Thermodynamics of Poly(tetrafluoroethylene) Solubility

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ABSTRACT: We have directly observed the dissolution behavior of poly(tetrafluoroethylene) (PTFE) in sealed glass tubes placed in aluminum heating blocks. Both oligomers of PTFE and other perfluorocarbons were studied as solvents for specially prepared, well-characterized low moleuclar weight PTFEs. Solution melting points and recrystallization temperatures were determined as well as the temperature above the solution melting point where liquid–liquid phase separation occurs. We have also modeled the phase behavior of PTFE–fluorocarbon systems using the Flory, Orwoll, Vrij theory and obtained qualitative agreement with the visual observations. Saturated perfluorocarbons with aliphatic ring structures and high critical temperatures were found to be the preferred solvents for allowing solubility at the lowest temperatures and pressures.

Introduction

Very little information concerning solution studies on poly(tetrafluoroethylene) (PTFE) appear in the literature. A patent was issued in 1950[1] on the plasticization of PTFE by perfluorocarbons. Chu et al.[2,3] made use of this early knowledge to make high temperature light scattering measurements of PTFE in a dilute solution using oligomers of both PTFE and poly(chlorotrifluoroethylene).

The first systematic study of the solution thermodynamics of these systems was made by Smith and Gardner.[4] They studied the melting point depression of PTFE in contact with oligomers and other perfluorocarbons using Flory–Huggins theory. In both cases (oligomers and other perfluorocarbons), a greater melting point depression was predicted with decreasing solvent molecular weight (MW). The limitation was that boiling point also decreased with MW in which case solubility was prevented at ambient pressure for solvents with boiling points much below 300 °C. Our objectives are to (1) experimentally verify the concepts proposed by Smith and Gardner[4] and (2) extend their ideas using a thermodynamic model which allows us to predict the effects of pressure on the phase behavior.

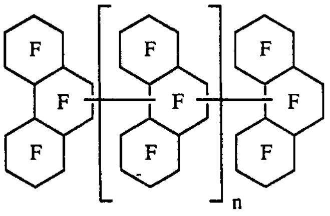
Experimental Section

The polymers used in the dissolution studies were noncommercial specially prepared PTFEs described previously.[5] Their MWD (molecular weight distributions) were estimated[5] and are listed in Table 1. The weight average MW ($\bar{M}_w$) varied from 340 000 to over 2 million. This is well below the MW for commercial polymers where $\bar{M}_n$ is estimated to be 20 million.[6] Therefore, one unique aspect of this work is the use of relatively low MW, characterized polymers. The MW is sufficiently low to rapidly accelerate the dissolution process while being high enough so that the L–L (liquid–liquid) phase behavior is only weakly dependent on MW.

Most of the perfluorinated solvents were obtained from PCR, Inc., of Gainesville, FL. Dodecafluorocyclohexane (C_6F_{12}), octafluoronaphthalene ($C_{10}F_8$), and perfluorotetracosane (n-$C_{24}F_{50}$) were obtained from the Aldrich Chemical Co. Perfluorotetradecahydrophenanthrene ($C_{14}F_{24}$) was obtained from both PCR and the ISC Division of the Rhône-Poulenc Co. (RP-ISC); the latter uses the tradename Flutec PP11. A mixture of isomers of perfluoroperhydrobenzylnaphthalene ($C_{17}F_{30}$), with the tradename Flutec PP25, was obtained from RP-ISC. A high-boiling oligomeric byproduct in the manufacture of Flutec PP11 was also obtained from RP-ISC. The latter is a gross mixture of perfluorocarbons whose generalized structure is shown below with n = 0 and 1, predominantly. The approximate boiling range of the components is 280–400 °C. Details of the characterization will be published at a later date.[7]

Table 1. PTFE Characterization

PTFE designation	$10^{-6}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
LMW	0.34	2.8
IMW	1.8	4.3
HMW	2.3	8.2


Flutec PP11 Oligomer

All materials were used as-received, with no additional purification except for perfluoroeicosane (n-$C_{20}F_{42}$). In this case, heating above about 200 °C caused a dark insoluble material to form with the as-received perfluorocarbon. This insoluble material became darker and seemed to increase in volume with increasing temperature. It would not melt at temperatures as high as 350 °C. Double distillation or sublimation was sufficient to prevent this formation. The purified material melted to a clear, colorless liquid which showed no signs of change up to 350 °C for extended periods of time. Gas chromatography, mass spectroscopy, and infrared spectroscopy failed to reveal the chemical nature of the impurity. We suspect a low level of metal catalyzed some reaction at high temperatures.

Non-perfluorocarbons were also used. Perfluorotrihexylamine was obtained from PCR, Inc. Polyhexafluoropropylene oxide oligomer was obtained from the DuPont Co. as Krytox 16350. The oligomer of poly(trifluorochloroethylene) was obtained from the Occidental Petroleum Co. as Fluorolube LG160.

Our experiments involved visually observing melting, swelling, and dissolution properties in sealed borosilicate glass tubes. Standard (1-mm) wall thickness, 8-mm outside diameter, borosilicate glass tubes were sealed at about 80–100-mm lengths and were loaded with solvent plus polymer to about one-half to two-thirds of capacity. The Corning Glass Co. literature lists allowable pressures in such a device as being 1.7 MPa. We tested four such tubes loaded with water, known to have a weakening effect on glass, particularly at high temperatures. These were slowly heated (50-deg intervals, holding for 15 min at each step change) and found to burst between 328 and 336 °C. The interior pressures at these temperatures were 12.5–13.9 MPa. It must be emphasized, however, that the Corning recommendation is the safe limit due to the unpredictable fracture behavior of a brittle material like silica glass. Certainly, experiments should not be

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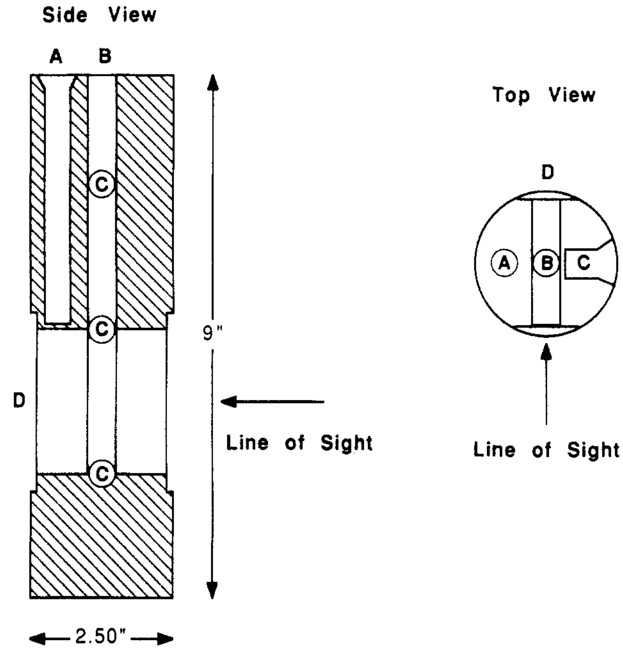

Figure 1. Schematic of the thermostated Al heating block for carrying out dissolution experiments.

carried out above the safe limit if they are not shielded. We found that we could safely work at higher pressures by shielding with a polycarbonate sheet and wearing heavy gloves when hands were placed behind the shield. Even though a loud explosion would occur during the occasional tube failure, the small volume of material precluded any danger with this simple shielding procedure.

We observed the dissolution of "virgin" polymer, which is in the form of micron sized particles. (By virgin we are referring to material which has never been melted.) For commercial PTFE, the melting of the virgin material is about 345 °C versus the premelted material's 327 °C melting point. We observed no significant difference in the DSC melting behavior for virgin versus the premelted low MW PTFEs. About 0.02–0.1 g of PTFE powder was loaded into the tubes followed by enough solvent to make 1–5% weight fraction solutions. The 10 and 20% solutions were made by premixing the polymer powder with liquid solvent into a paste and loading the paste into the tube with a wide bore syringe. The contents were then sealed under low vacuum ($\sim$4 kPa) using good glass blowing procedures to get a stress and defect-free enclosure. When volatile solvents were used, they were first cooled with liquid nitrogen prior to applying vacuum.

A schematic diagram for the aluminum heating block is shown in Figure 1. The sealed tubes were placed in tube "B" so they could be viewed through the slit "D" along the labeled "line of sight". Glass microscope slides were placed in the recesses on either side of the viewing slit to reduce heat loss and temperature gradients around the sample. A custom designed two-piece band heater was purchased from the Industrial Heater Co. (Bronx, NY) and bolted around the block. A controlling "J" type thermocouple was placed in hole "A". Monitoring "J" type thermocouples (three) were placed in the openings labeled "C". Glass wool insulation was placed over any uncovered metal plus the glass slides and the entire block was set on a heating plate to minimize thermal gradients. We were able to measure less than 0.5-deg discrepancy between all thermocouples at temperatures as high as 350 °C.

Differential scanning calorimetry was carried out under nitrogen pressure (2 MPa) in a Model 910 pressure DSC cell using a 9900 controller manufactured by TA Instruments (formerly DuPont Instruments). Samples consisted of cooled gel (5% weight fraction) from the above-described tube experiments. The samples were sealed in crimped standard aluminum pans with no pinholes to minimize solvent loss. If pinholes were used, we experienced considerable (60–90%) solvent loss. Without pinholes solvent loss was kept to 1–24%. When pinholes were not used, it was essential to gradually apply pressure to the cell so as not to crush the sample pans, which would result in a noisy signal. We would have liked to observe thermal effects when undissolved polymer was combined with solvent in the DSC pans but could not find a way of suitably sealing the DSC pans to prevent solvent loss during the dissolution process. Approximately 10-mg samples were used with heating and cooling rates of 10 °C/min.

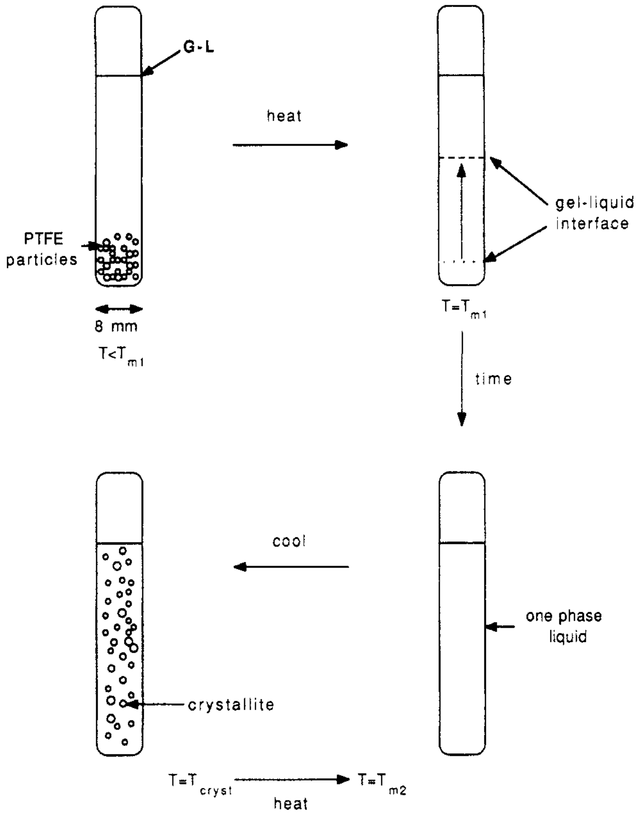

Figure 2. Schematic depicting the visual observations when dissolving PTFE and crystallizing the solutions followed by remelting.

Results

1. **General Observations.** The observations that were characteristic of all the cases where dissolution was observed are illustrated in Figure 2. When the sample temperature (T) is below the initial melting temperature (T_{m1}), solid, opaque, free-flowing PTFE powder is observed in equilibrium with the liquid solvent. The upper left drawing in Figure 2 depicts this case. The G–L in this drawing refers to the gas–liquid interface. As the sample nears T_{m1}, a decrease in opacity, particle swelling and some particle coalescence is observed. Thus, T_{m1} is the highest temperature at which crystals are visible. In our experiments, we heated the tubes in 5-deg increments (holding for 5 min at each temperature). As T_{m1} was approached, the temperature increments were decreased.

At, or slightly above, T_{m1} the mixture becomes perfectly clear. All the particles have completely coalesced and sufficient swelling has occurred to create a uniform, nonflowing mass at the bottom of the tube. The refractive index of the swollen polymer matches that of the solvent so closely that the human eye cannot detect the boundary between the swollen polymer and the solvent-rich phases. The only way we could detect the existence of the polymer-rich phase was to pick up the heating block and turn it on its side so that the solvent-rich phase would flow away, leaving the immobile polymer-rich phase at the bottom of the tube. The volume of the polymer-rich phase increases to a limiting value in a fairly short time (usually within 1 day for even the commercial polymer of at least 20 million MW). Then nothing appears to happen for an extended

Table 2. FOV Reduction Parameters

component	P^* (MPa)	V^* (cc/g)	T^* (K)	S^2	range P (Mpa)	range T (K)
PTFE	406.8	0.421 41	7090.4	0.10	0–40	603–645
n-C_6F_{34}	464.2	0.412 29	5674.3	0.07	0–10	499–593
n-$C_{20}F_{42}$	303.2	0.405 66	5982.9	0.06	0–10	572–625
$C_{10}F_{18}$	366.3	0.403 25	5094.2	0.05	0–10	472–536
$C_{14}F_{24}$	339.4	0.415 42	5860.3	0.06	0–10	539–617

period (several days for the HMW polymer) until the immobile phase starts to flow. Shortly after that point, the mixture becomes homogeneous. The sequence of events from initial melting, through the formation of a transient "gel"–liquid interface, ultimately ending in complete dissolution are represented by the pictures in the upper and lower right hand corners of Figure 2. ("Gel" refers to the immobile polymer-rich phase.)

Once dissolution occurred, the samples were cooled in the same fashion as the heating experiments (i.e. cooled in 5-deg increments holding 5 min at each temperature) to determine T_{cryst}, the temperature at which crystallites started to form. In both the heating and cooling experiments, we controlled the heating intervals well enough to determine T_{cryst} and T_m to about ±2 deg. The crystallites appeared as points of opacity uniformly distributed throughout the solution. At lower polymer concentrations these crystallites would sometimes settle to the bottom of the tube. Settling would not occur in the more concentrated solutions. Instead, a gel would form which we guess would be a highly swollen network of chains held together by crystallites. A second melting point, T_{m2}, was also determined upon heating, as previously described. The crystallization and remelting is illustrated in the bottom two pictures of Figure 2.

2. FOV Model Predictions. Theoretically generated phase diagrams allow systematic variation of temperature and pressure. These diagrams enhance the understanding of the experimental behavior since systematic variation of pressure was not experimentally available to us. Therefore, we will first show the calculated results.

Phase diagrams of some perfluorocarbon/PTFE mixtures were predicted using the Flory, Orwoll, Vrij (FOV) theory.[8,9] This allowed the prediction of the pressure and the temperature at which liquid–liquid phase separation should occur from solution. The reduction parameters characterizing the thermodynamic properties of the solvents were obtained by fitting the equation of state to pressure, volume, and temperature (*PVT*) data for each of the compounds. Since no experimental *PVT* data exist for many of the solvents considered here, data were generated for all solvents using the Hankinson, Brobst, and Thomson (HBT) technique.[10] This method can be used to predict the density of the liquid phase in the vicinity of the coexistence curve. Errors will result from this procedure. However, since we are only interested in the qualitative behavior of these systems, we will not be overly concerned with the quantitative details of the phase diagrams. The reduction parameters obtained from the above procedure (as well as for PTFE) are shown in Table 2. The parameters for PTFE were obtained by fitting to the experimental *PVT* data of Zoller.[11] The parameter S^2 is a measure of the goodness of fit and indicates almost perfect fits to the generated data which is to be expected for this rather limited pressure and temperature domain.

The vapor pressures of the solvents of interest were generated by the method of Lee and Kesler.[10] These results are shown in Figure 3 for three normal perfluoroalkanes, perfluorodecalin, and perfluorotetradecahydrophenanthrene. Many polymer solutions exhibit LCST (lower critical solution temperature) behavior in the vicinity of the critical temperature of the solvent. This is caused by the rapid decrease in density of the solvent in that temperature domain. For this reason, the generated *PVT* data were chosen so that it provided a description of the liquid at temperatures below the critical temperature.

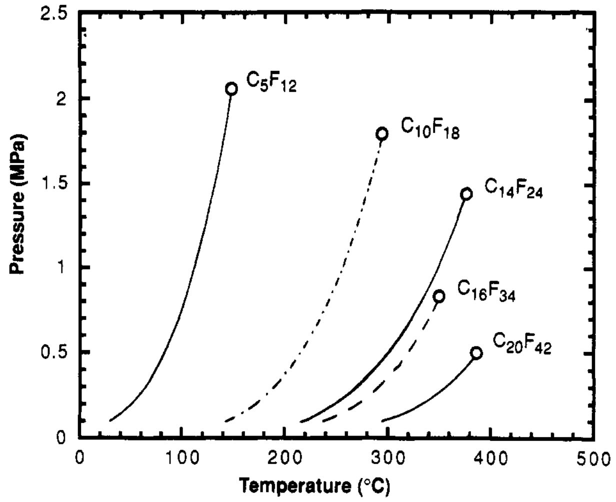

Figure 3. Vapor pressure curves for various perfluorocarbons. The open circles represent critical points.

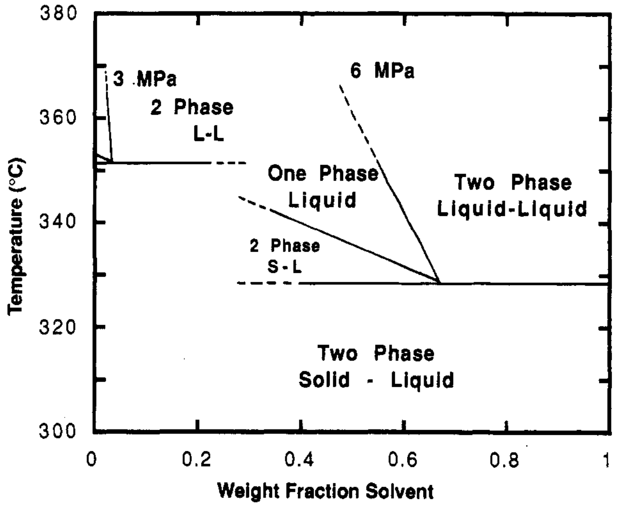

Figure 4. Phase diagram for PTFE with n-perfluorohexadecane predicted using FOV theory.

Representative examples of the phase diagrams calculated using this *PVT* data are illustrated in Figures 4 and 5 for PTFE in the 16 and 20 carbon n-perfluoroalkanes, respectively. In Figure 4, the phase diagrams at both 3- and 6-MPa pressure are illustrated; the lower pressure diagram is at the left of the figure. The liquidus curve is the nearly linear line with negative slope which starts at the pure polymer thermodynamic melting point (taken as 350 °C at atmospheric pressure). The liquidus curve is the melting point depression as a function of the polymer concentration and was computed via the Flory–Huggins equation, which is described in the next section. The Flory interaction parameter, χ, was set to zero and the polymer was assumed to be of high molecular weight. For the sake of clarity, the liquidus curves are discontinued near the center of the figure. A small rise in melting point has been observed as a function of pressure (~1 °C/MPa).[11,12] Below the liquidus, crystalline plus amorphous PTFE and solution are in equilibrium. For the 6-MPa case, immediately above the liquidus, a one-phase liquid region was predicted at solvent concentrations less than about 0.8

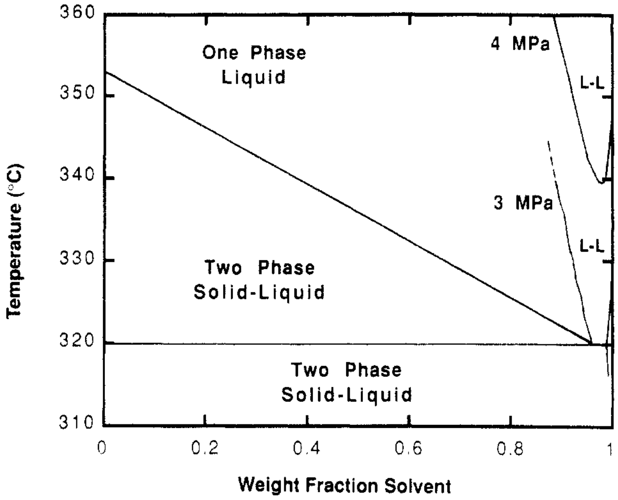

Figure 5. Phase diagram for PTFE with *n*-perfluoroeicosane predicted using FOV theory.

weight fraction. However, with increasing temperature, eventually a liquid PTFE-rich phase will separate from a solvent-rich phase. This explains the two-phase liquid–liquid (L–L) region at the upper right of Figure 4. At solvent concentrations greater than about 0.8 weight fraction, it is not possible to form a single-phase liquid solution; the liquidus curve cuts the L–L phase boundary such that the LCST is below the liquidus. At higher pressure, the boundary of this L–L region moves to higher temperatures until it is completely above the liquidus at all concentrations, as shown in Figure 5 for *n*-perfluoroeicosane. At the same time, the liquidus curve also moves to higher temperatures but with a much lower pressure dependence than the L–L boundary. In other words, there is a broader temperature range over which a stable solution can be obtained with increasing pressure under these conditions. Likewise, at lower pressure, a narrower temperature range is observed over which stability occurs. This is illustrated in Figure 4 for the case of $P = 3$ MPa. The liquidus curve drops a few degrees but the L–L boundary now intersects the liquidus line at less than 0.1 weight fraction of solvent. Thus, only a small area of solution stability is predicted at the far left of the figure. In this 3-MPa case, only a small degree of polymer swelling would be observed at high solvent concentrations. The minimum value of the liquidus curve would also be limited, so that only a small melting point depression is predicted at high solvent levels. For the 6-MPa case, more swelling would be expected as well as greater melting point depression because the one-phase region is predicted to occur at higher solvent levels than for the 3-MPa case. Thus, the melting point depression predicted by Smith and Gardner[4] should be limited by the LCST.

The L–L region forms because solvent density drops as its T_{CRIT} (critical temperature) is approached and it becomes entropically more favorable for phase separation to occur. Since an increase in solvent MW within a homologous series will result in increased T_{CRIT}, increasing MW will also result in an increased temperature at which L–L separation occurs. Figure 5 illustrates this for the higher MW 20 carbon *n*-perfluoroalkane. In this case, we see that a temperature range for solution stability exists at 3 MPa that is considerably larger than the narrower range predicted for the 16 carbon case at the same pressure. Experimental observations will be reported which are consistent with the picture predicted by this model.

3. PTFE Oligomers as Solvents. Smith and Gardner[4] used the Flory–Huggins theory, as shown in eq 1, to describe the melting behavior of PTFE–oligomer solutions. A major assumption was the athermal nature of these solutions.

Table 3. Solubility of PTFE in Oligomers (0.01 Weight Fraction)

solvent	T_m (°C) pred[b]	T_m (°C) obs	[a]T_{CRIT} (°C)
dodecafluoropentane (n-C_5F_{12})	237	ins	148
perfluorotetradecane (n-$C_{14}F_{30}$)	305	ins	300
perfluorohexadecane (n-$C_{16}F_{34}$)	310	ins	325
perfluoroeicosane (n-$C_{20}F_{42}$)	318	310	380
perfluorotetracosane (n-$C_{24}F_{50}$)	323	315	425

[a] Reference 7. [b] Melting points predicted at atmospheric pressure.

$$\frac{1}{T_{m2}} - \frac{1}{T_{m2}{}^{\circ}} = \frac{R}{\Delta H_{2U}}\frac{1}{n}(1 - v_2) \qquad (1)$$

In eq 1, T_{m2} and $T_{m2}{}^{\circ}$ are the diluted (solution) and undiluted thermodynamic polymer melting points. (T_{m2}, in this context, is assumed to be the same value as T_{m2} defined above for the visual observations of melting.) R is the gas constant, ΔH_{2U} is the polymer heat of fusion, n is the number of oligomer carbon atoms, and v_2 is the polymer volume fraction.

Table 3 lists the solution melting behavior in a series of perfluoro-*n*-alkanes from 5 to 24 carbon atoms at 1% volume fraction. The column labeled "pred" contains the T_{m2} predicted from eq 1 assuming $T_{m2}{}^{\circ} = 350$ °C, $\Delta H_{2U} = 4.6$ kJ/mol of CF_2. (These were the values used by Smith and Gardner.[4]) The experimentally observed melting points are in the column labeled "obs". T_{m1} and T_{m2} were found to have similar values; therefore an average value is listed under "obs". "Ins" was used to denote insoluble. Insolubility was indicated when there was no observable change up to 330 °C. That is, the polymer particles at the bottom of the tube remained opaque with no observable swelling even after passing the peak melting temperature one observes in a differential scanning calorimeter test for undiluted polymer. We feel that very little swelling occurred in these cases. If significant swelling had occurred, some coalescence would have been observed and the particles would have been less visible due to better matching of the refractive indices of polymer and solvent.

It is clear from the data in Table 3 that oligomers smaller than 20 carbon atoms do not dissolve the polymer at the autogenous pressures of these experiments. This is in agreement with the modeling predictions summarized in Figures 4 and 5. For the case of *n*-perfluorohexadecane (Figure 4), the pressure inside the tube would have to be greater than 6 MPa to get into the one-phase region at 0.01 weight fraction. The vapor pressure curves in Figure 3 show that the autogenous pressure was far less than the required 6 MPa. According to the phase diagram in Figure 5, we should not expect stable solutions with perfluoroeicosane at $P \leq 3$ MPa. The fact that we do obtain stable solutions at nearly atmospheric pressure indicates that the predicted L–L coexistence curves should be shifted to higher temperatures. This is not surprising considering the known quantitative accuracy of these predictions. However, qualitatively, the observations are consistent with the predictions and we would therefore expect a wider window of stability with higher MW solvents, like perfluorotetracosane. For those solvents that do dissolve PTFE, agreement between predicted and observed melting points in Table 3 is reasonable.

4. Nonoligomeric Perfluorocarbons as Solvents. The melting point depression of PTFE solutions in

Table 4. Solubility of PTFE in Cyclic Aliphatic Perfluorocarbons (0.01 Weight Fraction)

solvent	T_{m2} (°C)	V_1 @ RT (cm^3/mol)	T_{CRIT} (°C)
dodecafluorocyclohexane (C_6F_{12})	ins	<219[a]	184[b]
perfluoro-1,3-dimethylcyclohexane (C_8F_{16})	ins	219[c]	242[b]
perfluorodecalin ($C_{10}F_{18}$)	ins	242[c]	293[b]
perfluoro-1-methyldecalin ($C_{11}F_{20}$)	290 (ps)	261[c]	313[c]
perfluorodimethyldecalin ($C_{12}F_{22}$)	287 (ps)	284[c]	340[a]
perfluorotetradecahydrophenanthrene ($C_{14}F_{24}$)	278	340[e]	377[c]
perfluoroperhydrobenzylnaphthalene ($C_{17}F_{30}$)	285	378[c]	401[c]
PP11 oligomer	292	440[c,f]	>401[a]

[a] Estimated from neighboring analogues. [b] Reference 7. [c] Calculated from data in or taken directly from RP-ISC literature. [d] T_{m2} was not measured; this number is T_{m1}. [e] Calculated from the *PVT* data shown in Figure 8. [f] Calculated from the data in ref 10.

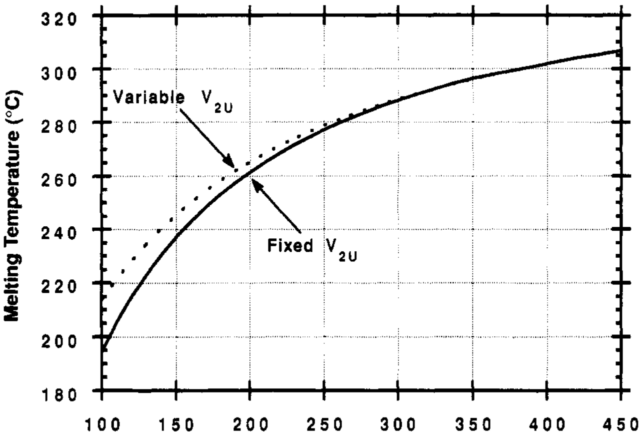

Figure 6. Effect of solvent molar volume on solution melting temperature for nonoligomeric perfluorocarbons.

nonoligomeric solvents has been described[4] using eq 2.

$$\frac{1}{T_{m2}} - \frac{1}{T_{m2}^{\circ}} = \frac{R}{\Delta H_{2U}} \frac{V_{2U}}{V_1} [1 - v_2 - \chi(1 - v_2)^2] \qquad (2)$$

In eq 2, V_1 and V_{2U} are molar volumes of the solvent and a CF_2 polymer unit, respectively, and χ is the polymer–solvent interaction parameter. For athermal solution conditions, $\chi = 0$. As solvent polarity increases, χ is also expected to increase, resulting in an increase of the solution melting point. Also, the melting point of athermal solutions is strongly affected by the solvent's molar volume. Of course, the critical temperature of the solvent will be just as important in determining the upper temperature limits of solubility as in the oligomer cases.

Table 4 summarizes the solution melting temperatures at 1% weight fraction observed as a function of solvent molar volume (V_1) and critical temperature (T_{CRIT}). Where data existed, V_1 was calculated from density values at room temperature. Dodecafluorocyclohexane is a solid at room temperature. We estimated V_1 for the liquid to be slightly lower than 219 cm^3/mol which is the value for its slightly higher MW "cousin", perfluoro-1,3-dimethylcyclohexane. The T_{CRIT} for perfluorodimethyldecalin was estimated from the quadratic equation wich was fit to the known critical temperatures of other cyclic, aliphatic perfluorocarbons. The T_{CRIT} for the PP11 oligomer is known only to be higher than that of its nearest counterpart, Flutec PP25.

Figure 6 illustrates the effect of V_1 on the solution melting point from eq 2, assuming $\chi = 0$ and 1% volume fraction polymer. (The use of 1% volume fraction in these calculations is not sufficiently different from the 1% weight fraction used in previous calculations to make a significant difference in the determination of T_{m2}.) The determination of T_{m2} shown in Figure 6 was made in two ways. First, V_{2U} was assumed to be constant at 30 cm^3/mol, as was done by Smith and Gardner.[4] However, V_{2U} will vary slightly with temperature and the results assuming this variability are also shown in Figure 6. V_{2U} was calculated in the latter case from the density data of Zoller[11] for a PTFE melt.

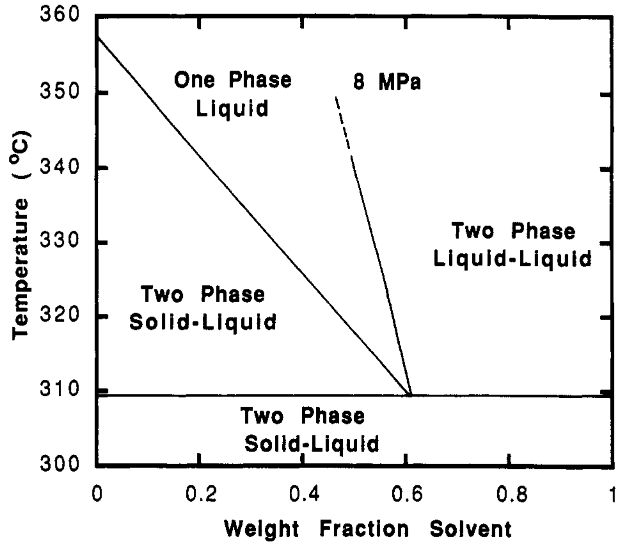

Figure 7. Phase diagram for PTFE with perfluorodecalin predicted using FOV theory.

The three lowest MW solvents do not dissolve or visibly swell the polymer up to 330 °C. This is probably due to their critical temperatures being too low and thus the upper temperature solubility limit falls below the liquidus under the conditions tested. Figure 7, the modeling prediction of the phase diagram at 8 MPa in perfluorodecalin, supports this contention. (Reduction parameters were again calculated from *PVT* data generated using the HBT method.[10]) Even at this relatively high pressure the one-phase liquid region is fairly narrow. The pressure in the glass tube probably never exceeded 2 MPa (see Figure 3) since the critical pressure for perfluorodecalin is only 1.5 MPa.[10] Therefore, it is not surprising that we did not observe any swelling for this case nor for the lower MW solvents which have even lower T_{CRIT}.

For solvents with T_{CRIT} at or below that of perfluorodecalin (293 °C) we observed virtually complete insolubility with no swelling. For solvents with T_{CRIT} at or above that of perfluorotetradecahydrophenanthrene (377 °C) complete dissolution occurs at autogenous pressures. For the two solvents, perfluoro-1-methyldecalin and perfluorodimethyldecalin, whose T_{CRIT} lies between these limits, only partial solubility was observed after several days. Therefore, we could only measure T_{m1} for these solvents, which appears as "T_{m2}" in Table 4, and used "ps" to denote partial solubility. We observed the crystals becoming transparent at the T_{m2} listed in Table 4 and, upon cooling, feathery, translucent material (which we assume to be PTFE) was observed in the solvent-rich upper layer. However, no combination of thermal history gave a homogeneous one-phase system. The predicted T_{m2} for the actual solutions (Figure 6) ranges from 295 °C for $C_{14}F_{24}$ to 306 °C for the PP11 oligomer. There is reasonable agreement with the observed and predicted values of T_{m2} with the expected trend of increasing melting point with solvent MW. It should also be mentioned that although

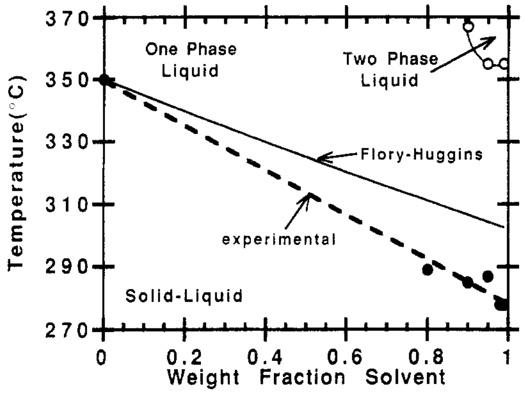

Figure 8. Phase diagram of LMW PTFE in $C_{14}F_{24}$. The solid and dashed lines represent the Flory–Huggins predictions and the experimental liquidus, respectively. The filled circles are the experimental values for T_{m2}, and the open circles, the experimentally observed L–L phase boundary. L–L phase separation is not predicted by FOV theory for this system to 377 °C at pressures slightly above the solvent's critical pressure.

Table 5. Solubility of PTFE in Aromatic Perfluorocarbons (0.01 Weight Fraction)

solvent	T_{m2} (°C)	V_1 @ RT (cm^3/mol)	T_{CRIT} (°C)
hexafluorobenzene (C_6F_6)	ins	115[a]	244[b]
octafluorotoluene (C_7F_8)	ins	142[a]	262[b]
octafluoronaphthalene ($C_{10}F_8$)	280[f]	160[c]	400[b]
decafluorobiphenyl ($C_{12}F_{10}$)	280	>187[d]	~400[e]

[a] Density value taken from the Aldrich Chemical Co. catalog. [b] Reference 7. [c] Reference 4. [d] Molar volume for the solid calculated from density given in the Aldrich Chemical Co. catalog. [e] Estimated to be similar to octafluoronaphthalene. [f] T_{m2} was not measured; this number is T_{m1}.

we found complete solubility in $C_{17}F_{30}$, considerable solvent degradation occurred at these temperatures, as evidenced by strong color formation. The T_{m2} recorded for $C_{17}F_{30}$ in Table 4 is in fact the T_{m1} and a rough estimate at that.

The mathematical model predicts a very uninteresting phase diagram (Figure 8) for PTFE in $C_{14}F_{24}$. Near the solvent's critical pressure, complete miscibility is predicted above the liquidus up to T_{CRIT}. We do observe an LCST for this system at pressures lower than the critical pressure; this will be discussed later in this paper.

An analogous set of data for some aromatic perfluorocarbons is listed in Table 5. As is the case for all the solvents discussed so far, those solvents with low T_{CRIT} do not dissolve PTFE under the autogenous pressure conditions in our glass tubes. This is true for hexafluorobenzene and octafluorotoluene. For hexafluorobenzene, no swelling was observed up to 234 °C when the tube exploded. For octafluorotoluene, no swelling was observed up to 266 °C, just past the critical temperature, when the tube exploded. These explosions occurred at unexpectedly low pressures on the basis of our previously described experience with water (bursting ~14 MPa). The maximum pressure for the aromatic solvents should be <3.5 MPa, the reported critical pressure[10] for hexafluorobenzene. We suspect, however, that some thermal degradation was the cause of the higher than expected pressure in the tubes. The low values of V_1 for the aromatics appears attractive for getting low solution melting points, an observation made by Smith and Gardner.[4] From Figure 6 we would predict a melting point of 244 °C in perfluoronaphthalene and slightly higher in decafluorobiphenyl if V_{2U} is assumed constant. If V_{2U} is allowed to vary with temperature, T_{m2} is predicted to be 250 °C. In both cases, T_{m2} should be considerably lower than for the aliphatic solvents. We observed, however, that melting occurred in the same range as the aliphatics. Solvent polarity is the expected cause and this will be addressed in the Discussion. In the case of all the nonoligomeric perfluorocarbons, the melting point depression (both predicted and observed) was much greater than for the oligomers.

Table 6. Solubility of LMW, IMW, and HMW in $C_{14}F_{24}$ and n-$C_{20}F_{42}$ (0.01–0.05 Weight Fraction)

property/solvent	$C_{14}F_{24}$	n-$C_{20}F_{42}$
T_{m1} (°C)	285–290	305–310
T_{cryst} (°C)	255–260	285–290
T_{m2} (°C)	275–287	310
LCST (°C)	355	345

5. **Non-Perfluorocarbons.** As a rule, non-perfluorocarbons do not dissolve PTFE.[4] A notable exception, as stated above, is oligomeric poly(trifluorochloroethylene).[3] We verified that this material is a solvent, but a poor one since the observed melting point of the 1% solution was 325 °C. Chu et al.[3] also concluded from their light scattering experiments that this chlorofluorocarbon is a poor solvent by virtue of its negative second virial coefficient. The very high melting point can be attributed to the solvent's polarity which will make $\chi > 0$ in eq 2. As observed by Smith and Gardner, the hexafluoropropylene oxide oligomer does not even swell the polymer. Our observations were made up to 340 °C.

We thought an interesting solvent not reported in the PTFE literature would be perfluorotrihexylamine. It is as nonpolar as many perfluorocarbons[13] and has a high boiling point (250–260 °C). It did cause the polymer to melt, coalescence, and swell considerably at 315 °C. But complete dissolution did not occur.

6. **Melting, Recrystallization, and Lower Critical Solution Temperatures.** All three polymer samples were dissolved in perfluoroeicosane and perfluorotetradecahydrophenanthrene in concentrations ranging from 1 to 5% weight fraction. A summary of the observations on these solutions appears in Table 6. Over the concentration and MW range tested, no appreciable differences were observed in the melting and recrystallization temperatures. From the magnitudes of the melting and recrystallization temperatures, it appears that once dissolved, a stable solution can be maintained 20–30° below the melting point. Using LMW polymer, we observed a lower critical solution temperature (LCST) of 345 and 355 °C, respectively, in the oligomer and cyclic perfluorocarbon. This is in qualitative agreement with the mathematical model which did not predict a LCST for $C_{14}F_{24}$ but did predict the LCST in n-$C_{20}F_{42}$ to be about 330 °C at 3 MPa.

Melting point depression and LCST data are plotted in Figure 8 for PTFE LMW in $C_{14}F_{24}$. Polymer weight fractions of 0.01–0.20 are represented with experimental data. (The densities of the polymer melt and solvent are less than 10% different; thus weight and volume fraction are, for our purposes, the same in this plot.) The solid line is the liquidus predicted from Flory–Huggins theory (eq 2). We used a value of 406 cm^3/mol for V_1 at 280 °C, as explained in the Discussion on "Pressure". The dashed line was the result of performing a linear regression on the melting data (T_{m2}). The experimental data are about 20 °C below the predicted values but the qualitative trend is the same. Discrepancies are probably the result of the athermal assumption. As explained in the preceding paragraph, no LCST was predicted at the lowest pressures usable by the model. The fact that we observed an LCST so close to the critical temperature of the solvent (377 °C), however, is in qualitative agreement with the model prediction. We observed no apparent LCST for the 20%

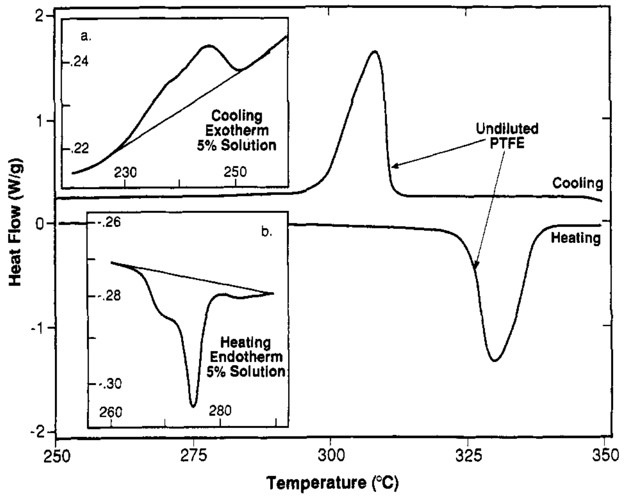

Figure 9. DSC behavior of PTFE solutions in $C_{14}F_{24}$ compared with undiluted polymer.

solution as high as 380 °C. Visibility was obscured, however, by bubbles forming which would not rise to the top of the solution due to extreme viscosity of the fluid. The bubbles form presumably due to decarboxylation of the polymer which has carboxylic acid end groups.

7. DSC Results. Although we visually observed what appeared to be melting and recrystallization in every soluble system tested, we performed DSC analysis to verify these observations. The thermal properties of the 5% weight fraction gel made from the LMW polymer and perfluorotetradecahydrophenanthrene were measured on heating and cooling. (Gel in this case refers to the thermoreversible gel formed on cooling the solution below T_{cryst}.) The scans for the gel are compared with 100% LMW polymer in Figure 9. The visual observations listed in Table 6 indicate that the last component of crystallinity in the gel (T_{m2}) melts between 275 and 280 °C while recrystallization is initiated between 255 and 260 °C. Insert a in Figure 9 shows the cooling exotherm for the 5% solution that one would expect on recrystallization. The onset of crystallization (highest exotherm temperature) for four trials ranged between 251 and 253 °C, in reasonable agreement with visual observations. The heating endotherm, represented by insert b, is expected when melting occurs and was observed to end between 280 and 290 °C, depending on where the baseline was drawn. For the endotherm shown, the baseline was drawn so that the end of the melting range appeared to be near 290 °C if you believe the high melting shoulder is real. The baseline could also have been drawn so that the end of melting would appear to be near 280 °C. In all cases, however, the end of melting and the start of recrystallization measured by DSC correspond closely to our visual observations.

Discussion

1. Pressure. Pressure, greater than the autogenous levels generated in these experiments, appears to be a very strong variable for increasing the range of solubility. As mentioned earlier, however, pressure increases the liquidus line 1 °C/MPa. The question is, would the L–L coexistence curve move to higher temperatures at a faster rate than this melting point increase?

For solvents with fairly high T_{CRIT}, only low pressure is needed to increase the solvent density to the point where miscibility is favorable. Many times, autogenous pressure is sufficient if T_{m2} is higher than the boiling point of the solvent and ambient pressure is sufficient if the boiling point is higher than T_{m2}. Consider the effect of pressure on one of these high T_{CRIT} solvents, $C_{14}F_{24}$, with a normal boiling point of 215 °C. Therefore, autogenous pressure is required to dissolve the polymer. According to Table 6, T_{m2} is between 275 and 280 °C. *PVT* data were collected on $C_{14}F_{24}$ by using a dilatometer supplied by Gnomix Research. Details of the procedure and the apparatus have been fully described elsewhere.[14] A surface was fitted to the data points, and this surface is shown in Figure 10. Figure 10 shows the specific volume as a function of temperature (20–250 °C) and pressure (10–100 MPa). The vapor pressure curve, calculated by the previously mentioned HBT method,[10] for $C_{14}F_{24}$ is plotted in Figure 3. At T_{m2}, Figure 3 shows that the vapor pressure is about 0.3 MPa. We can estimate the specific volume in Figure 10 to be 0.65 cm^3/g at 280 °C which translates to 406 cm^3/mol for V_1. Using eq 2, T_{m2} is found to be 303 °C, compared to 295 °C from the calculation based on the room temperature value for V_1 (340 cm^3/mol). This relatively large change in V_1 does not change the predicted T_{m2} very much. To regain the room temperature value of V_1 at 280 °C would require more than 100 MPa, which would raise the melting point about 100 °C. Even application of about 20 MPa would significantly reduce V_1 (reducing T_{m2} a few degrees) but the additional pressure would add 20 °C to the melting point. Therefore, we do not recommend increasing the pressure in miscible systems for the purpose of reducing the solution melting temperature.

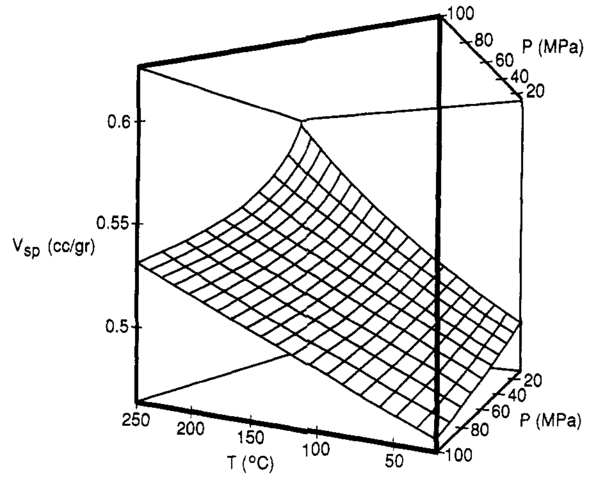

Figure 10. PVT data for $C_{14}F_{24}$. Heavy lines were used to delineate the front set of axes in the volume–temperature plane.

In the case of a solvent like perfluorodecalin, with which no miscibility was observed, modest pressure (~20 MPa) would probably be sufficient to get miscibility (as suggested by calculations used to generate Figure 7). Thus, pressure would gain solubility where it was not previously achieved. However, the melting point would not be lowered since the increased pressure would cause T_{m2} to increase by 20 °C above the 275 °C value predicted using eq 2.

For low MW oligomers (like C_5F_{12}), will increased pressure allow lower melting temperatures to be attained? In deriving eq 1 from the Flory–Huggins relationship, Smith and Gardner assumed that the ratio of the molar volume of a CF_2 unit in the polymer versus a unit in the diluent would be unity. This is a very bad assumption for the 5 carbon oligomer because at the predicted melting point (Table 3), the solvent is well above its T_{CRIT}. It would take tremendous pressures (at least 100 MPa) to reduce the molar volume to the level of the polymer. If there was no pressure penalty for this volume reduction, the Flory–Huggins relationship predicts T_{m2} to be 237 °C, as shown in Table 3. However, there is a 100 °C melting point penalty. We modeled the case of the 10 carbon oligomer and found that at least 30 MPa would be required for complete miscibility, and this would move the liquidus well above 300 °C for this oligomer. Thus, increasing pressure will not give lower melting solutions for these low molecular weight oligomers.

2. Solvent Polarity. Solution melting points would appear to be increased by solvent polarity on the basis of our experience with aromatic perfluorocarbon and oligomeric chlorotrifluoroethylene solvents. A polar solvent with PTFE would increase the value of the interaction parameter, χ, which in turn increases T_{m2}. The molar polar nature of aromatic hydrocarbons and perfluorocarbons has been established versus their nonpolar aliphatic counterparts by spectroscopic studies using solvatochromic dyes.[13] Solubility parameters[15] also show that aromatic perfluorocarbons (15.3–16.8 $MPa^{1/2}$) are more polar than aliphatic perfluorocarbons (11.3–12.7 $MPa^{1/2}$). The assymmetric nature of the chlorotrifluoroethylene oligomer leads to its polarity. The usual occurrence with polar solvents is insolubility with PTFE, as reflected by the insolubility in hexafluoropropylene oxide oligomer. It is interesting that perfluorotrihexylamine does not dissolve the polymer since the solvatochromic dye experiments indicate polarity equivalent to the linear and cyclic perfluoroalkanes.[13] If polarity were not a consideration in the case of octafluoronaphthalene and decafluorobiphenyl, their high T_{CRIT} and low molar volumes would lead us to expect a much lower T_{m2} than observed, as mentioned in the Results.

3. Swelling with Nonsolvents. Previous studies[16] reported swelling in PTFE below the melting temperature with nonsolvents. These studies were performed on commercial polymers which were fabricated into thin films. The fabrication process required heating above the virgin polymer's melting point to coalesce the cold-formed films. The combination of very high MW for the commercial polymer and the fact that fabrication required melting and recrystallization would make these films only partially crystalline and therefore the amorphous fraction would be susceptible to swelling. Our studies used micron-sized granules of virgin polymer which is considered to be nearly 100% crystalline. The lack of amorphous material would thus prevent any swelling below the melting temperature. Also, the granular particles, even if they were transparent, would scatter light, making it difficult to determine melting temperatures using a transparency criterion. In film form, the melting transition from cloudy to transparent would be much more apparent. Thus, there is no conflict with this earlier work.

Conclusions: Optimum Conditions for Solubility

Our criterion for good solubility was maximization of the area of one-phase miscibility on a temperature–concentration phase diagram. In the case of PTFE, this meant minimization of the liquidus temperature and maximization of the lower critical solution temperature (LCST). The liquidus temperature (T_{m2}) was lowest when the Flory–Huggins interaction parameter (χ) and the solvent molar volume (V_1) were minimized. The LCST was very strongly affected by the solvent T_{CRIT}; higher T_{CRIT} meant a higher LCST. Aliphatic perfluorocarbons, because of their low polarity, seemed to give the lowest interaction parameters with PTFE. The cyclic aliphatic perfluorocarbons appeared to give lower solution melting points than the normal perfluoroalkanes due to lower molar volume per equivalent MW. We have observed that those cyclic aliphatics with $T_{CRIT} > 340$ °C dissolved PTFE under autogenous pressure. The lowest observed melting occurred with solutions in $C_{14}F_{24}$; in this case, the effect of solvent molar volume on T_{m2} was not very great. $C_{14}F_{24}$ oligomers offered the advantage of being able to dissolve PTFE at ambient pressure without the disadvantage of raising T_{m2} appreciably.

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