

## Chain-Growth Polycondensation for Nonbiological Polyamides of Defined Architecture

Tsutomu Yokozawa,\* Toshinobu Asai, Ryuji Sugi, Shingo Ishigooka, and Shuichi Hiraoka

Department of Applied Chemistry  
Kanagawa University, Rokkakubashi  
Kanagawa-ku, Yokohama 221-8686, Japan

Received May 30, 2000

Many natural polymeric materials are perfect monodisperse macromolecules and are produced by the successive condensation of monomers with polymer end groups that are activated by enzymes.<sup>1–4</sup> Although these syntheses proceed via many complicated and tightly controlled processes, the overall process could be regarded as a kind of chain-growth polycondensation. In the polycondensation of artificial monomers, however, macromolecules with a wide range of molecular weights have been synthesized, because there is little difference of reactivity between monomers and polymer end groups, and step-growth polymerization occurs. If the polymer end groups become more reactive than monomers and the reaction of monomers with each other is prevented, chain-growth polycondensation would take place to yield artificial condensation polymers having well-defined molecular weights and narrow molecular weight distributions (MWD). Kinetic studies showed that some polycondensations involve more reactive polymer end groups than monomers, but the MWD of polymers were not evaluated.<sup>5</sup> The synthesis of poly-(2,6-dimethyl-1,4-phenylene oxide) by oxidative polymerization of 2,6-dimethylphenol<sup>6</sup> and by phase transfer catalyzed polycondensation of 4-bromo-2,6-dimethylphenol<sup>7</sup> also involved the reactive polymer end groups and did not show the behavior of a classic polycondensation. Percec conducted this polycondensation in the presence of chain initiators and obtained well-defined polyphenylene oxides.<sup>7</sup> However, the molecular weight values were much higher than the calculated values based on the [monomer]/[initiator] ratios, and polymers having a narrow MWD were obtained after precipitation; the crude polymerization mixture had a broad MWD. In the polycondensations of bifunctional nucleophilic monomers with bifunctional electrophilic monomers, polymers having a low polydispersity ( $M_w/M_n < 1.3$ ) were also prepared by phase transfer catalyst (PTC) techniques when polymer end groups were more reactive than monomers.<sup>8–10</sup> This type of polycondensation, however, could not control the molecular weight.

(1) For the biosynthesis of polypeptides, see: (a) Weissbach, H.; Pestka, S. *Molecular Mechanism of Protein Biosynthesis*; Academic Press: New York, 1977. (b) Bermek, E. *Mechanism of Protein Synthesis. Structure–Function Relations, Control Mechanisms, and Evolutionary Aspects*; Springer-Verlag: New York, 1985.

(2) For the biosynthesis of DNA, see: Kornberg, A. *Science* **1960**, *131*, 1503.

(3) For the biosynthesis of RNA, see: (a) Travers, A. *Nature* **1976**, *263*, 641. (b) Chamberlin, M. In *The Enzymes*; Boyer, P. D., Ed.; Academic Press: New York, 1982; Vol. 15, p 61.

(4) For the biosynthesis of *cis*-polyisoprene rubber, see: (a) Light, D. R.; Dennis, M. S. *J. Biol. Chem.* **1989**, *264*, 18589. (b) Light, D. R.; Lazarus, R. A.; Dennis, M. S. *J. Biol. Chem.* **1989**, *264*, 18598. (c) Dennis, M. S.; Light, D. R. *J. Biol. Chem.* **1989**, *264*, 18608.

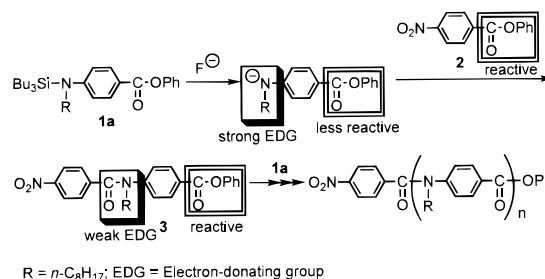
(5) (a) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. *J. Polym. Sci.* **1962**, *58*, 351. (b) Newton, A. B.; Rose, J. B. *Polymer* **1972**, *13*, 465. (c) Hibbert, D. B.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1739. (d) Robello, D. R.; Ulman, A.; Urankar, E. *J. Macromolecules* **1993**, *26*, 6718.

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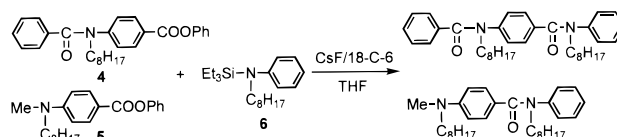
(7) (a) Percec, V.; Wang, J. H. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 63. (b) Percec, V.; Shaffer, T. D. *J. Polym. Sci. Part C: Polym. Lett.* **1986**, *24*, 439. (c) Percec, V.; Wang, J. H. *Polym. Bull.* **1990**, *24*, 493.

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### Scheme 1



### Scheme 2



Our previous work has shown that the Pd-catalyzed polycondensation of 4-bromo-2-octylphenol and carbon monoxide underwent chain-growth polycondensation from an initiator in the initial stage.<sup>11</sup> Another approach to chain-growth polycondensation was the polycondensation of solid monomer with PTC in organic solvent containing an initiator, where the reaction of monomers with each other was prevented.<sup>12</sup> The molecular weight was controlled but the MWD was a little broad ( $M_w/M_n < 1.3$ ). We now report the successful chain-growth polycondensation of phenyl 4-aminobenzoate derivatives **1** for aromatic polyamides having precisely controlled molecular weights and quite narrow MWD ( $M_w/M_n < 1.12$ ), where all of the experimental criteria of a living polymerization are exhibited even in polycondensation.

The expected course of polymerization of silylated **1a** with CsF in the presence of a small amount of reactive initiator **2** bearing an electron-withdrawing group is shown in Scheme 1. Thus, **1a** would react with **2** to yield amide **3** faster than with the acyl group of desilylated **1a** having the strong electron-donating aminylium anion group. Monomer **1a** would now react with **3** to yield a dimeric amide faster than with **1a** itself, because the amide group of **3** is the much weaker electron-donating group than the aminylium anion group of the monomer, and the acyl group of **3** would be more reactive than that of the monomer. Growth would continue in a chain polymerization manner with the conversion of the strong electron-donating aminylium anion of **1a** to the weak electron-donating amide group in polymer.

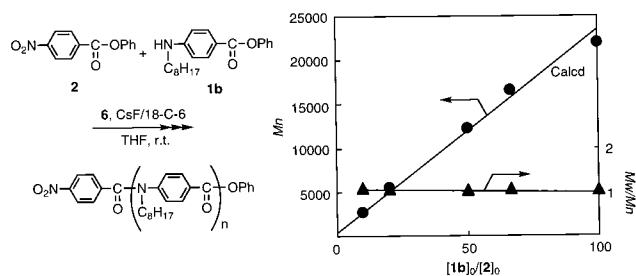
To estimate the reaction selectivity of monomer **1a** with the polymer end group (resulting in “chain-growth polymerization”) or with **1a** itself (resulting in “step-growth polymerization”), the reaction of monomer amino group model **6** with the 1:1 mixture of polymer terminal phenyl ester model **4** and monomer phenyl ester model **5** was carried out in the presence of CsF and 18-crown-6 in THF at room temperature (Scheme 2). The conversion ratio **4/5** was 95/5. Furthermore, the reaction of **6** with **4** and that of **6** with **5** were carried out, respectively. The reaction of **6** with **5** did not proceed when the reaction of **6** with **4** was completed. The results of model reactions indicate that monomer **1a** would react with the polymer end group with high selectivity and undergo chain-growth polycondensation.

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(11) Yokozawa, T.; Shimura, H. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 2607.

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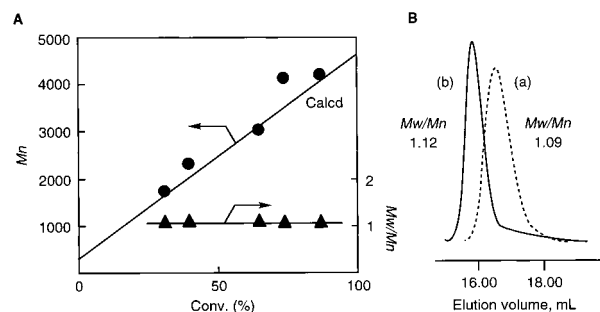
**Figure 1.**  $M_n$  and  $M_w/M_n$  values of poly**1b**, obtained with **6** and CsF/18-crown-6 in the presence **2** in THF at 25 °C, as a function of the feed ratio of **1b** to **2**.

The polymerization of **1a** was carried out in the presence of 1.0 equiv of CsF, 2.0 equiv of 18-crown-6, and phenyl 4-nitrobenzoate **2** as an initiator in THF at room temperature to yield a polyamide quantitatively, which was soluble in THF, chloroform, dichloromethane, *N,N*-dimethylformamide (DMF), and even toluene. In the polymerization with varying the feed ratio ( $[1a]_0/[2]_0$ ), the MWD of polymers was narrow ( $M_w/M_n = 1.16-1.20$ ) when the  $[1a]_0/[2]_0$  ratios were 10 or less but gradually increased up to 1.47 after that. Broad MWD in high  $[1a]_0/[2]_0$  ratios may be interpreted in terms of the hydrolysis of the silyl group of monomer **1a** with a very small amount of water coming from CsF and/or 18-crown-6. Hydrolyzed **1b** would not react as a monomer but eventually worked as an initiator, and the amount of **1b** could not be neglected in high  $[1a]_0/[2]_0$  ratios. Accordingly, we carried out the polymerization of **1b** by using *N*-triethylsilyl-*N*-octylaniline **6** as a base generated by CsF. Thus, the aminyl anion generated from **6** would abstract the proton of the amino group of **1b**, followed by polymerization in a similar manner of **1a**. If the reaction mixture was contaminated with a small amount of water, only **6** would be hydrolyzed and not affect monomer **1b**. In addition, the purification of **1b** and **6** was much easier than that of **1a**.

The polymerization of **1b** was carried out by using 1.1 equiv of **6** (Figure 1). The MWD of polymers was quite narrow and close to a monodisperse distribution, maintaining the  $M_w/M_n$  ratio below 1.1 over the whole  $[1b]_0/[2]_0$  range. The  $M_n$  values of polymers<sup>13</sup> were in agreement with the calculated values assuming that one polymer chain forms per unit **2** until  $M_n = 22\,000$ . This result implies that the polycondensation of **1b** proceeded from initiator **2** in a chain-growth polymerization manner like living polymerizations of vinyl monomers and cyclic monomers.<sup>14</sup> To elucidate whether chain-growth polymerization takes place in this polycondensation, the polymerization of **1b** was carried out in the presence of 5 mol % of **2**, and the  $M_n$  values and the  $M_w/M_n$  ratios were plotted against monomer conversion (Figure 2A). The  $M_n$  values increased in proportion to conversion, and the  $M_w/M_n$  ratios were less than 1.12 over the whole conversion range. This polymerization behavior agrees with the features of living poly-

(13) The  $M_n$ s of polyamides were estimated by gel permeation chromatography (GPC) based on polystyrene standards. However, the  $M_n$ s determined by GPC were in good agreement with those determined by <sup>1</sup>H NMR spectra.

(14) For a recent review of living polymerizations, see: Kobayashi, S. *Catalysis in Precision Polymerization*; John Wiley & Sons: New York, 1997.



**Figure 2.** Demonstration of chain-growth polycondensation. (A)  $M_n$  and  $M_w/M_n$  values of poly**1b**, obtained with **6** and CsF/18-crown-6 in the presence **2** in THF at 25 °C, as a function of monomer conversion. (B) GPC profile of the monomer addition experiment in THF at room temperature: (a) prepolymer ( $[1b]_0/[2]_0 = 20$ ), conversion = 98%,  $M_n = 4500$ ; (b) postpolymer ( $[added\ 1b]_0/[2]_0 = 24$ ), conversion = 187%,  $M_n = 10\,000$ .

merizations.<sup>14</sup> In general polycondensations that proceed in a step polymerization manner, the molecular weight does not increase much in low conversion of monomer and is accelerated in high conversion, and the  $M_w/M_n$  ratios increase up to 2.0. Consequently, Figure 2A shows that the polycondensation of **1b** proceeds in a chain-growth polymerization manner. The character of chain-growth polymerization of this polycondensation was further demonstrated by so-called “monomer-addition” experiments where a fresh feed of **1b** and **6** was added to the prepolymer ( $M_n = 4500$  ( $M_n(\text{calcd}) = 4780$ ),  $M_w/M_n = 1.09$ ) in the reaction mixture. The added **1b** feed was smoothly polymerized. The GPC chromatogram of the product (Figure 2B (b)) clearly shifted toward the higher molecular weight region, while retaining the narrow distribution ( $M_n = 10\,000$  ( $M_n(\text{calcd}) = 9970$ ),  $M_w/M_n = 1.12$ ).<sup>15</sup> This experiment implies that this polycondensation will enable us to synthesize block copolyamides having different aminoalkyl side chains and well-defined sequences. Furthermore, we anticipate that this polycondensation will provide new approaches for the design of nanoarchitectures, which have been achieved by living polymerizations of vinyl and cyclic monomers<sup>14</sup> and by stepwise synthesis of dendritic macromolecules<sup>16</sup> and linear oligomers.<sup>17</sup> Experiments along these lines are in progress.

**Acknowledgment.** This work was supported in part by a Grant-in-Aid (10650873) for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

**Supporting Information Available:** Synthesis of monomer **1b** and polymerization procedure (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) In the monomer-addition experiment, it was crucial to use 0.95 equiv of **6** in the first-stage polymerization. An excess amount of **6** did not react with the polymer end group during polymerization but did after the consumption of monomer to give the amide end group, which could not initiate the polymerization in the second-stage.

(16) For reviews, see: (a) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 885. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.

(17) For examples, see references in ref 12.