

Self-initiated Chain-growth Polycondensation for Aromatic Polyamides

Tsutomu Yokozawa,^{*†,††} Ryuji Sugi,^{†,††} Toshinobu Asai,[†] and Akihiro Yokoyama[†]

[†]Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686
^{††}“Synthesis and Control”, PRESTO, Japan Science and Technology Agency (JST)

(Received December 8, 2003; CL-031197)

The polycondensation of phenyl 4-(octylamino)benzoate (**1**) proceeded in a chain-polymerization manner to yield aromatic polyamides with low polydispersities ($M_w/M_n \leq 1.1$) even under normal conditions for step-growth polycondensation, in which initiator was not added. On the basis of the results of the polycondensations of **1** with initiator models, this self-initiated chain-growth polycondensation involves the formation of the dimer of **1**, which initiates the chain-growth polymerization faster than step-growth polymerization.

Polycondensation is generally initiated by the reaction of monomers with each other and propagated in a step polymerization manner to give polymer with a wide range of molecular weights; the polydispersity (M_w/M_n) approaches to 2.0 at high conversion of monomer. However, a few of polycondensations are initiated by the reaction of monomer with an initiator and propagated in a chain polymerization manner to yield polymer with a low polydispersity like living polymerization. For example, the polycondensation of phosphoranimines is initiated by PCl_5 to yield well-defined polyphosphazenes.¹ Dimethylsulfoxonium methylide polymerizes with trialkylboranes accompanying elimination of dimethylsulfoxide to afford polymethylenes with very low polydispersities.² The polycondensation of phenyl 4-(octylamino)benzoate **1** is initiated by phenyl 4-nitrobenzoate in the presence of base to give aromatic polyamides with low polydispersities.³ In the former two examples, the monomers do not react with each other essentially but react with the reactive species formed from the initiators and monomers, which are $-PR_2=N-PCl_3^+$ in the polymerization of phosphoranimines and trialkylboranes in the polymerization of the sulfoxonium ylide, respectively. In the last example, however, the monomer can react with each other even in the absence of the initiator, because the initiator and monomer have the same phenyl ester moiety as a polymerizable site.

This difference between the former two chain-growth polycondensations and the last one awoke our interest in whether **1** undergoes chain-growth polycondensation even without the initiator to yield polyamide with a low polydispersity or conventional step-growth polycondensation to give polyamide with a broad molecular weight distribution. One might think that the conventional polycondensation would occur in the absence of the initiator, because oligomers formed during reaction have the reactive amino group and phenyl ester moiety in both ends, and therefore those oligomers would react with each other. Herein we report that the polycondensation of **1** even without an initiator yields aromatic polyamides with very low polydispersities ($M_w/M_n \leq 1.1$)⁴ and prove that this polycondensation proceeds in a chain polymerization manner from dimer **3a** formed in situ (Figure 1).⁵ This self-initiated polymerization is a new type of chain-growth polymerization with a living polymerization na-

ture,⁶ because living polymerizations of vinyl monomers and cyclic monomers do not proceed in the absence of initiators.

The polycondensation of **1** was carried out with 1.0 equiv. of base (*N*-triethylsilyl-*N*-octylaniline (**2**), CsF, and 18-crown-6)³ in THF at room temperature. Surprisingly, the polymerization showed the behavior of living chain-growth polymerization; the molecular weight (M_n) values increased in proportion to monomer conversion and the M_w/M_n ratios were less than 1.2

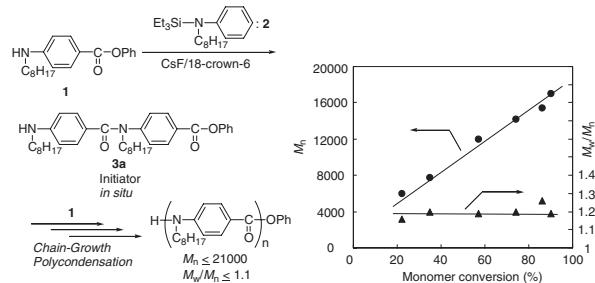


Figure 1. M_n and M_w/M_n values of poly**1**, obtained with **2** and CsF/18-crown-6 in THF at 25 °C, as a function of monomer conversion: $[1]_0 = [2]_0 = 0.67$ M; $[CsF]_0 = 0.67$ M; [18-crown-6] = 1.33 M.

Table 1. Polycondensation of **1** with **2**^a

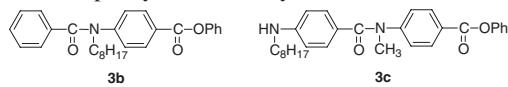
2, equiv	time	conversion, % ^b	M_n ^c	M_w/M_n ^c
0.9	24 h	89	15400	1.34
1.0	23 h	90	17000	1.19
1.2	4.3 h	88	18900	1.10
1.5	10 min	91	21300	1.07
	30 min	93	24400	1.15

^aPolymerization of **1** was carried out with **2** in the presence of CsF/18-crown-6 in THF ($[1]_0 = 0.67$ M; 1.0 equiv of CsF and 2.0 equiv of 18-crown-6 to **2**) at 25 °C. ^bMonomer conversion determined by HPLC. ^cDetermined by GPC based on polystyrene standards (eluent: THF)

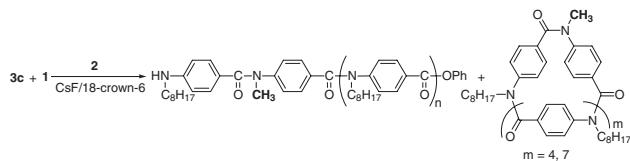
over the whole conversion range (Figure 1). Furthermore, as the amount of **2** was increased, the polymerization proceeded faster to yield polyamides with higher M_n values and lower polydispersities (Table 1). Especially, the polyamide with M_n of 21300 and M_w/M_n of 1.07 was obtained by the polycondensation with 1.5 equiv. of **2** only for 10 min. When this polymerization was conducted for 30 min, the GPC chromatogram of the product showed a small shoulder in the higher molecular weight region, and the M_n value and M_w/M_n ratio slightly increased, implying that small amount of polymers react with each other like step-growth polymerization. However, even if the reaction prolonged after that, the M_n values did not increase. Comparing the ¹H NMR spectra of the polyamides obtained by the polymerization for 10 and 30 min, the former spectrum showed the signals

of the aromatic protons adjacent to both the terminal amino and phenoxy carbonyl groups, whereas the latter one only showed the signal due to the terminal amino group. Disappearance of the phenyl ester end group in the polymerization for 30 min is ascribed to the conversion of the phenyl ester moiety into the amide end group by the reaction with **2**. Accordingly, this transformation into the inert amide end group is probably responsible for almost no step-growth reaction between polymers in high conversion. In the initial and middle stage of the polymerization, chain-growth polymerization would proceed much faster than step-growth polymerization.

The chain polymerization mechanism is best accounted for by different substituent effects between monomer and polymer; the aminyl anion of monomer **1** strongly deactivates the acyl group, whereas the amide linkage of polymer activates the polymer end acyl group, as described in the previous paper.³ What is then chain initiator species in this polymerization? We speculated that dimer **3a** generated in situ would initiate polymerization because the phenyl ester moiety of **3a** having the amide linkage is more reactive than that of **1**. With this assumption, the polymerization of **1** was carried out in the presence of phenyl 4-(*N*-benzoyl-*N*-octylamino)benzoate (**3b**) (6.1 mol %) as a model of dimer **3a**. The M_n value of polymer was 4160, which agreed with the calculated one of 4070, and the M_w/M_n ratio was 1.08. This result indicates that **3b** having the amide linkage at the para-position of the phenyl ester moiety worked as an initiator.



Furthermore, **1** was polymerized with 4.7 mol % of **3c** having the *N*-methyl group, which is distinguishable from dimer **3a** formed in situ, to yield polyamide with a higher M_n value ($M_n = 9000$, $M_w/M_n = 1.07$) than the calculated one (M_n (calcd) = 4300) and cyclic hexamer and nonamer containing one *N*-methyl group,⁷ respectively (Scheme 1). The ¹H NMR spectrum of the polyamide showed the signals of the *N*-methyl group and the *N*-methylene group of the terminal *N*-octyl group, the intensity ratio of which was 3/2, indicating that the polymer had **3c** unit as an initiator unit. Furthermore, the formation of these cyclic oligomers containing one **3c** unit is also best accounted for by initiation of oligomerization with **3c**, followed by cyclization. This consumption of **3c** for the production of the cyclic oligomers is probably responsible for the higher M_n value of the polymer obtained than the calculated value assuming that one polymer chain forms per unit **3c**.



Scheme 1.

Consequently, these results lead us to conclude that dimer **3a** generated in situ is in effect for the initiation of the polymerization of **1** without addition of initiator. On the basis of this initiation mechanism, we rationalize higher M_n values with increasing the amount of base **2** by suggesting that **3a** is formed by the reaction of **1** with the aminyl anion of **1**; fast generation of the aminyl anion of **1** with increasing the amount of **2** decreases

the reaction between the anion and **1**, resulting in decrease of concentration of **3a**.⁸

In conclusion, our present results demonstrate that monomer **1** undergoes chain-growth polycondensation even under normal conditions for step-growth polycondensation, where an initiator is not added. The polymerization probably involves the formation of the dimer of **1**, which initiates chain-growth polymerization faster than step-growth polymerization. This self-initiated living-like polymerization is a unique type of polymerization that would take place by monomers for polycondensation, which can react with each other to generate initiator species in situ.

This work was supported in part by a Grant-in-Aid (12450377) for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

- 1 a) C. H. Honeyman, I. Manners, C. T. Morrissey, and H. R. Allcock, *J. Am. Chem. Soc.*, **117**, 7035 (1995). b) H. R. Allcock, C. A. Crane, C. T. Morrissey, J. M. Nelson, S. D. Reeves, C. H. Honeyman, and I. Manners, *Macromolecules*, **29**, 7740 (1996). c) H. R. Allcock, S. D. Reeves, C. R. Denus, and C. A. Crane, *Macromolecules*, **34**, 748 (2001).
- 2 a) K. J. Shea, H. Zhu, J. R. Walker, M. M. Paz, and J. Greaves, *J. Am. Chem. Soc.*, **119**, 9049 (1997). b) K. J. Shea, B. B. Busch, and M. M. Paz, *Angew. Chem., Int. Ed. Engl.*, **38**, 1391 (1998). c) K. J. Shea, S. Y. Lee, and B. B. Busch, *J. Org. Chem.*, **63**, 5746 (1998). d) K. J. Shea, *Chem.—Eur. J.*, **6**, 1113 (2000). e) K. J. Shea, B. B. Busch, M. M. Paz, C. L. Straiger, J. M. Stoddard, J. R. Walker, X. Zhou, and H. Zhu, *J. Am. Chem. Soc.*, **124**, 3636 (2002).
- 3 a) T. Yokozawa, T. Asai, R. Sugi, S. Ishigooka, and S. Hiraoka, *J. Am. Chem. Soc.*, **122**, 8313 (2000). b) Y. Shibasaki, T. Araki, M. Okazaki, and M. Ueda, *Polym. J.*, **34**, 261 (2002).
- 4 It has been reported that condensation polymers with relatively low polydispersities ($M_w/M_n = 1.2$ –1.3) are obtained in a few of polycondensations of difunctional nucleophilic monomers with difunctional electrophilic monomers without addition of monofunctional compounds, see: a) V. Percec, ACS Symposium Series, American Chemical Society, Washington (1987), Vol. 326, p 96. b) V. Percec, T. D. Shaffer, and H. Nava, *J. Polym. Sci., Part C: Polym. Lett.*, **22**, 637 (1984). c) T. D. Shaffer and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 451 (1986). d) T. D. Shaffer and M. C. Kramer, *Makromol. Chem.*, **191**, 71 (1990). e) K. Miyatake, A. R. Hlil, and A. S. Hay, *Macromolecules*, **34**, 4288 (2001).
- 5 For examples of polycondensation without initiator that contains chain-growth polymerization mechanism in part in spite of not showing the nature of living polymerization, see a) R. W. Lenz, C. E. Handlovits, and H. A. Smith, *J. Polym. Sci.*, **58**, 351 (1962). b) A. B. Newton and J. B. Rose, *Polymer*, **13**, 465 (1972). c) W. Rissee and W. Heitz, *Makromol. Chem.*, **186**, 1835 (1985). d) V. Percec and T. D. Shaffer, *J. Polym. Sci., Part C: Polym. Lett.*, **24**, 439 (1986). e) D. B. Hibbert and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1739. f) D. R. Robello, A. Ulman, and E. J. Urakar, *Macromolecules*, **26**, 6718 (1993). g) K. Matyjaszewski, D. Greszta, J. S. Hrkach, and H. K. Kim, *Macromolecules*, **28**, 59 (1995).
- 6 Examples of self-initiated chain polymerization without living polymerization nature are thermal polymerization of styrene and copolymerization of donor and acceptor olefins: H. K. Hall, Jr., *Angew. Chem., Int. Ed. Engl.*, **22**, 440 (1983).
- 7 m/z Calcd for [cyclic hexamer + Ag]⁺ 1396.78, found 1396.93; m/z calcd for [cyclic nonamer + Ag]⁺ 2090.27, found 2090.59.
- 8 The increase of polymerization rate with increasing **2** may be attributed to involvement of abstraction of proton from **1** with **2** or generation of dimer **3a** in the rate-determining step.