 wt % lithium chloride (0.1 wt % LiCl/CH<sub>3</sub>OH), and precipitated polymer was washed by refluxing methanol and collected by filtration. The product (**PA2**) was dried overnight at room temperature under vacuum, giving 5.49 g: 85% yield. IR (KBr, cm<sup>-1</sup>): 1655 (C=O, amide).

**Amino Groups Modification of Polyamides PA1 and PA2 to Form PA1-a-PA1-c and PA2-a-PA2-c Amide-modified Polymers (PA1-a, PA1-b, PA2-a and PA2-b).** A typical experimental procedure for the synthesis of **PA1-a** from **PA1** is as follows:

A mixture of 0.5 g of **PA1**, 0.25 mL (3 mmol) of acetyl chloride, and 5 mL of NMP was stirred at room temperature for 2 h under nitrogen atmosphere, and then poured into 100 mL of methanol containing 0.1 wt % LiCl to precipitate the product. The product was filtered, washed with refluxing methanol, and dried overnight at room temperature under vacuum. IR (KBr, cm<sup>-1</sup>): C=O, amide: 1656 for **PA1-a**, 1654 for **PA1-b**.

**Imide-modified Polymer (PA1-c and PA2-c).** A typical experimental procedure for the synthesis of **PA1-c** from **PA1** is as follows:

A mixture of 0.5 g of **PA1**, 0.36 g (2.5 mmol) phthalic

anhydride and 5 mL NMP was stirred at room temperature for 2 h under nitrogen atmosphere. Then, 0.23 mL (2.5 mmol) of acetic anhydride, and 0.18 mL (2.5 mmol) of pyridine were added to the reaction mixture and temperature of the reaction mixture was raised to 100 °C and continuously stirred for 24 h. After cooling to room temperature, the mixture was poured into 100 mL of methanol containing 0.1 wt % LiCl. The product was precipitated, filtered, washed with refluxing methanol, and dried overnight at 120 °C under vacuum. IR (KBr, cm<sup>-1</sup>): 1654 (C=O, amide) and 1725, 1786 (C=O, imide).

**Model Reactions.** A mixture of amino compound (DAPB, p-APB or o-APB) and required benzoic acid was added in NMP under nitrogen atmosphere. 1.2 equivalent of (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonic acid diphenyl ester (**DBOP**), triethylamine relative to benzoic acid were added in the solution. The reaction mixture was stirred for 3 h at room temperature. The resulting solution was poured into water, and precipitated compounds were collected by filtration.

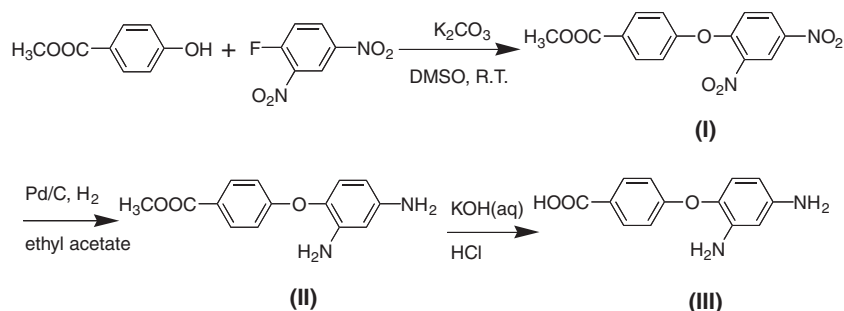
#### Films Preparation

A solution of 0.2 g of polymer in 1.0 mL of DMF was prepared. After filtration with a 0.5 μm filter, the solution was cast on a glass plate and heated at 100 °C for 1 h, 200 °C for 1 h and 300 °C for another hour in vacuum. Films were peeled from the glass plate by soaking in boiling water.

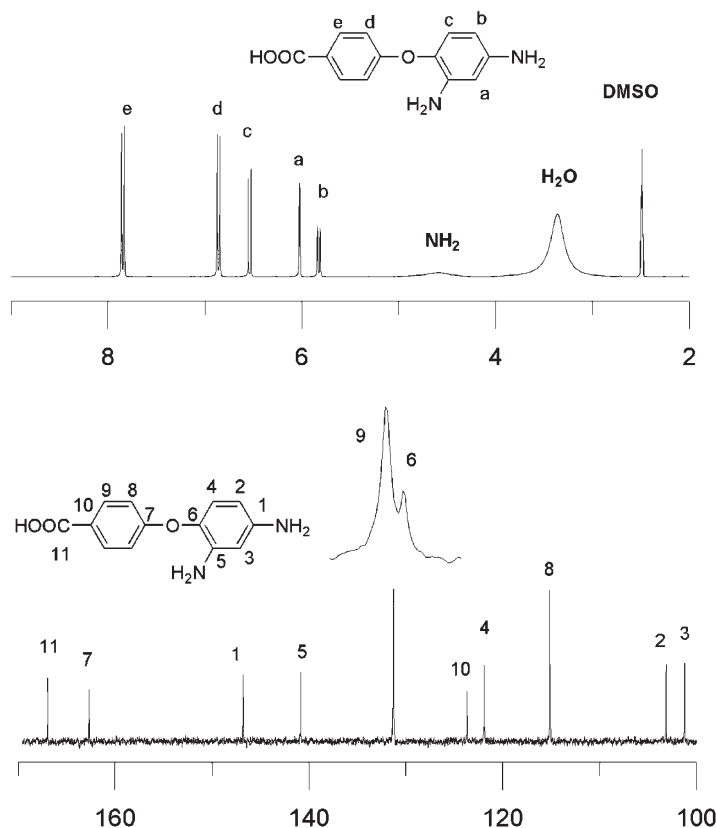
## RESULTS AND DISCUSSION

#### Monomer Synthesis

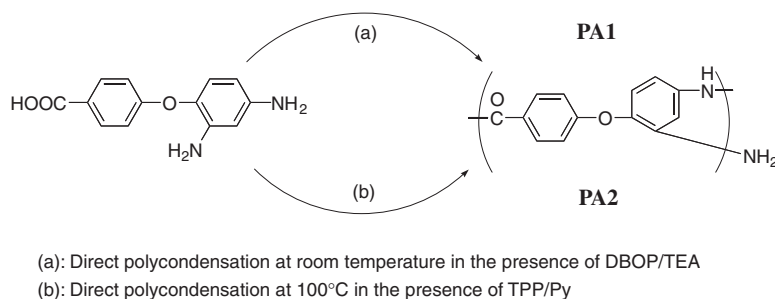
An ABB' type monomer, 4-(2,4-diaminophenoxy)benzoic acid (**III**), was prepared starting from 4-hydroxybenzoic acid methyl ester and 2,4-dinitrofluorobenzene, as shown in Scheme 1. 4-(2,4-Diaminophenoxy)benzoic acid methyl ester (**II**) was prepared by the catalytic reduction of 4-(2,4-dinitrophenoxy)benzoic acid methyl ester (**I**), which was derived by nucleophilic substitution of 4-hydroxybenzoic acid



Scheme 1.



**Figure 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of ABB' monomer (III) in  $\text{DMSO-}d_6$  at room temperature.



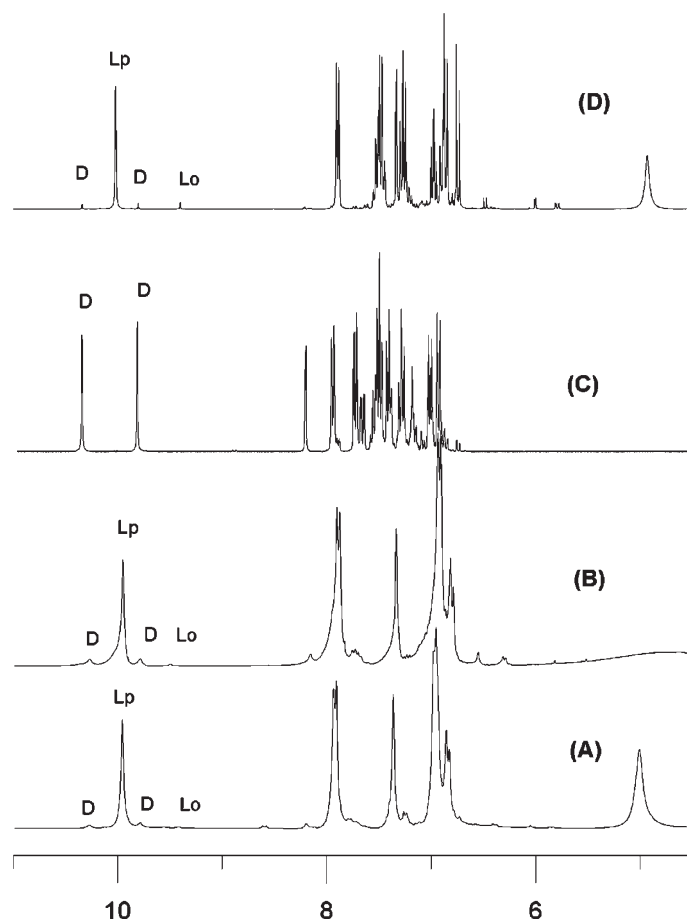
**Scheme 2.**

methyl ester with 2,4-dinitrofluorobenzene in the presence of potassium carbonate. Subsequent basic hydrolysis reaction of **II** in the potassium hydroxide aqueous gave 4-(2,4-diaminophenoxy)benzoic acid (**III**). The structure of the ABB' type monomer (**III**) as well as the intermediates was confirmed by elementary analysis, infrared spectra (IR), and  $^1\text{H}$  NMR spectra. The IR spectrum of **III** showed characteristic absorptions at 3382, 3472  $\text{cm}^{-1}$  due to NH stretching vibration and at 1688  $\text{cm}^{-1}$  due to carbonyl group of carboxylic acid. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **III** are presented in Figure 1 with peak assignments. The individual positions of chemical shifts for the aromatic protons were assigned distinctly one by one taking the shield effect into account. The  $^{13}\text{C}$  NMR spectrum of **III** exhibited 11 signals in the range  $\delta$

(ppm) 110.23–166.94. All these results confirm the structure of **III** to be proposed.

#### Polymer Syntheses

Direct polycondensations of the monomer were carried out in two different conditions as shown in Scheme 2. The direct polycondensation carried out in the presence of DBOP and triethylamine as condensation agents at room temperature gave polymer **PA1**, shown as route (a). The direct polycondensation of ABB' monomer was conducted at 100°C under nitrogen in the presence of triphenylphosphite and pyridine as condensing agents, giving a gray white polymer (**PA2**), shown as route (b). The absorption of 1652  $\text{cm}^{-1}$  attributed to the amide group were observed in the IR spectra of **PA1**. The NMR spectra of **PA1**

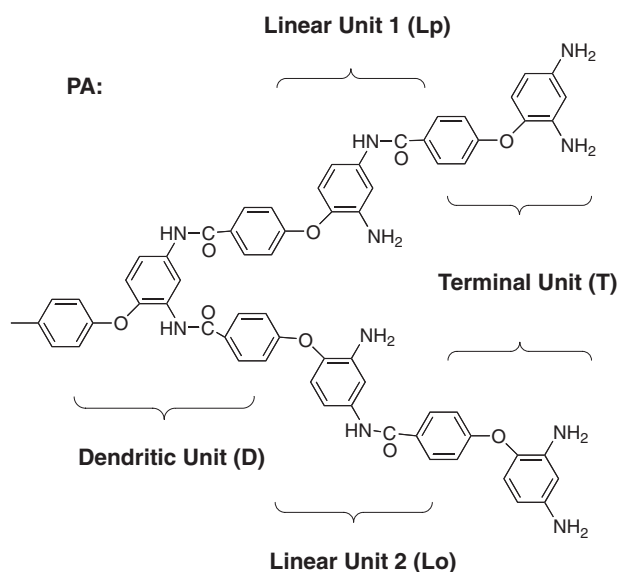


**Figure 2.**  $^1\text{H}$  NMR spectra of polymers (A) PA1 (B) PA2, and resulting mixture by the reaction of DBAP and benzoic acid in the ratios of (C) 1:2 (D) 1:1.

and **PA2** were similar as shown in Figure 2 (A and B spectra). In the  $^1\text{H}$  NMR spectrum of **PA1** (spectrum A in Figure 2), a major peak and three minor peaks at 9.43–10.29 ppm for amide protons, a peak at 5.02 ppm for the free amine end groups were observed.

In order to assign the peaks of amides (9.43–10.29 ppm) and calculate the degree of branching (DB), the model reactions for dendritic compound and competitive reaction of para- and ortho-amino groups were carried out by benzoic acid and a model diamine compound 1,3-diamino-4-phenoxybenzene (**DAPB**), which was synthesized by the nucleophilic substitution of phenol and 2,4-dinitrofluorobenzene in the presence of potassium carbonate and subsequent reduction of the nitro groups.<sup>3</sup> 4-Phenoxyphenylamine (**p-APB**) and 2-phenoxyphenylamine (**o-APB**) were also synthesized by the same procedure of **DAPB**. The reaction of **DAPB** and benzoic acid in the molar ratio of 1:2 gave a dendritic model compound. The  $^1\text{H}$  NMR of resulting mixture (spectrum C in Figure 2) showed two peaks at 10.37 and 9.84 ppm for the amide protons arose from para-amide and ortho-amide of dendritic structure. The competitive reaction of **DAPB** and benzoic acid (1:1) was also car-

ried out to investigate the relative reactivity of para- and ortho-amino groups. In the  $^1\text{H}$  NMR spectrum of resulting mixture (spectrum D in Figure 2), two minor peaks at 10.37, 9.84 ppm, one major peak at 10.12 ppm, and one minor peak at 9.52 ppm were observed. The two minor peaks at 10.37 and 9.84 ppm were attributed to the amide proton of ortho-reacted compound. *N*-(4-Phenoxy-phenyl)-benzamide and *N*-(2-phenoxy-phenyl)-benzamide were synthesized from **p-APB** and **o-APB** with benzoic acid, and these two amide proton peaks were observed at 10.15 and 9.58 ppm, respectively. Therefore, the major peak at 10.12 ppm was assigned to the amide proton of para-reacted compound and the minor peak at 9.52 ppm was the amide proton of ortho-reacted compound. The possible structure units of the present polyamide derived from ABB' type monomer **III** is shown in Scheme 3. Comparing the  $^1\text{H}$  NMR spectrum of **PA1** (spectrum A in Figure 2) with those of model mixtures, a major amide peak at 9.97 ppm was assigned to amide proton of para-reacted amide of linear unit ( $L_p$ ) and three minor peaks at 10.29, 9.80 ppm and 9.43 ppm were assigned to amide protons of dendritic unit (**D**) and ortho-amine reacted linear unit

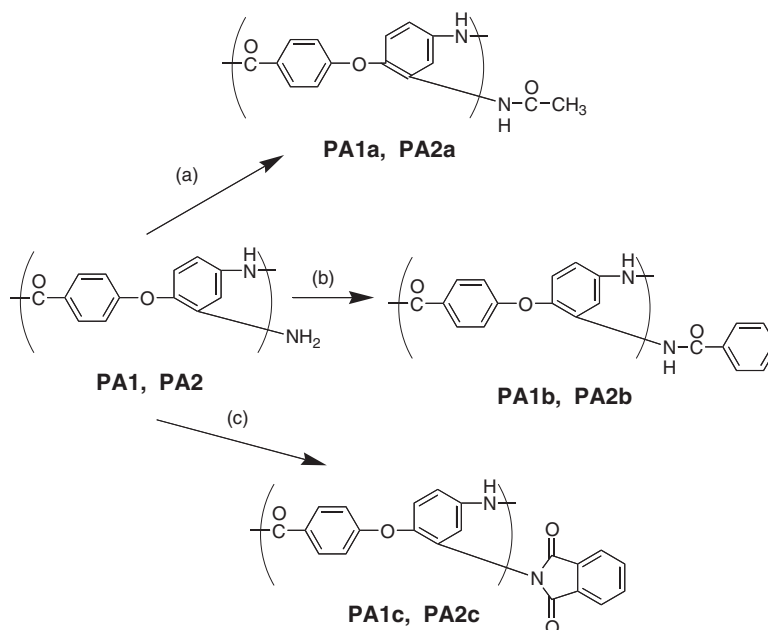


Scheme 3.

(L<sub>o</sub>), respectively. The DB of Frey equation<sup>4</sup> was modified to be  $DB = (2D)/(2D + L_p + L_o)$  for this case. From the integration of characteristic proton peaks (D, L<sub>p</sub> and L<sub>o</sub>), the DB was calculated to be 0.1. The IR spectrum of PA2 was determined to be similar with that of polymer PA1. The structure of PA2 was also confirmed by <sup>1</sup>H NMR, as shown in Figure 2B. The DB of PA2 was determined by the same manner as that of PA1 and calculated to be 0.2. The proton peaks attributed to the terminal unit at 6.56 and 6.31 ppm (relative to the peaks a and b

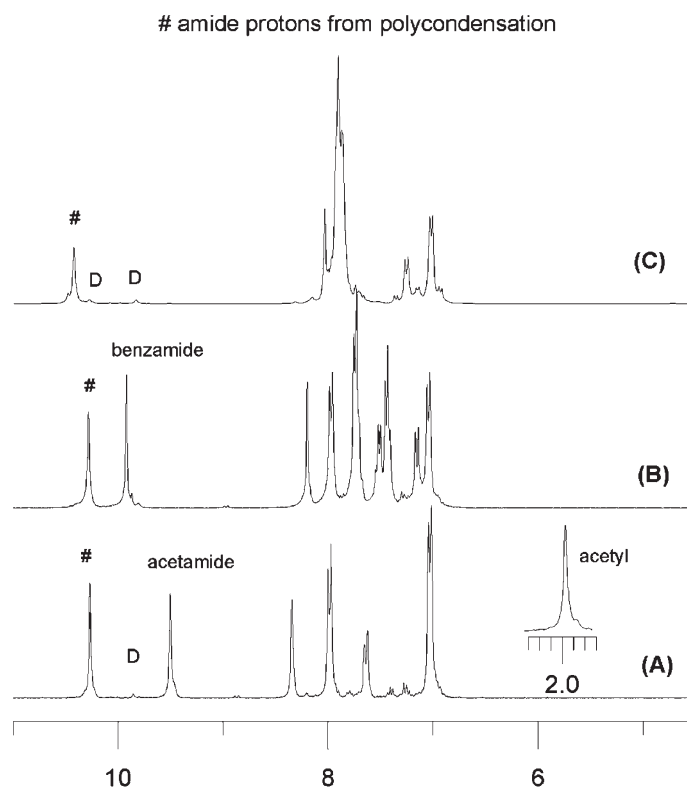
in Figure 1) were obviously observed. The result also means PA2 had higher DB than PA1.

As shown in Scheme 4, the free amine groups of PA1 and PA2 were reacted using acetyl chloride and benzoyl chloride as modification agents to prepare amide-modified polyamides (PA1a, PA2a, PA1b, PA2b). PA1 and PA2 were also reacted with phthalic anhydride to afford an imide-modified polyamide (PA1c and PA2c). IR spectra of amide-modified polyamides (PA1a, PA2a, PA1b and PA2b) showed characteristic absorptions at about 1655 cm<sup>-1</sup>. Imide-modified polyamide PA1c showed characteristic absorptions at 1786 and 1725 cm<sup>-1</sup> for functionalized imide and the amide characteristic absorption attributed to polycondensation shifted to 1664 cm<sup>-1</sup>. PA2c showed the similar IR spectrum with PA1c. The <sup>1</sup>H NMR spectra of modified polyamides from PA2 were similar to PA1. As an example, PA1a–PA1c are shown in Figure 3. The peak at 5.02 ppm for the free amine end group in <sup>1</sup>H NMR spectrum of PA1 (spectrum A in Figure 2) disappeared due to the functional-modification. In the spectrum of PA1a, new peaks at 9.50 and 1.98 ppm attributed to acetamide proton and acetyl group protons were observed. In addition, amide proton peak at 9.97 ppm attributed to polycondensation shifted to 10.28 ppm due to the modification. In the spectrum of PA1b, amide proton peak attributed to polycondensation shifted to 10.29 ppm and a new peak at 9.92 ppm attributed to benzamide proton was observed. In the spectrum of PA1c, amide proton peak attributed to polycondensa-



(a) Acetyl chloride, NMP, room temp., 2h (b) Benzoyl chloride, NMP, room temp, 2h  
(c) Phthalic anhydride, NMP, room temp., 2h; Acetic anhydride/pyridine, 100°C, 24h

Scheme 4.



**Figure 3.**  $^1\text{H}$  NMR spectra of end-modified polymers: (A) PA1a, (B) PA1b, (C) PA1c.

tion shifted to 10.50 ppm due to the modification. In addition, the amide proton peaks of dendritic structure (**D**), which were not affected by the modification, were also observed at 9.80 and 10.29 ppm in the spectrum of **PA1c**. However, in the spectra of **PA1a** and **PA1b**, one of the dendritic peaks at 10.29 was overlapped by the amide proton peak attributed to the main chain polyamide by polycondensation. The integrations of  $^1\text{H}$  NMR indicated that the modifications proceeded quantitatively.

The results of polymerizations and modifications are summarized in Table I. The polymers with lower

DB (**PA1** and **PA1a–c**) were prepared with weight-average molecular weight of 64000–74000, while the polymers with higher DB (**PA2** and **PA2a–c**) were prepared with weight average molecular weight of 39000–51000. The different reaction conditions resulted in different molecular weights. Also, the polyamides with lower DB, except **PA1c**, had higher inherent viscosities than polyamides with higher DB. All the polymers exhibit shape factor ( $\alpha$ ) higher than 0.5 and polymers with lower DB have higher shape factor. These data indicated the higher branching structures have lower entanglement of polymers. **PA1c**, whose terminal groups are larger, showed lower viscosity and lower shape factor. The reason has not been understood clearly. But it seems that the larger terminal groups diminished the chain entanglement.

Thermal properties and solubility of the resulting polyamides are summarized in Table II. The glass transition temperatures and 5% weight loss temperatures of the modified polyamides depended on the structure of end groups. However, the thermal properties were not influenced by the different DBs in range of 0.1–0.2. The resulting polymers were soluble in DMSO, DMF and NMP. These results are consistent with the results of polyamides with different DBs in the range of 0.32–0.84 derived from monomers contained prefabricated dendritic units.<sup>5</sup>

Films were cast from DMF solutions on glass plates. The mechanical properties of the films were

**Table I.** Preparations of polyamides and modified polyamides

Polymer	Yield (%)	$\eta_{\text{inh}}^{\text{a}}$	$M_{\text{w}}^{\text{b}}$	$M_{\text{w}}/M_{\text{n}}^{\text{b}}$	$\alpha^{\text{c}}$
<b>PA1</b>	93	0.73	63500	2.5	0.632
<b>PA1a</b>	93	0.73	64900	2.4	0.622
<b>PA1b</b>	95	0.66	72600	2.6	0.591
<b>PA1c</b>	95	0.39	74000	2.5	0.536
<b>PA2</b>	85	0.31	38700	1.9	0.594
<b>PA2a</b>	79	0.32	46600	1.8	0.619
<b>PA2b</b>	79	0.34	49200	1.9	0.578
<b>PA2c</b>	81	0.31	50600	2.0	0.527

<sup>a</sup>Measured at a concentration of 0.5 g/dL in NMP at 30 °C.

<sup>b</sup>Measured by GPC measurements in DMF containing 0.01 M LiBr with a triple detector array and determined using Viscotek TriSEC software. <sup>c</sup>Shape factor of Mark–Houwink equation.

**Table II.** Thermal properties and solubility of polyamides and modified polyamides

Polymer	$T_g$ (°C) <sup>a</sup>	$T_5$ (°C) <sup>b</sup>	Solubility <sup>d</sup>			
			DMSO	DMF	NMP	THF
<b>PA1</b>	n.o. <sup>c</sup>	367	++	++	+– <sup>e</sup>	–
<b>PA2</b>	n.o.	364	++	++	++	–
<b>PA1a</b>	237	327	++	++	++	–
<b>PA2a</b>	237	334	++	++	++	–
<b>PA1b</b>	246	362	++	++	++	–
<b>PA2b</b>	245	365	++	++	++	–
<b>PA1c</b>	290	456	++	++	++	–
<b>PA2c</b>	289	449	++	++	++	–

<sup>a</sup>Determined by DSC at a heating rate of 10 °C/min in nitrogen on second heating. <sup>b</sup> $T_5$  (5 wt % loss temperature) was determined by TG at a heating rate of 10 °C/min in nitrogen <sup>c</sup>Not observed <sup>d</sup>++: soluble at room temperature, +–: partially soluble, –: insoluble at room temperature; <sup>e</sup>soluble at heating

**Table III.** Mechanical properties of polyamides films<sup>a</sup>

Polymer	Appearance	Peel up	Strength (MPa)	Elongation (%)	Modulus (GPa)
<b>PA1</b>	C <sup>b</sup>	Yes	308	10	6.1
<b>PA1a</b>	C	Yes	171	4	5.0
<b>PA1b</b>	C	Yes	93	3	4.0
<b>PA1c</b>	C	No	—	—	—
<b>PA2</b>	C	Yes	200	4	6.3
<b>PA2a</b>	C	Yes	— <sup>d</sup>	—	—
<b>PA2b</b>	C	Yes	—	—	—
<b>PA2c</b>	D <sup>c</sup>	No	—	—	—

<sup>a</sup>Films were prepared from polymer solutions of DMF

<sup>b</sup>Continuous film <sup>c</sup>Discontinuous film <sup>d</sup>the continuous film exhibited poor physical properties with no mechanical strength

presented in Table III. All of the polyamides formed continuous films except **PA2c**. The film formed from **PA1c** was continuous but could not be peeled up continuously. **PA2a** and **PA2b** could be peeled up, but the continuous films exhibited poor physical properties with no mechanical strength. The ability of film forming is relation to the chain entanglements. The polyamides with amino end groups (**PA1** and **PA2**) had

the stronger tensile properties. The strong tensile strength might be caused from the hydrogen bonding of the amino groups. The lower DB polyamides showed better ability of film forming and higher tensile strength than the higher polyamides with the same terminal groups.

## CONCLUSIONS

Hyperbranched polyamides with different DBs were prepared by using DBOP/TEA as condensing agents at room temperature and TPP/Py at 100 °C from an ABB' type monomer. The thermal properties and solubility of the modified polyamides were not influenced by the different DBs, but were influenced by the structure of end groups. Strong films could be prepared from low degree of branching polymers and polymers with amino end groups.

## REFERENCES

1. Y. H. Kim and O. W. Webster, *Macromolecules*, **25**, 5561 (1992).
2. M. Jikei and M. Kakimoto, *Prog. Polym. Sci.*, **26**, 1233 (2001).
3. K.-L. Wang, M. Jikei, and M.-A. Kakimoto, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 3200 (2004).
4. D. Hölter, A. Burgath, and H. Frey, *Acta Polym.*, **48**, 30 (1997).
5. Y. Ishida, A. Sun, M. Jikei, and M.-A. Kakimoto, *Macromolecules*, **33**, 2832 (2000).
6. E. Malmström, M. Johansson, and A. Hult, *Macromolecules*, **28**, 1698 (1995).
7. P. Bharathi and J. S. Moore, *Macromolecules*, **33**, 3212 (2000).
8. M. Suzuki, A. Ii, and T. Saegusa, *Macromolecules*, **25**, 7071 (1992).
9. M. Suzuki; S. Yoshida, K. Shiraga, and T. Saegusa, *Macromolecules*, **31**, 1716 (1998).
10. L. J. Hobson and W. J. Feast, *Polymer*, **40**, 1279 (1999).
11. D. S. Thompson, L. J. Markoski, and J. S. Moore, *Macromolecules*, **33**, 6412 (2000).