# Anionic Ring-Opening Polymerization of Methyl 4,6-*O*-Benzylidene-2,3-*O*-carbonyl-α-D-glucopyranoside: A First Example of Anionic Ring-Opening Polymerization of Five-Membered Cyclic Carbonate without Elimination of $CO_2$

**Osamu Haba,* Haruka Tomizuka, and Takeshi Endo***

*Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan*

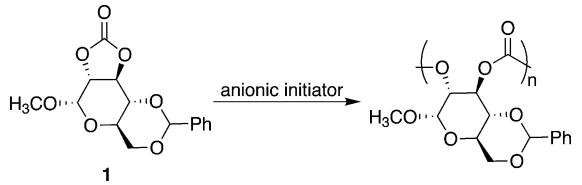
*Received November 12, 2004*
*Revised Manuscript Received February 22, 2005*

Aliphatic polycarbonates are very attractive materials because of their biocompatibility and biodegradability.[1−3] For their synthesis, two procedures have been used, i.e., (a) a polycondensation between activated carbonate derivatives and diols[4] and (b) a ring-opening polymerization of cyclic carbonates.[5−19] The latter should proceed by a chain polymerization and have potential to control molecular weight of the resulting polymer.

The anionic ring-opening behavior of the cyclic carbonates depends on their ring size. Six- or larger-membered cycles tend to polymerize smoothly to yield the corresponding polycarbonate at lower temperature (<100 °C) by anionic initiators.[5−19] In contrast, the anionic ring-opening polymerization of the five-membered ring is thermodynamically unfavorable and proceeds at higher temperature (>150 °C), causing elimination of carbon dioxide to give a copolymer consisting of both carbonate and ether linkages.[20−25]

In this paper, we report an anionic polymerization of a five-membered cyclic carbonate, methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-α-D-glucopyranoside (**1**),[26] which polymerizes at relatively low temperature below 60 °C without any elimination of carbon dioxide to produce polycarbonate repeating units (Scheme 1) despite the typical behavior of five-membered cyclic carbonates.

**Scheme 1. Anionic Ring-Opening Polymerization of 1**




**1**

Anionic ring-opening polymerizations of **1** were carried out with 0.04 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or potassium *tert*-butoxide (*t*-BuOK) as an initiator in tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF). After the initiator was added to the monomer solution, the polymerization proceeded homogeneously except for run 3, and the viscosity of the polymerization solutions increased. The resulting product was a white powdery polymer, which was insoluble in methanol and soluble in chloroform. Table 1 lists some results of the polymerization. When the polymerization was carried out at 60 °C, DBU was a more efficient initiator than *t*-BuOK, which gave a lower yield and number-average molecular weight ($M_n$) in both THF and DMF. The polymerization also proceeded smoothly even at 30 °C to give the polymer having $M_n$ of 14 000 g mol$^{-1}$ in 93% yield, although the rate of polymerization decelerated at 0 °C. Such temperatures are usually too low to polymerize other five-membered cyclic carbonates, and thus these results indicate that monomer **1** possesses higher polymerization ability despite the five-membered cyclic carbonate.

**Table 1. Anionic Ring-Opening Polymerization of 1[a]**

| run | initiator | solvent | temp, °C | yield,[b] % | $M_n$,[c] $10^3$ g mol$^{-1}$ | $M_w/M_n$[c] | $[\alpha]_D$[d] |
|---|---|---|---|---|---|---|---|
| 1 | *t*-BuOK | THF[f] | 60 | 79 | 6.1 | 1.41 | +61 |
| 2 | *t*-BuOK | DMF[g] | 60 | 55 | 4.0 | 1.27 | +61 |
| 3 | DBU[e] | THF | 60 | 93 | 10.5 | 1.38 | +68 |
| 4 | DBU | DMF | 60 | 71 | 8.4 | 1.41 | +69 |
| 5 | DBU | DMF | 30 | 93 | 14.0 | 1.49 | +73 |
| 6 | DBU | DMF | 0 | 30 | 5.2 | 1.27 | +80 |

[a] $[\mathbf{1}]_0$ = 3.0 mol L$^{-1}$; $[\mathbf{1}]_0/[I]_0$ = 25; time = 12 h. [b] Methanol-insoluble part. [c] Number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$) were determined by SEC eluted with DMF, calibrated using polystyrene standard. [d] Specific rotations, measured in $CHCl_3$ ($c$ = 1.0). [e] 1,8-Diazabicyclo[4.5.0]undec-7-ene. [f] Tetrahydrofuran. [g] *N,N*-Dimethylformamide.

To clarify the structure of the obtained polymer, methyl 4,6-*O*-benzylidene-2,3-bis-*O*-ethoxycarbonyl-α-D-glucopyranoside (**2**)[26] was prepared as a model compound for the carbonate repeating units. The $^{13}C$ NMR spectra of the obtained polymer (run 4 in Table 1) showed three sharp signals at 153.27, 101.48, and 96.95 ppm. These date agreed with that of **2** at 153.96, 101.31, and 97.26 ppm, which are assignable to carbonyl, benzylidene, and C1 carbons, respectively. In addition, the signals at 78.39, 75.07, 73.80, 68.56, 61.85, and 55.67 ppm in the spectrum of the polymer were compatible to C4, C2, C3, C6, C5, and methoxy carbons of **2** which appeared at 78.91, 74.22, 72.66, 68.53, 62.03, and 55.23 ppm, respectively. Thus, the spectrum of the obtained polymer agreed well with that of **2**. In the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the polymer (run 4 in Table 1), the molecular mass of the repeating units was found to be 308, corresponding to the carbonate repeating unit, and peak interval of 264, indicating the ether repeating unit, was not observed. These results indicate that the polymer essentially possesses the carbonate repeating units.

The obtained polymer was hydrolyzed using KOH in ethanol to further confirm of the polymer structure. If the elimination of carbon dioxide occurred during the anionic polymerization of **1**, the resulting polymer should contain polyether repeating units, which should be inert to hydrolysis. The polycarbonate repeating units should be hydrolyzed to give methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**3**). When the hydrolysis of the polymer (run 4 in Table 1) was carried out at ambient temperature for 3 h, the product was obtained by extracting with chloroform in 95% yield. Figure 1 shows the SEC chromatograms of the original polymer, the hydrolysis product, and the model compound **3** prepared from methyl α-D-glucopyranoside and benzaldehyde dimethyl acetal.[27] The peak due to the higher molecular

* Corresponding authors. O.H.: phone and Fax +81 238 26 3091; e-mail haba@yz.yamagata-u.ac.jp. T.E.: phone and Fax +81 238 26 3090; e-mail tendo@yz.yamagata-u.ac.jp.

10.1021/ma0476745 CCC: $30.25 
Published on Web 03/31/2005

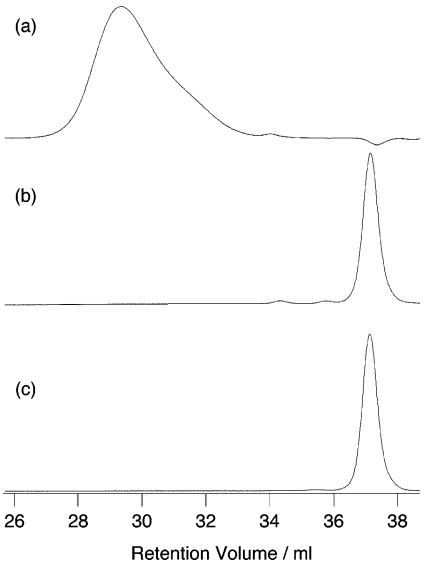



**Figure 1.** SEC chromatograms of (a) the original polymer (run 4 in Table 1), (b) the hydrolysis product, and (c) **3** eluted with DMF. The hydrolysis was carried out using KOH (8.5 equiv) in ethanol at room temperature for 3 h.

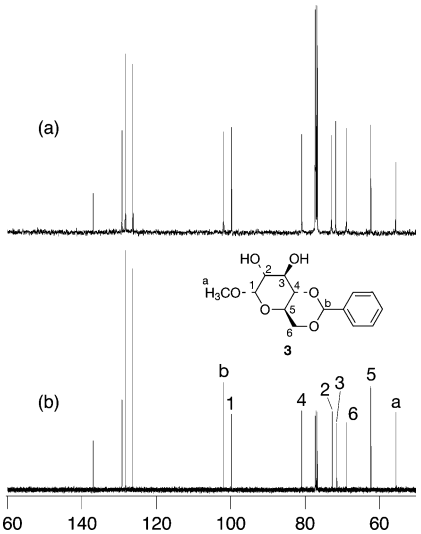



**Figure 2.** 125 MHz $^{13}C$ NMR spectra of (a) the hydrolysis product from the polymer (run 4 in Table 1) and (b) **3**.

weight in the chromatogram of the polymer was completely absent in that of the hydrolysis product, which instead shows a sharp peak at lower molecular weight corresponding with that of **3**. This indicates that the hydrolysis product contained no oligomeric or polymeric fractions, and the obtained polymer involves no polyether repeating units. HPLC analysis of the hydrolyzate indicated that it contains only one fraction having the same retention volume of **3**. Figure 2 shows $^{13}C$ NMR spectra of the hydrolysis product and **3**. These spectra completely agreed each other over the whole spectrum range. In addition, the specific rotation of the hydrolysis product was +109 ($CHCl_3$, *c* 1.0), which agreed with that of **3** (+109). Thus, the hydrolysis product could be characterized as **3**. These results should support that the anionic polymerization of **1** proceeded without elimination of carbon dioxide to give the polycarbonate containing no polyether moiety.

Thus, the anionic polymerization of **1** proceeded at a relatively low temperature without elimination of carbon dioxide to produce polycarbonate despite the thermodynamically unfavorable feature of the anionic polymerization of the usual five-membered cyclic carbonates. This may be caused by the ring strain of **1**, whose carbonate ring connects to a bicyclic and rigid *trans*-decalin fragment in trans fashion. To clarify this point, we are now in the progress of studying other five-membered cyclic carbonates having more simple structure.

**Supporting Information Available:** $^{13}C$ NMR spectra of the polymer and model compound **2** and MALDI-TOF MASS spectrum of the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Wang, H.; Dong, J. H.; Qiu, K. Y.; Gu, Z, W. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1301.
(2) Zhu, K. J.; Hendren, R. W.; Jensen, K.; Pitt, C. G. *Macromolecules* **1991**, *24*, 1736.
(3) Albertsson, A.-C.; Eklund, M. *J. Appl. Polym. Sci.* **1995**, *57*, 87.
(4) For example: Yokoe, M.; Aoi, K.; Okada, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2312.
(5) Sarel, S.; Pohoryles, L. A. *J. Am. Chem. Soc.* **1958**, *80*, 4596−4599.
(6) Kühling, S.; Keul, H.; Höcker, H. *Makromol. Chem.* **1990**, *191*, 1611−1622.
(7) Bialas, N. J.; Kühling, S.;. Keul, H.; Höcker, H. *Makromol. Chem.* **1990**, *191*, 1165−1175.
(8) Kühling, S.; Keul, H.; Höcker, H.; Buysch, H.-J.; Schön, N.; Leitz, E. *Macromolecules* **1991**, *24*, 4229−4235.
(9) Takata, T.; Matsuoka, H.; Endo, T. *Chem. Lett.* **1991**, 2091−2094.
(10) Kühling, S.; Keul, H.; Höcker, H.; Buysch, H.-J.; Schön, N. *Makromol. Chem.* **1991**, *192*, 1193−1205.
(11) Takata, T.; Kanamaru, M.; Endo, T. *Macromolecules* **1996**, *29*, 2315−2317.
(12) Takata, T.; Matsuoka, H.; Hirasa, T.; Matsuo, J.; Endo, T.; Furusho, Y. *Kobunshi Ronbunshu* **1997**, *54*, 974−981.
(13) Matsuo, J.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1375−1380.
(14) Murayama, M.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 919−923.
(15) Matsuo, J.; Aoki, K.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 4432−4438.
(16) Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1998**, *199*, 2489−2494.
(17) Shen, Y.; Chen, X.; Gross, R. A. *Macromolecules* **1999**, *32*, 2799−2802.
(18) Takata, T.; Murakawa, K.; Furusho, Y. *Polym. J.* **1999**, *31*, 1051−1056.
(19) Sanda, F.; Kamatani, J.; Endo, T. *Macromolecules* **2001**, *34*, 1564−1569.
(20) Carothers, W. J.; Natta, F. J. V. *J. Am. Chem. Soc.* **1930**, *52*, 314−326.
(21) Soga, K.; Hosoda, S.; Tazuke, Y.; Ikeda, S. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 219−229.
(22) Vogdanis, L.; Heitz, W. *Macromol. Chem. Rapid Commun.* **1986**, *7*, 543−547.
(23) Harris, R. F. *J. Appl. Polym. Sci.* **1989**, *37*, 183−200.
(24) Vogdanis, L.; Martens, B.; Uchtmann, H.; Hensel, F.; Heitz, W. *Macromol. Chem.* **1990**, *191*, 465−472.
(25) Lee, J.-C.; Litt, M. H. *Macromolecules* **2000**, *33*, 1618−1627.
(26) Doane, W. M.; Shasha, B. S.; Stout, E. I.; Russell, C. R.; Rist, C. E. *Carbohydr. Res.* **1967**, *4*, 445-.
(27) Evans, M. E. In *Methods in Carbohydrate Chemistry*; Whistler, R. L., BeMiller, J. N., Eds.; Academic Press: New York, 1980; Vol. 8, p 313.

MA0476745