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Impact of Backbone Architecture on the Solubility of Fluorocopolymers in Supercritical CO_2 and Halogenated Supercritical Solvents: Comparison of Poly(vinylidene fluoride-*co*-22 mol % hexafluoropropylene) and Poly(tetrafluoroethylene-*co*-19 mol % hexafluoropropylene)

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ABSTRACT: Cloud-point data to 270 °C and 2800 bar are presented for poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel) in supercritical fluid (SCF) C_3F_6, $CClF_3$, CHF_3, and CO_2. The impact of backbone architecture on intermolecular interactions and fluorocopolymer solubility is determined by comparing the phase behavior of Fluorel to that of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in the same SCF solvents. Good solvents for nonpolar FEP_{19} (SF_6 and C_3F_8) did not dissolve polar Fluorel even at temperatures in excess of 260 °C. Although the small dipole moments of C_3F_6 and $CClF_3$ interact favorably with the polar, vinylidene fluoride segments of Fluorel, the cloud-point curves in these two solvents exhibit a sharp rise in cloud-point pressures as the temperature is decreased. Apparently, dipolar interactions between vinylidene fluoride segments are much stronger than Fluorel−C_3F_6 or Fluorel−$CClF_3$ cross-interactions as the temperature is lowered. In contrast, quadrupolar CO_2 and dipolar CHF_3 are good solvents for Fluorel due to favorable polar, vinylidene fluoride segment−SCF solvent cross-interactions. However, at or near room temperature, CO_2 is a much better solvent for Fluorel than is CHF_3, which is speculated to be a result of specific interactions between CO_2 and the vinylidene fluoride segments.

Introduction

Poly(vinylidene fluoride) (PVDF) is an important polymer due to its chemical resistance, good mechanical properties, and unique electrical properties.[1,2] Copolymerization of vinylidene fluoride with a perfluorinated monomer produces a polar copolymer that has a very high dipole moment per unit volume.[1,3] Copolymers of vinylidene fluoride and hexafluoropropylene resist dissolution in hydrocarbons, aromatics, chlorinated solvents, acids, and alkalis, although they are soluble in many highly polar solvents including acetone, DMSO, and low molecular weight esters and ketones.[4−7] An understanding of fluoropolymer solubility is just beginning to unfold with many studies employing supercritical CO_2 to dissolve fluorinated polymers. The work presented here uses a variety of low molecular weight supercritical fluid (SCF) solvents to dissolve a polar fluorocopolymer of vinylidene fluoride and hexafluoropropylene to gain further insight into the intermolecular forces that control fluorocopolymer solubility. The results are compared and contrasted with those obtained with a nonpolar fluorocopolymer of tetrafluoroethylene and hexafluoropropylene in the same SCF solvents.

Mertdogan et al.[8] recently reported on the solubility of nonpolar poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in a wide variety of SCF solvents with special emphasis on supercritical CO_2. FEP_{19} dissolves in CO_2 as long as the temperature is greater than 185 °C and the pressure is at least 1000 bar. At high temperatures, elevated operating pressures are needed to increase the density of CO_2 to magnify CO_2−FEP_{19} dispersion interactions that depend on the polarizability per molar volume. However, FEP_{19} falls out of solution, regardless of the pressure, at temperatures below 185 °C because CO_2−CO_2 polar interactions are enhanced relative to CO_2−FEP_{19} interactions.[8] These data, coupled with the observation that polyethylene does not dissolve in CO_2, demonstrate that fluorinating a hydrocarbon polymer improves its solubility in CO_2, but the polymer must be somewhat polar to remain soluble in CO_2 at low to moderate temperatures.[9] For example, Rindfleisch, DiNoia, and McHugh[9] report that poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel) remains in solution in CO_2 to temperatures of ∼100 °C and pressures of 750 bar. Apparently, the dipole of vinylidene fluoride interacts favorably with the quadrupole of CO_2 so that the interchange energy favors Fluorel solubility to low temperatures where polar interactions are expected to be magnified.[10] In the present study, the solubility of Fluorel in a variety of SCF solvents is measured to demonstrate the impact of the polar nature of vinylidene fluoride as a comonomer with hexafluoropropylene relative to the same molar amount of tetrafluoroethylene with hexafluoropropylene, FEP_{19}, which is the nonpolar analog of Fluorel.

Before presenting the experimental results of this study, it is instructive to develop a molecular thermodynamic framework for interpreting the data. To a first approximation, the location of the cloud-point curve depends on the density of the solvent and the balance of the energetic interactions between polymer segments and solvent. The following expression shows the relation of the internal energy of a mixture, U_{mixture}, to the density for an isotropic, homogeneous solution:[11]

$$\frac{U_{\text{mixture}}}{kT} \approx \frac{3}{2} + \frac{2\pi\rho(P,T)}{kT} \sum x_i x_j \int \Gamma_{ij}(r,T)\, g_{ij}(r,\rho,T)\, r^2\, \mathrm{d}r \tag{1}$$

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Table 1. Weight-Average Molecular Weight (M_w), Glass Transition (T_g), and Melting Point Temperatures (T_m) for Poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel)[7] and Poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP$_{19}$)[13]

copolymer	M_w	T_g (°C)	T_m (°C)
Fluorel	85 000	−20	amorphous
FEP$_{19}$	210 000	~57	147

where x_i and x_j are mole fractions, $\Gamma_{ij}(r,T)$ represents the intermolecular pair potential energy of the solvent and the polymer segments, $g(r,\rho,T)$ is the radial distribution function, r is the distance between molecules, $\rho(P,T)$ is the solution density, P is the system pressure, T is the absolute temperature, and k is the Boltzmann constant. For the results presented here, an estimate of the solvent density at the cloud-point conditions is obtained using the Peng−Robinson equation of state.[12] Given that the internal energy of the mixture is roughly proportional to the density, the solubility of a polymer is expected to improve by increasing the system pressure or by switching to a denser SCF solvent. However, the polymer will dissolve only if the energetics of the interactions are weighted toward polymer segment−solvent interactions relative to polymer segment−segment or solvent−solvent interactions as described by the interchange energy, ω,

$$\omega = z\left[\Gamma_{ij}(r,T) - \frac{1}{2}(\Gamma_{ii}(r,T) + \Gamma_{jj}(r,T))\right] \tag{2}$$

where z is the coordination number, or number of different pairs in solution. An approximate form of the attractive part of the intermolecular potential energy, $\Gamma_{ij}(r,T)$, for small molecule mixtures is

$$\Gamma_{ij}(r,T) \approx -\left(C_1\frac{\alpha_i\alpha_j}{r^6} + C_2\frac{\mu_i^2\mu_j^2}{r^6kT} + C_3\frac{\mu_i^2Q_j^2}{r^8kT} + C_4\frac{\mu_j^2Q_i^2}{r^8kT} + C_5\frac{Q_i^2Q_j^2}{r^{10}kT} + \text{complex formation}\right) \tag{3}$$

where α is the polarizability, μ is the dipole moment, Q is the quadrupole moment, and C_{1-5} are constants.[10] As demonstrated in the Results and Discussion sections, this equation serves as a guide for qualitatively evaluating the effect of intermolecular interactions on polymer−solvent phase behavior. However, eq 3 is not expected to describe rigorously the interaction of a polymer segment with another segment or with the solvent since segmental motion is constrained by chain connectivity. The contribution of dispersion and polar interactions to the potential energy tends to outweigh induction interactions,[10] which are not shown in eq 3. Dispersion interactions, the first term in eq 3, depend only on the polarizability and not on temperature. However, dipolar and quadrupolar interactions are inversely proportional to temperature so that the importance of these interactions increases significantly as the solution temperature is lowered. Specific interactions such as complex formation can also contribute to the attractive pair potential energy. Wide ranges in temperature are investigated in this study to moderate the impact of polar interactions relative to dispersion interactions.

Table 1 presents the properties of Fluorel and FEP$_{19}$. The hexafluoropropylene repeat units in FEP$_{19}$ disrupt the stereoregularity of this copolymer, reduce the crystallinity, and lower the peak melting point from 327 °C for PTFE to 147 °C for FEP$_{19}$. Similarly, the hexafluoropropylene content in Fluorel disrupts the stereoregularity of this copolymer and renders it amorphous.[14] Vinylidene fluoride comonomer, with a dipole moment of 1.4 D,[15] introduces polarity into the backbone of Fluorel. Although the weight-average molecular weight of FEP$_{19}$ is larger than that for Fluorel, 210 000 versus 85 000, the impact of this difference is expected to be secondary relative to the difference in polarity between these two fluorocopolymers. Previous studies of polymer−SCF solvent phase behavior show only minor changes in the location of the cloud-point curves for polymers of different molecular weights when these molecular weights exceed ~100 000.[9,16]

Table 2. Physical Properties of the Solvents Used in This Study[a]

solvent	M_w	T_c (°C)	P_c (bar)	ρ_c (g/cm^3)	α (Å^3)	μ (D)	I_i (eV)
SF$_6$	146.1	45.5	37.6	0.735	5.46	0.0	14.4
C$_3$F$_8$	188.0	71.9	26.8	0.627	6.67	0.0	13.3
C$_3$F$_6$	150.0	94.0	29.0	0.510	6.04	0.4	10.6
CClF$_3$	104.5	28.8	38.7	0.579	4.58	0.5	12.9
CHF$_3$	70.0	26.2	48.6	0.528	2.65	1.6	14.8
CO$_2$	44.0	31.0	73.8	0.469	2.65	0.0	13.7

[a] Refs 10, 15, 17, and 18. [b] The polarizabilities, α, of the fluorinated solvents were calculated using the method of Miller and Savchik.[19] The dipole moments, μ, of C$_3$F$_8$ and C$_3$F$_6$ are assumed to be equal to those of propane and propylene, respectively. CO$_2$ also possesses a quadrupole moment of -4.3×10^{-26} erg$^{1/2}$ cm$^{5/2}$. The last column presents experimental values for the ionization potentials, I_i.[20−24,10]

Table 2 lists the properties of the three classes of SCF solvents chosen for this study. The cloud-point behavior of Fluorel is measured in two nonpolar perfluorinated solvents, perfluoropropane (C$_3$F$_8$) and sulfur hexafluoride (SF$_6$); in three polar fluorocarbons, hexafluoropropylene (C$_3$F$_6$), chlorotrifluoromethane (CClF$_3$), and fluoroform (CHF$_3$); and in carbon dioxide (CO$_2$). Both C$_3$F$_8$ and SF$_6$ readily dissolve FEP$_{19}$[8] and, therefore, are used in the present study. The slight polarity of C$_3$F$_6$ should make it a better solvent for Fluorel than for FEP$_{19}$. CClF$_3$ is examined since the magnitude of its dipole moment is similar to that of C$_3$F$_6$, although CClF$_3$ has a smaller polarizability. The impact of polarity is further studied by comparing the solubility of Fluorel in CHF$_3$ to the other SCF solvents since CHF$_3$ has a high dipole moment, but a very low polarizability, which is approximately the same value as that for CO$_2$. In the results presented here the cloud-point curve for Fluorel in CO$_2$ is extended to temperatures lower than those reported by Rindfleisch, DiNoia, and McHugh.[9]

Experimental Section

Experimental cloud-point data are obtained using equipment and techniques described in detail elsewhere.[8,25] Polymer solubilities are reported as cloud points obtained at a fixed polymer composition of ~5 wt %, the expected maximum in the $P-x$ isotherms.[8,16] The temperature range of these experiments is extended to 270 °C to modulate the impact of polar interactions. In addition, the pressure range of these experiments is extended to 3000 bar to obtain SCF densities that are high enough to facilitate the dissolution of Fluorel at very high temperatures.

Materials. Fluorel FC 2175 was kindly donated by 3M Co. FEP$_{19}$, C$_3$F$_6$, and C$_3$F$_8$ were kindly donated by DuPont Co. More detailed information on the characteristics of FEP$_{19}$ are given by Tuminello,[13] where FEP$_{19}$ is designated LMFEP-2. CClF$_3$ and SF$_6$ (both CP grade, 99.0% minimum purity) were obtained from MG Industries. CHF$_3$ (98% minimum purity) was obtained from Aldrich Chemical Co., Inc. CO$_2$ (bone dry

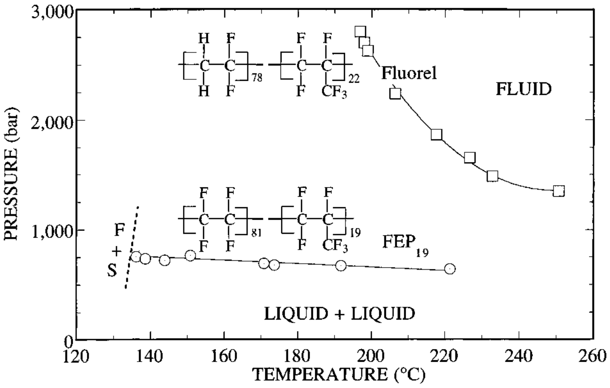

Figure 1. Comparison of the cloud-point curve of poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel), obtained in this study, to that of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in $CClF_3$, obtained by Mertdogan et al.[8] The crystallization boundary is denoted by the dashed line.

grade, 99.8% minimum purity) was obtained from Airgas Inc. All of the solvents were used as-received.

Results

The phase behavior results for the Fluorel−SCF solvent systems are presented in order of worst to best solvent for Fluorel and are compared to the phase behavior of the same solvents with nonpolar FEP_{19}. Fluorel does not dissolve in the two nonpolar solvents considered in this study, C_3F_8 and SF_6. This result is a bit surprising since temperatures as high as 260 °C were investigated where dispersion-type interactions are expected to dominate polar, vinylidene segment−segment interactions, as shown in eq 3. Nevertheless, despite the use of pressures in excess of 2600 bar to obtain high solvent densities that increase dispersion interactions, the interchange energy (eq 2) must still be dominated by polar Fluorel−Fluorel interactions relative to Fluorel−SCF solvent cross-interactions. These observations suggest that some solvent polarity is needed to dissolve Fluorel.

Figure 1 shows the phase behavior of Fluorel in $CClF_3$. The small dipole moment of $CClF_3$ provides sufficient Fluorel−$CClF_3$ polar interactions that allow Fluorel to dissolve in a temperature range where it did not dissolve in C_3F_8 or SF_6 even though these two solvents have higher polarizabilities. At 230 °C, $CClF_3$ dissolves Fluorel at 1500 bar, which is approximately 1000 bar greater than the pressure required to dissolve FEP_{19}, whose cloud-point curve is also shown in Figure 1. In addition, the cloud-point pressures of the Fluorel−$CClF_3$ system rise sharply as the temperature is lowered to 195 °C. The shape of the Fluorel−$CClF_3$ cloud-point curve is similar to that found for other polymer−solvent mixtures where one of the mixture components is nonpolar and the other is polar.[8,9,26] At temperatures below 195 °C, polar interactions between vinylidene fluoride segments dominate the interchange energy, which causes Fluorel to fall out of solution regardless of the SCF solvent density.

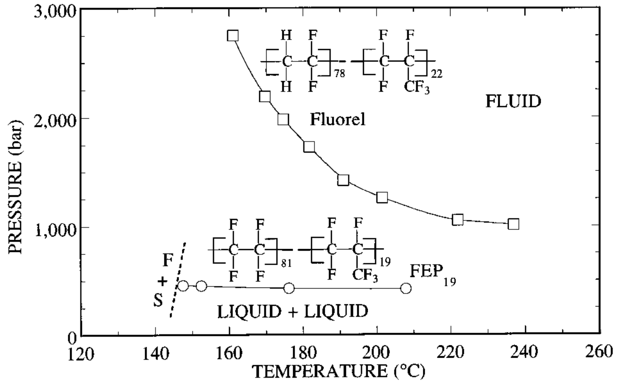

Figure 2. Comparison of the cloud-point curve of poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel), obtained in this study, to that of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in C_3F_6, obtained by Mertdogan et al.[8] The crystallization boundary is denoted by the dashed line.

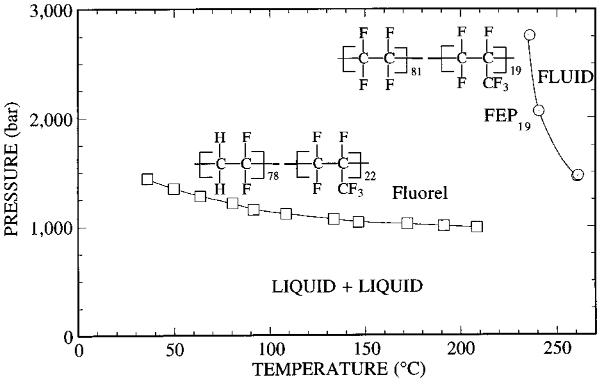

Figure 3. Comparison of the cloud-point curve of poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel), obtained in this study, to that of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in CHF_3, obtained by Mertdogan, Tuminello, and McHugh.[27]

Figure 2 shows that the Fluorel−C_3F_6 cloud-point curve is at lower pressures and lower temperatures relative to the Fluorel−$CClF_3$ curve shown in Figure 1. Even though both C_3F_6 and $CClF_3$ have essentially the same small dipole moment, C_3F_6 has a larger polarizability, which makes it a better solvent for Fluorel. Also shown in Figure 2 is a comparison of the cloud-point curves of Fluorel and of FEP_{19} in C_3F_6. The cloud-point pressures of FEP_{19} remain essentially constant at 600 bar over a wide temperature range. However, the cloud-point curve for the Fluorel system is at ~500 bar greater pressure at 220 °C and at ~1700 bar greater pressure at 170 °C. The sharp rise in pressure needed to dissolve Fluorel compared to FEP_{19} is likely due to the impact of the large dipole moment of Fluorel which is magnified at lower temperatures. Below 163 °C, Fluorel exhibits enhanced self-interactions, due to its large dipole moment, that outweigh cross-interactions between Fluorel and C_3F_6. Note that Fluorel has a lower molecular weight than FEP_{19}. The dramatic difference in the shape and pressures of the cloud-point curves of these two copolymers with both $CClF_3$ and C_3F_6 reinforces the assertion that the impact of copolymer molecular weight is secondary relative to any mismatch in the intermolecular potential energies of the copolymer and the solvent.

Figure 3 shows that Fluorel−CHF_3 cloud-point pressures remain constant at ~1100 bar from 210 to 80 °C and that they increase slightly as the temperature is reduced to ~30 °C. Although CHF_3 has a small polarizability, it has a large dipole moment which interacts favorably with the dipole moment of the vinylidene fluoride groups in Fluorel. The behavior of the Fluorel−CHF_3 cloud-point curve is in marked contrast to that of the FEP_{19}−CHF_3 cloud-point curve[27] which increase sharply at ~235 °C due to increased solvent−solvent, polar interactions. It is the polar self-interactions of

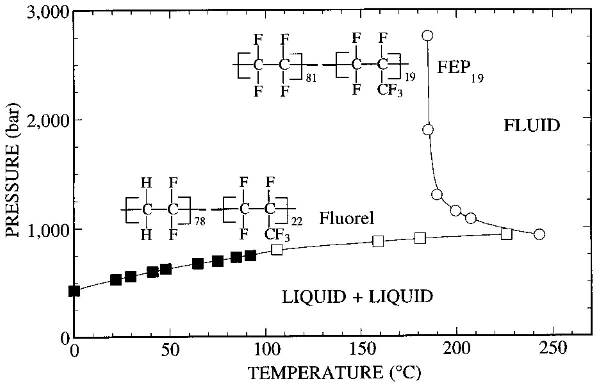

Figure 4. Comparison of the cloud-point curve of poly(vinylidene fluoride-*co*-22.0 mol % hexafluoropropylene) (Fluorel) to that of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}) in CO_2, obtained by Mertdogan et al.[8] The open squares are data of Rindfleisch, DiNoia, and McHugh,[9] and the closed squares are data obtained in this study.

CHF_3 that makes it such a poor solvent for nonpolar FEP_{19}.

Figure 4 shows a comparison of the cloud-point curves of FEP_{19} and of Fluorel in CO_2. The Fluorel–CO_2 data of Rindfleisch, DiNoia, and McHugh[9] are extended to lower temperatures and pressures. Polar interactions drive the FEP_{19} and the Fluorel curves in two different directions. Quadrupolar CO_2–CO_2 interactions dominate the phase behavior for FEP_{19} in CO_2, as is manifest in the sharp rise in cloud-point pressures with decreasing temperature.[8] However, dipole–quadrupole interactions between Fluorel and CO_2 overshadow these CO_2–CO_2 interactions as is manifest in a slight decrease in cloud-point pressure with decreasing temperature. In fact, relatively modest pressures are needed to dissolve Fluorel in CO_2 at temperatures as low as 0 °C.

The impact of polar interactions on the phase behavior of Fluorel is revealed with a comparison of cloud-point behavior in CO_2 relative to that in CHF_3. Although the cloud-point pressures of Fluorel in both solvents are approximately the same at 250 °C (see Figures 3 and 4), the cloud-point pressures for the Fluorel–CO_2 system decrease with decreasing temperature while those for the CHF_3 system increase. The magnitudes of dispersion interactions are expected to be similar in both solvents given that CO_2 and CHF_3 have essentially the same polarizability. In order to compare the polar moments of these two solvents, it is important to recognize that the impact of the dipole moment scales with the square root of the molar density whereas the impact of the quadrupole moment scales with the molar density to the $^5/_6$ power.[28] At their respective cloud-point conditions, the reduced quadrupole moment of CO_2 is ~67% of the value of the reduced dipole moment of CHF_3. It is interesting that CO_2 is a slightly better solvent than CHF_3 for Fluorel since CHF_3 is the more polar solvent and, in turn, is expected to interact more favorably with polar, vinylidene fluoride repeat units. The discrepancy between the anticipated and the actual phase behavior may be a consequence of additional forces of attraction governing the phase behavior of the Fluorel–CO_2 system. O'Shea and co-workers[29] and Kazarian and co-workers[30] present evidence that CO_2 can act as an electron acceptor to form Lewis acid–base complexes with polymers that possess electron-donating groups, such as fluorine atoms. Other studies have also suggested that CO_2 and fluorine molecules exhibit specific interactions which result in a high miscibility of CO_2 with fluorinated polymers.[30–32] Hence, the difference in the phase behavior with CO_2 relative to that with CHF_3 is attributed to complex formation between CO_2 and Fluorel, which is enhanced at low temperatures.

Discussion

A polymer is expected to dissolve in a given solvent when there is a balance of the interaction energies between polymer segment–segment, segment–solvent, and solvent–solvent pairs in solution. Since the intermolecular interaction potentials of the solvents used in this study are not the same, different temperatures and pressures are needed to achieve this balance in interchange energy for a given solvent as indicated by eqs 1–3. Previous studies with FEP_{19}[8] show that solvent molar density times polarizability, $\rho_i\alpha_i$, reduces the cloud-point data for seven different solvents to a single, linear function of temperature

$$\rho_i\alpha_i = (650.11 - 0.72459T)N_A \tag{4}$$

where ρ_i is calculated from the Peng–Robinson equation of state at cloud-point conditions, N_A is Avogadro's number, and T is the absolute temperature. Given pure solvent properties and a set of experimental cloud-point data for a single polymer–solvent system, this simple measure of solvent strength provides a means for estimating cloud-point pressures for nonpolar polymers with nonpolar solvents or with polar solvents at very high temperatures where polar interactions are diminished. This density–polarizability correlation tool does not predict when crystallization may occur or when polar interactions fix the phase behavior.

Unfortunately, $\rho_i\alpha_i$ does not correlate the cloud-point data for the Fluorel–SCF solvent systems. This is not surprising since the $\rho_i\alpha_i$ correlation, which is proportional to the square root of the internal energy, $(\Delta U_{SCF})^{0.5}$, is derived using only dispersion interactions while the Fluorel–SCF solvent phase behavior can be dominated by polar interactions. Although an equation of state could be used to determine ΔU_{SCF}, empirical temperature-dependent parameters are needed to account for polar interactions. It is possible, however, to use the principles of molecular thermodynamics to extend the $\rho_i\alpha_i$ correlation to include dipolar and quadrupolar interactions. The expression for the intermolecular pair potential energy

$$\Gamma_{ii}(r,T) \approx -\left(\frac{3I_i}{4}\frac{\alpha_i^2}{r^6} + \frac{2}{3}\frac{\mu_i^4}{r^6kT} + \frac{7}{40}\frac{Q_i^4}{r^{10}kT}\right) \tag{5}$$

where I_i is the ionization potential, is combined with eq 1 to calculate ΔU_{SCF}, defined as $[U_{SCF}(T,P) - U_{SCF}(T,P^{\text{ideal gas}})]$.[33] For this calculation the radial distribution function is set equal to 1 to obtain

$$\Delta U_{SCF} = 2\pi\rho_{SCF}(P,T)\, N_A\left[\left(\frac{1}{4}I_i\alpha_i^2 + \frac{2}{9}\frac{\mu_i^4}{kT}\right)\frac{1}{r^3} + \left(\frac{1}{40}\frac{Q_i^4}{kT}\right)\frac{1}{r^7}\right] \tag{6}$$

where $1/r^3$ is equal to the molar density of the pure SCF solvent, ρ_{SCF}.

If eq 6 is used to calculate $(\Delta U_{SCF})^{0.5}$, a single linear function of temperature is again obtained for FEP_{19} but a similar function is not found for the Fluorel data. Likewise, it is not possible to obtain a single function of ΔU_{SCF} vs T to represent the Fluorel data. Regular solution theory suggests that when the solubility parameter of the SCF solvent matches that of the copolymer, a single phase should be obtained. Hence, plotting $(\Delta U_{SCF}/v_{SCF})^{0.5}$ vs T should reduce each copolymer−SCF solvent data set to its own master curve since the solubility parameter for each copolymer is expected to be only a modest function of pressure. This approach proved to be inconsistent since it works for the Fluorel data but not for the simpler, nonpolar FEP_{19} data. More than likely, the correlations used in this study fail since none of the approaches account for polymer segment−segment interactions and, more importantly, polymer segment−solvent interactions. Further modeling studies are in progress with the Sanchez−Lacombe and SAFT equations of state to determine whether these equations can be used to model the observed phase behavior without resorting to arbitrary empirical corrections to account for polar interactions. In addition, further experimental studies are in progress with Fluorel-type copolymers with varying comonomer content.

Conclusions

Modest changes to the backbone architecture of a fluorocopolymer can have a significant impact on its solubility in a given SCF solvent. For example, the good solvents for nonpolar FEP_{19} proved to be nonsolvents for polar Fluorel. It is possible to dissolve Fluorel in solvents with small dipole moments, such as $CClF_3$ and C_3F_6, but higher pressures and temperatures are required than those needed to dissolve FEP_{19}. Conversely, Fluorel dissolves in polar CHF_3 at substantially lower pressures and temperatures than those required to dissolve FEP_{19}. Fluorel is much more soluble in CO_2 than is FEP_{19} due to the favorable interactions between the quadrupole moment of CO_2 and the dipole moment of the vinylidene fluoride repeat units. It is interesting that cloud points for Fluorel in CHF_3 and in CO_2 essentially superpose at high temperatures where polar interactions are reduced. However, as the temperature is lowered, the CHF_3 curve increases in pressure while the CO_2 curve decreases in pressure. The difference in phase behavior is attributed to complex formation between CO_2 and Fluorel, which is enhanced at low temperatures. Challenges remain for calculating polar fluorocopolymer−polar SCF solvent phase behavior.

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