

# 8

## Solubility of Poly(Tetrafluoroethylene) and Its Copolymers

WILLIAM H. TUMINELLO

### 8.1. INTRODUCTION

For many years a legend has been perpetrated that polytetrafluoroethylene (PTFE) and its perfluorinated copolymers are insoluble. Yet, a patent was issued as early as 1950 covering the plasticization of PTFE.<sup>1</sup> In the mid-1980s, Smith and Gardner<sup>2</sup> reviewed the subject of PTFE-perfluorocarbon solution thermodynamics and published some experimental data obtained at atmospheric pressure. They stressed the Flory–Huggins treatment of melting-point depression, assuming that enthalpic effects were unimportant so that these systems could be assumed to be athermal. In the 1990s, Tuminello and Dee<sup>3</sup> further refined the theoretical treatment of Smith and Gardner to include liquid-liquid phase separation and expanded the experimental database for solvents at their vapor pressures (autogenous). Chu and co-workers<sup>4,5</sup> have done some elegant characterization of PTFE in oligomers of tetrafluoroethylene and chlorotrifluoroethylene above 300°C.

Practicality has been an issue since many of the solvents referred to prior to 1994 have been quite expensive and the few others available have not had sufficient thermal stability to make them useful commercially. This chapter reviews our recent discovery of several commercially available cyclic perfluorocarbons as well as other halogenated fluids (and even carbon dioxide) as solvents for tetrafluoroethylene-containing polymers. We will describe solvation at atmospheric pressure, under autogenous conditions and under superautogenous

---

WILLIAM H. TUMINELLO • DuPont Company, Experimental Station, Wilmington, Delaware 19880-0356.

*Fluoropolymers 2: Properties*, edited by Hougham *et al.* Plenum Press, New York, 1999.

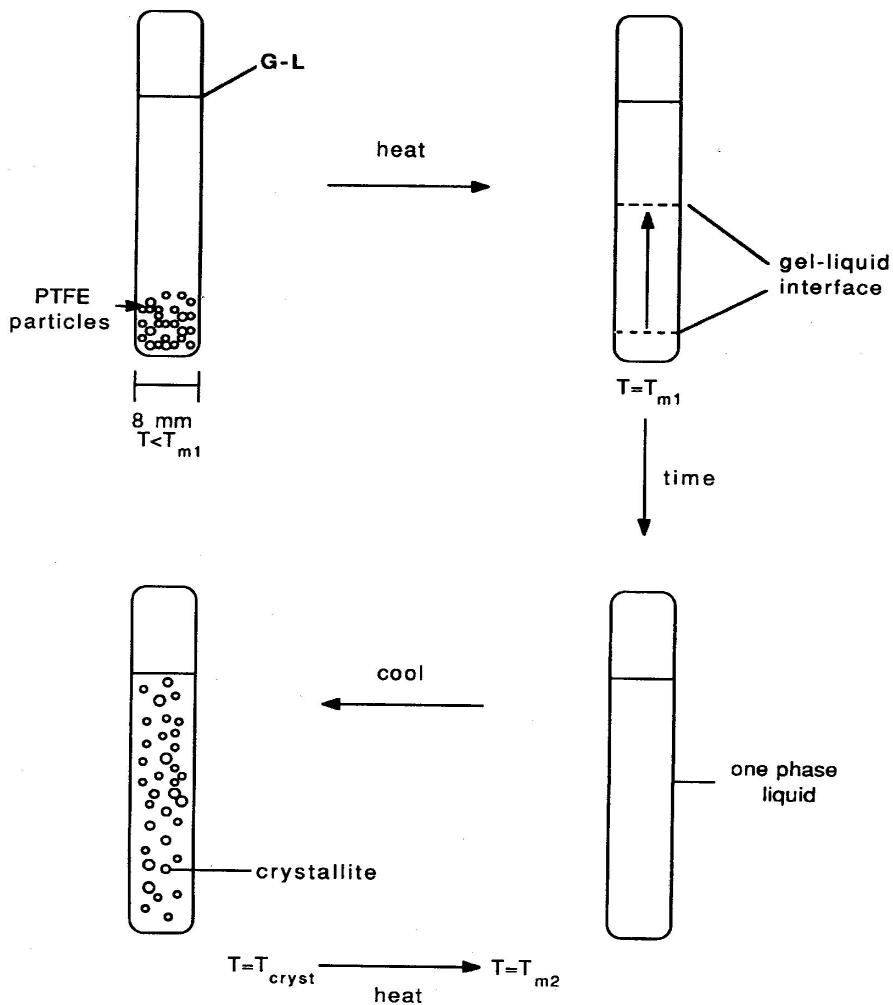
conditions (using externally applied pressure). The two studies will be tied together with a discussion on the solution thermodynamics of these polymers.

## 8.2. ATMOSPHERIC AND AUTOGENOUS PRESSURE

Polymer samples and solvents were sealed in borosilicate glass tubes (8-mm diameter). Visual determinations of dissolution, recrystallization, and liquid–liquid phase separation were made in a thermostated aluminum heating block.<sup>3,6</sup> The schematic in Figure 8.1 represents visual observations for low MW (molecular weight) PTFE in a liquid perfluorocarbon solvent. At low temperatures, the powder lies on the bottom of the tube. The gas–liquid solvent interface is represented as G–L. Upon heating to the solution melting point ( $T_{m1}$ ) the powder becomes transparent, swells with solvent, and coalesces at the bottom of the tube in the form of an immobile polymer-rich phase. As time passes the immobile phase continues to swell to a limit. The longer process of polymer chain diffusion into the solvent-rich phase continues until a homogeneous solution is obtained. Controlled cooling allowed us to determine the solution recrystallization temperature ( $T_{\text{cryst}}$ ). Controlled reheating confirmed the solution melting point ( $T_{m2}$ ). Further heating led to liquid–liquid phase separation observed as a cloud point. This is an example of LCST (lower critical solution temperature) behavior.

Figure 8.2 is a phase diagram representation of these observations. It is calculated based on thermodynamic information about the polymer (PTFE) and solvent, *n*-perfluoropentadecane.<sup>3</sup> Although this particular phase diagram represents behavior with externally applied pressure (8 to 10 MPa), the description applies to autogenous pressure behavior as well. If we consider a mixture with 0.95 weight fraction solvent at 10 MPa pressure, the solid polymer and the liquid are in equilibrium until the temperature is raised to slightly above 280°C. At this point, a one-phase solution is stable. Raising the temperature to about 350°C would cause liquid–liquid phase separation (LCST is reached) and we observe a cloud point.

If we were in the one-phase region at 10 MPa and were able to suddenly drop the pressure to 8 MPa, we would also observe a cloud point. The LCST boundary also moves to a higher temperature with increased solvent density in a homologous series of solvents. Thus, the same effect is observed by increasing the pressure, as explained above, or by raising the solvent MW. However, the solution melting point increases with solvent MW and pressure, creating competing effects. The increase in melting point with MW occurs because the melting point is strongly affected by solvent molar volume. An example of this effect is the solution behavior of PTFE in the homologous series C<sub>10</sub>F<sub>18</sub> (perfluorodecalin), C<sub>11</sub>F<sub>20</sub> (perfluoro-1-methyldecalin), and C<sub>14</sub>F<sub>24</sub> (Flutec PP11). Solution melting



**Figure 8.1.** Visual observations of melting, dissolution, and recrystallization of tetrafluoroethylene polymer-solvent mixtures.

and crystallization temperatures increase with solvent MW because of increased molar volume. Yet, PTFE is not soluble under autogeneous conditions in perfluorodecalin because the LCST is below the solid-liquid equilibrium line, similar to the behavior shown in Figure 8.2 for perfluoropentadecane at 8 MPa.

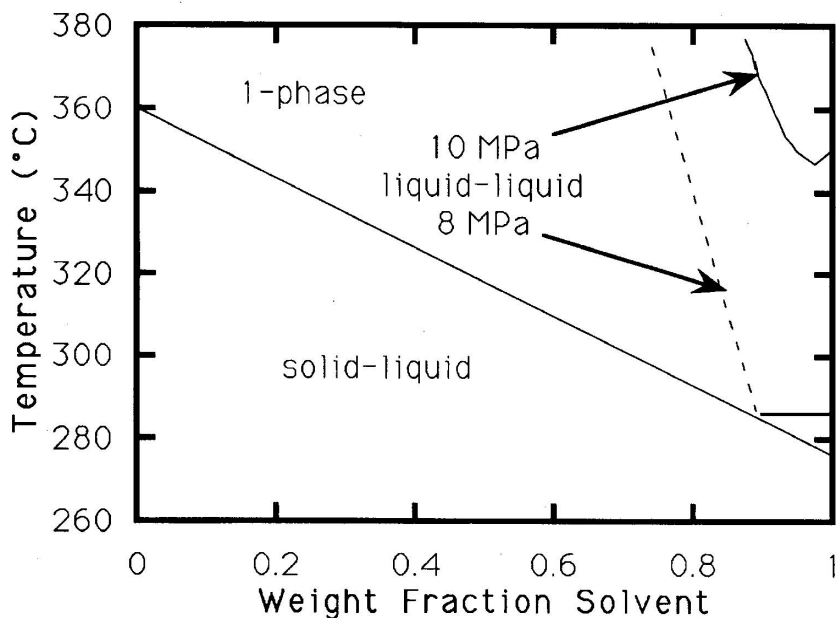


Figure 8.2. Phase diagram of PTFE and  $n\text{-C}_{15}\text{F}_{32}$ .

Table 8.1 lists some common perfluorocarbon solvents that have been used in our experiments and Table 8.2 lists many of the fluoropolymers that we have investigated. Many of the Flutec solvents can be obtained from British Nuclear Fuels, LTD, UK. The temperatures shown in Table 8.2 are for  $\text{C}_{14}\text{F}_{24}$  (Flutec PP11) as solvent. Temperatures can be slightly lower for lower-boiling solvents and slightly higher for higher-boiling solvents, like the oligomer. The bulk polymer melting points (defined for our purposes as the highest temperature at which crystallinity exists) are also given to demonstrate how solution melting and crystallization behavior parallels that of the bulk. A comparison of data in Tables 8.1 and 8.2 provides an approximate idea of which solvents are suitable for atmospheric pressure solutions.

$N$ -perfluoroalkenes are not as good solvents for perfluorocarbons as cyclic perfluoroalkanes.<sup>3</sup> The cyclic solvents give solutions with lower melting and crystallization temperatures and higher LCSTs.

Perfluoropolymers have an extremely low degree of intermolecular interaction. Thus, the entropy of mixing is the dominant driving force for solubility. Fluids that have even weak enthalpic interactions with themselves are poorer solvents for perfluoropolymers. For example, aromatic and other unsaturated perfluorocarbons are poorer solvents than their saturated counterparts. Using

Table 8.1. Commonly Used Perfluorocarbon Solvents


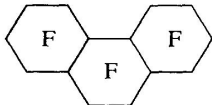
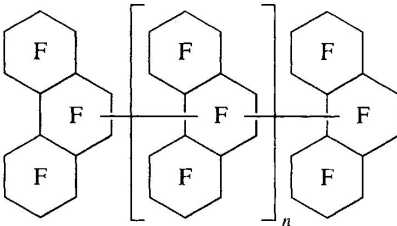
Solvent	Structure	Boiling point (°C)
Fluorinert <sup>R</sup> FC-75	C <sub>8</sub> F <sub>16</sub> O cyclic ethers (mainly perfluoro-2- <i>n</i> -butyltetrahydrofuran)	102
Perfluorodecalin		142
Flutec <sup>R</sup>		215
Flutec <sup>R</sup> (PP11 oligomer)		320–340 (Boiling range: 280–400)

Table 8.2. Solubility of TFE Polymers (1% w/w in C<sub>14</sub>F<sub>24</sub>)

Comonomer type	Comonomer concentration (mol %)	Solution		Bulk polymer T <sub>M</sub> (°C)
		T <sub>M</sub> (°C)	T <sub>cryst</sub> (°C)	
Homopolymer <sup>a</sup> (PTFE)	0	278	258	350
Perfluoropropylvinylether (PFA)	1	260	233	330
Hexafluoropropylene (FEP)	10	200	180	300
Hexafluoropropylene (low-melting FEP)	16	90	50	200
Hexafluoropropylene (amorphous FEP)	50	—	—	—
Ethylene <sup>b</sup> (Tefzel <sup>R</sup> )	50	260	230	300
EVE <sup>c</sup> (Nafion <sup>R</sup> )	12	100	50	200

<sup>a</sup>Relatively low MW PTFE samples were used with  $\bar{M}_w = 0.34$  to  $2.3 \times 10^6$  and  $\bar{M}_w/\bar{M}_n = 3$  to 8.

<sup>b</sup>Tefzel<sup>R</sup> is a nearly perfectly alternating copolymer of ethylene and TFE.

<sup>c</sup>EVE is CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF(CF<sub>3</sub>)-O-CF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>

strictly a molar volume argument, one can calculate a melting point of a 1% PTFE solution in octafluoronaphthalene as 250°C. Yet we observe the melting point to be about 280°C. The higher than predicted value is attributed to the polar interactions of this aromatic solvent.

### 8.3. SUPERAUTOGENOUS PRESSURE

Stainless steel cells fitted with sapphire windows were used to view solubility behavior with externally applied pressure.<sup>7-9</sup> Pressures as high as 200 MPa and temperatures as high as 330°C were employed. None of the solvents studied at superautogenous pressure would dissolve PTFE under autogenous conditions. Several perfluorocarbons with critical temperatures ranging from -46°C (CF<sub>4</sub>) to 293°C (perfluorodecalin) were studied with PTFE and low-melting FEP. Other solvents included chlorofluorocarbons, carbon dioxide, and sulfur hexafluoride. Solvent dipole and quadrupole moments, polarizability, and density were found to be strong variables controlling solubility. Mertdogan *et al.*<sup>9</sup> discuss these points in much more detail.

### 8.4. CONCLUSIONS

Owing to the exceedingly small intermolecular forces in perfluoropolymers, their solubility is dominated by entropy effects. Enthalpic interactions almost always decrease solubility because they tend to favor solvent-solvent mixing. Solution melting and crystallization temperatures have been observed to decrease with lower solvent molar volume, lower undiluted polymer melting point, cyclic perfluorocarbons, low solvent polarity, low pressure, and low polymer concentration. Maximizing solvent density by increasing pressure or solvent MW favors solubility by increasing the LCST temperature. Solution stability also increases with polymer concentration.

ACKNOWLEDGMENTS: The following people collaborated in this work: Dr. G. Dee (DuPont)—solution thermodynamics; Mr. D. Brill, Dr. G. Dee, and Dr. D. Walsh (DuPont) plus Dr. M. McHugh, Dr. M. Paulaitis, Mr. H. S. Byun, Mr. C. Kirby and Ms. C. Mertdogan (Johns Hopkins University)—solvents under superautogenous pressure; Dr. I. Bletsos, Dr. F. Davidson, and Dr. F. Weigert (DuPont) plus Dr. N. Simpson and Mr. D. Slinn (Rhone-Poulenc)—perfluorocarbon solvent characterization; Dr. C. Stewart (DuPont)—applications; Dr. R. Morgan (DuPont)—low-melting FEP inventor; Dr. R. Wheland (DuPont)—amorphous FEP inventor.

## 8.5. REFERENCES

1. J. D. Compton, J. W. Justice, and C. F. Irwin, U.S. Patent 2,510,078 (1950).
2. P. Smith and K. H. Gardner, *Macromolecules* 21, 2606 (1985).
3. W. H. Tuminello and G. T. Dee, *Macromolecules* 27, 669 (1994).
4. B. Chu, C. Wu, and J. Zuo, *Macromolecules* 20, 700 (1987).
5. B. Chu, Z. Wu, and W. Buck, *Macromolecules* 21, 397 (1988).
6. W. H. Tuminello, *Int. J. Polym. Analy. Charact.* 2, 141 (1996).
7. W. H. Tuminello, D. J. Brill, D. J. Walsh, and M. E. Paulaitis, *J. Appl. Polymer Sci.* 56, 495 (1995).
8. W. H. Tuminello, G. T. Dee, and M. A. McHugh, *Macromolecules* 28, 1506 (1995).
9. C. A. Mertdogan, H. S. Byun, M. A. McHugh, and W. H. Tuminello, *Macromolecules* 29, 6548 (1996).