Dissolution of Poly(tetrafluoroethylene)

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ABSTRACT: The dissolution behavior of poly(tetrafluoroethylene) (PTFE) is discussed. On the basis of the Flory-Huggins theory for melting point depression in polymeric systems, the requirements for dissolution of PTFE in perfluoroalkanes and other species are formulated. It is calculated that PTFE should dissolve at ambient pressure in its oligomers that have a chain length of 21 carbon atoms or more. These predictions are confirmed experimentally. A brief morphological study was made of structures generated from PTFE solutions. Spherulitic growths were obtained from quiescent solutions while "shish kebobs" resulted from sheared solutions of high molecular weight PTFE.

Introduction

Poly(tetrafluoroethylene) (PTFE) is notorious for its excellent high-temperature stability and for its extreme inertness to chemical attack and to virtually all common solvents.[1] These properties are highly useful and form the basis of many applications of PTFE in, e.q., corrosive atmospheres. By the same token, however, molecular characterization and manufacturing processes involving solutions of the polymer are impeded due to the lack of solvents. The only substances reported to dissolve 1-2% of PTFE at 290-310 °C are some perfluorokerosenes[2,3] and perfluorinated oils.[4]

In this paper, we made an attempt to formulate the requirements for dissolution of poly(tetrafluoroethylene) (PTFE) using simple arguments based on the Flory-Huggins[5] theory for melting point depression in polymeric systems. Theoretical and experimental results show that the dissolution behavior of PTFE is not unique and, in fact, closely resembles that of polyethylene.

Dissolution in Perfluoroalkanes

Much like the H-C-H groups in polyethylene, the F-C-F units of PTFE presumably are incapable of strong interactions with other substances to form, for example, hydrogen bonds that would facilitate the dissolution of the polymer. Accordingly, dissolution can be brought about only by an increased entropy upon mixing the polymer and the hypothetical solvent and by preventing strong repulsive interactions between the two species. In fact, an athermal solution is desired.

On the basis of these considerations, the most obvious candidates as solvents for poly(tetrafluoroethylene) are its oligomers, or rather the normal perfluoroalkanes. Only very moderate repulsion, if any, is expected between the polymer and the oligomer, provided that end-group effects do not play an important role, i.e., if the oligomeric chain is sufficiently long. Indeed, in the analogous polyethylene/normal paraffin case, it was found that the higher alkanes are good solvents for polyethylene and that the solutions approach athermal behavior for the long-chain paraffins.[6-8] In terms of the interaction parameter featured in the Flory-Huggins theory for polymer solutions, χ decreased at increasing number of carbons in the n-alkane to reach a value close to zero for chains with $n > 18$.[6,8,9] Obviously, the dissolution temperature, or the melting point of the polymer in the alkanes, increased at increasing carbon number[10] due to a reduced entropy of mixing. In principle, there is no reason to assume that the poly(tetrafluoroethylene)/normal perfluoroalkane systems would behave differently from their hydrogenated analogues. We will thus proceed to calculate the hypothetical phase diagrams of mixtures of PTFE and a variety of perfluoroalkanes of different chain length. It will be assumed that the polymer and the solvent are completely miscible in the liquid phase and immiscible in the solid state. The polymer liquidus curve, which, of course, is here of prime interest, will be calculated by using the commonly employed relation for melting point depression in polymeric systems following Flory and Huggins,[5] which in its most general form reads[11]

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

Here the subscript 1 refers to the diluent and 2 to the polymer. T_{m2}° and T_{m2} are the melting point (in kelvin) of the undiluted and diluted polymer, respectively. R is the gas constant, ΔH_U is the molar heat of fusion per structural unit, V_U refers to the molar unit volume, and v is the volume fraction. m and n are the respective numbers of structural units in the polymer and the diluent. It is common practice to take n equal to unity for small molecular solvents. In the present work we first deal with mixtures of the polymer with its oligomers, and we will, therefore, consider n and m to be the number of carbon atoms in the perfluoroalkane and the polymer, respectively. In this special case we take $V_{2U} = V_{1U}$ which is justified for long-chain perfluoroalkanes. As a first-order approximation χ, the Flory-Huggins interaction parameter, is assumed to be zero; i.e., the polymer solutions are supposed to behave athermally. This assumption, which is based on the experimental results obtained for the corresponding polyethylene long-chain paraffin mixtures,[6,8] will be discussed in more detail below. Substitution of $\chi = 0$ and $V_{2U} = V_{1U}$ in eq 1 yields the relationship

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

Since eq 2 assumes thermodynamic equilibrium between the polymeric solid and the solution, we need to substitute the thermodynamic equilibrium melting point and heat of fusion of infinitely large and 100% crystalline poly(tetrafluoroethylene) crystals. The latter value is reasonably well established to be 4.6 kJ/mol units.[12] The equilibrium melting point, on the other hand, is less well determined. Melt-crystallized PTFE has a typical peak melting temperature of about 327 °C.[12] This material is, however, semicrystalline and 327 °C is definitely too low a value for T_m°. A more appropriate estimation would be the end melting temperature of virgin ultrahigh molecular weight PTFE, which is known to be highly crystalline.[12] In our calculations we thus adopt $T_m^\circ = 350$ °C.[12,13]

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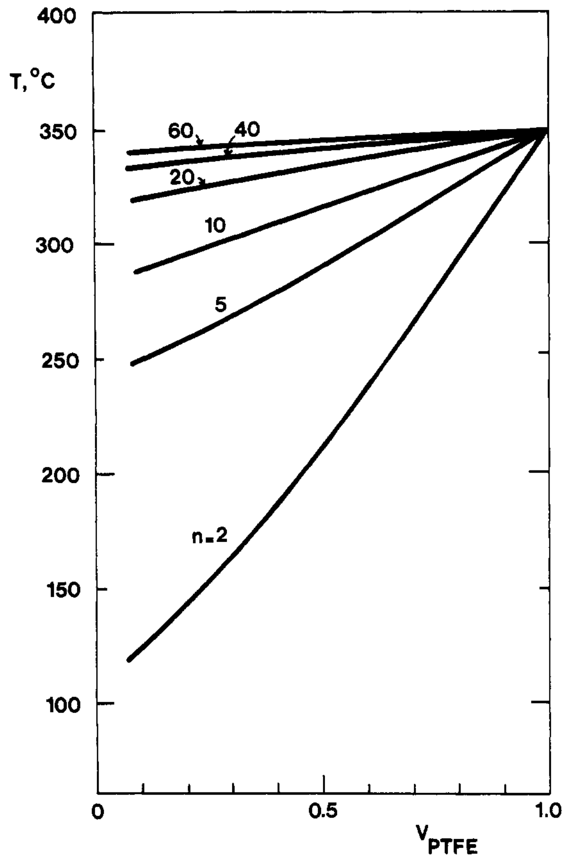


Figure 1. Equilibrium phase diagrams of poly(tetrafluoroethylene) (PTFE) and various perfluoroalkanes. The polymer liquidus curves were calculated by using eq 3.

Dealing with infinitely large macromolecules, the number of chain segments in the polymer $m = \infty$, which reduces eq 2 to

$$\frac{1}{T_{m2}} - \frac{1}{T_{m2}^{\circ}} = \frac{R}{\Delta H_{2U}} \frac{1}{n}(1 - v_2) \qquad (3)$$

The polymer liquidus curves calculated with eq 3 for various values of the perfluoroalkane length n are presented in Figure 1. Not surprisingly, the presented set closely resembles the one calculated by Wunderlich[14] for similar polyethylene/alkane systems. It can be seen that the expected melting point depression of the polymer by mixing with an oligomer or, in other words, the slope of the hypothetical PTFE liquidus rapidly diminishes with increasing length of the perfluoroalkane. As was briefly explained above, this is due to a reduced entropy of mixing for the longer oligomers.

A most instructive graph is obtained by plotting the calculated "dissolution temperatures" of PTFE in the perfluoroalkanes against their length (i.e., number of carbons), together with the thermal characteristics of these species. The latter data were taken from the literature[15,16] and partly obtained in this laboratory.[13] For the dissolution temperature, quite arbitrarily, the melting point of PTFE (T_m) in a mixture containing 10% by volume was chosen. This plot is presented in Figure 2. It reveals that the temperature where poly(tetrafluoroethyleen) is expected to dissolve to a 10% v/v level in the short perfluoroalkanes, such as, e.g., C_6F_{14}, is only at temperatures that exceed the boiling points of these materials by more than 150 °C. This obviously prevents the formation of a liquid solution of the polymer at ambient pressure. At most, sorption of the perfluoroalkanes in PTFE is envisaged.[17] The calculated dissolution temperature of the polymer in the oligomers with $13 \leq n \leq 22$ is found to be below the critical temperatures, but still above the boiling points of these materials. This suggests that dissolution of PTFE in its oligomers may be possible under pressure at temperatures in the vicinity of 300 °C. At $n \geq 23$, the dissolution temperature is exceeded by the boiling point of the perfluoroalkanes. The implication of this observation is that PTFE should dissolve at ambient pressure in its oligomers that have more than 22 carbon atoms.

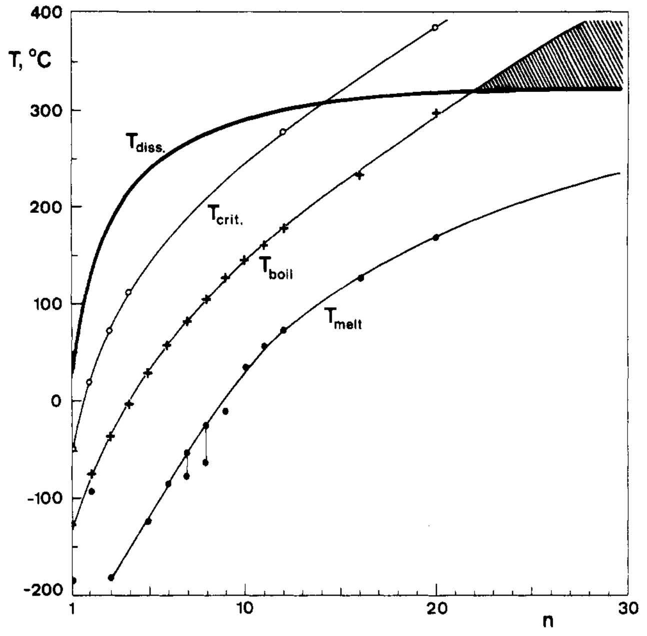


Figure 2. Dissolution temperatures of PTFE in its oligomers calculated with eq 3 at $v_2 = 0.1$ as a function of the oligomer carbon numer n. The melting, boiling, and critical temperatures of the perfluoroalkanes are also plotted. The shaded area indicates the region where ideal crystals are expected to dissolve at ambient pressure.

It should be noted that in the calculation of the dissolution temperature of PTFE in its oligomers using eq 3 a number of assumptions were made with regard to the values of various parameters. Before drawing some definitive conclusions, we will next examine the effect of these variables, such as T_m°, m, ΔH_{2U}, and χ on the polymer liquidus. First of all, it was assumed that thermodynamic equilibrium exists between the ideal polymer solid and the hypothetical solution. Accordingly, the values of T_{m2}°, ΔH_{2U}, and m relevant to this state were employed in the calculations. In practice these equilibrium conditions are rarely attained. The polymeric solid is composed of macromolecules with finite length (i.e., $m \neq \infty$); usually it is semicrystalline in nature and, as a result, is characterized by a lower melting point and heat of fusion than the corresponding values for perfect crystals. It turns out that variations in the number of units in the macromolecular chain, m, do not have a significant impact on the melting point depression of the polymer, provided that m exceeds 1000. Thus, the uncertainties arising from a lack of accurate knowledge of the value of m can be disregarded since in polymeric materials generally $m > 1000$.

The metastable, semicrystalline nature of ordinary macromolecular solids is difficult to incorporate in the treatment of melting and dissolution of polymeric materials. The reported attempts (e.g., ref 18) led to complicated and yet noncomplete descriptions. Nakajima and Hamada[6] demonstrated that for polyethylene/solvent systems the nonideality of the polymer solid state could be satisfactorily accounted for if the melting point of the defect polymer crystals was used for T_m° in the equation for the polymer liquidus, instead of the thermodynamic equilibrium melting temperature. This procedure was also found to be very useful in the calculation of polymer/diluent eutectic phase diagrams[9] and it will be employed hereafter. Similarly, the heat of fusion of the semicrystalline solid is substituted for ΔH_{2U} in eq 3. The experimental (peak) melting temperature of melt-crystallized poly(tetrafluoroethylene) is generally found in the range of 324–329 °C and the enthalpy of fusion is of the order of 2.6 kJ/mol units. Substitution of these values for $T_m°$ and ΔH_{2U} in eq 3 merely causes a downward shift by about 30–40 °C (depending on the length of the perfluoroalkanes) of the dissolution temperature vs. n curve, and its intersections with the critical, boiling, and melting point curves of the perfluoroalkanes are shifted to slightly lower values of n. Dissolution of semicrystalline PTFE to 10% v/v at ambient pressure is now expected to occur in its oligomers that have more than 20 C atoms at temperatures exceeding about 295 °C.

The Flory–Huggins interaction parameter χ was assumed to have the value zero in the calculations presented above. This, of course, is a first-order approximation for which no indications are available other than the presumable resemblance between the present systems and mixtures of polyethylene with long-chain alkanes. As was noted earlier, the latter systems behave nearly athermally provided that the alkanes are sufficiently long. It has been reported that solutions of polyethylene in the lower alkanes, such as, e.g., C_6H_{14} or C_8H_{18}, definitely cannot be characterized by χ values close to zero due to an increased effect of the end groups. The Flory–Huggins interaction parameters for such systems were found to be in the range from 0.3 to 0.4.[6,7] The quantity χ has a very strong influence on the melting point depression, and even small (positive) values cause a significant increase in the dissolution temperatures. Therefore, the T_{diss} vs. n curve in Figure 1 is highly inaccurate at low values of n, and the calculated dissolution temperatures should be regarded as the absolute lower boundary. It is, however, evident, by inspection of this graph, that the erroneous dissolution temperatures are found in a region which is not particularly of interest. Where dissolution of poly(tetrafluoroethylene) is anticipated (i.e., at $n > 20$) end-group effects are likely to be less important[6,8] and, consequently, χ will be close to zero.

The next step is, of course, to verify experimentally the presented hypothesis concerning the dissolution of PTFE in its oligomers. In order to obtain some reasonably accurate information about the interactions between perfluorinated compounds the phase diagrams of the variety of binary systems of the lower perfluoroalkanes were determined. As a typical example, relevant to the present study, the phase diagram of the system $C_{12}F_{26}/C_{20}F_{42}$ will be presented and discussed. The melting point/composition diagram (see Experimental Procedures for details) is given in Figure 3. This phase diagram is of the classical eutectic type, as is expected for two homologous chains differing sufficiently in length,[9,20] with the eutectic point located close to the axis of the lower melting constituent ($C_{12}F_{26}$). This result indicates that the two components are miscible in the liquid phase and completely immiscible in the solid state, as was assumed for the polymer/oligomer systems. The drawn liquidus lines were calculated with eq 1 with the subscripts 2 and 1 referring to, respectively, $C_{20}F_{42}$ and $C_{12}F_{26}$. In the calculation of the $C_{20}F_{42}$ liquidus the following values were used: $T_{m2}° = 162.4$ °C, $H_{2U} = 2.3$ kJ/mol units, $V_{2U} = V_{1U}$, $m = 20$, $n = 12$. Finally, χ was adjusted to give the best fit with the experimental results. The value used was $\chi = 0.04$, which indicates nearly athermal behavior. The $C_{12}F_{26}$ liquidus was also calculated with eq 1 simply by interchanging the subscripts 1 and 2 and m and n and substituting the appropriate values for each parameter. The enthalpy of fusion of $C_{12}F_{26}$ was determined to be 2.0 kJ/mol units and the melting temperature $T_m° = 74.4$ °C. The excellent agreement between the experimental melting point/composition diagram and the phase diagram calculated with $\chi = 0.04$ provides strong support for the assumptions made above in the calculations of the expected dissolution temperatures of PTFE in perfluoroalkanes with regard to the interactions between perfluorinated linear-chain molecules. It is noteworthy that the $C_{12}H_{26}/C_{20}H_{42}$ system behaves in a very similar way as the corresponding $C_{12}F_{26}/C_{20}F_{42}$ system. The experimental phase diagram can be described with eq 1 if χ has the value of 0.02,[21] which compares favorably with the Flory–Huggins interaction parameter for the $C_{12}F_{26}/C_{20}F_{42}$ system.

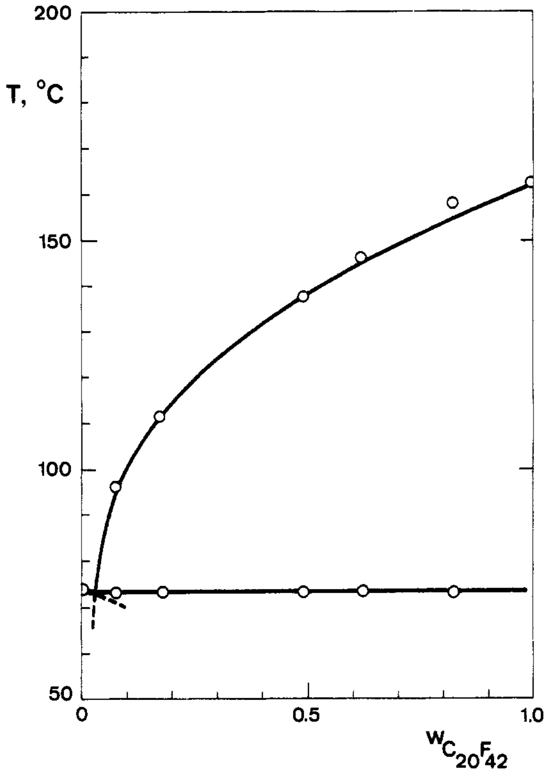


Figure 3. Phase diagram for the system $C_{12}F_{26}/C_{20}F_{42}$. Experimental melting points were obtained by DSC. Liquidus curves were calculated with eq 1 using $\chi = 0.04$.

The calculations in the previous section indicate that the expected dissolution temperatures of PTFE in $C_{12}F_{26}$ and $C_{20}F_{42}$ are respectively well above and very close to the boiling point of these compounds (170 and 297 °C). Indeed, microscopic studies performed by using a hot stage revealed that the perfluoroalkanes boiled before dissolution of PTFE occurred. Nevertheless, substantial swelling of the polymer was observed in mixtures with $C_{20}F_{42}$ at ~290 °C.

Unfortunately, the longer perfluoroalkanes (i.e., $n > 20$) were not available in high purity. The materials used hereafter, referred to as FC_{24} and FC_{60}, are mixtures of perfluorinated alkanes with a distribution of chain lengths around, respectively, $C_{24}F_{50}$ and $C_{60}F_{122}$. In particular, the FC_{60} mixture had a very broad distribution. As a result of the multicomponent nature of these perfluorinated samples, their mixtures with PTFE are not simple binary, and, strictly speaking, the binary calculations no longer apply. However, to a good approximation these PTFE/perfluoroalkane systems can be treated as quasi-binary.

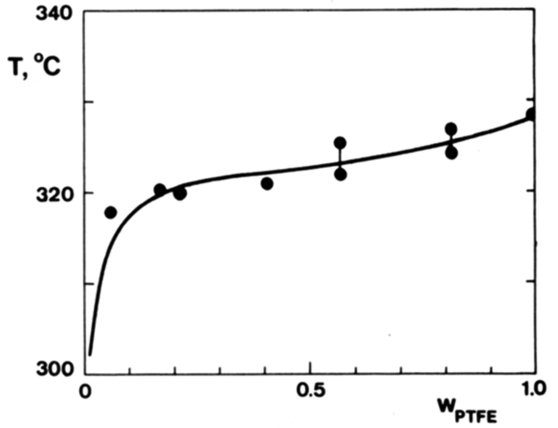


Figure 4. Phase diagram of PTFE/FC_{60}. Solid line calculated with relation 1 using $\chi = 0.01$.

Figure 5. Optical micrograph of spherulitic structures of PTFE obtained by crystallization from a 10% v/v solution in FC_{60}. Crossed polarizers.

Unlike $C_{20}F_{42}$, the sample designated FC_{24} did dissolve PTFE before excessive boiling occurred. A mixture containing 10% by weight of the polymer was placed in between microscope slides and slowly heated in the optical microscope. At a temperature of 295 °C the PTFE particles dissolved in the perfluoroalkane to give a clear solution. This dissolution temperature is remarkably close to the one calculated with eq 1 for pure $C_{24}F_{50}$. As a result of residual lower perfluoroalkanes the FC_{24} mixture exhibited a boiling range from 310 to 336 °C, which prevented the determination of the complete phase diagram with PTFE at ambient pressure.

Optical microscopy revealed that the FC_{60} mixture was also a solvent for poly(tetrafluoroethylene). The melting point/composition diagram of the system PTFE/FC_{60} could be determined without the aforementioned problem of excessive boiling at temperatures close to the melting temperature of the polymeric component. The experimental phase diagram is presented in Figure 4, together with the calculated polymer liquidus. This curve was calculated with eq 1 by using the following values: $T_{m2}° = 329$ °C, $\Delta H_{2U} = 2.6$ kJ/mol, $m = 1000$, $n = 60$, and $\chi = 0.01$ This calculation was made by assuming that this quasi-binary system can be described with the relations for binary mixtures.

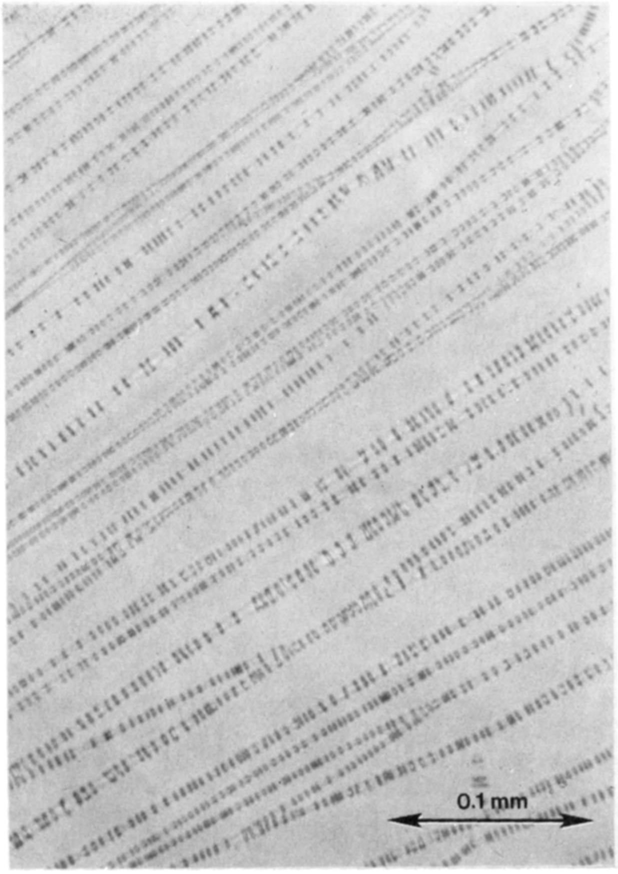


Figure 6. Optical micrograph of "shish-kebob-like" structures produced by cooling a sheared 10% v/v solution of ultrahigh molecular weight PTFE in FC_{60}.

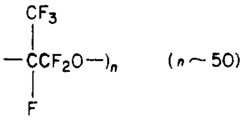
In a very brief morphological study the manner in which poly(tetrafluoroethylene) crystallizes from solution was investigated. It turned out that under quiescent conditions PTFE forms regular spherulitic structures from, e.g., a 10% solution in FC_{60} at temperatures below 304 °C. An optical micrograph taken with crossed polarizers of such spherulites is presented in Figure 5. Most interesting fibrillar structures were obtained by cooling a sheared solution of ultrahigh molecular weight (Teflon 7A) PTFE in FC_{60}. Figure 6 displays an optical micrograph of these fibrillar entities, which closely resemble the well-known shish kebobs obtained, for example, by crystallization of high molecular weight polyethylene from sheared solutions.[22] The lamellae grown perpendicular onto the polymer fibrils comprise the high molecular weight tail of the solvent mixture FC_{60}. The lower perfluoroalkanes were removed by sublimation from the crystallized sample.

It is interesting to reexamine some of the very few reports on the dissolution of PTFE. The first specific references to a solution of poly(tetrafluoroethylene), known to us, describe the use of a perfluorokerosene fraction having a boiling range of 130–240 °C at 10-mm pressure as a solvent.[2] It was reported that a solution containing 1% of PTFE was obtained by heating the polymer/solvent mixture in a sealed tube at 350 °C. Approximative correction[23] of boiling points to standard pressure yields a boiling range of about 270–400 °C for the perfluorokerosene fraction used. This indicates that the fraction most likely comprised perfluoroalkanes with chain lengths in the range from 18 to 30 C atoms. The observation that dissolution of PTFE in this perfluorinated kerosene occurred in a sealed tube (i.e., under pressure) at 350 °C is readily understood in the light of the foregoing discussion and, in fact, strongly supports the ideas presented.

In his chapter in the "Polymer Handbook",[3] Sperati notes that solutions containing 0.1–2% PTFE can be obtained in a perfluorokerosene $C_{21}F_{44}$ in the temperature range from 290 to 310 °C. This observation perfectly fits the predictions made in the theoretical part of this paper (see Figure 3). $C_{21}F_{44}$ has a boiling point of 310 °C, which prevents the dissolution of more than a few percent of PTFE at ambient pressure due to the increase in dissolution temperature with polymer concentration, i.e., the positive slope of the polymer liquidus.

Dissolution in Other Species

So far we have limited our discussions, calculations, and experiments completely to systems of poly(tetrafluoroethylene) and the perfluoroalkanes. Encouraged by the results obtained, we now turn to materials other than the PTFE oligomers. For obvious reasons,[24] we confined ourselves to the perfluorinated substances. Unfortunately, only a limited number of such species are available. The materials examined in this study are perfluorodecalin, octafluoronaphthalene, decafluorobenzophenone, and an oligomeric perfluorinated polyether



$$(-\underset{\displaystyle F}{\overset{\displaystyle CF_3}{C}}CF_2O-)_n \qquad (n \sim 50)$$

It was found that none of these species dissolved poly(tetrafluoroethylene). Microscopic observations and calorimetric measurements revealed that the first three substances boiled before dissolution was achieved, and the high-boiling perfluorinated oil did not cause any depression of the polymer melting point, nor formed a homogeneous liquid phase with the liquid polymer. The fact that no dissolution of PTFE occurred may be due to repulsive interactions between the polymer and the small molecules or the latter species may have boiling points that are well below the expected dissolution temperatures. Clearly, it is of interest to investigate the underlying cause of the observations.

In the experimental approach, the phase diagrams were determined of the four solvent candidates and the perfluoroalkane $C_{20}F_{42}$, which was used as a model compound for poly(tetrafluoroethylene). The results are presented in a combined melting temperature/composition diagram in which the $C_{20}F_{42}$ liquidus curves in the four solvents are collected (Figure 7). This diagram reveals that perfluorodecalin, octafluoronaphthalene, decafluorobenzophenone, and the perfluoro ether all are solvents for the PTFE oligomer. The solvent quality varies substantially, however, among these species as is apparent from the liquidus slopes. The dissolution temperature of $C_{20}F_{42}$ in octafluoronaphthalene and perfluorodecalin is around 100 °C. This is only slightly above T_{diss} in $C_{12}F_{26}$ (see Figure 3), which indicates that perfluorinated naphthalene and decalin are rather good solvents for linear perfluoroalkanes. (The reason why these substances did not dissolve PTFE will be discussed below.) The dissolution temperatures of $C_{20}F_{42}$ in decafluorobenzophenone and the perfluoro ether are substantially higher. This result points to an appreciable repulsive interaction between the components (i.e., $\chi \gg 0$), which is not too surprising in view of the different chemical nature of the solvents and the solute. It is then readily understood that these species do not dissolve PTFE. The entropy of mixing in the polymer system, required to balance the positive enthalpy of mixing, is only a fraction of that for the model $C_{20}F_{42}$/solvent systems.

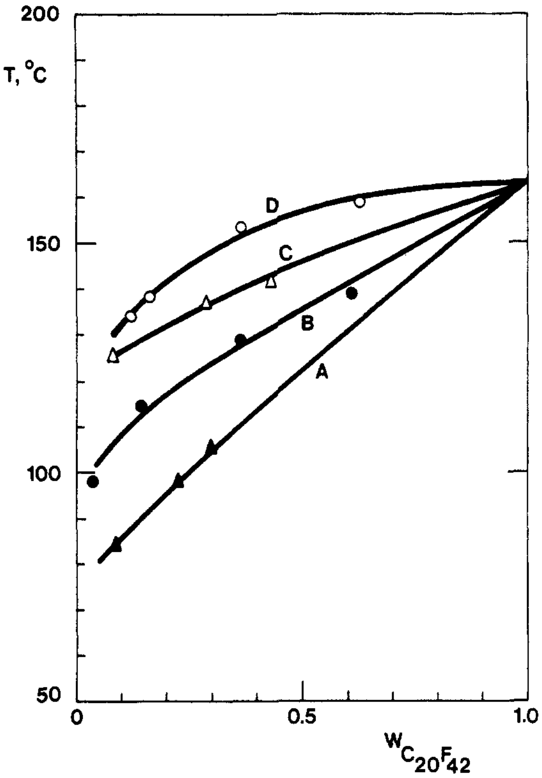


Figure 7. Liquidus curves of $C_{20}F_{42}$ in (A) octafluoronaphthalene, (B) perfluorodecalin, (C) decafluorobenzophenone, and (D) Krytox 143 AD determined by differential scanning calorimetry.

We now return to the problem why octafluoronaphthalene and perfluorodecalin, although very good solvents for $C_{20}F_{42}$, were incapable of dissolving PTFE. In a similar way as before, this discussion will focus on the polymer liquidus in hypothetical polymer/solvent systems. Starting with eq 1 for the melting point depression, we take the number of structural units in the solvent (n) to be unity, as is customary. As before, m is considered to be very large. Substitution of $n = 1$ and $m = \infty$ in eq 1 leads to the well-known relation for the polymer liquidus

$$\frac{1}{T_{m2}} - \frac{1}{T_{m2}^{\circ}} = \frac{R}{H_{2U}} \frac{V_{2U}}{V_1}[1 - v_2 - \chi(1 - v_2)^2] \qquad (4)$$

where V_1 refers to the molar volume of the solvent. Obviously, it can no longer be assumed that $V_1 = V_{2U}$, and, along with the Flory–Huggins interaction parameter χ, the quantity V_1 plays the dominant role in lowering the melting temperature of the polymer. A large melting point depression is expected with solvents having a small molar volume. In particular, small and highly polar molecules are characterized by low values of V_1. For example, water has V_1 = 18 cm^3/mol. Unfortunately, these polar substances are incapable of dissolving "nonpolar" polymers as polyethylene and poly(tetrafluoroethylene). All common nonpolar solvents, e.g., benzene, tetrachloromethane, cyclohexane, xylene, decalin, etc., have much larger molar volumes. V_1 of the above-mentioned species range at room temperature from 88 to 153 cm^3/mol.[25] Possible candidates as solvents for poly(tetrafluoroethylene), such as the

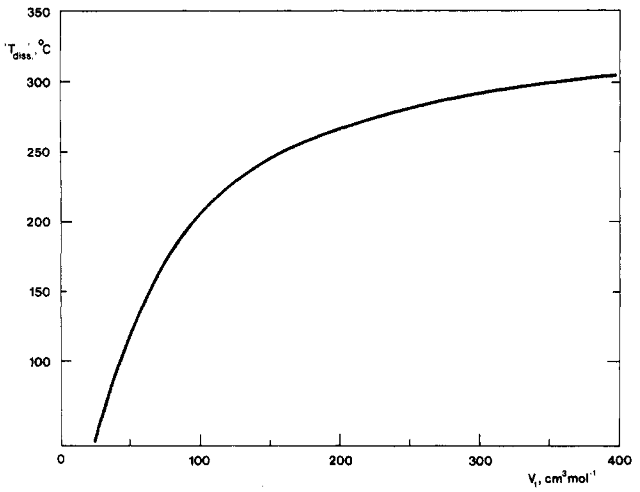


Figure 8. Dissolution temperatures of PTFE in hypothetical solvents calculated with eq 4 at $v_2 = 0.1$ using $\chi = 0$ as a function of the molar volume (V_1) of the solvent.

perfluorinated versions of these nonpolar solvents, have even larger molar volumes.

A set of liquidus curves was calculated with various values of V_1 ($T_{m2}° = 350$ °C, $\Delta H_{2U} = 4.6$ kJ/mol, and $V_{2U} = 30$ cm^3/mol). As a first-order approximation χ was assumed to be equal to zero. The results of these calculations are presented, as before, in a plot of the dissolution temperature (T_m at $v_2 = 0.1$) vs. the molar volume V_1 of the solvent (Figure 8). This graph indicates that the dissolution temperature of PTFE in a solvent with a molar volume of, e.g., 80 cm^3/mol can be as low as 180 °C if the solutions behave athermally. However, nonpolar substances having such relatively low molar volumes are invariably characterized by low boiling points. For instance, benzene has a room-temperature molar volume $V_1 = 83$ cm^3/mol, and its boiling point is only 80 °C; for cyclohexane: $V_1 = 104$ cm^3/mol, $T_{boil} = 81$ °C. The molar volumes of higher-boiling species, such as *p*-xylene ($T_{boil} = 139$ °C) and decalin ($T_{boil} = 196$ °C) are much larger (respectively, 123 and 153 cm^3/mol). The same rule holds, obviously, for perfluorinated substances, which in general have boiling points relatively close to those of their hydrogen analogues.[13] Thus, the requirement of a low value for V_1, to obtain a large depression of the polymer melting point, is concomitant with the solvent having a low boiling temperature, which prevents the dissolution of high-melting species. The compound perfluorodecalin ($T_{boil} = 143$ °C) has a room-temperature molar volume as high as 220 cm^3/mol (density at 20 °C = 1.928 g/cm^3). The calculations presented in Figure 8 indicate that PTFE should dissolve only at 268 °C in a suitable substance with $V_1 = 200$ cm^3/mol, which is well above the boiling point of perfluorodecalin. Similarly, the boiling point of octafluoronaphthalene, 218 °C, is below the estimated dissolution temperature of 245 °C, which was calculated with $V_1 = 150$ cm^3/mol. We thus find that these materials simply boil at too low temperatures to dissolve PTFE, much like the lower perfluorinated alkanes described in the previous section. A lower boundary boiling point for PTFE solvents obviously can be set at 350 °C, i.e., at the end melting point of the virgin polymer. Such required high-boiling temperatures (for nonpolar species) imply rather large molar volumes of the solvents, which, in turn, drastically limit the anticipated depression of the polymer melting temperature (Figure 8).

Concluding Remarks

In this study we addressed the problem of the dissolution behavior of poly(tetrafluoroethylene). It has been shown that PTFE dissolves at ambient pressure in its oligomers, provided that they have a chain length of 21 carbon atoms, or more. It was also demonstrated that the perfluorinated analogues of some common solvents, such as decalin or naphthalene, do exhibit favorable interactions with long perfluoroalkanes, but have boiling points that are too low to yield a liquid solution with PTFE at atmospheric pressure. This dissolution behavior was described, and could readily be understood, in terms of simple thermodynamic arguments.

It is concluded that the difficulties encountered in dissolving PTFE are not due to a unique chemical resistance of the polymer. The very high melting point of PTFE sets a lower limit for the boiling temperature of the solvent candidates, which, unfortunately, is surpassed only by very few suitable nonpolar organic species available. This conclusion, of course, was arrived at empirically already by previous authors.[3,28]

The theoretical calculation and experimental observation that PTFE dissolves only close to its melting point is not uniquely restricted to this polymer. In fact, many non-hydrogen-bond-forming crystalline polymers, such as polyethylene and isotactic polypropylene, dissolve just below their respective melting points (see, e.g., ref 26). Therefore, from a thermodynamic point of view, poly(tetrafluoroethylene) does not seem to be more insoluble than, for example, polyethylene. The finding that PTFE/perfluoroalkane systems closely resemble the corresponding PE/alkane mixtures and the fact that these systems can quite accurately be described by a similar thermodynamic interaction parameter strongly corroborate this view.

Finally, it should be noted that commercial PTFE (such as Teflon 6, 7A, etc.) generally is of a very high molecular weight, typically of the order of 10^7. The kinetic problems associated with the preparation of homogeneous solutions of any polymer of such very high molecular weight are tremendous, due to excessive high viscosities, and "gel" formation is most likely to occur. Such problems should be dealt with carefully, and not mistakenly be interpreted as indicating that the polymer does not dissolve.

Experimental Procedures

Materials. An experimental, relatively low molecular weight poly(tetrafluoroethylene) sample (estimated molecular weight 50 000[27]) was used throughout this study, unless indicated otherwise. This low molecular weight polymer was selected to avoid dissolution artifacts due to the extremely high viscosity of the normal, commercial materials.

The perfluoroalkanes $C_{12}F_{26}$ and $C_{20}F_{42}$ and the mixture referred to as FC_{24} were kindly made available to us by W. Mahler.

The mixture FC_{60} was obtained by evaporating at room temperature the dispersion liquid Freon from Vydax AR, leaving the desired product. It should be noted that, as a minor detail, the oligomeric molecules in this mixture have end groups that are different from the regular CF_3 units.

Perfluorodecalin, decafluorobenzophenone, and octafluoronaphthalene were purchased from PCR Research Chemicals, Inc., and were used as received.

The perfluorinated polyether was Krytox 143AD.

Measurements. Melting point, heats of fusion, and boiling points of the pure species and the melting temperature/composition diagrams of the binary mixtures were determined in the usual way[9,19] by means of differential scanning calorimetry (DSC). Additional optical microscopic observations were made with a Mettler temperature-regulated hot stage.

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Simulation of Upper and Lower Critical Phase Diagrams for Polymer Mixtures at Various Pressures

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ABSTRACT: A procedure is described for the simultaneous prediction of the binodal and spinodal curves of polymer mixtures at various pressures using a form of the equation-of-state theory of Flory and co-workers. The results of the calculation are compared with experimental results for the effect of pressure on the cloud points of both oligomer mixtures showing upper critical behavior and polymer mixtures showing lower critical behavior. The procedure successfully predicts the sign of the effect and its magnitude within the experimental and theoretical uncertainties for the systems studied.

Introduction

The equation-of-state theory of Flory and co-workers[1-4] has been widely used in describing the miscibility of polymer or oligomer mixtures. The ability of the theory to predict both upper critical solution temperature (UCST) and lower critical solution temperature (LCST) phase diagrams has been demonstrated by several authors.[5-7]

The effect of pressure on the miscibility of polymer–solvent mixtures and oligomer mixtures has been experimentally studied.[10-12] We have also studied the effect of pressure on the miscibility of polymer–polymer blends showing LCST behavior.[13] These studies have shown the following:

(a) For mixtures showing UCST behavior with negative heats of mixing the application of pressure causes the temperature range of miscibility to increase whereas for those with positive heats of mixing the temperature range of miscibility decreases.

(b) For high molecular mass polymer blends showing LCST behavior the effect of pressure increases the temperature range of miscibility.

In this paper we deal with the effect of pressure on both oligomer mixtures showing UCST behavior and high-polymer mixtures showing LCST behavior. Experimental results were obtained for samples of blends held in a pressure bomb and examined by measurement of turbidity during temperature scans. The apparatus, technique, and experimental results are described elsewhere.[11,13]

The theoretical procedure involves obtaining values of the hard-core pressure, volume, and temperature (P^*, V^*, and T^*) of the components from known physical data and a value of the contact interaction parameter, X_{12}, from heat of mixing measurements using oligomeric mixtures. The noncombinatorial contact parameter, Q_{12}, is then used as the only adjustable parameter to fit the minimum of the phase diagram to that of the experimental cloud point curve at atmospheric pressure. This value is then used to calculate the spinodal and binodal curves over the whole range of composition and pressure. The procedure used to calculate the binodal and spinodal curves has been described elsewhere[6-9,13] and will only be described briefly here. It should be pointed out that the assumption that both X_{12} and Q_{12} are independent of both temperature and pressure can only be approximate. Both temperature and pressure may change the interaction energies. Pressure may also cause configurational changes in molecules, an effect which has been found to be greatest for shorter chain lengths.[14]

Theory

To obtain the effect of pressure on the phase diagram of mixtures the hard-core properties of the pure compo-

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