# Well-Defined Star-Shaped Aromatic Polyamides from Chain-Growth Polymerization of Phenyl 4-(Alkylamino)benzoate with Multifunctional Initiators

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ABSTRACT: For the synthesis of well-defined star-shaped aromatic polyamides, triphenyl benzene-1,3,5tricarboxylate (**2a**), tetraphenyl benzene-1,2,4,5-tetracarboxylate (**2b**), and 1,3,5-tris(4-phenyloxycarbonylbenzyloxy)benzene (**3**) were synthesized and then employed as multifunctional initiators for the chaingrowth polymerization of phenyl 4-(octylamino)benzoate (**1**). The polymerization with **2a** or **2b** did not proceed smoothly from all of the phenyl ester moieties in the initiators and afforded polymers with high polydispersities. In contrast, initiator **3** having the benzyloxy spacers resulted in three-armed aromatic polyamide (**I**) with low polydispersity. Furthermore, the benzyloxy linkages of the core of **I** were cleaved by hydrogenolysis to yield a polymer with low polydispersity, the  $M_n$  of which was one-third that of **I**, indicating that **I** exactly possesses three arm chains of a uniform and controlled length. However, the polymerization at higher feed ratios of  $[1]_0/[3]_0$  afforded not only the three-armed polymer but also a linear polymer formed by self-polymerization of **1**.

## Introduction

The synthesis of well-defined star polymers has become an important field in macromolecular chemistry due to their unique spatial shapes and rheological properties. Among a variety of synthetic approaches to star polymers, living polymerization is the most appropriate for the synthesis of well-defined star polymers, which can be divided into three methods: (1) living polymerization with a multifunctional initiator, (2) coupling reaction of linear living polymers with a multifunctional coupling agent, and (3) linking reaction of linear living polymers with a divinyl compound. Method 1 can yield star polymers with a determined number of arms and has been successfully employed in various living polymerizations, including anionic,<sup>1</sup> cat-ionic,<sup>2</sup> radical polymerization,<sup>3</sup> and ring-opening processes.<sup>4</sup> However, polycondensation is not applicable to this method for the synthesis of well-defined star-shaped polymers because polycondensation does not proceed in a chain polymerization manner. Star-shaped condensation polymers have been prepared by copolycondensation of a star-center molecule with an AB-type monomer or with A<sub>2</sub> and B<sub>2</sub> monomers,<sup>5</sup> in which the arm lengths of the polymers obtained are not controlled. Well-defined star-shaped condensation oligomers have been synthesized by the coupling reaction between a star-center molecule and linear oligomers with monodispersity, which was prepared by sequential condensation procedure.6

We have developed condensative chain-growth polymerization,<sup>7</sup> which yields well-defined condensation polymers as well as block copolymers.<sup>8</sup> In this paper, we synthesize star-shaped aromatic polyamides by the chain-growth polymerization of phenyl 4-(octylamino)benzoate (1) on the basis of the multifunctional initiator method (method 1 mentioned above). The initiators employed herein possess tri- or tetraphenyl ester moieties per molecule, such as simple triphenyl benzene-1,3,5-tricarboxylate (**2a**) and tetraphenyl benzene-1,2,4,5tetracarboxylate (**2b**), and 1,3,5-tris(4-phenyloxycarbonylbenzyloxy)benzene (**3**) having the benzyloxy spacers (Scheme 1). The presence of a spacer unit in the initiator was found to be crucial for the synthesis of the star-shaped polyamides, and the polymerization behavior with **2a** or **2b** was different from that with **3**.

## **Experimental Section**

Measurements. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a JEOL ECA-600, 500, and FX-200 operating in the pulsed Fourier transfer (FT) modes, using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a JASCO FT/IR-410. Elemental analyses were performed by a Perkin-Elmer 2400 II CHN. The  $M_n$  and  $M_w/M_n$  of polymers were measured with a TOSOH HLC-8020 gel permeation chromatography (GPC) unit (eluent: tetrahydrofuran (THF); calibration: polystyrene standards) using two TSK-gel columns (2  $\times$ Multipore H<sub>XL</sub>-M). Isolation of polyamides was carried out with a Japan Analytical Industry LC-908 recycling preparative HPLC (eluent: chloroform) using two TSK-gel columns (2  $\times$ G 2000H<sub>HR</sub>). MALDI-TOF mass spectra were recorded on a Shimadzu/Krotos Kompact MALDI IV tDE in the reflection mode using laser ( $\lambda = 337$  nm). A sample solution of **3**, dithrarnol as a matrix, and silver trifluoromethanesulfonate as a cationizing salt was made in THF.

**Materials.** Phenyl 4-(octylamino)benzoate (1) and *N*-octyl-*N*-triethylsilylaniline were prepared according to the previously established procedures.<sup>7a</sup> Triphenyl benzene-1,3,5tricarboxylate (2a) was prepared according to the literature.<sup>9</sup> Phenyl benzoate (2c), CsF (Wako), and dehydrated tetrahydrofuran (dry THF; Kanto) as a solvent were used as received without purification. 18-Crown-6 (TCI) was dried under reduced pressure at 40 °C for more than 6 h prior to use.

Synthesis of Tetraphenyl Benzene-1,2,4,5-tetracarboxylate (2b). Into the mixture of phenol (4.6 g, 52 mmol) and benzene-1,2,4,5-tetracalboxylic acid (1.3 g, 5.0 mmol) was added phosphorus oxy chloride (2.2 mL, 24 mmol) at 120 °C with stirring. The reaction mixture was stirred at 120 °C for 8 h and poured into water, followed by extraction with CH<sub>2</sub>-

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Cl<sub>2</sub>. The combined organic layer was washed with 1 M NaOH and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo, and the residue was recrystallized from hexane–ethyl acetate to give 0.73 g of **2b** as a white solid (26%): purity >99% by HPLC; mp 147.1–150.8 °C. IR (KBr): 1737, 1590, 1486, 748, 688 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.58 (s, 2 H), 7.44 (t, J = 7.3 Hz, 8 H), 7.45–7.13 (m, 12 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.2, 150.6, 134.7, 130.7, 129.8, 126.6, 121.5. Anal. Calcd for C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>: C, 73.11; H, 3.97. Found: C, 73.25; H, 3.99.

Synthesis of Phenyl (4-Chloromethyl)benzoate (4). Into the mixture of phenol (3.2 g, 34 mmol) and triethylamine (4.3 mL, 31 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added a solution of 4-chloromethylbenzoyl chloride (4.9 g, 25 mmol) in  $CH_2Cl_2$ (100 mL) at 0 °C with stirring. The reaction mixture was stirred at ambient temperature for 15 h and poured into water, followed by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo, and the residue was recrystallized from hexane to give 4.6 g of 4 as a white solid (72%): mp 89.0-91.0 °C. IR (KBr): 2924, 1734, 1609, 1275, 1074, 742, 704 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ: 8.18 (d, J = 8.3 Hz, 2 H), 7.51 (d, J = 8.3 Hz, 2 H), 7.42 (t, J = 7.4 H)Hz, 2 H), 7.26 (t, J = 7.0 Hz, 1 H), 7.20 (d, J = 7.3 Hz, 2 H), 4.62 (s, 2 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ: 164.7, 150.9, 143.0, 130.7, 130.6, 129.6, 128.7, 126.0, 121.7, 45.3.

Synthesis of 1,3,5-Tris(4-phenyloxycarbonylbenzyloxy)benzene (3). The mixture of K<sub>2</sub>CO<sub>3</sub> (3.2 g, 23 mmol), phenyl (4-chloromethyl)benzoate (2.5 g, 10 mmol), KI (2.4 g, 15 mmol), and 18-crown-6 (0.19 g, 0.70 mmol) in acetone (10 mL) was stirred at 60 °C for 1 h, and a solution of phloroglucinol (0.38 g, 3.0 mmol) in acetone (1.8 mL) was added at 60 °C with stirring. The reaction mixture was stirred at 60 °C for 5 h. After cooling to room temperature, K<sub>2</sub>CO<sub>3</sub> was filtered off and poured into water, followed by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1) and was then recrystallized by hexane-ethyl acetate to give 0.13 g of **3** as a white solid (6%): purity >99% by HPLC; mp 180.0-181.5 °C. IR (KBr): 2924,  $1735, 1609, 1593, 1484, 1270, 1197, 1140, 1074, 743, 689 \text{ cm}^{-1}$ <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.21 (d, J = 8.0 Hz, 6 H), 7.55  $(d, J = 8.1 \text{ Hz}, 6 \text{ H}), 7.43 (t, J = 7.6 \text{ Hz}, 6 \text{ H}), 7.29-7.20 (m, J = 7.6 \text{ Hz}), 7.29-7.20 (m, J = 7.6 \text{ H$ 9 H), 6.27 (s, 3 H), 5.12 (s, 6 H).  $^{13}\mathrm{C}$  NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$ :  $164.9,\ 160.5,\ 151.0,\ 142.8,\ 130.6,\ 129.6,\ 129.3,\ 127.2,\ 126.0,$ 121.8, 95.3, 69.5. MALDI-TOF MS: m/z calcd for [3 + Ag]863.70; found 865.36. Anal. Calcd for C<sub>48</sub>H<sub>36</sub>O<sub>9</sub>: C, 76.18; H, 4.79. Found: C, 75.77; H, 4.55.

Polymerization Procedures. Monomer 1 was polymerized with initiator 3 for the preparation of polymers I-III. An example of the procedure is described for  $I.\ \mbox{CsF}$  (0.076 g, 0.5 mmol) was placed in a round-bottomed flask, equipped with a three-way stopcock, and dried at 250 °C under reduced pressure for 20 min. The flask was cooled to room temperature under an argon atmosphere. Into the flask was added a solution of 1 (0.165 g, 0.5 mmol), 3 (0.0076 g, 2 mol %), N-octyl-N-triethylsilylaniline (0.160 g, 0.5 mmol), and naphthalene (internal standard for HPLC analysis, 0.064 g, 0.5 mmol) in dry THF (1.25 mL) and a solution of 18-crown-6 (0.266 g, 1.0 mmol) in dry THF (0.25 mL) successively. After stirring at ambient temperature for 7 h, the reaction was quenched with saturated NH<sub>4</sub>Cl. A small portion of the THF layer was withdrawn by a syringe and analyzed by HPLC to determine the degree of consumption of 1 and extracted with CHCl<sub>3</sub>. The organic layer was washed with saturated NH<sub>4</sub>Cl and dried over anhydrous MgSO<sub>4</sub>. Concentration in vacuo gave crude product I as a yellow oil. The GPC trace of the crude poduct is shown in Figure 3A.  $M_n$ (GPC) = 8000 and  $M_w/M_n = 1.12$ . Subsequently, the residue was purified by preparative HPLC to give purified product I as a white powder. The <sup>1</sup>H NMR spectra and the GPC trace of I are shown in Figures 4A and 5A, respectively.  $M_n(NMR) = 11\ 000,\ M_n(GPC) = 8000,\ M_w/M_n = 1.12.$ 

**Hydrogenolysis of Triarmed Star Polymer.** Hydrogenolysis of the benzyl ether moieties of polymers I and II was performed to determine the length of arms. An example of the procedure is described for hydrogenolysis of I. A mixture of



**Figure 1.** (A) GPC profiles of polymer obtained in the polymerization of **1** with (i) **2a** and (ii) **2b**. (B) Time-conversion curves for the polymerization of **1** with **2a**, **2b**, or **2c** in the presence of *N*-octyl-*N*-triethylsilylaniline and CsF/18-crown-6 in THF ( $[1]_0 = [N$ -octyl-*N*-triethylsilylaniline]\_0 = [CsF]\_0 = 0.33 M, [18-crown-6]\_0 = 0.66 M) at 25 °C:  $[1]_0/[2a]_0 = 50.0$ ,  $[1]_0/[2b]_0 = 66.7$ ,  $[1]_0/[2c]_0 = 16.7$ . Initiator: (O) **2a**; ( $\blacklozenge$ ) **2b**; ( $\Box$ ) **2c**.



Elution Volume, mL

Figure 3. GPC profiles of polymers I, II, and III, obtained by the polymerization of 1 with 3 in the presence of N-octyl-*N*-triethylsilylaniline and CsF/18-crown-6 in THF ( $[1]_0$  = [N-octyl-N-triethylsilylaniline]<sub>0</sub> =  $[CsF]_0 = 0.33$  M, [18-crown- $[6]_0 = 0.66 \text{ M}$ ) at 25 °C:  $[1]_0/[3]_0 = 50.0 \text{ (A)}$ , 100 (B), and 200 (C).



product obtained by the hydrogenolysis of I.

5% Pd/C (0.010 g) and I (0.081 g) in ethyl acetate (10 mL) was stirried under  $H_2$  atmosphere at 50 °C for 20 h. Pd/C was filtered off, and the filtrate was concentrated in vacuo to give a crude product ( $M_n$ (GPC) = 4000 and  $M_w/M_n$  = 1.14), followed by purification with preparative HPLC to give 0.079 g of a core-

Figure 5. GPC profiles of (A) I and (B) the product obtained by the hydrogenolysis of I.

cleaved linear polymer as a white powder. The <sup>1</sup>H NMR spectra and the GPC trace of this product are shown in Figures 4B and 5B, respectively:  $M_n(NMR) = 3900, M_n(GPC) = 4000,$  $M_{\rm w}/M_{\rm n} = 1.14.$ 

Fractionation of III Using Preparative HPLC. Product **III** ( $M_n$ (GPC) = 16 800,  $M_w/M_n = 1.26$ ) was fractionated into two parts (III-a and III-b) using preparative HPLC. The product III (0.057 g) was dissolved in chloroform (3.0 mL), and the solution was injected into the preparative HPLC. The chromatogram of the eluent exhibted two peaks in the higher and lower molecular weight regions. The respective eluents were fractionated, concentrated, and dried in vacuo to give white powders. The <sup>1</sup>H NMR spectrum of III-a is shown in Figure 6B: 0.027 g (23%);  $M_{\rm n}(\text{GPC}) = 30\ 000, M_{\rm w}/M_{\rm n} = 1.07.$ The <sup>1</sup>H NMR spectrum of III-b is shown in Figure 6C: 0.012 g (10%);  $M_{\rm n}$ (GPC) = 15 400,  $M_{\rm w}/M_{\rm n}$  = 1.05.

# **Results and Discussion**

1. Chain-Growth Polymerization with Multifunctional Initiators 2. Simple benzenepoly(carboxylic acid) phenyl esters (2a and 2b) were first employed as multifunctional initiators. Thus, the polymerization of 1 with 2 mol % of trifunctional initiator  $2a ([1]_0/[2a]_0 =$ 50) and with 1.5 mol % of tetrafunctional initiator  $\mathbf{2b}$  $([1]_0/[2b]_0 = 66.7)$  was carried out in the presence of 1.0 equiv of N-octyl-N-triethylsilylaniline and CsF and 2.0 equiv of 18-crown-6 in THF at room temperature, respectively.<sup>7a</sup> The amounts of  $\mathbf{2}$  were chosen for the same length of arms in each star polymer  $([\mathbf{1}]_0/[-CO_2Ph]_0 =$ 



**Figure 6.** <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at 25 °C: (A) **III**, obtained by the polymerization of **1** with **3** in the presence of *N*-octyl-*N*-triethylsilylaniline and CsF/18-crown-6 in THF ( $[\mathbf{1}]_0 = [N\text{-}octyl-N\text{-}triethylsilylaniline]_0 = [CsF]_0 = 0.33$  M,  $[18\text{-}crown-6]_0 = 0.66$  M) at 25 °C:  $[\mathbf{1}]_0/[\mathbf{3}]_0 = 200$ . (B) **III-a** and (C) **III-b**, which were separated from **III** by preparative HPLC.

Scheme 2. Synthesis of Initiator 3 Having Benzyloxy Spacers



16.7). Figure 1A shows the GPC chromatograms of the polymers obtained in each polymerization for 3 h. Both of the GPC curves exhibit broad molecular weight distributions  $(M_w/M_n > 1.2)$ , implying that the arm lengths of those products were not completely controlled.

To check each polymerization behavior, the polymerization of 1 with 6 mol % of benzoic acid phenyl ester 2c ([1]<sub>0</sub>/[2c]<sub>0</sub> = 16.7) as a monofunctional initiator was conducted under the same initial concentrations of the phenyl ester moiety as for 2a and 2b. The polymerization rates from **2a** or **2b** would be the same as that from **2c**, if the polymerization is initiated and propagated smoothly from all the phenyl ester moieties of the initiators.<sup>8b</sup> As shown in the curves of monomer conversion against polymerization time (Figure 1B), the polymerization with both **2a** and **2b** was slower than that with 2c, which yielded a linear polyamide with lower polydispersity ( $M_n$ (GPC) = 4050,  $M_w/M_n$  = 1.15). Accordingly, the polymerization with 2a and 2b did not proceed homogeneously from all the initiation sites of 2. This might be caused by steric hindrance around the phenyl ester moieties in those initiators.

2. Chain-Growth Polymerization with Initiator **3.** (a) Synthesis of Initiator **3.** We prepared initiator **3** bearing benzyloxy spacers to avoid steric hindrance for initiation around the phenyl ester moieties (Scheme 2). Thus, 4-chloromethylbenzoyl chloride was converted to the corresponding phenyl ester 4, followed by etherification with phloroglucinol. The yield of 3 was only 6%, although similar etherification of 4 with phenol instead of phloroglucinol gave the corresponding ether in 66% yield. The low yield of **3** stemmed from C-alkylation of phloroglucinol, which is a well-known side reaction.<sup>10</sup> Indeed, the <sup>1</sup>H NMR spectra of the isolated byproducts showed the signal derived from C-alkylation at 4.0 ppm, the methylene protons of the benzyl group adjacent to an aromatic carbon.<sup>11</sup> However, this signal was not observed in the <sup>1</sup>H NMR spectrum of purified 3 (Figure 2). <sup>13</sup>C NMR spectroscopy, elemental analysis, analytical HPLC and mass spectroscopy indicated that 3 was essentially pure.

(b) Polymerization with Initiator 3. The polymerization with 2 mol % of 3 ( $[1]_0/[3]_0 = 50$ ) was completed in 7 h to yield a polymer I with  $M_n$ (GPC) of 8000 and  $M_w/M_n$  of 1.12 (Figure 3A), the polydispersity of which was lower than that of the polymer obtained with 2a and 2b under the same conditions. This result implies that each of the three phenyl ester moieties of 3 homogeneously initiated the polymerization of 1. Furthermore, the fact that the  $M_n$ (GPC) value of I was lower than the calculated value based on the feed ratio of  $[1]_0/[3]_0 (M_n(\text{calcd}) = 12\ 000)$  agreed with the feature of star-shaped polymers because the  $M_n$  values of linear polymer from 1 estimated by GPC were in good agreement with the theoretical values.<sup>12</sup>

In the <sup>1</sup>H NMR spectrum of I (Figure 4A), there can be seen characteristic signals of the benzyloxy group **b** and the aromatic proton **c** of the core unit, in addition to the signals of the repeating units d-i and the aromatic proton **a** at the ortho position of the terminal phenyl ester. The integral ratio of **c**:**b**:**a** is 3:6:6, and the signal of the benzyl proton of **3** at 5.1 ppm completely disappeared, indicating that one initiator molecule formed three polymer chains. The  $M_n$  values estimated by the integral ratio of the signal of the methylene in the repeating units (**f**) to that of the terminal group (**a**) was 11 000, which was in good agreement with the theoretical value mentioned above. These results indicate that **3** served as a trifunctional initiator to yield a three-armed polyamide.

To confirm the uniformity in length of the three arm chains of I, the benzyloxy linkages connected to the core were cleaved by hydrogenolysis. Figure 4B shows the <sup>1</sup>H NMR spectrum of the product after the hydrogenolysis of I at 50 °C for 20 h. Comparison between the spectra of Figure 4A,B shows complete conversion of the triarmed star polymer into a linear polymer because the signals b and c of the core unit in star polymer I completely disappeared and the signal of the methyl proton *j* derived from the benzyloxy group was observed, in which the integral ratio of j:a was 3:2. The  $M_n$  value of the product estimated similarly by the <sup>1</sup>H NMR spectrum was 3900, which was nearly one-third of the  $M_n$  value of I ( $M_n = 11000$ ). The GPC chromatogram of the product also shifted toward the low molecular weight region while retaining low polydispersity (Figure 5). This arm-cleavage experiment clearly indicates that I has three arm polyamide chains with a uniform and controlled length.

To synthesize the star polymers with higher molecular weights, the polymerization of 1 with 3 was carried out at higher feed ratios of  $[1]_0/[3]_0$ . The polymerization with 1 mol % of 3 ( $[1]_0/[3]_0 = 100$ ) was completed in 6 h to yield product II with  $M_n$ (GPC) of 15 100 and  $M_w/M_n$  of 1.16. The GPC chromatogram of II appeared in a higher molecular region than that of I, but a shoulder peak was observed in the lower molecular weight region (Figure 3B). In the polymerization with 0.5 mol % of 3 ( $[1]_0/[3]_0 = 200$ ) for 12 h, the GPC chromatogram of product III exhibited a bimodal (Figure 3C). The undesirable products in the lower molecular weight region seem to increase with decreasing 3 in the polymerization.

(c) Origin of Undesirable Products. Two peaks of bimoldal product III shown in Figure 3C were fractionated by preparative HPLC. In the <sup>1</sup>H NMR spectrum of isolated **III-a** ( $M_n$ (GPC) = 30 000,  $M_w/M_n$  = 1.07), the signal of a *singlet* of the aromatic proton **a** of the core at 6.2 ppm was observed, and the integral ratio of **a**:**b** was 3:6 (Figure 6B). Therefore, **III-a** is the three-armed polyamide yielded by the chain-growth polymerization of 1 from 3. The  $M_n$  value of **III-a** determined by <sup>1</sup>H NMR was 39 000, which was lower than calculated value on the basis of the feed ratios of  $[1]_0/[3]_0$  ( $M_n$ (calcd) = 47 000). On the other hand, the <sup>1</sup>H NMR spectrum of isolated III-b  $(M_n(GPC) = 15400, M_w/M_n = 1.05)$ showed the *doublet* signal e of the aromatic proton adjacent to the octylamino group at 6.2 ppm (Figure 6C),<sup>8c</sup> indicating a linear polyamide derived from selfpolymerization of 1. The fact that the  $M_{\rm n}$  of 14 000 determined by <sup>1</sup>H NMR was close to the  $M_n$ (GPC) value was also consistent with the feature of linear polymer from  $1.^{12}$  Accordingly, the  $M_n$  of **III-a** being lower than the theoretical  $M_{\rm n}$  is due to occurrence of not only chaingrowth polymerization from 3 but also self-polymerization of **1**. These results would suggest that the shoulder in the lower molecular weight region of sample II is also derived from the self-condensed linear polyamide without the **3** unit.

Cleavage of the arms of the isolated product III-a was attempted by hydrogenolysis at 50 °C for a week, but the linear polymer could not be obtained. It is probably difficult for long arm chains to be cleaved due to steric hindrance between the arms and the Pd/C catalyst for hydrogenolysis. However, sample II, obtained by the polymerization with 1 mol % of 3, underwent cleavage of the arms by hydrogenolysis at 50 °C for 3 days. Figure 7 shows the GPC chromatogram of II before and after hydrogenolysis. The main peak of II clearly shifted to the lower molecular weight region maintaing narrow distribution, and the peak became unimodal. Furthermore, the top position of this peak is surprisingly the same elution time as that of the shoulder peak of II before hydrogenolysis. This result implies that the degree of polymerization of each arm in star polymer II and that of the linear polyamide from the selfpolymerization of 1 were almost identical. In the case of product III, the  $M_n$  value of star polymer III-a ( $M_n$ = 39 000) was also nearly 3 times higher than that of the linear polymer **III-b** ( $M_n = 14000$ ).

We propose the polymerization mechanism as follows. We have recently reported that the polymerization of **1** without an initiator yields aromatic polyamides with low polydispersities  $(M_w/M_n \leq 1.1)$  and that this polymerization proceeds in a chain polymerization manner from the dimer of **1** formed in situ.<sup>13</sup> Accordingly, also in the polymerization of **1** with **3**, the dimer of **1** may be formed



**Figure 7.** GPC profiles of (A) **II** and (B) the product obtained by the hydrogenolysis of **II**.



**Figure 8.** GPC profiles of polymer obtained by the polymerization of **1** with **3** in the presence of *N*-octyl-*N*-triethylsilylaniline and CsF/18-crown-6 in THF ( $[1]_0 = [N$ -octyl-*N*triethylsilylaniline]\_0 = [CsF]\_0 = 0.33 M, [18-crown-6]\_0 = 0.66 M) at 25 °C:  $[1]_0/[3]_0 = 100$ .

in the early stage, and the chain-growth polymerization from the dimer and that from **3** would proceed at the same propagation rates to afford the linear polymer and the star polymer whose arm length is the same as that of the linear polymer. The propagation of both polymers can be seen by GPC traces of the polymerization of **1** with 1 mol % of **3** (Figure 8). The shoulder peak was observed in the middle stage of polymerization and shifted toward the higher molecular weight region, as well as the main peak, with polymerization time.

In the polymerization of 1 with a monofunctional initiator, no self-polymerization of 1 takes place as long as the feed ratio of  $[1]_0/[initiator]_0$  is 100 and less.<sup>7a</sup> In the polymerization with trifunctional initiator 3, however, the self-polymerization occurred even at the feed ratio of  $[1]_0/[initiator site of <math>3]_0 = 33$ , which is much less than 100. Easy occurrence of the self-polymerization in the polymerization of 1 with multifunctional initiator 3 is presumably ascribed to the low local concentration of the initiator site in the whole solution, except for the area around 3. Thus, monofunctional initiators homogeneously exist in the solution, whereas multifunctional initiators make both the area of high local concentration of the initiator units and the area of low local concentration of them where self-polymerization would be liable to occur. Contamination of the homopolymer in the synthesis of star polymers with multifunctional initiators turned out to be a unique problem in condensative chain-growth polymerization, in which there is a possibility of self-polymerization of monomers because it does not occur in the living addition polymerization method with multifunctional initiators.

### Conclusion

We have demonstrated that a condensative chaingrowth polymerization technique is applicable to preparation of star-shaped aromatic polyamides with controlled arm length by the use of multifunctional initiators. The polymerization of **1** with phenyl benzenepolycarboxylates (2a and 2b) as multifunctional initiators did not proceed homogeneously from each initiator site probably because of steric hindrance around the phenyl ester moieties in 2. In contrast, in the polymerization with trifunctional initiator **3** containing the benzyloxy spacers, the three phenyl ester moieties of 3 initiated polymerization of 1 homogeneously to yield a threearmed aromatic polyamide with a controlled arm length. However, the polymerization at higher feed ratios of  $[1]_0/$  $[3]_0$  afforded not only the three-armed polymer but also a linear polymer without the 3 unit from the selfpolymerization of **1**. This approach to star polymers by condensative chain-growth polymerization will permit the production of star block copolyamides having different aminoalkyl side chains and a well-defined sequence, as well as star block copolymers consisting of aromatic polyamide and polymers from the living polymerization of vinyl and cyclic monomers. Those results will be reported in the near future.

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