NOTE

Well-Defined Star-Shaped Poly(*p*-benzamide) via Chain-Growth Condensation Polymerization: Use of Tetra-Functional Porphyrin Initiator to Optimize Star Polymer Formation

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INTRODUCTION

Most star polymers with controlled molecular weight and low polydispersity are synthesized by living polymerization, in which only initiation and propagation reactions, but not chain transfer reaction, take place.¹ Accordingly, the obtained star polymers are generally not contaminated with linear polymers. Recently, we have developed chain-growth condensation polymerization,² a kind of living polymerization yielding condensation polymers with controlled molecular weight and narrow molecular weight distribution. However, synthesis of star-shaped poly(p-benzamide)s through this method, using multifunctional initiators, afforded not only the desired star-shaped poly(p-benzamide) via chain-growth polymerization, but also a linear poly(pbenzamide) via self-polycondensation of the monomer when the amount of the initiator was decreased. This contamination with linear polymer was more liable to occur as compared to the case of chain-growth condensation polymerization with a monofunctional initiator under the same conditions.³ In addition, separation of the products by means of high-performance liquid chromatography (HPLC) was necessary to confirm which product was the star polymer and which the linear polymer. However, by using an initiator containing porphyrin, the absorption maximum of which is around 430 nm and quite different from that of poly(p-benzamide), we could easily differentiate the star polymer bearing the porphyrin initiator unit from the linear polymer without this initiator unit by means of GPC with a variable-wavelength UV detector, and thus we could optimize the polymerization conditions for selective synthesis of star aromatic polyamides. Furthermore, there are rather few reports on the synthesis of porphyrin-cored star polymers with rigid arms, as compared with star polymers with flexible-coil polymer arms.⁴ For example, porphyrin-cored star polyfluorene was synthesized by Suzuki coupling polycondensation of bromofluorene boronic ester in the presence of a porphyrin having four iodofluorene moieties. In this polymerization, the length of the arms was not controlled and the molecular weight distribution was broad.⁵ Therefore, not only the synthesis, but also the properties of porphyrin-cored star polymers with well-defined rigid or semirigid arms remain to be fully established.

In this article, we investigated the chain-growth condensation polymerization of 4-(octylamino)benzoic acid esters 1 with porphyrin-cored tetra-functional initiator 3 under various conditions and optimized the conditions for selective synthesis of star-shaped poly(p-benzamide)s with suppression of the formation of linear selfcondensed polyamides (Scheme 1).

EXPERIMENTAL

Materials

Commercially available dehydrated tetrahydrofuran (stabilizer-free, Kanto) was used as a dry solvent.

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Scheme 1. Polymerization of 1 with 3.

Tetrakis(4-carboxyphenyl)porphine (TCPP, TCI), zinc-(II) acetate dihydrate (Aldrich), lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS, 1.0 M solution in THF, Aldrich) were used as received. 18-Crown-6 (TCI) was used after drying overnight under reduced pressure at 50 °C. *N*-Octyl-*N*-triethylsilylaniline (**2**) was prepared as described previously.⁶

Characterization

Conversion of monomers was determined by HPLC with a Japan Analytical Industry LC-909 HPLC unit (eluent: THF) using a JAIGEL column (1H-A). The $M_{\rm p}$ and $M_{\rm w}/M_{\rm n}$ values of polymers were measured with a TOSOH HLC-8120 gel-permeation chromatography (GPC) unit (eluent: THF; calibration: polystyrene standards) using two TSK-gel columns (2 \times Multipore H_{XI}-M). Isolation of polymer was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC unit (eluent: CHCl₃) using two TSK-gel columns $(2 \times \text{G2000H}_{\text{HR}}\text{-M})$. ¹H and ¹³C-NMR spectra were obtained on JEOL ECA-600 and ECA-500 spectrometers with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a JASCO FT/IE-410. Elemental analyses were performed using a Perkin-Elmer 2004 II CHN.

Synthesis of Initiator 3

Thionyl chloride (10 mL) was added to TCPP (0.494 g, 0.624 mmol), and the mixture was stirred at room temperature in darkness for 12 h. Excess thionyl chloride was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2 (30 mL) in the flask. To this solution was added a solution of triethylamine (0.70 mL, 5.4 mmol) and phenyl 4-(octylamino)benzoate (1.06 g, 3.25 mmol) in CH_2Cl_2 (5 mL). The mixture was

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stirred at room temperature in darkness for 1 h, and then the reaction was quenched with water. The organic layer was washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH₂Cl₂/hexane = 3/1) to give 0.982 g of porphyrin **3** without metallic cation as a purple solid (78%, m.p. 90–92 °C).

¹H NMR (600 MHz, CDCl₃, δ, ppm): 8.63 (s, 8 H), 8.24 (d, J = 8.3 Hz, 8 H), 7.98 (d, J = 7.8 Hz, 8 H), 7.65 (d, J = 8.2 Hz, 8 H), 7.43 (t, J = 7.8 Hz, 8 H), 7.33-7.27 (m, 12 H), 7.18 (d, J = 7.6 Hz, 8 H), 4.15 (t, J = 7.8 Hz, 8 H), 1.79 (quint, J = 7.7 Hz, 8 H), 1.47 (quint, J = 7.2Hz, 8 H), 1.42–1.25 (m, 32 H), 0.91 (t, J = 7.1 Hz, 12 H), -2.98 (s, 2 H). ¹³C NMR (150 MHz, CDCl₃, δ , ppm): 170.2, 164.4, 150.9, 148.6, 143.5, 135.4, 133.8, 131.3, 129.6, 127.7, 127.5, 127.19, 127.17, 126.1, 121.6, 119.2, 50.5, 31.8, 29.4, 29.3, 28.0, 27.0, 22.7, 14.1. IR (KBr, cm⁻¹): 3316, 3071, 2925, 1737, 1655, 1602, 1508, 1317, 1264, 754.

A solution of the above porphyrin (0.360 g, 0.180 mmol) and zinc(II) acetate dihydrate (0.322 g, 1.47 mmol) in CHCl₃ (36 mL) and MeOH (4 mL) was refluxed for 1 h. After cooling to room temperature, the reaction mixture was concentrated to dryness under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH₂Cl₂, then CH₂Cl₂/ methanol = 10/1) to give 0.389 g of **3** as a purple solid (95%, m.p. 115–116 °C).

¹H NMR (600 MHz, CDCl₃, δ, ppm): 8.72 (s, 8 H), 8.22 (d, J = 8.6 Hz, 8 H), 7.98 (d, J = 7.9 Hz, 8 H), 7.60 (d, J = 7.9 Hz, 8 H), 7.41 (t, J = 7.9 Hz, 8 H), 7.32–7.26 (m, 12 H), 7.17 (d, J = 7.6 Hz, 8 H), 4.11 (t, J = 7.6 Hz, 8 H), 1.76 (quint, J = 7.7 Hz, 8 H), 1.45 (quint, J = 7.2Hz, 8 H), 1.41–1.25 (m, 32 H), 0.91 (t, J = 6.9 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ , ppm): 170.2, 164.4, 150.8, 149.8, 148.6, 144.2, 135.1, 133.7, 131.9, 131.2, 129.6, 127.7, 127.5, 127.0, 126.1, 121.6, 120.1, 50.5, 31.8, 29.4, 29.3, 28.0, 27.0, 22.7, 14.1. IR (KBr, cm⁻¹): 3066, 2925, 1737, 1654, 1602, 1508, 1317, 1264, 754.

Anal. calcd for $C_{132}H_{128}N_8O_{12}Zn$: C, 76.08; H, 6.19; N, 5.38. Found: C, 75.72; H, 6.11; N, 5.28.

Polymerization of 1a with 2/CsF/18-crown-6

CsF (304 mg, 2.00 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure for 30 min. The flask was cooled to room temperature under an argon atmosphere. Into the flask were added a solution of phenyl 4-(octylamino)benzoate (1a) (651 mg, 2.00 mmol), 3 (52.4 mg, 25.1 µmol), 2 (639 mg, 1.99 mmol), and naphthalene (26.1 mg, 0.203 mmol, used as an internal standard for HPLC analysis) in dry THF (2.0 mL), and a solution of 18-crown-6 (1.06 g, 4.00 mmol) in dry THF (0.5 mL), successively. The mixture was stirred at ambient temperature for 6 h (monomer conversion = 96%), and the reaction was then quenched with saturated aqueous NH₄Cl. The whole was extracted with CHCl₃, and the organic layer was washed with water, and dried over anhydrous MgSO₄. After concentration in vacuo, the products were purified by preparative HPLC to give 407 mg of **4a** as a purple oil.

Polymerization of 1a by Slow Addition of 1a

CsF (61.9 mg, 0.407 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure for 30 min. The flask was cooled to room temperature under an argon atmosphere. Into the flask was added a solution of 3 (10.4 mg, 4.99 µmol), 18-crown-6 (219. mg, 0.829 mmol), and naphthalene (11.1 mg, 0.0866 mmol, used as an internal standard for HPLC analysis) in dry THF (1.0 mL). A solution of 1a (130 mg, 0.398 mmol) and 2 (123 mg, 0.386 mmol) in dry THF (1.0 mL) was slowly added dropwise over 15 min with stirring. The mixture was stirred at ambient temperature for an additional 31 h (monomer conversion = 84%), and the reaction was then quenched with saturated aqueous NH₄Cl. The whole was extracted with CHCl₃, and the organic layer was washed with water, followed by drying over anhydrous MgSO₄. Concentration in vacuo gave a crude product, whose $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ were determined by GPC ($M_{\rm n}=8800, M_{\rm w}/M_{\rm n}=1.70$). The residue was purified by preparative HPLC to give 31.4 mg of 4a as a purple oil.

Polymerization of 1b with LiHMDS

A round-bottomed flask equipped with a three-way stopcock was purged with argon and then charged with dry THF (0.4 mL) and 1.0 M LiHMDS in THF (0.41 mL, 0.41 mmol). The flask was cooled to $10 \,^{\circ}$ C under an argon atmosphere. A solution of methyl 4-(octylamino)-

benzoate (**1b**) (106 mg, 0.402 mmol) and **3** (10.3 mg, 4.94 μ mol) in dry THF (1.0 mL) at 10 °C was added at once into the flask containing LiHMDS with a syringe through the three-way stopcock in a stream of dry nitrogen, with stirring. Stirring was continued at 10 °C for 1.5 h, then the reaction was quenched with saturated aqueous NH₄Cl, and the whole was extracted with CH₂Cl₂. The organic layer was washed with 1 M NaOH and dried over anhydrous MgSO₄. Concentration *in vacuo* gave a crude product, whose M_n and M_w/M_n were determined by GPC ($M_n = 15,200, M_w/M_n = 1.07$). The residue was purified by preparative HPLC to give 89.4 mg of star **4b** as a purple oil (88%).

4b. $M_{\rm n} = 22,800$ (determined by ¹H NMR), $M_{\rm n}$ (calcd.) = 20,800, $M_{\rm w}/M_{\rm n} = 1.07$.

¹H NMR (500 MHz, CDCl₃, δ , ppm): 8.72 (s, 8 H), 7.96 (d, J = 6.9 Hz, 8 H), 7.86 (d, J = 8.6 Hz, 8 H), 7.60 (d, J = 7.5 Hz, 8 H), 7.20–6.90 (d, J = 8.2 Hz, 2n H), 6.90–6.40 (d, J = 8.2 Hz, 2n H), 4.17–3.03 (m, 2n H), 1.85–1.00 (m, 12n H), 1.00–0.70 (m, 3n H). IR (KBr, cm⁻¹): 3043, 2926, 2855, 1724, 1603, 1509, 848, 762, 706.

RESULTS AND DISCUSSION

The phenyl ester monomer **1a** was first polymerized from the Zn-porphyrin initiator **3** ([**1a**]₀/[**3**]₀ = 80) in the presence of 1.0 equivalent of *N*-octyl-*N*-triethylsilylaniline (**2**), CsF, and 2.0 equivalent of 18-crown-6 in THF at room temperature according to our reported procedure for the synthesis of star polyamides.³ Porphyrin initiator **3** without the metallic cation was not suitable, probably because the acidic protons of the initiator disturbed the polymerization. The products were analyzed by GPC with a UV detector at 254 and 430 nm. In the case of detection at 254 nm, the GPC elution curve was bimodal [Fig. 1(A)], whereas the GPC trace detected at 430 nm showed a monomodal peak, the M_n



Figure 1. GPC profiles of tetra-armed star polymers **4a**, obtained by the polymerization of **1a** with **3** ([**1a**]₀/[**3**]₀ = 79.7), detected by absorption measurement at (A) 254 nm ($M_n = 9700$, $M_w/M_n = 1.22$) and (B) 430 nm ($M_n = 11,400$, $M_w/M_n = 1.10$).

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Entry	$[\mathbf{1b}]_0/[3]_0$	Temp. (°C)	Conv. (%) ^b	$M_{ m n,\ calcd}$	$M_{ m n,~GPC}{}^{ m c}$	$M_{ m n, \ NMR}{}^{ m d}$	$M_{ m w}/M_{ m n}^{ m c}$
1	80.4	-10	95	19.500	9.500	18.800	1.33
2	80.6	-30	100	20,500	10.100	20.000	1.25
3	81.4	10	100	20,600	15.200	22.800	1.07
4	80.6	25	100	20,500	15,600	24,700	1.09
5	39.5	10	100	11,000	10,700	11,900	1.05
6	120.4	10	100	29,600	22,200	32,700	1.11
7	158.5	10	100	38,400	20,500	47,900	1.25

Table 1. Polymerization of 1b with 3^a

^aPolymerization of 1b with 3 was carried out in the presence of 1.0 equivalent of LiHMDS in THF ($[1b]_0 = 0.67$ M).

^b Determined by HPLC.

^cDetermined by GPC based on polystyrene standards (eluent: THF).

^d Determined by ¹H NMR.

value of which was identical with that of the main peak detected at 254 nm [Fig. 1(B)]. This means that the product corresponding to the main peak contains a porphyrin moiety, i.e., it is the desired porphyrin-cored star polymer **4a** with narrow molecular weight distribution. Accordingly, the minor peak detected at 254 nm was due to a linear polyamide formed by self-polycondensation of **1a**. When the feed ratio of monomer to initiator ([**1a**]₀/[**3**]₀) was decreased to 40 or to 20, the minor peak of the GPC elution curve decreased, but did not disappear.

Considering that a low concentration of the monomer would suppress the self-polycondensation of **1a**, we slowly added a solution of **1a** and **2** in THF to a solution of **3**, CsF, and 18-crown-6 in THF. Contrary to our expectation, the GPC elution curves detected both 254 nm and 430 nm showed broad molecular weight distributions ($M_w/M_n = 1.70$ and 1.51), respectively. Therefore, slow addition method caused not only self-polycondensation of **1a** but also production of star polymer with broad molecular weight distribution. This result implies that the base system using 2 was not strong enough to immediately abstract the proton of the amino group of 1a added slowly to the reaction mixture.

In our previous report,⁷ LiHMDS, which is a stronger base, was effective for the synthesis of linear poly(N-octyl-p-benzamide)s with defined molecular weight and narrow molecular weight distribution by polymerization of the methyl ester monomer 1b. Therefore, the polymerization of 1b was carried out by using LiHMDS in the presence of **3** ($[1b]_0/[3]_0 = 80$) at $-10 \degree C$ according to the procedure used for the synthesis of linear polyamide (Table 1, entry 1). The polymerization proceeded rapidly, and the minor peak in the GPC elution curve of the product became much smaller than that of the polymer obtained by polymerization with 2/CsF/18-crown-6 [Fig. 2(A) versus Fig. 1(A)]. The M_w/M_n ratios in Table 1 were calculated including the minor peak as an index of contamination of linear poly1b; the molecular weight distribution of star polymers was



Figure 2. GPC profiles detected by absorption measurement at 254 nm of tetraarmed star polymers **4b** obtained by the polymerization of **1b** with **3** in the presence of LiHMDS in THF ([**1b**]₀ = [LiHMDS]₀ = 0.67*M*; [**1b**]₀/[**3**]₀ = 80) at (A) -10 °C $(M_n = 9500, M_w/M_n = 1.33, \text{ entry 1})$, (B) -30 °C $(M_n = 10,100, M_w/M_n = 1.25, \text{ entry})$ 2) and (C) 10 °C $(M_n = 15,200, M_w/M_n = 1.07, \text{ entry 3})$.

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always narrow as shown in Figure 2. We next examined the polymerization temperature. Polymerization at -30 °C increased the formation of the linear polymer [entry 2, Fig. 2(B)], whereas the polymerization at 10 °C afforded only the tetra-armed star polymer 4b with a narrow molecular weight distribution [entry 3, Fig. 2(C)]. At room temperature, however, the minor peak of the linear polymer appeared again (entry 4). The star polymer formation favorable at higher temperature over self-polycondensation of 1b may be attributed to fast abstraction of the proton from the amino group of 1b with LiHMDS and fast reaction of deprotonated 1b with the tetra-functional initiator 3 at higher temperature. The self-polycondensation would be initiated by the reaction of 1b not deprotonated with the deprotonated **1b** because the amide anion strongly deactivates the ester moiety of 1b to prevent the deprotonated 1b from reacting with itself. Therefore, the fast generation of the deprotonated 1b would suppress selfpolycondensation. At room temperature, however, even the reaction between the deprotonated **1b** might take place, resulting in self-polycondensation.

Under the optimized conditions in hand, the polymerization was carried out with various feed ratios of monomer to initiator $([1b]_0/[3]_0)$ to synthesize star polymers **4b** with different arm lengths. The polymerization at the feed ratios $[1b]_0/[3]_0$ of 40 and 120 gave well-defined **4b**, the molecular weight values of which agreed well with the calculated values based on those feed ratios (entries 5, 6). At the ratio $[1b]_0/[3]_0$ of 159, however, the product was contaminated with self-condensed linear polymer, and the molecular weight distribution became broad (entry 7). Nevertheless, high-molecular-weight star polymer with low polydispersity was easily isolated by means of HPLC with SEC columns, because the molecular weight of the star polymer was sufficiently different from that of the linear polymer.

CONCLUSIONS

We investigated the chain-growth condensation polymerization method for the synthesis of well-defined star-shaped poly(*p*-benzamide) by using the porphyrincored tetra-functional initiator **3**. Because the objective star polymer has an absorption at 430 nm due to the porphyrin ring, the linear polymer formed as a by-product does not have this absorption, we were easily able to differentiate the star polymer from the linear polymer by GPC with UV detection and to optimize conditions for the selective synthesis of the star polymer. Thus, the methyl ester monomer **1b** was polymerized with LiHMDS in the presence of **3** at 10 °C to yield the star polyamide **4b** with controlled molecular weight and narrow molecular weight distribution. Studies of the properties of the porphyrin-cored star aromatic polyamides in comparison with those of general porphyrin-cored coil polymers are under way.

REFERENCES AND NOTES

- 1. Yusuf, Y.; Atilla, T. M. Prog Poly Sci 2006, 31, 1133.
- For recent reviews, see: (a) Yokozawa, T.; Yokoyama, A.; Chem Rec 2005, 5, 47; (b) Yokozawa, T.; Yokoyama, A. Prog Polym Sci 2007, 32, 147; (c) Yokoyama, A.; Yokozawa, T. Macromolecules 2007, 40, 4093.
- Sugi, R.; Hitaka, Y.; Yokoyama, A.; Yokozawa, T. Macromolecules 2005, 38, 5526.
- (a) Dichtel, W. R.; Baek, K.-Y.; Fréchet, J. M. J.; Rietveld, I. B.; Vinogradov, S. A. J. Polym Sci Part A: Polym Chem 2006, 44, 4939; (b) Beil, J. B.; Zimmerman, S. C. Macromolecules 2004, 37, 778; (c) High, L. R. H.; Holder, S. J.; Penfold, H. V. Macromolecules 2007, 40, 7157; (d) Hecht, S.; Vladimirov, N.; Fréchet, J. M. J. J Am Chem Soc 2001, 123, 18; (e) Jin, R.-H. J Mater Chem 2004, 14, 320.
- Li, B.; Xu, X.; Sun, M.; Fu, Y.; Yu, G.; Liu, Y.; Bo, Z. Macromolecules 2006, 39, 456.
- Yokozawa, T.; Asai, T.; Sugi, R.; Ishigooka, S.; Hiraoka, S. J Am Chem Soc 2000, 122, 8313.
- Yokozawa, T.; Muroya, D.; Sugi, R.; Yokoyama, A. Macromol Rapid Commun 2005, 26, 979.