Block Copolymerization of Cyclic Carbonate and Oxetanes in One-Shot Feeding

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A number of block copolymers has hitherto been synthesized by a variety of polymerizations and polymer reactions.[1] Among the preparations of block copolymers, the most versatile method is two-step chain polymerization of two monomers through a living polymer.[1b-d] Saegusa et al. have reported a unique block copolymerization, "one-shot block copolymerization", which involves successive polymerizations of each of two oxazoline derivatives, that are fed simultaneously, in a block copolymerization mode.[2] In this copolymerization, two monomers M_A and M_B can block copolymerize via a living mechanism and rates of both initiation and propagation of M_A are much larger than those of M_B. Recently, we have developed a novel block copolymerization in one-shot feeding between different kinds of monomers, oxetanes (**1**) and cyclic carbonate (**2**), which are preliminarily described in this paper.

An equimolar mixture of unsubstituted oxetane (**1a**) and 1,3-dioxan-2-one (**2**) was treated with methyl triflate (MeOTf; 5 mol %) as a cationic initiator at 0 °C in CH_2Cl_2. By ^1H NMR monitoring of the reaction progress (Figure 1), it was found that MeOTf and **1a** were immediately consumed with 1 and 3 h, respectively, but **2** remained completely unreacted. When the reaction temperature was raised up to room temperature (ca. 20 °C) after 6 h, **2** started to be consumed and was thoroughly exhausted in ca. 20 h. From the polymerization mixture, ether-insoluble polymer (**3a**; Scheme 1) was obtained in 83% yield. The ether-soluble part was determined as a mixture of low molecular weight copolymer and cyclic oligomers of **1a** from GPC, NMR, and GC data. In the copolymerizations of 3-*n*-octyloxetane (**1b**) and 3-benzyloxetane (**1c**) with **2** which were used for easy NMR analysis of the products, a similar behavior was observed (Table 1): **2** was hardly consumed until **1b** or **1c** was fully consumed until **1b** or **1c** was fully consumed in any case. While copolymer **3c** formed from **1c** and **2** could be purified as an ether-insoluble polymer, copolymer **3b** from **1b** and **2** was well soluble in ether and *n*-hexane; therefore, the absence of a homopolymer of **2** which is insoluble in ether and *n*-hexane was concluded. Copolymer **3b** was isolated by preparative HPLC. Although ^1H NMR spectra of any polymer obtained were almost the same as those of a mixture of two corresponding hompolymers (poly(**1b**) or poly(**1c**) and poly(**2**)), these polymers were eventually suggested as block copolymers of **1b** (**1c**) and **2** by the following results. The absence of a homopolymer of **1b** was confirmed by the absence of a methylene group adjacent to a hydroxy group derived from **1b** which was observed in a ^1H NMR spectrum of **3b**.

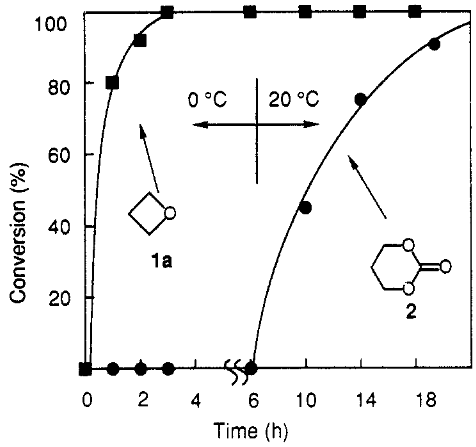

Figure 1. Time-conversion curves of the cationic copolymerization of **1a** and **2** with MeOTf (5 mol %) in CH_2Cl_2. The polymerization was carried out at 0 °C for 6 h, and thereafter the temperature was raised up to room temperature (20 °C).

Scheme I

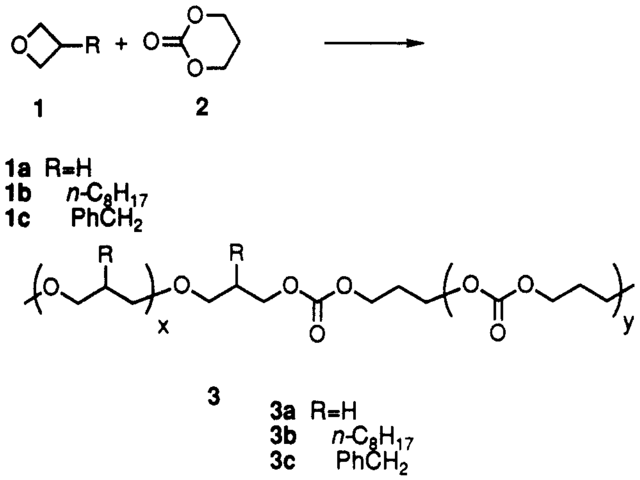

Figure 2 shows a typical GPC curve change during the polymerization of **1a** and **2** (before and after the consumption of **2**). The GPC curves were unimodal, and the initial curve (A) was clearly shifted to a high molecular weight region (B) by the consumption of **2** without a change in the curve mode. Meanwhile, the ^{13}C NMR signals observed for the polymers could be assigned to the proposed block copolymer structures **3** (Scheme 1), on the basis of the data for the corresponding poly(ether carbonate) and the homopolymers of **1a** and **2**.[3] A typical ^{13}C NMR spectrum of **3b** is shown in Figure 3. The most characteristic carbon signals, besides two major methylene carbon signals at 71.9 (a) and 64.2 ppm (d) which were of oxetane and carbonate units, respectively, appeared at

Table I. Cationic Copolymerization of 1 with 2[a]

oxetane	initiator (mol %)	solv[b]	temp (°C)	time (h)	conv[c] (%) 1	conv[c] (%) 2	yield (%)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]	$x/(x+y)$[c]	$y/(x+y)$[c]
1b	TMSOTf[e] (5)	$CDCl_3$	30	100	100	100	58[g] (**3b**)	4 600	1.30	37	63
1b	BF_3OEt_2 (5)	$CDCl_3$	30	12	100	62	74[g] (**3b**)	17 000	1.65	52	48
1b	BF_3OEt_2 (1)	CH_2Cl_2	0-30[f]	60[f]	100	40	60[g] (**3b**)	13 000	1.53	69	31
1c	MeOTf (5)	$CDCl_3$	30	100	100	100	33[h] (**3c**)	3 800	1.61	20	80

[a] Feed ratio 1:1. [b] [C] = 2 M. [c] Determined by ^1H NMR. [d] Number-average molecular weight, estimated by GPC (PSt standard). [e] Trimethylsilyl triflate. [f] Polymerization was carried out at 0 °C for 6 h at first, and then the temperature was raised up to 30 °C. [g] Isolated by preparative HPLC. [h] Ether-insoluble polymer.

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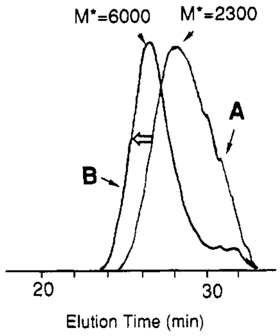


Figure 2. GPC curves of the reaction mixtures after 6 (A) and 18 h (B) in the cationic copolymerization of **1a** and **2** with MeOTf (5 mol %) in CH_2Cl_2 (conversion of the monomers; see Figure 1). M^* denotes the peak-top molecular weight.

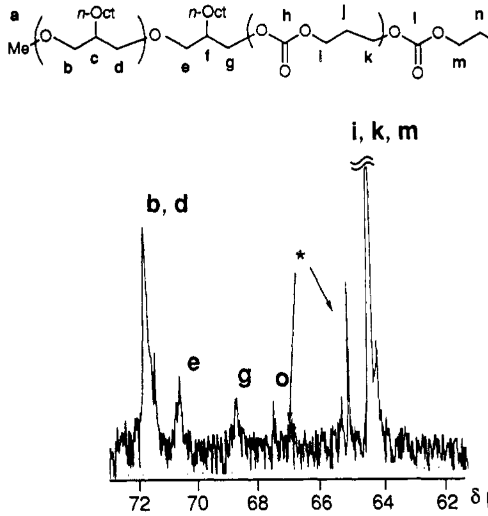


Figure 3. Partial ^{13}C NMR spectrum ($CDCl_3$) of copolymer **3b** ($\bar{M}_n$ 4600) around 65–75 ppm (Table 1, run 1). See ref 3. Chemical shifts of other signals are listed in ref 7.

70.9 (b) and 68.8 ppm (c) which could be assigned to those of the joint part between the two homopolymer units.

To confirm the occurrence of the block copolymerization, chemical and thermal properties of the copolymers were examined. When alkaline hydrolysis of copolymer **3b** ($\bar{M}_n$ 13 000, $\bar{M}_w/\bar{M}_n$ 1.53; unit ratio x:y = 31:69) with KOH in aqueous dioxane was carried out at 100 °C for 6 h, on poly(**1b**) without any carbonate unit was obtained as the polymeric product, which had an unimodal GPC curve ($\bar{M}_n$ 9000, $\bar{M}_w/\bar{M}_n$ 1.34).[4] Furthermore, DSC analysis of **3b** showed two T_gs at −76 and −26 °C which corresponded to those of the homopolymers poly(**1c**) (−76 °C) and poly(**2**) (−28 °C), respectively; these results strongly supported the block copolymer structures.

A mechanistic feature of this unique block copolymerization was studied by a different experiment in which an oxetane monomer (**1b**) was fed into the polymerization system of **2** before complete consumption of **2** under the same conditions (5 mol % of TMSOTf, 30 °C, $CDCl_3$). As shown in Figure 4, an equimolar amount of **1b** which was added at ca. 60% conversion of **2** was smoothly consumed in ca. 30 h. During the consumption of **1b**, the conversion of **2** was entirely kept at ca. 60% and did not take place again until **1b** completely disappeared in the system.[5]

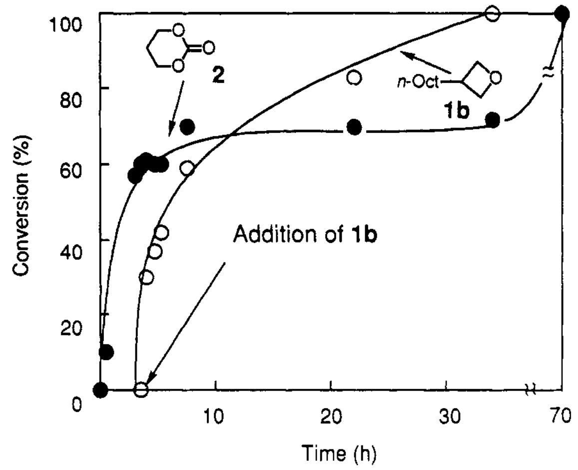
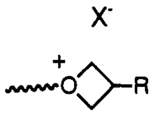


Figure 4. Time–conversion curves of the cationic copolymerization of **1b** and **2** with TMSOTf (5 mol %) in $CDCl_3$ at 30 °C. **1b** was added to the polymerization system of **2** after 3 h.

The remarkable time–conversion curves in addition to the selective formation of the block copolymers as mentioned above demonstrate that oxetane reacts much faster than cyclic carbonate with the propagating species (**4**[6] and **5**) independent of its structure, while **2** reacts slowly but sufficiently with the propagating species of oxetane (**5**) after most oxetane molecules are consumed, eventually leading to block copolymer.



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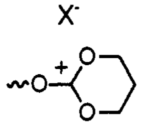

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References and Notes

(1) For example: (a) Hoffmann, A. S.; Bacckai, R *Highpolymers, Vol. XVIII, Copolymerization*; Ham, G. E., Ed.; John Wiley & Sons, Inc.: New York, 1964; Chapter VI, p 135. (b) Goodman, I. *Development of Block Copolymer I*; Goodman, I., Ed.; Applied Science Publishers Ltd.: Essex, U.K., 1982; Chapter 5, p 127. (c) *Ring-Opening Polymerization, Vol. I*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publisher: London, 1984; Chapter 5, p 218. (d) Cowie, J. E. *Comprehensive Polymer Science, Vol. 3, Chain Polymerization I*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Chapter 33, p 17. (e) Aoki, S.; Harita, Y.; Tanaka, Y.; Mandai, H.; Othu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2585. (f) Bucquoye, M.; Goethales, E. J. *Eur. Polym. J.* **1978**, *14*, 323.

(2) Saegusa, T.; Chujo, Y.; Aoi, K.; Miyamoto, M. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 1.

(3) Since the cationic homopolymerization of **2** proceeds accompanied by a small amount of decarboxylation, a homopolymer of **2** contains 1–3% of a trimethylene ether unit. Small signals at 65.1 and 67.0 ppm should be due to the trimethylene ether carbonate unit, because these signals can be observed in the ^{13}C NMR spectrum of poly(trimethylene ether carbonate) which is prepared from 1,5,7,11-tetraoxaspiro[5.5]undecane (Ariga, T.; Takata, T.; Endo, T., to be published).

(4) In the case of **3a** of Figure 2, $\bar{M}_n$ of the polymer obtained by the hydrolysis was 1300 ($\bar{M}_w/\bar{M}_n$ 2.05), while that of the prepolymer (product A) was 1800 ($\bar{M}_w/\bar{M}_n$ 1.72).

(5) Altough the polymer obtained by this experiment showed spectral characteristics similar to those of copolymer **3b**, the details of its microstructure are under investigation.

(6) Besides **4**, the triflate ester propagating species which should be in equilibrium with **4** is conceivable, when methyl and trimethylsilyl triflates are used.

(7) Signals of ^{13}C NMR spectrum (22.5 MHz, δ, $CDCl_3$) of block copolymer **3b** are 155.5 (l), 154.9 (h), 71.9 (b, d), 70.9 (e), 68.8 (g), 67.5 (o), 64.2 (i, k, m), 58.1 (a), 39.3 (c), 38.5 (f), 31.9 (j), 28.8 (n) ppm.