Copolymerization of Carbon Dioxide and Ethyl Vinyl Ether at Subcritical and Supercritical Conditions

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ABSTRACT: The copolymerization of carbon dioxide (CO_2) and ethyl vinyl ether (EVE) at subcritical and supercritical conditions was studied in the presence and absence of an aluminum triacetylacetonate [$Al(acac)_3$] catalyst. The experiments took place at 313–423 K and 4–15 MPa and for reaction times of 12–120 h. We confirmed that CO_2 could copolymerize with EVE with or without the $Al(acac)_3$ catalyst, regardless of whether the vessel wall material was Teflon or stainless steel. With the $Al(acac)_3$ catalyst, a maximum yield of 3.2% polymer was obtained at 338 K, 6 MPa, and 45 h. The maximum value of the average CO_2 fraction was about 50% (100% of the theoretical) at 338 K, 15 MPa, and 45 h. Results confirmed the mechanism and pathways proposed earlier by Soga et al. (1973). There was a trade-off between yield and the CO_2 fraction incorporated into the polymer as conditions changed from subcritical to supercritical. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3167–3174, 2003

Key words: copolymerization; catalysts; phase behavior

INTRODUCTION

Scientists have found new uses for carbon dioxide in polymer–nematic liquid crystal composite films,[1] polycarbonates,[2] and environmentally friendly polymer syntheses.[3–5] As CO_2 is a cheap and abundant carbon source, effective methods for the incorporation of CO_2 into new and existing products will depend on the number of possible reaction routes that polymer chemists have at their disposal. One method for the effective use of CO_2 is through copolymerization reactions.

Copolymerization of carbon dioxide with various monomers has attracted attention in the literature, as reviewed by Scholsky.[6] Inoue et al.[7] reported many early studies on the copolymerization of CO_2 and alkylene oxides in the presence of organometallic catalysts to form copolymers of polycarbonate. Jung et al.[8] studied the copolymerization of CO_2 and polypropylene oxide with an aluminum porphyrin system. Ree et al.[9] reported that the copolymerization of CO_2 and propylene oxide occurred with a zinc glutarate catalyst to give poly(propylene oxide). The success of these studies depended not only on the use of a suitable catalyst but also on the effective use of the activity of the monomer to drive the reaction. Numerous monomers have been copolymerized with CO_2,[10–17] but few reports exist on the copolymerization of CO_2 and simple compounds.

Soga and coworkers[18–19] found that vinyl compounds can copolymerize with CO_2 under the influence of suitable catalysts. They also reported that CO_2 copolymerizes with dienes (1,3-butadiene and 2,3-dimethyl-1,3-butadiene), apparently without a catalyst.[19] Typical reaction conditions of their study were mild, at 2–7.5 MPa and 330–490 K, which gave relatively low yields.[18,19] After a review of Soga's research, it became apparent that there still remained some points that are important for applied polymer research. The first point was brought up by various researchers on whether the stainless steel reactors used by Soga et al. could have served as a catalyst for cases where a reaction in the absence of catalyst was observed.[20] The second of these points was brought up in the review by Scholsky[6] and could be stated simply as whether manipulation of conditions, especially in the critical region, could bring about higher conversions and yields. In this work, our objective was to examine the copolymerization of CO_2 with ethyl vinyl ether (EVE) monomer in the absence and presence of a catalyst both at subcritical and supercritical conditions and to determine whether the reactor wall influenced the reaction. From our results, we provide conclusive evidence that changing the conditions of the reaction allowed manipulation of the reaction yield and the number fraction of CO_2 incorporated into the polymer and, further, that there were little or no catalytic effects of the stainless steel walls on the reaction.
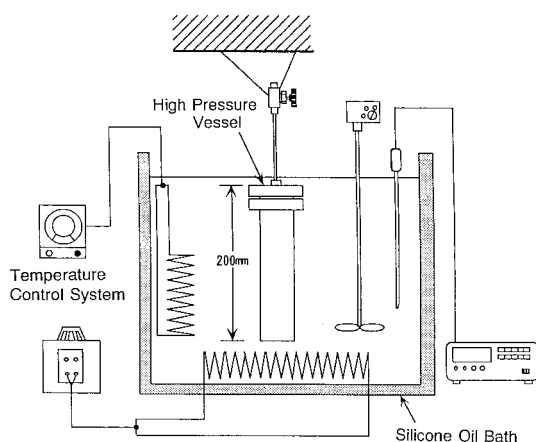
Figure 1 Schematic diagram of the experimental apparatus for polymerization.

EXPERIMENTAL

Both EVE and the catalyst, aluminum triacetylacetonate [Al(acac)$_3$], were extrapure grade and were purchased from Tokyo Kasei Co., Ltd. (Tokyo, Japan). The purity of EVE was higher than 98.0 mol %. In the experiments, EVE and Al(acac)$_3$ were used without further purification. Carbon dioxide (99.95 mol %) was supplied by Ekika Tansan Co., Ltd. (Tokyo, Japan), and was stored in a high-pressure vessel filled with reduced granular copper (40–80 mesh).

The experimental apparatus is shown in Figure 1 and consisted of a high-pressure reaction cell whose temperature was maintained with a silicone oil bath equipped with a temperature-control system. The cell was made of stainless steel (SS 304) with a height of 200 mm and an inner diameter of 40 mm (with an internal volume of about 200 cm^3) and was designed to stand up to 20 MPa of pressure. A Teflon liner was used for experiments to examine the catalytic effect of the reactor cell walls.

A high-pressure view cell, as shown in Figure 2, was used to study the reacting mixture visually. It was made of stainless steel (SS 304) with glass windows that were fused to a steel cap. The internal volume of the view cell was about 35 cm^3, and the pressure rating was about 20 MPa. Images in the cell were taken with a charade coupled device (CCD) camera and recorded onto video.

The loading of catalysts and reactants for both cells was as follows. First, CO$_2$ from a cylinder was fed into a high-pressure vessel. Next, the CO$_2$ was transferred and sent through a column of molecular sieves and filtered with a 0.5-μm filter. Catalysts (when used) and EVE monomer were added to the cell separately, the contents were frozen in liquid nitrogen, and air was removed with a vacuum (10^{-1} Pa). Then, CO$_2$ was admitted by a valve, and the entire cell and valve assembly was weighed on a 0–2 kg balance. Typical loadings for the reaction cell were 21 g of CO$_2$, 2.5 g of

EVE, and 0.1 g of catalyst. Loadings for the view cell were typically 4.2 g of CO$_2$, 0.5 g of EVE, and 0.02 g of catalyst. From the amount of CO$_2$ loaded, the pressure was calculated from the equation of state of Angus et al.[21] at given conditions with pure CO$_2$ assumed. The reaction was initiated by immersion of the vessel in the temperature bath held at the reaction temperature. After a given period of time, the vessel was removed from the bath and cooled in an ice-water bath. The unreacted CO$_2$ was slowly depressurized, and the reaction products were washed with a 0.1N hydrochloric acid–methanol (2:1) solution, extracted with diethyl ether, dried *in vacuo* overnight at 313 K, and weighed with a microbalance.

The composition of the polymers were determined with an elemental analyzer (CHN CORDER MT-5, Yanaco Co., Ltd. (Tokyo, Japan)). Product IR spectra were obtained with an IR spectrometer (FTIR-8100M, Shimazu Co., Ltd. (Kyoto, Japan)). Product NMR spectra of a 1% solution of CDCl$_3$ were measured with a 600-MHz NMR spectrometer (JNM-LA600, Nihon Denshi, Co., Ltd. (Tokyo, Japan)) at room temperature with tetramethylsilane as a standard. The molecular weights of the polymers were measured by gel permeation chromatography (GPC400, Shimazu Co., Ltd.) with a Shim-pack GPC-802 column with a refractive index detector and tetrahydrofuran as the mobile phase. Calibration plots for molecular weight were made on the basis of polystyrene standards.

RESULTS AND DISCUSSION

Soga et al.[18] reported that relatively weak Lewis acidic catalysts such as Al(acac)$_3$, Al(O—iPr)$_3$, and Al(OBu)$_3$ were suitable for the copolymerization. In this study, Al(acac)$_3$ was selected as a catalyst because it gave the largest product yield in preliminary experiments. Table I summarizes all of the experimental conditions. Runs 1–21 and 24 were made with catalyst. Runs 22, 23, and 25–27 were made in the absence of catalyst, and runs 24–27 were made with a Teflon-lined reaction cell.

Phase behavior

To confirm homogeneous reaction phase conditions, we observed the phase behavior of mixtures of EVE,
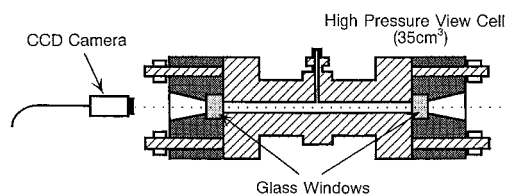
Figure 2 Schematic diagram of the experimental apparatus for phase behavior observation.

TABLE I
Experimental Conditions and Results for CO$_2$–EVE Copolymerization

Run No	T [K]	P [MPa]	Time [h]	EVE [g]	Al(acac)$_3$ [g]	CO$_2$ [g]	Yield [%]	x
1	338	6	13	2.490	0.118	24.80	1.75	0.121
2	338	6	24	2.600	0.116	24.80	1.99	0.214
3	338	6	36	2.490	0.124	24.80	2.57	0.232
4	338	6	45	2.510	0.117	24.00	3.16	0.361
5	338	6	72	2.723	0.108	24.20	2.08	0.424
6	338	6	96	2.687	0.108	25.20	1.88	0.428
7	338	6	120	2.692	0.112	23.80	1.82	0.451
8[a]	313	6	45	2.550	0.105	29.95	0.70	0.455
9[a]	323	6	45	2.734	0.104	27.01	0.85	0.386
10	353	6	45	2.651	0.105	25.01	2.54	0.332
11	368	6	45	2.583	0.103	24.29	2.38	0.272
12	383	6	45	2.580	0.105	22.07	2.07	0.243
13	398	6	45	2.705	0.105	18.93	1.93	0.216
14	413	6	45	2.653	0.104	17.88	1.93	0.188
15	423	6	45	2.590	0.112	16.44	1.94	0.157
16	338	4	45	2.698	0.105	14.98	0.92	0.308
17	338	7	45	2.713	0.107	31.02	2.50	0.375
18	338	8	45	2.679	0.110	37.58	1.74	0.379
19	338	10	45	2.732	0.108	53.40	1.51	0.415
20	338	12	45	2.745	0.108	78.72	1.25	0.450
21	338	15	45	2.520	0.107	120.64	0.85	0.482
22	338	6	45	2.728	—	25.53	1.14	0.338
23	338	6	45	2.590	—	25.55	1.67	0.310
24[b]	338	6	45	2.678	0.108	25.13	1.84	0.334
25[b]	338	6	45	2.695	—	25.49	0.91	0.342
26[b]	338	6	45	2.682	—	25.13	0.80	0.314
27[b]	338	6	45	2.678	—	25.97	0.90	0.325

T = temperature; P = pressure.
[a] Reaction at the vapor–liquid equilibrium phase condition.
[b] Reaction with a Teflon-lined cell.
[c] Yield is defined as g of polymer/g of EVE × 100%.

catalyst, and CO$_2$ in the high-pressure view cell and performed vapor–liquid equilibrium calculations with an equation of state. The catalyst, Al(acac)$_3$, was a crystalline solid. According to visual observations at 94 mol % CO$_2$ (catalyst-free base), the solution was homogeneous at 338 K and 6 MPa. This was also confirmed by the calculation of the phase behavior of the CO$_2$ + EVE system with the Soave–Redlich–Kwong (SRK) equation of state,[22] as shown in Figure 3. The binary interaction parameter (k_{12}) was estimated to be approximately 0.125 according to generalized correlations,[23] which were based on CO$_2$/n-paraffin systems. Because the reaction mixtures of this study were very rich in CO$_2$, the effect of k_{12} on the calculated results was small.

The range of the experimental conditions of this study were also overlaid onto the calculated phase behavior of CO$_2$–EVE, as shown in Figure 3. From the calculations, the initial conditions of each experiment could be expected to be homogeneous, although the effect of the catalyst on the reaction mixture was not considered. As shown in Figure 3, typical reaction conditions were those of a superheated vapor phase. Reaction conditions at higher pressures (10–15 MPa) were at supercritical conditions (runs 19–21 in Table
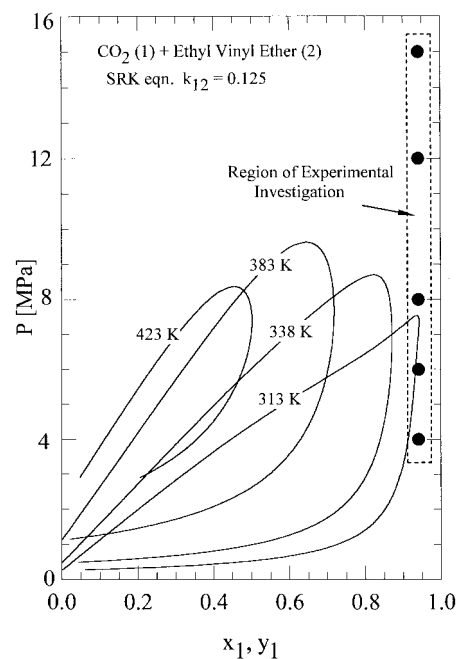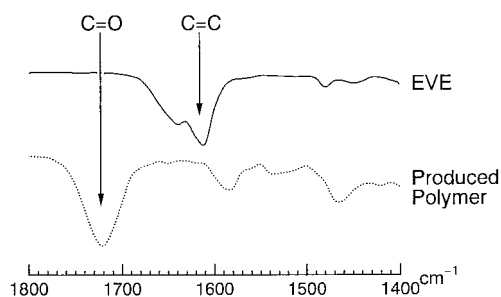

Figure 3 Calculated high pressure vapor–liquid equilibria of the CO$_2$–EVE system and the experimental range of the copolymerization.

Figure 4 IR spectra of EVE and the product polymer. Reaction conditions: 338 K, 6 MPa, and 45 h (run 4).

I). However, reaction conditions for runs 8 and 9 were within the region of vapor–liquid equilibrium, and therefore, these two runs proceeded under heterogeneous phase conditions. Experimental densities varied from $100–600$ kg/m^3.

Product analysis

Typical IR spectra of EVE and the product polymer are shown in Figure 4. In the spectrum, the characteristic absorption peak near 1630 cm^{-1} due to the C=C bond of EVE almost disappeared, and a strong peak near 1730 cm^{-1} due to the C=O bond appeared. Thus, the copolymerization of CO_2 and EVE took place at the experimental conditions. However, from the IR spectra, it was not easy to determine whether the carbonyl stretch belonged to the ester or ketone. Soga et al.[19] found that the carbonyl belonged mainly to the ketone from NMR analysis for CO_2–methyl vinyl ether copolymers and proposed a reaction mechanism for the copolymerization. Following Soga et al., we used NMR and concluded that the carbonyl belonged to the ketone group for the CO_2–EVE copolymers. The NMR spectra of the produced polymer at 338 K and 6 MPa is shown in Figure 5. Peaks b, d, f, h, i, j, k, and l could be assigned to each corresponding proton, as shown in Figure 5, whereas the spectra for protons a, c, e, and g could not be specified. From peaks d, i, j, and k, we concluded that the ketone group existed in the product copolymer and not in the ester group. The spectra had characteristic peaks very similar to those of the copolymer of methyl vinyl ether and CO_2 reported by Soga et al.[19]

For the copolymerization of CO_2 and EVE, the reaction can be expressed as follows:


$$(1)$$
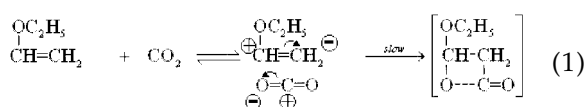
where the carbocation was probably the result of electron delocalization caused by the high local density of carbon dioxide. Soga et al.[19] proposed formation of a

four-member ring, β-lactone, that would most likely would be unstable. Equation (2) shows the random copolymerization of the probable β-lactone intermediate and the EVE homopolymer, following the work of Soga et al.:[19]


$$(2)$$
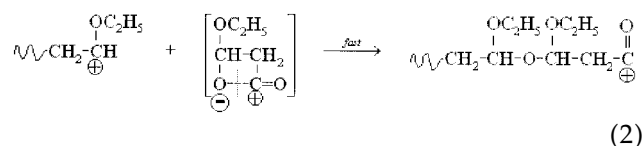
The homopolymerization of EVE could also occur through reaction of the EVE monomer with the carbocated species as shown by eq. (3):


$$(3)$$
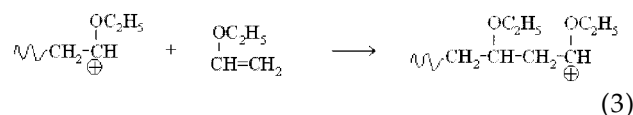
These detailed mechanisms were suggested by Soga et al.,[19] who did numerous detailed experiments, but their existence, for example, of the β-lactone intermediate, has not been confirmed.

The molecular weight distributions from GPC analysis are shown in Figure 6 for the copolymer obtained from the reaction at subcritical conditions (338 K, 6 MPa, and 45 h) and supercritical conditions (338 K, 15 MPa and 45 h reaction time). A bimodal molecular weight distribution was observed for copolymers obtained at other experimental conditions. The reaction products consisted of a large amount of lower molecular weight (200–600) materials and a small amount of higher molecular weight (1000–2000) materials as judged by the peak areas.

The molecular weight distributions, as shown in Figure 6, were different between the subcritical and supercritical conditions. Although the initial stages of the reaction could not be measured with this apparatus, we imagined that the reaction was not reversible and that there was a balance between polymer propagation and polymer decomposition. In the initial
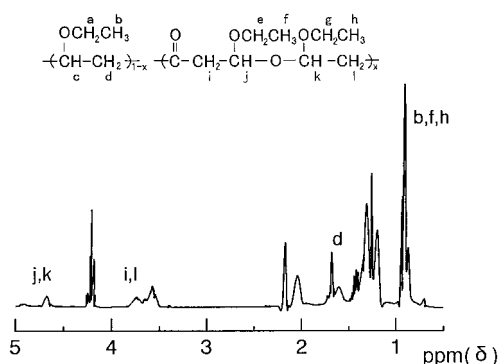
Figure 5 NMR spectra of the product polymer. Reaction conditions: 338 K, 6 MPa, and 45 h (run 4).
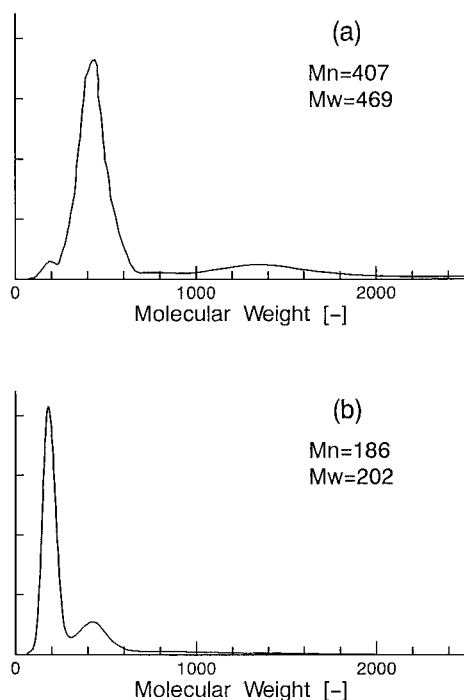
Figure 6 Molecular distribution of the produced polymer under (a) subcritical conditions of 338 K, 6 MPa, and 45 h (run 4) and (b) under supercritical conditions of 338 K, 15 MPa, and 45 h (run 21).

stage, possibly a small amount of high-molecular-weight polymers were formed. The amount of these higher molecular weight polymers was probably very small because of the progressively slower reaction rate. As time proceeded, decomposition of the polymer probably became favored, and as a result, many oligomers were produced. In this sense, we could say that the EVE–EVE copolymer seemed to be less stable than the EVE–CO₂ copolymer . This analysis was supported further by the average CO₂ fraction, which reached 100% of the theoretical value (i.e., 50% CO₂ content in the polymer).

The average molecular weight of the copolymer was generally in the range of 200–700 under the experimental conditions, which was of the same order of magnitude as the copolymer produced by Soga et al.[18,19] The average molecular weight decreased as the system pressure increased, which probably means that the decomposition of the produced copolymers became dominant as compared with the polymer propagation reactions at high-density conditions. It might be more appropriate to express the produced copolymers as oligomers, in view of the values of the molecular weights and molecular weight standards. However, to allow a convenient comparison with the study of Soga et al.,[15,16] we expressed the reaction products as copolymers.

IR, NMR, and elemental analyses confirmed that the copolymerization reactions proceeded according to

the mechanism proposed by Soga et al.[16] and resulted in polymers containing ether and ketone linkages. As pointed out by Soga et al.[16] and Scholsky[6] and also as understood from eqs. (2) and (3), the chemical formula of the copolymer was deduced to be

$$\{(CO_2)_x(C_4H_8O)_{(1-x)}\}_n \tag{4}$$
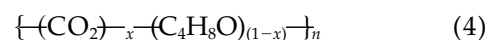
where n is the polymerization degree and x is the average fraction of CO₂ incorporated into the polymer by the reaction of eq. (3) in the monomer unit. In interpreting the figures, one should note that x represents a fraction between 0 to 1, and therefore, a 50% CO₂ content ($x = 0.5$) would give a monomer unit with a molecular weight of 59. If the monomer unit can be expressed by eq. (4), the following material balance constraints should hold for the three elements, C, H, and O, according to the elemental analysis data:

$$E_C/M_C = [4(1 - x) + x]/MM \text{ for C} \tag{5}$$

$$E_H/M_H = 8(1 - x)/MM \text{ for H} \tag{6}$$

$$E_O/M_O = [(1 - x) + 2x]/MM \text{ for O} \tag{7}$$

where E is the elemental analysis data of weight fraction, M is the atomic weight of the element, and MM is the molecular weight of monomer unit in Eq.(4). MM can be expressed as follows:

$$MM = 72 - 28x \tag{8}$$

Equations (5)–(7) can be used to determine the value of x in eq. (4). In the evaluations, the x values were determined from each of the equations, and then, the values were averaged. The obtained x values are given in Table I. The x values were derived from the assumption of an average molecular structure for the copolymer expressed by eq. (4).

Effect of reaction conditions

Time

The effect of reaction time on the product yield and the CO₂ fraction of in the monomer unit obtained for the reaction at 338 K and at 6 MPa is shown in Figure 7. The product yield increased with increasing reaction time up to 45 h, and then, it tended to decrease slightly. The maximum yield of the product based on EVE was estimated to be about 3%. As the copolymerization proceeded, the reaction phase probably became heterogeneous, which could be considered one of the reasons for the low yield of the reaction. However, the CO₂ fraction in the monomer unit increased with increasing reaction time up to 70 h, and then, it approached a constant
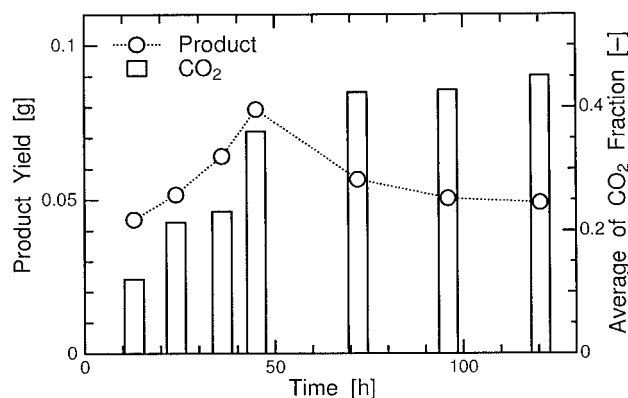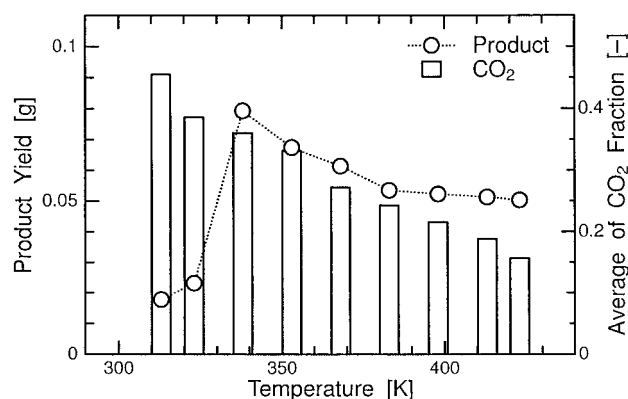
Figure 7 Effect of the reaction time on the product yield and average CO_2 fraction in the monomer unit at 338 K and 6 MPa.

Figure 9 Effect of the reaction pressure on the product yield and the CO_2 fraction in the monomer unit at 6 MPa and 45 h.
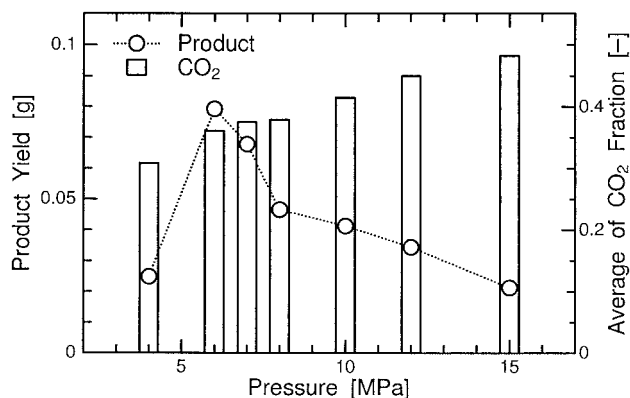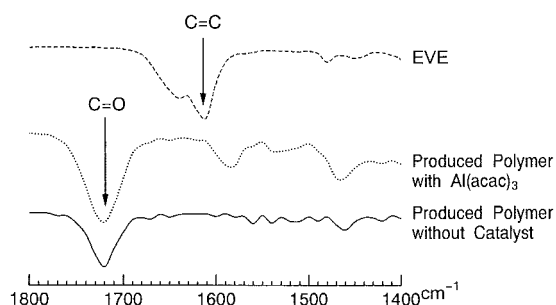
value. This could be explained as follows: it is known through many early studies that EVE homopolymer easily decomposes at higher temperatures.[24] Thus, the homopolymerized part of EVE in the monomer unit probably underwent selective decomposition at reaction times greater than 70 h.

Temperature

The effect of reaction temperature on the product yield and the CO_2 fraction is shown in Figure 8 for the reaction at 6 MPa and 45 h. At lower temperatures, the reaction rate was slow, which led to a low reaction yield. As the temperature increased, a maximum in the product yield was observed at around 338 K. However, the average CO_2 fraction in the monomer unit monotonically decreased. This was evidence that the EVE homopolymerization was faster than the rate of β-lactone formation at these conditions. At temperatures higher than 338 K, both the product yield and average CO_2 fraction decreased, which allowed us to

conclude that there was either decomposition of the EVE homopolymer part or the EVE–CO_2 complex in eq. (1).

Pressure

Figure 9 shows the effect of pressure on the product yield and average CO_2 fraction in the monomer unit for the reaction at 338 K and 45 h. As pressure increased, a maximum in the product yield was observed at around 6 MPa. The average CO_2 fraction in the polymer monotonically increased. In terms of eqs. (1) and (2), this means that the rate of β-lactone formation became comparable with the rate of EVE homopolymerization or that the rate of EVE homopolymerization was greatly retarded. A possible way to explain this effect at higher pressures (densities) is through the cage or clustering effect, as proposed by some authors.[25–27] In other words, higher pressures would lead to higher concentrations of CO_2 and higher local concentrations. Especially in the supercritical region, local density enhancement has been observed around solvated species by Wada et al.[28] or around excited complexes, which was clearly shown to have dramatic effects on reaction rates by Aizawa et al.[29] The incorporation of more CO_2 molecules into the polymer chain would lead to a less stable product that would be easily decomposed at atmospheric conditions or in the presence of water. Super and Beckman[30] discussed some of these factors in their review on copolymerizations with CO_2.

From the phase behavior, the reactions performed at pressures lower than 9 MPa could be considered to proceed in a superheated vapor phase, whereas those at higher pressures could be considered to proceed in a supercritical phase. The product yield had a maximum value at about 6 MPa, and the yield decreased with pressure at pressures higher than 6

Figure 8 Effect of the reaction temperature on the product yield and CO_2 fraction in the monomer unit at 6 MPa and 45 h.

Figure 10 IR spectra of EVE and the polymer produced with and without catalyst. Reaction conditions: 338 K, 6 MPa, and 45 h.

MPa. The CO$_2$ fraction in the monomer unit increased with increasing reaction pressure and was 50% at 15 MPa, which was much higher than any of the values reported by Soga et al.[19] The higher CO$_2$ fraction in the monomer unit might have been due to critical effects, as reported by several researchers, who reported higher yields for various polymerizations in CO$_2$ near the critical point.[10,11] The reason for this seems to be related to the dielectric constant of supercritical CO$_2$ and the stabilization of carbocation in supercritical CO$_2$. In this study, however, we found that the maximum product yield occurred at subcritical conditions of 338 K and 6 MPa. As discussed previously, a possible reason for this discrepancy was the selective decomposition of the polymer that could not be ignored under supercritical conditions. Because the average CO$_2$ fraction in the monomer unit at supercritical fluid conditions was higher than that at the subcritical vapor phase conditions, these results clearly show that the solvent power of CO$_2$ and the reactivity of CO$_2$ as a monomer had different temperature and density dependencies.

Catalyst and wall effects

Experiments were run with and without the catalyst and with and without the Teflon-lined reactor to confirm the reaction mechanism and possible wall effects. Typical IR spectra of the polymers obtained with and without catalyst are shown in Figure 10. In both spectra, the peak near 1630 cm^{-1} due to the C=C bond of EVE almost disappeared, and the peak near 1730 cm^{-1} due to the C=O bond appeared. So, the copolymerization of CO$_2$ and EVE also took place even in the absence of the catalyst. For both cases, the reaction products were identical. To ascertain the reproducibility of the reaction without catalyst, several experiments with the Teflon-lined reactor and without Al(acac)$_3$ were performed. In these cases (runs 25–27),

practically the same results were obtained. Product yields for the reactions without the catalyst decreased to one-half the yield with catalyst, but the CO$_2$ fractions were almost equal. Thus, the homopolymerization of EVE was mainly influenced by the catalyst. Reactions performed with the Teflon liner in the reaction cell gave product yields that were 20–30% lower than those obtained without the Teflon liner (runs 21 and 24 or runs 22–23 and 25–27). In these cases, there were no significant differences in the average CO$_2$ fraction incorporated into the polymers. Therefore, the reactor wall seemed to have little effect on the copolymerization and also on the homopolymerization of EVE.

CONCLUSIONS

Carbon dioxide copolymerized with EVE with or without the Al(acac)$_3$ catalyst. Increasing the reaction temperature decreased the yield, which could be attributed to selective polymer decomposition. Increasing the system pressure (density) decreased the yield but increased the average CO$_2$ fraction incorporated into the polymer. The maximum value of the average CO$_2$ fraction, about 50%, was much higher than the value of 23% obtained by Soga et al.

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