Impact of Melting Temperature on Poly(Tetrafluoroethylene-*co*-hexafluoropropylene) Solubility in Supercritical Fluid Solvents

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ABSTRACT: Experimental cloud-point data to 2800 bar and 250 °C are presented for binary mixtures of partially crystalline poly(tetrafluoroethylene-*co*-19 mol % hexafluoropropylene) (FEP_{19}) and amorphous FEP_{48} with CF_4, CO_2, and SF_6. It takes less pressure and lower temperatures to dissolve FEP_{48} compared to FEP_{19} in CF_4 and in SF_6. The sharp increase in the FEP_{48}−CO_2 cloud-point curve occurs at 20 °C lower temperature than the increase for the FEP_{19}−CO_2 system. Since the addition of hexafluoropropylene groups is not expected to significantly change the type of interactions between an average segment of the copolymer with that of the solvent, the increased ease of dissolving FEP_{48} is associated with the greater free volume expected for this more highly branched amorphous copolymer.

Introduction

Recently several articles have reported on the solubility of amorphous as well as crystalline fluorocopolymers in supercritical fluid (SCF) solvents.[1−4] A general trend observed in these studies is that the cloud-point curve rises sharply in pressure with decreasing temperature if the fluorocopolymer is nonpolar and the SCF solvent is polar, or vice versa. The shape of the cloud-point curve reflects the temperature sensitivity of the interchange energy, which is the balance of intermolecular interactions between polymer segment−segment, segment−solvent, and solvent−solvent pairs in solution. For mixtures of nonpolar and polar components, the sharp rise in the cloud-point curve with decreasing temperature is a consequence of the enhanced self-interactions between the polar component in solution since polar interactions dominate nonpolar, dispersion interactions, which are much less sensitive to temperature.[5]

With semicrystalline fluorocopolymers, the cloud-point curve terminates at a crystallization temperature below which it is not possible to obtain a single phase regardless of the pressure. Superficially, the topology of the cloud-point curve in the case of a semicrystalline fluorocopolymer−SCF system is very similar to that of polar fluorocopolymer−nonpolar SCF or nonpolar fluorocopolymer−polar SCF systems. For the nonpolar poly(tetrafluoroethylene-*co*-19 mol % hexafluoropropylene) (FEP_{19})−CO_2 system, it is not readily apparent that the sharp increase in cloud-point pressure is due to the polar character of CO_2 since FEP_{19} crystallizes in CF_4 at ~189 °C at 2000 bar which is a few degrees *higher* than the cloud-point temperature of FEP_{19} in CO_2 at this pressure.[2] The turbidity of the solution makes it difficult to determine if the second phase contains solid crystals in solution. However, it is possible to deduce whether crystals are present by measuring the temperature needed to a obtain a single phase when the solution is isobarically heated at a fixed rate. With CF_4, the temperature must be increased by ~25 °C beyond the crystallization boundary at a fixed pressure of 2000 bar to obtain a clear, single phase. The magnitude of this temperature overshoot is similar to the supercooling found for PTFE in non-SCF fluorocarbon solvents.[6] With CO_2 and the same heating rate, the temperature must be increased by 1−2 deg beyond the liquid−liquid boundary to obtain a single phase, which strongly suggests that there are no FEP_{19} crystals in solution.[2] Hence, the sharp rise in the FEP_{19}−CO_2 cloud-point curve is attributed to the quadrupolar nature of CO_2 which makes it too polar for nonpolar FEP_{19} even at 185 °C.[2−4]

In this paper, cloud-point data of poly(tetrafluoroethylene-*co*-48 mol % hexafluoropropylene) (FEP_{48})−SCF solvent mixtures are compared to those previously reported for FEP_{19}−SCF solvent mixtures[2] with supercritical CO_2, SF_6, and CF_4. Since FEP_{48} is totally amorphous, crystallinity is not a factor when interpreting which intermolecular interactions govern the topology of the cloud-point curve. Table 1 lists the physical properties of the two fluorocopolymers used in this study. It is important to note that although the peak melting temperature of FEP_{19} is 147 °C, its melting temperature is expected to increase at a rate of 1.0 °C/10 bar, the rate observed for PTFE.[1,9] Therefore, hydrostatic pressure increases the melting temperature, but the solubility of the SCF solvent in the FEP_{19}-rich liquid phase reduces the melting temperature. Hence, the high-pressure melting points observed for FEP_{19} in SCF solvents (e.g., 189 °C in CF_4 at 2000 bar) are a result of a balance between these two competing effects.

Table 2 lists the properties of the solvents. The cloud-point curves for the nonpolar FEP_x copolymers in nonpolar SF_6 and CF_4 are expected to be fixed by dispersion interactions that scale with solvent polarizability. The polar character of CO_2 can be assessed by comparing the shapes of the FEP_x−CO_2 cloud-point curves to those of the same FEP_x copolymer in CF_4 since

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Table 1. Physical Properties of the FEP_x Copolymers Used in This Study[a]

HFP content (mol %)	M_w	peak melting temp (°C)
19	210 000	147
48	191 000	

[a] More detailed information on the characteristics of FEP_{19} are given by Tuminello,[7] where FEP_{19} is designated LMFEP-2, and by Mertdogan et al.[8] The HFP content of the copolymers was determined spectroscopically and the weight-average molecular weight was calculated from low strain rate melt viscosity.

Table 2. Physical Properties[a] of the Supercritical Fluids Used Here[10,11]

	mol wt	critical temp (°C)	critical pressure (bar)	polarizability 10^{25} (cm^3)	dipole moment (D)
CO_2	44.0	31.0	73.8	26.5	0.0
CF_4	88.0	−45.6	37.4	28.6	0.0
SF_6	146.1	45.5	37.6	54.6	0.0

[a] The polarizability is calculated using the method of Miller and Savchik.[12] The quadrupole moment of CO_2 is -4.3×10^{-26} erg$^{1/2}\cdot$cm$^{5/2}$.

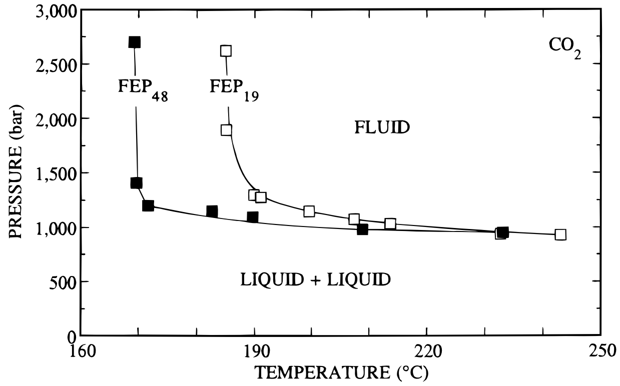

Figure 1. Impact of hexafluoropropylene content on the solubility of poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer with 19 mol % HFP (FEP_{19})[2] and 48 mol % HFP (FEP_{48}) in CO_2.

these two SCF solvents have virtually the same polarizability which fixes the nonpolar character of the solvent.[4]

Experimental Section

Experimental cloud-point data are obtained using equipment and techniques described in detail elsewhere.[2,13] Polymer solubilities are reported as cloud-points obtained at a fixed polymer composition of ~5 wt %, the expected maximum in the $P-x$ isotherms.[2,14–16] Each cloud-point is reproduced two or three times at each temperature with a scatter of approximately ±3.4 bar.

Materials. The FEP_{19} and FEP_{48} were kindly donated by DuPont. CO_2, 99.8% minimum purity, was obtained from Airgas Inc. CF_4 and SF_6, both 99.0% minimum purity, were obtained from MG Industries. The solvents are used as received.

Results

Figure 1 shows a comparison of experimental cloud-point data for FEP_{19} and FEP_{48} in CO_2. Both cloud-point curves exhibit the same characteristic shapes even though FEP_{19} can crystallize and FEP_{48} is amorphous. At high temperatures it takes approximately 1000 bar to dissolve either FEP_x copolymer in CO_2. The need for high pressure is a consequence of the small polarizability of CO_2 that reflects the weak nonpolar character of CO_2. Increasing the hexafluoropropylene (HFP) comonomer content from 19 to 48 mol % shifts the low-temperature portion of the cloud-point curve from 190 to 170 °C. The sharp upturn in cloud-point pressure in both cases is a consequence of quadrupolar interactions between CO_2 molecules that makes the interchange energy unfavorable for dissolving nonpolar FEP_x. Crystallinity does not play a role in fixing the topology of the $FEP_{48}-CO_2$ cloud-point curve and, on the basis of previous studies,[2–4] it does not play a role with the $FEP_{19}-CO_2$ system.

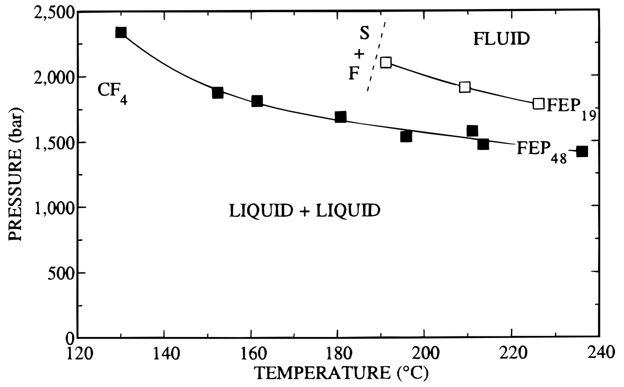

Figure 2. Impact of hexafluoropropylene content on the solubility of poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer with 19 mol % HFP (FEP_{19})[2] and 48 mol % HFP (FEP_{48}) in CF_4. The crystallization boundary is denoted by a dashed line.

Figure 2 shows the cloud-point curves for FEP_{19} and FEP_{48} in CF_4. At temperatures greater than 190 °C, the FEP_{48} curve is shifted 400 to 500 bar lower in pressure compared to the FEP_{19} curve. The large difference in pressure between the two cloud-point curves cannot be explained on the basis of the small difference in molecular weights of these two copolymers. The location of the cloud-point curve is determined both by the energy of interaction and by the entropy of mixing. The entropic term includes the combinatorial entropy of mixing, and it also contains the configurational entropy of mixing, the so-called equation of state contribution that is related to the free volume difference between the solvent and the polymer. Adding HFP groups to the backbone of FEP_x copolymers has only a modest effect on the energetics of interaction, but it does increase the free volume of the copolymer, which favors dissolution of the copolymer. Hence, the decrease in cloud-point pressure is a consequence of the increased free volume of FEP_{48} relative to that of FEP_{19}. Similar trends are observed with the phase behavior of supercritical ethane and propane with linear, low-density polyethylene (LLDPE) with differing amounts of chain branching.[17] It takes higher pressures to dissolve the LLDPE with the smallest number of chain branches as compared to the LLDPE with the largest number of chain branches in either ethane or propane.[17]

The $FEP_{48}-CF_4$ curve extends to temperatures lower than 190 °C since it does not crystallize. Both cloud-point curves exhibit only a small negative slope since nonpolar, dispersion interactions dominate in these cases. The FEP_x-CF_4 cloud-point curves are 500–1000 bar higher in pressure compared to the FEP_x-CO_2 curves since the strength of dispersion interactions roughly scales with density and CF_4 is less dense than CO_2 at comparable pressures and temperatures.[2]

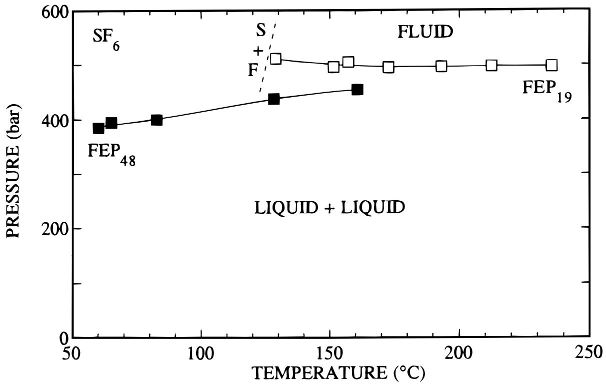

Figure 3. Impact of hexafluoropropylene content on the solubility of poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer with 19 mol % HFP (FEP_{19})[2] and 48 mol % HFP (FEP_{48}) in SF_6. The crystallization boundary is denoted by a dashed line.

Figure 3 shows the impact of HFP content on the cloud-point curves of FEP_x in SF_6. In this case, the cloud-point pressures are well below 1000 bar since SF_6 has a much larger polarizability than CO_2 or CF_4. The FEP_{48} curve superposes with the FEP_{19} curve at temperatures greater than 120 °C, but it exhibits a slight positive slope as the temperature is lowered. Again, the cloud-point pressures decrease with increasing HFP content in FEP_x due to the decreased difference in copolymer−solvent free volumes.

Conclusions

The results presented here reinforce the conclusion that the melting point of a polymer has only a secondary effect on the topology of the cloud-point curve as long as the copolymer does not crystallize at operating conditions.[2,3,17] For the FEP_x copolymers, the impact of adding hexafluoropropylene to the backbone results in an increased number of branch points that increases the free volume of the copolymer. Lower pressures are then needed to obtain a single phase in the region of pressure−temperature space where entropic contributions dominate enthalpic contributions to the Gibbs free energy. The topology of the cloud-point curves of nonpolar FEP_x copolymers in CO_2 is a consequence of the quadrupolar nature of CO_2 which causes the cloud-point curve to sharply increase in pressure when the interchange energy is dominated by CO_2−CO_2 interactions. The results presented here substantiate the assertion that the melting point of FEP_x copolymers, with at least 19 mol % HFP content, does not change the characteristic shape of the cloud-point curve in quadrupolar CO_2 but show that increased HFP content can shift the cloud-point curve to lower temperatures. If polarity is added to the backbone of the copolymer, it is possible to avoid a sharp increase in pressure with decreasing temperature in the presence of CO_2 due to favorable CO_2-polar segment interactions.[3,4]

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