Chain-Growth Condensation Polymerization of 4-Aminobenzoic Acid Esters Bearing Tri(ethylene glycol) Side Chain with Lithium Amide Base

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ABSTRACT: Chain-growth condensation polymerization of *p*-aminobenzoic acid esters **1** bearing a tri(ethylene glycol) monomethyl ether side chain on the nitrogen atom was investigated by using lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base. The methyl ester monomer **1a** afforded polymer with low molecular weight and a broad molecular weight distribution, whereas the polymerization of the phenyl ester monomer **1b** at -20 °C yielded polymer with controlled molecular weight ($M_n = 2800-13,400$) and low polydispersity ($M_w/M_n = 1.10-1.15$). Block copolymerization of **1b** and 4-(octylamino)benzoic acid methyl ester (**2**) was further investigated. We found that block copolymer of poly**1b** and poly**2** with defined molecular

weight and low polydispersity was obtained when the polymerization of **1b** was initiated with equimolar LiHMDS at -20 °C and continued at -50 °C, followed by addition of **2** and equimolar LiHMDS at -10 °C. Spherical aggregates were formed when a solution of poly**1b** in THF was dropped on a glass plate and dried at room temperature, although the block copolymer of poly**1b** and poly**2** did not afford similar aggregates under the same conditions. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1357–1363, 2010

KEYWORDS: block copolymers; chain-growth condensation polymerization; living polymerization; polyamides; self-assembly

INTRODUCTION Oligomers and polymers containing aromatic rings in the backbone and oligo(oxyethylene) units in the side chain possess unique character derived from the different solvophobicity of the backbone and side chain.¹⁻⁹ For example, *m*-phenyleneethynylene oligomers bearing tri(ethylene glycol) side chains fold to a helix in polar solvents, such as acetonitrile.¹ We have reported that poly(*p*-benzamide)⁵ and poly(naphthalenecarboxamide)⁶ bearing methyl-substituted tri(ethylene glycol) as a chiral side chain on the nitrogen atom take helical structures in solution, whereas the corresponding poly(*m*-benzamide) takes a chiral conformation in solution.⁷ Furthermore, poly(*m*-benzamide)s bearing triand tetra(ethylene glycol) side chains on the nitrogen atom are soluble in water and exhibit lower critical solution temperatures (LCST) in water.⁸

These aromatic polyamides, except the poly(*p*-benzamide), were synthesized in a controlled manner by chain-growth condensation polymerization of the corresponding aromatic amino acid esters with lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base.¹⁰ However, the poly(*p*-benzamide) with the chiral tri(ethylene glycol) side chain was prepared by polymerization with a prototype base system using *N*-octyl-*N*-(triethylsilyl)aniline/CsF/18-crown-6, instead of commercially available LiHMDS.⁵ This silyl aniline is readily hydrolyzed by moisture in air. *N*-Alkyl poly(*p*-benzamide)s have already been synthesized by polymerization with LiHMDS, but a polymerization method using LiHMDS for the synthesis of poly(*p*-benzamide) bearing oligo(oxyethylene) side chains has not been established. An oligo(oxyethylene) side chain on the amide anion would have a strong affinity for the lithium cation derived from LiHMDS, and this is expected to reduce the reactivity of the amide anion. Furthermore, the amide anions of *para*-aminobenzoic acid ester monomers are less reactive than those of the *meta*-substituted counterparts because of the electron-withdrawing resonance effect of the ester moiety in the para monomer. Therefore, the polymerization of *N*-oligo(oxyethylene) 4-aminobenzoic acid esters with LiHMDS is thought not to proceed in the same manner as that of the *meta*-substituted counterparts.

In this article, we report LiHMDS-promoted chain-growth condensation polymerization of 4-aminobenzoic acid esters **1** bearing a tri(ethylene glycol) monomethyl ether side chain on the nitrogen atom and the copolymerization of **1** and 4-(octylamino)benzoic acid methyl ester **2** with LiHMDS (Scheme 1). Self-assembly of poly**1** and the block copolymer was also examined.

EXPERIMENTAL

Materials

Commercially available dehydrated tetrahydrofuran (stabilizer-free, Kanto) and $\rm CH_2Cl_2$ (Kanto) were used as dry

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SCHEME 1 A: Polymerization of **1**. B: Block copolymerization of **1** and **2**.

solvents. Lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS, 1.0 M solution in THF, Aldrich) was used as received. N,N,N',N'-Tetramethylethylenediamine (TMEDA) was distilled over CaH₂. Methyl 4-(octylamino)benzoate (**2**)¹⁰ and phenyl 4-methylbenzoate (**3**)¹¹ were prepared as described previously.

Characterization

Conversion of monomer was determined by HPLC with a Japan Analytical Industry LC-909 HPLC unit (eluent: THF) using a JAIGEL column (1H-A). The $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ values of polymers were measured with a TOSOH HLC-8120 gel-permeation chromatography (GPC) unit (eluent: THF; volume flow rate: 1 mL/min; calibration: polystyrene standards) using two TSK-gel columns (2 \times Multipore H_{XL}-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 G2000H_{HR}-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/IR-410. Scanning electron microscopy (SEM) was carried out with a Hitachi S-4000. Samples were prepared by dropping a THF solution of polymer on a glass slide, and allowing it to dry under THF vapor at 25 °C for 3 days. This glass plate was sputter-coated with carbon before SEM analysis.

Synthesis of Monomer 1

Monomer $\mathbf{1}$ was synthesized by the procedure as shown in Scheme 2.

Synthesis of 4-{2-[2-(2-Methoxyethoxy)ethoxy]acetylamino} benzoic Acid Methyl Ester (4a)

A mixture of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (6.0 mL, 39 mmol), methyl 4-aminobenzoate (4.5 g, 30 mmol), and 4-(dimethylamino)pyridine (DMAP, 4.8 g, 39 mmol) in dry CH_2Cl_2 (45 mL) was stirred at 0 °C for 10 min. Into the flask was added *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (7.5 g, 39 mmol) with stirring at 0 °C. The reaction mixture was stirred at room temperature for 65 h, and then the reaction was quenched with water, followed by extraction with CH_2Cl_2 . The combined organic layer was washed with 1 M HCl and saturated aqueous NaHCO₃,

and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 5/1) to give 5.1 g of **4a** as a yellow viscous oil (54%).

¹H NMR (500 MHz, CDCl₃, δ, ppm): 8.97 (br s, 1 H), 8.06 (d, J = 8.9 Hz, 2 H), 7.62 (d, J = 8.9 Hz, 2 H), 4.13 (s, 2 H), 3.90 (s, 3 H), 3.79–3.77 (m, 2 H), 3.74–3.72 (m, 4 H), 3.60–3.58 (m, 2 H), 3.37 (s, 3 H). ¹³C NMR (126 MHz, CDCl₃, δ, ppm): 168.6, 166.6, 141.6, 130.7, 125.7, 119.1, 71.7, 71.2, 70.7, 70.4, 70.0, 58.9, 51.9. IR (neat, cm⁻¹): 3332, 2882, 1719, 1282, 1176, 1109, 858.

Synthesis of 4-{2-[2-(2-Methoxyethoxy)ethoxy]ethylamino}benzoic Acid Methyl Ester (1a)

A three-necked flask, equipped with a dropping funnel, a reflux condenser, and a gas inlet tube, was purged with argon and then charged with 1.15 M borane-THF complex in THF (15 mL, 17 mmol). The solution was cooled to 0 °C under an argon atmosphere with stirring for 10 min. A solution of **4a** (4.1 g, 13 mmol) in dry THF (20 mL) was added dropwise from the dropping funnel, and the mixture was refluxed for 3.5 h. After cooling to room temperature, 6 M HCl (23 mL) was added to it, and the whole was heated under reflux for 1 h. The solution was diluted with water and neutralized to approximately pH 8 with NaHCO₃, then extracted with Water and dried over anhydrous MgSO₄. The



SCHEME 2 Synthesis of Monomer 1.

solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 7/1) to give 2.6 g of **1a** as an orange viscous oil (67%).

¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.86 (d, J = 8.9 Hz, 2 H), 6.57 (d, J = 8.9 Hz, 2 H), 4.69 (br s, 1 H), 3.84 (s, 3 H), 3.71 (t, J = 5.2 Hz, 2 H), 3.67–3.65 (m, 6 H), 3.57–3.55 (m, 2 H), 3.39 (s, 3 H), 3.35 (q, J = 4.6 Hz, 2 H). ¹³C NMR (126 MHz, CDCl₃, δ , ppm): 167.2, 152.0, 131.4, 118.1, 115.5, 71.8, 70.4, 70.2, 69.1, 61.8, 58.9, 51.4, 42.8. IR (neat, cm⁻¹): 3369, 2876, 1704, 1607, 1278, 1109, 771.

Synthesis of 4-{2-[2-(2-Methoxyethoxy)ethoxy]acetylamino} benzoic Acid Phenyl Ester (4b)

A mixture of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (8.0 mL, 52 mmol), phenyl 4-aminobenzoate (8.6 g, 40 mmol), and DMAP (6.4 g, 52 mmol) in dry CH_2Cl_2 (180 mL) was stirred at 0 °C for 10 min. Into the flask was added EDCI (10.0 g, 52 mmol) with stirring at 0 °C. The reaction mixture was stirred at room temperature for 48 h, and then the reaction was quenched with water, followed by extraction with CH_2Cl_2 . The combined organic layer was washed with 1 M HCl and saturated aqueous NaHCO₃, and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 2/1) to give 12.8 g of **4b** as a pale yellow viscous oil (83%).

¹H NMR (600 MHz, CDCl₃, δ , ppm): 9.05 (br s, 1 H), 8.17 (d, J = 8.9 Hz, 2 H), 7.81 (d, J = 8.9 Hz, 2 H), 7.42 (t, J = 7.4 Hz, 2 H), 7.23 (t, J = 7.5 Hz, 1 H), 7.21 (d, J = 7.7 Hz, 2 H), 4.12 (s, 2 H), 3.80–3.78 (m, 2 H), 3.75–3.73 (m, 4 H), 3.61–3.59 (m, 2 H), 3.38 (s, 3 H). IR (neat, cm⁻¹): 3332, 2882, 1719, 1282, 1176, 1109, 858.

Synthesis of 4-{2-[2-(2-Methoxyethoxy)ethoxy]ethylamino}benzoic Acid Phenyl Ester (1b)

A three-necked flask, equipped with a dropping funnel, a reflux condenser, and a gas inlet tube, was purged with argon and then charged with 0.98 M borane-THF complex in THF (40 mL, 39 mmol). The solution was cooled to 0 °C under an argon atmosphere with stirring for 10 min. A solution of 4b (11.6 g, 30 mmol) in dry THF (50 mL) was added dropwise from the dropping funnel, and the mixture was refluxed for 3 h. It was then cooled to room temperature, 6 M HCl (5 mL) was added to it, and the whole was heated under reflux for 1 h. The solution was diluted with water and neutralized to approximately pH 8 with NaHCO₃, then extracted with CH₂Cl₂. The combined 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 (ethyl acetate/hexane = 3/4) to give 4.6 g of **1b** as an orange oil (43%).

¹H NMR (600 MHz, CDCl₃, δ , ppm): 8.01 (d, J = 8.6 Hz, 2 H), 7.40 (t, J = 8.1 Hz, 2 H), 7.23 (t, J = 7.4 Hz, 1 H), 7.19 (d, J = 8.4 Hz, 2 H), 6.63 (d, J = 8.6 Hz, 2 H), 4.80 (s, 1 H), 3.74 (t, J = 5.2 Hz, 2 H), 3.71–3.65 (m, 6 H), 3.59–3.56 (m, 2 H), 3.40 (s, 3 H), 3.38 (t, J = 5.3 Hz, 2 H). ¹³C NMR (126 MHz, CDCl₃, δ , ppm): 165.3, 152.6, 151.3, 132.2, 129.3, 125.4, 121.9, 117.4, 111.7, 72.0, 70.6, 70.4, 69.2, 59.0, 42.9. IR (neat, cm⁻¹): 3369, 2876, 1704, 1607, 1278, 1109, 771.

Polymerization

Polymerization of 1b

A round-bottomed flask equipped with a three-way stopcock was purged with argon and then charged with dry THF (0.5 mL) and 1.0 M LiHMDS in THF (0.50 mL, 0.50 mmol). The solution was cooled to -20 °C with stirring under an argon atmosphere. A solution of 1b (0.180 g, 0.50 mmol) and 3 (0.0053 g, 0.025 mmol) in dry THF (0.5 mL) at -20 °C was added at once with a syringe into the flask containing LiHMDS through the three-way stopcock under a stream of dry nitrogen. Stirring was continued at -20 °C for 4 h, then the reaction was quenched with saturated aqueous NH₄Cl, and the whole was extracted with CH₂Cl₂. The organic layer was washed with water and dried over anhydrous MgSO₄. Concentration in vacuo gave a crude product, whose M_n and $M_{\rm w}/M_{\rm n}$ were determined by GPC ($M_{\rm n}=4000,\ M_{\rm w}/M_{\rm n}=$ 1.15). The residue was purified by preparative HPLC to give 0.063 g of poly**1b** as a yellow viscous oil (46%).

Poly**1b**: $M_n = 6400$ (determined by ¹H NMR), M_n (calcd.) = 5500, $M_w/M_n = 1.15$.

¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.08 (d, J = 7.2 Hz, 2n H), 6.89 (d, J = 7.9 Hz, 2n H), 4.15–3.88 (m, 2n H), 3.79–3.46 (m, 10n H), 3.39–3.30 (m, 3n H). IR (neat, cm⁻¹): 3059, 2873, 1644, 1603, 1509, 1107, 849.

Synthesis of Block Copolymer

A round-bottomed flask equipped with a three-way stopcock was purged with argon and then charged with dry THF (0.5 mL) and 1.0 M LiHMDS in THF (0.50 mL, 0.50 mmol). The solution was cooled to -20 °C with stirring under an argon atmosphere. A solution of 1b (0.180 g, 0.50 mmol) and 3 (0.0053 g, 0.025 mmol) in dry THF (0.5 mL) at -20 °C was added at once with a syringe into the flask containing LiHMDS through the three-way stopcock under a stream of dry nitrogen. After having been stirred for 10 min at -20 °C, the mixture was cooled to -50 °C with stirring. Stirring was continued at -50 °C for 6 h, then 0.1 mL of the solution was withdrawn and quenched with saturated aqueous NH₄Cl to measure the M_n value and M_w/M_n ratio of poly**1b** $[M_n \text{ (GPC)} = 3600, M_w/M_n = 1.11]$. Immediately after the sampling, the reaction mixture was warmed to -10 °C, and then 1.0 M LiHMDS in THF (0.50 mL, 0.50 mmol) at room temperature was slowly added, followed by fast addition of a solution of 2 (0.123 g, 0.47 mmol) in dry THF (1.0 mL) at -10 °C. The mixture was stirred at -10 °C for 15 h. The reaction was quenched with saturated aqueous NH₄Cl, and the whole was extracted with CHCl₃. The organic layer was washed with water and dried over anhydrous MgSO₄. Concentration in vacuo gave a crude product, whose M_n and $M_{\rm w}/M_{\rm n}$ were determined by GPC ($M_{\rm n}=6700,~M_{\rm w}/M_{\rm n}=$ 1.15). The residue was purified by preparative HPLC to give 0.188 g of the block copolymer of poly1b and poly2 as a yellow viscous oil (75%).

Entry	Additive ^b	Temp. (°C)	Time (days)	M _{n calcd.}	<i>M</i> _{n GPC} ^c	$M_{\rm w}/M_{\rm n}^{\rm c}$
1	-	0	12 ^d	_e	600	1.22
2	LiCl	0	7 ^d	_e	900	1.30
3	TMEDA ^f	0	9	5,500	2,100	1.63
4	-	25	2	5,500	1,700	1.72
5	LiCl	25	3	5,500	1,200	1.52
6	TMEDA ^f	25	2	5,500	1,600	1.73

TABLE 1 Polymerization of 1a^a

^a Polymerization of **1a** with **3** was carried out in the presence of 1.0 equiv. of LiHMDS in THF ([**1a**]₀/[**3**]₀ = 20, [**1a**]₀ = 0.33 M).

^b Five equivalents.

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

Poly**1b**-*b*-poly**2**: $M_n = 10,000$ (determined by ¹H NMR), M_n (calcd.) = 10,200, $M_w/M_n = 1.15$.

¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.16–6.98 (m, 2(n+m) H), 6.89 (d, J = 8.0 Hz, 2n H), 6.77 (d, J = 8.0 Hz, 2m H), 4.03–3.90 (m, 2n H), 3.85–3.74 (m, 2m H), 3.68–3.48 (m, 10n H), 3.35 (s, 3n H), 1.57–1.44 (m, 2m H), 1.39–1.08 (m, 10m H), 0.87 (t, J = 7.0 Hz, 3m H). IR (KBr, cm⁻¹): 3065, 2926, 2856, 1569, 1017, 949, 763.

RESULTS AND DISCUSSION

Polymerization of Methyl Ester Monomer 1a

The methyl ester monomer **1a** bearing a tri(ethylene glycol) monomethyl ether side chain on the nitrogen atom was polymerized in the presence of phenyl 4-methylbenzoate (3) $([1a]_0/[3]_0 = 20)$ as an initiator and 1.0 equiv. of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base⁹ in THF under several conditions (Table 1). The polymerization at 0 °C, like the polymerization of 4-(octylamino)benzoic acid methyl ester (2) with LiHMDS, proceeded very slowly, and 1a was not completely consumed even after 12 days (entry 1). Addition of 5 equiv. of LiCl¹²⁻¹⁴ gave similar results (entry 2). In contrast, addition of 5 equiv. of TMEDA^{8,15-18} resulted in complete consumption of **1a** (entry 3), implying that the unusually slow polymerization of 1a stems from coordination of the lithium cation to the tri(ethylene glycol) side chain on the nucleophilic nitrogen atom. However, the polymerization was still slow, and afforded polymer with a

TABLE 2 Po	olymerization of 1b ^a
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 $^{\rm d}$ 1a was not completely consumed.

^e Not calculated because the conversion of **1a** was not determined.

^f N, N, N', N'-Tetramethylethylenediamine.

low molecular weight and a broad molecular weight distribution ($M_n = 2100, M_w/M_n = 1.63$).

The polymerization was then carried out at room temperature. The monomer **1a** was completely consumed even in the absence of LiCl or TMEDA, but the M_n value of the polymer obtained was lower than the calculated value based on the feed ratio of $[1a]_0/[3]_0$ and the molecular weight distribution was broad (entry 4). LiCl or TMEDA was not effective for controlling polymerization of **1a** at room temperature, giving similar polymers with low M_n and broad molecular weight distribution (entries 5 and 6). We speculated that the low reactivity of **1a** might reduce the difference of activation energy between the reaction of **1a** with the polymer end group, leading to chain-growth polymerization, and the selfcondensation of **1a**, leading to step-growth polymerization.

Polymerization of Phenyl Ester Monomer 1b

We next polymerized more reactive phenyl ester monomer **1b** in the presence of **3** ([**1b**]₀/[**3**]₀ = 20) and LiHMDS (Table 2). The polymerization proceeded rapidly at -10 °C, and the molecular weight of the obtained polymer became larger than in the case of the polymerization of **1a** (entry 1). However, the GPC elution curve showed a shoulder in the higher-molecular-weight region [Fig. 1(A)]. In the polymerization at -20 °C, the minor shoulder disappeared, and the molecular weight distribution became narrower [entry 2, Fig. 1(B)]. At -30 °C, however, a shoulder appeared again in the higher-molecular-weight region [entry 3, Fig. 1(C)]. Therefore, the optimum temperature for the polymerization of **1b**

Entry	[1b] ₀ /[3] ₀	Temp. (°C)	Time (h)	<i>M</i> _{n calcd}	M _{n GPC} ^b	<i>M</i> _{n NMR} ^c	$M_{\rm w}/M_{\rm n}^{\rm b}$
1	20.0	-10	2.5	5,500	4,200	6,200 ^d	1.20
2	20.0	-20	4	5,500	4,100	6,400	1.15
3	20.0	-30	5	5,500	3,800	5,600	1.16
4	10.0	-20	2	2,900	2,200	2,800	1.11
5	31.2	-20	2	8,200	4,800	7,200	1.10
6	50.0	-20	4	13,500	7,500	13,400	1.10

 $^{\rm a}$ Polymerization of 1b with 3 was carried out in the presence of 1.0 equiv. of LiHMDS in THF ([1b]_0 = 0.33 M).

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

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^c Determined by ¹H NMR.

^d Polymer in the shoulder was removed with preparative HPLC.



FIGURE 1 GPC profiles of poly**1b** obtained by the polymerization of **1b** with **3** in the presence of LiHMDS in THF ([**1b**]₀/[**3**]₀ = 20, [**1b**]₀ = 0.33 M) at (A) -10 °C ($M_{n GPC} = 4200$, $M_w/M_n = 1.20$, entry 1 in Table 2), (B) -20 °C ($M_{n GPC} = 4100$, $M_w/M_n = 1.15$, entry 2), and (C) -30 °C ($M_{n GPC} = 3800$, $M_w/M_n = 1.16$, entry 3).

was -20 °C. These temperature effects can be accounted for by assuming that the shoulder was due to products generated by the coupling reaction of chain-growth polymer and selfcondensed polymer. In the polymerization at -10 °C, the deprotonated **1b** would be sufficiently reactive to undergo self-polymerization. At -30 °C, abstraction of the proton from the amino group of **1b** with LiHMDS would be slow, and the reaction of undeprotonated **1b** with deprotonated **1b** would take place, resulting in self-condensation of **1b**.

With the optimized conditions in hand, the polymerization was carried out with various feed ratios of monomer to initiator ($[\mathbf{1b}]_0/[\mathbf{3}]_0$) to synthesize poly**1b** with different values of molecular weight. The M_n value was determined by ¹H NMR, because the M_n value of poly**1b** obtained by GPC based on polystyrene standards deviated from the real M_n value. The polymerization at the $[\mathbf{1b}]_0/[\mathbf{3}]_0$ ratios of 10, 31, and 50 gave well-defined poly**1b**, the molecular weight values of which agreed well with the calculated values based on those feed ratios. The molecular weight distributions were all narrow (entries 4–6).

Synthesis of Block Copolymers

Since we have already established a method for the chaingrowth condensation polymerization of 4-(octylamino)benzoic acid methyl ester (2) with LiHMDS,¹⁰ one-pot block copolymerization of **1b** and **2** with LiHMDS was investigated [Scheme 1(B)]. Such a block aromatic copolyamide having hydrophilic tri(ethylene glycol) and hydrophobic octyl side chains might afford unprecedented self-assembled structures. In this block copolymerization, the polymerization order is important, because the phenyl ester monomer **1b** would be



FIGURE 2 GPC profiles of poly1b as a prepolymer (dashed line) and poly1b-*b*-poly2 as a postpolymer (solid line) obtained by two-stage polymerization of 1b ([1b]₀/[3]₀ = 20) and 2 ([added 2]₀/[3]₀ = 20) with 3 in the presence of LiHMDS in THF. The data in parentheses are M_n GPC and M_w/M_n values of the product in this order, unless otherwise stated. A: Polymerization of 1b with 2.0 equiv. of LiHMDS at -20 °C (3800, 1.28) followed by 2 (8100, 1.37). B: Polymerization of 1b with 1.0 equiv. of LiHMDS at -20 °C (3300, 1.13) followed by 2 with 1.0 equiv. of LiHMDS (5700, 1.33). C: Polymerization of 1b with 1.0 equiv. of LiHMDS at -20 °C for 10 min and at -50 °C for 6 h (3600, 1.11) followed by 2 with 1.0 equiv. of LiHMDS at -10 °C [M_n GPC = 6700, M_n NMR = 10,000 (M_n calcd = 10,200), M_w/M_n = 1.15].

converted to the methyl ester monomer 1a, the polymerization of which was uncontrolled as mentioned earlier, by transesterification if the methyl ester monomer 2 were polymerized in the first stage of the one-pot copolymerization. Thus, **1b** was polymerized first in the presence of **3** as an initiator ($[1b]_0/[3]_0 = 20$) and LiHMDS (2.0 equiv.) in THF at -20 °C, and then a fresh feed of 1 equiv. of 2 ([2]₀/[3]₀ = 20) was added to the reaction mixture. The GPC elution curve of the product was shifted toward the higher-molecular-weight region, but showed a shoulder in the region of the prepolymer peak, indicating that not all of the end groups of the prepolymer, poly1b, initiated polymerization of 2, and a part of poly1b remained unreacted [Fig. 2(A)]. The large excess of LiHMDS in the first stage was thought to have reacted with a part of the terminal phenyl ester moiety of poly1b, inactivating it.

On this assumption, LiHMDS equivalent to each monomer was added in both the first and second stage. Thus, **1b** was polymerized in the presence of **3** ($[1b]_0/[3]_0 = 20$) and 1.0 equiv. of LiHMDS in THF at -20 °C to give a prepolymer. A fresh feed of 1.0 equiv. of LiHMDS and **2** ($[2]_0/[3]_0 = 20$) were added to the prepolymer in the reaction mixture. The shoulder in the GPC elution curve of the product became

Entry	Poly 1b			Poly 1b - <i>b</i> -Poly 2						
	[1b] ₀ /[3] ₀	Reaction Time (h)	<i>M</i> _{n GPC} ^b	$M_{\rm w}/M_{\rm n}^{\rm b}$	[2] ₀ /[3] ₀	Reaction Time (h)	$M_{ m n\ calcd.}$	<i>M</i> _{n GPC} ^b	M _{n NMR} c	$M_{\rm w}/M_{\rm n}^{\rm b}$
1	20.0	6	3,600	1.11	20.4	15	10,200	6,700	10,000	1.15
2	20.0	8	3,300	1.10	43.3	18	15,500	7,700	14,900	1.19
3	10.0	3	1,900	1.14	50.0	15	14,400	9,500	15,900	1.10
4	40.0	20	5,600	1.12	13.3	8	14,100	6,100	14,400	1.26

TABLE 3 Block Copolymerization of 1b and 2^a

^a Polymerization of **1b** with 1.0 equiv. of LiHMDS was carried out in THF at -20 °C for 10 min then at -50 °C for the indicated period, followed by polymerization of **2** with 1.0 equiv. of LiHMDS at -10 °C.

^b Determined by GPC based on polystyrene standards (eluent: THF). ^c Determined by ¹H NMR.



FIGURE 3 SEM images of poly1b selfassembled from a THF solution on a glass plate. A and B: 10 wt % Solution of poly1b $(M_{n \text{ NMR}} = 6400, \text{ entry 2 in Table 2})$. C: 5 wt % of the same polymer. D: 5 wt % of poly1b $(M_{n \text{ NMR}} = 13,400, \text{ entry 6 in Table 2})$.

smaller, but still remained [Fig. 2(B)]. A small amount of LiHMDS might have reacted with the terminal phenyl ester moiety to give an unreactive amide terminal moiety, probably because the phenyl ester terminal moiety was too reactive at -20 °C. Polymerization at a temperature lower than -20 °C might prevent this termination reaction. Accordingly, the polymerization of **1b** was initiated at -20 °C for 10 min, then the reaction mixture was stirred at -50 °C for 6 h, followed by addition of LiHMDS and **2** to the prepolymer in the reaction mixture at -10 °C. The GPC elution curve of the product did not show a shoulder and was shifted toward the higher-molecular-weight region, while the polydispersity remained below 1.20, indicating successful production of the block copolymer of poly**1b** and poly**2** [Fig. 2(C)].

Under the optimized conditions in hand, poly1b-b-poly2 with different compositions was synthesized by varying the feed ratio of **1b** to **2** (Table 3). The M_n value of the block copolymers agreed well with the calculated value, and the molecular weight distribution was narrow. It should be noted that the block copolymer with the longer poly**1b** segment (entry 4) is soluble not only in general organic solvents but also in water.

Self-Assembly

We studied self-assembly of the obtained block copolymer (Table 3, entry 4). Dilute aqueous, chloroform, and THF solutions of the block copolymer were dropped on a glass plate and dried at room temperature. However, the scanning electron microscopy (SEM) images of these samples did not show any assembled structures; flat films might have been formed.

On the other hand, SEM images of a sample prepared similarly from a solution of homopolymer, poly**1b**, in THF revealed the formation of 10–25 μ m spherical aggregates, whose diameter was independent of the molecular weight of poly**1b** (Fig. 3). These aggregates were not formed from solutions in other

organic solvents, such as chloroform and 2-propanol. Furthermore, other *N*-alkyl poly(*p*-benzamide)s did not afford spherical aggregates from a THF solution. Therefore, interactions between the tri(ethylene glycol) side chain in poly**1b** and THF and/or different solubility of the tri(ethylene glycol) side chain and aromatic polyamide backbone in THF may underlie the formation of these aggregates. Further studies are necessary to establish the reason for the formation of the spherical aggregates from the homopolymer, poly**1b**.

CONCLUSIONS

We have demonstrated that the tri(ethylene glycol) monomethyl ether side chain on the nitrogen atom of 4-aminobenzoic acid esters **1** makes the polymerization of **1** with LiHMDS sluggish, compared to the polymerization of the *N*alkyl counterparts, and the phenyl ester **1b** is necessary for controlled chain-growth condensation polymerization. By using this established polymerization method, poly**1b**-*b*poly(*N*-octyl-4-benzamide) was synthesized by the successive polymerization of **1b** and **2** in one pot in the presence of initiator **3** and LiHMDS. The obtained block copolymer did not self-assemble, but when a THF solution of poly**1b** was allowed to dry on a glass plate, spherical aggregates were formed. Synthesis and properties of star polymers containing poly**1b** will be reported elsewhere.

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