

COPOLYMERIZATION OF 1,2-EPOXY CYCLOHEXANE AND CARBON DIOXIDE USING CO₂ AS BOTH REACTANT AND SOLVENT

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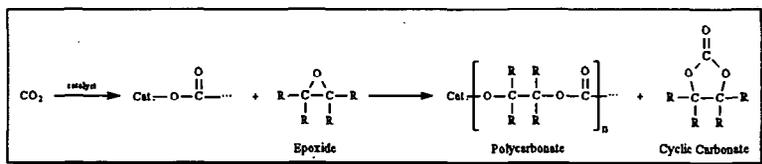
ABSTRACT

The copolymerization of 1,2-epoxy cyclohexane (cyclohexene oxide; CHO) and carbon dioxide was performed using no other solvent than carbon dioxide itself. A CO₂-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 polymer/g Zn. The best results were obtained at temperatures from 100-110°C and at mole fractions of CHO above X_{CO₂}=0.15. This polymer was >90% polycarbonate with weight average molecular weights (M_w) ranging from 50,000-180,000.

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 CO₂ at high pressures. At supercritical conditions the solubility parameter, dielectric constant and density of carbon dioxide are all comparable to that of liquids, while the surface tension and viscosity are comparable to gases. With modifications to equipment (to accommodate pressure) CO₂ can be substituted for some organic solvents while achieving or enhancing end results. This technique has been successfully employed, in such operations as extractions¹ and emulsion/dispersion polymerizations.^{2,3} In each of these cases the CO₂ acts as the extracting medium or solvent, its advantages being high rates of diffusion and easy recovery of products.

In the literature other researchers have shown that CO₂ can be successfully used as a reactant in organic polycarbonate synthesis (Scheme 1). Cyclic carbonates and polycarbonates have been formed using CO₂ and a variety of catalyst systems, many of which are zinc-based.⁴⁻³⁰ The nature of these catalysts has required use of an appropriate organic solvent to homogenize the reaction mixture,



Scheme 1: Phosgene-Free Polycarbonate Synthesis Using CO₂ as a Reactant

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 polymer/g Zn) with the exception of Darenbourg's catalyst³⁰ (which gave ~366 g polymer/g catalyst for the CHO/CO₂ copolymerization). The catalysts Darenbourg developed include (2,6-diphenylphenoxide)₂Zn(diethyl ether)₂, (2,6-diphenylphenoxide)Zn(THF) and (2,4,6-tri-*tert*-butylphenoxide)₂Zn(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 catalysts developed by ARCO²⁵, but which has been modified to allow solubilization in supercritical carbon dioxide. Other researchers have shown that molecules constructed of fluoroether, fluoroalkyl or silicones are soluble to varying extents in carbon dioxide.^{1-5,31} Therefore, the procedure for synthesizing the catalysts consists of taking the half-ester of maleic anhydride and attaching a CO₂-soluble tail, by way of a hydrocarbon spacer. Allowing the synthesized molecule to complex with ZnO creates the active catalyst. The catalyst structure can not be specifically determined, due to the catalyst's inability to crystallize, but a representative drawing of the catalyst's molecular formula is shown in Figure 1.

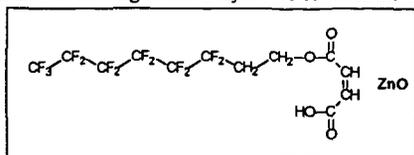
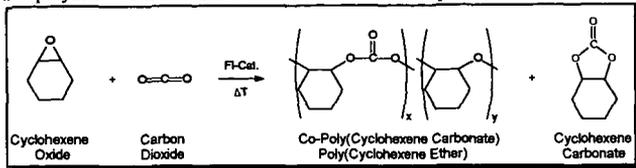


Figure 1: Fluorinated Half-Ester Complexed with ZnO (8.44% Zn by weight)

This work will explore the copolymerization of CO₂ and cyclohexene oxide (CHO) to synthesize polycyclohexene 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-



Scheme 2: Polycyclohexene Carbonate from CO₂ and Cyclohexene Oxide

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 polycyclohexene carbonate formed will be discussed.

EXPERIMENTAL

Materials: Cyclohexene Oxide (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure over CaH₂. The purified CHO monomer was then transferred under N₂ to flasks equipped with stopcocks, and stored under N₂ until used. Methylene chloride (99.9% assay) and anhydrous methyl alcohol (99.9% assay) were used to separate and precipitate the reactor products (Malinkrodt Specialty Chemicals Co.; Paris, KY)

Research Grade CO₂ (Aircro Special Gases; Riverton, NJ) and Supercritical Grade CO₂ (Liquid Carbonic; Chicago, IL) were 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-perfluoroalkyl Catalyst: A flask was charged with 8.56 g (87.3 mmoles) of maleic anhydride, then flushed with N₂. The maleic anhydride was heated at 55°C and melted. Tridecafluorooctanol, 31.8 g (87.3 mmoles), was flushed with N₂ and transferred via a Teflon needle to the melted maleic anhydride. A solution of 0.73 ml (5.24 mmoles) of triethyl amine in 15 ml of toluene was next transferred to the mixture. [Note: both the amine and toluene were distilled from calcium hydride.] The mixture was stirred and heated at 55°C overnight. Upon cooling, the perfluoroalkyl monoester that formed was isolated by vacuum filtration and vacuum dried at 50°C overnight to recover 34 g (84% yield). The perfluoroalkyl monoester was purified by recrystallizing it 5 times in hexane or 2 times in benzene. Purified perfluoroalkyl monoester, 12 g (27.26 mmoles) and zinc oxide, 2.22 g (27.26 mmoles) was added to a 250 ml three necked flask, equipped with condenser, mechanical stirrer and N₂ inert gas. Both solids were flushed with N₂, then 100 ml anhydrous 1,1,2-trichlorotrifluoroethane was transferred over the solids. The mixture was refluxed at 50°C for 24 hours. The synthesized Zn-perfluoroalkyl catalyst was recovered by filtration with a pressure funnel. The filtrate was stripped to dryness and vacuum dried at room temperature overnight. The Zn-perfluoroalkyl catalyst collected was 13.4 g (90.6% yield).

Polymerization of Polycyclohexene Carbonate: All reactions were performed in 50 ml heated reactors (Pressure Products Industries; Warminster, PA) capable of 6000 psig maximum working pressure at 340°C, and equipped with magnetically driven mixers. An air driven, gas booster compressor (Haskel Inc; Burbank, CA) was used to generate CO₂ pressure.

In a typical polymerization, the catalyst was weighed and placed into the reactor body under a natural atmosphere. The reactor was then sealed and flushed with flowing nitrogen at an inlet pressure of 100 psig and atmospheric outlet pressure for ½ - 2 hours. During this time, a measured amount of CHO was added to an addition piping under N₂ atmosphere using a graduated, glass syringe. The addition piping was then attached vertically to the reactor inlet. CO₂ 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 heated to the reaction temperature. Once the reaction temperature was reached, pressurized CO₂ was added slowly (~200 psi increase in reactor pressure, letting temperature reach within 1°C of the reaction temperature each time) until the destination pressure and temperature were reached, a process which lasted 30-45 minutes. After the reaction was completed, the reactor was cooled to below 30°C and the gaseous reactor contents slowly bubbled through methylene chloride. The liquid and solid reactor contents were collected using methylene chloride to dissolve them from the reactor body and head. The reactor body and head were again rinsed with methylene chloride and this rinse was combined with the products obtained from the first reactor wash to make-up the total reaction products.

Purification of Products: The reactor rinse, the solvent used for collecting gaseous reactor contents, and reactor wash were combined and filtered. The solvent was removed under vacuum and the solid or viscous liquid reactor products were then dried in vacuo and weighed to determine the "Crude" yield. A concentrated solution was then made by dissolving the dried reactor products in a small amount of methylene chloride; this solution was then added to a large volume of methanol

from which a white, solid product precipitates. The precipitate was filtered and both the solid precipitate and the filtered solution were retained. The solid was re-dissolved in methylene chloride, concentrated and re-precipitated in fresh methanol two additional times. The solid was dried under vacuum at $\sim 50^{\circ}\text{C}$, and then weighed to determine the methanol-insoluble fraction of the product. The three methanol solutions collected from the precipitations were combined and the methanol removed under vacuum at $50\text{-}70^{\circ}\text{C}$. Residual solids were dried under vacuum at $\sim 50^{\circ}\text{C}$ to recover the methanol-soluble fraction of the product.

Characterization of Polymers: Polymer molecular weights were measured using gel permeation chromatography (GPC, Waters 150CV) and polystyrene standards. The fraction of polycarbonate repeat units was determined using a Bruker MSL 300 NMR.

RESULTS AND DISCUSSION

Poly(cyclohexene carbonate) was synthesized at different polymerization temperatures, while keeping the pressure constant, to determine the effects on the polymer product. Each reaction was run for 24 hours and the catalyst to monomer ratio of {moles of Zn} to {moles of cyclohexene oxide (C.O.)} was also kept constant. The reactor volume is unchanging, though, and the same volume of C.O. and weight of catalyst were used throughout this series. Therefore, the number of moles of CO_2 that are loaded into the reactor at constant pressure decreases as the temperature is increased throughout the temperature series. Another way to say this is that the mole fraction of C.O. increases as the temperature increases. This relationship is shown by following the mole fraction of C.O. on Table 1.

Table 1 also shows other results of the varying temperature reaction series. In Table 1 the polymer yield is presented in another form, g Polymer/g Zn, to indicate the catalysts' activity at different conditions. For comparison purposes, previous Zinc-based catalysts for the formation of polycarbonate from epoxides generally give 10-40 g Polymer/g Zinc. At higher temperatures the catalyst selectivity towards polymer decreases favoring the formation of MeOH-soluble products.

Changing the reaction pressure also has an effect on the reaction products. In a separate series of reactions the pressure was changed while the temperature remained constant at $109\text{-}110^{\circ}\text{C}$ and the polymerization was allowed to react for 24 hours. And while the catalyst to monomer ratio of {moles of Zinc} to {moles of C.O.} was kept the same as the other series, this set of experiments was done with half of the reactants as the variable temperature experiments. This means that there was more CO_2 present in the reaction mixture or that the reactions were run at lower mole fractions of C.O.. Again the same volume of C.O. and weight of catalyst were used over the entire range of pressures, therefore more CO_2 was present as the reaction pressure increased. This relationship is represented by a decrease in the mole fraction of C.O. with increasing pressures as shown in Table 2. The effect of this variation is not clear, but it seems that at these mole fractions the percentage of by-products formed is independent of pressure.

Table 2 also shows the yield results as a function of the changing pressure. The depression in yields at 4000 psig can not be attributed to the phase behavior in this set of experiments. Although, the yield depression shown at 4000 psig though 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 psig can be partially explained by the fact that the product yields decrease as the mole fraction of C.O. decreases. In the changing pressure experiments, the number of moles of CO_2 introduced at constant temperature increase as the pressure is increased. Therefore, the mole fraction of C.O. decreases and this results in decreasing yields.

A series of five reactions were run at varying mole fractions of C.O. to study the effect on the reaction products. These reactions were run for 24 hours at a constant pressure of 2000 psig and a constant temperature of $109\text{-}110^{\circ}\text{C}$. The catalyst to monomer ratio of {moles of Zinc} to {moles of C.O.} 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 C.O. was varied.

The product yields show a decreasing trend at lower mole fractions of C.O. This could be attributed to lower solvating properties at low mole fractions of C.O. The $\text{CO}_2\text{-C.O.}$ system could require certain co-solvent properties (a large enough solvating power for reactants and products) in order for good yields to be achieved. When the required co-solvent properties are not met, due to a large excess of CO_2 , the reaction system might prefer to produce MeOH-soluble products rather than the desired polycarbonate polymer.

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 an order of magnitude higher turnovers than previously reported and the catalyst has high selectivity towards 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 CO₂ 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 to best operating conditions for this synthesis.

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TABLE 1: EFFECT OF TEMP. ON POLYCYCLOHEXENE CARBONATE FORMATION

Conditions: P=2000 psig, t=24 hours, $N_z/N_{C_0} = 3.3 \times 10^3$

T (°C)	CONV.	SEL.	% CAR. (NMR)	X_{C_0}	g POLY g Zn	M_w ($\times 10^{-3}$)	M_w/M_n
60	5.7%	0.2%	58%	0.11	1.30	—	—
70	11%	6.3%	92%	0.12	41.1	120	27
80	28%	22%	81%	0.15	146	232	11
80	30%	17%	89%	0.13	116	109	5.8
90	—	9.1%	87%	0.15	61.5	114	6.6
90	11%	0.08%	80%	0.16	0.53	104	5.0
100	57%	30%	95%	0.16	203	174	14
100	79%	68%	93%	0.16	457	109	6.4
110	65%	50%	97%	0.18	328	195	12
110	84%	69%	96%	0.16	440	68.1	4.2
120	75%	61%	94%	0.20	406	56.2	3.6
130	60%	45%	87%	0.21	307	43.4	3.0
172	50%	2.4%	29%	0.24	15.8	9.8	2.4

TABLE 2: EFFECT OF PRES. ON POLYCYCLOHEXENE CARBONATE FORMATION

Conditions: t=24 hours; T=110°C; $N_z/N_{C_0} = 3.3 \times 10^3$

P (psig)	CONV.	SEL.	% CAR. (NMR)	X_{C_0}	g POLY g Zn	M_w ($\times 10^{-3}$)	M_w/M_n
1000	70%	50%	86%	0.20	329	59.1	3.7
2000	75%	57%	91%	0.10	408	60.4	5.4
3000	63%	45%	83%	0.061	297	74.1	4.4
3000	57%	37%	92%	0.062	254	66.2	4.9
4000	32%	17%	89%	0.049	114	89.6	5.6
4000	28%	14%	96%	0.050	115	60.8	4.1
5000	49%	32%	87%	0.047	229	55.8	3.0
5000	30%	7%		0.040	40.2	38.5	2.7

TABLE 3: EFFECT OF X_{C_0} ON POLYCYCLOHEXENE CARBONATE FORMATION

Conditions: 2000 psig, t=24 hours; T=110°C; $N_z/N_{C_0} = 3.3 \times 10^3$

X_{C_0}	CONV.	SEL.	% CARB. (NMR)	M_w ($\times 10^{-3}$)	M_w/M_n	g POLY g Zn
0.28	82%	65%	96%	106	3.3	421
0.18	65%	50%	97%	195	12	328
0.16	84%	69%	96%	68.1	4.2	440
0.10	75%	57%	91%	68.7	5.1	408
0.023	59%	4.8%	65%	23.8	1.8	35.0