Solubility of CF_2-Modified Polybutadiene and Polyisoprene in Supercritical Carbon Dioxide

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ABSTRACT: The cloud-point behavior of fluorinated polyisoprenes (FPI) and fluorinated polybutadienes (FPBD) in supercritical fluid (SCF) CO_2 are reported at temperatures from 60 to 170 °C and pressures from 1000 to 3000 bar. These fluorinated polymers were prepared by the addition of difluorocarbene (CF_2) to the parent polydienes yielding a *gem*-difluorocyclopropane repeating unit, a segment containing both fluorine and a significant dipole moment. Neither the unmodified polyisoprene starting material nor the hydrogenated variant dissolves in CO_2 up to temperatures of 155 °C and pressures of 2600 bar. Both FPI and FPBD dissolve in CO_2, but pressures in excess of 1000 bar are needed to obtain a single phase. The PFI and PFBD cloud-point curves exhibit temperature minima at approximately 60 and 80 °C, respectively, likely due to an increase in CO_2-CO_2 and polymer−polymer interactions relative to polymer$-CO_2$ interactions. As the amount of CF_2 incorporation in FPI samples decreases, the cloud-point curves shift to higher pressures and to higher temperatures. In a series of FPBD samples, an increase in cloud-point pressure with increase in molecular weight is initially large for molecular weights less than 10^5 and then becomes much less at higher molecular weights, as also observed for other polymer−SCF solvent mixtures. This methodology for incorporation of fluorine into macromolecules leads to significant enhancement of solubility in CO_2.

Introduction

Supercritical fluid (SCF) solvents, and particularly CO_2, are being actively investigated as media for polymerization processes,[1] polymer purification and fractionation processes,[2] and as environmentally preferable solvents for solution coatings and powder formation processes.[3] A fundamental understanding of the underlying physics and chemistry of SCF−polymer phase behavior is required to fully exploit SCF-based polymer processing. This understanding comes from systematic phase behavior and modeling studies.[4] However, quantitative solution models for polymer$-CO_2$ systems still struggle with the challenges of accounting for intra- and intersegmental interactions and the density dependence of the intermolecular potential functions of these highly compressible solutions. Nevertheless, it is possible to glean insight into the solvent character of supercritical CO_2 from the principles of molecular thermodynamics.

For example, the polarizability of CO_2, which fixes the magnitude of nonpolar, mean-field CO_2-CO_2 interactions, is similar in value to that of methane, a very weak SCF solvent. Yet supercritical CO_2 is a much stronger solvent than methane since nonpolar interactions scale with solvent density,[5] and CO_2 density is easily increased with pressure. Hence, many polymer$-CO_2$ phase behavior studies show that polymer solubility remains very low even at high temperatures where nonpolar interactions are expected to dominate, unless the system pressure is exceptionally high (i.e., unless the density of CO_2 is increased considerably).[4] Another molecular feature of CO_2 is that it has a substantial quadrupole moment due to the difference in electron affinities between oxygen and carbon. The strength of polar interactions is inversely proportional to temperature since polar interactions depend on the relative orientation between molecules. Therefore, it is possible to dissolve a nonpolar polymer in CO_2 if the temperature is high enough to reduce the magnitude of CO_2-CO_2 quadrupolar interactions relative to CO_2−polymer segment dispersion interactions. However, CO_2 is a poor solvent for highly polar polymers since dipole−dipole (i.e., segment−segment) interactions outweigh quadrupole interactions, especially at low temperatures.[4] The challenge that is partially addressed in this paper is to ascertain the level of polarity needed for hydrocarbon-based polymers to dissolve in CO_2 at modest pressures and temperatures.

Temperature-sensitive specific interactions can also contribute to the attractive pair-potential energy between CO_2 and a polymer segment. Kazarian et al.[6] showed that polymers with electron-donating groups, such as carbonyls, exhibit specific CO_2−segment interactions on the order of 1 kcal/mol between the electron-accepting carbon atom of CO_2 and the electron-donating carbonyl oxygen in the polymer. Many studies have also shown or suggested that the Lewis acidic carbon atom of CO_2 interacts with a lone pair of electrons on fluorine in a C−F bond. For example, high-pressure fluorine NMR has been used to elucidate specific CO_2−fluorocarbon interactions in low molecular weight fluorocarbon solvents[7] and fluorocarbon repeat units in fluorinated polymers and copolymers.[8] Hence, fluorinating a polymer promotes its solubility in supercritical CO_2. However, McHugh and co-workers have also demon-

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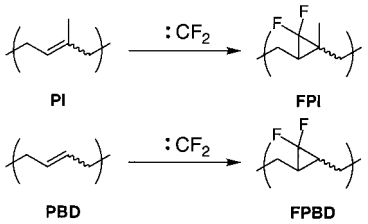

Figure 1. Chemical structures of the polydienes and their CF_2-modified analogues.

Table 1. Characteristics of the Polyisoprene[a] and CF_2-Modified Polyisoprenes Used in This Study

entry	% CF_2[b]	10^3M_w[c]	10^3M_n[c]	PDI[c]
1	0	$28._0$	$26._9$	1.04
2[d]	0	$35._2$	$32._9$	1.07
3	90[e]	$48._0$	$43._9$	1.09
4	~99	$49._3$	$45._0$	1.10
5	50[f]	$42._4$	$39._6$	1.07

[a] The parent polyisoprene contained 93% 4,1 repeat units and 7% 4,3 repeat units as determined by ^{1}H NMR spectroscopy. [b] Mol % CF_2 incorporation as determined by ^{1}H NMR spectroscopy. [c] Determined by SEC (using PS standards). [d] This sample was completely hydrogenated to the corresponding polyolefin poly(ethylene-*alt*-propylene). [e] The 10% unreacted olefins consisted of 64% 4,1 and 36% 4,3 regioisomers as determined by ^{1}H NMR spectroscopy. [f] The unreacted olefins were 89% 4,1 and 11% 4,3 regioisomers as determined by ^{1}H NMR spectroscopy.

Table 2. Characteristics of the CF_2-Modified Polybutadienes[a] Used in This Study

entry	% CF_2	10^3M_w[b]	10^3M_n[b]	PDI[b]
1	98	222	$96._8$	2.28
2	~99	$81._3$	$60._0$	1.45
3	98	$31._2$	$25._5$	1.22

[a] The starting PBD contained 95% 1,4 repeat units and 5% 1,2 repeat units as determined by ^{1}H NMR spectroscopy. [b] Determined by SEC (using PS standards).

strated that just fluorinating a polyolefin is not sufficient to impart CO_2 solubility at modest operating temperatures; the polymer must also have a measurable polar moment.[9]

In the work presented here, CO_2−polymer phase behavior studies are reported with model fluorinated polymers prepared by the chemical modification of polybutadiene (PBD) and polyisoprene (PI) with difluorocarbene (CF_2).[10,11] Several CF_2-modified PBD and PI polymers were prepared with varying amounts of CF_2 incorporation, and phase behavior measurements were performed to ascertain the impact of fluorination on polymer solubility in CO_2. There are two special features to the chemistry employed in this study for the preparation of model fluorinated polymers. First, the level of fluorine incorporation can be systematically tuned by controlling either the reaction stoichiometry or time. Second, the incorporation of the CF_2 moiety is by addition to a carbon−carbon double bond forming a *gem*-difluorocyclopropane repeat unit. This repeat unit contains both atomic fluorine and a significant dipole moment. The structures of the repeat units are shown in Figure 1, and Tables 1 and 2 provide information on the polymer architecture, the CF_2 content, and the molecular weight for the polymers used in this study. The effect of molecular weight is assessed with three CF_2-modified PBD materials that have essentially identical CF_2 content but with molecular weights between 3.0×10^4 and 2.2×10^5. The effect of CF_2 content is ascertained from cloud-point curves of the modified PI samples with 50, 90, and 99% incorporation of CF_2 groups and with essentially identical degrees of polymerization. Although polyolefins are not expected to be soluble in CO_2,[12−15,16] cloud-point measurements were nonetheless performed with an unmodified PI and a completely hydrogenated PI.

Experimental Section

The model polymers used in this study were prepared as described previously.[11] Some modifications to the general experimental procedure were made since the original report.[17] Molecular weights (M_w and M_n) were measured by size exclusion chromatography (SEC) on a Hewlett-Packard series 1100 liquid chromatography system equipped with a Hewlett-Packard 1047A refractive index detector. The system was fitted with three Jordi poly(divinylbenzene) columns of 500, 10^3, and 10^4 Å porosities calibrated with polystyrene standards (Polymer Laboratories). The columns and detector were maintained at 40 °C. SEC measurements were performed with a flow rate of 1 mL/min using tetrahydrofuran as the mobile phase. Samples were dissolved in THF (10 mg/mL) and passed through a 0.2 μm filter prior to injection.

Even though the CF_2-modified PBD and PI polymers were extensively purified with different liquid solvents, very small amounts of "impurities" made the single-phase CO_2−polymer solutions slightly murky. (The formation of small amounts of poly(tetrafluoroethylene) is possible under the experimental conditions.) Hence, the polymer samples were further cleaned by dissolving them in a warm solution of acetone plus cyclohexane. The polymer−acetone−cyclohexane solution is allowed to cool overnight, and a very small, polymer-rich lower phase is decanted from the slight yellowish upper phase. More cyclohexane is slowly added to the recovered lower phase to precipitate the polymer, which is subsequently dried in a vacuum oven. Cloud points with the purified polymer were indistinguishable from those of the original samples although now the single-phase, CO_2−polymer solutions were very clear, and the single-phase to two-phase cloud points occurred over a very small pressure interval.

Described elsewhere are the equipment and techniques used to obtain CO_2−polymer cloud points.[9,18] Fixed polymer concentrations of approximately 2−4 wt % are used for each cloud point since this concentration range is expected to be close to the maximum in the pressure−composition isotherms.[9,19−21] The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. These cloud points have been compared in our laboratories to those obtained using a laser light setup where the phase transition is the condition of 90% drop off in light transmitted through the solution. Both methods gave identical results within the reproducibility of the data. Cloud points with a scatter of approximately ±4.0 bar are reproduced 2−3 times at each temperature that is held to within ±0.3 °C. For measurements performed with the unsaturated polyolefins approximately 0.5 wt % (based on polymer weight) of 2,6-di-*tert*-butyl-4 methylphenol, obtained from Aldrich Chemical Co., was added as an inhibitor to the solution to ensure the integrity of the polymer; this is at a low enough concentration to have no measurable effect on the phase behavior.

Results and Discussion

Rindfleisch and co-workers reported that polyolefins do not dissolve in supercritical CO_2.[14] Nevertheless, the solubility of PI in CO_2 was checked in the present study. The PI parent material (entry 1, Table 1) did not dissolve in CO_2 to temperatures of 155 °C and pressures of 2400 bar. Another baseline set of experiments was performed with the same parent PI after complete hydrogenation (entry 2, Table 1). Once again, this polyolefin (i.e., polyethylene-*alt*-polypropylene) did not dissolve in CO_2 to temperatures of 150 °C and pressures

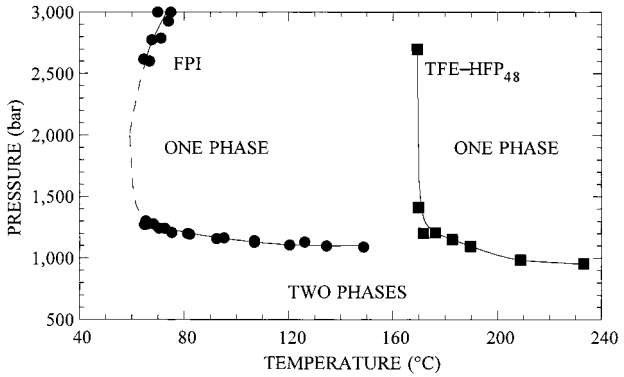

Figure 2. Phase behavior of FPI (filled circles, 90% CF_2 substitution, entry 3, Table 1) in CO_2 compared to that of poly(tetrafluoroethylene-*co*-48 mol % hexafluoropropylene) (TFE−HFP_{48}, M_w = 191 kg/mol) (filled squares) in CO_2 as reported by McHugh and co-workers.[22] The dashed line represents the expected shape of the cloud-point curve in the region where it was not possible to obtain reliable experimental data.

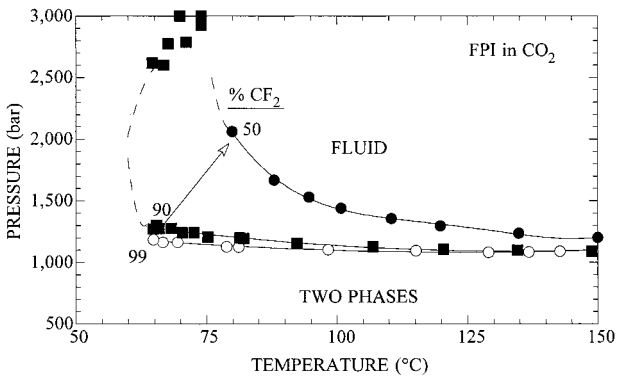

Figure 3. Effect of CF_2 modification level in FPI samples on dissolution conditions (open circles, entry 4, Table 1: ∼99%; filled squares, entry 3, Table 1: 90%; filled circles, entry 5, Table 1: 50%). The dashed lines represent the expected shape of the cloud-point curves in the regions where it was not possible to obtain reliable experimental data. The high-pressure branch was not obtained for the 99% CF_2-modified sample.

of 2600 bar. In these instances CO_2 is too polar to dissolve a relatively nonpolar polydiene or polyolefin.

Figure 2 shows the phase behavior of a highly (90%) CF_2-modified PI (FPI, entry 3, Table 1) in CO_2 compared to that of poly(tetrafluoroethylene-*co*-48 mol % hexafluoropropylene) (TFE−HFP_{48}) in CO_2 as measured by McHugh and co-workers.[22] There are several striking features of this phase diagram. The most obvious feature is that FPI is soluble in CO_2 at moderate temperatures, albeit at high pressures. At temperatures near 150 °C, dispersion interactions are expected to be the dominant type of FPI−CO_2 interaction. Since dispersion interactions scale with the product of polarizability and density[5,9,23] and the polarizability of CO_2 is very low, pressures in excess of 1000 bar are needed to obtain a single phase at these temperatures. The density of pure CO_2 is between 0.9 and 1.2 g/cm^3 at the temperatures and pressures of the FPI−CO_2 cloud-point curve shown in Figure 2.

Another interesting feature of the phase behavior of this FPI−CO_2 mixture is that the low-pressure branch of the FPI cloud-point curve does not change significantly over a temperature range from 150 to 60 °C. With 90% CF_2 substitution this FPI polymer has sufficient polarity to interact favorably with the quadrupole moment of CO_2 so that CO_2−FPI segment interactions dominate CO_2−CO_2 and FPI segment−segment interactions. When a CF_2 group is inserted across a double bond of the PI chain, a cyclopropyl group is created with a net dipole moment that is expected to be normal to the chain backbone. In comparison, TFE−HFP_{48} dissolves in CO_2 at higher temperatures than observed with FPI even though TFE−HFP_{48} is not expected to have a significant permanent dipole moment.[22] The TFE−HFP_{48}−CO_2 phase behavior demonstrates that fluorinating a polyolefin increases its solubility in CO_2, presumably due to the highly polar character of the C−F bond relative to the C−H bond. However, simply fluorinating a polyolefin is not sufficient to keep it dissolved in CO_2 as shown with TFE−HFP_{48}, which falls out of solution at temperatures less than ∼170 °C[22] where CO_2−CO_2 interactions overwhelm TFE−HFP_{48}−CO_2 interactions. The combination of atomic fluorine and the polar difluorocyclopropane unit in FPI enhances CO_2−polymer interactions and thus renders polymer solubility at low to moderate temperatures.

The other striking feature of the FPI phase behavior is the sharp increase in the cloud-point pressure at temperatures near 60 °C, shown as a dashed line in Figure 2. Reliable data in this region of the phase diagram are difficult to obtain since the thermal mass of the view cell apparatus makes it more facile to obtain isothermal data rather than isobaric data. Also, since the level of CF_2 modification is only 90%, there is likely a small concentration of chains with less than 90% CF_2 that fall out of solution at these temperatures and, hence, make the single phase appear murky. The steep portion of the cloud-point curve in this temperature region represents fluid to liquid + liquid transitions, as expected with the noncrystalline FPI, and not fluid to liquid + solid transitions.[17,22] At temperatures less than ∼60 °C it is not possible to obtain a single phase regardless of the pressure or CO_2 density. The portion of the cloud-point curve that reappears at very high pressures exhibits a slight positive slope and can be termed an upper-critical-solution temperature (UCST) curve since a single phase is obtained as the temperature is increased isobarically. Since UCST behavior is typically associated with endothermic mixtures, the positive slope of the UCST curve is likely the result of the mixture volume being larger than the sum of the pure component parts,[24] which suggests that FPI chains do not readily pack into very dense CO_2. Of course, the very high solution densities also magnify any dissimilarities in the intermolecular potential functions of CO_2 and FPI, which makes it difficult to attribute phase separation solely to entropic or enthalpic considerations. In fact, it is worth noting that the overall shapes of the FPI and TFE−HFP_{48} curves are similar to those observed for binary polymer mixtures consisting of a polar and a nonpolar component, which suggests that the phase behavior is fixed by enthalpic factors.[4] More extensive phase behavior studies are needed to resolve this issue unequivocally.

Figure 3 shows the impact of CF_2 modification on the solubility of FPI in CO_2. As the amount of CF_2 incorporation decreases, the cloud-point curve shifts to higher pressures and temperatures. Reliable cloud-point data can be obtained for the 50% FPI−CO_2 sample to ∼80 °C, below which the solution becomes murky, indicating that a small amount of CO_2-insoluble material is present. At temperatures slightly higher than 80 °C the

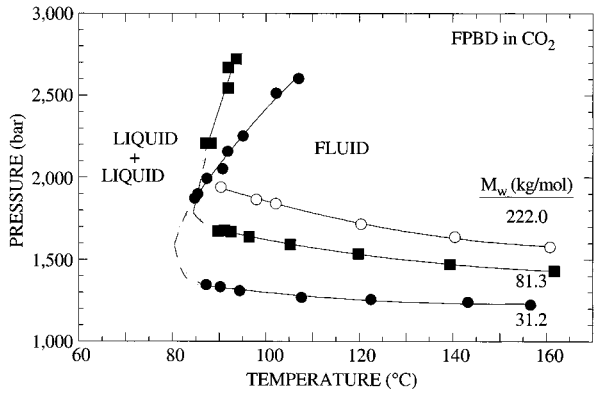

Figure 4. Effect of molecular weight on the phase behavior of FPBD in CO_2 (filled circles, entry 3, Table 2; filled squares, entry 2, Table 2; open circles, entry 1, Table 2.) The dashed lines represent the expected shape of the cloud-point curve in the regions where it was not possible to obtain reliable experimental data. Data were not obtained for the high-pressure branch of the 221 kg/mol sample.

pressure was increased to 3000 bar (the maximum pressure of the apparatus); however, the 50% FPI solution remained a single phase, suggesting that the high-pressure branch of the cloud-point curve, if it exists, is at exceptionally high pressures. Increasing the level of fluorination to essentially complete conversion of the PI double bonds (~99%) leads to modest decreases in dissolution pressure and temperature as compared to the 90% FPI sample. No attempt was made to determine the high-pressure branch of the cloud-point curve of the 99% FPI sample.

The impact of molecular weight is demonstrated in Figure 4 with the CF_2-modified PBD (FPBD)−CO_2 system. Each of the FPBD polymers used here have at least 98% of the double bonds replaced with CF_2 groups (Table 2). The increase in cloud-point pressure with increasing molecular weight shown with the low-pressure portion of the cloud-point curves in Figure 4 has also been observed with many other polymer−SCF solvent mixtures.[4] As with the FPI−CO_2 system, a sharp increase in cloud-point pressure is observed in the neighborhood of 85 °C for the two low-molecular-weight FPBD curves, and UCST-like behavior is observed for the FPBD−CO_2 mixtures.

It is interesting to note that the cloud-point pressures for 99% CF_2-modified FPI (Figure 3) are *lower* than those observed for 100% CF_2-modified FPBD at comparable molecular weights (Figure 4). Also, the temperature at which the FPBD curve exhibits a rapid increase in pressure is higher than that observed with FPI. A reason for the differences in the phase behavior for these systems is related to the differences in the contact or cohesive energies between segments of the polymer, two solvent molecules, or a segment of the polymer and a solvent molecule. Note that the polar CF_2 group occurs in every six-carbon repeat group in FPI compared to every five-carbon repeat group of FPBD, which means that an FPI repeat group is less polar per unit volume. Hence, FPI segment−segment polar interactions are less than those for FPBD, but evidently there is still sufficient polarity to maintain strong FPI segment−CO_2 polar interactions since FPI remains dissolved in CO_2 to temperatures as low as 60 °C. The other structural difference between the two types of repeat groups is the CH_3 branch in FPI, which means that FPI is less densely packed than FPBD. The volume change on mixing FPI with CO_2 is expected to be less than that for FPBD mixed with CO_2 which reduces the entropy penalty associated with dissolving an ordered dense polymer with a less ordered solvent.[25] Unfortunately, the structural differences between FPI and FPBD affect both energetic and entropic considerations that fix solubility levels. More detailed studies are needed to uncouple or resolve unequivocally these two considerations.

Conclusions

Recent advances in the ability to synthesize model polymers provide the opportunity to design experimental studies that reveal which specific structures readily dissolve in supercritical CO_2. In the present study we show that hydrocarbon-based polydienes can dissolve in CO_2 if a CF_2 moiety is incorporated across a carbon−carbon double bond, forming a *gem*-difluorocyclopropane-containing repeat unit. Importantly, this moiety contains both fluorine and a significant dipole moment; some amounts of dipolar interactions are needed between the repeat group in the polymer and CO_2 to maintain a single phase at low-to-moderate temperatures. Although we demonstrated that CF_2-modified PBD and PI dissolve in supercritical CO_2, very high pressures were needed to obtain a single phase. Further work is in progress to synthesize hydrocarbon-based macromolecules that will dissolve in CO_2 at low pressures.

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cane and squalane do dissolve in CO_2 as long as the system temperature is greater than 30 °C for hexadecane and 60 °C for squalane. At "cold" temperatures it is not possible to form a single phase regardless of the pressure since CO_2-CO_2 quadrupolar self-interactions dominate CO_2-alkane dispersion and induction cross-interactions.

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