Synthesis of Poly(naphthalenecarboxamide)s with Low Polydispersity by Chain-Growth Condensation Polymerization

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ABSTRACT: Condensation polymerization of 6-(*N*-substituted-amino)-2-naphthoic acid esters (**1**) was investigated as an extension of chain-growth condensation polymerization (CGCP). Methyl 6-(3,7-dimethyloctylamino)-2-naphthoate (**1b**) was polymerized at −10 °C in the presence of phenyl 4-methylbenzoate (**2**) as an initiator and lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base. When the feed ratio $[\mathbf{1a}]_0/[\mathbf{2}]_0$ was 10 or 20, poly(naphthalenecarboxamide) with defined molecular weight and low polydispersity was obtained, together with a small amount of cyclic trimer. However, polymer was precipitated during polymerization under similar conditions in $[\mathbf{1a}]_0/[\mathbf{2}]_0 = 34$. To increase the solubility of the polymer, monomers **1c** and **1d** with a tri(ethylene glycol) (TEG) monomethyl ether side chain instead of the 3,7-dimethyloctyl side chain were synthesized. Polymerization of the methyl ester monomer **1c** did not proceed well, affording only oligomer and unreacted **1c**, whereas polymerization of the phenyl ester monomer **1d** afforded well-defined poly(naphthalenecarboxamide) together with small amounts of cyclic oligomers in $[\mathbf{1d}]_0/[\mathbf{2}]_0 = 10$ and 29. The polymerization at high feed ratio ($[\mathbf{1d}]_0/[\mathbf{2}]_0 = 32.6$) was accompanied with self-condensation to give polyamide with a lower molecular weight than the calculated value. Such undesirable self-condensation would result from insufficient deactivation of the electrophilic ester moiety by the electron-donating resonance effect of the amide anion. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3020–3029, 2011

KEYWORDS: chain-growth condensation polymerization; living polymerization; molecular weight distribution/molar mass distribution; naphthalene; polyamides; polycondensation

INTRODUCTION Living polymerization has enormously progressed over the last few decades,[1–10] and is indispensable for the production of nanoarchitecture, which serves as the backbone of nanotechnology. However, it remains important to develop new living polymerization methods to extend the range of well-defined polymers that can be accessed.

We have developed a novel living polymerization, chain-growth condensation polymerization (CGCP), which can provide condensation polymers with controlled molecular weight and low polydispersity. To achieve chain-growth polymerization in condensation polymerization while suppressing conventional step-growth polymerization, selective activation of the polymer end group is necessary. In the synthesis of well-defined *N*-substituted polybenzamides, we have used two kinds of substituent effects for the selective activation of the polymer end group.[6,11–13] In the polymerization of *p*-substituted monomer, the strong electron-donating *resonance* effect of the amide anion deactivates the electrophilic ester moiety at the *para* position, resulting in the suppression of self-condensation of the monomer. Once the monomer has reacted with the ester moiety of an initiator or the polymer end group, the amide anion of the monomer is converted to an amide linkage, which is a much weaker electron-donating group than the amide anion, and so the newly extended polymer terminal ester moiety becomes more reactive than the ester moiety of the monomer bearing the amide anion. Accordingly, another monomer is selectively reacted with the polymer end group, and chain growth continues (Scheme 1).[12] In the polymerization of *m*-substituted monomer, the amide anion can deactivate the electrophilic ester moiety at the *meta* position through the electron-donating *inductive* effect, and self-condensation is suppressed.[13] The following amidation of the monomer induces the activation of the newly elongated polymer end group as in the *p*-substituted monomer. In general, *inductive* effects become much weaker through three or more successive carbon–carbon σ bonds, whereas resonance effects can work between functional groups not only at the *para* position of benzene but also at the 1,5- or 2,6-positions of naphthalene. Therefore, we were interested to know whether the long-distance resonance effects in the naphthalene ring can be utilized for CGCP. If so, monomers available for CGCP could be not only simply extended from those with a benzene backbone to those with a naphthalene backbone but also utilized for

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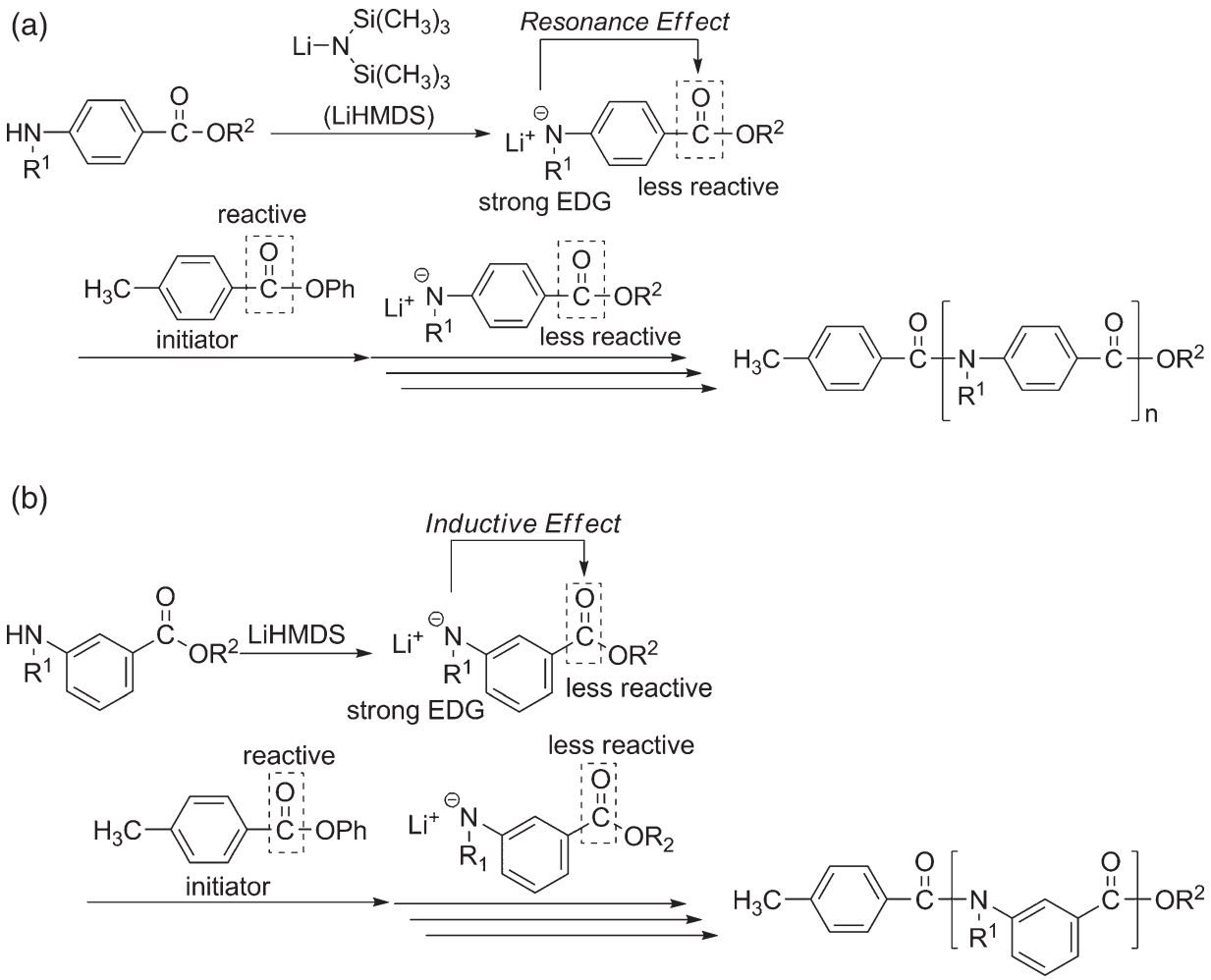


SCHEME 1 CGCP of (a) *p*-substituted and (b) *m*-substituted benzene-based monomers.

more fused aromatic system, for instance pyrene and porphyrin, which have interesting properties. However, resonance effect also becomes weak as the distance between the functional groups is longer. If the amide anion cannot sufficiently convey the electron-donating effect on the ester moiety through the resonance effect, self-condensation of monomer would be caused, resulting in difficulty on controlling molecular weight and polydispersity of the obtained polymer.

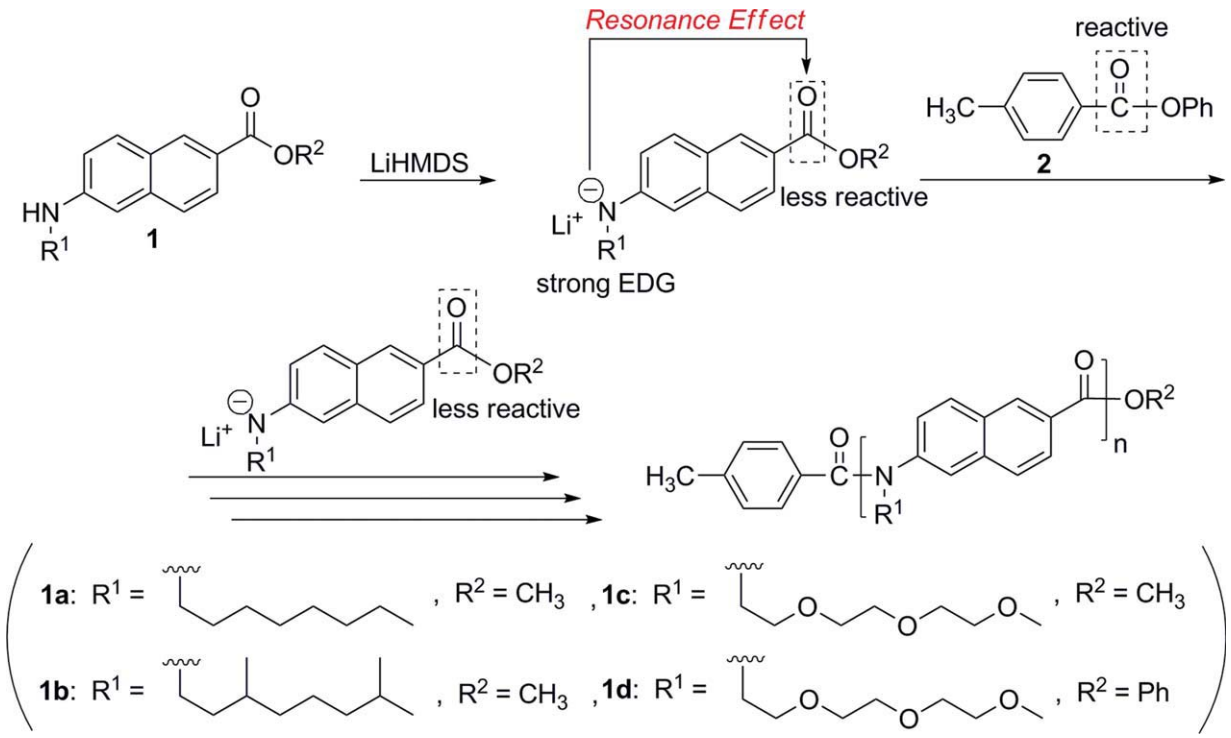
In this article, we focus on the condensation polymerization of 6-amino-2-naphthoic acid esters (**1**) bearing an alkyl or a tri(ethylene glycol) (TEG) side chain on the amino group in the presence of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base and phenyl 4-methylbenzoate (**2**) as an initiator. We found that the polymerization proceeded in a chain-growth polymerization manner to yield poly(naphthalenecarboxamide)s with defined molecular weight and low polydispersity (Scheme 2). This result demonstrates that the resonance effect at the 2,6-position of naphthalene ring is sufficient for CGCP, working in the same way as in CGCP of the benzene-based monomers that we have hitherto reported.

RESULTS AND DISCUSSION

Polymerization of Monomers with Alkyl Side Chain

The methyl ester monomer **1a** having an octyl side chain was first polymerized in the presence of **2** ($[\mathbf{1a}]_0/[\mathbf{2}]_0 = 10$) and 1.0 equiv of LiHMDS in tetrahydrofuran (THF) at −10 °C (Scheme 2). However, the produced polymer was precipitated in the reaction mixture within 1 h. The *N*-octyl side chain, which permits polyamides with the benzene backbone to dissolve in THF,[12–14] was not effective to solubilize polyamide with the naphthalene backbone.

To suppress precipitation of polymer during polymerization, we synthesized monomer **1b** bearing a 3,7-dimethyloctyl side chain, which was easily derived from citronellal. The polymerization of **1b** with initiator **2** and LiHMDS was carried out under several conditions (Table 1). At the feed ratio $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 10$, at which poly**1a** was



SCHEME 2 CGCP of naphthalene-based monomers.

precipitated during polymerization, the polymerization proceeded homogeneously throughout to yield polymer with low polydispersity. The number-average molecular weight (M_n) value of the obtained polymer, determined from the ^{1}H NMR spectrum, agreed well with the theoretical value of M_n on the basis of the feed ratio (Entry 1).

The polymerization at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$ also proceeded homogeneously, although the reaction solution increased in viscosity, to afford polymer with double the initial M_n value (Entry 2). The polymerization at this feed ratio was studied in more detail. As the polymerization progressed, the gel permeation chromatography (GPC) elution curve of the product was shifted toward the higher molecular weight region, maintaining low polydispersity (Fig. 1). The M_n values and M_w/M_n ratio, determined by GPC, were plotted as a function of monomer conversion, and these relationships showed that the M_n value increased in proportion to conversion, being consistent with the theoretical M_n value based on the feed ratio, and M_w/M_n remained at 1.1 over the whole conversion range (Fig. 2). These results clearly demonstrate that the polymerization proceeds via the CGCP mechanism.

However, the GPC traces had a small peak in the low molecular weight region after 5 min, the intensity of which remained almost unchanged (Fig. 1). This product was

TABLE 1 Polymerization of **1b** with **2**[a]

						M_n			
Entry	$[\mathbf{1b}]_0/[\mathbf{2}]_0$[b]	$[\mathbf{1b}]_0$	Temperature (°C)	Time (h)	Conversion[c] (%)	Calculated[d]	GPC[e]	NMR[f]	M_w/M_n[e]
1	10.0	0.44	−10	18	100	3,240	3,680	2,780	1.15
2	20.0	0.45	−10	4	99	6,340	5,720	5,540	1.13
3	34.0	0.45	−10	3.5	93	10,670	8,180	–	1.20
4	32.8	0.15	−10	6	100	10,300	7,450	–	1.20
5	32.7	0.044	−10	18	93	10,270	5,200	–	1.22
6	34.0	0.148	0	4	98	10,670	7,720	–	1.20

[a] Polymerization was carried out in the presence of 1.0 equiv of LiHMDS in THF.
[b] Feed ratio of the monomer **1b** to the initiator **2**.
[c] Estimated by HPLC (eluent: THF).
[d] Calculated from the feed ratio of $[\mathbf{1b}]_0/[\mathbf{2}]_0$.
[e] Determined by GPC based on polystyrene standards (eluent: THF).
[f] Determined by ^{1}H NMR.

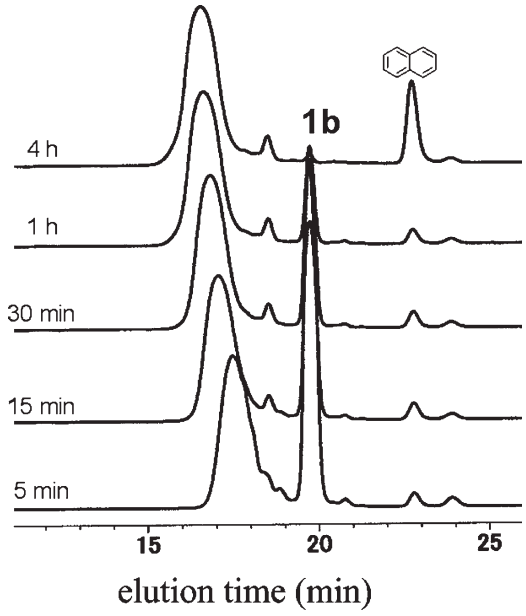


FIGURE 1 GPC profiles of the product obtained by the polymerization of **1b** with 5 mol % of **2** in the presence of LiHMDS in THF at −10 °C (Table 1, Entry 2).

isolated by high-performance liquid chromatography (HPLC) and analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. It turned out to be a cyclic trimer of **1b**, which had been synthesized in a different manner by Azumaya and coworkers.[15] This cyclic trimer, the amount of which did not increase with the progress of polymerization, was probably formed by self-condensation of **1b** in the early stage of polymerization, where deprotonated **1b** could react with **1b** untreated with base. As the polymerization of the corresponding *p*-substituted benzene monomer did not afford cyclic oligomers as byproducts under the same conditions,[14] the proton abstraction by the base from the amino group of **1b** might be slower than that in the benzene monomer, resulting in the occurrence of the reaction of deprotonated **1b** with nondeprotonated **1b**. This decrease in the acidity of the amino group of **1b** can be ascribed to a weaker electron-withdrawing resonance effect of the ester moiety at the 2-position of the naphthalene ring, compared with the ester moiety at the *para* position of the benzene monomer.

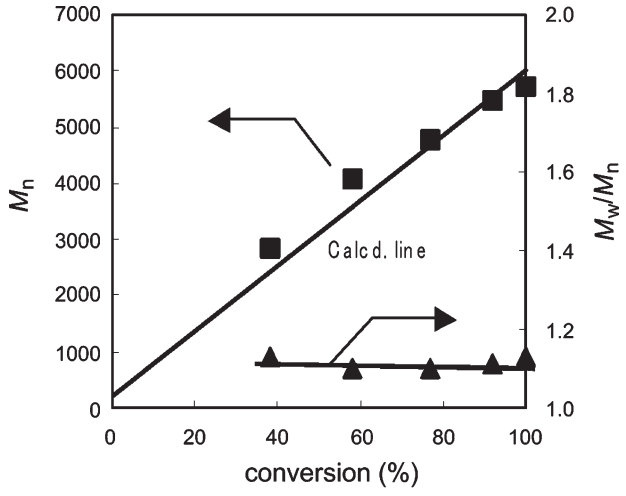


FIGURE 2 M_n and M_w/M_n values of poly**1b**, obtained by polymerization with 5 mol % of **2** in the presence of LiHMDS in THF at −10 °C (Table 1, Entry 2).

The polymerization was further carried out at the feed ratio $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 34$. The reaction mixture became slightly turbid after 1 h, and then polymer was precipitated at 3 h. The M_n value of the obtained polyamide was lower than the theoretical value, and M_w/M_n was slightly increased (Entry 3). To suppress the precipitation, the polymerization was carried out in dilute solution (Entry 4). The polymerization proceeded homogeneously, but again the M_n value did not reach the theoretical value and the M_w/M_n was slightly increased (Entries 4 and 5). Low concentration might be liable to induce self-condensation of **1b**, resulting in polymer with lower molecular weight. The polymerization at 0 °C did not afford good results, either, because of precipitation of polymer during polymerization (Entry 6). As a consequence, the polymerization of **1b** can be well controlled up to the feed ratio $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$, although even then, a small amount of cyclic trimer was formed in the early stage of the polymerization.

Polymerization of Monomers with Oligo(ethylene glycol) Side Chain

To increase the solubility of poly(naphthalenecarboxamide), we synthesized monomers with an oligo(ethylene glycol) side chain. The oligo(ethylene glycol) side chain not only provides good solubility in a variety of solvents but also affords unique functionality.[16–23] Indeed, *m*-substituted polybenzamides with an oligo(ethylene glycol) side chain showed a lower critical solution temperature in water.[23] However, CGCP of some monomers with an oligo(ethylene glycol) side chain is more difficult than CGCP of those with an alkyl side chain, because oligo(ethylene glycol) has high affinity for lithium cation, inducing undesired reactions.[24,25]

The methyl ester monomer **1c** bearing a TEG side chain was first polymerized with LiHMDS in the presence of 10 mol % of **2** at −10 °C for 24 h in a similar manner to that described for **1b** (Scheme 1). However, an oligomer with $M_n = 780$ was obtained and unreacted monomer was recovered. As in the polymerization of *m*-substituted benzene monomers with an oligo(ethylene glycol) side chain,[24] the polymerization was then carried out in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), which is known to strongly coordinate lithium cation, but similar results were obtained. We next increased the reactivity of the ester moiety of the monomer by changing to phenyl ester. Thus, the phenyl ester monomer **1d** was polymerized with 1.0 equiv of LiHMDS in the presence of initiator **2** ($[\mathbf{1d}]_0/[\mathbf{2}]_0 = 10$) at −10 °C to afford polymer with a slightly broadened molecular weight distribution (Table 2, Entry 1). When the polymerization was examined at lower temperature, −20 °C, to suppress self-condensation, the GPC profile of the product showed a narrower molecular weight

TABLE 2 Polymerization of **1d** with **2**[a]

Entry	$[\mathbf{1d}]_0/[\mathbf{2}]_0$[b]	Additive	Temperature (°C)	Time (h)	M_n		M_w/M_n[d]
					Calculated[c]	GPC[d]	
1	10.0	None	−10	1	3,370	3,460	1.23
2	10.0	None	−20	2	3,370	3,130	1.18
3	10.0	None	−30	2	3,370	3,170	1.17
4	28.6	None	−30	19	9,430	5,690	1.16
5	10.0	LiCl	−30	2	3,370	3,190	1.17
6	32.6	LiCl	−30	5	10,490	6,800	1.21

[a] Polymerization was carried out in the presence of 1.0 equiv of LiHMDS in THF ($[\mathbf{1d}]_0$ = 0.44 M).
[b] Feed ratio of the monomer **1d** to the initiator **2**.
[c] Calculated from the feed ratio of $[\mathbf{1d}]_0/[\mathbf{2}]_0$.
[d] Determined by GPC.

distribution (Entry 2). Further lowering the polymerization temperature to −30 °C also yielded polyamide with controlled molecular weight and narrow molecular weight distribution (Entry 3). Although the GPC profile of the products showed a small peak, which might be due to cyclic oligomers [Fig. 3(a)], the controlled M_n and narrow polydispersity of the products suggest that the polymerization of **1d** at −20 and −30 °C proceeded mainly in a chain-growth polymerization manner. On the other hand, when the polymerization was carried out with a smaller amount of the initiator **2** ($[\mathbf{1d}]_0/[\mathbf{2}]_0$ = 28.6), the M_n value of the polymer was not consistent with the calculated value [Entry 4, Fig. 3(b)], and the GPC profiles of the product showed a shoulder in the higher molecular weight region, as well as a small peak in the lower molecular weight region [Fig. 3(b)], although no polyamide precipitate was seen, indicating that the side chain improved the solubility of the polyamide. The shoulder peak might be attributed to coupling between the chain-growth and the self-condensation polyamides, and self-condensation would also result in the formation of cyclic oligomers, observed as the small peak. We thought that the undesirable self-condensation probably resulted from insufficient deactivation of the electrophilic ester moiety by the electron-donating resonance effect of the amide anion due to the longer distance between the positions 2 and 6 of the naphthalene ring, compared with the positions 1 and 4 of *p*-substituted benzene ring.

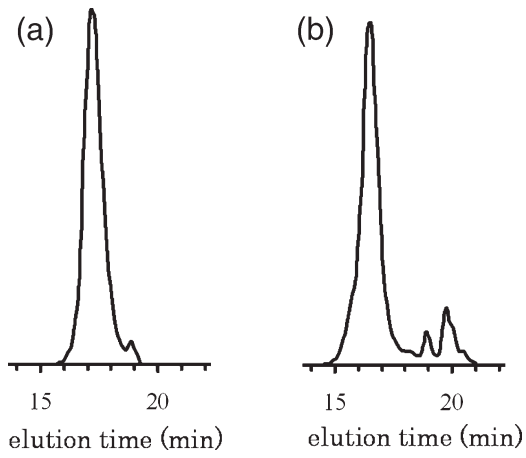


FIGURE 3 GPC profiles of the products obtained by the polymerization of **1d** with 1.0 equiv of LiHMDS in the presence of **2** in THF. The polymerization was carried out at −30 °C with the feed ratio (a) $[\mathbf{1d}]_0/[\mathbf{2}]_0$ = 10.0 for 2 h (Table 2, Entry 3) and (b) $[\mathbf{1d}]_0/[\mathbf{2}]_0$ = 28.6 for 19 h (Entry 4).

To suppress the self-condensation completely, the polymerization was carried out in the presence of LiCl as an additive, as we expected stabilization of the amide anion to reduce the nucleophilicity.[26] When the polymerization was carried out at the feed ratio of $[\mathbf{1d}]_0/[\mathbf{2}]_0$ = 10.0 in the presence of 5.0 equiv of LiCl to **1d**, the M_n value of the polymer was consistent with the calculated value (Entry 5). However, polymerization at high feed ratio ($[\mathbf{1d}]_0/[\mathbf{2}]_0$ = 32.6) was accompanied with self-condensation, affording polyamide with a lower molecular weight than the calculated value (Entry 6). Thus, we found that the introduction of the TEG side chain into the naphthalene monomer improved the solubility of the poly(naphthalenecarboxamide) in THF, and that CGCP proceeded well at low feed ratios.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standards of ^{1}H NMR spectra in $CDCl_3$ and CD_3OD were tetramethylsilane (0.00 ppm) and the midpoint of CD_3 (3.35 ppm), respectively, and the internal standards of ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 were the midpoints of $CDCl_3$ (77.0 ppm) and CD_3 (39.8 ppm), respectively. IR spectra were recorded on a JASCO FT/IR-410. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. The conversion of monomers during the polymerization was determined by HPLC with a Japan Analytical Industry LC-909 HPLC unit (eluent: THF) fitted with a JAIGEL column (1H-A). The M_n and M_w/M_n values of polymers were measured on a Shodex GPC-101 GPC unit equipped with

Shodex UV-41, Shodex RI-71S, and two Shodex KF-804L columns (bead size = 7 μm, pore size = 200 Å). THF was used as the eluent (temperature = 40 °C, flow rate = 1 mL/min). Calibration was carried out using polystyrene standards. The isolation of polyamides was carried out with a Japan Analytical Industry LC-908 recycling preparative HPLC (eluent: chloroform) using two TOSOH TSK-gel columns (2 × G2000H_{HR}). Commercially available dehydrated THF (stabilizer-free, Kanto), dehydrated dichloromethane (Kanto), dehydrated methanol (Kanto), and dehydrated *N*,*N*-dimethylformamide (Wako) were used as dry solvents. LiHMDS (1.0 M) solution in THF (Aldrich) and 1 M borane–THF complex in THF (Kanto) were used as received. TMEDA was distilled over CaH_2 before use.

Synthesis of 1a

Into a solution of 6-amino-2-naphthoic acid methyl ester (1.004 g, 4.99 mmol) in dry THF (14 mL), *n*-octanal (0.77 mL, 5.0 mmol), glacial acetic acid (0.31 mL, 5.5 mmol), and $NaBH(OAc)_3$ (1.589 g, 7.5 mmol) were successively added (Scheme 3). The mixture was stirred at room temperature for 14 h. The reaction was quenched with aqueous $NaHCO_3$, and the whole was extracted with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 8/1) followed by recrystallization from hexane to afford monomer **1a** as white solid (0.76 g, 48%). mp 92.3–94.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (br s, 1H), 7.93 (dd, J = 8.6 and 1.7 Hz, 1H), 7.70 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 6.89 (dd, J = 8.9 and 2.3 Hz, 1H), 6.78 (br s, 1H), 3.94 (s, 3H), 3.23 (t, J = 7.2 Hz, 2H), 1.69 (quint, J = 7.4 Hz, 2H), 1.48–1.22 (m, 10H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz) 167.7, 148.1, 138.0, 131.0, 130.5, 126.0, 125.9, 125.6, 122.9, 118.4, 103.3, 51.9, 43.7, 31.8, 29.4, 29.3, 29.2, 27.2, 22.6, 14.1; IR (KBr) 3372, 2954, 2922, 2855, 1691, 1624, 1536, 1491, 848, 815 cm^{-1}.

Synthesis of 3,7-Dimethyloctanal (3)

A mixture of 5% Pd/C (156 mg, 5 mol %), citronellal (1.512 g, 9.802 mmol), and ethyl acetate (120 mL) was stirred at room temperature for 2 h under an H_2 atmosphere. The reaction mixture was filtered through Celite and the filtrate was concentrated under vacuum to afford **3** as colorless liquid (1.526 g, 99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (t, J = 2.3 Hz, 1H), 2.39 (ddd, J = 16.0, 7.7, and 2.0 Hz, 1H), 2.22 (ddd, J = 16.0, 8.0, and 2.6 Hz, 1H), 2.11–1.98 (m, 1H), 1.53 (m, 1H), 1.39–1.09 (m, 6H), 0.97 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 6H); IR (neat) 2955, 2928, 2870, 2717, 1725, 1560, 1466, 1409, 1383, 1366, 1215, 1147, 1119, 1091, 1050, 880 cm^{-1}.

Synthesis of 1b

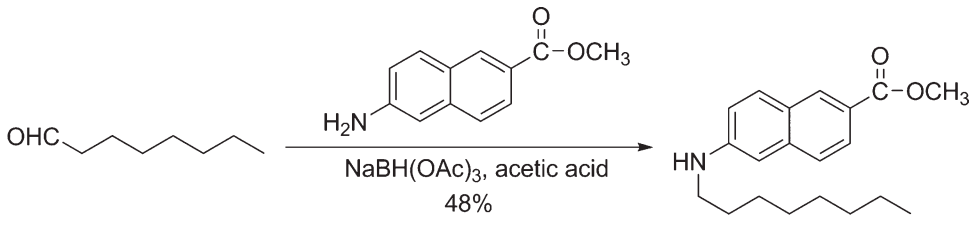
Into a solution of 6-amino-2-naphthoic acid methyl ester (797.5 mg, 3.96 mmol) in dry dichloromethane (50 mL) at 0 °C, **3** (752 mg, 4.75 mmol) and $NaBH(OAc)_3$ (1.097 g, 5.15 mmol) were successively added (Scheme 4). The mixture was stirred at 0 °C for 1 h and at room temperature for 1 h. The reaction was quenched with aqueous $NaHCO_3$, and the whole was extracted with dichloromethane. The collected organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography [SiO_2, hexane/EtOAc = 8/1 (twice), hexane/dichloromethane = 1/1] to afford pale red solid (1.2195 g, 95%). mp 90.7–91.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (br s, 1H), 7.93 (dd, J = 8.6 and 1.7 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 6.88 (dd, J = 8.6 and 2.3 Hz, 1H), 6.77 (br s, 1H), 3.97 (br s, 1H), 3.94 (s, 3H) 3.31–3.18 (m, 2H), 1.76–1.49 (m, 5H), 1.41–1.10 (m, 5H), 0.97 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 147.4, 137.8, 131.0, 130.5, 126.4, 126.0, 125.8, 123.3, 118.6, 104.4, 51.9, 42.2, 39.2, 37.2, 36.3, 30.9, 28.0, 24.7, 22.7, 22.6, 19.6; IR (KBr) 3389, 2928, 1689, 1624, 1537, 1494, 1479, 1434, 1418, 1382, 1343, 1297, 1214, 1133, 1101, 851, 817 cm^{-1}.

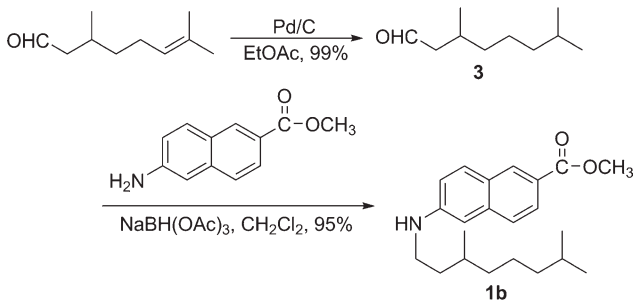
Synthesis of 4

To a mixture of 6-amino-2-naphthoic acid (5.00 g, 26.8 mmol) and dry methanol (250 mL) at 0 °C, thionyl chloride (52 mL, 0.71 mol) was added dropwise, and the whole was stirred at room temperature overnight under an argon atmosphere. The reaction mixture was poured into water, neutralized with saturated aqueous $NaHCO_3$, and extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/2) to give **4** as pale red solid (4.73 g, 88%). mp 163.0–164.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 1.1 Hz, 1H), 7.94 (dd, J = 8.6 and 1.7 Hz, 1H), 7.76–7.74 (m, 1H), 7.58 (d, J = 8.6 Hz, 1H), 6.98–6.96 (m, 2H), 4.04 (br s, 2H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 146.5, 137.4, 131.1, 130.9, 126.6, 125.9, 125.7, 123.8, 118.6, 107.8, 52.0; IR



SCHEME 3 Synthesis of **1a**.



SCHEME 4 Synthesis of **1b**.

(KBr) 3405, 3340, 3236, 2945, 1688, 1620, 1577, 1509, 1481, 1438, 1393, 1350, 1299, 1212, 1133, 1103, 983, 955, 914, 876 cm^{-1}.

Synthesis of 5

To a mixture of **4** (103 mg, 0.511 mmol), 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (0.1 mL, 0.7 mmol), 4-(dimethylamino)pyridine (DMAP; 79.2 mg, 0.648 mmol), and dry dichloromethane (20 mL) at 0 °C, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 124 mg, 0.646 mmol) was added, and the whole was stirred at room temperature for 1 h. Water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/2) to give **5** as yellow viscous liquid (156 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (br s, 1H), 8.54 (br s, 1H), 8.38 (d, J = 2.0 Hz, 1H), 8.04 (dd, J = 8.6 and 1.7 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.64 (dd, J = 8.6 and 2.3 Hz, 1H), 4.17 (s, 2H), 3.97 (s, 3H), 3.82–3.80 (m, 2H), 3.77–3.74 (m, 4H), 3.62–3.60 (m, 2), 3.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 167.2, 137.1, 136.2, 130.6, 130.1, 129.6, 127.8, 126.4, 125.8, 120.7, 116.3, 71.7, 71.2, 70.7, 70.4, 70.1, 59.0, 52.1; IR (neat) 3511, 3335, 2948, 2882, 1933, 1717, 1631, 1608, 1582, 1542, 1496, 1483, 1436, 1407, 1391, 1342, 1287, 1246, 1201, 1099, 1029, 990 cm^{-1}.

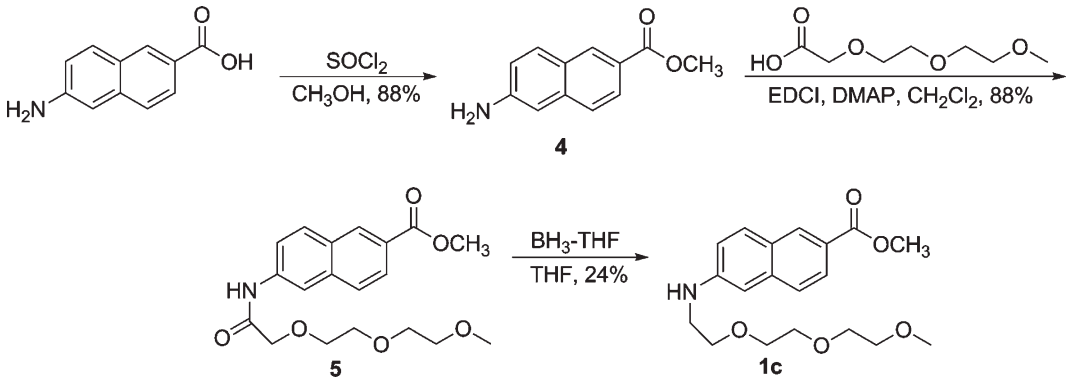
Synthesis of 1c

A three-neck flask equipped with a dropping funnel, a reflux condenser, and a gas inlet tube was purged with argon and then charged with 1.01 M borane–THF complex in THF (14.6 mL, 14.8 mmol; Scheme 5). A solution of **5** (3.42 g, 9.86 mmol) in THF (30 mL) was added dropwise from the dropping funnel at 0 °C, and the mixture was stirred at room temperature for 30 min, then refluxed for 4 h. After the mixture had cooled to room temperature, 6 M hydrochloric acid (3.0 mL) was added, and the whole was heated at reflux for 1 h. It was allowed to cool to room temperature, then diluted with water, neutralized to pH ~ 8 with $NaHCO_3$, and extracted with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 1/2) to give **1c** (797 mg, 24%) as pale yellow viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (br s, 1H), 7.92 (dd, J = 8.6 and 1.7 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 6.91 (dd, J = 8.9 and 2.3 Hz, 1H), 6.74 (d, J = 2.0 Hz, 1H), 4.69 (br s, 1H), 3.91 (s, 3H), 3.71 (t, J = 5.2 Hz, 2H), 3.65–3.61 (m, 6H), 3.53–3.51 (m, 2H), 3.37–3.35 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 148.0, 137.8, 131.0, 130.4, 126.2, 125.9, 125.7, 123.1, 118.7, 103.6, 71.9, 70.5, 70.3, 69.2, 59.0, 51.9, 43.1; IR (neat) 3512, 3374, 3059, 2948, 2877, 2047, 1927, 1714, 1623, 1577, 1530, 1493, 1459, 1436, 1417, 1403, 1382, 1288, 1209, 1096, 1028, 990, 967, 939, 915, 853 cm^{-1}.

Synthesis of 6

To a mixture of 6-amino-2-naphthoic acid (5.20 g, 28.8 mmol), $NaHCO_3$ (4.67 g, 55.6 mmol), and dry THF (840 mL) at 0 °C, benzyl chloroformate (2.0 mL, 14 mmol) was added, and the whole was stirred at room temperature for 1 h. Further benzyl chloroformate (2.0 mL, 14 mmol) was added to the reaction mixture at 0 °C, and the whole was stirred at room temperature for 17 h, then poured into water, adjusted to pH around 1 with 1 M hydrochloric acid, and extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. The residue was recrystallized from THF–$CHCl_3$ to give **6** as white solid (8.20 g, 92%). mp 236.8–239.7 °C.



SCHEME 5 Synthesis of **1c**.

^{1}H NMR (500 MHz, CD_3OD): δ 8.56 (br s, 1H), 8.17 (br s, 1H), 8.03 (dd, J = 8.6 and 1.7 Hz, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.63 (dd, J = 8.9 and 2.0 Hz, 2H), 7.50–7.48 (m, 2H), 7.44–7.41 (m, 2H), 7.39 (t, J = 7.3 Hz, 1H), 5.28 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 167.8, 153.7, 139.3, 136.7, 136.1, 130.6, 130.4, 128.8, 128.6, 128.5, 128.4, 127.6, 126.6, 126.0, 120.3, 113.4, 66.3; IR (KBr) 3314, 3061, 3033, 2954, 2895, 2852, 2685, 2639, 2565, 1670, 1634, 1579, 1542, 1501, 1428, 1307, 1242, 1066 cm^{-1}.

Synthesis of 7

To a mixture of **6** (8.19 g, 25.5 mmol), phenol (3.16 g, 33.5 mmol), DMAP (4.05 g, 33.2 mmol), and dry DMF (500 mL) at 0 °C, EDCI (6.35 g, 33.3 mmol) was added, and the whole was stirred at room temperature for 17 h. Then, water was added, and the mixture was extracted with dichloromethane. The organic layer was washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated. The residue was purified by recrystallization from $CHCl_3$ to give **7** as colorless needles (7.21 g, 71%). mp 193.4–196.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (br s, 1H), 8.17 (dd, J = 8.6 and 1.7 Hz, 1H), 8.12 (br s, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.47–7.35 (m, 8H), 7.31–7.24 (m, 3H), 6.92 (br s, 1H), 5.27 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 165.1, 153.7, 151.1, 139.9, 136.7, 136.6, 131.6, 130.8, 129.9, 129.2, 128.8, 128.53, 128.46, 128.1, 126.3, 125.9, 124.6, 122.3, 120.6, 113.4, 66.4; IR (KBr) 3324, 3182, 3094, 3066, 3030, 2954, 1714, 1631, 1584, 1552, 1483, 1348, 1285, 1226, 1190, 1163, 1139, 1047 cm^{-1}.

Synthesis of 8

To a mixture of **7** (4.31 g, 10.9 mmol) and dry dichloromethane (450 mL), Et_3SiH (7.0 mL, 44 mmol), Et_3N (1.22 mL, 8.66 mmol), and $PdCl_2$ (0.583 g, 3.29 mmol) were added and the whole was stirred at room temperature for 1.5 h. The reaction mixture was filtered through Celite and concentrated. Then, dry dichloromethane (500 mL) and trifluoroacetic acid (30 mL) were added to the residue at room temperature, and the mixture was stirred at room temperature for 0.5 h. After neutralizing with saturated aqueous $NaHCO_3$, the mixture was extracted with dichloromethane, and the organic layer was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified with silica gel column chromatography (AcOEt/hexane = 2/3) to give **8** as pale red solid (2.61 g, 92%). mp 193.2–194.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (d, J = 1.1 Hz, 1H), 8.07 (dd, J = 8.6 and 1.7 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.44 (dd, J = 8.6 and 7.6 Hz, 2H), 7.29–7.24 (m, 3H), 7.02–7.00 (m, 2H), 4.09 (br s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 151.2, 146.9, 137.8, 132.0, 131.1, 129.4, 126.6, 126.2, 125.9, 125.7, 123.0, 121.8, 118.8, 107.8; IR (KBr) 3414, 3343, 3238, 3057, 1708, 1640, 1618, 1478, 1431, 1390, 1348, 1290, 1202, 1188, 1065, 869 cm^{-1}.

Synthesis of 9

To a mixture of **8** (2.49 g, 9.50 mmol), 2-[2-(2-methoxyethoxy)-ethoxy]acetic acid (1.9 mL, 12 mmol), DMAP (1.51 g, 12.4 mmol), and dry dichloromethane (250 mL) at 0 °C, EDCI (2.38 g, 12.4 mmol) was added, and the whole was stirred at room temperature for 2 h, then poured into water and extracted with dichloromethane. The organic layer was washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 4/1) to give **9** as yellow viscous liquid (3.43 g, 86%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (br s, 1H), 8.72 (br s, 1H), 8.44 (d, J = 1.7 Hz, 1H), 8.18 (dd, J = 8.6 and 1.7 Hz, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.67 (dd, J = 8.9 and 2.3 Hz, 1H), 7.45 (dd, J = 8.3 and 7.4 Hz, 2H), 7.31–7.25 (m, 3H), 4.19 (s, 2H), 3.84–3.81 (m, 2H), 3.79–3.75 (m, 4H), 3.63–3.62 (m, 2H), 3.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 168.6, 165.1, 150.9, 137.3, 136.4, 131.3, 130.1, 129.4, 129.3, 127.9, 125.8, 125.6, 125.5, 121.6, 120.7, 116.1, 71.5, 71.1, 70.5, 70.3, 69.9, 58.8; IR (neat) 3334, 3065, 2881, 1731, 1692, 1630, 1580, 1541, 1494, 1407, 1391, 1342, 1281, 1241, 1188, 1106, 1024, 942 cm^{-1}.

Synthesis of 1d

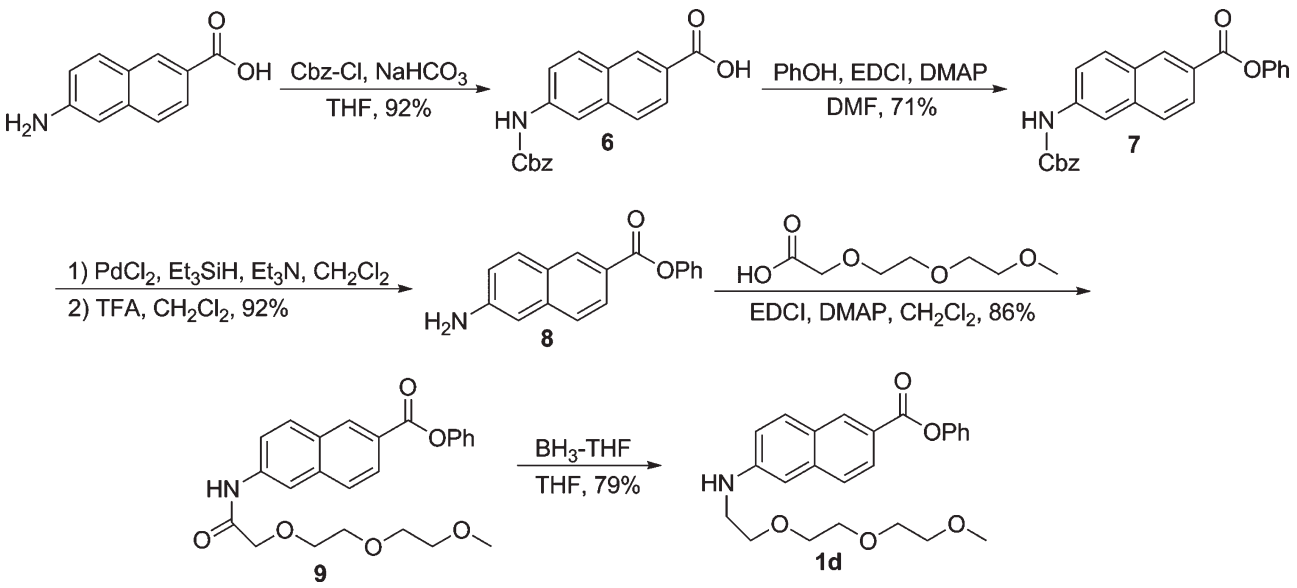
A three-neck flask, equipped with a dropping funnel, a reflux condenser, and a gas inlet tube, was purged with argon and then charged with 1.20 M borane–THF complex in THF (9.5 mL, 11 mmol; Scheme 6). A solution of **9** (3.19 g, 7.53 mmol) in THF (100 mL) was added dropwise from the dropping funnel, and the mixture was stirred at room temperature for 30 min, refluxed for 4 h, and allowed to cool to room temperature. Then, 6 M hydrochloric acid (5.0 mL) was added, and the whole was refluxed for 1 h. After cooling to room temperature, the mixture was neutralized to pH $\sim$ 8 with $NaHCO_3$, and extracted with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 1/3) to give **1d** (2.42 g, 79%) as pale yellow viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, J = 1.4 Hz, 1H), 8.06 (dd, J = 8.6 and 1.7 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.65 (d, J = 8.9 Hz, 1H), 7.44 (dd, J = 8.4 and 7.5 Hz, 2H), 7.29–7.24 (m, 3 H), 6.97 (dd, J = 8.9 and 2.6 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 4.67 (br s, 1H), 3.80 (t, J = 5.2 Hz, 2H), 3.72–3.67 (m, 6H), 3.58–3.56 (m, 2H), 3.45 (t, J = 5.2 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.7, 151.2, 148.3, 138.2, 131.8, 130.6, 129.4, 126.2, 126.1, 125.9, 125.6, 122.3, 121.8, 118.9, 103.6, 71.9, 70.6, 70.5, 70.3, 69.2, 59.0, 43.1; IR (neat) 3334, 3065, 2881, 1731, 1692, 1630, 1580, 1541, 1494, 1407, 1391, 1342, 1281, 1241, 1188, 1106, 1024, 942 cm^{-1}.

Polymerization

Synthesis of Poly1b

A flask equipped with a three-way stopcock was purged with argon and then charged with 1.0 M LiHMDS in THF (0.4 mL, 0.4 mmol). The flask was cooled to −10 °C under



SCHEME 6 Synthesis of **1d**.

an argon atmosphere with stirring. A solution of monomer **1b** (130.9 mg, 0.4022 mmol), initiator **2** (2.5 mg, 0.012 mmol), and naphthalene (51.6 mg, 0.403 mmol) as an internal standard in dry THF (0.5 mL) cooled to −10 °C was added all at once into the flask containing LiHMDS via a syringe through the three-way stopcock in a stream of dry nitrogen. The reaction mixture was stirred at −10 °C for 4 h, then the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by preparative HPLC (eluent: $CHCl_3$) using a polystyrene gel column to give poly**1b** (65.1 mg) as brown solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81–7.75 (m, 1H), 7.53–7.41 (m, 1H), 7.37–7.21 (m, 2H), 7.18–7.02 (m, 2H), 4.12–3.88 (m, 2H), 1.72–1.01 (m, 10H), 0.95–0.69 (m, 9H).

Synthesis of Poly1d

The polymerization was carried out as in **1b**, using 1.0 M LiHMDS in THF (0.4 mL, 0.4 mmol) and a solution of **1d** (164 mg, 0.400 mmol) and **2** (8.5 mg, 0.040 mmol) in dry THF (0.5 mL). After the reaction mixture had been stirred at −10 °C for 1 h, the reaction was quenched, and the mixture was extracted and purified in the same manner as in **1b** to give poly**1d** (127 mg) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.14 (m, 6H), 4.25–4.09 (m, 2H), 3.85–3.46 (m, 10H), 3.30–3.27 (m, 3H).

CONCLUSIONS

We have extended the range of monomers that undergo CGCP, leading to well-defined aromatic polyamides, from benzene monomers to naphthalene monomers, and we describe the synthesis of poly(naphthalenecarboxamide)s with alkyl and TEG side chains and its limitations. The polymerization of **1b** bearing a 3,7-dimethyloctyl side chain in the presence of initiator **2** and LiHMDS gave well-defined poly(naphthalenecarboxamide), together with a very small amount of a cyclic trimer, formed by self-condensation of **1b** in the early stage of the polymerization, in $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 10$ and 20. Attempts to obtain higher molecular weight polymers resulted in the formation of polymer insoluble in the reaction solvent. On the other hand, polymerization of **1d** with the TEG side chain yielded poly(naphthalenecarboxamide) with high solubility, but the molecular weight was well controlled only in $[\mathbf{1d}]_0/[\mathbf{2}]_0 = 10$. Polymerization at higher feed ratio was accompanied with self-condensation to afford polyamides via chain-growth and step-growth polymerization, so that the M_n value of the polymer did not reach the theoretical value. The undesirable self-condensation is accounted for by insufficient deactivation of the electrophilic ester moiety by the electron-donating resonance effect of the amide anion, due to the greater distance between the positions 2 and 6 of the naphthalene ring, in comparison with the corresponding *p*-substituted benzene monomer, which can undergo CGCP without self-condensation until the feed ratio reaches 100.

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