Control of Molecular Weight Distribution in Polycondensation Polymers. Polyamide Synthesis

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ABSTRACT: Synthesis of the aromatic polyamide with a narrow molecular weight distribution (M_w/M_n) was investigated *via* polycondensation. The new monomers, metal amide anions of 4-(*N*-octylamino)benzoylbenzoxazolin-2-thione (**2**) was prepared to prevent conventional polycondensation. The number average molecular weights (M_n)s of the resulting polymer could be controlled varying the feed ratio of **2** and *p*-nitrobenzoyl chloride in the range of 10^3 – 10^4 maintaining narrow M_w/M_n s (~ 1.15). The kinetic plots of the polymerization gave a linear relationship between polymerization time and $-(1/[I]_0) \ln([M]/[M]_0)$, and the rate of the polymerization was estimated as $116.4 \text{ mol}^{-1} \text{ h}^{-1}$.

KEY WORDS Controlled Polymerization / Polycondensation / Aromatic Polyamide / LiCl / Grignard Reagent / Low Polydispersity / Condensative Chain Polymerization /

Controlled and living polymerizations allow the synthetic approach of well-defined polymers with controlled molecular weights (M_n), molecular weight distributions (M_w/M_n), and terminal functionalities.¹ It has been realized in polymerizations of numerous molecules *via* anionic,² cationic,³ radical,⁴ coordination,⁵ and group transfer systems.⁶ However, most of these have strict limitations on the monomer structures for stabilization of propagating species in order to avoid side reactions such as termination and chain transfer. On the other hands, in step-growth polymerization, which generally possesses polymers having functionalities in their backbone, M_n as well as M_w/M_n is somewhat difficult to control due to the statistical nature in its mechanism; the initiation, propagation, and termination reactions are essentially identical. Basic principle in polycondensation is that stoichiometric imbalance in monomer feed ratio decreases the degree of the polymerization, and that the polymerization should obey the Carothers equation to yield polymers with infinity at 100% conversion under ideal conditions. Thus, the M_n and M_w/M_n control in step-growth polymerization is one of the most attractive subjects in polymer chemistry. Lenz *et al.* reported that the M_n s of the poly(phenylene sulfide)s obtained by the aromatic nucleophilic substitutions of alkali metal 4-halothiophenoxides are higher than those predicted by the Carothers equation probably because of the different reactivity between the thiophenoxides in the monomers and those in the polymer chain ends.⁷ Poly(*p*-phenylene sulfone) was synthesized by the self-condensation of sodium 4-halobenzenesulfonate,

where the addition of a small amount of 4-fluorophenyl sulfone greatly increases the yield of the resulting polymer, presumably by acting as an initiator for a chain-type polymerization.⁸ The phase transfer catalyzed oxidative polymerization of 4-bromo-2,6-dimethylphenol in the presence of 2,4,6-trimethylphenol or 4-*tert*-butyl-2,6-dimethylphenol was investigated to control M_n and M_w/M_n .⁹ Although the M_n s of the resulting polymers increased with the feed ratio of the monomer and initiator, those were different from calculated values. The phase transfer catalyzed polymerization of 4-bromomethyl-2-*n*-octyloxybenzoate was also investigated by Yokozawa *et al.*¹⁰ The M_n of the resulting polyester was controlled up to 4000 with less than 1.3 of M_w/M_n . The first critical synthesis of a polymer with controlled M_n (~ 20000) and M_w/M_n (~ 1.1) was achieved in the polyamide synthesis using 4-(*N*-octylamino)benzoic acid phenylester.¹¹ They also reported the synthesis of the aromatic polyethers with low M_w/M_n values (~ 1.1), but the attainable M_n was less than 5000 because of the poor solubility of resulting polymers.¹² Although their method for polyamide synthesis provide the higher level control of M_n and M_w/M_n in polycondensation than the others, it requires complicated process with peculiar reagents such as *N*-triethylsilyl-*N*-octylaminobenzene and CsF as a base to generate “monomer”, and excess amounts of 18-crown-6-ether as solubilizing agent for CsF. Ensure the concept for the chain-growth polycondensation of various monomers, the polymerization method must be simplify enough to be applicable in various monomers. We here describe a new synthetic method to obtain a polyamide with controlled M_n and M_w/M_n in polycon-

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densation process using conventional bases.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried over sodium and distilled before use under nitrogen. NaH was washed with hexane twice, and used under nitrogen atmosphere. Organo lithium and Grignard reagents were used as received. Diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**DBOP**) was prepared according to the literature.¹³ 4-(*N*-Octylamino)benzoic acid was prepared according to the literature.¹⁴ Lithium chloride was dried at 180°C for 2 h under reduced pressure. All other reagents and solvents were used without further purification.

Measurements

FT-IR spectra were measured on a Horiba FT-720 spectrometer. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX300S spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Plgel 5 μ m MIXED-C) eluted with CHCl₃ at a flow rate of 1.0 mL min⁻¹ calibrated by standard polystyrene samples. Preparative high pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry LC-908 equipped with two consecutive gel columns, JAIGELS 1H and 2 H, detected with refractive index and ultraviolet at 254 nm using chloroform as an eluent with a flow rate of 3.8 mL min⁻¹.

Synthesis of 4-(*N*-octylamino)benzoylbenzoxazolin-2-thione (**1**)

To a solution of 4-(*N*-octylamino)benzoic acid (10 g, 40.1 mmol) and triethylamine (5.9 mL, 42 mmol) in NMP (26 mL) was added **DBOP** (18.6 g, 48.6 mmol) at 25°C. The mixture was stirred at the temperature for 30 min, then at 50°C for 2 h. The resulting solution was poured into 100 mL of 3 wt% aqueous NaHCO₃ solution, filtered, washed with H₂O several times, dissolved in CH₂Cl₂, dried over MgSO₄, and filtered. The filtrate was concentrated under reduced pressure, and the residue was recrystallized from methanol, then ethyl acetate/hexane (1/1 in volume ratio) to obtain yellow curdy (57% yield). IR (KBr) ν 3378 (N-H), 2915 (C-H aromatic), 2853 (C-H aliphatic), 1662 cm⁻¹ (active amide). ¹H NMR (CDCl₃, 25°C) δ 0.89 (t, 3H, CH₃), 1.18–1.52 (m, 10H, CH₂), 1.60–1.70 (m, 2H, CH₂), 3.20 (q, 2H, CH₂), 4.62 (b, 1H, amide), 6.56 (d, 2H, aromatic), 7.16–7.41 (m, 4H, aromatic), 7.78 (d,

2H, aromatic); ¹³C NMR (CDCl₃, 25°C) δ 14.2 (CH₃), 22.8, 27.3, 29.4, 29.5, 32.0, 43.6 (CH₂), 110.4, 112.0, 112.1, 118.2, 125.0, 125.3, 132.0, 134.6, 147.9, 154.7 (aromatic), 165.6 (C=O), 179.4 (C=S); Elemental Anal. Calcd for C₂₂H₂₆N₂O₂S: C; 69.02, H; 6.85, N; 7.32, S; 8.38. Found: C; 68.58, H; 6.33, N; 7.04, S; 7.97.

Polymerization

All polymerization reactions were carried out with the following general procedure: All glass vessels were heated *in vacuo* before use, filled with and handled in a stream of dry nitrogen. Into a flask equipped with a three way stop-cock, 1.45 g (3.79 mmol) of **1**, 2.40 g (56.9 mmol) of LiCl, and 25 mL of THF were placed under nitrogen. The solution was cooled to -40°C, and then 5.68 mL (5.68 mmol) of EtMgBr solution in THF was slowly added to give light yellow monomer solution. After 30 min at the temperature, 0.0353 mg (0.190 mmol) of *p*-nitrobenzoyl chloride was charged to start the polymerization. The light yellow reaction solution was kept stirring at the temperature for another 24 h, and then quenched with *p*-toluidine. The resulting mixture was poured into 100 mL of 3 wt% aqueous NaHCO₃ solution, filtered, washed with H₂O several times, dissolved in CH₂Cl₂, dried over MgSO₄, and filtered. The filtrate was concentrated under reduced pressure to give a brown viscous solid. It was purified by a preparative HPLC providing colorless viscous in 93% yield. IR (KBr) ν 2923 (C-H aromatic), 2854 (C-H aliphatic), 1650 cm⁻¹ (amide). ¹H NMR (CDCl₃) δ 0.87 (t, 3H, CH₃), 1.16–1.38 (m, 10H, CH₂), 1.42–1.68 (m, 2H, CH₂), 2.32 (s, terminal CH₃), 3.72–4.00 (m, 2H, CH₂), 6.70–6.88 (d, 2H, aromatic), 6.99–7.16 (d, 2H, aromatic), 7.52 (d, terminal aromatic), 7.81 (d, terminal aromatic), 7.97 (d, terminal aromatic); ¹³C NMR (CDCl₃, 25°C) δ 14.2 (CH₃), 22.7, 27.1, 28.0, 29.4, 29.5, 32.0, 50.7 (CH₂), 126.9, 129.7, 134.6, 144.8, (aromatic), 169.0 (amide); Elemental Anal. Calcd for (C₁₅H₂₁NO)_n: C; 72.94, H; 8.78, N; 6.02. Found: C; 72.77, H; 8.42, N; 6.22.

Reaction of *p*-Nitrobenzoyl Chloride with **1**

Into a flask equipped with a three way stop-cock, 0.3825 g (1.0 mmol) of **1**, 0.6360 g (15 mmol) of LiCl, and 4.5 mL of THF were placed under nitrogen. The yellow solution was cooled to -40°C, and then 1.1 mL (1.1 mmol) of EtMgBr solution in THF was slowly added through a syringe. After 30 min at the temperature, 0.1856 g (1.0 mmol) of *p*-nitrobenzoyl chloride was charged, and the resulting red colored solution was kept stirring for another 30 min. Then 0.1072 g (1.0 mmol) of *p*-toluidine was added into the reaction mixture, and the solution was gradually warmed to

25°C for 30 min. The resulting solution was poured into 100 mL of 3 wt% aqueous K_2CO_3 solution, filtered, washed with 3 wt% of HCl in H_2O , H_2O several times, dissolved in CH_2Cl_2 , dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure to give a brown solid. This was purified by silica gel column chromatography (hexane/ethyl acetate = 2/1 in volume ratio; 92% yield) (**3**). $M_p = 60-62^\circ C$. IR (KBr) ν 3428 (N–H amide), 2927 (C–H aromatic), 2854 (C–H aliphatic), 1650, 1600 (amide), 1515 cm^{-1} (NO_2). 1H NMR ($CDCl_3$) δ 0.87 (t, 3H, CH_3), 1.16–1.42 (m, 10H, CH_2), 1.57–1.71 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 3.94 (t, 2H, CH_2), 7.12 (t, 4H, aromatic), 7.45 (q, 4H, aromatic), 7.57 (b, 1H, amide) 7.75 (d, 2H, aromatic), 8.02 (d, 2H, aromatic); ^{13}C NMR ($CDCl_3$, $25^\circ C$) δ 14.3, 21.1 (CH_3), 22.9, 27.3, 28.2, 29.4, 29.5, 32.1, 50.9 (CH_2), 121.0, 123.5, 125.8, 128.1, 129.8, 129.9, 134.3, 134.9, 135.6, 142.6, 145.9, 148.7 (aromatic), 164.7, 168.0 (amide); Elemental Anal. Calcd for $C_{29}H_{33}N_3O_4$: C; 71.44, H; 6.82, N; 8.62. Found: C; 71.79, H; 7.19, N; 8.50.

Kinetic Study

The kinetic study for the polymerization of **2** generated by the reaction of **1** with $EtMgBr$ in the presence of $LiCl$ was carried out in THF at $-40^\circ C$. The monomer concentration $[M]$ on time t was estimated by the integration ratios of signals at 7.8 and 6.8 ppm corresponding to aromatic protons of monomer and polymer, respectively, in 1H NMR spectra.

RESULTS AND DISCUSSION

Monomer Synthesis

For investigation of condensative chain polymerization, we first prepared 4-(*N*-octylamino)benzoyl-benzoxazolin-2-thione (**1**) as a monomer precursor in order to endow adequate solubility¹¹ both to monomer and resulting polymer (Scheme 1). The selective formation of the active amide **1** was confirmed by IR, 1H , and ^{13}C NMR spectroscopies. Monomers **2** were then prepared from the reaction of **1** with commercially available bases such as NaH , *n*-BuLi, $EtMgCl$, $EtMgBr$, and *sec*-BuMgBr.

Polymerization

Table I summarizes the results of the polymerization of monomers **2** initiated by *p*-nitrobenzoyl chloride (1/20 equiv to the monomer) in THF at $-40^\circ C$ for 3 h in the presence and absence of $LiCl$ as an additive (Scheme 2). Using NaH as a base, the solution of **2** became heterogeneous, and its conversion into the polymer was very low even in the presence of $LiCl$

Scheme 1.

Table I. Synthesis of Polyamide with Several Bases^a

Run	Base	Conv ^b %	M_n^c	M_w/M_n^c
1	NaH	2	<i>d</i>	<i>d</i>
2	$NaH+LiCl$	4	<i>d</i>	<i>d</i>
3	<i>n</i> -BuLi	45	1200	1.37
4	<i>n</i> -BuLi+ $LiCl$	42	5100	1.60
5	$EtMgBr$	10	400	1.37
6	$EtMgBr+LiCl$	91	6800	1.19
7	$EtMgCl+LiCl$	38	4800	1.20
8	<i>sec</i> -BuMgBr+ $LiCl$	40	3900	1.20

^aConditions; $[M]_0 = 0.15\text{ M}$, $[M]_0/[I]_0 = 20$, $[LiCl]_0/[M]_0 = 15$, $[Base]_0/[M]_0 = 1.5$, in THF at $-40^\circ C$ for 3 h. ^bDetermined by 1H NMR. ^cDetermined by GPC ($CHCl_3$, PSt standard). ^dNot determined.

Scheme 2.

(runs 1 and 2). Monomer **2** generated with *n*-BuLi was converted to the polymer about 45%, though the M_w/M_n values were very high mainly because of the self-condensation of **2** (runs 3 and 4). Then, the Grignard reagents were employed as bases (runs 5–8). Although the monomer **2** generated with $EtMgBr$ could not be polymerized efficiently (run 5), in conjunction with $LiCl$ the polymerization proceeded smoothly to give the corresponding polyamide with a narrow M_w/M_n (= 1.19) in high conversion (run 6). Instead

Table II. Synthesis of Polyamide^a

Run	[LiCl] ₀ /[M] ₀	Temp °C	Conb ^b %	M _n ^c	M _w /M _n ^c
1	0	25	2	<i>d</i>	<i>d</i>
2	5	25	45	3090	2.06
3	15	25	37	6120	1.54
4	15	0	34	14420	1.44
5	15	-40	91	6800	1.18
6	15	-78	3	<i>d</i>	<i>d</i>
7	15(MgCl ₂)	-40	2	<i>d</i>	<i>d</i>

^aConditions; [M]₀ = 0.15 M, [M]₀/[I]₀ = 20, [LiCl]₀/[M]₀ = 0–15, [EtMgBr]₀/[M]₀ = 1.5, in THF for 3 h. ^bDetermined by ¹H NMR. ^cDetermined by GPC (CHCl₃, PSt standard). ^dNot determined.

Scheme 3.

of EtMgBr, EtMgCl was employed to generate **2** for the chain-growth polymerization. Although the self-condensation could be avoided in THF at -40°C for 3 h without the addition of the initiator, the rate of the polymerization was very low (run 7). Such a slow propagation was observed as well, when the polymerization was conducted using **2** generated with *sec*-BuMgBr in the presence of LiCl (run 8). Therefore, EtMgBr in conjunction with LiCl was selected to generate **2** for study of condensative chain-polymerization.

Table II summarizes the results of the polymerization of **2** generated with EtMgBr initiated by *p*-nitrobenzoyl chloride (1/20 equiv to **2**) in THF at various temperatures for 3 h in the presence and absence of LiCl (Scheme 3). In the absence of LiCl, no polymer was obtained at 25°C (run 1). Increasing the amounts of LiCl, conversions of **2** increased up to about 40%, and *M_w*/*M_n* values became smaller (runs 1–3). In order to achieve higher control of the polymerization, the reaction temperature was varied from 25 to -78°C. The corresponding polyamide with a narrow *M_w*/*M_n* was obtained in 91% conversion at -40°C. At much lower temperature (-78°C) or using MgCl₂ instead of LiCl as an additive, the polymerization hardly proceeded probably because of its insufficient reactivity of **2** or insolubility of MgCl₂ in THF, respectively (runs 6 and 7).

Investigation of Monomer Stability

To clarify the stability of **2** derived from **1**, its solution in THF was held at -40°C in the presence of LiCl for 30 min. It was then quenched with H₂O, and extracted from ether. The active amide **1** was quantita-

Scheme 4. **Scheme 5.**

tively recovered, confirmed by ¹H NMR spectroscopy. On the contrary, only 16% of **1** was recovered when the THF solution of **2** was kept at 0°C in the presence of LiCl for 30 min. The other products were 39% of 4-(*N*-octylamino)benzoic acid and 45% of oligomers. These indicated that *in-situ* generated monomer **2** were stable below -40°C, and if the temperature was raised up to 0°C, **2** was converted to carboxylic acid probably through a ketene derivative (Scheme 4).

Since the monomer **2** solution in THF was found to be stable at -40°C in the presence of LiCl, then the equimolar reaction of **2** with *p*-nitrobenzoyl chloride, followed by quenching with *p*-toluidine was investigated as a model reaction in the polymerization (Scheme 5). The final product **3** was isolated by silica gel column chromatography, and characterized by ¹H, ¹³C NMR, IR, and elemental analyses. In the ¹H NMR spectrum, in addition to signals due to **1** unit of *a*–*d*, *h*, and *i* at 0.87, 1.16–1.42, 1.57–1.71, 3.95, 7.12, and 7.75 ppm, respectively, signals assignable to end groups (*e*–*g*, *j*, and *k*) were observed at 2.32, 7.45, 7.12, 7.45, and 8.02 ppm, respectively (Figure 1). The yield of **3** was estimated as 92%, indicating that the initiation and termination of the polymerization might be occurred without any side reactions.

Figure 1. ^1H NMR spectrum (300 MHz, CDCl_3) of the model compound obtained by the reaction of 4-nitrobenzoic acid chloride with **1** in the presence of LiCl and EtMgBr, followed by the reaction with *p*-toluidine in THF.

Table III. Synthesis of Polyamide^a

Run	$[M]_0/[I]_0$	Conv ^b %	M_n calc	M_n^b NMR	M_w/M_n^c
1	20	99	4800	4700	1.15
2	40	98	9300	9100	1.13
3	50	99	11700	10900	1.15
4	100	91	21300	20100	1.17

^aConditions; $[M]_0 = 0.15\text{ M}$, $[\text{LiCl}]_0/[M]_0 = 15$, $[\text{EtMgBr}]_0/[M]_0 = 1.5$, in THF at -40°C for 24 h. ^bDetermined by ^1H NMR. ^cDetermined by GPC (CHCl_3 , PSt standard).

Polymerization of Metal Amide **2** in the Presence of LiCl

Table III summarizes the results of the polymerization of **2** generated with EtMgBr changing the feed ratio of **2** and initiator. The polymers with narrow M_w/M_n s (1.13–1.17) were obtained quantitatively, where the M_n s determined from the integration ratio in ^1H NMR could be tailored by varying the feed ratio and the values showed good agreement with theoretical ones (runs 1–4).

Figure 2 shows the kinetic plots of the polymerization obtained in run 1 in Table III based on a first order equation as follows.

$-\text{d}[M]/\text{d}t = k[P^*][M]$ (P^* ; polymer propagating end)

$-\ln\{[M]/[M]_0\} = kt$ (I ; initiator, $[M]_0$; initial monomer concentration)

The kinetic plots of the polymerization gave a linear relationship between polymerization time and $-(1/[I]_0)\ln([M]/[M]_0)$. This indicated that the polymerization of **1** should proceed *via* chain growth manner without termination like monomer transformation reaction described in Scheme 4. The rate constant of

Figure 2. Relationships between time and $-(1/[I]_0) \times \ln([M]/[M]_0)$ in the polymerization obtained in run 1 in Table III based on a first order equation.

Figure 3. Dependence of M_n and M_w/M_n of the resulting polyamide on $[M]_0/[I]_0$. A broken line showed the theoretical value, $M_{n(\text{calc})}$ calculated by the feed ratio of the monomer to initiator, and a solid line with $\blacklozenge$ did the measured value $M_{n(\text{NMR})}$ by ^1H NMR.

the polymerization was determined as $116.4\text{ mol}^{-1}\text{ h}^{-1}$.

Figure 3 shows the dependence of the M_n on $[M]_0/[I]_0$ ratio obtained in the polymerization of Table III. The M_n increased linearly with the feed ratio of monomer and initiator maintaining narrow M_w/M_n s. Thus, the polycondensation in this system proceeded *via* chain growth manner.

Figure 4 illustrates the ^1H NMR spectrum of the polyamide obtained in the polymerization with *p*-nitrobenzoyl chloride in THF at -40°C for 24 h, followed by the end capping reaction with *p*-toluidine. In addition to signals *a*–*d*, *h*, and *i* assignable to polymer backbone, signals *k*, *i'*, *j*, and *e* assignable to aromatic and methyl protons of initiating and terminal ends were observed at 7.97, 7.81, 7.52, and 2.32 ppm, respectively. The integration ratio of signals between *j* and *e* was 2:2.92, which was in good agreement with the

Figure 4. ^1H NMR spectrum (300 MHz, CDCl_3) of the polyamide obtained in the polymerization with *p*-nitrobenzoic acid chloride in THF at -40°C for 24 h, followed by the end capping reaction with *p*-toluidine. * is derived from solvent (CH_2Cl_2).

Scheme 6.

theoretical value of 2:3. The M_n calculated from the integration ratio of *j* and *i* was 4000, very close to theoretical one ($M_n = 3900$) calculated from the feed ratio of the monomer and initiator. These results also supported that the polycondensation in this system proceeds *via* chain growth manner.

Scheme 6 illustrates a plausible polymerization mechanism in this system. The initiator, *p*-nitrobenzoyl chloride may be attacked by the metal amide of *in situ* generated monomer **2** to afford the neutral amide bond. The reactivity of the resulting active amide against the monomer may be higher than that of the monomer itself whose carbonyl group is inactivated with the strong electron-donating effect of the metal amide. As a result, the monomer may selectively attack on the polymer propagating end (chain growth polymerization mechanism) to give the polymer with controlled M_n and

M_w/M_n , whereas the polymerization obey polycondensation mechanism of releasing 2-mercaptobenzoxazole in each step.

SUMMARY

In this article, we have demonstrated the synthesis of an aromatic polyamide with a narrow M_w/M_n *via* polycondensation mechanism. New monomer **2** having long alkyl group, active amide, and counter metal cation was designed to prevent conventional polycondensation. The M_n s of the obtained polymer could be controlled by the amount of *p*-nitrobenzoyl chloride in the range of 10^3 – 10^4 maintaining narrow M_w/M_n s (~ 1.15). The ^1H NMR spectroscopic and kinetic studies clearly indicated that the polycondensation in this system proceeded *via* the chain growth mechanism.

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