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Copolymerization of 1,2-Epoxycyclohexane and Carbon Dioxide Using Carbon Dioxide as Both Reactant and Solvent

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ABSTRACT: The copolymerization of 1,2-epoxycyclohexane (cyclohexene oxide, CHO) and carbon dioxide was performed using no other solvent than carbon dioxide itself. A CO_2-soluble, ZnO-based catalyst was synthesized and used to catalyze the polymerization. Polymerizations were conducted at different temperatures, pressures, and mole fractions of CHO giving rise to polymer yields as high as 69% with catalyst activities as high as 400 g of polymer/g of Zn. The best results were obtained at temperatures of 100−110 °C and at mole fractions of CHO above $X_{CHO} = 0.15$. This polymer was >90% polycarbonate with weight average molecular weights (M_w) ranging from 50 000 to 180 000.

Introduction

Recent advances involving the use of carbon dioxide to replace organic solvents have attracted attention due to environmental concerns and the interesting properties of CO_2 at high pressures. At supercritical conditions the solubility parameter, dielectric constant, and density of carbon dioxide are comparable (order of magnitude) to those of liquids, while the surface tension and viscosity are comparable to those of gases. With modifications to equipment (to accommodate pressure) CO_2 can be substituted for some organic solvents while achieving or enhancing end results. This technique has been successfully employed, in such operations as extractions[11] and emulsion/dispersion polymerizations.[2−5] In each of these cases the CO_2 acts as the extracting medium or solvent, it's advantages being high rates of diffusion and easy recovery of products.

In the literature other researchers have shown that CO_2 can be successfully used as a reactant in organic polycarbonate synthesis (Scheme 1). Cyclic carbonates and polycarbonates have been formed using CO_2 and a variety of catalyst systems, many of which are zinc-based.[6−30] The nature of these catalysts has required the use of an appropriate organic solvent to homogenize the reaction mixture, but a few examples can be found in the literature where reactions were performed in the absence of any solvent.[23−25,30] The literature contains data on a large number of catalyst systems, where the yields of copolymer were as high as 70%. Unfortunately, the catalyst activities were usually low (5−40 g of polymer/g of Zn) with the exception of Darensbourg's catalyst[30] (which gave ∼366 g of polymer/g of Zn for the 1,2-epoxycyclohexane (CHO)/CO_2 copolymerization). The catalysts Darensbourg developed include (2,6-diphenylphenoxide)$_2$Zn(diethyl ether)$_2$, (2,6-diphenylphenoxide)$_2$Zn(THF)$_2$, and (2,4,6-tri-*tert*-butylphenoxide)$_2$Zn(diethyl ether)$_n$, $n < 2$.[30] These catalysts employ mononuclear Zn(II) phenoxide derivatives with bulky substituents to enhance the activity of the Zn(II) complexes.

This work describes the use of a new catalyst based on the methylene chloride-soluble catalyst developed by ARCO (catalysts exhibit activities of ∼9 g of polymer/g of Zn)[26] but which has been modified to allow solubilization in supercritical carbon dioxide. Other researchers have shown that molecules constructed of fluoro ether, fluoroalkyl, or silicones are soluble to varying extents in carbon dioxide.[1−5,31] Therefore, a procedure for synthesizing the catalyst was devised that consists of first making a CO_2-soluble half-ester/half-acid from maleic anhydride and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanol and then reacting it with ZnO to create the active catalyst. The catalyst structure can not be specifically determined, due to an inability to isolate a single catalyst crystal, but a representative drawing of the catalyst's components is shown in Figure 1. The catalyst will absorb water from the air and lose some of its activity, but this effect has not been quantified. Anaerobic conditions were used for these reactions to obtain the best possible results in the copolymerization of CO_2 and cyclohexene oxide (CHO) to synthesize poly(cyclohexene carbonate) (PCHC), without using organic solvents. The reaction studied (Scheme 2) forms a copolymer which includes a small amount of ether repeat units and the 1:1 adduct 1,2-cyclohexene carbonate (CHC). The effects of running this reaction at various pressures, temperatures, and mole fractions of the epoxide on the yield and nature of the poly(cyclohexene carbonate) formed will be discussed.

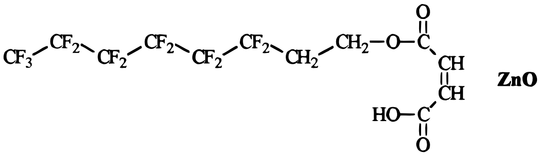

Figure 1. Fluorinated catalyst containing 8.44% Zn by wt as determined by elemental analysis.

Experimental Section

Materials. Cyclohexene oxide (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure over CaH_2. Methylene chloride (99.9% assay) and anhydrous methyl alcohol (99.9% assay) were used to separate and precipitate the reactor products (Mallinckrodt Specialty Chemicals Co., Paris, KY). Both the amine and the toluene used in the catalyst synthesis were distilled from calcium hydride. Maleic anhydride briquettes were used fresh, and the remainder were disposed of due to exposure to air. Tridecafluorooctanol (97%) was used without further purification.

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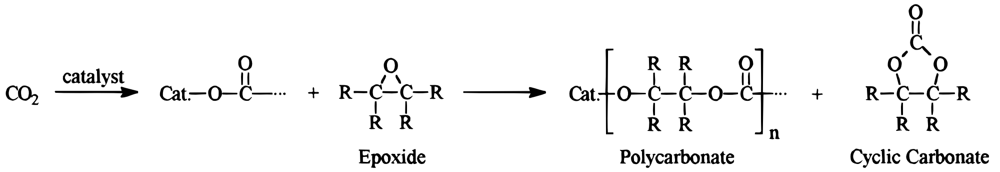
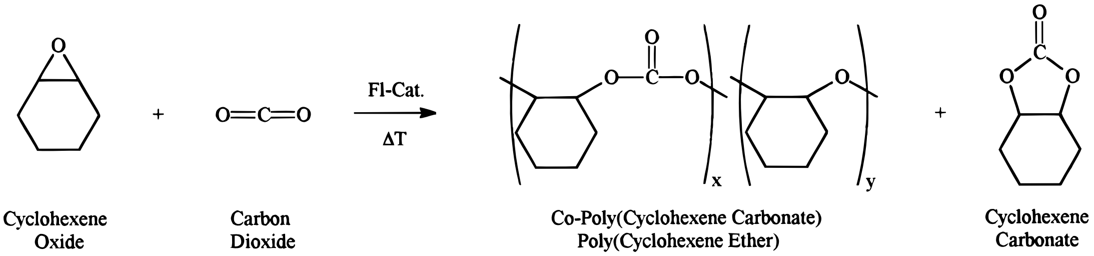
Scheme 1. Phosgene-Free Polycarbonate Synthesis Using CO_2 as a Reactant



Scheme 2. Poly(cyclohexene carbonate) from Carbon Dioxide and Cyclohexene Oxide



Supercritical grade CO_2 (Liquid Carbonic, Chicago, IL) was used after passing through a series 62, high-pressure purifier, which removes oil and water from gas and liquid systems (Liquid Carbonic). Nitrogen with 99.99% purity (Liquid Carbonic) was passed through the high-pressure purifier and then into the reactor without further purification.

Synthesis of Zn-fluoroalkyl Catalyst. A flask was charged with 8.56 g (87.3 mmol) of maleic anhydride and then flushed with N_2. The maleic anhydride was heated to 55 °C, and then tridecafluorooctanol (31.8 g, 87.3 mmol), which had been flushed with N_2, was transferred to the maleic anhydride. A solution of 0.73 mL (5.24 mmol) of triethylamine in 15 mL of toluene was next transferred to the mixture. The mixture was stirred and heated at 55 °C overnight. Upon cooling, the fluoroalkyl monoester that precipitated was isolated by vacuum filtration and vacuum dried at 50 °C overnight to recover 34 g (84% yield). The fluoroalkyl monoester was purified by recrystallizing in hexane or benzene. Analysis of the purified fluoroalkyl monoester using ^1H NMR shows peaks at 2.55 (m, 2H, $-CH_2-$), 4.57 (t, 2H, $-CH_2-O-$), 6.38 and 6.42 ppm (d, 1H, $-CH=CH-$). ^{13}C NMR shows peaks at 25 (t, 1C, $-CH_2-$), 58 (s, 1C, $-CH_2-O-$), 106−121 (m, 6C, all CF), 130 and 132 (s, 1C, $-C=C-$), 166 and 168 ppm (s, 1C, both $-C(O)-$).

Purified flouroalkyl monoester (12 g, 27.26 mmol) and zinc oxide (2.22 g, 27.26 mmol) were added to a 250 mL three-necked flask, equipped with a condenser. Both solids were flushed with N_2; then 100 mL of anhydrous 1,1,2-trichlorotrifluoroethane was transferred over the solids. The mixture was stirred and refluxed at 50 °C for 24 h. The resulting Zn-fluroalkyl catalyst was recovered by filtration with a pressure funnel. The filtrate was stripped to dryness and vacuum-dried at room temperature overnight. The Zn-fluroalkyl catalyst collected was 13.4 g (90.6% yield). Analysis of the purified Zn-fluoroalkyl catalyst using ^1H NMR shows peaks at 2.61 (m, 2H, $-CH_2-$), 4.42 (t, 2H, $-CH_2-O-$), 6.15 and 6.35 ppm (d, 1H, $-CH=CH-$). ^{13}C NMR shows peaks at 31 (t, 1C, $-CH_2-$), 57 (s, 1C, $-CH_2-O-$), 107−122 (m, 6C, all CF), 127 and 136 (s, 1C, $-C=C-$), 166 and 173 ppm (s, 1C, both $-C(O)-$).

Polymerization of Poly(cyclohexene carbonate). All reactions were performed in 50 mL autoclave type reactors (Pressure Products Industries, Warminster, PA) equipped with magnetically driven mixers. In a typical polymerization, the catalyst was weighed and placed into the reactor body and then the reactor was flushed with nitrogen. During this time, a measured amount of CHO was added to an addition piping under an N_2 atmosphere. The addition piping was then attached vertically to the reactor inlet. The ends of the addition piping were flushed with CO_2 or N_2 during the installation. CO_2 at its vapor pressure (≈850 psi at 25 °C) was then used to 'push' the CHO into the reactor. After the injection of monomer, the reactor was isolated and brought to the reaction pressure and temperature, a process which lasted 30−45 min. After the reaction was completed, the liquid and solid reactor contents were collected using methylene chloride.

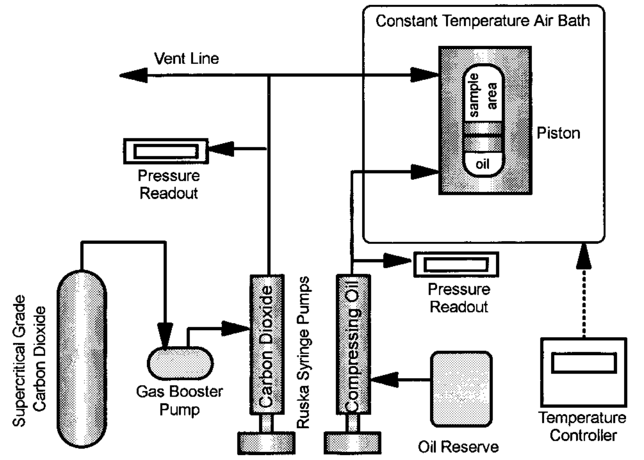


Figure 2. D. B. Robinson high-pressure, variable volume view cell.

Purification of Products. The reaction products dissolved in methylene chloride were filtered, and then the solvent was removed under vacuum. The reaction products were then dried in vacuo and weighed to determine the "crude" yield. The reaction products were further purified by reprecipitation from methylene chloride into methanol to obtain a methanol-soluble (low molecular weight) and a methanol-insoluble (high molecular weight) product.

Characterization of Polymers. Polymer molecular weights were measured using gel permeation chromatography (GPC; Waters 150CV) and polystyrene standards. THF, at a flow rate of 1.0 mL/min (35 °C), was used as mobile phase solvent. The instrument was equipped with ultrastyragel columns with pore sizes of 10^4, 10^3, 500, and 100 Å in series. The fraction of polycarbonate repeat units was determined using a Bruker MSL 300 NMR instrument.

Phase Behavior Determination. The phase behavior of the reaction mixtures was observed in a variable volume, high-pressure view cell (D. B. Robinson and Assoc., Edmonton, Alberta, Canada), a simplified schematic of which is shown in Figure 2. In a typical bubble point behavior experiment, the sample area of the cell is loaded with the desired volume of CHO and then the cell is sealed and heated to the desired operating temperature. Once the desired temperature is achieved, a measured quantity of CO_2 at 2000 psig and room temperature (~23 °C) is added isothermally and isobarically. Once the desired amount of CO_2 is added, the cell pressure is increased to 6000 psig. The cell is mixed for 20 min at 6000 psig to achieve equilibrium of the cell contents. Next, the cell pressure is lowered until the bubble point is observed.

When the mole fraction of CHO was decreased to below the critical point of the mixture for a particular temperature, the phase behavior of the mixture changed from a bubble point to

Table 1. Poly(cyclohexene carbonate) Synthesized at Various Temperatures[a]

T (°C)	X_{CHO}	% carb (NMR)	M_w ($\times 10^{-3}$) (GPC)	M_w/M_n (GPC)	turnover (g of polymer/ g of Zn)
60	0.12	58			1.30
70	0.12	92	120	27	41.1
80	0.15	81	299	13	146
80	0.14	89	109	5.8	116
90	0.16	87	114	6.6	61.5
90	0.16	80	104	5.0	0.53
100	0.18	95	174	14	203
100	0.17	93	109	6.4	457
110	0.18	97	195	12	328
110	0.17	96	68.1	4.2	440
120	0.20	94	57.9	3.7	411
130	0.20	87	43.4	3.0	307
172	0.24	29	9.8	2.4	15.8

[a] Conditions: $P = 2000$ psig; $t = 24$ h; $N_{\mathrm{Zn}}/N_{\mathrm{CO}} = 3.3 \times 10^{-3}$.

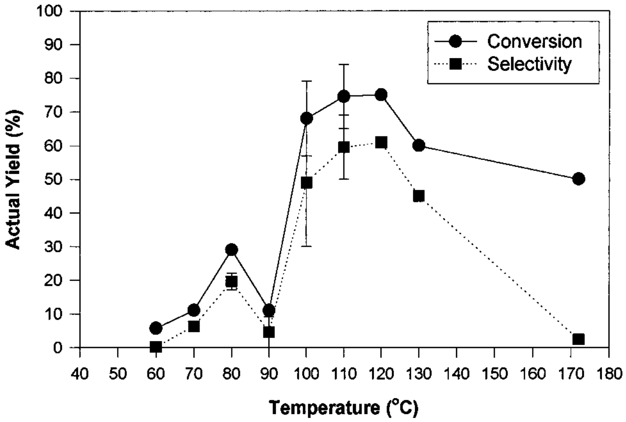


Figure 3. Effect of temperature on conversion and selectivity. Conditions: $P = 2000$ psig; $t = 24$ h; $N_{\mathrm{Zn}}/N_{\mathrm{CHO}} \sim 3 \times 10^{-3}$.

a dew point at the phase boundary. When a dew point is reached tiny droplets of liquid "dew" form throughout the solution, clouding it drastically, and then very slowly settle forming a tiny drop of a second phase at the bottom of the cell. When observing a dew point the pressure in the cell was dropped very slowly until the droplet formation and subsequent settling was observed; this point was labeled the dew point pressure. By noticing when the phase behavior changed from forming bubble points to dew points, the critical point of the mixture could be located.

Results and Discussion

Poly(cyclohexene carbonate) was synthesized at different polymerization temperatures, while keeping the pressure and catalyst to monomer ratio (mol of Zn:mol of CHO) constant, to determine the effects on the polymer product. Each reaction was run for 24 h to ensure that equilibrium conditions were reached. The reactor volume is unchanging, though, and the same volume of CHO was used throughout this series. Therefore, the mole fraction of CHO increases as the temperature increases, as shown in Table 1. The effect of reaction temperature is shown in Figure 3. In the figure the solid line depicts the percent of the theoretical weight that was formed by all products, both MeOH-soluble and- insoluble, while the broken line shows the percent of the theoretical weight that is MeOH-insoluble polymer. Those reactions which were repeated to test the validity of the depression at 90 °C are designated on Figure 3 by data with error bars, where the error bars represent the high and low value of two runs.

In Table 1 the polymer yield is presented as g of polymer/g of Zn, showing values ranging from 1.3 at 60 °C to over 400 at 100−120 °C. In comparison, previous zinc-based catalysts for the formation of polycarbonate from epoxides generally gave ~5−370 g of polymer/g of Zn.[6−30] For the copolymerization of cyclohexene oxide and CO_2, Kuran[29] was able to achieve 74.5% conversion with 70% selectivity using a diethylzinc-based homogeneous catalyst, and Darensbourg[30] achieved yields of 300−366 g of polymer/g of Zn. Also shown in Table 1 is the tendency for the catalyst to produce MeOH-soluble products at higher temperatures. In general, as the temperature is increased past the optimum, the conversion remains high but the percentage of MeOH-soluble products increases (the molecular weight decreases). This behavior has been observed by others during the copolymerization of CO_2 and propylene oxide (epoxypropane).[15,19,23,29]

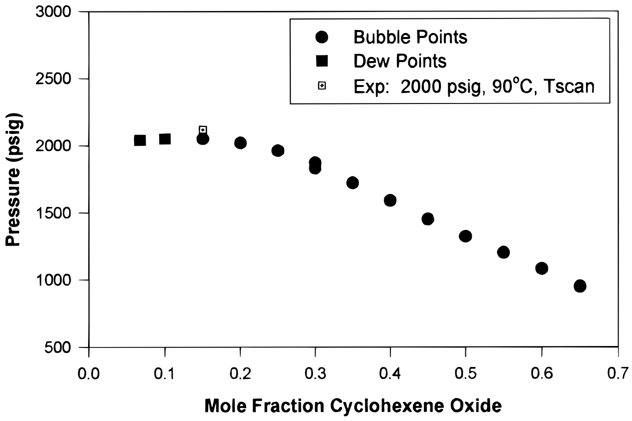


Figure 4. Phase behavior of cyclohexene oxide and CO_2 at 90 °C.

An unexpected result is the depression in yields at 90 °C. Figure 4 shows the phase behavior of CHO/CO_2 mixtures at 90 °C, showing that the experiment run at 90 °C is close to both the liquid−vapor phase boundary and the critical point of the CHO−CO_2 mixture. A reaction environment under these conditions would involve large variations in local concentrations and density even though the global concentration and density are constant. These conditions could affect the reaction in some way to decrease the product yields. However, the high rate of mixing should provide favorable mass transport, regardless of the phase behavior. Thus, it is not certain as to why the depression at 90 °C occurs.

In a separate series of reactions the pressure was varied while the temperature remained constant at 109−110 °C and the polymerization time was set at 24 h. Again, the same volume of CHO and weight of catalyst were used for each reaction, and thus the mole fraction of CHO decreased with increasing pressures as shown in Table 2. Figure 5 shows the yield as a function of the changing pressure. The data with error bars are reactions that were repeated to test the validity of the unexpected yield depression at 4000 psig. It does not appear likely that the depression at 4000 psig is due to the phase behavior in this set of experiments. Figure 6 shows the phase behavior of CHO/CO_2 mixtures at 110 °C, as well as points (open circles and squares) which indicate the pressure and composition of polymerizations performed, and shows that the run at 4000 psig is not close to a CHO/CO_2 phase boundary. Although the yield depression shown at 4000 psig can not be explained from what we know about the phase behavior of this system, the general trend of decreasing yields for the experiments run at 3000, 4000, and 5000

Table 2. Poly(cyclohexene carbonate) Synthesized at Different Pressures[a]

P (psig)	X_{CHO}	% carb (NMR)	M_w ($\times 10^{-3}$) (GPC)	M_w/M_n (GPC)	turnover (g of polymer/ g of Zn)
1000	0.20	86	59.1	3.7	329
2000	0.10	91	60.4	5.4	408
3000	0.064	83	64.3	3.7	297
3000	0.064	92	66.2	4.9	254
4000	0.050	89	53.0	3.5	114
4000	0.050	96	60.8	4.1	115
5000	0.047	87	37.0	1.9	229

[a] Conditions: $T = 109-110$ °C; $t = 24$ h; $N_{Zn}/N_{CO} = 3.3 \times 10^{-3}$.

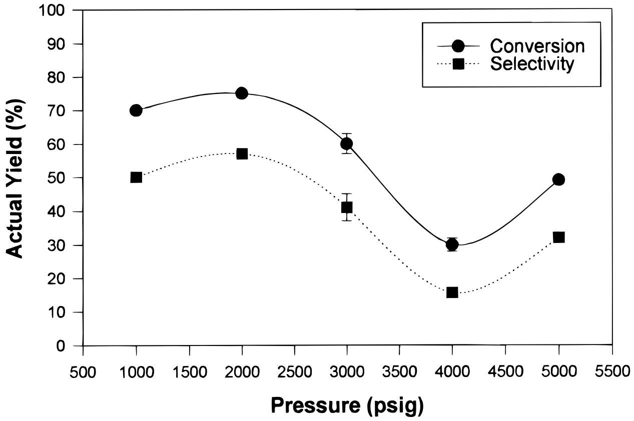


Figure 5. Effect of pressure on conversion and selectivity. Conditions: $T = 109-110$ °C; $t = 24$ h; $N_{Zn}/N_{CHO} \sim 3 \times 10^{-3}$.

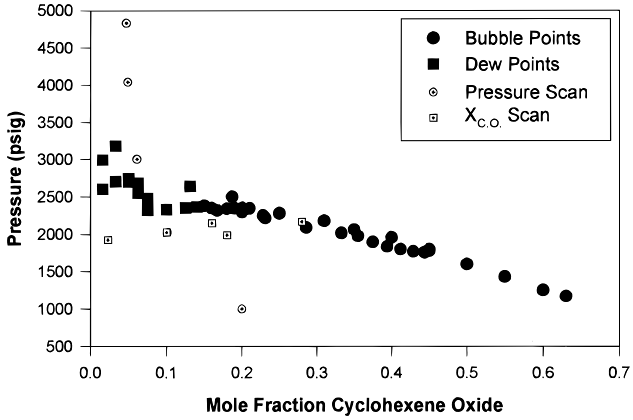


Figure 6. Phase behavior of CO−CO_2 mixtures at 110 °C.

psig can be partially explained by the fact that the product yields apparently decrease as the mole fraction of CHO decreases. This behavior is illustrated by Figure 7, which shows the product yields as a function of changing mole fraction.

Here, a series of five reactions were run at varying mole fractions of CHO to study the effect on the reaction products. These reactions were run for 24 h at a constant pressure of 2000 psig and a constant temperature of 109−110 °C. The catalyst to monomer ratio (mol of Zinc:mol of CHO) was again kept constant. Table 3 shows the characterization results of the polymer product from this series. In this series of reactions, *only* the mole fraction of CHO was varied.

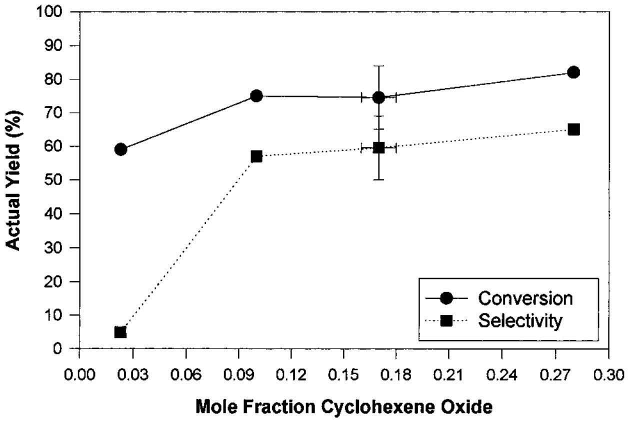


Figure 7. Effect of the CHO to CO_2 ratio on conversion and selectivity. Conditions: $P = 2000$ psig; $t = 24$ h; $T = 109-110$ °C; $N_{Zn}/N_{CHO} \sim 3 \times 10^{-3}$.

Table 3. Poly(cyclohexene carbonate) Synthesized at Various CO to CO_2 Ratios[a]

X_{CHO}	% carb (NMR)	M_w ($\times 10^{-3}$) (GPC)	M_w/M_n (GPC)	turnover (g of polymer/ g of Zn)
0.30	96	106	3.3	421
0.18	97	195	12	328
0.17	96	68.1	4.2	440
0.10	91	60.4	5.4	408
0.022	65	21.6	1.8	35.0

[a] Conditions: $T = 109-110$ °C; $P = 2000$ psig; $t = 24$ h; $N_{Zn}/N_{CO} = 3.3 \times 10^{-3}$.

Figure 7 shows the yields of products as a function of the mole fraction between 0.28 and 0.023. As mole fraction of CHO decreases below 0.10, the yield of MeOH-insoluble polymer drops significantly, although the overall yield of material is affected only slightly. This could be due to the poorer solvating power of the monomer mixture at low mole fractions of CHO. The CO_2−CHO system may require certain cosolvent properties (a large enough solvating power for reactants, catalyst, and products) in order for good yields of high polymer to be achieved. When the required cosolvent properties are not met, due to a large excess of CO_2, the reaction system produces MeOH-soluble products rather than the desired polycarbonate high polymer. This characteristic seems to be caused by a low mole fraction of CHO rather than from operating in the two-phase region. If X_{CHO} is high enough ($X_{CHO} \geq 0.15$), reactions performed in the two-phase region will still result in good yields of high polymer.

The percentage of carbonate repeat units in the MeOH-insoluble polymer was determined by ^1H NMR spectroscopy. The proton NMR results are consistent with a polycarbonate homopolymer which contains a small percentage of polyether linkages. Figure 8 shows a representative NMR of the purified, MeOH-insoluble product synthesized at 2000 psig and 80 °C. The peaks (a = 4.8 ppm, s; b = 3.5 ppm, s) can be attributed as follows, while the other peaks present on the NMR are attributable to the protons present on the cyclohexane ring. By integrating the NMR spectra and comparing the areas under peaks a and b, the percentage of carbonate linkages can be determined. Tables 1−3 show the NMR results for the three reaction series and show that the polymer with ~90% carbonate linkages is formed over a wide range of temperatures and pressures. The polymer with a low percentage (≤65%) of carbonate repeat units is formed at either very high temperatures (172 °C), very low temperatures (60 °C), or low mole fraction of CHO ($X_{CHO} = 0.023$).

Gel permeation chromatography (GPC) was used to characterize the MeOH-insoluble products via comparison with polystyrene standards. Tables 1−3 report the

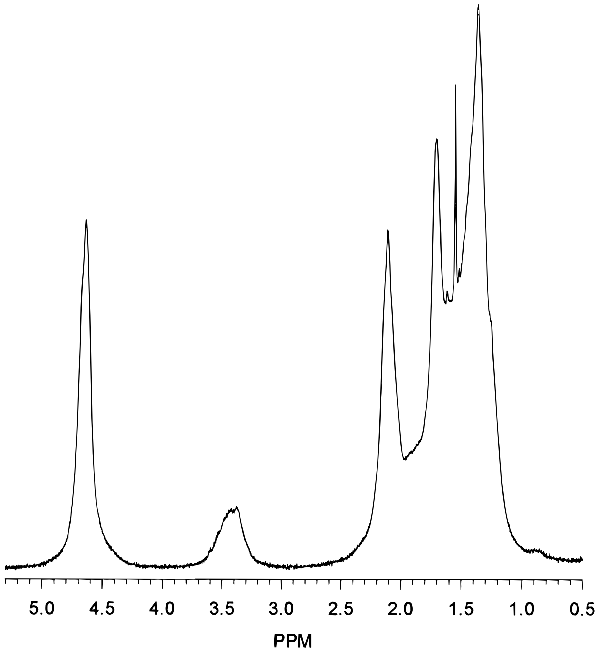


Figure 8. ^1H NMR peak assignments for CO_2−CHO copolymer.

polymer's weight average molecular weight (M_w) as well as the polydispersity index. As the tables show, polymers between 50 000 and 150 000 M_w were generated at a variety of temperatures and pressures. The broad polydispersity indexes are thought to be caused by different rates of initiation of the Zn species. Due to an inability to obtain a single catalyst crystal, nothing could be learned about its structure, but it is assumed that when the ZnO complexes to the monoester it forms multiple active species which initiate at different rates, leading to a broader range of molecular weights than would be obtained if only one species was present.

Conclusions

A system for synthesizing polycarbonate from epoxides, which uses a CO_2-soluble catalyst and CO_2 as a reactant and the only solvent, can produce high polymer at high turnover rates. Polycarbonates containing >90% polycarbonate linkages with weight average molecular weights of 50 000−150 000 are obtained. Although the effects of pressure seem to point to 2000 psig and 110 °C as the best conditions for this polymerization, further studies operating in other regimes of the phase diagram might prove enlightening. The zinc-based, CO_2-soluble catalyst system shows 1 order of magnitude higher turnovers than previously reported, and the catalyst has high selectivity toward polymer under certain conditions. More work needs to be done to fully understand this system, especially in the area of phase behavior. In a system where CO_2 is both reactant and solvent, the phase behavior of the system can influence the results, and this influence needs to be completely understood to determine the best operating conditions for this synthesis.

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