

# Dissolving Poly(tetrafluoroethylene) in Low Boiling Halocarbons

WILLIAM H. TUMINELLO,\* DONALD J. BRILL, DAVID J. WALSH,<sup>†</sup> and MICHAEL E. PAULAITIS<sup>‡</sup>

The DuPont Company, Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356

## SYNOPSIS

An apparatus and methodology are described for dissolving poly(tetrafluoroethylene) in relatively low boiling perhalocarbons at temperatures as high as 330°C and up to about 20 MPa pressure. Cloud points are reported for these solutions with the following solvents: *n*-perfluorohexane, perfluorodecalin, Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and Fluorinert® FC-75 (a perfluorocarbon ether). Most of the solutions were studied above the critical temperatures of their solvents. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It has been shown<sup>1</sup> that high temperatures are necessary for dissolving high melting fluoropolymers, like poly(tetrafluoroethylene) (PTFE) in perfluorocarbons, the preferred solvents. In many cases, confining the liquid/polymer mixture under its autogenous pressure is sufficient to enable dissolution at temperatures higher than the normal boiling point of the liquid. If the boiling point is too low, however, the autogenous pressure of the mixture is not sufficient to enable dissolution. Theory predicts that many fluids that are nonsolvents at low pressure can become solvents at higher pressures.<sup>2</sup> Tuminello and Dee<sup>1</sup> applied this theory to the dissolution of PTFE in perfluorocarbons. They predicted that perfluorocarbons, such as perfluorodecalin, that were not solvents under autogenous conditions would be solvents at higher pressures. This report describes the experiments done to dissolve PTFE in liquids previously considered nonsolvents.

## EXPERIMENTAL

The apparatus used to measure cloud points at elevated pressures is illustrated in Figure 1(a,b). The

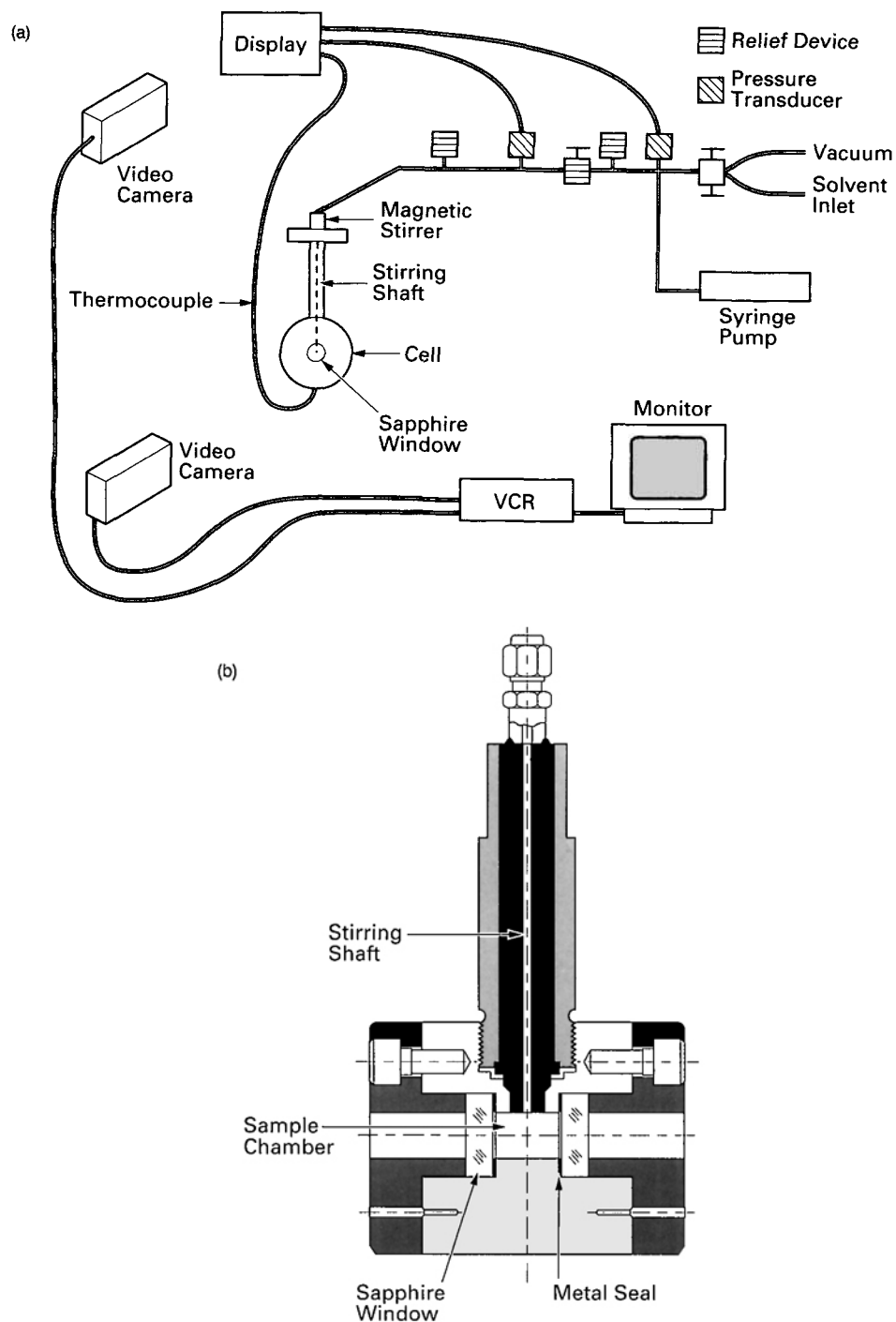
design is a modification of a high pressure apparatus described previously.<sup>3</sup> The high pressure cell consists of a stainless steel cylinder with two sapphire windows at opposite ends. The cylinder is approximately 2.5 in. O.D. and 2.25 in. long with a 0.5 in. I.D. by 0.9 in. inner chamber with a volume of about 3.0 cm<sup>3</sup>. The sapphire windows are sealed with custom-designed Helicoflex nickel-plated seals. The steel block was placed inside an aluminum heating block for temperature control. The windows permit observations of cloud points using a video camera and monitor. The cell also has two ports for temperature measurement, stirring, and solvent feed. The thermocouple was located in the lower port (not shown) and a stirring shaft was placed in the upper port. The upper port also acted as a feedline for the solvent, allowing control of the pressure within the chamber. The stirrer was sealed within the pressure chamber and was driven by a magnetic coupling. The cell was tested at 315°C, 31 MPa pressure with no evidence of leaks.

The experimental procedure was as follows. Polymer was loaded into the cell, which was then evacuated overnight. The polymer was a specially prepared low molecular weight PTFE designated PTFE-6.<sup>4</sup> The cell was then either heated to nearly 300°C before adding solvent or the solvent was added at ambient temperature with subsequent heating. Dissolution was obtained by adjusting pressure at constant temperature. Cloud points were measured as the pressure at which turbidity was first observed in the transparent solution at a specific temperature. Measurements were made in

\* To whom correspondence should be addressed.

<sup>†</sup> Present address: The DuPont Company, Sabine River Works, Orange, TX 77631.

<sup>‡</sup> Present address: Department of Chemical Engineering, University of Delaware, Newark, DE 19716.

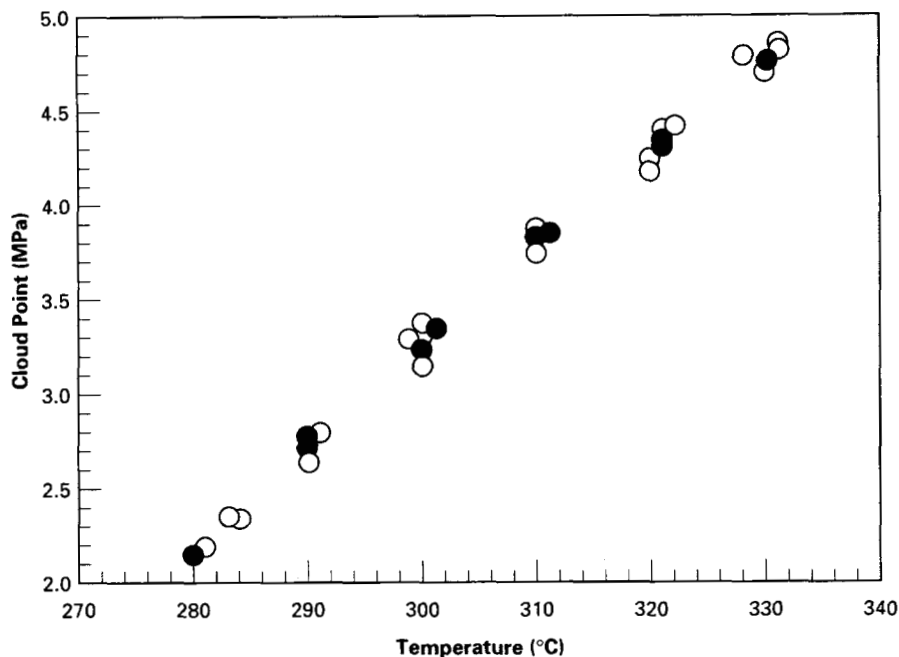


**Figure 1** (a) High pressure, high temperature cell with auxiliary equipment. (b) Close up of high pressure, high temperature cell.

series as the temperature both increased and decreased. No significant differences were observed between the measurements with increasing or decreasing temperature.

The solvents were used as received. *n*-Perfluorohexane ( $n\text{-C}_6\text{F}_{14}$ ) and perfluorodecalin ( $\text{C}_{10}\text{F}_{18}$ )

were obtained from PCR, Inc. Freon<sup>®</sup> 113 ( $\text{CCl}_2\text{FCClF}_2$ ) was obtained from VWR Scientific at 99.8% minimum purity. Fluorinert<sup>®</sup> FC-75, obtained from the 3M Company, is a perfluorinated ether consisting mainly of perfluoro(2-*n*-butyltetrahydrofuran).

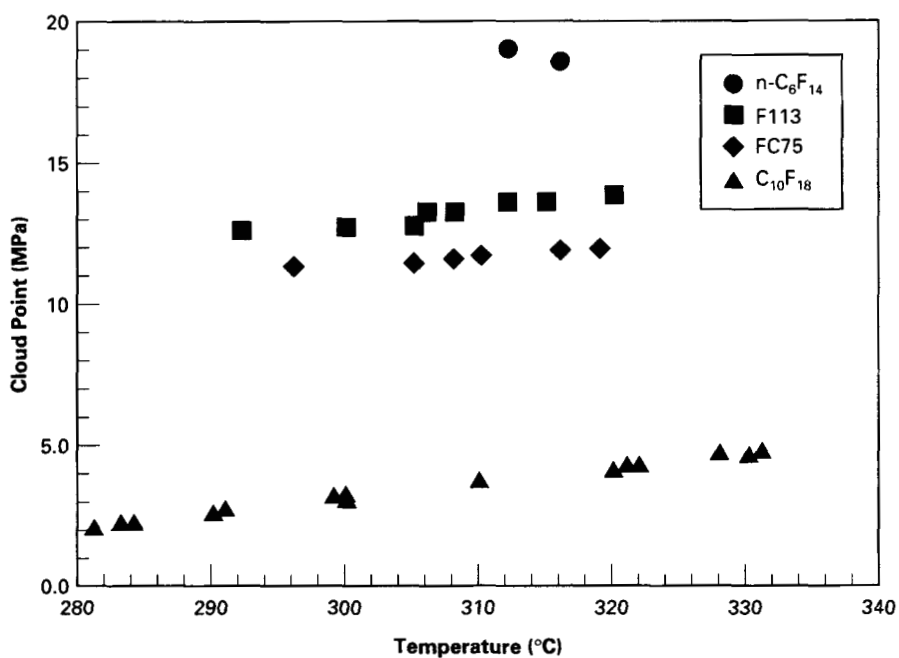


**Figure 2** Measured cloud point pressures for perfluorodecalin solutions. (○) 0.26% w/w polymer; (●) 0.52% w/w polymer.

## RESULTS

Solutions containing 0.26% w/w polymer in perfluorodecalin were prepared at 285°C, 4.1 MPa. Cloud points were obtained over a range of temperatures from 280 to 331°C. The data for two separate

experiments are plotted in Figure 2. The experiment was repeated at twice the polymer concentration, with identical results. These results are also plotted in Figure 2. A one-phase homogeneous solution is present to the left of the data points and liquid-liquid phase separation occurs to the right. It ap-



**Figure 3** Comparison of cloud point pressures for all solutions.

**Table I** Solvent Critical Temperatures

Solvent	$T_{\text{CRIT}}$ (°C)
<i>n</i> -Perfluorohexane	176
Freon® 113	214
Fluorinert® FC-75	231
Perfluorodecalin	293

peared that crystallization started to occur slightly below 280°C. This was observed as the onset of turbidity as temperature was lowered at constant pressure. Similar observations were made for PTFE solutions with higher boiling solvents.<sup>1</sup>

Solutions containing 0.25% w/w polymer were prepared in perfluoro-*n*-hexane at 305°C, 22.3 MPa. In this case, recrystallization appeared to occur at about 295°C. Cloud points were obtained at 312 and 316°C. The cloud points are shown in Figure 3 compared with perfluorodecalin solution data at the 0.26% polymer concentration.

Freon® 113, 0.17% polymer solutions were prepared at 305°C, 13.8 MPa. Recrystallization appeared to start at about 288°C. The measured cloud points are shown in Figure 3.

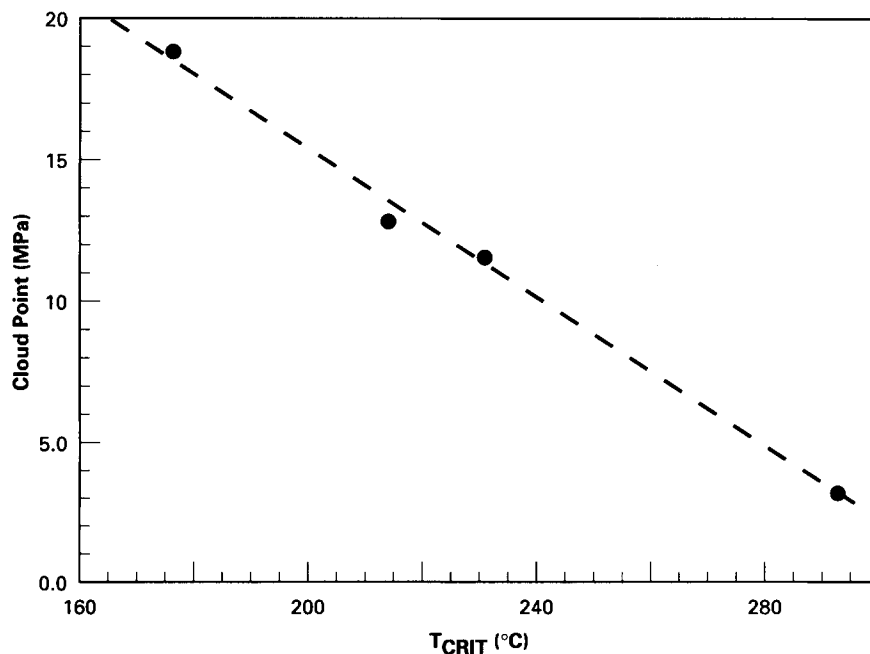
A solution of 0.15% polymer in Fluorinert® FC-75 was prepared at 303°C, 18.7 MPa. Recrystalli-

zation appeared to start near 296°C. Cloud points are shown in Figure 3.

We had expected carbon tetrachloride to be a solvent due to the significant degree of swelling it causes in PTFE.<sup>5</sup> However, we observed that this normally very stable liquid began to discolor badly at around 210°C, which may have been caused by catalytic degradation on the walls of our apparatus.

## DISCUSSION

The calculated phase diagram for PTFE in perfluorodecalin at 8 MPa indicated that the polymer would swell but there would not be complete dissolution above the solution melting point.<sup>1</sup> We obviously obtained complete solution at lower pressures. Also the liquidus line for solid-liquid equilibrium calculated from the Flory-Huggins equation indicated a solution melting point of about 280°C. We observed crystallization starting at this temperature. The predicted melting point is therefore lower than observed because about 20°C supercooling was previously observed for PTFE crystallizing from solution.<sup>1</sup> The Flory-Huggins prediction assumed a polymer-solvent interaction parameter of zero. Possibly the low solvent density at temperatures above the solvent's critical temperature would cor-



**Figure 4** Cloud point at 300°C vs. solvent critical temperature. The dashed line is a linear fit to the data.

respond to a different value for this parameter, thus raising the expected solution melting point.

In almost every case, dissolution was observed at temperatures above the critical temperature ( $T_{\text{CRIT}}$ ) of the solvent. The only exceptions were the solutions in perfluorodecalin below 293°C.  $T_{\text{CRIT}}$  for each solvent is listed in Table I. The data for perfluorodecalin, perfluorohexane and Freon® was obtained from Reid et al.<sup>6</sup> We determined the temperature at which the liquid-gas interface disappeared in a sealed borosilicate glass tube for FC-75. Because this is not a pure material, disappearance of the interface occurred over the temperature range 228–233°C. The average of this range is listed in the table. The cloud points at 300°C are plotted vs.  $T_{\text{CRIT}}$  (°C) for each of the solvents in Figure 4. A linear relation denoted by the dashed line is a least squares linear fit to obtain

$$P_{\text{CP}} = 41.8 - 0.1319T_{\text{CRIT}} \quad (1)$$

where  $P_{\text{CP}}$  refers to the cloud point (MPa) at 300°C.

The authors wish to thank Dr. Andrew E. Feiring for suggesting the use of Freon® 113.

## REFERENCES

1. W. H. Tuminello and G. T. Dee, *Macromolecules*, **27**, 669 (1994).
2. D. K. Carpenter, in *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Vol. 15, H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., J. I. Kroschwitz, Editor-in-Chief, Wiley, New York, 1989, pp. 419–480.
3. T. M. Bergstresser and M. E. Paulaitis, *ACS Symp. Ser.*, **329**, 138 (1987).
4. W. H. Tuminello, T. A. Treat, and A. D. English, *Macromolecules*, **21**, 2606 (1988).
5. H. W. Starkweather, *Macromolecules*, **18**, 1222 (1985).
6. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Liquids and Gases*, 4th ed., McGraw-Hill, Mexico, 1987, Appendix A.

Received September 21, 1994

Accepted November 1, 1994