Cationic Ring-Opening Polymerization of Seven-Membered Cyclic Carbonate with Water−Hydrogen Chloride through Activated Monomer Process

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ABSTRACT: Controlled ring-opening polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC), with H_2O/HCl·Et_2O initiator system was investigated. The molecular weight (M_n) of the obtained polymer could be controlled by the amount of H_2O in the range of 10^3-10^4 maintaining a low polydispersity ratio (M_w/M_n = 1.11−1.17). The second portion of the monomer after completion of the first polymerization was converted quantitatively to give the corresponding polymer with a low M_w/M_n. The kinetic and ^{1}H NMR spectroscopic studies suggested that the nucleophilic attack of H_2O to the monomer activated with hydrogen chloride afforded α-hydroxyl-ω-carbonic acid, followed by decarboxylation reaction to give α,ω-dihydroxyl compound. It was suggested that the chain growth in this system was the attack of the terminal hydroxyl group to the monomer activated with hydrogen chloride.

Introduction

Living polymerization attracts much attention in ring-opening polymerization as well as vinyl polymerization, because it can form polymers with controlled molecular weights and polydispersities. Recent remarkable advance of polymerization catalysts has developed a wide variety of living ring-opening polymerization systems. For example, Teyssie et al. have proved the living nature of coordination polymerization of ϵ-caprolactone.[1] Inoue and Aida have reported an exceptionally clean coordination process based on aluminum porphirines to yield living diblock and triblock polyoxiranes.[2] Living coordination ring-opening polymerization of lactones using aluminum alkoxides has been well established, which allows the synthesis of polyester chains with controlled molecular weights, low polydispersity ratios, and well-characterized chain end groups.[3] On the other hand, cationic controlled ring-opening polymerization of cyclic ethers via an activated monomer mechanism has been reported by Penczek et al.[4] Cationic ring-opening polymerization of cyclic acetals,[5] lactones,[6] and cyclic carbonates[7] through activated monomer mechanism has been also reported by several groups. Recently, we have demonstrated that the combination of trifluoroacetic acid and an alcohol enables to reduce unfavorable reactions in the ring-opening polymerization of cyclic carbonates to give the corresponding polymers in good yields ($M_n \sim 6000$, $M_w/M_n < 1.24$).[7] We have preliminarily reported that HCl·Et_2O is the most effective catalyst for the polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC), to obtain the corresponding polycarbonate with a controlled molecular weight ($M_n \sim 15\,000$) and a low polydispersity ratio ($M_w/M_n < 1.17$) under mild conditions.[8] In this paper, we describe the mechanistic aspect of 7CC polymerization initiated with H_2O catalyzed by HCl·Et_2O on the basis of NMR spectroscopic and kinetic analyses.

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Experimental Section

Materials. CH_2Cl_2, $CHCl_3$, and $CDCl_3$ were distilled sequentially over CaH_2 and P_2O_5 under nitrogen. THF was dried over sodium and distilled before use under nitrogen. H_2O was distilled prior to use. *n*-Butyl alcohol (BuOH) and 1,4-butanediol [$Bu(OH)_2$] were distilled over CaH_2 under nitrogen. 7CC was prepared according to the literature and stored at −20 °C under nitrogen atmosphere.[9] Acetic acid, bromoacetic acid, and trifluoroacetic acid were dried over P_2O_5 and then distilled under nitrogen. A 1.0 M HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification.

Measurements. ^{1}H NMR spectra were recorded with a JEOL Lambda-500 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns (G2500HXL and G4000HXL) eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14B equipped with FID detector using *n*-dodecane as an internal standard (column packing SE-30, gradient temperature of 100−230 °C, 15 °C/min).

Polymerization. All polymerization reactions were carried out with the following general procedure: All glass vessels were heated in vacuo before use, filled with and handled in a stream of dry nitrogen. To 0.80 g (5.0 mmol) of 7CC were added 0.0045 g (0.25 mmol) of H_2O and 4.8 mL of CH_2Cl_2. The polymerization was initiated by the addition of 250 μL (0.25 mmol) of HCl solution (1 M) in Et_2O at 25 °C. After a set time, the reaction mixture was poured into 300 mL of methanol/*n*-hexane (50/50, volume ratio) containing 5 mL of triethylamine to precipitate a polymer. The precipitate was filtered, washed sequentially with methanol (5 mL) and *n*-hexane (5 mL), and dried at 25 °C for 5 h in vacuo.

Results and Discussion

Table 1 summarizes the results of the polymerization of 7CC with H_2O/HCl initiator system at 25 °C (Scheme 1). In the presence of H_2O, the polymers (P7CC) with low M_w/M_n's (1.11−1.17) were obtained in almost quantitative yields where the M_n could be tailored by changing the ratio between $[M]_0$ and $[H_2O]_0$ (runs 2−5, 7, and 8). No polymer was obtained in the absence of

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Table 1. Polymerization of 7CC[a]

run	$[M]_0$:$[H_2O]_0$	time (h)	solvent	yield (%)	M_n[b]	M_w/M_n[b]
1	30:0	4	CH_2Cl_2	0	—[c]	—[c]
2	15:1	4	CH_2Cl_2	95	3000	1.17
3	30:1	4	CH_2Cl_2	96	4700	1.15
4	45:1	4	CH_2Cl_2	98	6000	1.17
5	60:1	4	CH_2Cl_2	98	10000	1.11
6	15:1	0.5	CH_2Cl_2	61[d]	—[c]	—[c]
7[e]	15:1	0.5	CH_2Cl_2/Et_2O	98	2800	1.15
8	12:1	15	THF	90	2600	1.11

[a] Conditions: 25 °C, $[M]_0 = 1$ M, $[HCl]_0 = 0.04$ M. [b] Determined by GPC (THF, polystyrene standards). [c] Not determined. [d] Conversion. [e] $[HCl]_0 = 0.5$ M, $CH_2Cl_2/Et_2O = 1/1$ (vol/vol).

Scheme 1

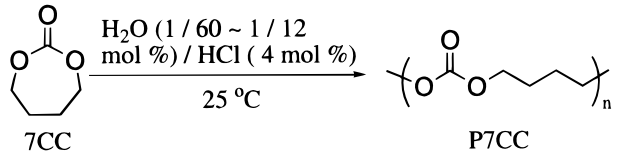


Table 2. ^1H and ^{13}C NMR Chemical Shifts (ppm) of 7CC in the Absence and Presence of $HCl·Et_2O$ in $CDCl_3$ at 25 °C[a]

run	additive	α-proton	β-proton	^{13}C=O
1	none	4.21	1.95	155.40 (154.49)[b]
2	$HCl·Et_2O$	4.21[b]	1.95[b]	—[c] (154.54)[b]
3	CF_3CO_2H	4.28	1.99	159.40 (155.01)[b]

[a] Conditions; [7CC] = 0.10 M, [HCl] = 0.11 M. [b] In Et_2O and $CDCl_3$ (1/1 volume ratio). [c] Not measured.

Table 3. Polymerization of 7CC with Protonic Acids in the Presence and Absence of H_2O[a]

run	initiator	conv[b] (%)
1	CH_3CO_2H	0
2	CH_3CO_2H/H_2O	0
3	CH_3BrCO_2H	0
4	CH_2BrCO_2H/H_2O	0
5	$HCl·Et_2O$	0
6	$HCl·Et_2O/H_2O$	100
7	CF_3CO_2H	44
8	CF_3CO_2H/H_2O	100

[a] Conditions: 25 °C, 3 h, $[M]_0 = 1$ M, $[H^+]_0 = 0.04$ M, $[H_2O] = 0.05$ M, solvent; CH_2Cl_2. [b] Determined by ^1H NMR.

H_2O, indicating that $HCl·Et_2O$ had no ability to polymerize 7CC by itself (run 1). When $[HCl]_0$ increased from 0.04 to 0.5 M, the propagation rate was accelerated to give the polymer for 0.5 h quantitatively (runs 6 and 7). The polymerization also proceeded quantitatively in THF instead of CH_2Cl_2 without incorporation of THF unit into the polymer for 15 h (run 8).

Table 2 shows the ^1H and ^{13}C NMR chemical shifts of the α- and β-methylene protons of the carbonate group and the carbonyl carbon on 7CC in the absence and presence of HCl and CF_3CO_2H in dry $CDCl_3$ at 25 °C. In the presence of CF_3CO_2H, these signals clearly shifted into lower field compared to the case of 7CC alone (run 3). This shift was also observed for ^{13}C NMR in the case of HCl, although the tendency was not so large (run 2). Anyhow, it could be mentioned that the monomer was activated by a protonic acid, probably by coordination at the carbonyl oxygen. No signal was observed assignable to a ring-opened structure of 7CC.

Table 3 summarizes the results of cationic ring-opening polymerization of 7CC with $HCl·Et_2O$ besides CH_3CO_2H, CH_2BrCO_2H, and CF_3CO_2H in the presence and absence of H_2O at 25 °C in CH_2Cl_2 for 3 h. Although

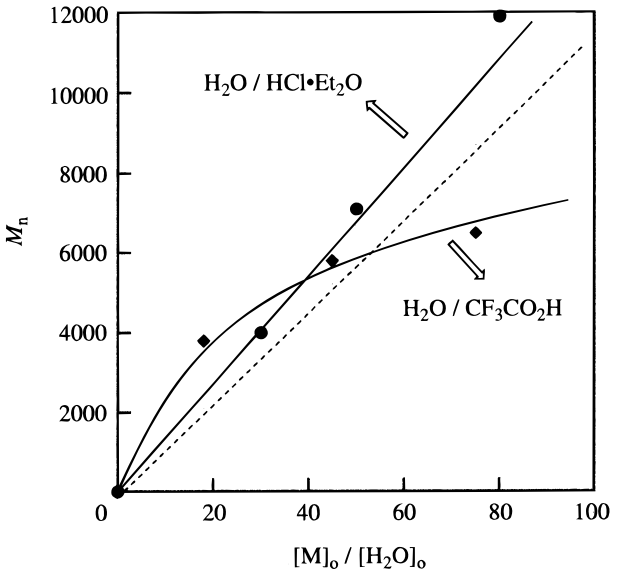


Figure 1. Relationships between $[M]_0/[H_2O]_0$ and M_n of P7CC obtained by the polymerization of 7CC: (●) with $H_2O/HCl·Et_2O$ at 25 °C for 4 h, (◆) with H_2O/CF_3CO_2H at 0 °C for 12 h. A broken line showed the theoretical value calculated by the feed ratio of the monomer to initiator. $[M]_0 = 1$ M in CH_2Cl_2, $[H^+]_0 = 0.04$ M.

CF_3CO_2H polymerized 7CC even in the absence of H_2O probably through a conventional cationic mechanism, CH_3CO_2H and CH_2BrCO_2H showed no activity for 7CC polymerization in both the presence and absence of H_2O. This tendency may be explained in conjunction with the acidity of the acid additives. HCl by itself was not effective for the polymerization despite the stronger acidity in aqueous medium (run 5),[10,11] while in the presence of H_2O, 7CC was quantitatively converted to afford the polymer (run 6). Using $HCl·Et_2O$ along with H_2O, the M_n of the obtained polymer increased linearly as the $[M]_0/[H_2O]_0$ ratio, keeping close to the theoretical values (Figure 1). Using CF_3CO_2H along with H_2O, the M_n increased as the $[M]_0/[H_2O]_0$ ratio but did not show good agreement with the theoretical value assuming one polymer chain per initiator. Considering these results, the role of $HCl·Et_2O$ on the polymerization of 7CC in the presence of H_2O should be definitely only an activator of the monomer. As a result, monodisperse P7CC was obtained via a single propagation mechanism. To confirm the living nature of the present system, 30 equiv of 7CC was first polymerized to obtain the polymer of $M_n = 3500$ in a quantitative conversion. The polymer showed the same M_n even after 24 h, and then the same amount of monomer was charged into the reaction mixture to restart again the polymerization. The GPC curve completely shifted to a higher M_n field, where the M_n of the final polymer was twice that of the starting polymer, keeping a low M_w/M_n (Figure 2). These results clearly showed that the propagating center did not react with the carbonate moieties in the polymer backbone, and the active site was still "living" even for 24 h after the monomer was entirely converted into the polymer.

The results in Tables 1 and 3 and Figure 1 suggest that the polymerization is initiated with H_2O to proceed via an activated monomer mechanism (AM mechanism). Thus, the propagating center of the polymer is considered as a primary alcohol. Figure 3 shows the kinetic plots of the polymerization with $H_2O/HCl·Et_2O$ in CH_2Cl_2 at 25 °C based on a first-order equation as follows,

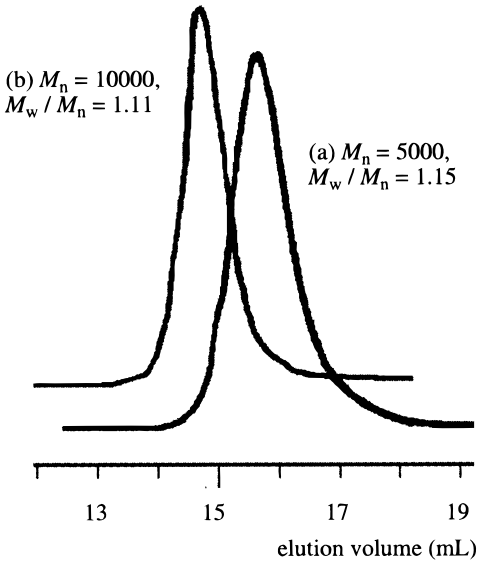


Figure 2. GPC traces of P7CC obtained by the polymerization with $H_2O/HCl{\cdot}Et_2O$ in CH_2Cl_2 at 25 °C: (a) 30 equiv of 7CC for 4 h, (b) the further addition of 30 equiv of 7CC for 24 h.

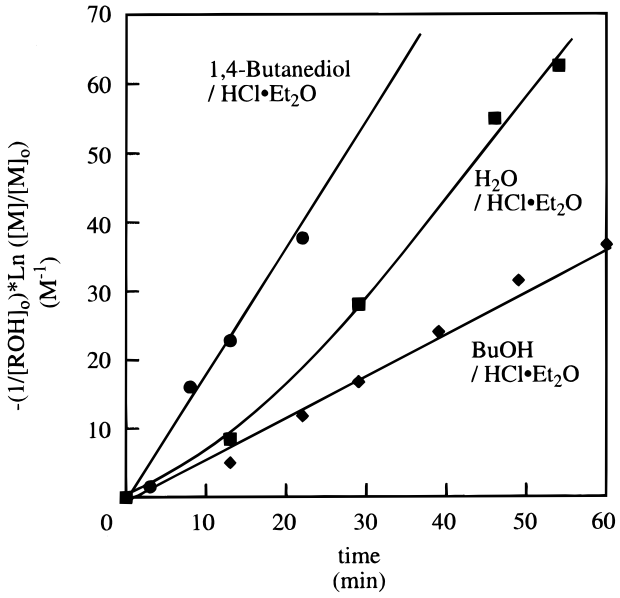


Figure 3. Relationships between time and $-[ROH]_0^{-1} \ln([M]/[M]_0)$ in the polymerization of 7CC in CH_2Cl_2 ($[M]_0$ = 1 M, $[HCl{\cdot}Et_2O]_0$ = 0.04 M) at 25 °C initiated with (●) $Bu(OH)_2/HCl{\cdot}Et_2O$, (■) $H_2O/HCl{\cdot}Et_2O$, and (◆) $BuOH/HCl{\cdot}Et_2O$.

along with 1,4-butandiol/$HCl{\cdot}Et_2O$ and $BuOH/HCl{\cdot}Et_2O$ systems proceeding via the AM mechanism to compare their polymerization behavior.

$$-d[M]/dt = k_p[ROH]_0[M]$$

(ROH = H_2O, BuOH, and $Bu(OH)_2$)

$$-[ROH]_0^{-1} \ln\{[M]/[M]_0\} = k_p t$$

The kinetic plots of the polymerization with alcohols in conjunction with HCl obeyed linear variations that indicated the rapid exchange between the carbonyls of the monomer molecules. On the other hand, the kinetic curve of the polymerization with $H_2O/HCl{\cdot}Et_2O$ initiator showed deviation at the early stage of the polymerization; i.e., the polymerization behavior with $H_2O/HCl{\cdot}Et_2O$ seems similar to that with $BuOH/HCl{\cdot}Et_2O$ in the early stage (<15 min), but as a result of acceleration, it showed a similar tendency to the 1, 4-butanediol/$HCl{\cdot}Et_2O$ initiator system.

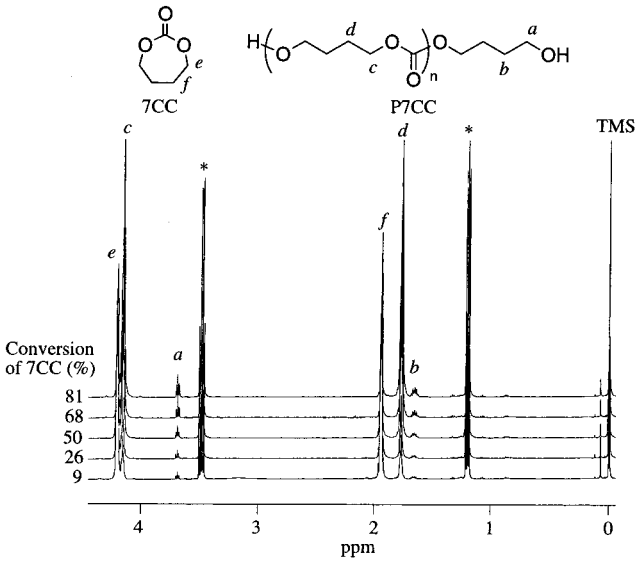


Figure 4. ^1H NMR spectra (500 MHz, $CDCl_3$) of P7CC obtained by the polymerization with $H_2O/HCl{\cdot}Et_2O$ in CH_2Cl_2 ($[M]_0$ = 1 M, $[HCl{\cdot}EtO]_0$ = 0.04 M) at 25 °C. The asterisk represents signals due to diethyl ether.

Figure 4 illustrates the time dependence of the ^1H NMR spectra of P7CC obtained in the polymerization with H_2O/HCl catalyst in CH_2Cl_2 at 25 °C for 4 h. Signals *a* and *b* assignable to α- and *β*-methylene protons of a terminal hydroxyl group were observed at 3.68 and 1.66 ppm, respectively, in addition to the signals *c* and *d* of the P7CC unit. No signal was observed at 3.40−3.46 ppm assignable to methylene protons adjacent to an ether unit, indicating that the polymerization was not accompanied by random decarboxylation, a typical side reaction in the cationic ring-opening polymerization of cyclic carbonates.[12] It is noticeable that the intensities of the α- and *β*-proton signals of the terminal OH group increased during the polymerization. Its observation would be explained by a selective decarboxylation reaction at the carbonic acid polymer end, because the obtained polymer showed low M_w/M_n. Considering the increase of the −OH group, the kinetic plot of polymerization of 7CC with $H_2O/HCl{\cdot}Et_2O$ in Figure 3 can be reillustrated as Figure 5, exhibiting a linear relationship, that is, good obedience to a first-order reaction in any region. Therefore, it can be concluded that decarboxylation occurs from HOCOO terminal only when H_2O is used, resulting a polymer with telechelic −OH terminals. Alcohol (ROH) provides a polymer with carbonate (ROCOO−) and OH terminals. This result also indicates the single active site of the polymerization of 7CC in this system.

Scheme 2 illustrates a plausible polymerization mechanism of 7CC in this system. H_2O may attack the monomer activated by $HCl{\cdot}Et_2O$ to form the adduct (A). The hydroxyl group of the adduct (A) initiates the polymerization by the attack to the activated monomer. The propagation involves the activated monomer cationic mechanism like in oxirane polymerization reported by Penczek et al.[4] However, in the 7CC polymerization with $H_2O/HCl{\cdot}Et_2O$, it is accompanied by the transformation of the carbonic acid end of the adduct (A) into a hydroxyl group via decarboxylation. CF_3CO_2H serves not only as an activator of 7CC but also as an initiator

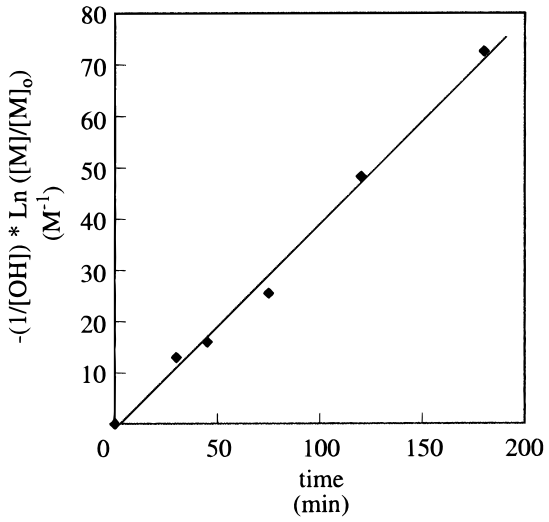
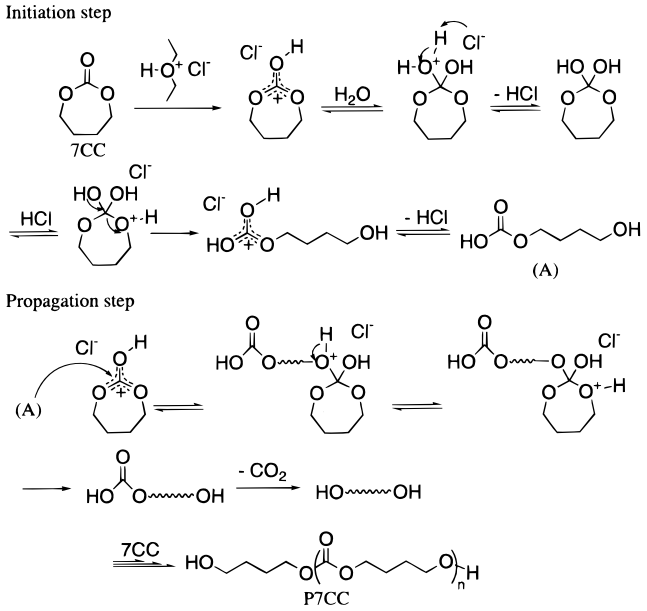


Figure 5. Relationship between time and $-[OH]^{-1}$ ln([M]/[M]$_0$) in the polymerization of 7CC with H_2O/HCl·Et_2O in CH_2Cl_2 ([M]$_0$ = 1 M, [HCl·EtO]$_0$ = 0.04 M) at 25 °C.

Scheme 2



of conventional cationic ring-opening polymerization of 7CC, providing the polymer with a relatively high M_w/M_n ratio. On the other hand, HCl·Et_2O serves only as an activator of 7CC. In CH_2Cl_2 solution, the acidity of HCl·Et_2O would be smaller than CF_3CO_2H, probably due to the effect of Et_2O. HCl·Et_2O may coordinate the carbonyl group of the polymer like that of monomer, providing a secondary oxonium ion, but the nucleophilic attack of the terminal OH group may be ignored probably due to the inherent low reactivity of the unstrained secondary oxonium ion. This may suppress a backbiting reaction, resulting in the living character of the polymerization.

Summary

In this article, we could demonstrate a controlled polymerization of a seven-membered cyclic carbonate, 7CC, based on the simple combination of H_2O and hydrogen chloride. The M_n of the polymer could be controlled by the amount of H_2O in the range of 10^3−10^4, maintaining a low M_w/M_n (1.11−1.17). The polymer propagating end was still active for 24 h after the complete consumption of the monomer. Kinetic and ^{1}H NMR spectroscopic studies suggested that a single active species of −OH group at the polymer end selectively attacked the monomer activated with hydrogen chloride to cause living polymerization.

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