Hyperbranched Polymers

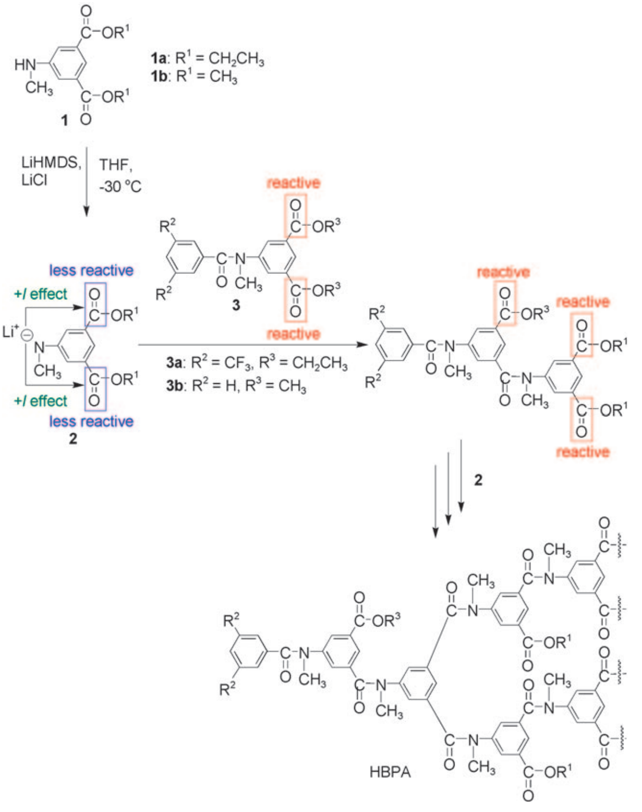
DOI: 10.1002/ange.200901714

Synthesis of Well-Defined Hyperbranched Polyamides by Condensation Polymerization of AB_2 Monomer through Changed Substituent Effects**

*Yoshihiro Ohta, Shuichi Fujii, Akihiro Yokoyama, Taniyuki Furuyama, Masanobu Uchiyama, and Tsutomu Yokozawa**

Hyperbranched polymers have received considerable attention in recent years because of their unusual properties that arise from their unique molecular architecture and convenient synthesis by one-step polymerization of AB_m ($m \geq 2$) type monomers.[1] The physical properties of hyperbranched polymers depend on the chemical composition, molecular weight, molecular weight distribution, and degree of branching (DB), so a challenging goal is the development of general AB_2 polymerization methods that achieve controlled molecular weight and narrow molecular weight distribution. The basic approach to these controlled polymerizations is selective reaction of the monomer with a core molecule and the polymer ends in a manner similar to chain-growth polymerization. Several attempts have been reported that use chain-growth ring-opening isomerization polymerization of cyclic latent AB_2 monomers from a core molecule,[2] polymerization from a core molecule on an insoluble solid support,[3] slow addition of monomers to a core molecule,[4] and reactive core molecules.[5] Polymers with controlled molecular weight and low polydispersity (weight-average/number-average molecular weight, $M_w/M_n < 1.3$) were generally obtained when the monomer/core ratio was less than about 100. Above that, however, the molecular weight distribution became broad[4b] or the deviation of the observed molecular weight from the calculated one increased even when polymers with low polydispersity were obtained.[4c,d] These results probably arose from self-polymerization of AB_2 monomers at high feed ratio.[4b]

Herein, we propose a new approach to controlled polymerization of AB_2 monomers by utilizing the change of substituent effects between monomer and polymer. In the condensation polymerization of 5-(methylamino)isophthalic acid ethyl ester (**1a**) as an AB_2 monomer with a base, the amide anion of **2** deactivates both the ester moieties in **2** through the inductive effect (+I effect) to suppress the self-polymerization of **2**, and **2** selectively reacts with a core molecule (initiator) **3** and the terminal ester moieties of polymer to afford a well-defined hyperbranched polymer (Scheme 1), in a similar manner to that in which AB-type monomers undergo chain-growth condensation polymerization.[6] Here, we report that control over the molecular weight ($M_n = 2370$–39300) of hyperbranched polyamide (HBPA) was achieved by varying the ratio of the monomer to the core from 7 to 200, while retaining very low polydispersity ($M_w/M_n \leq 1.13$), in the polymerization of **1a** with core molecule **3**. We also utilized this approach to synthesize a block copolymer of linear and hyperbranched aromatic polyamides by means of a convenient one-pot monomer addition method.



Scheme 1. Condensation polymerization of AB_2 monomer **1** from core initiator **3** by making use of changed substituent effects.

---

[*] Y. Ohta, S. Fujii, Prof. Dr. A. Yokoyama, Prof. Dr. T. Yokozawa
Department of Material and Life Chemistry, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686 (Japan)
Fax: (+81) 45-413-9770
E-mail: yokozt01@kanagawa-u.ac.jp
T. Furuyama, Dr. M. Uchiyama
Advanced Elements Chemistry Laboratory
Institute of Physical and Chemical Research
RIKEN, Hirosawa, Wako-shi, Saitama 351-0198 (Japan)

[**] This work was supported in part by a Grant-in-Aid (Grant 19550128) for Scientific Research and a Scientific Frontier Research Project from the Ministry of Education, Culture, Sports, Science, and Technology (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901714.

The polymerization of **1a** was first carried out by addition of **1a** over 40 min to a mixture of 1.1 equivalent of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) and 6.7 mol% **3a** as a core initiator in THF at −30 °C. Further stirring at −30 °C for 1 h afforded HBPA with a relatively narrow molecular weight distribution ($M_w/M_n = 1.28$; Supporting Information, Figure S1). The M_n value of the hyperbranched polymer estimated by gel-permeation chromatography (GPC) is generally lower than the real M_n value, and therefore the M_w value was determined with a multiangle laser light scattering (MALLS) detector. To facilitate comparison with the theoretical value (M_n(calcd)) based on the monomer/core feed ratio, the M_n value designated as M_n(MALLS) was calculated by division of the M_w value from MALLS by the M_w/M_n ratio from GPC. According to this, the M_n(MALLS) of the obtained HBPA was 3500.

To confirm the branched structure, model compounds of the dendritic and linear units were synthesized, and the ^{1}H NMR spectrum of HBPA was compared with those of the model compounds (Supporting Information, Figure S2). The ^{1}H NMR spectrum of HBPA showed separately the signals of the dendritic (D), linear (L), and terminal (T) units, and the DB of the HBPA calculated by use of the Fréchet formula[7] was 0.52. This DB value is close to the theoretical value of 0.5 in the general polymerization of an AB_2 monomer.[8]

The polymer end group of the HBPA was analyzed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry with dithranol as matrix in the presence of sodium trifluoroacetate as cationizing salt. The mass spectrum of HBPA contains two series of peaks (Figure 1a). One corresponds to the Na^+ adducts of HBPA with the core **3a** unit and the other comes from HBPA without the **3a** unit, in which the focal amino group has reacted intramolecularly with one of the ester moieties to form a cyclic structure. This result means that the polymerization of **1a** involves not only selective reaction of **1a** with **3a** and the polymer ends, but also self-polymerization of **1a**. We speculated that **1a** would be too reactive for self-polymerization to be suppressed, and so the reactivity of the amide anion **2** was decreased by the use of LiCl.[9] Thus, the polymerization of **1a** with 6.7 mol% **3a** was carried out in the presence of 5 equivalents of LiCl. The M_w/M_n ratio became 1.11 (Supporting Information, Figure S3), and the M_n value (M_n(MALLS) = 3920) was in fair agreement with the calculated value, assuming that one core molecule forms one HBPA molecule (M_n(calcd) = 3570). The DB value of HBPA was 0.52. The MALDI-TOF mass spectrum contains only one series of peaks corresponding to the Na^+ adduct of HBPA with the core **3a** unit (Figure 1b).[10]

Furthermore, when the polymerization of **1a** was carried out with various feed ratios of **1a** to **3a** ($[\mathbf{1a}]_0/[\mathbf{3a}]_0$), the observed M_n value of the HBPA increased in proportion to the $[\mathbf{1a}]_0/[\mathbf{3a}]_0$ ratio up to 200, and a narrow polydispersity was retained (Figure 2a).[11] The gel-permeation chromatogram of HBPA obtained even at a monomer/core feed ratio of 200 showed a very narrow, monomodal peak (Figure 2b). Consequently, the polymerization of the AB_2 monomer **1a** with LiHMDS in the presence of LiCl proceeds in a chain-growth polymerization manner from the core **3a**.

As the AB_2 monomer **1a** was added to a mixture of the core **3a** and base for 40 min in this polymerization, one might think that the chain-growth polymerization from the core would stem not from the changed substituent effects, but from slow monomer addition (SMA), although it took more than 12 h for controlled synthesis of hyperbranched polymers by the reported SMA method.[4] Accordingly, the polymerization of **1a** was carried out by the addition of **1a** and **3a** ($[\mathbf{1a}]_0/[\mathbf{3a}]_0 = 15$) at once to a mixture of LiHMDS and LiCl. The obtained HBPA also possessed a controlled molecular weight and narrow molecular weight distribution (M_n(MALLS) = 3450 (M_n(calcd) = 3570), $M_w/M_n = 1.17$; Supporting Information, Figure S6). This finding indicates that this controlled polymerization of AB_2 monomer is governed not by SMA, but by the change of substituent effects between the monomer and polymer.

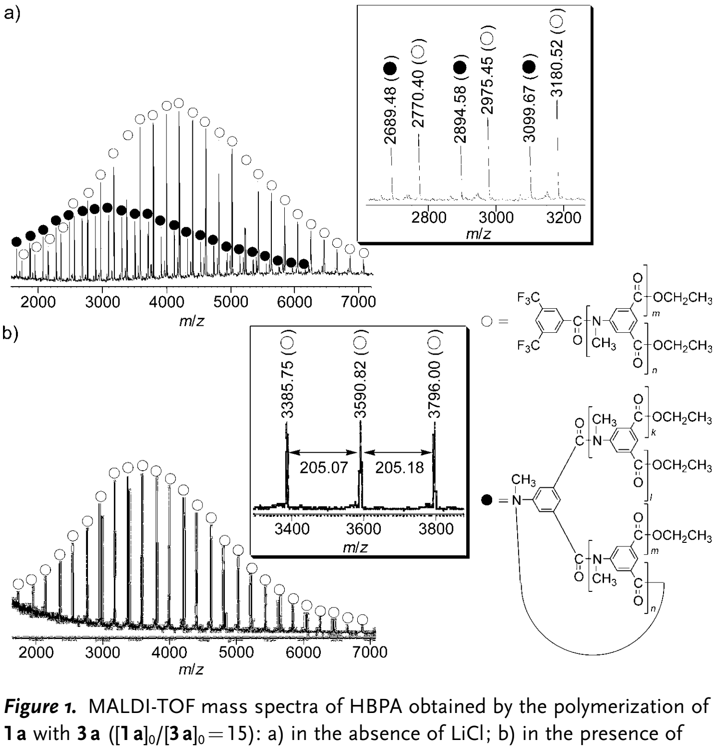


Figure 1. MALDI-TOF mass spectra of HBPA obtained by the polymerization of **1a** with **3a** ($[\mathbf{1a}]_0/[\mathbf{3a}]_0 = 15$): a) in the absence of LiCl; b) in the presence of LiCl.

In addition, density functional theory (DFT) calculations were performed to estimate the change of substituent effects. We examined the propagation reaction of a methyl ester monomer **1b** with a dimethyl ester core **3b** and the self-condensation of **1b** as model reactions (Scheme 1) by using the DFT (B3LYP/6-31G*) method. Although the effect of LiCl is important and remains to be elucidated, in this instance we calculated only the substituent effects for the sake of simplicity. The activation energies for the propagation and self-condensation are 25.7 and 29.2 kcal mol^{-1}, respectively. On the basis of the geometries, energies, and vibrational frequencies obtained, the theoretical rate constants were then evaluated at 243 K and 1 atm. The reaction rate constant for the propagation (3.8×10^{-11} s^{-1}) is 1.4×10^3-fold greater than that for the self-

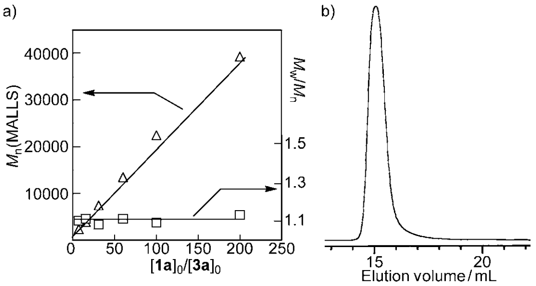


Figure 2. a) M_n and M_w/M_n values of HBPA as a function of the feed ratio of **1a** to **3a**. b) GPC profile of HBPA obtained by the polymerization of **1a** with **3a** ([**1a**]$_0$/[**3a**]$_0$ = 200).

condensation ($2.7\times10^{-14}\,s^{-1}$) and, hence, is consistent with the experimental tendency that propagation was favored over self-condensation by virtue of the substituent effects.

Finally, with this established polymerization method, we tried to synthesize a well-defined diblock copolymer of linear and hyperbranched polymer in one pot.[12] Thus, methyl 3-(4-octyloxybenzylamino)benzoate (**4**)[13] was polymerized in the presence of an initiator **5** ([**4**]$_0$/[**5**]$_0$ = 20), 2.2 equivalents of LiHMDS, and 11 equivalents of LiCl to give a prepolymer (Figure 3a; M_n = 6230 (M_n(calcd) = 6900), M_w/M_n = 1.10). A fresh feed of **1a** ([**1a**]$_0$/[**5**]$_0$ = 20) was added to the prepolymer in the reaction mixture, and the added **1a** was smoothly polymerized. The gel-permeation chromatogram of the product (Figure 3b) was clearly shifted toward the higher-molecular-weight region, while retaining a narrow molecular weight distribution (M_n(MALLS) = 10900 (M_n(calcd) = 11500), M_w/M_n = 1.14), which indicated successful production of the linear–hyperbranched block copolymer from **4** and **1a**.

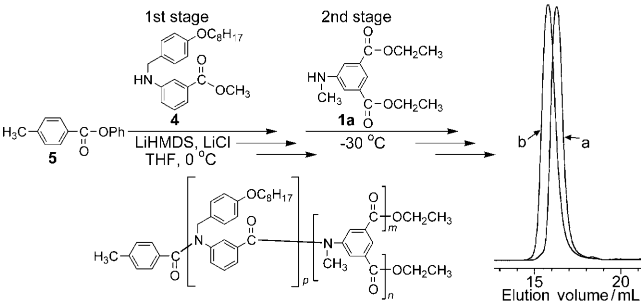


Figure 3. GPC profiles of polymers in the block copolymerization of **4** and **1a**: a) poly**4** as a prepolymer ([**4**]$_0$/[**5**]$_0$ = 20, M_n = 6230, M_w/M_n = 1.10); b) poly**4**-*b*-HBPA ([**1a**]$_0$/[**5**]$_0$ = 20, M_n(MALLS) = 10900, M_w/M_n = 1.14).

In conclusion, hyperbranched aromatic polyamides, with a degree of polymerization in the range of 7–200 and very low polydispersity ($M_w/M_n \leq 1.13$), can be synthesized by simple condensation polymerization of an AB_2 monomer. These results demonstrate that AB_2 condensation polymerization involving a change of substituent effects between the monomer and polymer to suppress self-polymerization is very effective for the controlled synthesis of hyperbranched polymers. Furthermore, this established method enables the synthesis of block copolymers of linear and hyperbranched polymers by a convenient monomer addition method in one pot, and other architectures including hyperbranched polymers should also be accessible in the same way. Studies of other controlled condensation polymerizations of AB_2 monomers on the basis of changed substituent effects are under way.

Experimental Section

Typical polymerization procedure: LiCl (0.152 g, 3.59 mmol) was placed in a flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure. The flask was cooled to room temperature under an argon atmosphere, and then charged with 1.0 M LiHMDS in THF (0.720 mL, 0.720 mmol). The flask was cooled to −30 °C under an argon atmosphere with stirring. A solution of **3a** (0.0053 g, 0.011 mmol) and naphthalene (internal standard, 0.0096 g, 0.075 mmol) in dry THF (1.0 mL) was added to the flask under dry nitrogen, followed by a solution of **1a** (0.163 g, 0.649 mmol) in dry THF (4.0 mL) dropwise over about 40 min at −30 °C with stirring under dry nitrogen. The mixture was stirred at −30 °C for 1 h, and then the reaction was quenched with sat. NH_4Cl. A small portion of the THF layer was withdrawn into a syringe and analyzed by GC to determine the conversion of **3a** and **1a** (conversion = 100 %). After that, the whole was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (2.0 mL), and the solution was added to hexane (150 mL). After filtration, the insoluble material was washed with hexane and dried in desiccator to give HBPA as a white solid (0.113 g, 82 %, M_n(MALLS) = 13500, M_w/M_n = 1.11). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55–8.41 (aromatic), 8.11–7.89 (aromatic), 7.87–7.57 (aromatic), 7.53–7.30 (aromatic), 7.25–6.90 (aromatic), 4.46–4.11 (COOCH_2CH$_3$), 3.51–2.81 (N-CH$_3$), 1.43–1.12 ppm (COOCH$_2$$CH_3$).

Synthesis of linear–hyperbranched block copolymer: LiCl (0.305 g, 7.19 mmol) was placed in a flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure. The flask was cooled to room temperature under an argon atmosphere, and then charged with 1.0 M LiHMDS in THF (1.45 mL, 1.45 mmol). The flask was cooled to 0 °C under an argon atmosphere with stirring. A solution of **5** (0.0069 g, 0.033 mmol) and naphthalene (internal standard, 0.0105 g, 0.819 mmol) in dry THF (1.0 mL) was added to the flask under dry nitrogen, followed by a solution of **4** (0.240 g, 0.650 mmol) in dry THF (0.6 mL) dropwise over about 20 min at 0 °C with stirring under dry nitrogen. The mixture was stirred at 0 °C for 20 min, then 0.3 mL of the solution was withdrawn and quenched with sat. NH_4Cl to measure the M_n value and M_w/M_n ratio of poly**4** (the GPC trace is shown in Figure 3a: M_n(GPC) = 6230, M_n(NMR) = 7470, M_w/M_n = 1.10). Immediately after the sampling, the mixture was cooled to −30 °C, then a solution of **1a** (0.163 g, 0.649 mmol) in dry THF (4.0 mL) was added dropwise to the mixture over about 40 min at −30 °C with stirring under dry nitrogen. The mixture was stirred at −30 °C for 1 h, then the reaction was quenched with sat. NH_4Cl. The whole was extracted with CH_2Cl_2, and the organic layer was washed with brine, followed by drying over anhydrous $MgSO_4$. After concentration under reduced pressure, the residue was dissolved in CH_2Cl_2 (1.0 mL), and the solution was added to hexane (30 mL). After filtration, the insoluble material was washed with hexane and dried in a desiccator to give HBPA as a white solid (0.276 g, 77 %, M_n(MALLS) = 10900, M_w/M_n = 1.14). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50–8.44 (aromatic), 8.05–7.89 (aromatic), 7.84–7.55 (aromatic), 7.53–7.29 (aromatic), 7.25–6.86 (aromatic), 6.85–6.62 (aromatic), 6.41–6.23 (aromatic), 4.96–4.55 (N-CH$_2$), 4.42–4.17 (COOCH_2CH$_3$), 3.94–3.73 (OCH_2CH$_2$C$_5$H$_{10}$CH$_3$), 3.56–2.82 (N-CH$_3$), 2.21–2.16 (CH_3C$_6$H$_4$), 1.73 (OCH$_2$$CH_2C_5H_{10}CH_3$), 1.46–1.20 ($OCH_2CH_2C_5H_{10}CH_3$ and $COOCH_2CH_3$), 0.88 ppm ($OCH_2CH_2C_5H_{10}CH_3$).

Received: March 30, 2009

Keywords: block copolymers · hyperbranched polymers · polymerization · substituent effects

---

[1] a) Y. H. Kim, *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1685; b) B. Voit, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2679; for a recent report on the synthesis of hyperbranched conjugated polymers, see: c) J. Tolosa, C. Kub, U. H. F. Bunz, *Angew. Chem.* **2009**, *121*, 4680; *Angew. Chem. Int. Ed.* **2009**, *48*, 4610.

[2] a) M. Suzuki, A. Ii, T. Saegusa, *Macromolecules* **1992**, *25*, 7071; b) M. Suzuki, S. Yoshida, K. Shiraga, T. Saegusa, *Macromolecules* **1998**, *31*, 1716.

[3] P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1997**, *119*, 3391.

[4] a) A. Sunder, R. Hanselmann, H. Frey, R. Mülhaupt, *Macromolecules* **1999**, *32*, 4240; b) P. Bharathi, J. S. Moore, *Macromolecules* **2000**, *33*, 3212; c) A. Möck, A. Burgath, R. Hanselmann, H. Frey, *Macromolecules* **2001**, *34*, 7692; d) R. K. Kainthan, E. B. Muliawan, S. G. Hatzikiriakos, D. E. Brooks, *Macromolecules* **2006**, *39*, 7708.

[5] D. P. Bernal, L. Bedrossian, K. Collins, E. Fossum, *Macromolecules* **2003**, *36*, 333.

[6] A. Yokoyama, T. Yokozawa, *Macromolecules* **2007**, *40*, 4093.

[7] C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583.

[8] H. Frey, D. Hölter, *Acta Polym.* **1999**, *50*, 67.

[9] S. K. Varshney, J. P. Hautekeer, R. Fayt, R. Jérôme, Ph. Teyssié, *Macromolecules* **1990**, *23*, 2618.

[10] The MALDI-TOF mass spectra of the HBPAs during polymerization also contain only one series of peaks (Supporting Information, Figure S4).

[11] For GPC profiles of HBPA obtained with various feed ratios of $[\mathbf{1a}]_0/[\mathbf{3a}]_0$, see Figure S5 in the Supporting Information; the results are summarized in Table S1.

[12] Several linear–hyperbranched block copolymers have been synthesized in two or more pots: a) E. Barriau, A. G. Marcos, H. Kautz, H. Frey, *Macromol. Rapid Commun.* **2005**, *26*, 862; b) A. G. Marcos, T. M. Pusel, R. Thomann, T. Pakula, L. Okrasa, S. Geppert, W. Gronski, H. Frey, *Macromolecules* **2006**, *39*, 971; c) F. Wurm, J. Nieberle, H. Frey, *Macromolecules* **2008**, *41*, 1184.

[13] T. Ohishi, R. Sugi, A. Yokoyama, T. Yokozawa, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4990.