Ring-Opening Polymerization of Ethylene Carbonate and Depolymerization of Poly(ethylene oxide-*co*-ethylene carbonate)

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ABSTRACT: The ring-opening polymerization of ethylene carbonate (EC) using KOH as initiator was investigated by changing the EC/KOH ratios and the reaction temperatures. The ratio of the rate of polymerization to chain scission increases as the temperature rises. Hydrolysis results and polymer composition data indicate that polymer chains are formed initially by attack of the active polymer chain end (the alcoholate anion) on ethylene carbonate: one attack at the carbonyl group followed by two attacks at the methylene group. Reactions that decrease the molecular weight and carbonate content in the polymer continue as long as the carbonate links are present. A relationship between carbonate content and degree of polymerization was derived using both decarboxylation and bimolecular elimination reactions for the kinetic equations; this fit the experimental data very well.

Introduction

Ring-opening polymerization of cyclic monomers depends on both thermodynamic and kinetic factors. Thermodynamically, the free energy change (ΔG_p) should be negative.[1−5] The free energy change in the polymerization can be determined by the enthalpy and entropy changes (ΔH_p and ΔS_p) and temperature (T):

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{1}$$

For most cyclic monomers, such as cyclic ethers, lactones, and cyclic siloxanes, ΔH_p and ΔS_p are both negative; they can polymerize only below a certain temperature called the ceiling temperature.[1] Some cyclic monomers, such as cyclooctasulfur and *N*,*N*-diethylamine-1,3,2-dioxaphosphorinane, with $\Delta H_p > 0$ and $\Delta S_p > 0$, can polymerize only above a certain temperature called the floor temperature.[1] If $\Delta H_p < 0$ and $\Delta S_p > 0$, the monomers can polymerize at any temperature; if $\Delta H_p > 0$ and $\Delta S_p < 0$, polymerization is thermodynamically forbidden.

Five-membered aliphatic cyclic carbonates, such as ethylene carbonate and propylene carbonate, are unique in ring-opening polymerization. Their ceiling temperature is below 25 °C, but they have been polymerized above 100 °C. The repeat units of the resultant polymers were a mixture of monomeric units (carbonate units) and the corresponding oxide units, which means that CO_2 is lost during the polymerization (eq 2). Probably the evolution of the CO_2 makes ΔS_p positive, so this polymerization becomes thermodynamically possible at high temperature.

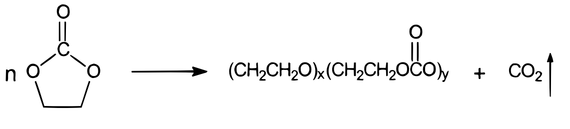

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Table 1. Five Reaction Conditions Used in This Study

	EC/KOH mole ratio	reaction temp (°C)
case I	1000/1	180
case II	200/1	180
case III	20/1	180
case IV	1000/1	150
case V	1000/1	200

Ethylene carbonate could be polymerized using Lewis acids, transesterification catalysts, or bases as initiators or as polymerization catalysts.[7−13] When Lewis acids or transesterification catalysts were used, normally the resultant polymers contained about 40−50 mol % of ethylene carbonate units (reaction temperature was 150−170 °C and reaction time was 70−100 h).[7−11,13] When base was used, the resultant polymers contained 10−20 mol % of ethylene carbonate links (reaction temperature was about 150 °C and reaction time was 72−98 h).[12] The polymerization mechanism of ethylene carbonate using a basic catalyst has not been reported as far as we know.

In this paper, ethylene carbonate was polymerized with KOH as initiator to study the polymerization mechanism.

Experimental Section

Materials. Ethylene carbonate (EC, from Acros Organics) was dried over P_2O_5 and then fractionally distilled under vacuum.[14] KOH (Fisher Scientific) was dried under vacuum at 110 °C for 3 days using an Abderhalden-type drying apparatus; then it was ground into powder in a porcelain dish under nitrogen or argon atmosphere in a glovebox. The KOH powder was directly used as initiator. The other chemicals were obtained from Fisher Scientific and used without further purification.

Polymerization Procedure. A three-neck 250 mL round-bottomed flask containing a magnetic stirring bar was equipped in a glovebox with a gas inlet/outlet and condenser under nitrogen or argon atmosphere. Then 1.5 mol (132.09 g) of EC and a measured amount of powdered KOH were added to the round-bottomed flask in the glovebox. The mole ratios of EC/KOH used in these systems were 1000/1, 200/1, and 20/1. The

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Table 2. 180 °C Reaction Results (EC/KOH mole ratio = 1000/1), Case I

reacn time (h)	convn[a] (%)	carbonate unit content[b] (mol %)	oxide unit content[c] (mol %)	vinyl end group content[d] (mol %)	molecular weight[e] ($\bar{M}_n/\bar{M}_w$)	PDI[f]	M_n and M_w after hydrolysis[e] ($\bar{M}_n/\bar{M}_w$)	$M_{n,hyd}$[g]	stage
2	26.2	31.8	68.2	0.00	3620/5220	1.45	188/252	132	I
3	39.4	22.7	77.3	0.00	4500/5850	1.30	200/272	184	
5	73.7	19.8	81.2	0.00	5700/7350	1.29	220/310	212	
9	93.5	17.0	83.0	0.00	6900/9040	1.31	240/340	248	
12	98.4	16.9	83.1	0.00	6600/9600	1.45	250/350	249	
15.5	99.9	16.9	83.1	0.00	6400/8960	1.40	260/370	249	II
19	100	17.0	83.0	0.00	5100/7600	1.48	270/380	245	
22	100	15.5	84.5	0.00	2300/3270	1.42	280/430	249	
25	100	14.3	85.7	0.53	1800/2913	1.62	280/430	258	
28	100	13.1	86.9	1.13	1630/2410	1.48		273	
31.5	100	10.2	89.8	2.04	1250/1860	1.49	290/430	313	
33	100	7.3	92.7	2.00	950/1530	1.61		359	
38	100	5.9	94.1	2.24	640/1200	1.88	330/500	335	
42.5	100	4.0	96.0	2.65	530/943	1.78	340/570	347	

[a] Determined from eq 3. [b] Determined from eq 4. [c] Determined from eq 5. [d] Determined from eq 11. [e] Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. [f] Polydispersity index = $\bar{M}_n/\bar{M}_w$. [g] Determined from eq 7.

Table 3. 180 °C Reaction Results (EC/KOH mole ratio = 200/1), Case II

reacn time (h)	convn[a] (%)	carbonate unit content[b] (mol %)	oxide unit content[c] (mol %)	vinyl end group content[d] (mol %)	molecular weight[e] ($\bar{M}_n/\bar{M}_w$)	PDI[f]	stage
1	32.6	25.2	74.8	0.00	1880/3420	1.82	I
2	62.1	18.2	81.8	0.00	3700/4920	1.33	
3	91.8	16.5	83.5	0.00	4200/5910	1.41	
4	96.9	15.7	84.3	0.00	4550/6280	1.53	
5	99.1	15.1	84.9	0.00	4050/6960	1.58	
7.5	100	14.1	85.9	0.30	3900/7100	1.82	II
10	100	13.5	86.5	0.67	2610/4950	1.90	
14	100	10.4	89.6	1.87	1680/2660	1.58	
18	100	6.9	93.1	3.27	870/1690	1.94	
24.5	100	0.0	100.0	4.33	530/960	1.81	
31	100	0.0	100.0	4.41	420/770	1.83	
39	100	0.0	100.0	4.45	410/760	1.85	
52	100	0.0	100.0	5.13	420/760	1.81	
62	100	0.0	100.0	4.37	430/770	1.79	

[a] Determined from eq 3. [b] Determined from eq 4. [c] Determined from eq 5. [d] Determined from eq 11. [e] Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. [f]Polydispersity index = $\bar{M}_w/\bar{M}_n$.

Table 4. 180 °C Reaction Results (EC/KOH mole ratio = 20/1), Case III

reacn time (h)	convn[a] (%)	carbonate content[b] (mol %)	oxide content[c] (mol %)	vinyl end group content[d] (mol %)	molecular weight[e] ($\bar{M}_n/\bar{M}_w$)	PDI[f]	stage
0.5	69.5	24.6	75.4	0.00	850/1300	1.53	I
1.5	100	13.4	86.6	0.00	1040/1470	1.41	
2.5	100	9.2	90.8	1.32	580/980	1.69	II
3	100	7.3	92.7	1.73	460/740	1.61	
4	100	0.2	99.8	2.58	310/520	1.68	
5	100	0	100	1.89	290/510	1.76	
7	100	0	100	1.94	280/500	1.79	
9	100	0	100	1.88	290/490	1.69	
12	100	0	100	1.99	280/500	1.78	

[a] Determined from eq 3. [b] Determined from eq 4. [c] Determined from eq 5. [d] Determined from eq 11. [e] Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. [f] Polydispersity index = $\bar{M}_n/\bar{M}_w$.

reaction mixture was stirred at 150, 180, or 200 °C. There were five reaction conditions, shown in Table 1. Ultrahigh purity grade nitrogen or argon gas was continuously passed through the flask during the reaction. About 2 mL of the reaction mixture was sampled at given times using a syringe to prevent air and moisture contamination of the reaction (Tables 2−6). They were directly used for NMR measurements. For GPC measurement, a neutralized sample was used; the reaction mixture was dissolved in THF and neutralized to pH 7 using acetic acid.

Hydrolysis of Polymers. A 0.5 g sample of polymer was added to 5−20 mL of 0.6 N KOH in ethanol. The volume of KOH solution was chosen so that the KOH equivalent exceeded that of the polymer carbonate content. (Determination of the carbonate content will be discussed in the Results and Discussion section.) Normally, a 1.5-fold molar excess of KOH was used. The mixture was stirred at room temperature for 3 h. The reaction mixture was neutralized using 0.1 N HCl aqueous solution and then filtered. Solvent was removed from the filtrate using a rotary evaporator; a viscous liquid was obtained. The viscous liquid was a mixture of poly(ethylene glycol)s; no carbonate groups were left by ^{1}H NMR. For a reaction mixture that contained monomer (EC), the monomer was removed before the hydrolysis as follows. First, 1.0 g of the reaction mixture was dissolved in 2.0 g of ethanol, and the solution was poured into 100 mL of ether. Viscous polymer precipitated while the monomer (EC) remained dissolved in the ether. The ether layer was then decanted from the reaction. The polymer was washed with ether several times until no monomer was left in the polymer.

Characterization. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained using a Varian Gemini 200 spectrometer with $CDCl_3$ as solvent. Molecular weights were obtained using a Waters model 590 gel permeation chromatography instrument (GPC) equipped with one Phenogel GPC guard column, two Waters Styragel HR 4E columns, and a refractive index detector. THF was used as eluent at a flow rate of 1 mL/min at 40 °C. A calibration plot was constructed using ethylene glycol, tri(ethylene glycol), tetra(ethylene glycol), penta(ethylene glycol), hexa(ethylene glycol), and poly(ethylene glycol) standards (molecular weights ranged from 440 to 18 000).

Results and Discussion

EC (1.5 mol) was bulk polymerized with different amounts of KOH: 0.075, 0.0075, and 0.0015 mol, at 180 °C. Also, 1.5 mol of EC was polymerized with 0.0015 mol of KOH at 150 and 200 °C, Table 1.

The EC/KOH ratio mentioned above might not be exactly correct. Commercial KOH always contains 10−15 wt % of water, and complete removal of the water requires fusion in a vacuum.[15] Three days under vacuum at 110 °C might not have been enough to totally dry the KOH. However, the main concern of this paper is not quantitative analysis but developing a polymeriza-

Table 5. 150 °C Reaction Results (EC/KOH mole ratio = 1000/1), Case IV

reacn time (h)	convn[a] (%)	carbonate unit content[b] (mol %)	oxide unit content[c] (mol %)	vinyl end group content[d] (mol %)	molecular weight[e] ($\bar{M}_n/\bar{M}_w$)	PDI[f]	stage
1				0.00	990/1050	1.06	I
3	9.0	30.0	70.0	0.00	2000/2300	1.15	
5	18.3	25.7	74.3	0.00	4800/5460	1.14	
8	28.3	23.1	76.9	0.00	5460/6740	1.23	
10	36.8	23.3	76.6	0.00	5700/7500	1.31	
13	39.5	23.0	77.0	0.00	5800/7410	1.23	
15	43.2	22.8	77.2	0.00	5900/7530	1.28	
18	52.1	22.1	77.8	0.00	5960/8130	1.36	
24	60.7	21.6	78.4	0.00	5700/7780	1.36	
29	68.5	20.9	79.1	0.00	5390/7410	1.37	
34	76.6	20.1	79.9	0.00	5070/7380	1.46	
37	81.3	19.4	80.6	0.00	5020/7540	1.50	
42	86.0	18.7	81.3	0.00	4550/7020	1.54	
45	90.5	18.2	81.8	0.00	4410/7000	1.58	
51	95.7	18.2	81.8	0.00	4290/6970	1.62	
58.5	100	15.9	84.1	0.00	3980/6390	1.61	II
64.5	100	15.5	84.5	0.00	3640/5850	1.61	
75	100	15.1	84.9	0.00	3060/5240	1.71	
83	100	15.1	84.9	0.01	2810/4860	1.73	
94	100	13.1	86.9	0.01	2400/4140	1.73	

[a] Determined from eq 3. [b] Determined from eq 4. [c] Determined from eq 5. [d] Determined from eq 11. [e] Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. [f] Polydispersity index = $\bar{M}_w/\bar{M}_n$.

Table 6. 200 °C Reaction Result (EC/KOH mole ratio = 1000/1), Case V

reacn time (h)	convn[a] (%)	carbonate unit content[b] (mol %)	oxide unit content[c] (mol %)	vinyl end group content[d] (mol %)	molecular weight[e] ($\bar{M}_n/\bar{M}_w$)	PDI[f]	stage
1	25.1	28.9	71.1	0.00	5390/6930	1.29	I
2	46.1	20.9	79.1	0.00	7500/10100	1.35	
3	73.7	19.0	81.0	0.00	8970/11190	1.25	
3.5	85.2	18.9	81.1	0.00	8730/11280	1.29	
4	93.4	17.1	82.9	0.00	8420/11410	1.36	
4.5	95.8	17.0	83.0	0.00	8270/11260	1.36	
5	98.6	16.7	83.3	0.00	8000/10890	1.36	
5.5	99.0	16.7	83.3	0.00	7720/10480	1.36	
7	99.3	16.0	84.0	0.00	6700/9190	1.37	
8	100	16.1	83.9	0.52	5810/8300	1.43	II
9	100	15.8	84.2	0.77	4410/7070	1.60	
11.5	100	14.3	85.7	1.13	3100/4210	1.39	
14	100	11.9	88.1	1.03	1800/3100	1.72	
16	100	10.5	89.5	2.34	1220/2080	1.71	
19	100	9.9	90.1	2.88	980/1870	1.91	
25	100	5.9	94.1	3.35	760/1530	2.01	
32	100	3.5	96.5	4.84	460/1030	2.24	

[a] Determined from eq 3. [b] Determined from eq 4. [c] Determined from eq 5. [d] Determined from eq 11. [e] Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. [f] Polydispersity index = $\bar{M}_w/\bar{M}_n$.

tion mechanism, so a small amount of possible water impurity will not affect the conclusions. Water in this polymerization acts similarly to KOH in that each molecule generates a polymer molecule.

About 2 mL of the reaction mixture was sampled at a given time to determine conversion, polymer molecular weight, and composition (Tables 2−6). For case I (see Table 1 for conditions), as soon as the system was heated, KOH started to dissolve in the reaction medium, and after about 30 min, all the KOH was dissolved. So the monomer/initiator ratio, 1000/1, is valid after about 30 min. From the beginning of the reaction, gas evolved vigorously from the reaction mixture. Vigorous gas evolution continued for 19 h, and then diminished. No gas evolution could be detected after 33 h. The color of the reaction mixture changed during the reaction. Initially the reaction mixture was water white. As soon as the reaction started, the color changed to light yellow (1−12 h), darkened to yellow (12−28 h), to dark yellow (28−38 h), and finally to brown (>38 h). For cases II and III, the KOH powder dissolved completely after 45 min and 2 h, respectively. Gas also evolved vigorously at the beginning of the reaction, and continued until 8 and 2 h for cases II and III, respectively. The colors of the reaction mixtures for these cases changed in the same pattern as for case I, but much faster. For case IV, gas evolution was observed for 94 h, the maximum reaction time. The color of reaction mixture changed very slowly. For case V, little, if any, gas evolved after 11.5 h, and the color of the reaction mixture changed very quickly. A noticeable feature of all the reactions was that the color changed to light yellow as soon as the reaction started.

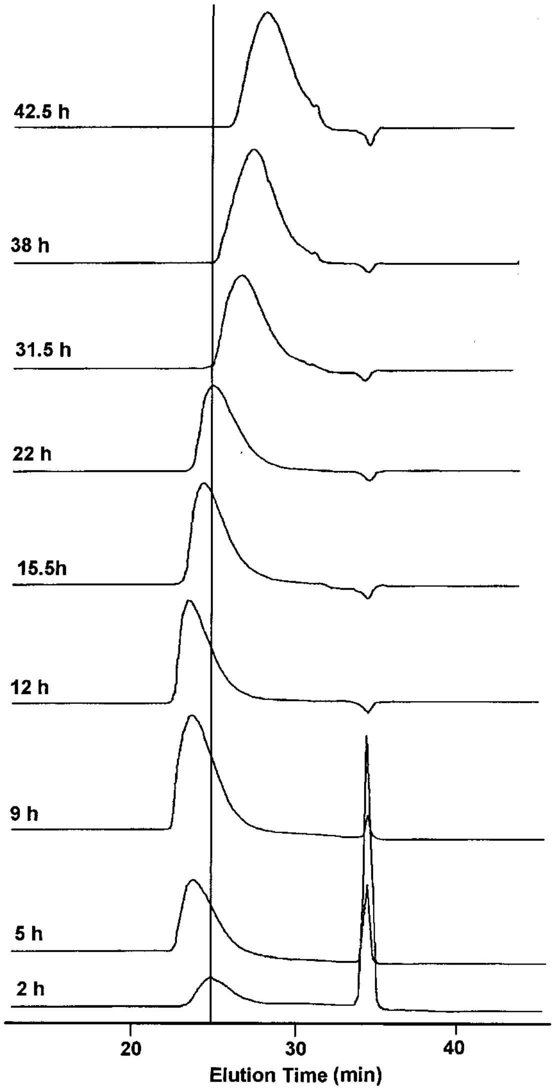


Figure 1. Gel permeation chromatography results for case I (EC/KOH = 1000/1, 180 °C).

GPC and NMR spectra were taken for the samples. Figure 1 shows the molecular weight (GPC) change of the reaction mixture with reaction time for case I. The sharp peaks at about 34 min are due to the monomer and the broad peak at earlier elution times is due to the polymer. In the early stage of reaction (1−9 h), both

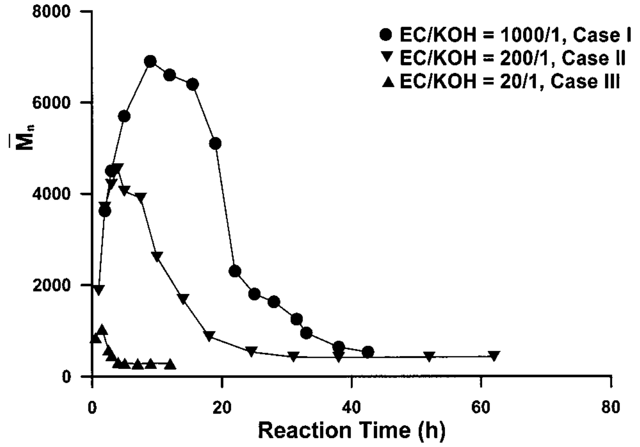


Figure 2. Number-average molecular weight ($\bar{M}_n$) vs time curves for three 180 °C cases (cases I, II, and III).

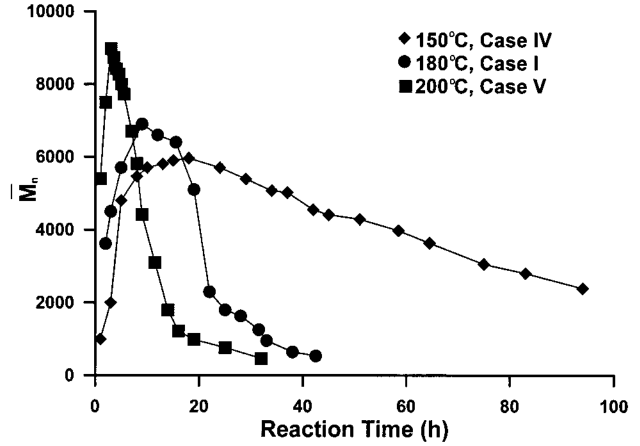


Figure 3. Number-average molecular weight ($\bar{M}_n$) vs time curves for three EC/KOH = 1000/1 cases (cases I, IV, and V).

monomer and polymer peaks are visible, with the monomer peak intensity decreasing while the intensity of the polymer peak increases. After 12 h, only the polymer peak is visible. The molecular weight of the polymer increases (the elution time decreases) as the reaction time increases up to 12 h and then starts to decrease. GPC number and weight-average molecular weights are listed in Table 2. Molecular weight changes for cases II, III, IV, and V were also observed and are listed in Tables 3–6.

Figure 2 shows the molecular weight change with reaction time for the three 180 °C cases (cases I, II, and III). For every case, molecular weight first increases, reaches a maximum, and then decreases. The times to reach the maximum molecular weight increased as the EC/KOH mole ratios increased; they were about 1.5, 4, and 9 h for EC/KOH = 20/1, 200/1, and 1000/1, respectively. The lower the KOH concentration (the higher the EC/KOH ratio), the higher the maximum $\bar{M}_n$.

Figure 3 shows the change in $\bar{M}_n$ as a function of reaction time for the three cases where EC/KOH = 1000/1 (cases I, IV, and V). The higher the reaction temperature, the higher the maximum molecular weight of the polymer and the shorter the time to reach the maximum molecular weight. At 180 and 200 °C, the molecular weight decreases rapidly at first after reaching its maximum and subsequently decreases slowly.

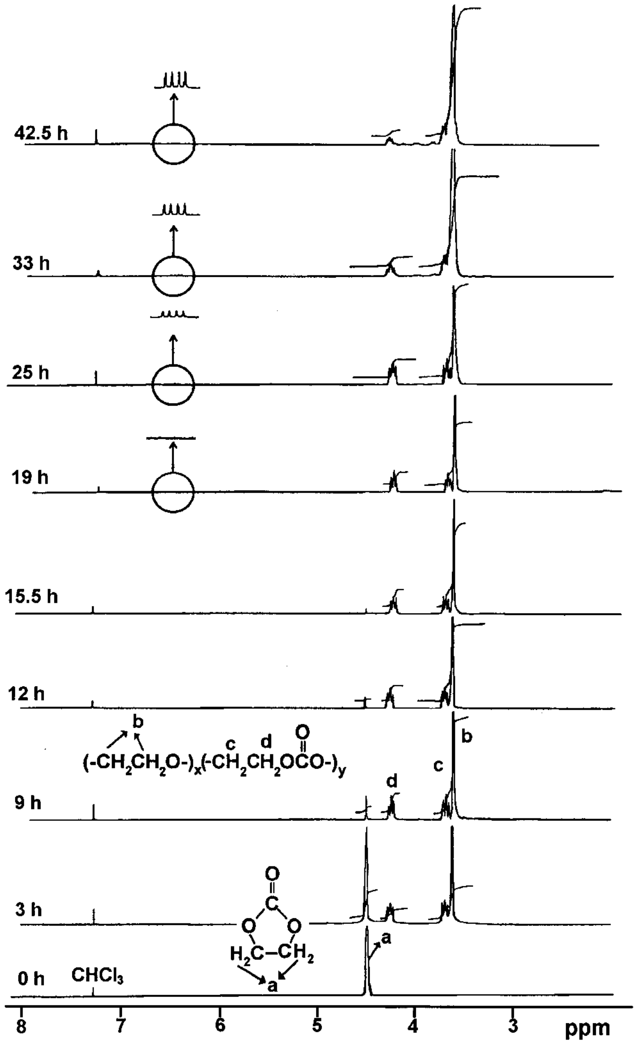


Figure 4. ^{1}H NMR spectra for case I (EC/KOH = 1000/1, 180 °C).

At 150 °C (case IV), the molecular weight decreases slowly after reaching the maximum.

The maximum $\bar{M}_n$'s obtained for cases I, II, IV, and V were 6900, 4550, 5960, and 8970. Considering the monomer/initiator ratios, these values are very low. For case III, the maximum $\bar{M}_n$, 1050, was obtained at 1.5 h. The maximum $\bar{M}_n$ calculated from the monomer/initiator ratio (20/1) and the polymer composition at 1.5 h for case III is 970. In case III, the initiator, KOH, totally dissolved after 2 h. Therefore, the monomer/initiator ratio should be larger than 20/1 at 1.5 h. So in case III, we can also assume that the maximum $\bar{M}_n$ obtained is smaller than that calculated from the monomer/initiator ratio. These results indicate that chain degradation occurred from the beginning of the polymerization. The chain degradation reactions will be explained in the later section of this paper.

The polymer chemical structure was studied by NMR as a function of reaction time and temperature. Figure 4 shows the ^{1}H NMR spectra of the samples for case I. As the reaction time increased, the peak intensity of the proton due to monomer (EC) (singlet at 4.54 ppm) decreased. After 19 h the polymer structure shows clearly. As expected, it contains ethylene oxide and ethylene carbonate units (eq 2).

By peak integration of these spectra, the monomer conversion and the polymer composition can be calcu-

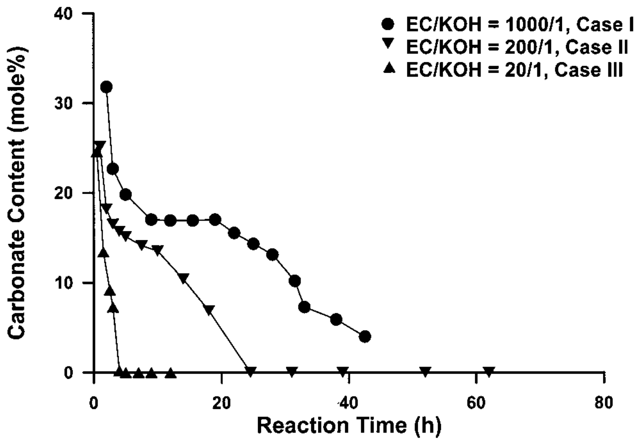


Figure 5. Carbonate content vs time curves for three 180 °C cases (cases I, II, and III).

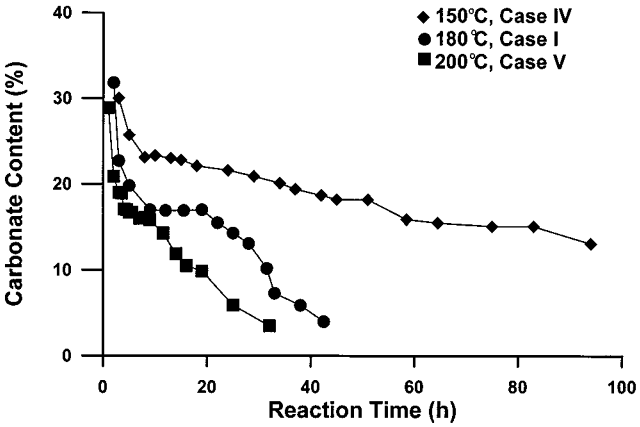


Figure 6. Carbonate content vs time curves for three EC/KOH = 1000/1 cases (cases I, IV, and V).

lated. The degree of conversion was calculated as follows:

$$\text{conversion (\%)} = \frac{A_b + A_c + A_d}{A_a + A_b + A_c + A_d} \times 100 \quad (3)$$

where A_a, A_b, A_c, and A_d are the intensities of the a, b, c, and d protons, respectively (Figure 4). The conversions for all cases were calculated and are listed in Tables 2–6. Figure 5 shows the time vs conversion curves for the three 180 °C cases. The times to reach 100% conversion for EC/KOH = 20/1, 200/1, and 1000/1 cases were 1.5, 7.5, and 19 h, respectively.

The polymer composition was calculated by comparing the area of the multiplet at 3.50–3.66 ppm, assigned to the ethylene oxide (EO) unit, with that of two triplets at 3.70 and 4.26 ppm, assigned to the ethylene carbonate (EC) unit, as follows (Figure 4).

$$\text{EC content (mole \%)} = \frac{A_c + A_d}{A_b + A_c + A_d} \times 100 \quad (4)$$

$$\text{EO content (mol \%)} = 100 - \text{EC content (mol \%)} \quad (5)$$

The composition changes for all the cases were calculated and are listed in Tables 2–6. Interestingly, the EC content is always below 32 mol % even in the earliest stage of the polymerization. Figures 5 and 6 show the changes of the carbonate content in the polymer with reaction time for all the cases. In general the carbonate content changes in three steps. At first, the carbonate content decreases rapidly from about 30 mol % to about 17–23%. In the second step, it tends to plateau. It decreases steadily to zero in the third step. The structure changes of the reaction mixture and the polymer structure were also confirmed by ^{13}C NMR (Figure 7).

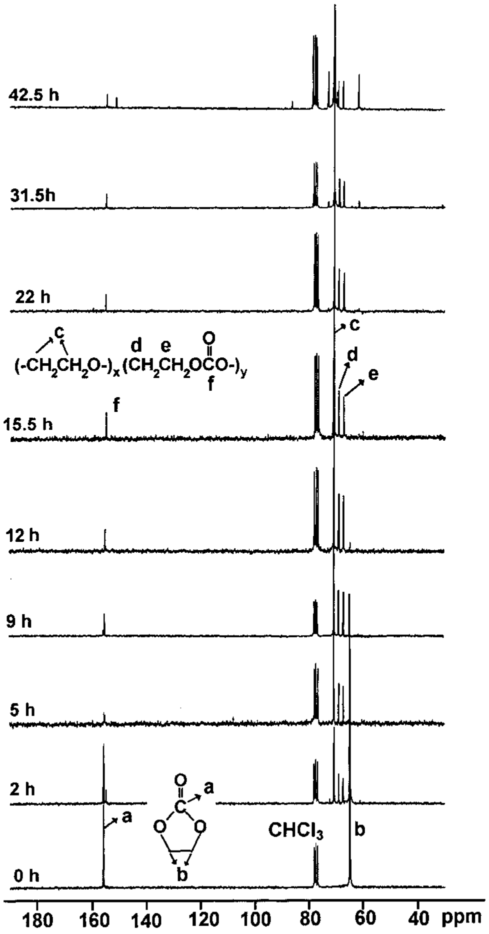
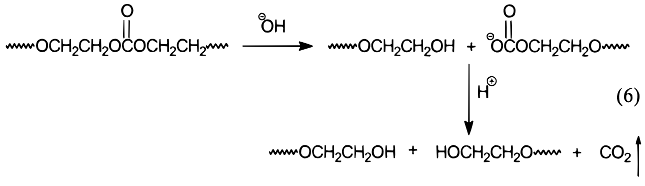


Figure 7. ^{13}C NMR spectra for case I (EC/KOH = 1000/1, 180 °C).

The oxide sequences in the polymer backbone were converted to poly- or oligo(ethylene glycol)s; the carbonate linkage can be easily hydrolyzed[7,16,17] under basic conditions as follows:



$$\sim\sim OCH_2CH_2O\overset{O}{\overset{\|}{C}}OCH_2CH_2\sim\sim \xrightarrow{{}^{\ominus}OH} \sim\sim OCH_2CH_2OH + {}^{\ominus}O\overset{O}{\overset{\|}{C}}OCH_2CH_2O\sim\sim$$
$$\xrightarrow{H^{\oplus}} \sim\sim OCH_2CH_2OH + HOCH_2CH_2O\sim\sim + CO_2\uparrow \quad (6)$$

Figure 8 shows the GPC results of the hydrolyzed polymers of case I. In the early stage of the reaction a major peak was observed at 31.8 min elution time. The elution times of ethylene, diethylene, triethylene, and tetraethylene glycols were 32.8, 32.3, 31.8, and 31.4 min, respectively. So, in the early stages a major polymer structure comprises two oxide units and a carbonate unit (EC–EO–EO repeating unit). As the reaction time increased, the average oxide unit length increased (the elution time of the hydrolyzed polymer fragments increased). The $\bar{M}_n$'s and $\bar{M}_w$'s after hydrolysis for case I are listed in Table 2.

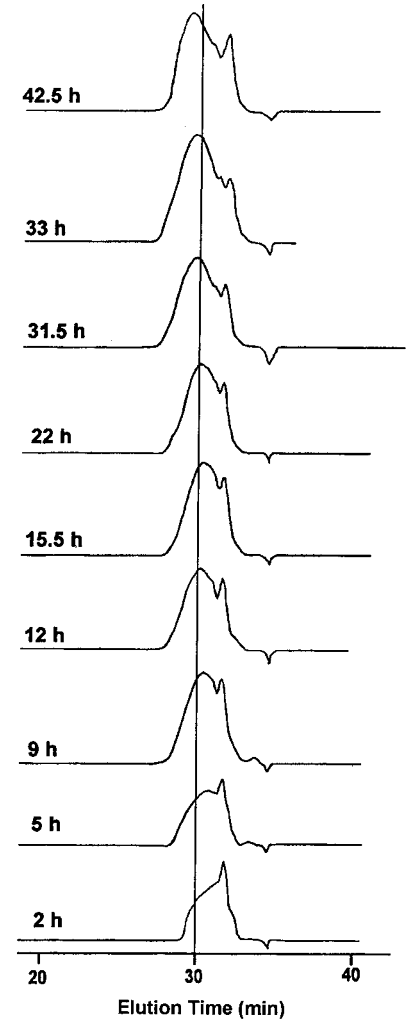


Figure 8. Gel permeation chromatography results after hydrolysis for case I.

$\bar{M}_n$'s after hydrolysis ($\bar{M}_{n,\mathrm{hyd}}$) can also be calculated from the $\bar{M}_n$'s and oxide/carbonate contents of the polymers as follows:

$$\bar{M}_{n,\mathrm{hyd}} = \frac{\bar{X}_n}{(1 + N_{\mathrm{EC}})} \times 44.05 \tag{7}$$

Here, $\bar{X}_n$ is the number-average degree of polymerization and N_{EC} is the average number of carbonate units per polymer chain. They can be calculated as follows:

$$N_{\mathrm{EC}} = \bar{X}_n \times C_{\mathrm{EC}} \tag{8}$$

$$\bar{X}_n = \bar{M}_n/\mathrm{FW}_{\mathrm{av}} \tag{9}$$

C_{EC} is the carbonate unit mole fraction in the polymer and $\mathrm{FW}_{\mathrm{av}}$ is the average molecular weight of a backbone unit.

$$\mathrm{FW}_{\mathrm{av}} = C_{\mathrm{EC}} \times 88.06 + C_{\mathrm{EO}} \times 44.05 \tag{10}$$

C_{EO} is the oxide unit mole fraction in the polymer, which can be obtained from ^1H NMR spectra, and 88.06 and 44.05 are the unit molecular weights of EC and EO, respectively. $\bar{M}_{n,\mathrm{hyd}}$'s of case I are listed in Table 2 and they showed quite good agreement with the experimental values.

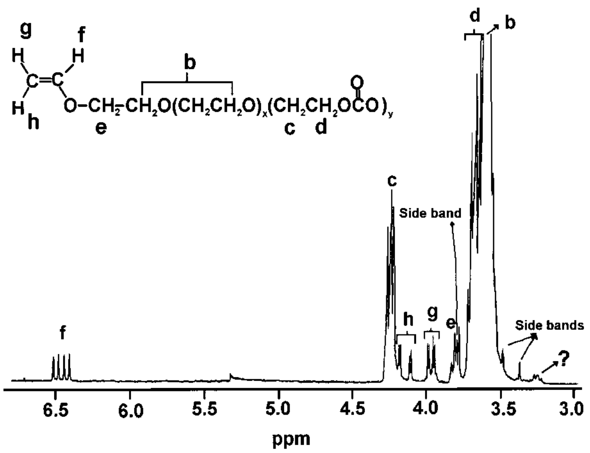


Figure 9. Magnified ^1H NMR spectrum for case I after 42.5 h reaction.

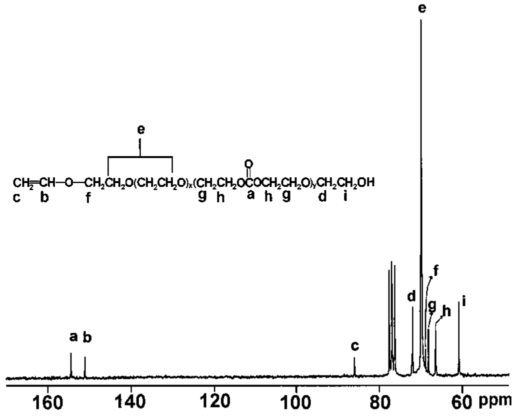
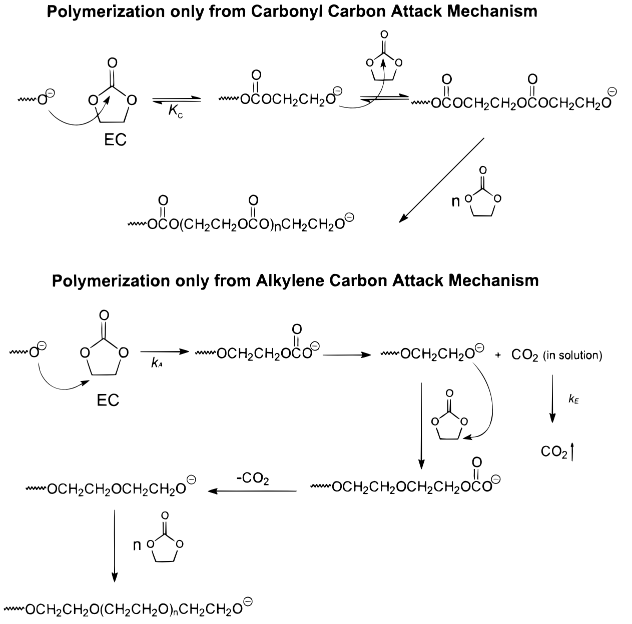


Figure 10. Magnified ^{13}C NMR spectrum for case I after 42.5 h reaction.

One interesting feature found in the ^1H NMR spectra of the samples is the three deshielded quartets at 3.98, 4.16, and 6.47 ppm and a triplet at 3.82 ppm that started to appear after a certain reaction time. For case I the peaks started to appear after 25 h, as shown in Figure 4. Figure 9 shows peak assignments for the ^1H NMR spectrum of case I after 42.5 h reaction. Proton **f** (chemical shift, $\delta \sim 6.47$ ppm) is strongly affected by the electronegative ether unit and is split by proton **h** (coupling constant, $J \sim 14.37$ Hz) and by proton **g** ($J \sim 6.75$ Hz). The proton **h** ($\delta \sim 4.16$ ppm) signal is split by proton **f** ($J \sim 14.37$ Hz) and by proton **g** ($J \sim 2.11$ Hz). The proton **g** ($\delta \sim 3.98$ ppm) signal is split by proton **f** ($J \sim 6.75$ Hz) and by proton **h** ($J \sim 2.11$ Hz). Four peaks are shown in the 3.77–3.86 ppm range. One peak at 3.81 ppm was attributed to a sideband, so the triplet at 3.82 ppm ($J \sim 4.58$ Hz) was attributable to methylene protons (**e** protons) next to a vinyl ether group. The ^{13}C NMR spectrum (Figure 10) confirms the chemical structure of the case I, 42.5 h reaction. In ^{13}C NMR, a hydroxyethyl end group was also detected (**d** and **i** carbon peaks at 72.59 and 61.40 ppm), which was not seen in the ^1H NMR spectrum. The vinyl end group molar ratios of the polymers, listed in Tables 2–6, were calculated by comparing the quartet at 6.47 ppm (1H) and the polymer backbone peaks (4H), the multiplet at

Scheme 1



3.50–3.66 ppm, and two triplets at 3.70 and 4.26 ppm as follows.

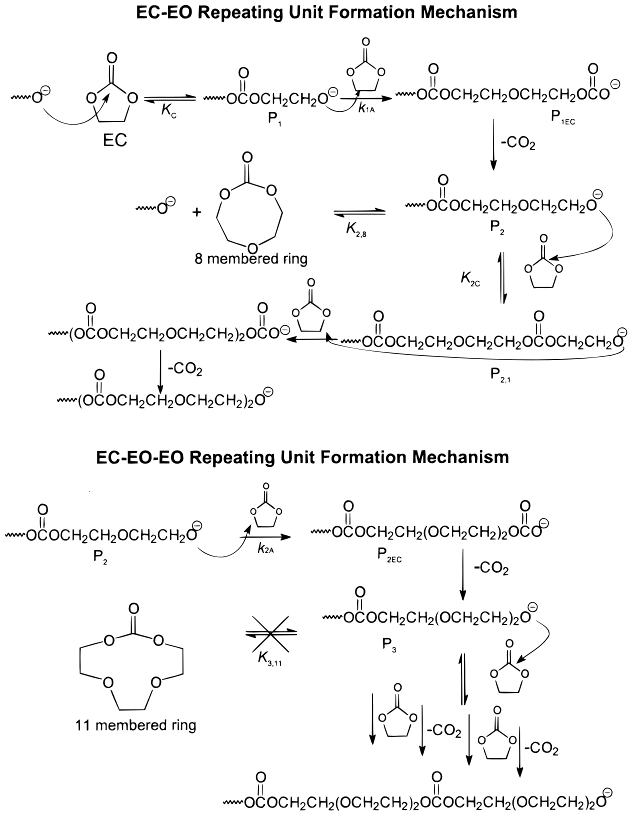
$$\text{vinyl end group content (mol \%)} = \frac{4A_f}{A_b + A_c + A_d + A_e + 4A_f} \quad (11)$$

A_b, A_c, A_d, A_e, and A_f are the intensities of protons b, c, d, e, and f, respectively (Figure 9). The vinyl groups started to appear after the conversion reached 100%, and the concentration increased as the oxide content approached 100 mol %; then they did not change with further heating.

To summarize the above results, the reactions seemed to divide into two stages. During stage I, conversion and molecular weight increase. In stage II, no monomer is left, and the carbonate content and molecular weight of the polymers decrease with time, which indicates that chain cleavage occurs. These stages for all the cases are listed in Tables 2–6.

There are two possible routes to react the monomer during stage I. One is by attack at the carbonyl carbon and the other is by attack at the alkylene carbon (Scheme 1). Kinetically, carbonyl attack is favored over alkylene attack.[13,17–19] However, the carbonyl attack (K_C) is reversible, and the only way to obtain a high molecular weight poly(ethylene carbonate) is when the polymerization is performed below the ceiling temperature. The polymers obtained in our experiments contained both carbonate and oxide links, the maximum carbonate content found was 32 mol %. Previous papers also mentioned that thermodynamically the cyclic monomer (EC) is favored over the polymer.[12] On the contrary, the attack on the alkylene carbon is irreversible, and is accompanied by decarboxylation. Rokicki et al.[20] reported the loss of CO_2 above 150 °C from potassium carbonates, such as 2-(1-phenoxy)propyl potassium carbonate. The probable reaction to get polymer from EC is by alkylene attack. However, if the polymerization proceeded only by this reaction, the resulting polymer backbone should be all oxide units. This was not the case.

Scheme 2



Therefore, the most probable EC polymerization mechanism under basic conditions should be a combination of an alkylene carbon attack and a carbonyl carbon attack.

Hydrolysis results show that the EC–EO–EO repeating unit is the major structural unit of the initial polymer. The GPC curves after polymer hydrolysis in the early stage of the reaction (Figure 8, 2 and 5 h) show a diethylene glycol shoulder (32.3 min) on a large single peak from triethylene glycol. This shows that EC–EO repeat unit formation happens, but at much lower frequency than that of EC–EO–EO repeat unit formation. The EC contents at the beginning of the reactions (low conversion) for cases I, IV, and V, 31.8, 30.0, and 28.9 mol %, also confirm this mechanism. For cases II and III, the EC content in the initial polymers was lower, about 25 mol %, probably because decarboxylation was already occurring due to the high base content. The decarboxylation reaction will be examined in a later section.

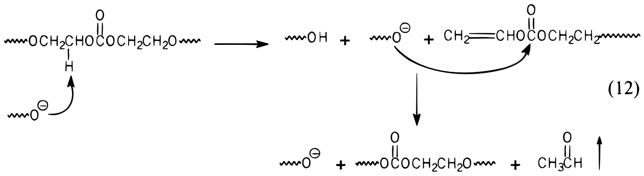
Scheme 2 shows a possible EC polymerization mechanism under basic condition to form the EC–EO–EO repeating unit and the EC–EO repeating unit. In the first step, the active chain end attacks the carbonyl carbon of EC to form P_1. This equilibrium is to the left side (EC and active end) as mentioned above. Some of P_1 can react with another EC to form P_{1EC} by an attack on the alkylene. This is irreversible. P_2 is then formed by the loss of CO_2. Then there is another equilibrium, $K_{2,8}$, between P_2 and the eight-membered ring formed by the intramolecular cyclization of P_2. This equilibrium is reversible and should be toward the P_2 side. If the alcoholate ion end of P_2 attacks the carbonyl carbon of EC (K_{2C}), $P_{2,1}$ will be formed. This reaction is reversible. Then an EC–EO unit can be formed by one alkylene carbon attack, followed by decarboxylation as shown in

Scheme 2, EC−EO Repeating Unit Formation Mechanism. The major reaction of P_2 that leads to chain growth is attack on the alkylene carbon of EC (k_{2A}) to form P_{2EC}, followed by its decarboxylation to form P_3. Intramolecular cyclization of P_3 would produce an 11-membered ring ($K_{3,11}$ equilibrium). However, 11-membered ring formation by intramolecular cyclization is rare. It is well-known that five- and six-membered rings form easily by intramolecular cyclization reactions. As the ring size increases from the seven-membered ring, intramolecular cyclization becomes harder, and cyclization is very unlikely if it produces 9- to 12-membered rings. The detailed studies of intracyclization vs linear polymerization can be found elsewhere.[21,22] We can therefore assume that P_3 is highly favored compared to the 11-membered ring in $K_{3,11}$ equilibrium. By repetition of this mechanism, one carbonyl carbon attack (K_C) and two alkylene carbon attacks (k_{1A} and k_{2A}), polymers with EC−EO−EO repeating units can be formed.

The polymerization mechanisms described above were hypothesized using the assumption that the active center is the alcoholate anion, even though the carbonate anion preferentially exists in the reaction mixture. The alcoholate anion is a much stronger nucleophile than the carbonate anion. For all-base polymerization of lactones, except for the strained β-propiolactone, the alcoholate anion was the active center.[1,18,23−25] It is reasonable therefore to expect that the active center for the nonstrained EC polymerization is the alcoholate anion.

In stage I, carbonate content decreases. If the CO_2 is lost only during the polymerization step, the polymer oxide content should not change. If the EC is polymerized following the EC−EO−EO repeat unit formation mechanism, shown in Scheme 2, the carbonate content should always be about 33 mol %. For case I, at the beginning of the reaction, the EC content was 31.8 mol %, while at the end of stage 1 the EC content was down to 18.8 mol %. The difference between the two should be due to the loss of the carbonate group in the polymer chain. There are two possible decarboxylation mechanisms, one is intramolecular while the other is intermolecular, as shown in Scheme 3.

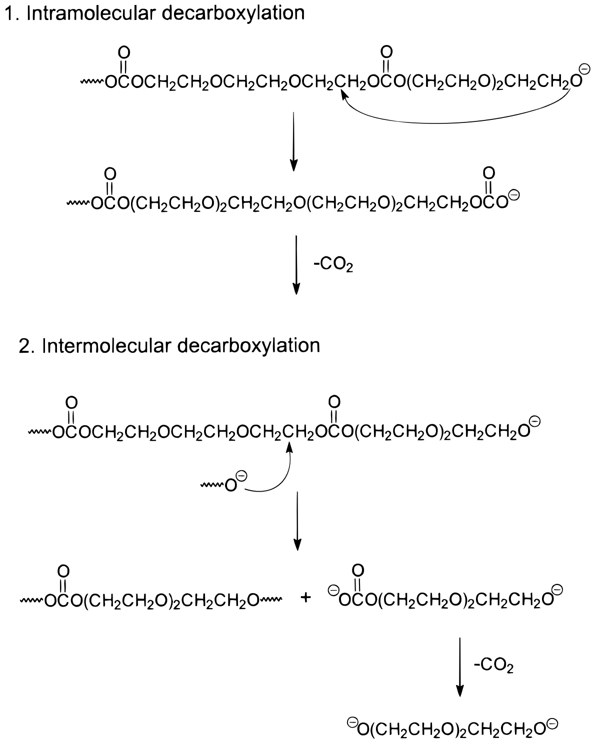
During the polymerization, water white liquid distilled from the reaction mixture and was collected. ^1H NMR analysis showed that the liquid was acetaldehyde. The probable route for the formation of the acetaldehyde is shown in eq 12. When acetaldehyde is formed, it decreases the molecular weight of the polymer for the following reasons: (1) The anion attack cleaves the polymer molecule. (2) One backbone unit is lost by the formation of one acetaldehyde molecule (eq 12). (3) If the acetaldehyde polymerizes, which was observed in poly(ethylene terephthalate) thermal degradation,[26] water is a byproduct. One water molecule can generate two active sites. The color change of the reaction mixture may be indicative of acetaldehyde polymerization; the water white color of the reaction mixtures changed to light yellow as soon as the reaction started and darkened as the reaction proceeded. There might be other side reactions which decrease the molecular weight, such as radical chain reactions, observed during the thermal degradation of polyethers and poly(ethylene terephthalate).[27,28] However these reactions occur at higher temperatures; there is no evidence for them in the present study.



(12)

Scheme 3

Decarboxylation from the Carbonate Group in the Polymer Chain



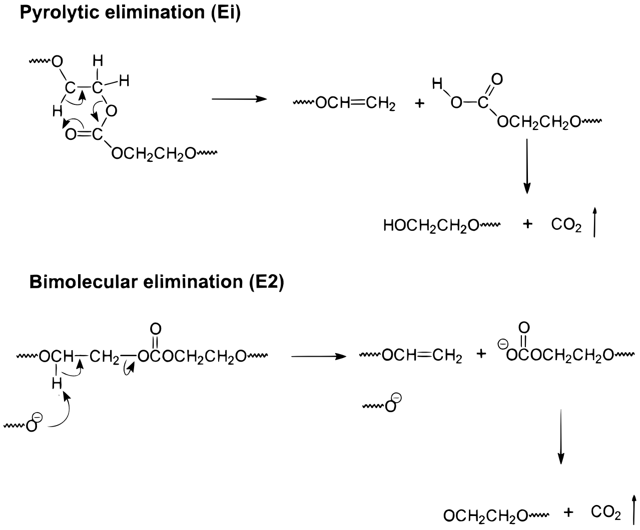
In stage II, all the EC has reacted. In this stage, carbonate content and molecular weight decrease with time, which indicates that polymer chain is cleaved, with CO_2 loss. The decarboxylation reaction, shown in Scheme 3, rationalizes the decrease of carbonate content, but cannot explain the chain cleavage. In stage II, vinyl end groups begin to form, which must be related to the chain cleavage. The vinyl end group can be formed by two possible elimination mechanisms (Scheme 4). One is pyrolytic elimination (Ei) and the other is bimolecular elimination (E2).[28] Ei does not seem to happen. Because Ei is a first-order reaction, it can happen as soon as carbonate groups are incorporated into the polymer backbone. However, vinyl groups only started to form in stage II.

E2 elimination is possible whenever there are carbonate groups in the backbone and enough alcoholate anions present. The E2 mechanism results in chain cleavage and also rationalizes the decrease in carbonate content. If the decrease of carbonate content is due only to bimolecular elimination (Scheme 4) and decarboxylation (Scheme 3), then eq 13 should be valid in stage II.

$$-\mathrm{d}[\mathrm{Car}]/\mathrm{d}t = k_{\mathrm{E2}}[\mathrm{RO}^-][\mathrm{Car}] + k_{\mathrm{decar}}[\mathrm{RO}^-][\mathrm{Car}] \quad (13)$$

[Car] is the concentration of carbonate groups in the polymer, and k_{E2} and k_{decar} are the rate constants for the E2 reaction and decarboxylation. In eq 13, k_{E2} is

Scheme 4



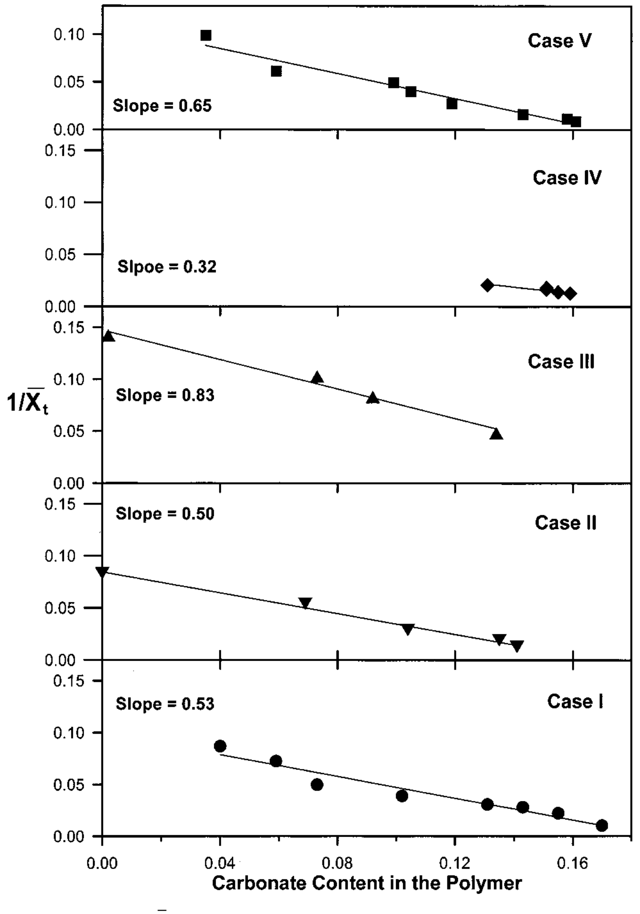


Figure 11. $1/\bar{X}_t$ vs carbonate content curves. The solid line is a fit using eq 17. The slope is $k_{E2}/(K_{E2} + K_{decar})$.

related only to chain cleavage. This is shown in eq 14,

$$d[\mathrm{Car}]_{E2}/dt = k_{E2}[\mathrm{RO}^-][\mathrm{Car}] \qquad (14)$$

where $[\mathrm{Car}]_{E2}$ is the concentration of carbonate groups in the polymer chain that will be cleaved by the E_2 reaction. Then, dividing eq 14 by eq 13, we can eliminate the $[\mathrm{RO}^-]$ term.

$$d[\mathrm{Car}_{E2}] = -[k_{E2}/(k_{E2} + k_{decar})]\, d[\mathrm{Car}] \qquad (15)$$

Table 7. Data for Equation 17

reacn time (h)	[Car][a] (fraction)	FW_{av}[b]	$\bar{M}_n$	$\bar{X}_t$[c]	case
19	0.170[d]	51.48	5100	99.07[e]	I
22	0.155	50.82	2300	45.26	
25	0.143	50.29	1800	35.79	
28	0.131	49.76	1630	32.75	
31.5	0.102	48.48	1250	25.78	
33	0.073	47.21	950	20.12	
38	0.059	46.59	643	13.80	
42.5	0.040	45.76	527	11.52	
7.5	0.141[d]	50.20	3900	77.68[e]	II
10	0.135	49.94	2610	52.26	
14	0.104	48.58	1680	34.58	
18	0.069	47.04	870	18.50	
24.5	0	44.05	530	12.05	
1.5	0.134[d]	49.90	1040	20.84[e]	III
2.5	0.092	48.05	580	12.07	
3	0.073	47.21	460	9.74	
4	0.002	44.09	310	7.03	
58.5	0.159[d]	51.00	3980	78.05[e]	IV
64.5	0.155	50.82	3640	71.63	
75	0.151	50.64	3060	60.42	
83	0.151	50.64	2810	55.49	
94	0.131	49.76	2400	48.23	
8	0.160[d]	51.08	5810	113.73[e]	V
9	0.158	50.95	4410	86.55	
11.5	0.143	50.29	3100	61.64	
14	0.119	49.24	1800	36.56	
16	0.105	48.62	1220	25.09	
19	0.099	48.36	980	20.27	
25	0.059	46.60	760	16.31	
32	0.035	45.54	460	10.10	

[a] Carbonate content in the polymer. [b] Average molecular weight of backbone unit in the polymer, calculated from eq 10. [c] Average number of backbone units in the polymer. [d] Initial carbonate content, $[\mathrm{Car}]_0$, in stage II. [e] Initial average number of backbone units in the polymer, X_0 in stage II.

Upon integrating eq 15, we obtain eq 16. Cleavage occurs only during an E2 reaction. If carbonate mole fraction in the polymer is used for the units of [Car] and $[\mathrm{Car}]_{E2}$, $[\mathrm{Car}]_{E2,t} - [\mathrm{Car}]_{E2,0}$ can be rewritten as $1/\bar{X}_t - 1/\bar{X}_0$, where $\bar{X}_t$ and $\bar{X}_0$ are the degrees of polymerization at a given time and at the beginning. Therefore, the relationship of carbonate content vs degree of polymerization is given by eq 17. Good straight-line plots,

$$[\mathrm{Car}]_{E2,t} - [\mathrm{Car}]_{E2,0} = [k_{E2}/(k_{E2} + k_{decar})]([\mathrm{Car}]_0 - [\mathrm{Car}]_t) \qquad (16)$$

$$(1/\bar{X}_t - 1/\bar{X}_0) = [k_{E2}/(k_{E2} + k_{decar})]\,([\mathrm{Car}]_0 - [\mathrm{Car}]_t) \qquad (17)$$

Figure 11, show that this equation gives a good representation of our data (Table 7). From the slope of the line, we can get the ratio between the elimination (k_{E2}) and the unimolecular decarboxylation (k_{decar}) rates, which is shown in Figure 11. The slopes of cases I and II (relatively small amount of initiator) are identical within experimental error, while that of case III (relatively large amount of initiator) is larger than those of cases I and II. As the reaction temperature increases for the three EC/KOH = 1000/1 cases (cases I, IV, and V), the slope increases, indicating that raising the temperature raises the elimination rate relative to the bimolecular cleavage rate.The bimolecular elimination rate constant was found to obey the Arrhenius relationship, $k_{E2}/(k_{E2} + k_{decar}) = A \exp(-E^{\ddagger}/RT)$ ($r^2 = 0.991$), and the apparent activation energy is ~23.9 kJ/mol.

Conclusions

Our studies show that $-OCO_2CH_2CH_2OCH_2CH_2$-OCH_2CH_2- (EC−EO−EO) is the major backbone repeat in the early stage of the ring-opening polymerization of ethylene carbonate in basic condition. These repeats can be formed by the combination of two alkylene carbon attacks and one carbonyl carbon attack by the active chain end, as shown in Scheme 2. However the carbonate content in the polymer decreased throughout the polymerization by intermoecular and intramolecular decarboxylation reactions (Scheme 3). Once all the monomer was consumed, bimolecular elimination (E2, Scheme 4) was postulated to happen. The E2 elimination reaction generates vinyl end groups.

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