

Condensative Chain Polymerization in Solid–Liquid Phase. Synthesis of Polyesters with a Defined Molecular Weight and a Narrow Molecular Weight Distribution by Polycondensation

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Synthesis of polymers and materials of controlled architectures is of current interest in both industrial and academic research. These challenges are being met partly through the use of living polymerizations. In polycondensation, however, polymers of controlled architectures have not been synthesized except for stepwise synthesis of dendritic macromolecules¹ and linear oligomers.² We have proposed that one approach to control polycondensation with the formation of macromolecules having a defined molecular weight and a narrow molecular weight distribution is to make polycondensation proceed in a chain-growth reaction manner from an initiator like living polymerizations.^{3,4} We call this type of polycondensation “Condensative Chain Polymerization” according to the recent IUPAC recommendations.⁵ Previous work in this group has shown that 4-trimethylsilyloxybenzoyl chloride has the possibility of undergoing condensative chain polymerization by model reactions⁴ and that the polycondensation of a 4-bromophenol derivative and carbon monoxide can proceed in a chain polymerization manner in the initial stage.⁶ An important thing for successful condensative chain polymerizations is to prevent the reaction of monomers with each other leading to step polycondensations. It occurred to us that the polymerization of solid monomers dispersed in the organic solvent with a phase transfer catalyst (PTC) would be an attractive route to condensative chain polymerizations. Thus, solid monomers do not react with each other and the monomer transferred to organic solvent with PTC would react with an initiator and the polymer end group in organic solvent (Scheme 1). Although all the advantages of PTC techniques have been applied to polymer synthesis,⁷ especially in condensation polymers, no study has been reported on the control over the molecular weight and polydispersity of condensation polymers by PTC. Herein we report

(1) For a recent review, see: Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 885.

(2) For examples of stepwise synthesis of linear oligomers, see: (a) Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (b) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841. (c) Nelson, J. C.; Young, J. K.; Moore, J. S. *J. Org. Chem.* **1996**, *61*, 8160. (d) Godt, A.; Ziener, U. *J. Org. Chem.* **1997**, *62*, 6137. (e) Jones, L.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388. (f) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed.* **1994**, *33*, 1360. (g) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376. (h) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348. (i) Sadighi, J. P.; Singer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 4960. (j) Huang, S.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 4908.

(3) Possible condensative chain polymerizations are shown by the polycondensations of alkali 4-halothiophenoxide and sodium 4-halobenzenesulfinate, respectively, although the polymerization mechanisms are not exactly clear because of insolubility of polymers. See: (a) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. *J. Polym. Sci.* **1962**, *58*, 351. (b) Robello, D. R.; Ulman, A.; Urankar, E. *Macromolecules* **1993**, *26*, 6718.

(4) Yokozawa, T.; Horio, S. *Polym. J.* **1996**, *28*, 633.

(5) Mita, I.; Stepto, R. F. T.; Suter, U. W. *Pure Appl. Chem.* **1994**, *66*, 2483.

(6) Yokozawa, T.; Shimura, H. *J. Polym. Sci. Polym. Chem. Ed.* **1999**, *37*, 2607.

(7) For reviews, see: (a) Imai, Y. *J. Macromol. Sci. Chem.* **1981**, *A15*, 833. (b) Imai, Y. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 1095. (c) Tagle, L. H. In *Handbook of Phase Transfer Catalysis*; Sasson, Y., Neumann, R., Eds.; Blackie Academic & Professional: London, 1997; p 200.

Scheme 1

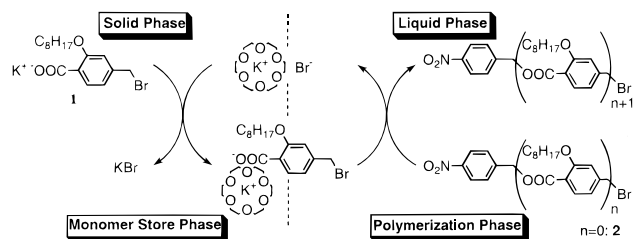


Table 1. Effect of the Amount of 18-Crown-6 on Polymerization of **1** in the Presence of 10 mol % of **2**^a

18-crown-6, mol %	M_n^b	M_w/M_n^b
2	2900	1.49
5	2800	1.45
7	2700	1.47
10	2400	1.36
15	2500	1.45
30	2500	1.57
100	2500	2.13

^a Polymerization of **1** was conducted in acetone ($[I]_0 = 0.33$ M) at 25 °C for 24–48 h (conversion = 100%). ^b Determined by GPC based on polystyrene standards using THF as solvent.

the polycondensation of potassium 4-bromomethyl-2-*n*-octyloxybenzoate (**1**)⁸ with 18-crown-6⁹ in acetone in the presence of 4-nitrobenzyl bromide (**2**) as an initiator to yield polyesters with a defined molecular weight and a narrow molecular weight distribution ($M_w/M_n < 1.3$).

We first optimized the amount of 18-crown-6 for this polymerization. By the use of a large amount of 18-crown-6, step polymerizations would occur because the concentration of monomer in solvent becomes higher than that of an initiator, and the reaction of the monomers with each other would take place. On the other hand condensative chain polymerizations would occur by the use of a small amount of 18-crown-6, but the polydispersity would become broad because it is difficult to propagate homogeneously from each initiator by a small supply of monomer. The polymerization of **1** was carried out in acetone¹⁰ in the presence of 10 mol % of **2** at various amounts of 18-crown-6 at room temperature for 24–48 h (conversion = 100%) (Table 1). Equimolar amounts of 18-crown-6 and **2** were found to yield polyester with the narrowest polydispersity.

To elucidate whether chain polymerization or step polymerization takes place in this polycondensation, the polymerization of **1** was carried out in the presence of 7 mol % of **2** at room temperature, and the polymer molecular weights, polydispersities, and the ratios of end group to initiator unit in polymer were plotted against monomer conversion (Figure 1). The ratios of end group

(8) For examples of the polycondensation of alkali bromomethylbenzoates, see: (a) Cameron, G. G.; Buchan, G. M.; Law, K. S. *Polymers* **1981**, *22*, 558. (b) Inoki, M.; Akutsu, F.; Kitayama, Y.; Kasashima, Y.; Naruchi, K. *Polym. J.* **1996**, *28*, 1103. For an example of the polycondensation of bromomethylbenzoic acids using triethylamine, see: Pinkus, A. G.; Subramanyam, R.; Hariharan, R. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 1031.

(9) For examples of polycondensation with PTC involving the reaction of alkali carboxylates with alkyl halides, see: (a) Ueda, M.; Sakai, N.; Imai, Y. *Koubunshi Ronbunshu* **1981**, *38*, 443. (b) Cameron, G. G.; Law, K. S. *Polymers* **1981**, *22*, 272. (c) Kielkiewicz, J.; Kuran, W.; Pogorzelska, B. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 255. (d) Rokichi, G.; Kielkiewicz, J.; Marciniak, B. *Polimery* **1982**, *27*, 374. (e) Kuran, W.; Rokicki, G.; Kielkiewicz, J. Polish Patent PL 122 553; *Chem. Abstr.* **1986**, *101*, 73283h. (f) Klemm, D.; Geschwend, G. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 431. (g) Hurdac, N.; Bordieanu, V.; Simionescu, C. *Polym. Bull.* **1992**, *28*, 639.

(10) The polymerization of **1** was carried out in the presence of 10 mol % of **2** in various kinds of solvent (toluene, diethyl ether, THF, dichloromethane, chloroform, and acetone) and the polymerization in acetone yielded the polymer having the narrowest polydispersity.

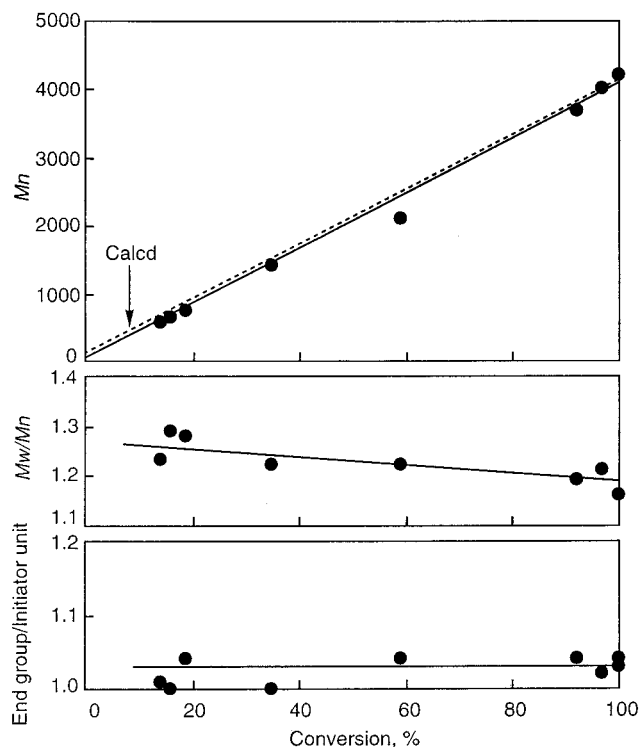


Figure 1. M_n , M_w/M_n , and the ratio of end group to initiator unit values of poly1, obtained with 7 mol % of **2** and 18-crown-6 in acetone at 25 °C, as a function of monomer conversion: $[1]_0 = 0.33$ M; $[2]_0 = [18\text{-crown-6}]_0 = 0.023$ M.

to initiator unit were determined by the ^1H NMR spectra after the reaction of the polymer end groups with an excess amount of potassium 4-methoxyphenolate.¹¹ The molecular weight¹² increased in proportion to conversion, and the M_w/M_n ratios were less than 1.3 over the whole conversion range. The ratios of end group to initiator unit were constantly about 1.0 irrespective of conversion. This polymerization behavior agrees with the features of living polymerizations of vinyl monomers and cyclic monomers. In general polycondensations that proceed in a step polymerization manner, the molecular weight does not increase much at low conversion of monomer and is accelerated at high conversion. The ratios of end group to initiator unit would be larger than 1.0 in the initial stage because monomers react with not only an initiator but also other monomers. This ratio would approach 1.0 in the last stage, as polymer chains that have not reacted with the initiator react with the end group of polymer chains having the initiator unit.¹³ Consequently, Figure 1 shows

(11) Polymer model compound, 4'-nitrobenzyl 4-bromomethyl-3-*n*-octyloxybenzoate was reacted with 5 equiv of 4-methoxyphenol in the presence of 4.5 equiv of potassium hydroxide in dichloromethane and water containing a catalytic amount of tetrabutylammonium bromide as a phase transfer catalyst for 24 h to give the corresponding 4-methoxyphenyl ether in 99% yield (HPLC yield) without hydrolysis of the ester linkage of the polymer model compound.

(12) The polymer molecular weights were estimated by gel permeation chromatography (GPC) based on polystyrene standards. However, the molecular weights determined by GPC were in good agreement with those determined by ^1H NMR. For example, M_n (GPC) = 4490, M_n (NMR) = 4480.

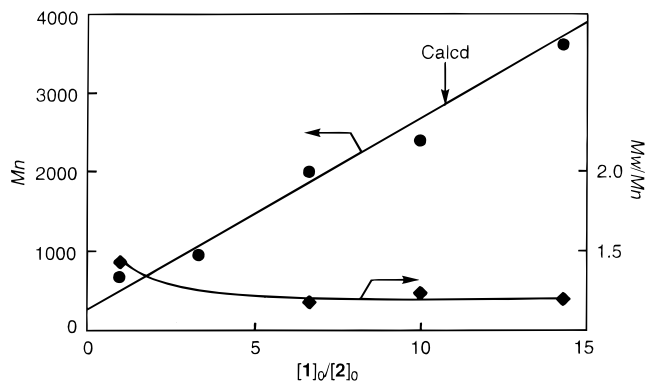


Figure 2. M_n and M_w/M_n values of poly1, obtained with **2** and 18-crown-6 in acetone at 25 °C, as a function of feed ratio of **1** to **2**: $[1]_0 = 0.33$ M; $[2]_0 = [18\text{-crown-6}]_0 = 23\text{--}330$ mM; conversion = 100%.

that the polycondensation of **1** proceeds not in a step polymerization manner but in a chain polymerization manner.

In another series of experiments, **1** was polymerized with varying feed ratio ($[1]_0/[2]_0$). As shown in Figure 2, the polymer molecular weights obtained at 100% conversion were directly proportional to the $[1]_0/[2]_0$ ratio. The observed M_n values were in good agreement with those calculated with the assumption that one initiator molecule forms one polymer chain. The polydispersities M_w/M_n ratio of polymer stayed less than 1.3 over the whole range of the $[1]_0/[2]_0$ ratio.¹⁴ This also agrees with the features of chain polymerizations.

In conclusion, our results demonstrate that the polycondensation of solid monomer **1** with PTC in organic solvent containing initiator **2** enable us to synthesize condensation polymers having a defined molecular weight and a narrow molecular weight distribution. This polycondensation involves a chain polymerization from the initiator in the solvent phase without the reaction of solid monomers with each other. We are confident that an example of the control over the molecular weight and polydispersity of condensation polymers by virtue of a simple PTC technique will render considerable impulse to the development of polymer synthesis, since PTC techniques have been successfully applied to a wide range of polycondensations, including industrial production of polymers. Studies of condensative chain polymerization of other monomers with PTC are currently under way.

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Supporting Information Available: A synthetic scheme for **1**, procedures of polymerization, and the etherification of the polymer model compound and the polymer end group (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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(13) This polymerization behavior was observed in the polymerization of the same monomer in an aqueous–organic biphasic system using PTC. See: Hiyama, N.; Suzuki, H.; Yokozawa, T. *Polym. Prepr. Jpn.* **1999**, *48*, 307.

(14) When the $[1]_0/[2]_0$ ratios were 20 or above, the polymers having the molecular weights close to the calculated values were obtained as well as oligomers without the initiator **2** unit.