1506 *Macromolecules* **1995,** *28,* 1506−1510

Dissolving Perfluoropolymers in Supercritical Carbon Dioxide

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Received September 6, 1994®

ABSTRACT: A copolymer of TFE (tetrafluoroethylene) and HFP (hexafluoropropylene) was dissolved in supercritical (SC) CO_2 at about 200 °C and 100 MPa. The copolymer contained 19.3 mol % HFP and had an ultimate melting point of 200 °C. Theoretical predictions for phase diagrams of CO_2 with TFE homo- and copolymers indicate solubility at ≥100 MPa for all systems. The temperature requirements for solubility are about 300 °C and greater for PTFE [poly(tetrafluoroethylene)], with lower temperatures required for the copolymers. The experimental results for the low-melting HFP copolymers are reasonably consistent with these phase diagrams, leading us to believe that PTFE should be soluble near the predicted conditions.

Introduction

Determining the solubility of perfluorinated polymers represents a significant experimental and theoretical challenge. A recent study by Tuminello and Dee[1] describes the solubility behavior of poly(tetrafluoroethylene) (PTFE) in a variety of perfluorocarbons. Very high temperatures are needed to dissolve PTFE, mainly to overcome the nonpolar attractive forces between polymer segments that become magnified in the stereoregular structure of the polymer's crystalline phase. However, Tuminello and Dee did not consider nonhalocarbon solvents in their study.

One solvent of special interest is CO_2 since, if it can dissolve PTFE, it could be much more cost effective than expensive perfluorocarbon solvents. Unfortunately, there is only circumstantial experimental evidence to support the claim that CO_2 can dissolve perfluoropolymers. Krukonis[2] has shown in fractionation studies that supercritical (SC) CO_2 at modest temperatures and pressures is a suitable solvent for oligomeric perfluoropolyethers and poly(chlorotrifluoroethylene). In another study, DeSimone et al.[3] reported successfully dissolving hydrofluorocarbon polymers in CO_2, again at modest operating conditions. It is tempting to extrapolate the results from these CO_2 studies and suggest that CO_2 is a suitable solvent for other perfluorinated polymers. However, this extrapolation is generally not warranted based on other experimental evidence. It is well known that even if a solvent dissolves the polymer repeat unit in its oligomeric form, it in no way means that the solvent dissolves the high polymer.[4] Enick verified this principle when he determined that CO_2 readily dissolves perfluorohexane[5] but does not dissolve PTFE.[6] It should also be noted that the solubility behavior of hydrofluorocarbon polymers, such as the ones used by DeSimone and co-workers, can be quite different from that of perfluoropolymers. Chu, Wu, and Buck[7] demonstrated that poly(ethylene-*co*-tetrafluoroethylene) copolymers are soluble in polar solvents such as diisobutyl adipate. However, results from our own work show that diisobutyl adipate does not even swell PTFE and its copolymers such as TFE−HFP and TFE−PPVE. (HFP is hexafluoropropylene and PPVE is perfluoropropyl vinyl ether.)

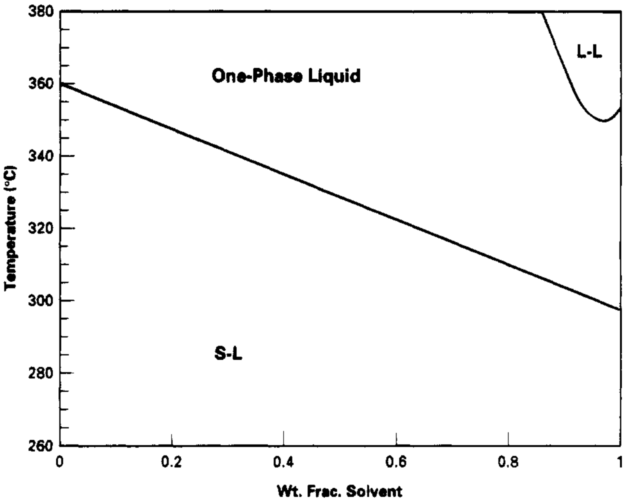

Figure 1. Predicted phase diagram for the system PTFE/n-$C_{15}F_{32}$ at 10 MPa. "L−L" refers to the two-phase liquid region. "S−L" refers to the region where solid polymer is in equilibrium with the liquid solvent.

Before we present the results obtained in the present study, it is worthwhile to briefly describe the type of phase behavior to be expected with perfluoropolymer−solvent systems. The phase diagram shown in Figure 1 for PTFE plus n-$C_{15}F_{32}$ will be used to illustrate this behavior. The part of Figure 1 of importance in this study is the section near 90 wt % solvent since polymer solubility measurements, or cloud points, are normally determined with less than approximatey 10 wt % polymer in solution. At the solvent-rich end of the diagram the crystalline solid polymer phase coexists with the polymer amorphous phase and a pure solvent phase below the liquidus line, which indicates the melting point depression. Above the liquidus a single-phase liquid is obtained. As the temperature increases, the liquid density decreases until eventually the liquid phase splits into two liquid phases at the lower critical solution temperature (LCST). The LCST can be raised by increasing the solvent density either by increasing the system pressure or by switching to a higher molecular weight solvent from the same homologous series. Conversely, the two-phase, liquid−liquid region can be

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® Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-1506$09.00/0

extended to lower temperatures by decreasing the pressure (or solvent molecular weight) until the liquidus line is intersected. If this occurs then it is not possible to obtain a single liquid phase when working with solvent-rich mixtures. The behavior depicted in Figure 1 is similar to that expected with CO_2 as the solvent. Of course the critical temperature of CO_2 is so far removed from the temperatures needed to melt perfluoropolymers that elevated pressures will be required to endow CO_2 with sufficient density to dissolve the liquefied perfluoropolymer.

Our objectives in this brief paper are to demonstrate, both theoretically and experimentally, that CO_2 can dissolve perfluoropolymers. Since the experimental determination of perfluoropolymer solubility in CO_2 requires operation at elevated temperatures and pressures, our first approach will be to theoretically generate the phase diagrams expected for perfluoropolymer–CO_2 mixtures. The accuracy of the calculated phase diagrams will then be verified by experimentally determining the solubility of a TFE–HFP perfluorocopolymer containing 19.3 mol % HFP.

Phase Diagram Development

The approach used to predict the phase diagrams for polymer–solvent systems at elevated temperatures and pressures combines several equations of state to best mimic pure component and mixture behavior. While it is preferable to use a single equation of state to generate the entire phase diagram, this is not possible since no single equation of state is capable of describing the properties of a pure solid polymer, an expanded solvent, and polymer–solvent mixtures comprised of components which have large differences in their molecular sizes.

1. Melting Point Depression. Consider first how the melting point of a pure perfluoropolymer is affected by pressure in the presence of a solvent. In this instance the Flory–Huggins theory[8] is used to predict the liquidus curve. Equation 1 is an expression of this theory.

$$\frac{1}{T_{m2}} = \frac{1}{T^{\circ}_{m2}} - \frac{R}{\Delta H_{2U}}\frac{V_{2U}}{V_{1U}}\left[\frac{\ln v_2}{m} + \left(\frac{1}{m} - \frac{1}{n}\right)(1 - v_2) + \chi(1 - v_2)^2\right] \qquad (1)$$

where T_{m2} and T°_{m2} are the diluted and undiluted equilibrium melting temperatures of the polymer, respectively, R is the gas constant, ΔH_{2U} is the enthalpy of fusion for PTFE and its copolymers, V_{1U} and V_{2U} are the molar volumes of solvent and a CF_2 group of polymer, respectively, v_2 is the volume fraction of polymer, m is the number of chain carbon atoms in the polymer, n is the number of solvent structural units, usually taken as 1 for CO_2 and most solvents, and χ is the polymer–solvent interaction parameter.

For these calculations, the equilibrium melting temperature and the heat of fusion are taken as 350 °C and 4600 J/mol of CF_2 group for PTFE.[9] The melting points for the copolymers are assumed to be the highest temperature for the melting endotherm from a DSC plot. Table 1 summarizes these melting points for all the polymers studied. Since the melting point of pure PTFE increases 1 °C/MPa,[10] the same pressure dependence is applied to all the fluoropolymers studied. The molar volume of a CF_2 group of perfluoropolymer is obtained using the Tait equation as presented by Zoller.[10] The value of m, the number of chain atoms in the polymer, is fixed at 6000; we have found little effect on melting point depression (on the order of a 1% change) for values of m as low as 200.

Table 1. TFE-Based Fluoropolymers

comonomer type	mol %	T°_{m2} (°C)
homopolymer	- - -	350
PPVE[a]	~1	319
HFP[b]	~10	281
HFP[b]	19.3	200

[a] Perfluoropropyl vinyl ether. [b] Hexafluoropropylene.

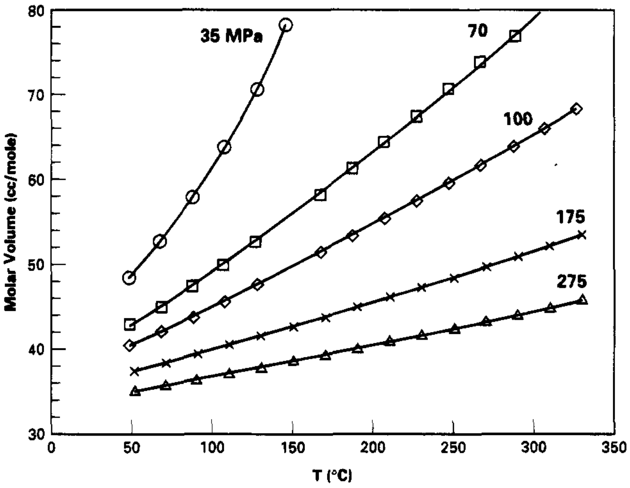

Figure 2. Higher density *PVT* behavior for CO_2 predicted by modeling the experimental data.

Molar volume data for CO_2 were taken from the literature.[11] The Flory equation of state[12] was used to interpolate the sparse data for CO_2 above 100 MPa pressure employing the following parameters: $P^* = 556.76$, $V^* = 0.599322$, $T^* = 2571.5$. The molar volume of CO_2, calculated from the Flory equation, is plotted in Figure 2 for the denser fluid states as a function of temperature and pressure. The lines connecting the points are the second-order polynomial fits at each pressure.

The polymer–solvent interaction parameter, χ, is obtained using a regular solution relationship. Equation 2 is one way of making this determination.[13]

$$\chi = 0.34 + \frac{V_{1U}}{RT}(\delta_1 - \delta_2)^2 \qquad (2)$$

where T is the absolute temperature and δ_1 and δ_2 are the Hildebrand solubility parameters for solvent and polymer, respectively. A major limitation of this equation is that the minimum value of χ is predicted to be 0.34 whereas there are many examples of values lower than this.[13] The reported solubility parameter[14] for PTFE and copolymers with HFP, 12.3 $(\mathrm{MPa})^{0.5}$, is used for all the fluoropolymers in this study. The solubility parameter for carbon dioxide is approximated using eq 3 as suggested by Hildebrand and Scott.[15]

$$\delta_1 = a^{0.5}/V_{1U} \qquad (3)$$

where a is the van der Waals interaction parameter. For CO_2, $a = 3.64 \times 10^5$ J·cm^2/mol^2.[16] By this relationship, δ_1 is strictly a function of molar volume. The strong effect of molar volume, and thus pressure, on δ_1 is shown in Table 2. Looking at Table 2 tells us that we should get a good match between polymer and solvent solubility parameters when V_{1U} is between about 45 and 55 cm^3/mol. King et al.[17] calculated δ_1 for

Table 2. Calculated Solubility Parameter versus Molar Volume for CO_2

V_{1U} (cm^3/mol)	δ_1 ($(MPa)^{0.5}$)
35	17.2
40	15.1
45	13.5
50	12.1
55	11.0
60	10.0
65	9.21

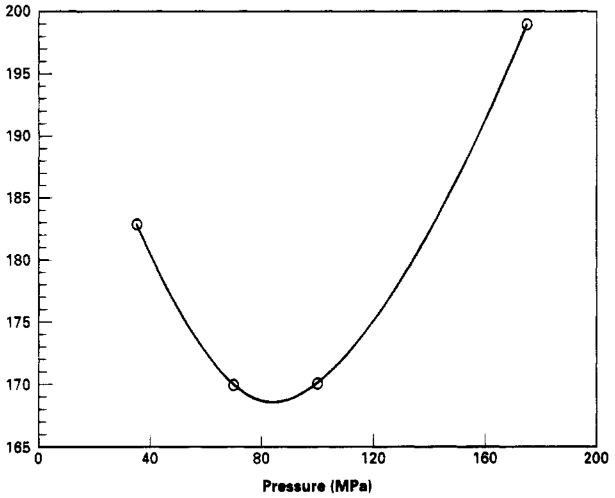

Figure 3. Prediction of the melting point as a function of pressure for the low-melting HFP copolymer at a volume fraction of 0.01 in CO_2.

subcritical CO_2 liquid to be 11.7 $(MPa)^{0.5}$ at 25 °C with a molar volume of 61.7 cm^3/mol. This is in reasonable agreement with the value of about 10.0 $(MPa)^{0.5}$ for the equivalent molar volume in Table 2. In addition, Vermue et al.[18] calculated δ_1 for SC CO_2 to be 13.1 $(MPa)^{0.5}$ at a molar volume of 53 cm^3/mol; the analogous Table 2 value is 11.5 $(MPa)^{0.5}$.

Figure 3 shows the effect of pressure on the melting point depression as predicted from eq 1 for the low-melting HFP copolymer at a fixed concentration of 1 vol %. A minimum is observed due to the competing effects of shrinking molar volume for CO_2 and the increase in T°_{m2} with pressure via the Clausius–Clapeyron relationship. At lower pressures the molar volume of carbon dioxide decreases fairly rapidly with pressure, making this effect dominant and causing the melting point to decrease by up to 15 °C. At higher pressures, however, the molar volume of CO_2 does not decrease rapidly enough to compensate for the increase in the polymer melting point induced by hydrostatic pressure.

2. Liquid–Liquid Phase Separation. As shown in Figure 1 a liquid–liquid phase separation can occur at elevated temperatures and pressures. The Sanchez–Lacombe (SL) equation-of-state theory[19] is used to predict the phase behavior of the liquid mixture according to the methodology outlined by Sanchez.[4] As a first approximation, the reduction parameters used in the SL equation to describe the volumetric behavior of PTFE are used for the copolymers considered in this study. This was done because no volumetric data were available for these copolymers. The reduction parameters for PTFE–$P^* = 277.1$ MPa, $V^* = 0.46851$ cm^3/g, and $T^* = 641.0$ K–are obtained from molar volume data at temperatures above 330 °C[10] and are assumed to be temperature independent.

3. Phase Diagrams. Since pressure, or conversely carbon dioxide density, has a large effect on the predicted phase behavior, phase diagrams are generated at 60, 92, and 100 MPa. It can be implied from Figure 4 that at 60 MPa some swelling is observed for all of the fluoropolymers listed in Table 1 but that a single-phase region is only achieved at polymer concentrations greater than 50–60 wt %. The solvent-rich branch of the liquid–liquid region is not explicitly shown in Figure 4 as it is essentially 100 wt % pure carbon dioxide. The temperatures at which swelling should be observed are relatively high, about 210 °C for the low-melting HFP copolymer and 370 °C for PTFE. Although not shown, qualitatively similar behavior is calculated at 70 MPa except that the polymer-rich branch of the liquid–liquid coexistence region is now predicted to fall between about 40 and 50 wt % polymer. The range of melting points at 70 MPa decreases to about 200–360 °C.

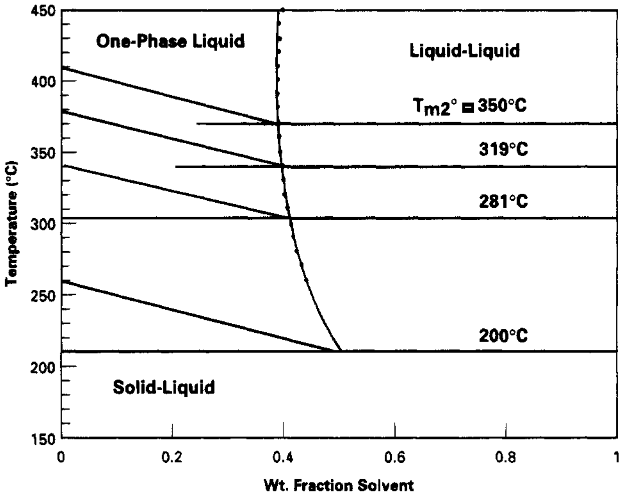

Figure 4. Predicted phase diagram for four perfluoropolymers in CO_2 at 60 MPa. The polymers have thermodynamic melting points ranging from 200 to 350 °C as shown in the figure and listed in Table 1.

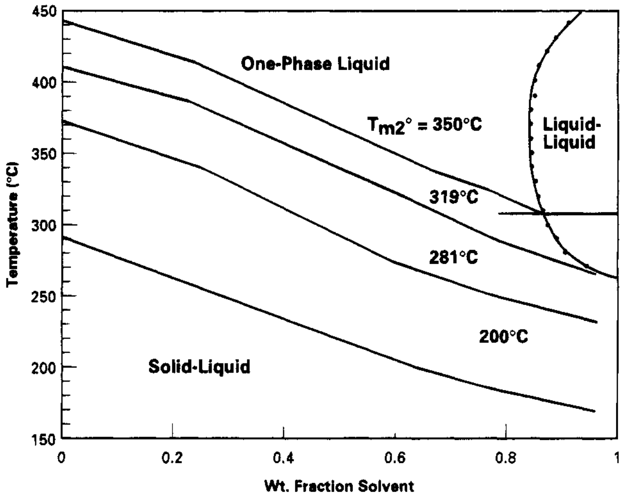

Figure 5. Predicted phase diagram for the four perfluoropolymers shown in Figure 4 with CO_2 at 92 MPa.

In Figure 5, the phase diagram at 92 MPa reveals qualitatively different behavior. The liquid–liquid coexistence curve has a semicircular shape versus the parabolic shapes seen at lower pressures. A single phase is predicted above about 170 °C for the low-melting HFP (19 mol %) copolymer and about 230 °C for the high-melting HFP (10 mol %) copolymer. Both of these copolymer–carbon dioxide mixtures are predicted to remain a single phase until the temperature

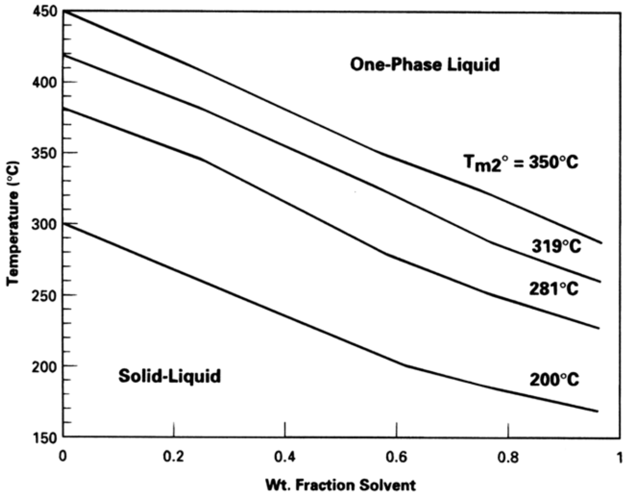

Figure 6. Predicted phase diagram for the four perfluoropolymers shown in Figure 4 with CO_2 at 100 MPa.

is raised above about 260 °C. Complete miscibility of the PPVE copolymer in carbon dioxide is borderline at about 260 °C since the predicted liquidus curve essentially intersects the LCST at the solvent side of the diagram. The predicted behavior of PTFE–carbon dioxide mixtures in Figure 5 shows that a single phase is not observed for polymer concentrations less than about 10 wt %.

Figure 6 shows that the liquid–liquid region does not appear on the phase diagram if the system pressure is increased to 100 MPa. The temperatures at which stable single phases are formed are very close to those shown in Figure 5 since the pressure is only 8 MPa higher in Figure 6. Although this is a modest pressure increase, the solutions remain a single phase to temperatures as high as 450 °C.

Experimental Section

The relatively low melting HFP copolymer used in our experimental solubility studies was kindly supplied by Dr. R. A. Morgan of The DuPont Co. in Parkersburg, WV. Morgan determined that this polymer had 19.3 mol % HFP, a shear viscosity of 1200 Pa·s at 372 °C, and a shear stress of 44 800 Pa. Its peak melting point by DSC was about 147 °C.

The thermodynamic melting points of the polymers listed in Table 1 are estimated as the highest temperatures at which the melting endotherm persists. This is based on DSC melting behavior reported in this paper obtained with about 10 mg samples at a heating rate of 10 °C/min following a "quench" cooling from the melt.

The solubility measurements presented here are obtained using the high-pressure, variable-volume cell shown in Figure 7 and described in detail elsewhere.[20] The cell, which is capable of operating to 276 MPa and 220 °C, is fitted with a 1.9 cm thick sapphire window to allow visual observation of the phases. By moving a piston located within the cell, the polymer–solvent mixture is compressed to the desired pressure as measured with a Heise gauge (Dresser Industries, Model CM-108952, 0–3450 ± 13.5 bar). The temperature of the cell is measured to within 0.4 °C using a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Keithley Instruments, Inc., Model 195T, accuracy ±0.03%). The mixture inside the cell is viewed with a video monitor using a camera coupled to a boroscope (Olympus Corp., Model F100-024-000-55) placed against the outside of the sapphire window. The solution in the cell is mixed with a stir bar activated by an external magnet beneath the cell. All of the solubility observations reported here are made while the cell is heating from room temperature.

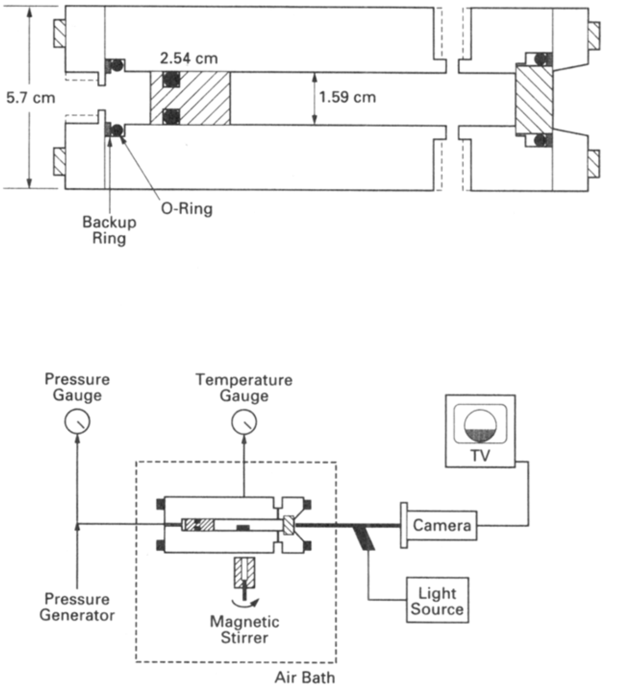

Figure 7. Schematic diagram of the dissolution apparatus and auxiliary equipment.

Experimental Results

Two series of solubility measurements in carbon dioxide are described. They comprised concentrations of 1.2 and 5.5 wt % of the TFE–HFP copolymer with 19 mol % HFP. For both concentrations, this copolymer appears "fluffy" and quickly settles after agitation when dispersed in carbon dioxide. The experiment with 5.5% polymer is described first.

The first evidence of any swelling was observed at about 146 °C and 110 MPa, at which point the particles did not settle but remained suspended. At 165 °C and 110 MPa the polymer-rich phase appears swollen and elongates when agitated by the stir bar. The elongated strands of swollen polymer then appear to dissolve into the more mobile CO_2-rich phase. Evidence that dissolution has actually occurred came in the form of observing a cloud point in the CO_2-rich phase upon dropping the pressure to about 90 MPa. This cloud point represents the pressure at which complete opacity was observed. But the change from complete transparency to opacity occurs gradually over a broad pressure range from about 110 to 90 MPa. At about 215 °C, a homogeneous phase is obtained that appears slightly cloudy with a low apparent viscosity since it is easily stirred with the stir bar apparatus. The cloud point pressure is now about 131 MPa at 215 °C. It is possible that the cloudiness is due to a small, insoluble amount of high TFE content copolymer present in the sample. However, it is also plausible that the cloudiness is due to small amounts of insoluble material leached from the highly swollen Viton O-rings used to seal the window and piston of the cell.

In the second experiment the concentration of copolymer is reduced to 1.2 wt % and EPDM O-rings are used to minimize O-ring swelling in the presence of high-pressure carbon dioxide. We were not able to dissolve this TFE–HFP copolymer completely in carbon dioxide to temperatures of 193 °C and pressures of 193 MPa. A water leak was suspected at the higher temperatures. The differences in polymer concentration in both experiments only seemed to affect the volume of gel-like polymer-rich phase produced in the intermediate temperature range between the onset of coalescence and the attainment of homogeneity.

Conclusions

The observations of copolymer solubility in carbon dioxide are remarkably close to the behavior predicted in Figures 4–6. The first observance of polymer dissolving in the CO_2 at 165 °C is quite close to our prediction of about 170 °C. The cloud point at this temperature was observed to be about 90 MPa, also close to the predicted behavior. The broad range of temperature and pressure over which solubility was observed could be due to a wide range in polymer composition. If the latter statement is true, this could affect our phase diagram predictions, since we assumed that comonomer concentration would not affect the LCST.

The results obtained in this preliminary study suggest very convincingly that carbon dioxide can indeed be a suitable solvent for perfluoropolymers. The calculated phase diagrams provide a guide for further experimentation. In particular, it is vitally important that the experiments are performed over extended temperature and pressure ranges. Further experimentation is in progress to expand the data base of perfluoropolymers in carbon dioxide as well as other supercritical fluid solvents using a cell that does not have elastomeric seals. As these data bases are developed, it will be possible to refine the calculations used to predict the phase behavior of perfluoropolymer systems and the data themselves may suggest novel uses for simple supercritical fluids, especially carbon dioxide.

Acknowledgment. The authors wish to thank Bruce Hasch for his skillful assistance in performing the dissolution experiments.

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