

Aromatic Polyethers with Low Polydispersities from Chain-Growth Polycondensation

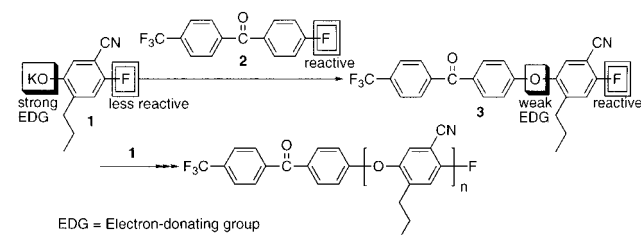
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Received June 19, 2001

The development of living polymerization for the preparation of polymers with controlled molecular weights and narrow polydispersities is among the most significant accomplishments in polymer synthesis.¹ However, those well-defined polymers have not been synthesized by polycondensation, which proceeds in a step-polymerization manner, except for the cationic polycondensation of phosphoranimes yielding well-defined polyphosphazenes.² We have proposed that the polycondensation, like living polymerization, would be attained by chain-growth polycondensation,³ where the monomer reacts with only the polymer end group, not with other monomers,⁴ and we have been successful in achieving a chain-growth polycondensation by using phenyl 4-(*N*-octylamino)benzoate as a monomer and *N*-octyl-*N*-triethylsilylaniline as a base generated by CsF.⁵ In this polycondensation, we took advantage of different substituent effects between monomer and polymer; the aminyl anion of monomer strongly deactivates the phenyl ester moiety of monomer, whereas the amide linkage of polymer activates the polymer end phenyl ester moiety. Therefore, monomer reacted with only the polymer end group, and the polycondensation proceeded in a living polymerization manner.

The acyl group of this monomer is thought to play an important role in chain-growth polycondensation, because the strong electron-donating aminyl anion can be changed to the weak electron-donating amide linkage by bonding to the strong electron-withdrawing acyl group. Accordingly, monomers having the acyl group or carbonyl group as an electrophilic site are expected to undergo chain-growth polycondensation to yield well-defined condensation polymers such as polyesters, polythioesters, and polyketones, and so forth. An extension of chain-growth polycondensation awoke our interest in whether monomers having no acyl group as an electrophilic site also undergo chain-growth polycondensation. It would be more difficult to achieve such a chain-growth polycondensation, because the substituent effects on the reactive site are not expected to change much between monomer and polymer. We now report that the polycondensation of a potassium 4-fluorophenolate derivative **1**, which has no acyl group as an electrophilic site, also proceeds via chain-growth

Scheme 1



polycondensation to yield a polyether having a controlled molecular weight and low polydispersity ($M_w/M_n \leq 1.1$).

The expected course of polymerization of **1** in the presence of a small amount of reactive initiator **2** bearing an electron-withdrawing group is shown in Scheme 1. Thus, **1** would react with **2** to yield ether **3** faster than with the aromatic fluorine of **1** having the strong electron-donating phenoxide group. Monomer **1** would now react with **3** to yield a dimeric ether faster than with **1** itself, because the ether linkage of **3** is a weaker electron-donating group than the phenoxide group of **1**, and the aromatic fluorine 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 phenoxide group of **1** to the weak electron-donating ether linkage in polymer.

We also think another polymerization course for the chain-growth polycondensation of **1**, in which phenoxide is the propagating end group instead of fluorine. If potassium 4-methoxyphenoxide **4** having the electron-donating group is used as an initiator, **4** would react with **1**, and the ether linkage formed would make the polymer terminal phenoxide more reactive than the phenoxide of the monomer, because ether linkage has a stronger electron-donating character than fluorine. With the above two assumptions, the polymerizations of **1** with 7 mol % of **2** and **4** were carried out at 150 °C in sulfolane, respectively. Surprisingly, the polymerization of **1** with **4** did not proceed, whereas the polymerization with **2** took place to yield a polymer with low polydispersity (Figure 1). This result implies that not only the reaction of **4** with **1** but also the reaction of monomers **1** with each other did not take place under this condition, and that the polymerization of **1** in the presence of **2** did not involve step polymerization but was initiated with **2**.

To elucidate whether chain-growth polymerization takes place in this polycondensation, the polymerization of **1** was carried out in the presence of 7 mol % of **2**, and the M_n values,⁶ the M_w/M_n ratios, and the ratios of end group to initiator unit in polymer 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 1.1 over the whole conversion range. The ratios of end group to initiator unit, which were easily determined by the ¹⁹F NMR spectra of polymer, were constantly about 1.0, irrespective of conversion. This polymerization behavior agrees with the features of living polymerizations.¹ In general polycondensations that proceed in a step polymerization manner, the molecular weight does not increase much in low conversion of the monomer and is accelerated in high conversion, and the M_w/M_n ratios increase up to 2.0. The ratios of end group to initiator unit would be larger than 1.0 because monomers react with not only an initiator but also other monomers. Consequently, Figure 2a shows that the polycondensation of **1** proceeds in a chain-growth polymerization manner. In another series of experiments, **1** was polymerized with varying feed ratio ($[1]_0/[2]_0$). As shown in Figure 2b, the observed M_n values of polymers were in good

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

(2) (a) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035. (b) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740. (c) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50. (d) Allcock, H. R.; Reeves, S. D.; Denus, C. R.; Crane, C. A. *Macromolecules* **2001**, *34*, 748.

(3) (a) Yokozawa, T.; Horio, S. *Polym. J.* **1996**, *26*, 633. (b) Yokozawa, T.; Shimura, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2607. (c) Yokozawa, T.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 11573.

(4) For examples of polycondensation in which the reaction of monomer with polymer end group is faster than that of monomers with each other, although the polymerization behavior does not show the character of living polymerization, see: (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) Risse, W.; Heitz, W. *Makromol. Chem.* **1985**, *186*, 1835. (d) Percec, V.; Shaffer, T. D. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 439. (e) Hibbert, D. B.; Sandall, J. P. *B. J. Chem. Soc., Perkin Trans. 2* **1988**, 1739. (f) Percec, V.; Wang, J. H. *Polym. Bull.* **1990**, *24*, 493. (g) Percec, V.; Wang, J. H. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 63. (h) Robello, D. R.; Ulman, A.; Urankar, E. *J. Macromolecules* **1993**, *26*, 6718.

(5) Yokozawa, T.; Asai, T.; Sugi, R.; Ishigooka, S.; Hiraoka, S. *J. Am. Chem. Soc.* **2000**, *122*, 8313.

(6) The M_n values of polymer were estimated by the ¹H NMR spectra based on the ratios of signal intensities of the repeating units to the initiator unit.

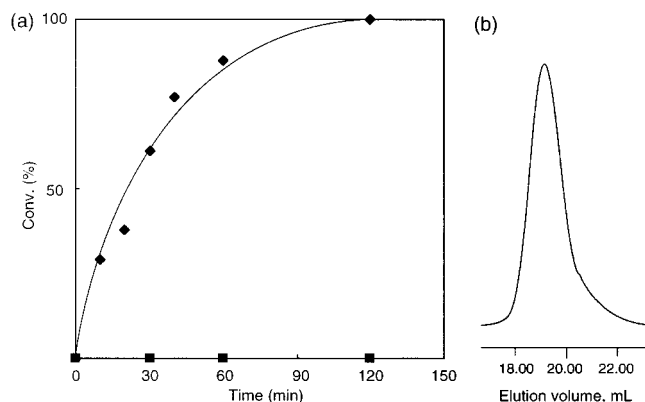


Figure 1. (a) Time-conversion curves for the polymerization of **1** in the presence of initiator in sulfolane at 150 °C: $[1]_0 = 0.17$ M; $[\text{initiator}]_0 = 11.7$ mM. Initiator: (◆) **2**; (■) **4**. (b) GPC profile of poly**1** obtained in the polymerization of **1** with **2** for 40 min.

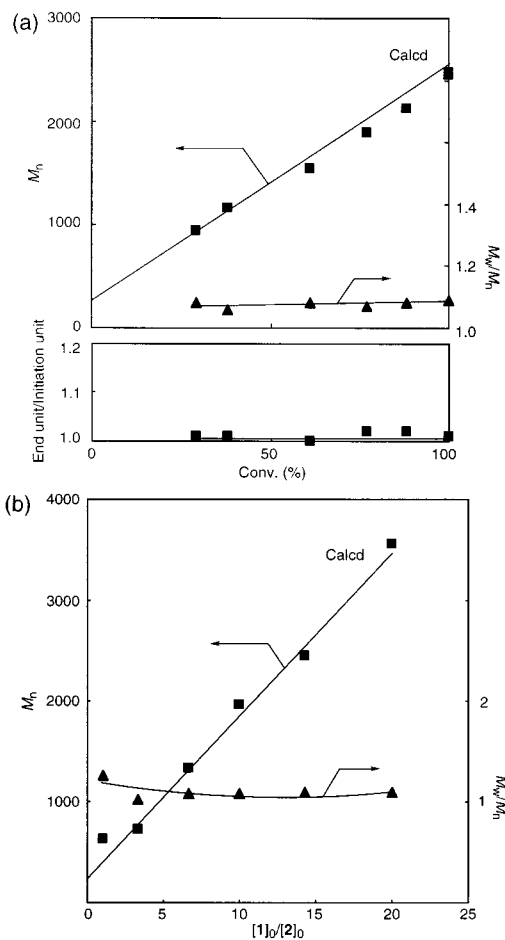


Figure 2. (a) M_n and M_w/M_n values of poly**1** and the ratios of end group to initiator unit in poly**1**, obtained in the presence of **2** in sulfolane at 150 °C, as a function of monomer conversion: $[1]_0 = 0.17$ M; $[2]_0 = 11.7$ mM. (b) M_n and M_w/M_n values of poly**1**, obtained in the presence of **2** in sulfolane at 150 °C, as a function of the feed ratio of **1** to **2**: $[1]_0 = 0.17$ M; $[2]_0 = 8.3$ – 167 mM; conversion = 100%.

agreement with those calculated with the assumption that one initiator molecule forms one polymer chain. The M_w/M_n ratios were less than 1.1 when the $[1]_0/[2]_0$ ratios were more than 1.0.⁷ This also agrees with the features of chain-growth polymerization.

This successful chain-growth polycondensation would be based on the different reactivity of aromatic fluorines between the polymer end group and monomer **1** as we expected; initiator **2** and the polymer end group are more reactive than **1**. It has been reported that more reactive aromatic fluorines show the signals

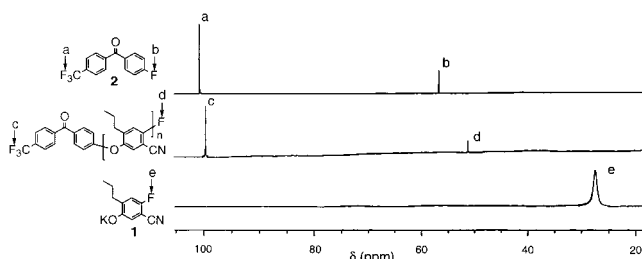


Figure 3. ^{19}F NMR spectra of **2** and **1** in $\text{DMSO-}d_6$ and that of polymer end group in CDCl_3 at 25 °C.

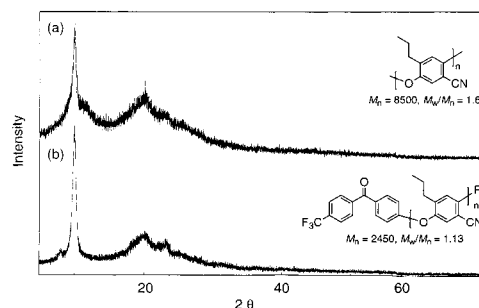


Figure 4. XRD pattern: (a) poly**1** obtained by ordinary polycondensation without **2** in sulfolane at 180 °C: $[1]_0 = 0.33$ M; (b) poly**1** obtained in the presence of **2** at 150 °C in sulfolane: $[1]_0 = 0.17$ M; $[2]_0 = 11.7$ mM.

in the lower field in the ^{19}F NMR spectra,⁸ and the ^{19}F NMR spectra of **1**, **2**, and the polymer end group were measured to estimate their reactivities (Figure 3).⁹ The signal of **2** appeared in the lowest field, and the signal of the polymer end group and that of **1** appeared in the higher field in this order, which is identical with the order of reactivities that chain-growth polycondensation requires.

We found that the polyether having initiator **2** unit with low polydispersity was less soluble in organic solvent than the polyether obtained by ordinary polycondensation without **2**. Furthermore the powder X-ray diffraction (XRD) pattern of both polymers showed that the crystallinity of the polymer obtained by chain-growth polycondensation was higher than that of the polymer obtained by ordinary polycondensation, even though the molecular weight of the former polymer was lower than that of the latter polymer (Figure 4). This implies that the crystallinity of condensation polymers could be controlled by polydispersity.

Our present results demonstrate that not only monomers having the acyl group but also monomers without the acyl group undergo chain-growth polycondensation like living polymerization to yield condensation polymers with low polydispersities. We anticipate that many kinds of condensation polymers with low polydispersities could be produced by chain-growth polycondensation, and that novel physical properties of well-defined condensation polymers could be discovered. 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 **1**, polymerization procedure, and measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(7) When the $[1]_0/[2]_0$ ratios were 25 or above, the polymer was precipitated during polymerization.

(8) Lozano, A. E.; Jimeno, M. L.; Abajo, J.; Camp, J. G. *Macromolecules* **1994**, *27*, 7164.

(9) The ^{19}F NMR spectrum of polymer was measured in CDCl_3 , because the polymer was not soluble in DMSO . However, it was confirmed that there was little difference of the chemical shift of the signal b of **2** between in $\text{DMSO-}d_6$ and in CDCl_3 .