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Phase Behavior of Oxygen-Containing Polymers in CO_2

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ABSTRACT: The cloud point curves of a series of oxygen-containing polymers in CO_2 were measured to attempt to deduce the effect of oxygen functional groups within a polymer on the polymer/CO_2 phase behavior. The addition of an ether oxygen to a hydrocarbon polymer, either in the backbone or the side chain, enhances "CO_2-philicity" by providing sites for specific interactions with CO_2 as well as by enhancing the entropy of mixing by creating more flexible chains with higher free volume. Ab initio calculations show that both ether and ester oxygens provide very attractive interaction sites for CO_2 molecules. The binding energy for an isolated ether oxygen with CO_2 is larger in magnitude than that for a carbonyl oxygen/CO_2 complex. However, acetate functionalized polymers are more CO_2-soluble than polymers with only ether functionalities—possibly because acetate functional groups contain a total of three binding modes for CO_2 interactions, compared with only one for the ether functional group. Experiments clearly indicate that adding a single methylene group as a spacer between a polymer backbone and either an ether or acetate group exhibits a strong deleterious effect on phase behavior. This effect cannot be explained from our ab initio calculations.

Introduction

Substantial effort has been devoted to developing uses for carbon dioxide as a process solvent because CO_2 is inexpensive and relatively nonhazardous. Unfortunately, CO_2 is generally considered to be a feeble solvent for polar and high-molecular weight materials, although it can solubilize low-molecular weight, volatile compounds. A full understanding of the solvent character of CO_2 has remained a challenge for researchers for more than two decades. To illustrate this, the literature notes that the solvation power of CO_2 has been likened to toluene on the basis of Fourier transform infrared (FT-IR) spectroscopy,[1] to hexane[2] and to pyridine[3] on the basis of thermodynamic solubility parameter calculations, and to acetone on the basis of hydrogen-bond-accepting tendency.[4] However, these descriptions have been discarded over the years because many materials that are soluble in these solvents have been found to be insoluble in CO_2. Carbon dioxide's large quadrupole moment has been suggested as being at least partially responsible for its weak solvent character.[5,6] CO_2 has also been likened to fluorocarbons owing to its low "polarizability per volume", a measure of the strength of van der Waals interactions. It has been reported that CO_2 exhibits a lower polarizability per volume, and hence weaker solvent power toward nonpolar hydrocarbons, than either ethane or ethylene.[7]

Some, but interestingly not all, fluorinated alkane, acrylate, and ether polymers are miscible with CO_2 at much lower pressures than their nonfluorous counterparts.[8,9,10] The origin of the miscibility of these fluorinated polymers has been closely scrutinized by researchers to support design of new CO_2-philic materials. Attempts to explain the CO_2-philic character of fluorinated polymers have employed both spectroscopic and theoretical studies to determine whether there exist any specific interactions between CO_2 and these molecules, and if so, what the nature of these interactions is. For example, Yee et al.[11] used FT-IR to investigate the possibility of specific interactions between CO_2 and hexafluoroethane (C_2F_6). They found no evidence of specific attractive interactions between the F atoms and CO_2, and in fact CO_2 was found to be more repulsive to C_2F_6 than C_2H_6. The authors consequently attributed the observed enhanced solubility of fluorocarbons to the highly repulsive nature of fluorocarbon−fluorocarbon interactions, making the solute−solute interactions less favorable than solute−solvent interactions. Possible specific interactions between F and CO_2 were also investigated by NMR spectroscopy. Dardin et al.[12] compared ^1H and ^{19}F NMR chemical shifts of *n*-hexane (C_6H_{14}) and perfluoro-*n*-hexane (C_6F_{14}) in CO_2. They reported that no extraordinary solvent−solute interactions were present between C_6H_{14} and CO_2, whereas they observed a chemical shift in the C_6F_{14} spectra, which they ascribed to C_6F_{14}−CO_2 van der Waals interactions.[13] Kazarian et al.[14] found evidence for weak CO_2−F interactions in poly(vinyl fluoride) by observing a small splitting in the CO_2 bending mode. In contrast, Yonker and Palmer[15] used ^1H and ^{19}F NMR to show that neither fluoromethane (CH_3F) nor trifluoromethane (CHF_3) exhibit significant specific attractive interactions with CO_2. Taylor et al.[16] attributed this discrepancy in the NMR results to the electronic and structural difference between the molecules in comparison.

Theoretical studies have also resulted in contradictory findings. On the basis of restricted Hartree−Fock-level ab initio calculations, Cece et al.[17] suggested that there exist specific interactions between CO_2 and the fluorines of C_2F_6. Han and Jeong,[18] however, disagreed with these results, noting that Cece et al.[17] did not take into account basis-set superposition error (BSSE) corrections during their calculations. Using similar ab initio calculations but accounting for BSSE corrections, Diep et al.[19] reported no evidence of CO_2−F interactions in perfluorinated compounds that would explain the superior solubility of fluorocarbons versus hydrocarbons. Furthermore, interactions

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between hydrocarbons and CO_2 were found to be even stronger than those between fluorocarbon analogues and CO_2.[19] Raveendran and Wallen[20] computationally investigated the effect of stepwise fluorination on the CO_2-philicity of methane in an effort to address the existence of F−CO_2 interactions, and to explain the fundamental difference in the nature of interactions of fluorocarbons and hydrocarbons with CO_2. Their calculations showed that there is an optimum degree of fluorination for maximum CO_2-philicity. Their results for comparison of methane (CH_4) and perfluoromethane (CF_4) indicated that CO_2−fluorocarbon and CO_2−hydrocarbon interactions are energetically comparable; however, they are different in nature. In partially fluorinated systems, the fluorine atom acts as a Lewis base toward the electron-deficient carbon atom of CO_2, and the hydrogen atoms, having increased positive charge due to the neighboring fluorine, act as Lewis acids toward the electron-rich oxygen atoms of CO_2. Shoichet, Enick, and co-workers[21] investigated the effect of semifluorination of a polymer with both experimental and theoretical methods. They found that the copolymer poly(tetrafluoroethylene-*co*-vinyl acetate) exhibits an optimum fraction of tetrafluoroethylene; having more or less than the optimum fraction leads to an increase in the cloud point pressure. The optimum fraction of tetrafluoroethylene was attributed to CO_2 interacting with both fluorinated and nonfluorinated parts of the polymer, such that the polymer simultaneously displays both Lewis acid and Lewis base character.[21]

A different scenario emerges from a recent study by Fried and Hu,[22] who used second-order Møller−Plesset (MP2) perturbation calculations with the 6-311++G** basis set in an effort to identify the nature of specific interactions between CO_2 and fluorinated substituent groups of polymers. These authors investigated interactions of CO_2 with three fluoroalkanes (CF_4, CF_3CH_3, and $CF_3CH_2CH_3$) and three alkanes (CH_4, CH_3CH_3, and $CH_3CH_2CH_3$). They reported that quadrupole−dipole interactions are important contributors to the total energy of interaction, with $CF_3CH_2CH_3$ having the maximum quadrupole−dipole interaction energy of 11.5 kJ/ mol. By contrast, the interaction energy between propane and CO_2 is 6.88 kJ/mol, attributable to dispersion forces and other interactions. In experimental studies by McHugh and co-workers,[5,23] the favorable miscibility of fluorocarbons has been attributed to polar−quadrupole interactions between fluorinated polymers and CO_2, given CO_2's large quadrupole moment. These authors suggest that CO_2's large quadrupole moment works against solubilizing predominantly nonpolar polymers, because CO_2 self-interactions dominate, especially at low temperatures. The authors also noted that fluorination imparts solubility to the polymer provided that polarity is also introduced to the polymer via such fluorination. However, a high level of fluorination produces an adverse effect on miscibility due to the dominance of dipole−dipole interactions between the polymer chains.[5,23] Clearly, there is considerable controversy in the literature surrounding the origin of the miscibility of fluorinated polymers in CO_2.

In the mid-1990s, using FT-IR, Kazarian et al.[14] reported the existence of specific interactions between the carbon atom of CO_2 and lone pairs on the oxygen of a carbonyl. They argued that this complex formation is most probably of a Lewis acid−Lewis base nature. The Lewis acid character of CO_2 has also been explored by FT-IR in a number of studies[24,25] and also measured computationally.[26,27,28] In these studies, it was shown that the carbonyl oxygen interacts with the carbon atom of CO_2, but the geometry and strength of the interaction may vary depending on adjacent groups. Experimental findings also revealed that one can achieve miscibility of an otherwise immiscible polymer in CO_2 via incorporation of carbonyl groups.[29,30] Meredith et al.[31] reported that CO_2 can interact with other Lewis base groups, such as tributyl phosphate and a tertiary alkyl amine. Recently, Raveendran and Wallen[27] reported the presence of attractive specific interactions between CO_2 and the S═O sulfonyl group in dimethyl sulfoxide on the basis of ab initio calculations.

Because CO_2 is a weak solvent, O'Neill et al.[7] hypothesized that a CO_2-philic material should exhibit weak self-interactions. The authors have shown that many of the compounds exhibiting CO_2-philic character (e.g., fluoroacrylates, siloxane polymers, polyethers) exhibit low surface tension, which suggests low cohesive energy density and hence weak self-interactions.

Fluorinated acrylate polymers are the most CO_2-philic high molecular weight materials identified to date, and hence the intense interest in probing the underlying phenomena that govern the phase behavior of fluorinated polymer−CO_2 mixtures is understandable. Such work is also critical to the design of nonfluorous CO_2-philes as well, as it focuses on the nature of specific interactions between solute functional groups and CO_2. Fluorinated materials are generally expensive; some are environmentally suspect, and hence design of a nonfluorous CO_2-phile would be of interest scientifically and commercially.

We hypothesize that a CO_2-philic material should possess a relatively low cohesive energy density, a relatively low glass transition temperature (high flexibility and high free volume), and a number of Lewis base groups to promote polymer−CO_2 interactions. We previously showed that CO_2 can have as strong and favorable interactions with an ether oxygen as with a carbonyl oxygen.[28] Similarly, in another study, it was suggested on the basis of infrared spectroscopy and ab initio calculations that van der Waals complex formation occurs between the dimethyl ether oxygen atom and CO_2 carbon atom.[32] Upon consideration of the lower contribution of ether oxygens (compared to carbonyls) to the cohesive energy density of a material,[33] and the flexibility and rotational freedom gained by addition of an ether oxygen, utilization of ether groups in the design of a CO_2-philic material could be more important than the carbonyl group if the former is judiciously integrated into the polymer structure.

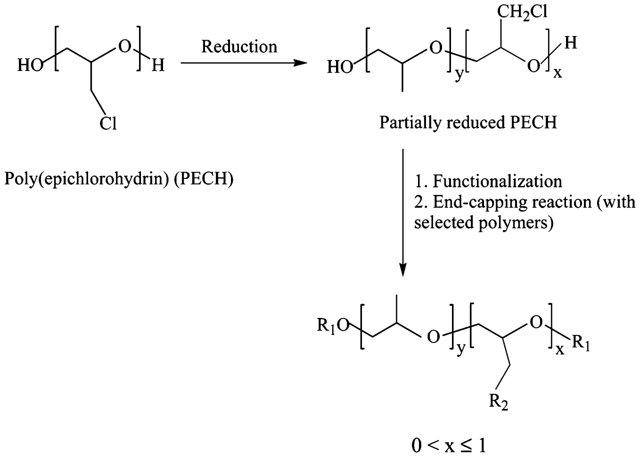
In this study, we incorporated ether and carbonyl oxygens into relatively simple (structurally) polymer chains in various ways and systematically assessed the effect of such groups on the phase behavior of the polymers. End group effects were also assessed for some polymers via the replacement of CO_2-phobic hydroxyl groups with CO_2-philic acetate groups. Polymers investigated here include methyl acetate-functionalized poly(propylene glycol), methyl ether-functionalized poly(propylene glycol), polypropylene, poly(propylene glycol) dimethyl ether, poly(vinyl ethyl ether), poly(vinyl acetate), poly(vinyl methyl ether), and poly(allyl acetate).

We have employed quantum chemical ab initio calculations to complement the experimental studies in this work. The geometric and energetic properties of CO_2 with various polymer moieties have been computed. Quantum chemical calculations cannot provide a complete description of the CO_2−polymer system. However, the calculations are valuable for identifying specific interaction sites on polymers that may improve CO_2 solubility of the polymer.

Experimental Methods

Materials. Poly(propylene glycol) with number-average molecular weights of 2000, 2700, and 3500, poly(vinyl ethyl ether) (M_n

Scheme 1. Schematic for Synthesis of Partially Reduced and Functionalized Polymers with Ether Oxygen in the Backbone[a]



[a] R_1 = H and R_2 = O-CO-CH_3, methyl acetate-functionalized poly(propylene glycol); R_1 = H and R_2 = O-CH_3, methyl ether-functionalized poly(propylene glycol); R_1 = CO-CH_3 and R_2 = O-CO-CH_3, methyl acetate-functionalized poly(propylene glycol) diacetate; R_1 = CO-CH_3 and R_2 = O-CH_3, methyl ether-functionalized poly(propylene glycol) diacetate.

= 3800), *N*-methylmorpholine, lithium aluminum hydride (95%), sodium hydride (60% in mineral oil), methyl iodide (99.5%), lithium aluminum hydride (1 M in tetrahydrofuran, THF), potassium acetate, sodium methoxide (0.5 M in methanol), anhydrous THF, and anhydrous *N*,*N*-dimethylformamide (DMF) were obtained from Aldrich. Sodium potassium tartrate was purchased from Fisher Scientific. Poly(epichlorohydrin) (85% in 1,3-dioxolane, nominal number-average molecular weight of 2600) was received as a generous gift from 3M. Poly(*n*-butyl acrylate) with nominal number-average molecular weight of 10 000 (78 repeat units) was purchased from Polysciences, Inc. Poly(vinyl methyl ether) with M_n = 3850 and polydispersity index (PDI) = 1.05 was purchased from Polymer Source Inc. High molecular weight (M_n = 120 000) poly(vinyl ethyl ether) was purchased from Scientific Polymers, Inc. Low molecular weight atactic poly(propylene) (number-average molecular weight of 425 and 1000, in hexane) was obtained as a generous gift from Sunoco Chemicals. All materials were used as received unless otherwise noted below.

Synthesis of Partially Functionalized Poly(propylene glycol)s. In order to achieve varying degrees of substitution on a polyether backbone of constant chain length and chain length distribution, we performed a series of reactions on poly(epichlorohydrin) (PECH). PECH was first partially reduced, to an epichlorohydrin/propylene glycol copolymer, by use of lithium aluminum hydride ($LiAlH_4$). The remaining chloromethyl groups were later reacted to incorporate either ether or acetate side chains (Scheme 1).

Partial reduction of poly(epichlorohydrin) to form epichlorohydrin/propylene glycol copolymer was adapted from an existing procedure.[34] Details of all synthesis procedures are given in the Supporting Information. The polymer was characterized by ^1H NMR as follows: δ 1.1 [br s, 3H, -CH_2-CH(CH_3)-O], 3.8 (br s, 3H, -CH_2-CH-O), 3.6 (br s, 2H, -CH_2-Cl).

Methyl acetate-functionalized poly(propylene glycol)s were synthesized according to the procedure used by Cohen.[35] ^1H NMR characterization gave the following: δ 1.13 [br s, 3H, -CH_2-CH(CH_3)-O], 2.07 (s, 3H, -O-CO-CH_3), 3.6 (br s, 3H, -CH_2-CH-O), 4.2 (br s, 2H, -CH_2-O-CO-CH_3).

Methyl ether-functionalized poly(propylene glycol)s were synthesized according to the procedure given in the Supporting Information. ^1H NMR results were as follows: δ 1.13 [br s, 3H, -CH_2-CH(CH_3)-O], 3.71 (br s, 8H, -CH_2-CH-O, -CH_2-O-CH_3, -O-CH_3).

Hydroxyl end groups of the functionalized poly(propylene glycol)s were capped by reacting with a large excess of acetoyl chloride. End-capping was performed on the following polymers: poly(propylene glycol) (PPG) (M_n = 2000), 100% acetate-functionalized PPG, 12% methyl acetate-functionalized PPG, 12% methyl ether-functionalized PPG, and homopolymer of epichlorohydrin (PECH). To verify the completion of the reaction, an FT-IR spectrum was taken. The -OH peaks at 1080 and 1060 cm^{-1} and a broad peak at approximately 3500 cm^{-1} disappeared as the hydroxyl groups were replaced by the acetate. On the polymers without acetate substitution in the backbone, the methyl protons on the acetate end groups were easily visible in the ^1H NMR spectrum at 2.1 ppm.

Low molecular weight poly(propylene) (PP) was purified by removing solvents (hexane and residual water) under vacuum; removal of the solvents was verified by ^1H NMR. The PP (M_n = 1000) was received as an amorphous, white solid mixed with crystalline beads of high molecular weight PP. A gel-permeation chromatogram provided by Sunoco Chemicals indicated that a majority of the sample had a number-average molecular weight of 1000. The mixture was placed in hexane, which dissolved the PP 1000, while the high molecular weight material remained as an insoluble solid. The high molecular weight material was filtered, and the hexane was removed under reduced pressure, leaving poly(propylene) at the desired molecular weight of 1000.

Poly(propylene glycol) dimethyl ether was synthesized via reaction of the hydroxyl end groups in poly(propylene glycol) (M_n = 3500) with methyl iodide. Upon concentration, a pale-yellow, viscous polymer was obtained. The peak at 3480 cm^{-1} in the FT-IR and at 3.92 ppm in ^1H NMR, each corresponding to the -OH end groups in the poly(propylene glycol), disappeared following reaction. Absence of these peaks in the modified polymer indicated that effectively all of the -OH groups in the poly(propylene glycol) were capped.

Allyl acetate cannot generally be polymerized to chain lengths beyond seven repeat units, and hence poly(allyl acetate) was synthesized via modification of poly(allyl alcohol), which itself was synthesized via reduction of poly(*n*-butyl acrylate) (with nominal number-average molecular weight of 10 000) with $LiAlH_4$ following an existing procedure.[36] A very tough, white polymer was obtained (7.3 g, 87% yield). ^1H NMR (300 MHz, DMSO-d_6) gave the following: δ 1.2−1.5 (br s, 3H, CH_2-CH), 3.4 (br s, 2H, CH_2-OH), 4.3 (br s, 1H, -OH). ^1H NMR (300 MHz, D_2O): δ 1.2−1.5 (br s, 3H, CH_2-CH), 3.4 (br s, 2H, CH_2-OH), 4.7 (br s, 1H, water); shifting of the peak at 4.3 ppm in DMSO-d_6 to 4.7 ppm in D_2O is due to proton exchange between -OH and D_2O.

Poly(allyl acetate) was synthesized via acetylation of poly(allyl alcohol) by acetic anhydride according to an earlier procedure.[37] ^1H NMR (300 MHz, C_6D_6) gave δ 1.5 (br s, 3H, -CH_2-CH-), 2.0 (s, 3H, -O-CO-CH_3), 4.2 (br s, 2H, -CH_2-O-CO-CH_3).

Phase Behavior Measurements. Nonsampling phase behavior measurements of the polymer−CO_2 systems were performed in the same way as described earlier.[28] All measurements were carried out at 22 °C, therefore, CO_2 was in the liquid state in all the systems studied. Cloud point determination was repeated three times. Typical variability in the cloud point measurements was less than $\pm$0.7 MPa. The error bars for the cloud point measurements are roughly the size of the data points in the figures.

Theory/Calculations. Quantum chemical modeling has been employed by many groups as a method to help clarify the interactions between CO_2 and polymers.[17,19−22,26−28,38] There are several limitations to the use of ab initio quantum mechanical methods to describe CO_2−polymer systems. The CO_2−CO_2 and (approximate) CO_2−polymer interactions can be computed, but current methods are not capable of accurately describing polymer−polymer interactions. Effects of temperature, entropy, and pressure cannot be explicitly included—statistical mechanical methods are needed for these factors. Notwithstanding these serious limitations, quantum methods are still able to provide insight that statistical mechanical methods and equation of state modeling cannot. Statistical mechanical methods rely on empirical potentials and so lack true predictive power unless the potential energy surfaces can be described with sufficient accuracy. Ab initio methods can provide accurate interaction energies, and extensive quantum calculations can be used to develop potential models. The goal of our work is to compute the ground-state geometries and energetics of CO_2−polymer interactions—specifically in order to compare ether and carbonyl functional groups.

Quantum mechanical methods cannot be directly applied to modeling of true polymer−CO_2 systems because of the large number of atoms involved and the aperiodic nature of the polymer. We have therefore divided the polymer into representative segments or moieties and have performed calculations for CO_2 interacting with these segments. Generally, we chose moieties that contain important functional groups, such as the ether and the carbonyl oxygens, as surrogates for the polymers. Complexes of ether oxygen/CO_2 and carbonyl oxygen/CO_2 are weakly interacting, bound mainly by dispersion (van der Waals) forces. High-level theories and large basis sets are required to fully capture the properties of those weakly bound systems. Computationally efficient methods, such as density functional theory, are not generally accurate for dispersion complexes.[39−46] The coupled cluster method, CCSD(T), is one of the most accurate levels of theory available. However, the systems that we are interested are too large for the CCSD(T) method, given current available computing resources. Therefore, we chose the MP2 level of theory to perform calculations as a compromise between accuracy and efficiency. Our previous calculations indicate that MP2 is acceptable for these types of calculations.[28] We carried out geometry optimizations at the MP2/6-31+g(d) level of theory and basis set. The 6-31+g(d) basis set was chosen as a compromise between completeness and efficiency. Optimizations were started from several different initial configurations, in which CO_2 molecules were placed around oxygens of the polymer moieties. We performed single-point energy calculations on geometries obtained from optimizations with a much larger basis set (aug-cc-pVDZ). The binding energies reported here are taken as the difference between the total energies of the cluster and the constituent molecules making up the cluster, each relaxed to their (local) minimum energy configuration. Negative energies are more favorable with this definition of binding energy. Counterpoise (CP) corrections[47] were applied to all binding energies to approximately account for basis set superposition error, which has considerable impact on the accuracy of results for weakly bound complexes.[19] We used the average of raw and CP-corrected energies as an approximation for energies at the complete basis set (CBS) limit. This approximation was found to be fairly accurate in our previous calculations[21,28,48] and also in agreement with the findings of Feller and Jordan.[49] Hence, in this paper, we report only the averages of MP2/aug-cc-pVDZ CP corrected and uncorrected interaction energies. Gaussian 98[50] was used for all the calculations.

Results and Discussion

We computed interaction energies of CO_2 with models of the repeat units of poly(vinyl acetate) (PVAc), poly(vinyl methyl ether) (PVME), poly(vinyl ethyl ether) (PVEE), and poly(allyl acetate), namely, isopropyl acetate (IPA), methyl isopropyl ether (MIE), ethyl isopropyl ether (EIE), and isobutyl acetate (IBA). We have also studied methyl isobutyl ketone (MIK) in order to investigate carbonyl/CO_2 interactions.

We identified one favorable binding mode for the ether or ester oxygen with CO_2 and two different binding modes for the carbonyl oxygen/CO_2 complex from our calculations. The two carbonyl oxygen/CO_2 binding geometries, A and B in Figure 1, mainly differ in the orientation of CO_2 with respect to the different R groups of the carbonyl-containing molecule (see Figure 1). The calculated binding energies for these systems are summarized in Table 1. Note that the binding energies reported in Table 1 are about 4−5 times larger in magnitude than the kinetic energy available to a CO_2 molecule at the temperature of the experiments. Hence, these binding modes are likely to be important, even at room temperature.

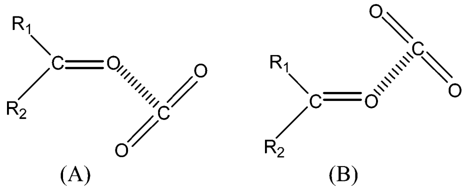


Figure 1. Schematic of the two different binding geometries for the carbonyl oxygen/CO_2 complex identified from ab initio calculations.

Table 1. Interaction Energies with CO_2

molecules[a]	interaction energies (kJ/mol) ether oxygen/ CO_2	carbonyl oxygen/ CO_2 (A)	carbonyl oxygen/ CO_2 (B)
IPA	−14.8	−14.2	−15.9
MIE	−18.0	N/A	N/A
EIE	−18.6	N/A	N/A
IBA	−15.1	−14.1	−14.3
MIK	N/A	−13.6	−16.0

[a] IPA, isopropyl acetate; MIE, methyl isopropyl ether; EIE, ethyl isopropyl ether; IBA, isobutyl acetate; MIK, methyl isobutyl ketone.

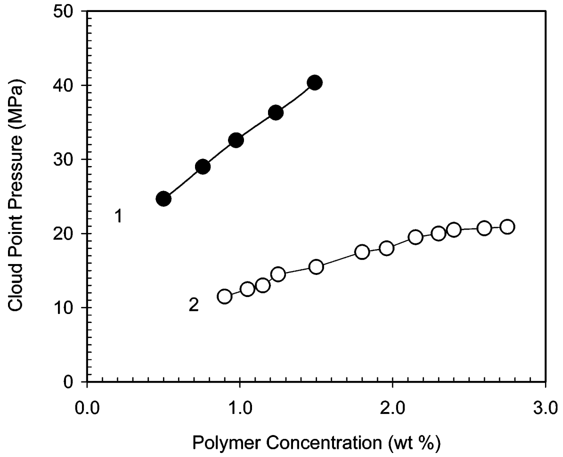
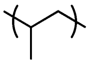
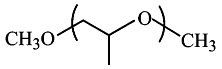
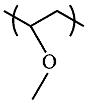
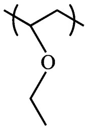
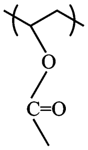
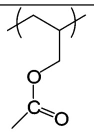


Figure 2. Phase behavior of mixtures of CO_2 with (1) polypropylene (PP, $M_n = 425$,●) and (2) poly(propylene glycol) monomethyl ether (PPG-MME, $M_n = 1000$, ○), at 22 °C. PPG-MME is more CO_2-philic than PP, despite having a molecular weight more than twice that of PP.

It has previously been assumed that the carbonyl oxygens are the most important sites for CO_2 interactions with acetate-containing molecules. A number of studies have been carried out to characterize carbonyl oxygen/CO_2 interactions,[26,38,51] yet none have considered the impact of the ether-like ester oxygen in the acetate group. However, there have been two studies on the interaction of CO_2 with isolated ethers.[32,52] Our ab initio calculations, summarized in Table 1, clearly show that binding energies of CO_2 with ester oxygens in acetate groups and with isolated ethers are as large in magnitude as those associated with carbonyl sites. For example, the binding energy of CO_2 with the ester oxygens in both IPA and IBA is comparable with the CO_2 binding to the carbonyl oxygens. Furthermore, isolated ethers (MIE and EIE) have binding energies larger in magnitude than those in an isolated carbonyl (MIK). Note that the calculations presented here are for small molecules and do not account for the entropic and polymer−polymer contributions to solubility. Hence, one cannot directly predict the solubility of polymers from these calculations. Nevertheless, these results indicate that ether-containing polymers have favorable sites for CO_2−polymer interactions and should therefore be good candidates for CO_2-soluble polymers.

Our experiments confirm that the presence of ether oxygens in a polymer does lower miscibility pressures in CO_2. Figure 2 shows the phase behavior of poly(propylene) (PP, $M_n = 425$)

Table 2. Surface Tension of the Polymers Used to Assess the Effect of Oxygen on Phase Behavior[59,60]

Polymer	Structure	Surface Tension (mN/m) at 20 °C
1. Poly(propylene) (PP)		31
2. Poly(propylene glycol)-dimethylether (PPG-DME)		31
3. Poly(vinyl methyl ether) (PVME)		29
4. Poly(vinyl ethyl ether) (PVEE)		36
5. Poly(vinyl acetate) (PVAc)		36
6. Poly(allyl acetate)		n/a

and poly(propylene glycol) monomethyl ether (PPG-MME, $M_n = 1000$)[53] in CO_2. We observed that poly(propylene) with a number-average molecular weight of 1000 is not miscible with CO_2 at concentrations above 0.5 wt % at pressures below 50 MPa. PPG-MME is miscible with CO_2 at much lower pressures than PP, despite the higher molecular weight *and* inclusion of a terminal hydroxyl group. Note that both polymers exhibit the same surface tension, as seen in Table 2 by comparison with poly(propylene glycol) dimethyl ether (PPG-DME), $CH_3O(CH_2CHCH_3O)_nCH_3$, which is similar to PPG-MME, $CH_3O(CH_2CHCH_3O)_nH$. Hence, solute self-interaction is not an overriding factor. The phase behavior results suggest that the ether oxygens in PPG-MME are responsible for its superior miscibility compared to that of PP, in agreement with our ab initio calculations. In addition to providing a site for specific interactions, it is likely that the presence of oxygen in the PPG-MME enhances the entropy of mixing compared with polypropylene. High molecular weight PPG exhibits a lower T_g than atactic polypropylene, suggesting higher flexibility and free volume in the former. In addition, the value for σ, the ratio of the actual chain dimension to that of a freely rotating chain, is higher for atactic polypropylene, suggesting that polypropylene is a stiffer chain. In summary, the addition of the ether oxygen to the backbone has a dramatic effect on phase behavior, apparently via the creation of sites for specific interactions with CO_2 and secondarily via enhancement of chain flexibility and thus entropy of mixing.

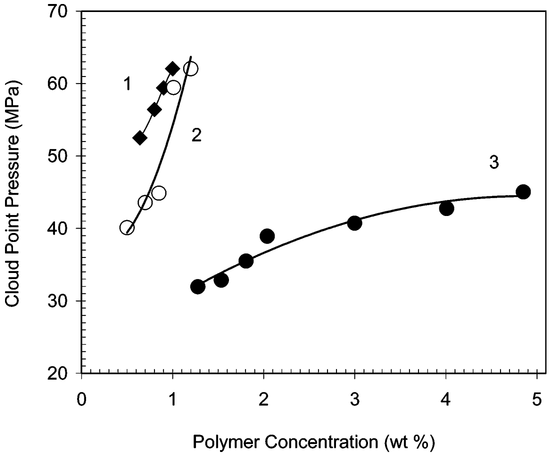


Figure 3. Phase behavior of CO_2 mixtures with (1) PPG-DME ($M_n = 3500$) (◆), (2) PVME ($M_n = 3850$) (○), and (3) PVEE ($M_n = 3800$) (●) at 22 °C. The effect of the location of oxygen (backbone versus side chain) on the cloud point curve can be seen by comparing 1 and 2. PVME has a lower cloud point pressure curve despite having a higher molecular weight than PPG-DME. The effect of the poly(vinyl alkyl ether) chain length on the phase behavior can be seen by comparing curves 2 and 3. PVEE is substantially more CO_2-philic than PVME.

The polymer–CO_2 phase behavior of two isomeric polymers of similar molecular weight—namely, PVME and PPG-DME, structures 2 and 3 of Table 2—was tested to assess the effect of oxygen placement within the polymer on the cloud point curves (Figure 3). As seen from Figure 3, placement of oxygen in the side chain has a positive effect on miscibility pressures (note that the PPG has a slightly lower molecular weight), although miscibility pressure curves show similar trends. The lower miscibility pressures of PVME can be attributed to relatively weaker self-interaction (lower surface tension, Table 2). Although the longer side-chain branches of PVME might be expected to enhance free volume and hence the entropy of mixing,[54] the T_g of high molecular weight PVME is substantially higher than that of PPG, and the σ parameter for PVME is also substantially higher. The theoretical calculations do not differentiate between the PVME/CO_2 and the PPG-DME/CO_2 interactions, because the moieties used to represent these two polymers are identical. In summary, PVME is somewhat more CO_2-philic than PPG, possibly owing to slightly weaker self-interaction in PVME, but the exact source of the differences between these two polymers is not entirely clear.

The phase behavior of PVME-3850 and PVEE-3800 is compared in Figure 3, where PVEE differs from PVME only by an extra methylene unit in the side chain. Despite the relatively higher surface tension and thus the higher cohesive energy density, PVEE is apparently more CO_2-philic than PVME. It has been suggested that as the side-chain length increases, the polymer gains more free volume and thus the glass transition temperature decreases, resulting in enhanced entropy of mixing; this is indeed the case here, where high molecular weight PVEE exhibits a T_g of −60 °C versus −31 °C for PVME. Therefore, we surmise that the relatively better miscibility of PVEE (versus PVME) is entropically driven, although the ether oxygen in PVEE may also be more accessible to CO_2 for Lewis acid–Lewis base interactions due to the increased free volume.

We have calculated the geometries and energetics of model ethers with CO_2 in order to identify specific interactions between CO_2 and the ether oxygens. A single optimized geometry was

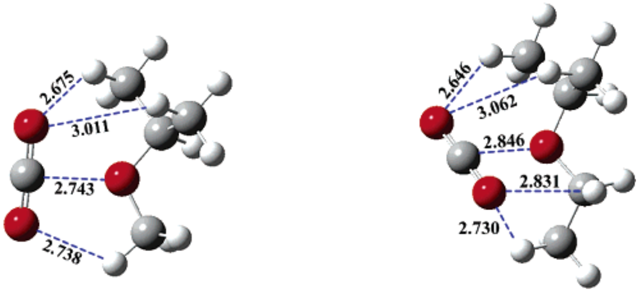


Figure 4. Optimized geometries for the methyl isopropyl ether (MIE)/CO_2 complex (left) and for the ethyl isopropyl ether (EIE)/CO_2 complex (right). Interaction energies are −18.0 and −18.6 kJ/mol for MIE/CO_2 and EIE/CO_2, respectively.

obtained for the MIE/CO_2 dimer (analogue to PVME), shown in Figure 4. The interaction energy for this system is −18.0 kJ/mol. The charge on the ether oxygen is −0.684, as computed from a natural bond order (NBO) population analysis. We also identified a single optimized binding geometry for the EIE/CO_2 complex (analogue to PVEE), also shown in Figure 4. The interaction energy is −18.6 kJ/mol and the NBO charge on the ether oxygen is −0.690. The small difference in the interaction energies between CO_2 and the ether oxygens in MIE and EIE is not responsible for the differences in the phase behavior shown in Figure 3.

In summary, when one compares the behavior of PPG, PVME, and PVEE, it is clear that PVEE is the most CO_2-philic. Oddly, of the three polymers, PVEE also exhibits the highest surface energy, suggesting that PVEE exhibits the strongest self-interactions. PPG exhibits weaker self-interaction (lower surface tension) and is also a very flexible, high free volume material, yet PVEE exhibits substantially lower miscibility pressures. Our calculations do not reveal any clues to the origin of this behavior; a complete explanation of the effect of molecular structure on phase behavior in CO_2 is clearly still lacking.

Having observed that ether oxygens in the side chain can reduce the miscibility pressures of polymers in CO_2, and knowing that incorporation of an ether oxygen into the backbone (polyether) increases the chain flexibility and thus improves the miscibility, we prepared and tested methyl ether-substituted PPG. We observed that these polymers were essentially CO_2-insoluble. It should be noted that the structure of the methyl ether-functional PPGs closely resemble that of a branched poly(ethylene oxide), which is known to exhibit poor miscibility in CO_2.[53] In summary, despite the methyl ether-functionalized epichlorohydrin repeat unit ($R_2 = OCH_3$, Scheme 1) being an isomer of the CO_2-philic PVEE (structure 4 in Table 2), the methyl ether-functionalized PPG is CO_2-insoluble. While this effect appears drastic, it is not without precedent. McHugh and colleagues,[23] as well as Enick, McHugh, and co-workers,[55] showed that the miscibility pressures of poly(methyl acrylate) and poly(vinyl acetate) differ by hundreds of megapascals, despite being isomers.

The phase behavior of PVEE/CO_2 is compared with that of PVAc/CO_2 in Figure 5. As shown in Table 2, these polymers exhibit the same cohesive energy density and their side-chain lengths are also essentially the same. The miscibility pressures for PVAc-3090 ($M_n = 3090$) are lower than those of PVEE-3800 ($M_n = 3800$) in CO_2. The differences in phase behavior may be due to differences in molecular weight and we therefore have measured the cloud point pressures of PVAc-7700 ($M_n = 7700$) in CO_2 for comparison. We see from Figure 5 that the miscibility pressures for PVAc-7700 are comparable with those of PVEE-3800 at 3, 4, and 5 wt % concentrations, although at more dilute concentrations the PVEE-3800 is more CO_2-soluble. Although not illustrated in the figure, PVAc with a molecular weight of 193 000 (2244 repeat units) exhibits miscibility with CO_2 at 67.6 MPa at ~5 wt %,[55] while PVEE with a molecular weight of 120 000 (1667 repeat units) is not miscible with CO_2 at 3.5 wt % at a pressure of 241 MPa and at elevated temperatures. These results indicate that PVAc is slightly more CO_2-philic than PVEE at low molecular weight, with the difference becoming more dramatic as the polymer length increases.

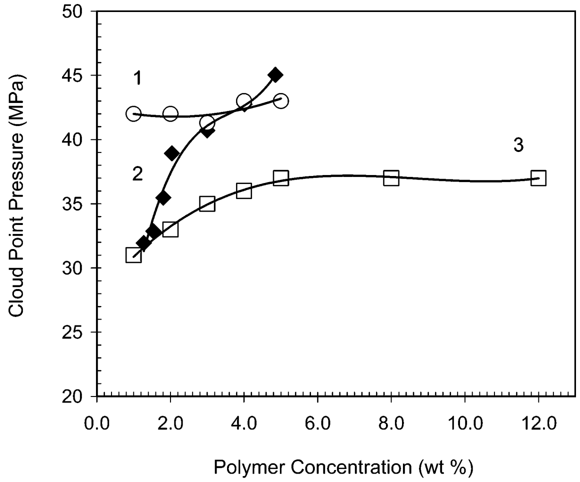


Figure 5. Phase behavior of mixtures of CO_2 with (1) PVAc-7700 (○), (2) PVEE-3800 (◆), and (3) PVAc-3090 (□) at 22 °C. PVAc is more CO_2-philic than PVEE at comparable molecular weights.

We used the IPA molecule as a reference to investigate the interactions of CO_2 with acetate groups and ether groups. We compared the interaction of CO_2 with the two oxygen-containing groups in IPA with CO_2/ether binding energies for MIE and EIE. Three different binding configurations were identified and are shown in Figure 6. The interaction energies are −14.8, −14.2, and −15.9 kJ/mol for ester oxygen binding and carbonyl oxygen binding modes A and B, respectively (see Figure 1 and Table 1). The NBO charges for the ester oxygen and the carbonyl oxygen of the IPA are −0.681 and −0.715, respectively. The interaction energies for the MIE/CO_2 and the EIE/CO_2 complexes are substantially higher than that of ether oxygen binding in the IPA/CO_2 complex (see Table 1). This indicates that isolated ether oxygens are more favorable than ester oxygens where interaction with CO_2 is concerned. The slightly more negative charge on the isolated ether oxygen (about −0.69) is consistent with this observation, since the larger charge gives a more favorable Lewis acid−Lewis base interaction. However, this small difference of charges cannot completely explain the 3.2−3.8 kJ/mol difference in the interaction energies; the geometry also plays a role in the observed binding energy differences.

The distance between the ether oxygen and the carbon of the CO_2 molecule (O⋯C) for the MIE/CO_2 dimer is 2.743 Å (Figure 4), while the corresponding distance for the IPA/CO_2 dimer is 2.897 Å (Figure 6). The shorter O⋯C distance for the MIE/CO_2 dimer contributes to the stronger interaction energy. Note that a MIE molecule has one less methyl group than an IPA molecule and hence has less steric hindrance for CO_2 approaching the ether oxygen; we believe this accounts for the shorter binding distance.

The O⋯C distance for the EIE/CO_2 dimer is 2.846 Å (Figure 4), which is slightly shorter than for IPA/CO_2. In addition, we observe one extra “hydrogen bond” (H⋯O) for the EIE/CO_2 dimer (Figure 4) as compared with MIE/CO_2 and IPA/CO_2. The

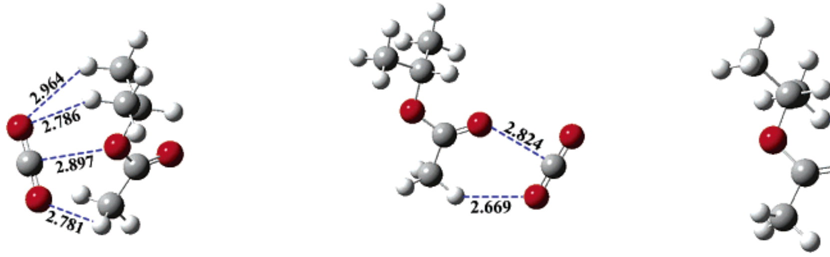


Figure 6. Optimized binding geometries for the isopropyl acetate (IPA)/CO_2 complex. Interaction energies are −14.8, −14.2, and −15.9 kJ/mol for the binding modes from left to right.

H···O distances for the EIE/CO_2 dimer are all well within the definition of a C−H···O "hydrogen bond".[56] This extra hydrogen bond contributes to the larger interaction energy.

Table 1 clearly shows that the binding energies of CO_2 with ester oxygens are smaller in magnitude than binding energies for isolated ether oxygens. However, PVAc (the polymeric analogue to IPA), is considerably more soluble in CO_2 than the polymeric analogues of MIE (PVME) and EIE (PVEE). The higher solubility of PVAc may be due to the fact that the acetate group has more binding modes available for CO_2, compared with the ether polymers. PVAc has three binding modes per monomer unit, one with the ester oxygen and two with the carbonyl oxygen (see Figure 6). The ether monomers can only accommodate one CO_2 near the ether oxygen. Therefore, the total interaction energy of an IPA/CO_2 dimer surpasses that of MIE/CO_2 and EIE/CO_2 dimers. In other words, "quantity" is more important than "quality", at least in this case.

In summary, PVAc is more CO_2-philic than PVEE, despite having comparable cohesive energy density (and hence comparable self-interaction strength). Furthermore, high molecular weight PVAc exhibits a higher T_g than PVEE, which would suggest that PVEE exhibits greater chain flexibility and higher free volume. Nevertheless, PVAc exhibits lower miscibility pressures. It is possible that the ester oxygen of PVAc provides rotational freedom to the carbonyl group, facilitating carbonyl−CO_2 interactions.[28]

One might imagine that the interaction of CO_2 with either the ether oxygen in PVEE or the ester oxygen in PVAc would not be as favorable as carbonyl oxygen−CO_2 interactions due to steric hindrance from the long polymer backbone chain. If that were true, only the carbonyl group in PVAc would be involved in Lewis acid−Lewis base interactions with CO_2. In an effort to assess the accessibility issue, methyl acetate-functionalized PPGs with various degrees of substitution [0% (PPG), 12%, and 100%] were studied (Scheme 1). Interestingly, we observed that addition of methyl acetate side chains to the polyether backbone of PPG shifts the miscibility pressure curve to higher pressures rather than lower, as can be seen from Figure 7. In other words, PPG (curves 5 and 6) is more CO_2-philic than *any* of the methyl acetate-functionalized PPGs (see curves 1−4). Note that the PDI is exactly the same for curves 1−4 because they were synthesized from the same PECH starting material. These results are consistent with the CO_2 insolubility of the methyl ether-functionalized PPG—the presence of the single methylene group between either the methyl ether or the acetate and the backbone has a severe deleterious effect on phase behavior. We have attempted to account for this effect through ab initio calculations. The IBA molecule has a similar structure to IPA, albeit with a CH_2 group spacer between the isopropyl group and the ether oxygen. Similar to IPA, we obtained three optimized geometries for the IBA/CO_2 complex, shown in Figure 8. The interaction energies for these three binding geometries are −15.1, −14.1, and −14.3 kJ/mol, respectively, giving an average binding energy of −14.5 kJ/mol. The average binding energy for the IPA/CO_2 dimer is −15.0 kJ/mol, as can be seen from Table 1. Although the trend in binding energies is consistent with the experiments, a difference in binding energy of 0.5 kJ/mol is not considered significant. The NBO charges for the ether oxygen and the carbonyl oxygen of IBA are −0.675 and −0.707, respectively. These are smaller in magnitude than the charges on the IPA oxygens (see above). The difference in charges on the oxygens is also consistent with the weaker interactions. However, the differences in interaction energies and partial charges are not large enough to explain the dramatic differences in solubilities observed in experiments. We therefore conclude that other factors influence the solubility that cannot be captured by ab initio calculations.

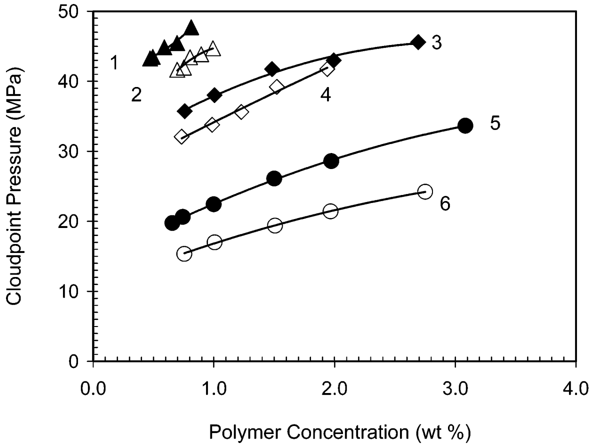
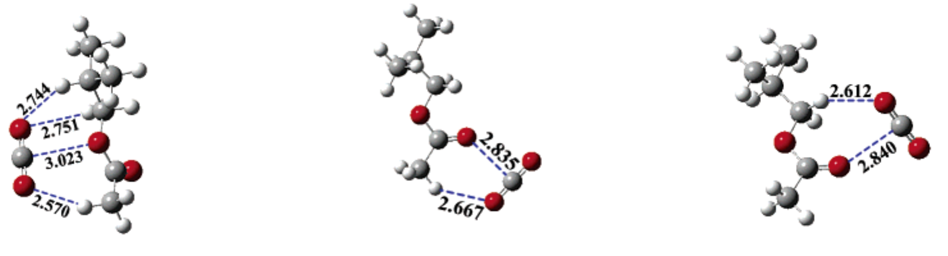


Figure 7. Effects of the degree of methyl acetate substitution and of acetate end-capping on the phase behavior of CO_2 at 22 °C for mixtures of CO_2 + (1) 100% methyl acetate functional PPG (M_n = 3253, 28 repeat units, ▲), (2) 100% methyl acetate functional PPG diacetate (M_n = 3337, 28 repeat units,△), (3) 12% methyl acetate functional PPG (M_n = 1830, 28 repeat units,◆), (4) 12% methyl acetate functional PPG diacetate (M_n = 1914, 28 repeat units,◇), (5) 0% methyl acetate functional PPG (M_n = 2000, 34 repeat units, ●), and (6) 0% methyl acetate functional PPG diacetate (M_n = 2084, 34 repeat units, ○). These results indicate that methyl acetate functionalization diminishes CO_2-philicity and that end-capping of polymers with acetates rather than hydroxyls increases CO_2-philicity.

From the data described above, it appeared that addition of a single methylene group between either pendent methyl ether or acetate groups and the polymer backbone created a serious adverse effect on miscibility with CO_2. To confirm this, we prepared the analogue of PVAc with this additional methylene group, that is, poly(allyl acetate). It has been shown previously that poly(vinyl acetate)s are miscible with CO_2 at relatively moderate pressures.[23,55] Poly(allyl acetate) was synthesized as described above. Consistent with our results for the functional polyethers, poly(allyl acetate) with molecular weight of 7800 (78 repeat units) is not miscible with CO_2 at pressures up to 60 MPa and concentrations at or above 0.8 wt %. By contrast, poly(vinyl acetate) with molecular weight of 7700 (89 repeat units)



ether oxygen/CO_2 carbonyl oxygen/CO_2 (A) carbonyl oxygen/CO_2 (B)

Figure 8. Optimized binding geometries for isobutyl acetate (IBA)/CO_2 complex. Interaction energies are −15.1, −14.1, and −14.3 kJ/mol for the binding modes from left to right.

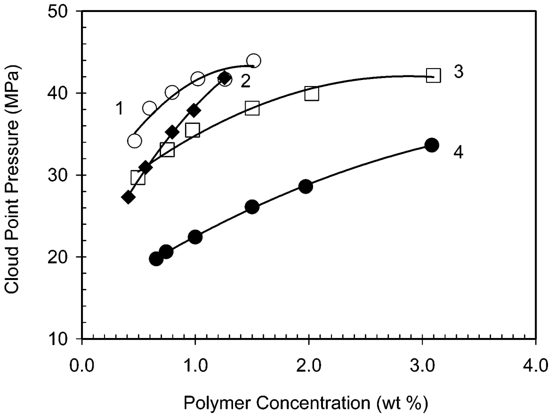


Figure 9. Comparison of miscibility of functional and nonfunctional PPGs on the basis of molecular weight at 22 °C for mixtures of CO_2 + (1) 44% methyl acetate functional PPG ($M_n = 2347$, ○), (2) PPG ($M_n = 2700$, ◆), 3) 22% methyl acetate-functional PPG ($M_n = 1991$, □), and (4) PPG ($M_n = 2000$, ●). The methyl acetate side chain, rather than molecular weight, is responsible for diminished CO_2-philicity.

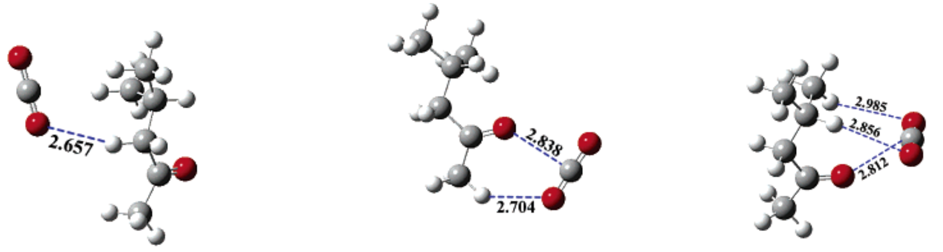
is miscible with CO_2 at pressures of ca. 43 MPa at concentrations ranging from 0.5 to 5 wt % (Figure 5).[55] These results are entirely consistent with our data for methyloxymethyl- and methyl acetate-functionalized polyethers—it is clear that incorporation of an extra methylene unit increases miscibility pressures dramatically.

Hydroxyl end groups have a detrimental effect on the solubility of the polymers in CO_2 because they participate in strong self-interactions via hydrogen bonding. The effect of terminal hydroxyl groups on phase behavior has been previously observed for poly(isobutylene)[57] and poly(ethylene oxide).[58] To determine the effect of hydroxyl end groups on the phase behavior, they were capped with acetoyl chloride, leaving a CO_2-philic acetate group on each end of the polymer chains. The cloud point pressure curve of 0% (PPG), 12%, and 100% methyl acetate-functionalized PPGs with their acetate end-capped analogues (Scheme 1) are compared in Figure 7. As seen in the figure, acetate end-capping lowers the miscibility pressures of the methyl acetate-functionalized polymers. The polymers exhibited a drop of about 3−7 MPa in the cloud point pressures when their end groups are capped with methyl acetate rather than a proton, despite the small molecular weight increase. Note that the PDI values for the capped and uncapped polymers are identical in each case.

We also tested whether the observed CO_2/polymer phase behavior of methyl acetate-functionalized PPGs compared to nonfunctional PPG (Scheme 1), shown in Figure 7, was the result of an increase in molecular weight due to substitution. As seen in Figure 9 (compare curves 2 and 4), the miscibility pressure of PPGs does increase substantially when the number-average molecular weight increases from 2000 to 2700. The PPG with molecular weight of 3500 was previously reported to be immiscible with CO_2 at moderate temperature,[55] although solubility can be attained at elevated temperatures.[55] One might argue, therefore, that the high miscibility pressure of the methyl acetate-functionalized PPGs is a result of the increase in molecular weight upon substitution. However, when we compare the phase behavior of the methyl acetate-functionalized PPG (on an equivalent molecular weight basis) with nonfunctional PPG, we can see that a 22% acetate-functionalized PPG with a molecular weight of 1991 (curve 3 of Figure 9) exhibits cloud point pressures 10 MPa higher than that of PPG with about the same molecular weight (curve 4 of Figure 9). Similarly, despite its lower molecular weight, miscibility pressures of a 44% acetate-functionalized PPG (with molecular weight of 2347) are higher than those for unaltered PPG with molecular weight 2700. Therefore, we can conclude that addition of the methyl acetates, and in particular the methylene spacer, causes the poor miscibility of functional PPGs.

We have performed ab initio calculations on isolated carbonyl oxygen/CO_2 complexes. We chose the MIK molecule, which contains only one carbonyl oxygen, as a model carbonyl oxygen compound. We identified two optimized binding geometries for the carbonyl oxygen/CO_2 interaction, A and B, shown in Figure 10. These modes are analogous to the A and B geometries shown in Figure 1. The interaction energies for the two binding geometries are −13.6 and −16.0 kJ/mol, respectively. We also performed optimization calculations by placing the CO_2 molecule on the opposite side of the carbonyl oxygen, where an ester oxygen would exist in an IPA molecule. This calculation resulted in a very weak binding mode (Figure 10), which contains virtually only H···O interactions and has an interaction energy of −7.5 kJ/mol. This is a much weaker binding than for the ether oxygen site on the IPA molecule.

The interaction energy of geometry A of the MIK/CO_2 dimer is slightly lower than that of the IPA/CO_2 dimer, in spite of the very similar binding geometries for the two dimers. The interaction energies for mode A are −13.6 and −14.2 kJ/mol for MIK/CO_2 and IPA/CO_2, respectively. The isolated carbonyl oxygen of MIK is less electron-rich than the carbonyl oxygen of an IPA molecule, having NBO charges of −0.660 and −0.715 for the MIK and IPA carbonyl oxygens, respectively. The existence of the ester oxygen in the acetate molecule enhances the electronegativity of the carbonyl oxygen, which results in more favorable interactions with CO_2. The lower charge could result in slightly weaker O···C binding for the MIK/CO_2 complex. The lower interaction energy, coupled with the loss of the ester oxygen binding site, will very likely decrease the CO_2-philicity of the MIK molecule and also of polymers containing only ketone functional groups, relative to polymers with acetate groups. Experiments are needed to verify this prediction.



hydrogen/CO_2 carbonyl oxygen/CO_2 (A) carbonyl oxygen/CO_2 (B)

Figure 10. Optimized binding geometries for methyl isobutyl ketone (MIK)/CO_2 complex. Interaction energies are −7.5, −13.6, and −16.0 kJ/mol for the binding modes from left to right.

One might expect that binding mode B for MIK would likewise be weaker than the corresponding mode B for IPA. However, the energies are roughly the same at −16.0 and −15.9 kJ/mol for MIK/CO_2 and IPA/CO_2, respectively. There are two reasons for the increased binding for mode B relative to mode A in MIK/CO_2. First, the carbon on CO_2 is closer to the carbonyl oxygen in mode B than in mode A, which increases the Coulombic interaction potential. Second, there are two O···H interactions between the oxygens on CO_2 and hydrogens on MIK, whereas for mode A there is a single hydrogen bond.

Conclusion

The phase behavior of a series of model oxygen-containing polymers in CO_2 was measured to attempt to assess the importance of oxygen functional groups on CO_2/polymer phase behavior. While there are many issues yet to be resolved, we can conclude that adding an ether oxygen to a hydrocarbon polymer, in either the backbone or the side chain, enhances "CO_2-philicity" by providing sites for specific interactions with CO_2 as well as by enhancing the entropy of mixing by creating more flexible chains with higher free volume. Ab initio calculations show that ether and ester oxygens provide very attractive interaction sites for CO_2 molecules. The importance of the ester oxygens in acetate groups seems to have been ignored in previous computational studies. The binding energy for an isolated ether oxygen with CO_2 is larger in magnitude than that for a carbonyl oxygen/CO_2 complex. However, acetate-functionalized polymers are experimentally known to be more CO_2-soluble than polymers with only ether functionalities. Our calculations indicate that the reason for this may be that acetate functional groups contain a total of three binding modes for CO_2 interactions, compared with only one for the ether functional group. In summary, the addition of an ester oxygen has two positive effects on interactions with CO_2. First, it provides a much stronger attractive site than a CH_2 group for CO_2 interactions. Second, it makes the carbonyl oxygen more electron-rich and hence more favorable for CO_2 binding.

There are a number of effects that continue to defy explanation. For example, it is clear that adding a single methylene group as a spacer between a polymer backbone and either an ether or acetate group results in a strong deleterious effect on phase behavior; neither our ab initio calculations nor conventional thermodynamic theories provide any guidance to the origin of this effect.

In future, we propose to examine design of materials where the placement of oxygen-containing functional groups not only provides sites for interaction with CO_2 but also renders neighboring protons more acidic, providing possible sites for interaction with CO_2's oxygen atoms. Further, because our calculations show that isolated ether groups exhibit stronger interactions with CO_2 than carbonyls, we will examine polymers with multiple ether groups.

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Supporting Information Available: Details of polymer synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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