Design and Synthesis of Low Cost, Sustainable CO₂-philes

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Research conducted in the 1990s has demonstrated that one can design compounds which are "CO₂-philic", that is, they exhibit miscibility with CO₂ at pressures significantly below that of conventional alkyl-functional analogues. The use of such CO₂-philic functional groups in the design of surfactants and chelating agents has allowed successful implementation of CO₂ in processes such as emulsion polymerization, heavy metal extraction, and others. However, the high cost of widely used fluorinated CO₂-philes can render the economics of a CO₂ process unfavorable. Consequently, we have investigated the design of CO₂-philes composed of only carbon, hydrogen, and oxygen. Using fundamental data on the thermophysical behavior of CO₂ as a guide, we focused on the design and synthesis of functionalized polyethers and copolymers of cyclic ethers and carbon dioxide that were found to be soluble in liquid and supercritical carbon dioxide. By choosing the proper amount of incorporated carbon dioxide, we can generate propylene oxide–CO₂ copolymers that exhibit lower miscibility pressures than fluoroethers with the same number of repeat units.

Introduction

Significant effort has been devoted to the use of supercritical carbon dioxide (scCO₂) as a process solvent because it is environmentally benign, nontoxic, nonflammable, and inexpensive. Because of its low critical temperature (31.17 °C) and moderate critical pressure (73.8 bar),[1] the supercritical state of carbon dioxide is easily reached, another potential advantage for practical application. The limitations of CO₂ as a process solvent are primarily related to its relatively feeble solvent power. Consequently, much previous work has focused on the design of materials which are "CO₂-philic", that is, they exhibit miscibility in CO₂ under mild conditions (temperatures $T < 100$ °C and pressures $P < 200$ bar). Based on experimental observations, many polymers have been classified as either "CO₂-philic" or "CO₂-phobic". Despite the observation that almost all monomers are soluble in carbon dioxide, hydrocarbon polymers have, in general, very limited solubility in CO₂ at temperatures below 80 °C.[2–8] Amorphous fluoropolymers and silicones essentially define the CO₂-philic classification. To take advantage of the useful properties of CO₂ as a process solvent, amphiphiles with CO₂-philic functionality have been generated. DeSimone et al.[9] used fluoroacrylate homopolymers and fluoroacrylate–styrene copolymers as dispersing agents in dispersion polymerization of methyl methacrylate in CO₂. Beckman et al.[10] studied dispersion polymerization of methyl methacrylate using methyl methacrylate–hydroxyethyl methacrylate copolymers grafted with perfluoropropylene oxide as stabilizers. These copolymers contain highly CO₂-philic graft chains and a backbone that exhibits affinity with the growing polymer particles. Fluoroether functional amphiphiles have also been used to extract heavy metals,[11,12] solubilize proteins,[13,14] and support emulsion polymerization.[15]

Fluoroacrylate and fluoroether polymers are very soluble in CO₂ and have been readily used as amphiphiles, but they are very expensive (on the order of $1/gram). The design and development of a CO₂-philic hydrocarbon polymer with solubility comparable to that of fluoroethers would allow production of chelating agents, surfactants, and catalysts which would be 10–100 times less expensive than their fluorinated counterparts.

Polymer Design

After examining the characteristics that render fluorinated and silicone polymers soluble in carbon dioxide, we proposed that a CO₂-philic material will be a copolymer in which each structural unit has specific qualities that will optimize the copolymer's solubility in carbon dioxide (Figure 1). We therefore proposed that a CO₂-philic hydrocarbon polymer should be a copolymer of the following:[16]

(A) Monomer 1 (M_1), which contributes to high flexibility, high free volume, and weak solute/solute interactions (low cohesive energy density or interfacial tension). Generally, low T_g and steric parameter values are used as evidence for high flexibility and free volume in polymeric materials. These factors combine to create a favorable entropy of mixing for the copolymer in CO₂, as well as weak solute/solute interactions, easing dissolution into CO₂.

(B) Monomer 2 (M_2), which produces specific solute/solvent interactions between the polymer and CO₂ through a Lewis base group (e.g., carbonyl group) in the side chain or backbone of the polymer.

Ideally, interactions between M_1 and M_2 should be enthalpically unfavorable, further helping to promote dissolution in carbon dioxide. It is possible that this feature is a strong contributor to the low miscibility pressures of fluoroacrylate polymers in CO₂, in that interactions between the fluorinated side chains and acrylate backbone of this material are likely to be unfavorable. Because use of a homopolymer of either M_1 or M_2 only serves to optimize part of the free energy, if both monomer 1 and monomer 2 are chosen in the proper proportions, then the copolymer should be more soluble than either of the homopolymers.

In our previous work, we explored the effect of Lewis base functionalization, a major part of our overall hypothesis, on the phase behavior of a model silicone

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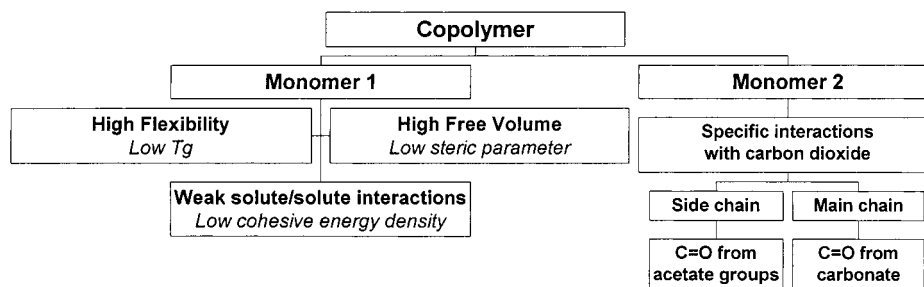† Present address: Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213.
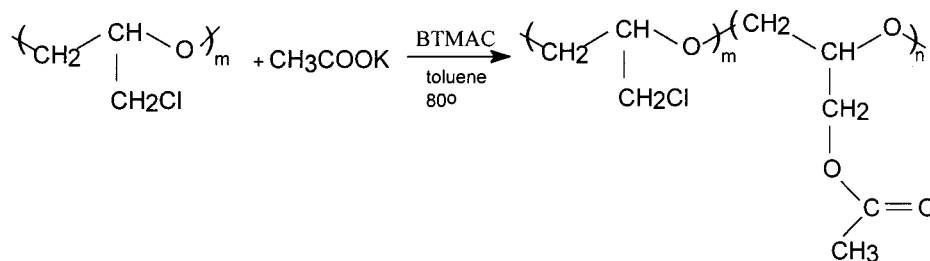
Figure 1. CO_2-philic material design.

Figure 2. Modification of poly(epichlorohydrin) with acetate groups.

in CO_2.[17] Silicones are considered CO_2-philic, although not in the same class as fluorinated ethers and acrylates. We have observed that silicones exhibit UCST-type behavior at room temperature (as the temperature increases, the pressure required to solubilize a given amount of material drops), which suggested that the enthalpy of mixing of these materials with CO_2 might be improved through the incorporation of Lewis bases in side chains. Silicones exhibit among the lowest T_g values (150 K) and steric parameters (1.39) observed for synthetic polymers, and hence, it appeared that chain flexibility (and thus the entropy of mixing) was not an area requiring extensive improvement. Functionalized silicones were prepared via the hydrosilation of model dimethyl siloxane hydromethyl siloxane oligomers over a platinum catalyst. Allyl acetate or 1-hexene was used to generate the side chains, to allow us to compare the efficacy of adding Lewis base groups to simply adding methylene units. The phase behavior results were quite dramatic, in that addition of five acetate functional side chains to the silicone oligomer lowered the cloud point curve by over 2500 psi at room temperature. We also observed that addition of simple alkyl side chains raised the cloud point curves to higher pressures, consistent with expectations.

In the present paper, we show that functionalization of polyethers with carbonyl groups in the side chain or incorporation of carbonyls into the backbone significantly lowers the cloud point pressures of such polyethers in CO_2. We have probed the effect of placement of carbonyl groups in the polymer (backbone versus side chain) and also the effect of the number of these groups in polymers of different molecular weights.

Experimental Section

Materials. All syntheses were carried out in a purified argon atmosphere. Monomers and solvents were purified as described previously.[18] Ethylene oxide was used as received. Epichlorohydrin (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure. Carbon dioxide and argon (both 99.99% purity from Praxair, Pittsburgh, PA) were passed through high-pressure purifiers before use. All other chemicals were

obtained from Aldrich Chemicals and used as received, unless otherwise noted.

Synthesis of Acetate-Functionalized Poly(epichlorohydrin). Low-molecular-weight poly(epichlorohydrin) was used as the starting material to produce acetate-modified polymers with varying acetate content. In a typical polymerization reaction, boron trifluoride diethyl ether (1.5 mL, 0.0118 mol) was added dropwise to a solution of 20 mL of epichlorohydrin (0.2557 mol) in 44 mL of toluene over 30 min at room temperature. After 4 h, the catalyst was deactivated with aqueous NaOH, and the organic phase was separated and dried over $CaCl_2$. The solvent was removed under reduced pressure at 50 °C, and the polymer was analyzed using NMR spectroscopy and GPC. Poly(epichlorohydrin) with seven repeat units was produced with a yield of 90−95%. To generate higher-molecular-weight polymers (e.g., 25 repeat units), methylaluminoxane (kindly supplied by Akzo Nobel) was used as the initiator. The polymerization was stopped with methanolic hydrochloric acid, and the polymer solution was filtered and processed as above.

For modification with acetate groups, the polymer was reacted with potassium acetate using a phase transfer catalyst (benzyltrimethylammonium chloride) in toluene (Figure 2). The reaction mixture was heated to 50−80 °C for 24 h. The solution was allowed to cool to room temperature, and the remaining catalyst and potassium acetate were removed by filtration. The polymer solution was washed rapidly three times with cold water to remove any unreacted potassium acetate and then dried with magnesium sulfate. The solvent was removed under reduced pressure. The amount of acetate incorporated was determined by ^{13}C NMR spectroscopy from the ratio of the CH_2Cl peak at 43−45 ppm to the CO peak from acetate at 170−171 ppm. The maximum degree of modification was 45%.

Synthesis of Poly(glycidyl acetate). Polymers containing only acetate groups in the side chain were synthesized by polymerization of glycidyl acetate in a manner similar to that for epichlorohydrin, using a sterically hindered aluminum catalyst of the type $[(H_5C_6)_3C-O]_2-Al-O-CH(CH_3)_2$. The glycidyl acetate
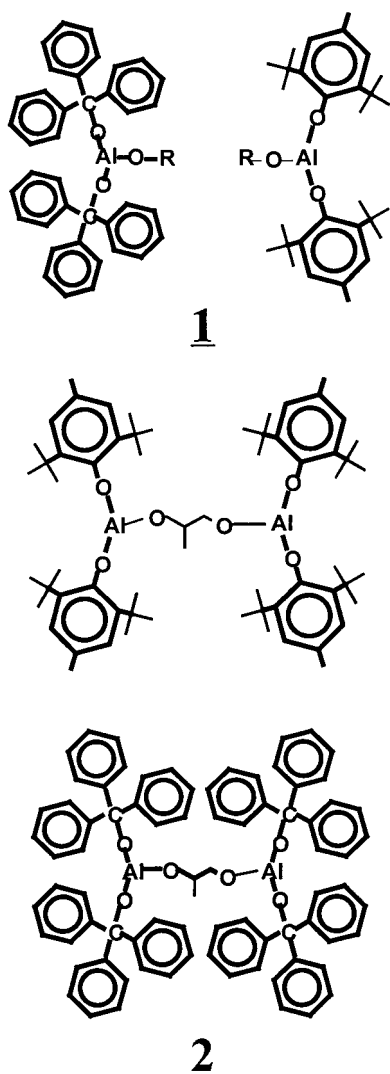
Figure 3. Sterically hindered aluminum catalysts used in the copolymerization of cyclic ethers and carbon dioxide.

was synthesized according to the procedure described in the literature.[19]

Synthesis of Catalysts for Oxirane/CO₂ Copolymerization. The catalysts were synthesized under argon in glass flasks that were heated to 200 °C and then evacuated and flushed with inert gas three times. The catalysts used for the copolymerization of propylene oxide and carbon dioxide are monofunctional (**1**) or difunctional (**2**) sterically hindered aluminum alkoxides or phenoxides (Figure 3). First, triisobutylaluminum is reacted with tri(phenyl)methanol or a sterically hindered phenol and then with an appropriate alcohol or glycol.[20] The ^{27}Al NMR spectra of the catalysts showed that the sterically hindered aluminum catalysts exhibit essentially only pentacoordination. If the Al atom were hexacoordinated, then the ^{27}Al NMR spectrum would also show a peak at 0 ppm, but the pentacoordinated species only shows a peak at appoximately 60 ppm. These NMR results suggest that the catalysts exhibit one species of active site (unlike previously reported catalysts for the polymerization of oxiranes and carbon dioxide); which perhaps explains the living character of the polymerizations that we subsequently observed.

In a typical experiment, 10 mL of triisobutyl aluminum (TIBA), as a 1.0 M solution in toluene, is reacted with 5.207 g (0.02 mol) tri(phenyl)methanol at 40° for

2−4 h, and then 0.77 mL (0.01 mol) of 2-propanol is added dropwise, and the mixture stirred for 2 h. The suspension of catalyst in toluene is then cooled to room temperature, the solvent is removed with a syringe, and the catalyst is washed twice with a small amount of dried toluene. The remaining solvent is then removed under vacuum at 50 °C. The aluminum catalysts with sterically hindered phenoxide substituents were used as a toluene solution.

Copolymerization of Cyclic Ethers and Carbon Dioxide. Copolymerization of cyclic ethers and carbon dioxide was performed in either a 25 or 35 mL high-pressure reactor equipped with a magnetic stirrer and pressure and temperature indicators. Prior to the experiment, the reactor was heated to 200 °C, evacuated, and then cooled to room temperature under an argon blanket. The desired amount of aluminum catalyst was introduced to the reactor under an argon blanket, and the reactor was sealed and evacuated for 15−20 min and then finally flushed with argon. The soluble aluminum compounds were used as a toluene solution and introduced with a syringe. The oxirane was added alone using a syringe or as a mixture with CO_2 using a high-pressure syringe pump (High-Pressure Equipment Co.). After injection of the reagents, the reactor was isolated and heated to the prescribed temperature (40−60 °C). After the desired time, the pressure was slowly released, and the reaction was terminated with methanolic hydrochloric acid. The polymer solution was filtered, processed, and analyzed as previously described.[16,20,21] The amount of carbonate incorporated into the polymer was determined from the integrals of the ether proton peaks at approximately 3.4−3.6 ppm and the carbonate-bound protons at 4.8 ppm from ^1H NMR spectrum. The reaction of cyclic ethers and carbon dioxide produces copolymers consisting of both ether and carbonate linkages.

Synthesis of Acetate-Terminated Poly(propylene oxide). Poly(propylene) oxide (monobutyl ether) with 7 or 21 repeat units was reacted with an excess of acetyl chloride in toluene for 24 h; the residual reactant and solvent were subsequently removed under vacuum.

Analyses. All ^1H NMR spectra were recorded on a Bruker DMX 300 instrument with the polymers dissolved in chloroform-d with tetramethylsilane used as the internal reference. The ^{27}Al NMR (75.468 MHz) spectra of the catalysts were recorded as previously described.[18,21] Molecular weights of the product polymers were determined using a Waters 150CV gel permeation chromatograph, equipped with 10^4, 10^3, 500, and 100 Å Ultrastyragel columns. THF was used as the eluent, and calibration was performed using polystyrene standards. IR spectra were recorded on a Mattson Genesis II FTIR spectrophotometer. The phase behavior of the polymers was studied in a variable-volume high-pressure view cell, equipped with a stirrer and temperature and pressure controllers.

Results and Discussion

Polyethers are known to exhibit low T_g's (190−230 K) and relatively low cohesive energy densities. Polyethers are also more CO_2-philic than many other polymers but significantly less so than fluorinated polymers or silicones.[8] To create model hydrocarbon CO_2-philes, we incorporated carbonyl groups into polyethers by side-chain acetate functionalization and by copolymerization of oxiranes and CO_2. Carbonyls have
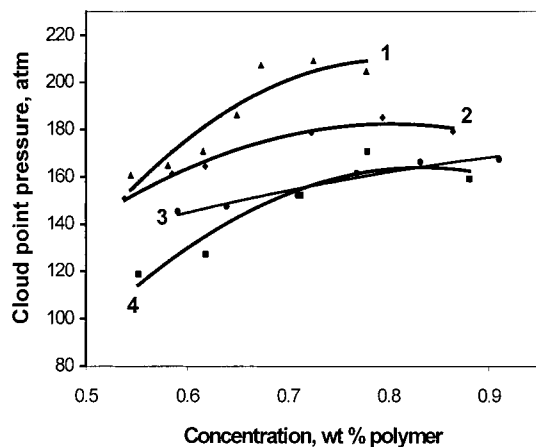
Figure 4. Phase behavior of acetate-functionalized epichlorohydrin $N = 25$ repeat units: (1) 33% acetate, (2) 40% acetate, (3) PO homopolymer (also 25 repeat units), (4) 45% acetate.
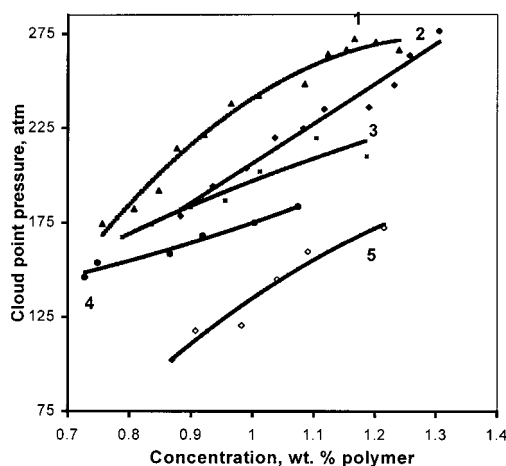

Figure 5. Phase behavior of acetate-functionalized poly(epichlorohydrin) $N = 7$ repeat units: (1) epichlorohydrin homopolymer, (2) 28% acetate, (3) 100% acetate, (4) 33% acetate, (5) 38% acetate.

been shown to interact favorably with carbon dioxide,[16,17,22] so we examined the effect of C=O placement in polyethers, as well as the effect of the extent of functionalization with carbonyl groups.

The Effect of Side Chain Functionalization on Solubility. A homopolymer of epichlorohydrin (25 repeat units) exhibits cloud point pressures above the limits of our instrument (400 atm, or 6000 psi) for concentrations greater than 0.5 wt %. As one can see from Figure 4, although the homopolymer of epichlorohydrin is insoluble under our operating conditions, the acetate-modified polymers are soluble in CO_2, and their cloud point pressures decrease as the amount of acetate is increased. Thus, a polymer modified with 45% acetate exhibits lower cloud point pressures than a homopolymer of propylene oxide of the same chain length.

We also modified a lower-molecular-weight (seven repeat units) poly(epichlorohydrin) with different amounts of acetate groups and compared the solubilities of the two polymers (Figure 5). The cloud points drop by 100 atm as the percent of acetate incorporated into the polymer moves from 28 to 38%, but yet the cloud point pressures of 100% acetate are higher. We conclude that the acetate groups act like a bound cosolvent but that, as the amount of acetate increases, a point of diminishing returns is reached. McHugh et al.[23] observed that the cloud point of poly(acrylates) in CO_2 dropped as the amount of cosolvent (acrylate) increased,
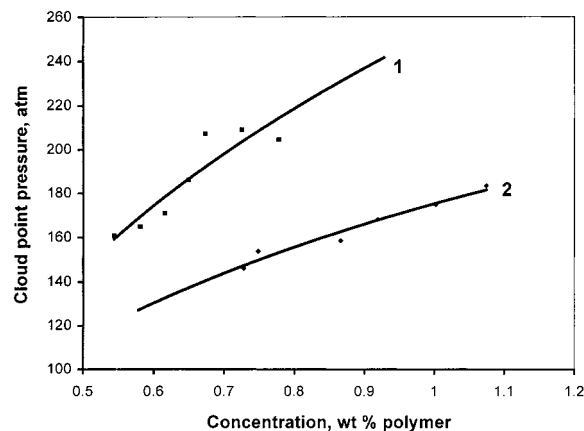

Figure 6. Phase behavior of functionalized poly(epichlorohydrin) with 33% acetate: (1) $N = 25$ repeat units, (2) $N = 7$ repeat units.
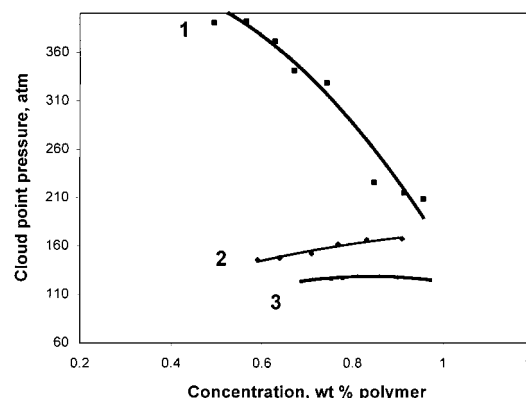

Figure 7. Phase behavior of PO–CO_2 copolymer with $N = 25$ repeat units: (1) PO/CO_2 copolymer 56% carbonate, (2) PO homopolymer, (3) PO/CO_2 copolymer 40% carbonate.

but they too reached a point of diminishing returns with cosolvent addition. In our case, although increasing the amount of acetate enhances CO_2–polymer interactions, it also stiffens the chain and likely enhances polymer–polymer interactions as well. Comparing poly(epichlorohydrin) with 7 and 25 repeat units (Figure 6) with the same amount of acetate (33%), we see that the cloud points of the two differ by as much as 70 atm, as expected.

The Effect of Backbone Carbonyl Groups on Solubility. Another option for probing the effect of carbonyl groups on the solubility of the polymer is to incorporate them into the backbone of the polymer. This was done by copolymerizing either propylene oxide (PO), ethylene oxide (EO), or cyclohexene oxide (CHO) with CO_2 using sterically hindered aluminum catalysts. These catalysts are living in character (yields in the range of 200–1200 g of polymer/g of catalyst) with one type of site available for polymerization and can be monofunctional or difunctional. The extent to which CO_2 is incorporated into the polymer depends on the temperature and pressure at which the polymerization is carried out, as well as the nature of the sterically hindered substituents attached to the aluminum atoms and the oxirane type.

When we compare PO/CO_2 copolymers with 25 repeat units (Figure 7), one can see that a copolymer with 56% carbonate is less CO_2-philic than a homopolymer of PO, but a polymer with 40% carbonate exhibits miscibility pressures lower than those of the homopolymer. A polycarbonate homopolymer (i.e., a completely alternating CO_2/propylene copolymer) with 25 repeat units
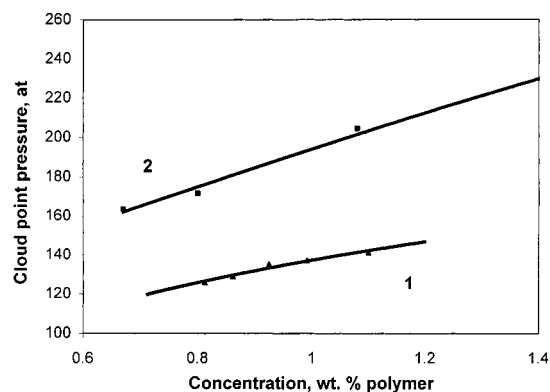
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Figure 8. Phase behavior of $PO-CO_2$ copolymers vs poly-(fluoroether): (1) PO/CO_2 copolymer with $N = 220$ repeat units, 15% carbonate; (2) Krytox, $N = 176$ repeat units (ref 24).
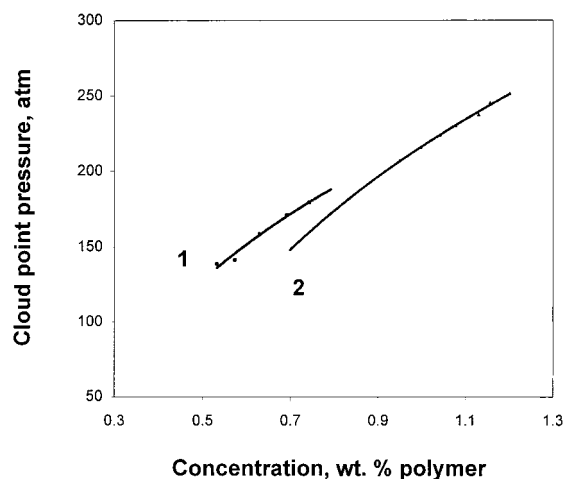

Figure 9. Phase behavior of $EO-CO_2$ copolymer vs PEO: (1) EO/CO_2 copolymer with $N = 103$, 33.7% carbonate; (2) PEO, $N = 16$.

displays miscibility pressures beyond the limits (6000 psi) of our instrument. These results are consistent with our initial design hypothesis (Figure 1) that, if the correct proportions of monomer 1 and monomer 2 are chosen, the copolymer should be more soluble than either of the homopolymers.

PO/CO₂ copolymers are apparently more CO₂-philic than fluoroether polymers, in that the cloud points of a 250 repeat unit PO/CO_2 copolymer (15.4% carbonate) are signifivcantly lower than those for a poly(perfluoroether) with 175 repeat units (Figure 8). This behavior is quite dramatic as poly(perfluoroethers) are one of the most CO₂-philic polymers known to dateand the PO/CO_2 copolymers are likely to be at least $^1/_{100}$ the cost of the fluorinated materials.

The phase behavior of other oxirane/CO₂ copolymers was also examined. Ethylene oxide (EO) was copolymerized with carbon dioxide, and we found that an EO/CO_2 copolymer with 103 repeat units had almost the same phase behavior (Figure 9) as a homopolymer of EO with only 16 repeat units (an EO homopolymer with 103 units would be essentially insoluble in this pressure range).

We also synthesized copolymers of cyclohexene oxide and CO₂, for which one might suppose that the chain would be less flexible because of the cyclohexane rings. Miscibility pressures for these types of copolymers (as for others) are a function of molecular weight and incorporated carbon dioxide (as carbonate units). For example, the data in Figure 10 show that miscibility
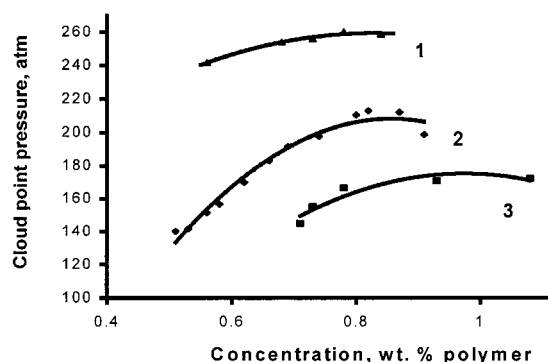

Figure 10. Phase behavior of $CHO-CO_2$ copolymers with high content of carbonate units: (1) 47% carbonate, $N = 27$; (2) 40% carbonate, $N = 20$; (3) 50% carbonate, $N = 16$.
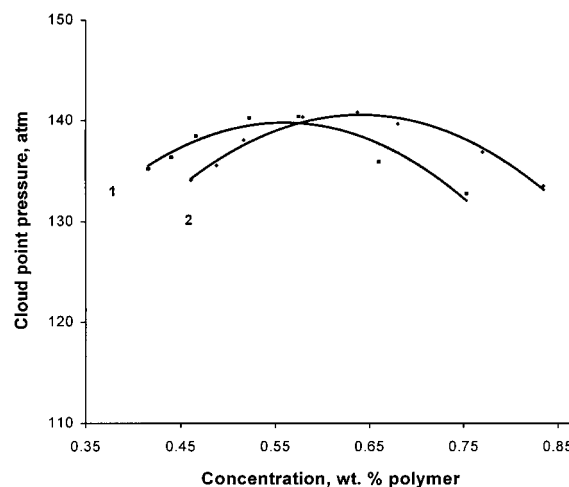

Figure 11. Phase behavior of $CHO-CO_2$ copolymers with low content of carbonate units: (1) 8.8% carbonate, $N = 124$; (2) 2.3% carbonate, $N = 88$.

pressures increase upon increasing chain length at (relatively) constant percentage of carbonate, as expected. However, as shown in Figure 11, the amount of carbonate required to render these copolymers CO₂-philic is apparently much lower than the levels in the materials in Figure 10. Figure 11 shows that copolymers with less than 10% carbonate repeats exhibit miscibility pressures below 150 atm. The cloud point curves for $CHO-CO_2$ copolymers with $N = 124$ repeat units (8.8% carbonate) and $N = 88$ repeat units (2.3% carbonate) show almost the same behavior despite differing by 36 repeat units. That the CHO/CO₂ copolymers are so CO₂-philic is somewhat surprising—the results in Figure 11 may be attributed to increased chain flexibility upon introduction of carbonate repeats into a poly(CHO) or unfavorable enthalpic interactions between carbonate and cyclohexyl groups.

It should be also noted that the solubility of low-molecular-weight polymers in carbon dioxide is affected by the nature of the end groups. We observed that monohydroxy-terminated polyethers are more soluble than a difunctional homologue with the same number of repeated units but less soluble than an acetoxy-terminated polyether (Figure 12). Again, addition of an acetate group provides a superior response to addition of an alkyl group.

Conclusion

The solubility of polyethers in CO₂ is dramatically affected by addition of either acetate groups in the side
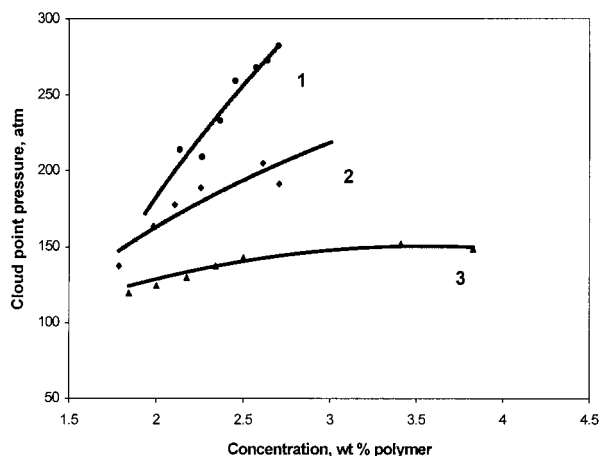
Figure 12. Phase behavior of poly(propylene glycol) diol (**1**), poly-(propylene glycol) monobutyl ether (**2**), and poly(propylene glycol) acetate (**3**) with 21 repeat units.
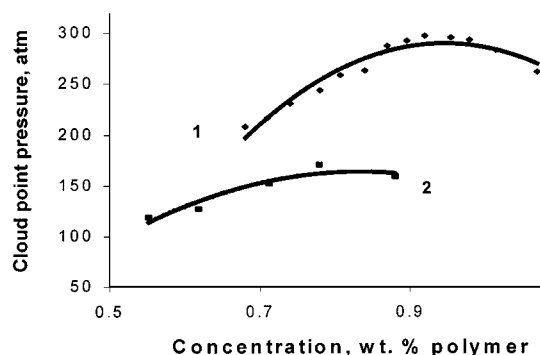

Figure 13. Phase behavior of epichlorohydrin/CO_2 copolymer compared to acetate-modified poly(epichlorohydrin): (1) ECH/CO_2 copolymer, $N = 17$, 25% carbonate; (2) modified PECH, $N = 25$, 45% acetate.

chain or carbonate groups in the backbone of the polymer. Miscibility pressures of polyethers modified with acetate groups decrease as the acetate content increases, but a point is reached beyond which additional acetate content raises cloud point pressures. This is consistent with our original hypothesis. The oxirane/CO_2 copolymers were very soluble even to the point where a PO/CO_2 copolymer was more soluble than a poly(perfluoroether). Still, the question remains "is it better to put carbonyl groups in the side chain or the backbone?" Figure 13 shows that a copolymer of epichlorohydrin and CO_2 with 17 repeat units and 25% carbonate is less soluble than a poly(epichlorohydrin) with 25 repeat units modified with 45% acetate groups. However, we do not know whether 25% is the optimum level of carbonate linkages in the ECH/CO_2 copolymer for maximum solubility (or whether 45% acetate is also optimal). There must be a balance between the favorable entropic effects from chain flexibility and the enthalpic effects created by solute/solvent interactions, and hence, work is in progress to provide a better understanding of this energetic balance.

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