Copolymerization of CO2 and Cyclohexene Oxide

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Abstract

Generation of high value polymers from carbon dioxide is of general technological interest given that CO2 is both inexpensive and relatively easy to handle on an industrial scale. Previous work on the use of CO2 as a comonomer has focused primarily on development of new catalysts, and the effects of conventional process variables such as temperature and concentration on the polymerization outcome have not been examined in great detail. Recently, we, as well as Darensbourg and colleagues, have shown that one can generate zinc-based catalysts for the polymerization of CO2 and cyclohexene oxide which produce over 400 grams of polymer per gram of metal. In this paper, we use a product of the reaction between zinc oxide and the fluorinated half-ester of maleic anhydride to generate copolymers of CO2 and cyclohexene oxide where CO2 is both reactant and sole solvent. In general, we found that the outcome of the polymerization depends greatly on the proximity to the ceiling temperature and the critical cyclohexene oxide concentration, and also on the phase behavior of the cyclohexene oxide-CO2 binary.

Introduction

Carbon dioxide is an inexpensive, abundant material whose use is not burdened by any particularly onerous safety hazards. Generation of high value polymers from CO2, a raw material with essentially no value, is naturally of great interest to various members of the industrial polymer community. While CO2 is relatively difficult to activate for polymerization compared to CO or SO2, previous work has shown that an interesting variety of polymeric materials can be generated using CO2 as a comonomer [1-13].

In particular, a number of research groups have focused on generation of cyclic carbonates and polycarbonates from CO2 and cyclic ethers, many using zinc-based catalysts [1,2,18 and references therein]. The nature of these catalysts has required 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 [14-17]. The literature contains

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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 Darensbourg's catalyst [17] (which gave ~366 g polymer/g Zn for the CHO/CO2 copolymerization). The catalysts Darensbourg developed include (2,6-diphenylphenoxide)2Zn(diethyl ether)2, (2,6-diphenylphenoxide)2Zn(THF)2 and (2,4,6-tri-*tert*-butylphenoxide)2Zn(diethyl ether)n, n<2. 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 polymer/g Zn) [19], 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 [20-25], and thus our catalyst employs a fluorinated ligand.

Most of the previous work on use of CO2 as a monomer has focused on catalyst preparation and performance, and thus the effects of typical process variables (concentration and temperature) on polymerizations involving CO2 have not been explored in depth; nowhere near as thoroughly as for typical radical, ionic, and coordinative chain polymerizations. Further, CO2 is attracting significant research activity not only for its use as a raw material, but also as an environmentally-benign solvent. While most of the previous work has evaluated polymerizations of gaseous CO2 and cyclic ethers in organic solvents, use of pressures above the liquid-vapor boundary for CO2 (approximately 6.2 MPa at 298K) or in the supercritical regime (above 304K and pressures generally above 7.6 MPa) would allow use of CO2 as both reactant and solvent. In this case we should include pressure as a process variable whose effects should be evaluated.

Experimental

Materials. Cyclohexene Oxide (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure over CaH2. 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. Tridecafluoroctanol (97%) was used without further purification.

Supercritical Grade CO2 (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 mmoles) of maleic anhydride, then flushed with N2. The maleic anhydride was heated to 55oC and then tridecafluoroctanol (31.8 g; 87.3 mmoles), which had been flushed with N2 was transferred to the 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. The mixture was stirred and heated at 55oC overnight. Upon cooling, the fluoroalkyl monoester that precipitated was isolated by vacuum filtration and vacuum dried at 50oC 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 ppm (m, 2H, -CH2-), 4.57 ppm (t, 2H, -CH2-O-), 6.38 and 6.42 ppm (d, 1H, -CH=CH-). 13C NMR shows peaks at 25 ppm (t, 1C, -CH2-), 58 ppm (s, 1C, -CH2-O-), 106-121 ppm (m, 6C, all CF), 130 and 132 ppm (s, 1C, -C=C-), 166 and 168 ppm (s, 1C, both -C(O)-).

Purified flouroalkyl monoester, 12 g (27.26 mmoles) and zinc oxide, 2.22 g (27.26 mmoles) were added to a 250 mL three necked flask, equipped with a condenser. Both solids were flushed with N2, then 100 mL anhydrous 1,1,2-trichlorotrifluoroethane was transferred over the solids. The mixture was stirred and refluxed at 50oC for 24 hours. 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 ppm (m, 2H, -CH2-), 4.42 ppm (t, 2H, -CH2-O-), 6.15 and 6.35 ppm (d, 1H, -CH=CH-). 13C NMR shows peaks at 31 ppm (t, 1C, -CH2-), 57 ppm (s, 1C, -CH2-O-), 107-122 ppm (m, 6C, all CF), 127 and 136 ppm (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 N2 atmosphere. The addition piping was then attached vertically to the reactor inlet. The ends of the addition piping were flushed with CO2 or N2 during the installation. CO2 at its' vapor pressure (≈850 psi at 25oC), 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 minutes. After the reaction was completed, the liquid and solid reactor contents were collected using methylene chloride.

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 (35oC), was used as mobile phase solvent. The instrument was equipped with ultrastyragel columns with pore sizes of 104 A, 103 A, 500 A and 100 A in series. The fraction of polycarbonate repeat units was determined using a Bruker MSL 300 NMR.

Phase Behavior Determination. The phase behavior of the reaction mixtures was observed in a variable volume, high pressure view cell (D.B. Robinson and Associates; Edmonton, Alberta, Canada) [26,29]. 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 CO2 at 2000 psig and room temperature (~23oC) is added isothermally and isobarically. Once the desired amount of CO2 is added, the cell pressure is increased to 6000 psig. The cell is mixed for 20 minutes 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 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

Unless otherwise noted, all polymerizations were run for 24 hours with a constant ratio of Zn:CHO of 3.3 x 10-3. The term "conversion" describes the total amount of product generated, while selectivity includes only the methanol-insoluble portion of the product. Regarding nomenclature, [CHO] refers to the concentration of cyclohexene oxide in moles/liter, while XCHO is the mole fraction of cyclohexene oxide in a CO2/CHO mixture.

Phase Behavior of CHO/CO2 and Catalyst/CO2 Mixtures

We have previously described the phase behavior of the cyclohexene oxide-CO2 binary [26]; P-x diagrams at 383K and 405K in Figure 1. The points in Figure 1 are experimental data while the solid line represents the prediction of the Peng-Robinson equation of state using an interaction parameter (kij) of 0.05 [26]. As expected, the phase boundary moves to higher pressure as the temperature increases, yet the results also reveal anomalous behavior at low CHO concentration. The actual phase boundary must curve back (as shown by the Peng-Robinson projections) forming a closed loop which intersects the vertical axis (at XCHO = 1) at the vapor pressure of cyclohexene oxide, yet it appears instead to shift instead to higher pressures at low XCHO. We analyzed the material from the view cell before and after the variable volume measurements, and found (via 1H NMR) that a small amount of the CHO had homopolymerized to polyether during the phase measurements at the higher temperatures (generation of the complete phase boundaries can take 12 hours). It is difficult to exclude atmospheric moisture from the sample while loading the variable volume view cell, and thus water may be the initiator for the polyether formation. If CHO and CO2 are mixed in a small batch reactor which is thoroughly flushed with nitrogen, no polyether results after 24 hours at 383K. Because the amount of polymer formed is small, it only significantly effects the phase behavior at lower CHO concentrations. The true phase behavior of the CO2-CHO binary at low CHO concentration will most likely follow the projection of the Peng-Robinson equation of state, as shown in Figure 1.

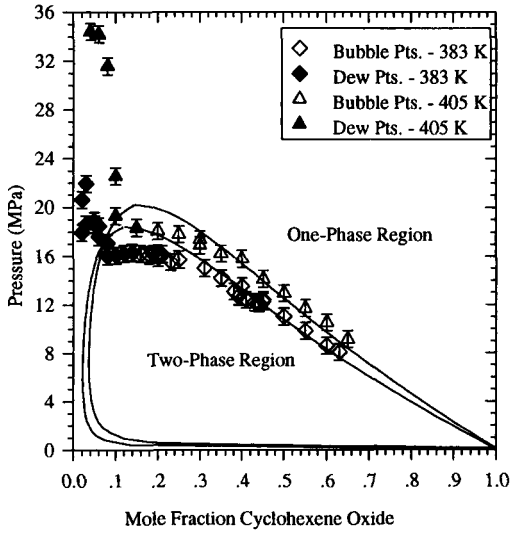

Figure 1: P-x diagram for binary mixtures of cyclohexene oxide and carbon dioxide at 383K and 405K. Lines are predictions of the Peng-Robinson equation

Although the catalyst was designed to exhibit higher solubility in CO2 than an analogous alkyl-functional material (which is insoluble), even the fluorinated analog is not completely soluble at all pressures under consideration (see Figure 2). We have also observed that the catalyst is miscible with CHO and CHO-rich mixtures with CO2. Thus, in polymerizations conducted in initially two-phase CO2-CHO mixtures, the catalyst will partition between the phases.

Phase Behavior of CHO/CO2/Polymer Mixtures

By performing polymerizations in the variable volume view cell, we were able to observe the phase behavior during polymerization. For example, Figure 3 shows the phase behavior vs time of a polymerization of CO2 and cyclohexene oxide at 13.8 MPa, 383K, and with an initial XCHO of 0.18. At the onset of the reaction, two phases were apparent, a CHO-rich phase at the

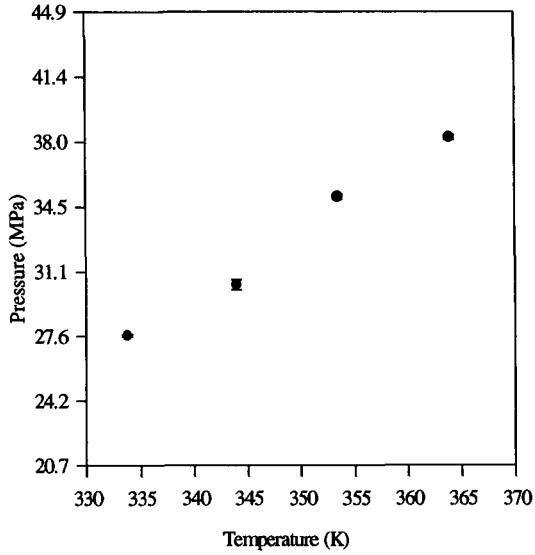

Figure 2: PT diagram for a 1.8 wt. % binary mixture of fluorinated catalyst (reaction product of zinc oxide and fluorinated half-ester of maleic anhydride) and carbon dioxide.

bottom of the cell with a CO2-rich phase above. Given that the catalyst is miscible with CHO at 383K, and that 13.8 MPa is below the cloud point pressure of the catalyst at 383K (Figure 2), we assume that the catalyst resides primarily in the lower CHO-rich phase.

As can be seen in Figure 3, a presumably polymer-rich phase appears approximately one hour after the addition of CO2 and catalyst to the cyclohexene oxide. This third phase grows steadily thereafter, eventually consuming all of the second, originally CHO-rich phase. Following the disappearance of the middle phase, the upper phase begins to grow cloudy. Initially during this period, cessation of stirring allows suspended material in the upper phase to settle, resulting in clearing. However, by seven hours into the polymerization, the upper phase remains cloudy even after stirring is halted. After 24 hours it was difficult to determine the location of the interface between upper and lower phases.

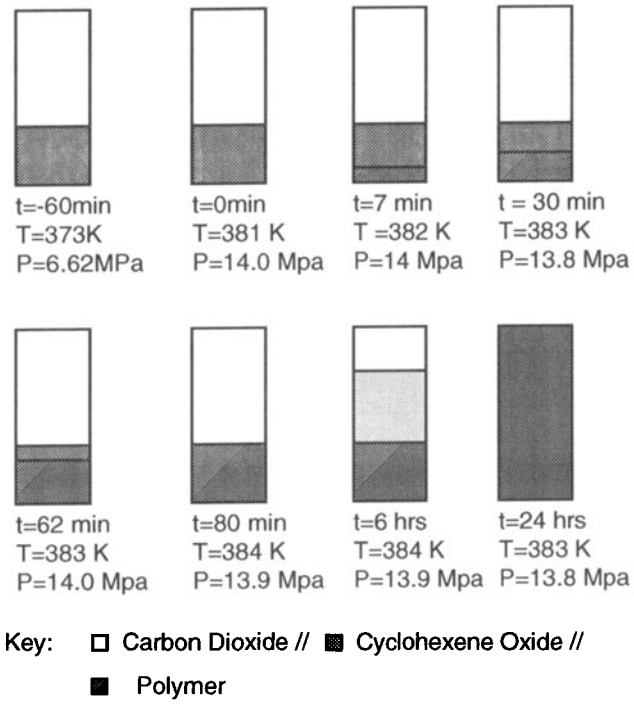

Figure 3: Reaction mixture of cyclohexene oxide, carbon dioxide, and catalyst at 13.8 Mpa versus time. t = 0 on plot is 1 hour following addition of carbon dioxide and catalyst to the cyclohexene oxide.

We draw the following conclusions from this behavior. First, because CHO, catalyst, and CO2 will all partition between the two original phases, we can assume that polymerization will occur in each phase. Presumably the rate within the lower (CHO-rich) phase will be much higher, given that the bulk of the CHO and catalyst will reside in the lower phase, and given the equilibrium nature of the polymerization as described later. Thus we observe initially the formation of the third (polymer-rich phase) and its growth.

The behavior evident towards the end of the polymerization is interesting, in that the reluctance of the mixture to separate suggests that the system is closer to a phase boundary (the densities of the two phases are closer) at this point than earlier in the polymerization. This can be rationalized if we consider the CHO-CO2 binary as a single pseudo-component, and assume that the polymer/solvent P-x diagram in this system exhibits a maximum (Upper Critical Solution Pressure, or UCSP) at low concentration, as is typical. If so, then increasing the polymer concentration moves the system farther from the UCSP, and thus the phase boundary moves to lower pressure.

Effect of Pressure, XCHO, and [CHO] on Polymerization at 383K

We initially assumed that the phase behavior of the system would play a significant role in determining the extent of polymerization and the characteristics of the polymer product. As such, we performed a series of polymerizations at 383K using the phase behavior of the CHO-CO2 binary as a guide (see Figure 1). Polymerizations were performed where pressure varied at constant XCHO, and also where XCHO was varied at constant P. Increasing XCHO at constant P is essentially the same as increasing [CHO] at constant pressure. Pressures were chosen such that (a) all polymerizations were conducted in the single phase regime of the CHO/CO2 binary, or (b) all were performed starting with a two-phase mixture, and finally (c) where the phase boundary was crossed as XCHO increased.

Maintaining a constant mole fraction while varying pressure required increasing the charge of CHO to the reactor as P increased, given that the density of CO2 increases with pressure. Thus the concentration of CHO (moles/volume) also increased as P increased, despite a constant XCHO. To further examine the effects of concentration and pressure, a series of experiments was also performed where P was varied at constant [CHO], rather than constant XCHO. In this series of reactions XCHO actually declines as pressure increases at constant [CHO] (ie., the charge of CHO to the reactor is constant and the amount of CO2 added increases as P increases). On the phase diagram (Figure 1), a locus of points where P varies at constant XCHO is a vertical line, while a series where [CHO]varies at constant P is a curve which shifts asymptotically to lower values of XCHO as P increases

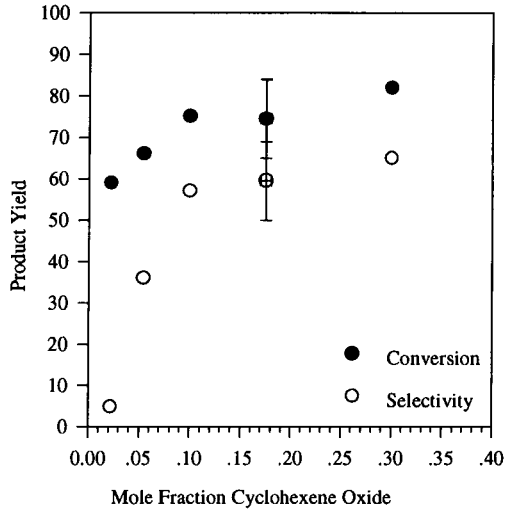

Figure 4a: Product yield and selectivity from copolymerization of carbon dioxide and cyclohexene oxide at 383K after 24 hours at P = 13.8 MPa

Effect of Varying XCHO at Constant Pressure

Figure 4a and 4b show the effect of increasing XCHO (and thus increasing [CHO]) on conversion and selectivity at P = 13.8 MPa and 27.6 MPa, where polymerization at the former takes place initially in a two-phase mixture initially while the latter allows a single phase initially (see Figure 1). Increasing XCHO leads to significantly greater yields (all reactions were run for 24 hours), and also greater selectivity. Polymerization, for example, at 13.8 MPa and an XCHO of 0.02 produces only low molecular weight (methanol-soluble) polymer while reaction at a mole fraction of 0.1 generates nearly 80% yield, with 60% high polymer. In addition, as shown in Figure 5, decreasing the initial concentration of CHO decreases the fraction of carbonate repeat units in the polymer.

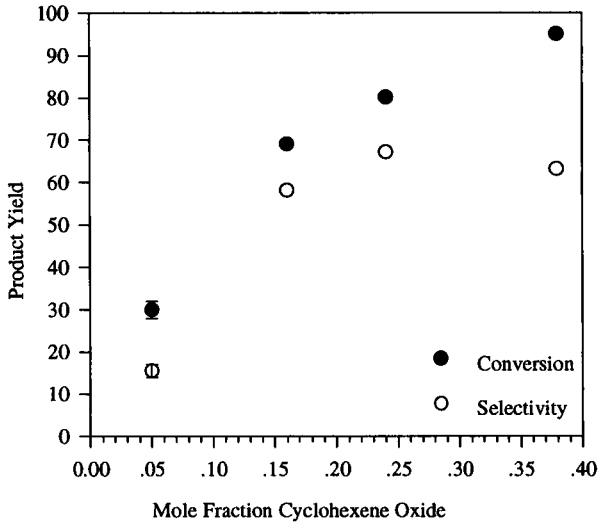

Figure 4b: Product yield and selectivity from copolymerization of carbon dioxide and cyclohexene oxide at 383K after 24 hours at P = 27.6 MPa

The behavior in Figures 4a, 4b, and 5, where initial [CHO] governs % carbonate and selectivity for high polymer, suggests that equilibrium thermodynamics governs the outcome of the reaction. As we reduce [CHO] at constant P, we might expect to encounter polymerization difficulties due to an approach to the critical monomer concentration (the same would hold true for [CO2]). Supporting this, we have observed a decrease in both yield and selectivity as the initial [CHO] drops, yet we have also observed lower % carbonate (higher polyether content) in the copolymer as [CHO] drops, seemingly in contradiction with what one might expect upon approaching [M]c for cyclohexene oxide. We would propose the following outline, a slight modification to Lowery's theory for copolymerization influenced by equilibrium [27], to account for our observations:

1. CO2 can only react with a CHO-functional chain end (r1 = 0), while CHO can react with either a CO2-functional or CHO-functional chain end (r2≠ 0) thus allowing a mixture of carbonate and ether linkages to form, the relative amounts depending upon the reactivity ratio. Given the

high % carbonate achieved in the majority of our polymerizations, the rate of addition of CHO to a CHO chain end is apparently much lower than that of a CO2 to a CHO chain end.

2. Unlike in Lowery's original model, both monomers (CO2 and CHO) can depolymerize,

3. CHO's in carbonate repeat units can depolymerize much more readily than CHO's in ether repeat units.

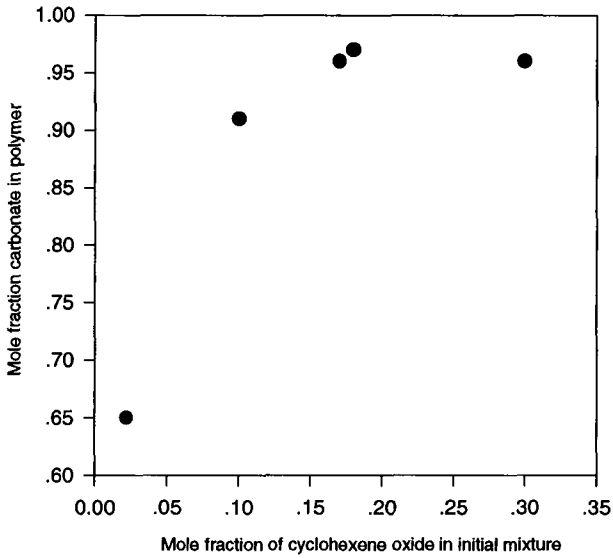

Figure 5: Effect of initial XCHO on mole fraction carbonate in the polymer at 383K, 24 hours reaction time, and P = 13.8 MPa

Points (1) and (2) account for the tendency to generate primarily polycarbonate at concentrations above the [CHO]c, and the observation that low [CHO] lead to low yields. Lowery's model showed that dilution of the monomer more prone to depolymerization reduces its fraction in the copolymer. Point (3) above accounts for our observation that while low [CHO] gives low yields and low selectivities, it also produces a polymer with a higher polyether content.

Lowery's model assumed variable depropagation rates owing to penultimate effects and thus our hypothesis is a specific case of Lowery's overall framework.

The hypothesis that each monomer can depropagate, plus knowledge of the phase behavior of the CHO/CO2 binary, can help to explain why it appears that conducting the polymerization in the two-phase regime gives better results than analogous reactions conducted in the initially one-phase regime (at high pressures). Here we use the term nominal [CHO] to describe the total amount of cyclohexene oxide added to the reactor, divided by reactor volume. For a single phase system, the nominal [CHO] equals the actual [CHO] during polymerization. However, adding an amount of CHO to CO2 which places one in the 2-phase envelope in P-x space (see Figure 1) forms CO2-rich and CHO-rich phases. Given that the tie-line for the mixture is horizontal, all nominal [CHO]'s within the phase envelope will lead to formation of a CHO-rich phase of constant concentration (only the phase volume will change as one changes the nominal [CHO] within the 2-phase envelope). The catalyst will partition between the phases, but considering the phase behavior for the catalyst in pure CO2, it appears likely that most of the catalyst will reside in the CHO-rich phase. In any event, the concentration of CHO in the CO2-rich phase will likely be too low (below [CHO]c) to support polymerization. Only when the nominal [CHO] is low enough (or high enough) to form a single phase will the nominal [CHO] be equal to the actual [CHO] during polymerization. Thus, the yield at 27.9 MPa appears to drop off faster as [CHO] decreases than analogous reactions run at 13.8 MPa, but in fact, at 13.8 MPA the [CHO] in the CHO-rich phase remains constant as the nominal [CHO] drops, until we cross the phase boundary. At this point nominal [CHO] equals actual [CHO] available for polymerization, and the equilibrium monomer concentration governs the behavior, leading to a sharp drop-off in yield.

Regarding the effect of pressure, we ran series of polymerizations varying pressure at both constant XCHO, and constant [CHO]. We would expect pressure to affect the reaction outcome in two ways. First, it is known that pressure governs the rate constant through its effect on the

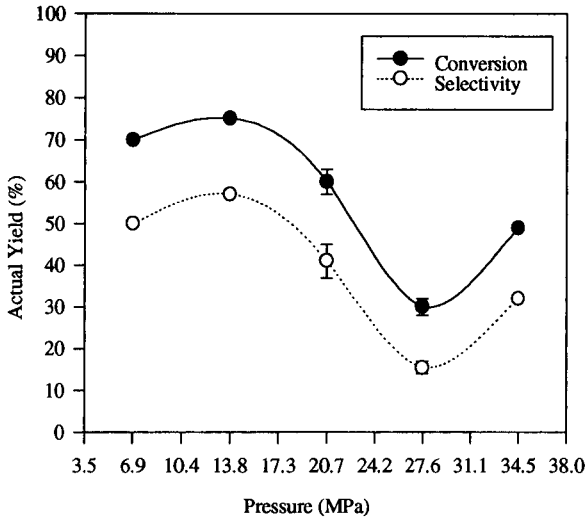

Figure 6: Effect of pressure on product yield for copolymerization of carbon dioxide and cyclohexene oxide at 383K and constant [CHO].

volume change upon activation [28], although this effect would not likely be large over the pressure range (5 to 30 MPa) that we studied (assuming a volume change upon activation comparable to those commonly encountered in free-radical chain polymerizations). Second, assuming that the volume change upon polymerization is negative, increasing pressure will raise the ceiling temperature and lower the equilibrium monomer concentration [28]. Thus increasing pressure at 383K should lead to higher yields/selectivities by lowering [CHO]c. However, as shown in Figure 6, this appears not to be the case. The yield drops above 17 MPa, exhibits a minimum, then increases again (the drop and subsequent increase are indeed reproducible). Once again, this behavior can be explained via examination of the phase behavior. At low pressures, the polymerizations in Figure 6 were run in the two phase regime, and thus the [CHO] in the CHO-rich phase (where most of the catalyst resides) is much higher than the nominal [CHO]. At pressures above the phase boundary (17 MPa), actual [CHO] equals nominal [CHO], and thus by raising the pressure from a point below the phase boundary to a point above, the concentration of CHO for the polymerization actually drops suddenly, leading to the observed drop in yield above

17 MPa. As pressure increases further, [CHO]c drops as suggested above, and thus the yield increases again.

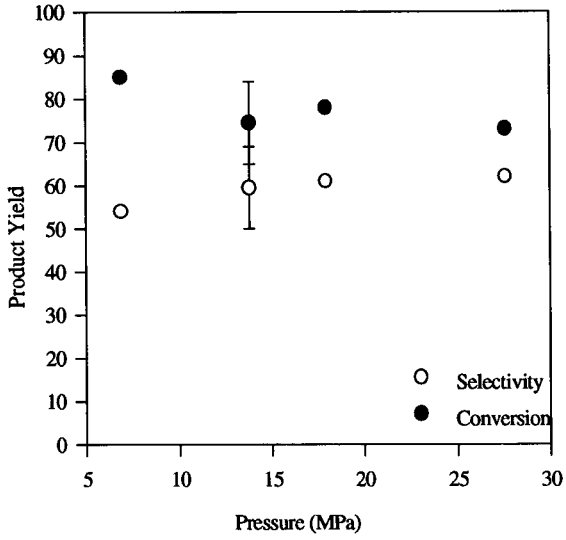

Figure 7a: Effect of pressure on product yield for copolymerization of carbon dioxide and cyclohexene oxide at 383K and constant XCHO = 0.15.

We also examined the effect of changing pressure at constant XCHO, ie. series of points which would appear as vertical slices through the phase diagram in P-x space. However, increasing pressure at constant XCHO means that [CHO] will increase while P increases, given that the density of CO2 increases as P increases. At a mole fraction of 0.15 (Figure 7a) increasing pressure leads to little obvious effect in either yield or selectivity. Although each of these series include points both above and below the phase boundary, the nominal [CHO]'s are high enough such that crossing the phase boundary does not drop the concentration close enough to [CHO]c to cause problems. However, the behavior of the series at a mole fraction of 0.05 is more complex (Figure 7b). At very low pressures, low yields of high polymer result, possibly because this point occurs in the single phase region or because we are now below [CO2]c. As pressure is increased, and the two-phase region is entered, the [CHO] in the CHO-rich phase is sufficiently high to allow

for relatively efficient polymerization. As the phase boundary is again crossed (above 15 MPa) the yield of high polymer again drops, as the nominal [CHO] equals the actual. Yield rises at higher pressures owing to the drop in [CHO]c as pressure increases.

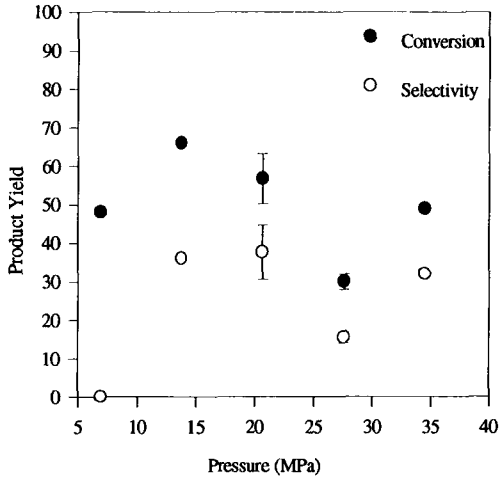

Figure 7b: Effect of pressure on product yield for copolymerization of carbon dioxide and cyclohexene oxide at 383K and constant XCHO = 0.05.

Effect of Temperature on Polymerization at 13.8 MPa

A series of polymerizations were run employing a constant [CHO] and pressure (13.8 MPa) while varying the temperature, as shown in Figure 8. Interpretation of these results is not straightforward, as a number of factors influenced the outcome of the polymerization. First, the nominal XCHO will increase as temperature increases (from XCHO = 0.12 at 333K to 0.24 at 445K), as the density of CO2 decreases at constant pressure. Second, the rate constant for the reaction will increase as per a typical Ahrenius expression. Third, if the polymerization is governed by equilibrium thermodynamics as suspected, we may approach a ceiling temperature as temperature increases. Finally, while the system at 13.8 MPa and 333K starts as a single phase, both the monomer and the catalyst will exhibit two-phase behavior at higher temperatures at 13.8 MPa.

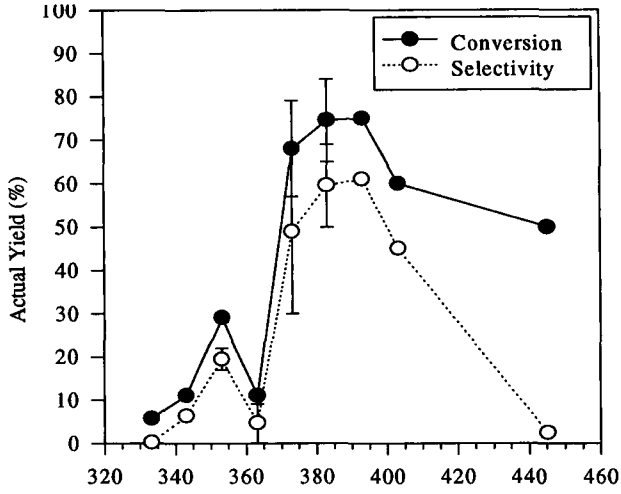

Figure 8: Effect of temperature on product yield for copolymerization of carbon dioxide and cyclohexene oxide at 13.8 MPa

At temperatures below 363K, the monomer-CO2 mixture exhibits a single phase at 13.8 MPa. As temperature increases, conversion increases as both the rate constant and [CHO] increase. At 363K, the XCHO employed in the reaction is almost exactly at the critical point of the CHO-CO2 mixture while the catalyst is still soluble in CO2. The large concentration fluctuations present near the critical point may be the cause for the low conversion at 363K. As temperature increases beyond 363K, the CHO-CO2 mixture (and the catalyst-CO2 mixture) exhibits 2-phase behavior at 13.8 MPa, and thus the polymerization occurs primarily in the CHO-rich phase, where [CHO]actual is much higher than the nominal [CHO]. This fact, plus the effect of increasing temperature on the rate constant, lead to increasing conversion with increasing temperature above 363K. Finally, at temperatures above 403K, the ceiling temperature begins to play a role and conversion drops.

Molecular Weight

Molecular weights were measured for all of the methanol-insoluble products. As in our previous work, we observed Mw's generally in the 50,000 - 200,000 range with very broad molecular weight distributions (2 - 12) [18,29]. No obvious trends in molecular weight of the methanol-insoluble material vs. either pressure or concentration were observed.

Summary

In summary, the P-x behavior of the copolymerization of cyclohexene oxide and carbon dioxide where CO2 is the sole solvent, can be explained by a combination of equilibrium thermodynamics of polymerization plus the phase behavior of the CHO-CO2 binary. If the polymerization temperature rises above the ceiling temperature (which is apparently slightly above 413K) or if [CHO] falls below the critical value, the yield of high polymer drops to essentially zero. Because the CHO-CO2 binary exhibits phase demixing at low pressures, one must remember that the nominal concentration of CHO (moles of CHO added to the reactor divided by reactor volume) is not the actual [CHO] during the initial stages of polymerization. Phase splitting into CHO-rich and CHO-poor phases will allow polymerization to high molecular weight polymer, even when nominal [CHO] is below [CHO]c. It is therefor advantageous to operate in the 2-phase regime because:

(a) polymerization to high polymer can be achieved at lower pressures than would be required for a single phase system

(b) the presence of a high XCO2 in the CHO-rich phase plasticizes this phase to the point where mass transfer limitations are not observed.

The resulting polymer is so heavily plasticized by the carbon dioxide that the reactor can be easily stirred at temperatures well below the Tg0 (408K) of the polymer.

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