

# Synthesis and Properties of Hyperbranched Polyamides Containing Fluoroalkyl Groups at the Branch Ends

Ayu Sugiyama, Ryohei Hayakawa, Yu Nagase

Department of Applied Chemistry, Graduate School of Engineering, Tokai University,  
1117, Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan,  
Tel: +81-463-58-1211, Fax: +81-463-51-2012, e-mail: yunagase@keyaki.cc.u-tokai.ac.jp

Hyperbranched aromatic polyamides with carboxyl groups at the chain ends were synthesized by polycondensation of a few  $AB_x$  ( $AB_2$ ,  $AB_4$ ,  $AB_8$ ) type monomers based on 5-(4-aminophenoxy)isophthalic acid, which consisted of different degree of branch (DB). Then, a fluoroalkyl group was introduced into the branch ends by a polymer reaction of the hyperbranched polyamide with 2-perfluorobutylethanol. In addition, the surface properties of the polymer films were investigated by XPS analysis and measurements of contact angle of water and diiodomethane. It was found that the surface properties were affected by the degree of branch, where the hyperbranched polymer having  $DB=0.72$  containing fluoroalkyl group exhibited the very low surface free energy.

Key words: Hyperbranched polymer/ Aromatic polyamide/ Fluoroalkyl group/ Degree of branch/ Surface property

## 1. INTRODUCTION

Recently, dendritic macromolecules, such as dendrimers and hyperbranched polymers, have been paid much attention due to their unique shapes and physical properties, for example, the end group-rich structure, the low viscosity and higher solubility compared to linear polymers [1-4]. It is also well-known that dendrimers and hyperbranched polymers are generally amorphous, even if the linear analogues are known as crystalline polymers. On the other hand, the hyperbranched polymer are synthesized by one-step polymerization using  $AB_x$  monomer ( $x \geq 2$ ), while the dendrimers are usually synthesized by stepwise reaction with several steps. Therefore, hyperbranched polymers are suitable to synthesize a large-scale production and wide range of applications. Hyperbranched polymers are not composed of a uniform structure, which consist of three sorts of unit structures, such as dendritic, linear, and terminal units, and the ratio of dendritic and terminal units against all units is called a degree of branch (DB). In addition, the several functional groups could be easily introduced into the linear and terminal units of hyperbranched polymers, where the polymer surface would be efficiently covered with the functional groups of the branch ends.

M. Jikei *et al.* have investigated the preparations of hyperbranched polycondensation type aromatic polymers, such as polyamide and polyimide, and the effect of linear and branch structures on physical properties [5-8]. We have been studying the preparation of hyperbranched aromatic polyamides by polycondensations of  $AB_2$ ,  $AB_4$ , and  $AB_8$  type monomers, for the purpose of controlling the degree of branch and investigating the effect of branch structures on the physical properties of polymers. In this study, the introduction of a fluoroalkyl group into the branch ends of hyperbranched aromatic polyamide was carried out by a polymer reaction based on the esterification. Furthermore, the surface property of hyperbranched polyamides having different degree of branch with a fluoroalkyl group at the branch ends was investigated to reveal the effect of the degree of branch on the surface property of hyperbranched polymers.

## 2. EXPERIMENTAL

### 2.1 Synthesis of methyl 5-(4-nitrophenyloxy)isophthalate (1)

$K_2CO_3$  (6.46 g, 47.5 mmol) was added to a solution of methyl 5-hydroxyisophthalate (10.0 g, 47.5 mmol) and *p*-fluoronitrobenzene (5 ml, 47.5 mmol) in 95 ml of DMSO. Under an argon atmosphere, the mixture was stirred for overnight at r. t., and it was poured into excess water to precipitate the product. Then, the obtained product was purified by recrystallization with chloroform/hexane.

Yield: 13.1 g (83.4 %).

$^1H$ -NMR,  $\delta$  (400 MHz,  $CDCl_3$ , ppm): 3.96 (6H, s), 7.05 (1H, d,  $J=2.20$  Hz), 7.07 (2H, d,  $J=2.20$  Hz), 7.94 (2H, d,  $J=1.47$  Hz), 8.25 (2H, m); IR,  $\nu$  (KBr,  $cm^{-1}$ ): 3098, 2955, 2849, 1730 (C=O), 1606, 1520 (C=C), 1342 ( $NO_2$ ), 1238, 1110 (C-O-C).

### 2.2 Synthesis of 5-(4-nitrophenyloxy)isophthalic acid (2)

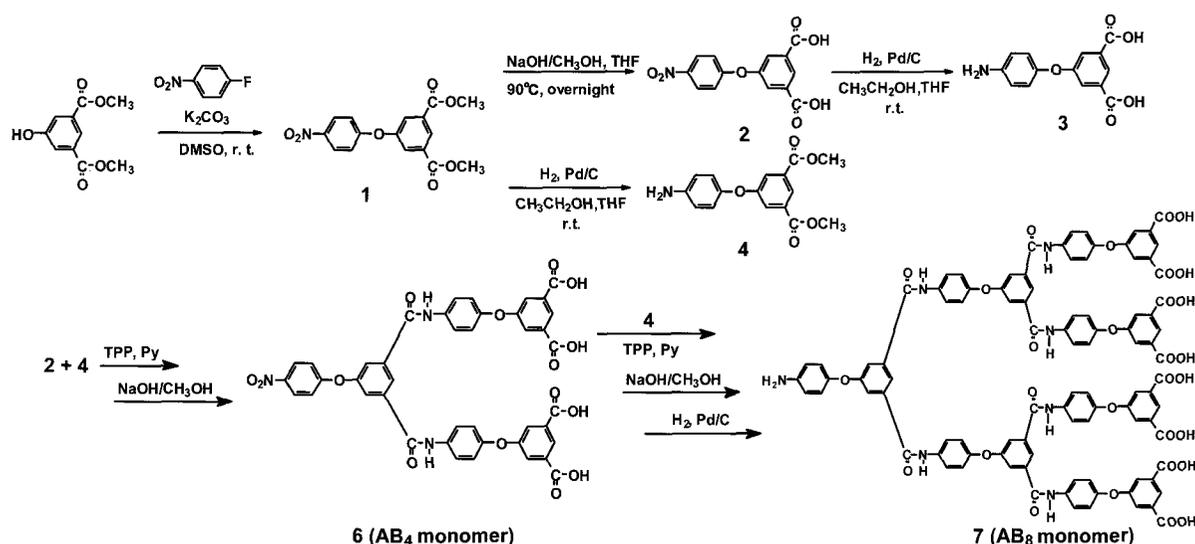
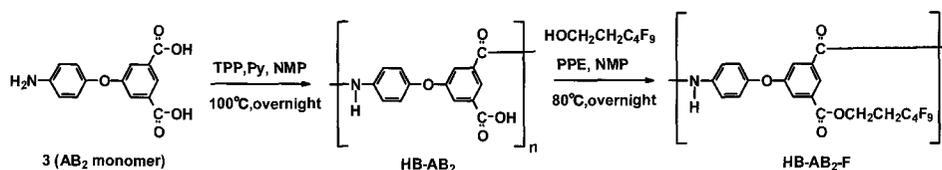
Compound **1** (7.00 g, 21.1 mmol) was dissolved in 100 ml of THF, and the solution of NaOH (6.00 g, 150 mmol) dissolved in 150 ml of methanol was added. After the mixture was refluxed for 30 min, the mixture was dissolved into excess water, and conc. HCl was added until it became acidic to afford **2** as a white powder.

Yield: 6.21 g (94.4 %).

$^1H$ -NMR,  $\delta$  (400 MHz,  $CDCl_3$ , ppm): 2.52 (2H, d,  $J=0.977$  Hz), 7.22 (2H, d,  $J=8.55$  Hz), 7.84 (2H, m), 8.25 (1H, d,  $J=0.977$  Hz); IR,  $\nu$  (KBr,  $cm^{-1}$ ): 3080-2554, 1701 (C=O), 1610 (C=C), 1411 (OH), 1585, 1342 ( $NO_2$ ), 1371, 1256 (C-O), 1101 (C-O-C).

### 2.3 Synthesis of 5-(4-aminophenyloxy)isophthalic acid (3, $AB_2$ monomer)

Compound **2** (2.50 g, 8.25 mmol) was dissolved in 100 ml of THF and 100 ml of ethanol, and 5% Pd/C powder (0.351 g, 0.165 mmol) was suspended in the solution. Then, the reaction vessel was purged with hydrogen and the mixture was stirred at r. t. for overnight. After Pd/C was filtered off, the solvents were removed

Scheme 1 Syntheses of AB<sub>2</sub>, AB<sub>4</sub> and AB<sub>8</sub> monomers.Scheme 2 Syntheses of hyperbranched polymers (HB-AB<sub>2</sub> and HB-AB<sub>2</sub>-F<sub>4</sub>).

under reduced pressure to obtain **3** as a white powder.

Yield: 2.20 g (98.2 %).

<sup>1</sup>H-NMR,  $\delta$  (400 MHz, CDCl<sub>3</sub>, ppm): 6.64 (2H, d,  $J=8.30$  Hz), 6.81 (2H, d,  $J=6.84$  Hz), 7.55 (2H, s), 8.21 (1H, s); IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3422 (N-H), 2871, 1701 (C=O), 1587, 1506 (C=C), 1304 (C-O), 1252 (COC), 1204 (C-N).

#### 2.4 Synthesis of methyl 5-(4-aminophenoxy)-isophthalate (**4**)

Compound **4** was prepared from **1** by the similar reduction as the procedure to prepare **3**, which was an intermediate of AB<sub>4</sub> and AB<sub>8</sub> monomers.

Yield: 5.00 g (87.9 %).

<sup>1</sup>H-NMR,  $\delta$  (500 MHz, CDCl<sub>3</sub>, ppm): 3.91 (6H, s), 6.79 (2H, d,  $J=8.75$  Hz), 6.87 (2H,  $J=8.73$  Hz), 7.75 (2H, s), 8.33 (1H, s); IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3450, 3369 (N-H), 2951, 1726 (C=O), 1595, 1510 (C=C), 1259 (C-O-C).

#### 2.5 Syntheses of AB<sub>4</sub> and AB<sub>8</sub> monomers (**5** and **6**)

AB<sub>4</sub> and AB<sub>8</sub> monomers were prepared by condensation of **2** with **4**, followed by the hydrolysis of methyl ester unit and the hydrogenised reduction of the nitro group similar to the procedure to prepare **2** and **3**. The typical procedure of the condensation reaction was as follows;

To a solution of **2** (0.60 g, 1.99 mmol) and **4** (1.50 g, 4.98 mmol) in 7.00 ml of NMP, triphenyl phosphate (TPP, 1.37 ml) and pyridine (Py, 0.41 ml) were added. Then, the mixture was stirred at 100°C for 24 hours. The product was obtained after the reprecipitation of this solution into excess methanol.

Yield: 2.78 g (95.2%).

<sup>1</sup>H-NMR,  $\delta$  (400 MHz, DMSO, ppm): 7.11 (4H, m), 7.55 (4H, m), 7.74 (4H, m), 7.89 (4H, m), 7.97 (2H, m),

8.05 (2H, m), 8.11 (2H, m), 8.19 (2H, m), 8.24 (1H, s), 10.4 (2H, d); IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3380 (N-H), 1724 (C=O), 1652 (C=C), 1328 (NO<sub>2</sub>), 1238 (C-O-C).

#### 2.6 Polymerizations

Hyperbranched polyamides were prepared by polycondensations of AB<sub>2</sub>, AB<sub>4</sub> and AB<sub>8</sub> monomers. The typical procedure of the polymerization of AB<sub>2</sub> monomer was described below.

**3** (2.00 g, 7.33 mmol), TPP (4.03 ml, 14.7 mmol), and Py (1.19 ml, 14.7 mmol) were dissolved in 7.33 ml NMP, the mixture was degassed for 1 hour until reduced pressure. And then it was stirred at 100°C for 24 hours under an argon atmosphere. Finally, the solution was poured into excess amount of methanol containing 0.1 wt.% of lithium chloride, and the reprecipitations from its NMP solution to methanol were carried out a few times to remove the condensation reagents.

Yield; 1.87 g (93.5%).

IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3315 (N-H), 3069, 1719 (C=O), 1589, 1504 (C=C), 1458, 1408 (C-N), 1296, 1213 (C-O-C).

#### 2.7 Polymer reactions

Fluorinated hyperbranched polyamides were prepared by esterifications of HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub> with 2-perfluorobutylethanol. The typical procedure of the polymer reaction to prepare HB-AB<sub>2</sub>-F<sub>4</sub> was described below. The condensation reagent, poly(phosphoric ester) (PPE), was prepared according to the literature [9].

HB-AB<sub>2</sub> (0.3 g, 1.1 mmol), 2-perfluorobutylethanol (0.44 ml, 5.5 mmol) and PPE (2.39 ml) was dissolved in 3.7 ml of NMP. Under an argon atmosphere, the mixture was stirred for overnight at 80°C. Then, the mixture was poured into methanol to precipitate the polymer.

Yield; 0.31 g (95%).

IR,  $\nu$  (KBr,  $\text{cm}^{-1}$ ): 3367 (N-H), 3076, 1739 (C=O), 1591, 1506 (C=C), 1458, 1408 (C-N), 1312 (C-O), 1194 (C-O-C), 1136 (C-F).

## 2.20 Characterization

$^1\text{H-NMR}$  spectra were conducted with a BRUKER Ultra Shield AVANCE 500 MHz FT-NMR and the chemical shifts were estimated in ppm units with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded with a Shimadzu FTIR-8400 spectrometer. Gel permeation chromatography (GPC) was carried out to determine the number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights with a Tohso HCL-802A instrument by using THF as eluent, equipped with four columns of TSK gels G5000H<sub>6</sub>, G4000H<sub>6</sub>, G3000H<sub>6</sub> and G2000H<sub>6</sub>. The elution was detected by RI and Laser light scattering detectors using Tohso LS-8000. The surfaces of polymer films were analyzed with an X-ray photoelectron spectroscope (ULVAC-PHI Quantum 2000 XPS). The take-off angle of photoelectrons was adjusted to be 90 degree. The measurement of contact angle was conducted at r. t. with DROPMASTER 700 by Kyowa Interface Science.

## 3. RESULTS AND DISCUSSION

### 3.1 Preparation of hyperbranched aromatic polyamides.

The synthetic routes of AB<sub>2</sub>, AB<sub>4</sub> and AB<sub>8</sub> monomers were shown in Scheme 1. Starting material, **1**, was prepared from methyl 5-hydroxyisophthalate and *p*-fluoronitrobenzene by the conventional Williamson etherification. Then, the intermediates for the monomers, **2** and **4**, were prepared by the hydrolysis of the ester unit and reduction reaction of nitro group, respectively, and AB<sub>2</sub> monomer, **3**, was easily obtained by the similar reduction of **2**. On the other hand, AB<sub>4</sub> and AB<sub>8</sub> monomers were prepared in high yields by the condensation of **2** and **4**, followed by the hydrolysis and the reduction. From these monomers, three kinds of hyperbranched polyamides with different degree of branch, HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub>, were obtained easily by an ordinary polycondensation using triphenyl phosphate and pyridine as condensation reagents. The yields and molecular weights of these polymers are summarized in Table 1.

All of the obtained polymers were soluble in THF and aprotic polar solvents such as NMP, DMF and DMSO, but insoluble in water and other ordinary organic solvents. The solubility of polymers would be due to the backbone component which consisted of aromatic polyamide. In general, aromatic polyamides were hardly soluble in THF, therefore, the solubility of the obtained polymers would be due to their branch structures. The degree of branch (DB) of the polymers was estimated by the ratio of peak intensities in  $^1\text{H-NMR}$  spectra, where the three peaks derived from amide protons of terminal, linear, and dendritic units were observed at 10.6, 10.5 and 10.4 ppm, respectively, as shown in Fig. 1. As listed in Table 1, the degree of branch of the hyperbranch polyamides could be efficiently controlled by changing the monomer structures.

Next, the introduction of perfluorobutyl group into the branch ends of these hyperbranched polyamides was

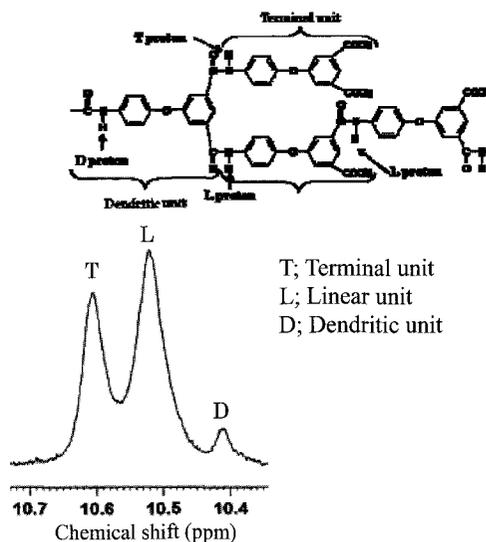


Fig. 1  $^1\text{H-NMR}$  spectrum of amide protons of HB-AB<sub>2</sub>.

Table 1 Characterizations of hyperbranched polyamides.

Code	Yield (%)	$M_w$ ( $\times 10^4$ ) <sup>a)</sup>	DB <sup>b)</sup>	DS (mol%) <sup>c)</sup>
HB-AB <sub>2</sub>	93.5	1.33	0.44	-
HB-AB <sub>2</sub> -F <sub>4</sub>	95.0	4.15	-	88.5
HB-AB <sub>4</sub>	80.8	3.39	0.72	-
HB-AB <sub>4</sub> -F <sub>4</sub>	98.1	3.62	-	60.4
HB-AB <sub>8</sub>	96.0	4.11	0.83	-
HB-AB <sub>8</sub> -F <sub>4</sub>	95.2	5.07	-	75.0

a) Determined by GPC, detected by laser light scattering detector based on polystyrene standards. b) Degree of branch, which was estimated by  $^1\text{H-NMR}$ . c) Degree of substitution, which was estimated by  $^1\text{H-NMR}$ .

carried out by the esterification using poly(phosphoric ester) (PPE) as a condensation reagent to afford HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub>, as shown in Scheme 2 and Table 1. This polymer reaction proceeded smoothly, however, the substitution of the perfluorobutyl group was not completed, where the degree of substitution (DS) was 60 – 88 mol% as listed in Table 1. DS was estimated by the ratio of the peak intensities in  $^1\text{H-NMR}$  spectrum at amide proton (10.4-10.6 ppm) and perfluorobutylethyl proton (3.8, 4.1 ppm). Probably, the complete substitution of the branch ends would be difficult because of the low reactivity of the inert carboxyl group in the branched polymers in their solution. By the way, the solubility of the fluorinated polymers was almost same as the starting polyamides.

### 3.2 Surface property of fluorinated hyperbranched polyamides

In the case of hyperbranched polymers, the branch ends would be concentrated on the surface of polymer rather than the backbone component. Therefore, the perfluorobutyl group of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> would strongly affect the surface property of the polymer films, although the degree of substitution was not completed in the polymer reaction. In addition, the degree of branch would be also effective to the surface modification. From these points of view, the surface property of the fluorinated hyperbranched polyamides was investigated as described below.

The thin films of these polymers were prepared by

coating of their DMSO solutions on glass plates, and the

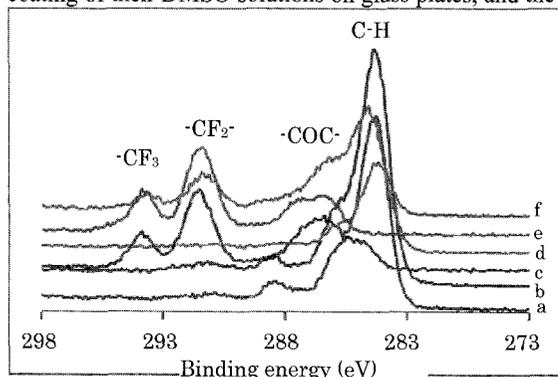


Fig. 2 XPS spectra of hyperbranched polymers. (a) HB-AB<sub>2</sub>, (b) HB-AB<sub>4</sub>, (c) HB-AB<sub>8</sub>, (d) HB-AB<sub>2</sub>-F<sub>4</sub>, (e) HB-AB<sub>4</sub>-F<sub>4</sub>, (f) HB-AB<sub>8</sub>-F<sub>4</sub>.

Table 2 Atomic contents of polymer surfaces measured by XPS.

code	DS (mol%)		C (%)	N (%)	O (%)	F (%)	F/C
HB-AB <sub>2</sub>	-	Obs.	73.8	4.9	21.3	-	-
		Theo.	73.7	5.2	21.1	-	-
HB-AB <sub>2</sub> -F <sub>4</sub>	88.5	Obs.	39.7	1.1	17.9	41.3	1.04
		Theo.	59.8	3.1	12.4	24.7	0.41
HB-AB <sub>4</sub>	-	Obs.	75.1	3.8	20.3	-	-
		Theo.	73.7	5.3	21.0	-	-
HB-AB <sub>4</sub> -F <sub>4</sub>	60.4	Obs.	34.3	0.1	15.4	50.2	1.46
		Theo.	62.8	3.6	14.3	19.3	0.31
HB-AB <sub>8</sub>	-	Obs.	75.0	3.5	21.5	-	-
		Theo.	72.7	4.6	22.7	-	-
HB-AB <sub>8</sub> -F <sub>4</sub>	75.0	Obs.	53.4	2.6	20.7	23.4	0.44
		Theo.	59.8	2.8	13.8	23.6	0.39

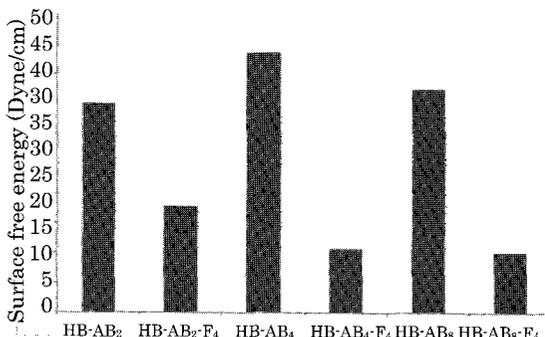


Fig. 3 Surface free energies of polymer films.

films were dried at 100 °C for 24 hours. Then, the measurements of X-ray photoelectron spectroscopy (XPS) was carried out on the film surface. As seen in Fig. 2, the fluoroalkyl group was confirmed clearly on the surface of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> films, and the atomic contents was estimated from each peak intensity as listed in Table 2. The observed atomic contents of HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub> were almost as same as the theoretical values. On the contrary, the observed values of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> were different from the theoretical ones, where the contents of carbon and fluorine atoms became higher. Consequently, the films of such hyperbranched polyamide containing fluoroalkyl end groups were efficiently covered with fluoroalkyl groups.

Fig. 3 indicated the surface free energy of each polymer film, which was calculated according to

Owens-Wendt method [10] by the measurements of contact angles of water and diiodomethane on the film surfaces. The values of surface free energy of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> were clearly decreased as compared with those of HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub>, respectively. Especially, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> consisting of the high DB of 0.72 and 0.83 exhibited the very low surface free energy. Thus, the higher degree of branch would be very effective to modify the polymer surface by covering the branch end groups.

#### 4. CONCLUSION

We succeeded in the control of degree of branch for hyperbranched polyamide by using different kinds of monomers such as AB<sub>2</sub>, AB<sub>4</sub> and AB<sub>8</sub> type monomers. In addition, the introduction of a fluoroalkyl group into the branch carboxyl ends proceeded smoothly with high yield by polymer reaction of HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub> with 2-perfluorobutylethanol using PPE. Furthermore, according to the measurements of XPS analysis, the surface properties of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> were different each other, which were affected by the degree of branch of each polymer. The values of surface free energy of HB-AB<sub>2</sub>-F<sub>4</sub>, HB-AB<sub>4</sub>-F<sub>4</sub> and HB-AB<sub>8</sub>-F<sub>4</sub> were lower than those of HB-AB<sub>2</sub>, HB-AB<sub>4</sub> and HB-AB<sub>8</sub>, which decreased as the increase of degree of branch. Therefore, the higher degree of branch would be effective to concentrate the branch-end groups on the polymer surface.

Consequently, hyperbranched polymers would be useful as surface modification agents, where the surface was efficiently covered with branch ends. From this study, it was found that the higher degree of branch is more effective to modify the polymer surface, and it was also important to have a film-forming ability. However, in general, dendritic macromolecules are difficult to produce a thin film because the intermolecular interaction is not so strong. Therefore, as the second step of this study, the preparations of hyperbranched polymers having a good film-forming property are now in progress.

#### 5. REFERENCES

- 1) D. A. Tomalia, A. M. Naylor, W. A. Goddard, III, *Angew. Chem., Int. Ed. Engl.* **29**, 138 (1990).
- 2) B. I. Voit, *Acta Polym.* **46**, 87 (1995)
- 3) J. M. J. Fréchet, C. J. Hawker, I. Gitsov, J. W. Leon, *J. Macromol. Sci., Pure Appl. Chem.* **A33**, 1399 (1996).
- 4) C. J. Hawker, R. Lee, and J. M. J. Fréchet, *J. Am. Chem. Soc.* **113**, 4583 (1991)
- 5) M. Jikei, S. H. Chou, M. Kakimoto, S. Kawauchi, T. Imase, J. Watanabe, *Macromolecules*, **32**, 2061 (1999)
- 6) M. Jikei, K. Fujii, G. Yang, M. Kakimoto, *Macromolecules*, **33**, 6228 (2000)
- 7) Y. Ishida, A. C. F. Sun, M. Jikei, M. Kakimoto, *Macromolecules*, **33**, 2832 (2000)
- 8) K. Yamanaka, M. Jikei, M. Kakimoto, *Macromolecules*, **33**, 1111 (2000)
- 9) Y. Kanaoka, K. Tanizawa, E. Sato, O. Yonemitsu, Y. Ban, *Chem. Pharm. Bull.* **15**, 593 (1967)
- 10) D. K. Owens, and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969)