

## Thermodynamic Phase Behavior of Fluoropolymer Mixtures with Supercritical Fluid Solvents

Hun-Soo Byun<sup>†</sup> and Young-Ho Yoo

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea  
(Received 28 April 2004 • accepted 24 June 2004)

**Abstract**—Cloud-point experimental data were presented at temperatures up to 260 °C and pressures up to 2,500 bar for poly(vinylidene fluoride) (PVDF) [ $M_w=180,000$  and  $275,000$ ] in  $\text{CO}_2$ ,  $\text{CHF}_3$ ,  $\text{CHClF}_2$ , and dimethyl ether (DME). Also, phase behavior curves were shown for the PVDF [ $M_w=180,000$ ] in  $\text{CO}_2$  with 1-propanol and 1-pentanol. Poly(vinyl fluoride) does not dissolve in  $\text{CO}_2$  even at 215 °C and 2,500 bar, while poly(vinylidene fluoride) does dissolve in  $\text{CO}_2$  at 220 °C and pressures of 1,700 bar. To dissolve poly(vinylidene fluoride) in dimethyl ether, pressures in excess of 200 bar and temperatures in excess of 165 °C are needed. The cloud-point behavior between the ternary PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ -DME mixture shows a temperature range of 100-195 °C and pressure range of 350-1,360 bar by adding the 11, 29, and 60 wt% DME in cosolvent. The phase behavior for PVDF [ $M_w=180,000$ ]- $\text{CHF}_3$ -9, 19, and 40 wt%  $\text{CHClF}_2$  system shows a temperature at below 200 °C and pressure up to 1,700 bar. The effect of  $\text{CHClF}_2$  as a cosolvent for PVDF [ $M_w=275,000$ ] in  $\text{CO}_2$  decreased with the pressure increasing 10, 26, 40 and 61 wt% of cosolvent ( $\text{CHClF}_2$ ) contents. Also, the effect of 15 and 40 wt% DME for the PVDF [ $M_w=275,000$ ]- $\text{CHF}_3$  mixture shows temperature ranges of 120-206 °C and pressures up to 1,570 bar.

Key words: Phase Behavior, Poly(vinylidene fluoride), Supercritical Fluid Solvents, 1-Alcohol, Fluoropolymer

### INTRODUCTION

Supercritical fluid solvents have been used in polymer processes such as monomer polymerization [DeSimone et al., 1992], fractionation [Mertdogan et al., 1997], extraction [Chang et al., 2000], swelling [Chun and Kim, 2002] and sustainable industries [Sarbu et al., 2000; Perrut, 2000]. Also, supercritical fluid solvents have been an attractive alternative to incompressible organic liquid solvents, since they can have liquid-like dissolving power while exhibiting transport properties of a gas. Particularly, supercritical carbon dioxide has been touted as the solvent of choice for many industrial applications because it is nonhazardous, inexpensive, nonflammable, nontoxic, and readily available.

Fluoropolymers are useful for a wide range of applications since they possess a unique combination of chemical, mechanical, and electrical properties. The solubility fluoropolymers depend on the number of fluorinated side groups and on the molecular weight of the hydrocarbon main chain. Especially, poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF) are important polymers due to chemical resistance, hard (good) mechanical properties and unique electrical properties [Newman et al., 1979; Hsu and Geil, 1984]. In the reported related research in this work, Lora et al. [1999] recently reported on the solubility of poly(vinyl fluoride) and poly(vinylidene fluoride) in supercritical  $\text{CH}_2\text{F}_2$  and  $\text{CO}_2$  and in  $\text{CO}_2$  with acetone, dimethyl ether, and ethanol. The experimental data of reported cloud-point are presented at temperature to 245 °C and pressure to 2,700 bar for the binary and ternary systems. Also, Mertdogan et al. [1996, 1999] reported on the solubility of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in supercritical  $\text{CO}_2$  and halogenated

supercritical solvents, and cosolvency effect of  $\text{SF}_6$  on the solubility of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in supercritical  $\text{CO}_2$  and  $\text{CHF}_3$ .

In this work, the high pressure phase behavior of fluoropolymers (PVDF:  $M_w=180,000$  and  $275,000$ ) in compressed liquid and supercritical  $\text{CO}_2$ ,  $\text{CHF}_3$ , dimethyl ether and  $\text{CHClF}_2$ , with  $\text{CO}_2$  in 1-propanol and 1-pentanol was measured at temperatures up to 260 °C and pressures as high as 2,500 bar.

### EXPERIMENTAL SECTION

The cloud-point curves for the fluoropolymer-supercritical low molecular weight hydrocarbon mixtures were determined at pressures up to 3,000 bar and temperatures to 250 °C. Fig. 1 shows the schematic diagram of the experimental apparatus used for the fluo-

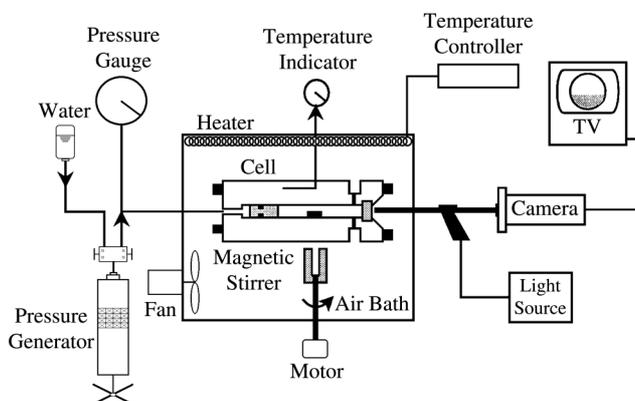


Fig. 1. Schematic diagram of the high-pressure experimental apparatus used in this study.

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: hsbyun@yosu.ac.kr

ropolymer-SCF solvent phase behavior studies [Byun, 2002; Byun and Choi, 2002].

Experimental cloud-point data were obtained by using a high-pressure, variable-volume view cell. The variable-volume cell used to obtain the cloud-point curves was a static-type with a 1.59 cm I.D., an O.D. of 7.0 cm, and a working volume of  $\sim 28 \text{ cm}^3$ . A 1.9 cm thick sapphire window was fitted in the front part of the cell to allow observation of the phases. Typically  $0.500 \pm 0.002 \text{ g}$  of fluoropolymer was loaded into the cell which was subsequently purged at room temperature with the solvent of interest at 3 to 6 bar to remove any entrapped air and organic solvents. Generally,  $7.0$  to  $10.0 \pm 0.020 \text{ g}$  of solvent were transferred into the cell gravimetrically by using a high-pressure bomb. For the fluoropolymer-solvent-monomer systems, the liquid monomer was transferred into the cell to within  $\pm 0.002 \text{ g}$  by using a syringe. The fluoropolymer mixture was compressed to the desired operating pressure by moving a piston located within the cell. The piston was moved by using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-108952, 0 to 3,450 bar, accurate to within  $\pm 3.5$  bar). The temperature of the cell was measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, model 7563, accuracy to within  $\pm 0.005\%$ ). The system temperature was typically maintained to within  $\pm 0.2 \text{ }^\circ\text{C}$  below  $200 \text{ }^\circ\text{C}$ , and  $\pm 0.4 \text{ }^\circ\text{C}$  above  $200 \text{ }^\circ\text{C}$ . The mixture inside the cell could be viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. A fiber optic cable connected to a high density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope was used to transmit light into the cell. The solution in the cell was well mixed by using a magnetic stir bar activated by an external magnet beneath the cell.

At a fixed temperature, the solution in the cell was compressed to a single phase. The solution was maintained in the one-phase region at the desired operating temperature for at least 30-40 min so that the cell could reach thermal equilibrium. The pressure was then slowly decreased until the solution reached cloud-point. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. The cell was again pressurized to a single phase, at least 150 bar above the cloud-point pressure, and maintained for at least 10 minutes. Cloud point measurements were repeated at least twice at each temperature, and were typically reproducible to within  $\pm 3.0$  bar at the highest temperatures. In the P-T region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within  $\pm 5.0$  bar. Typi-

cally, the lowest temperature of the cloud-point curves presented in this work represents either the highest pressure of the experimental apparatus or the location of the crystallization boundary of the fluoropolymer.

**Materials:** Poly(vinylidene fluoride) [ $M_w=180,000$ ,  $M_w/M_n=2.53$  and  $M_w=275,000$ ,  $M_w/M_n=2.57$ ] were obtained from Aldrich Chemical Co., Inc. Also, poly(vinyl fluoride) [fluoride content 41%,  $T_g=41 \text{ }^\circ\text{C}$ ] was obtained from Scientific Polymer Products, Inc. The 1-propanol (99.5% purity) and 1-pentanol (98% purity) were obtained from Aldrich Chemical Co. and Junsei Chemical Co., respectively. Carbon dioxide (99.9% minimum purity) was obtained from Daesung Oxygen Co. (Yeosu, Chonnam). Fluoroform (98+ % minimum purity) was obtained from Aldrich Chemical Co., Inc.  $\text{CHClF}_2$  (99.9% minimum purity) was obtained from Dongil Gas Co. Dimethyl ether (99.9% minimum purity) was obtained from Yeosu NCC Company. All of the solvents were used as received.

## RESULTS AND DISCUSSION

The properties of the solvents and cosolvents used in this study are shown in Table 1 [Reid et al., 1987; Daubert and Danner, 1989]. For the poly(vinylidene fluoride)-solvents systems,  $\text{CO}_2$ ,  $\text{CHF}_3$ ,  $\text{CHClF}_2$  and DME were used as solvents. For the poly(vinylidene fluoride)-solvents-cosolvents, 1-propanol and 1-pentanol were used as cosolvents.

$\text{CO}_2$  have the critical pressure, critical temperature, critical density and polarizabilities. However,  $\text{CO}_2$  has a quadrupole moment but does not have a dipole moment.  $\text{CHF}_3$  has the critical pressure, critical temperature, critical density, dipole moment and polarizabilities.  $\text{CHClF}_2$  possesses a dipole moment (1.4 D). DME has both polarizability and dipole moment. The dipole moment increases in the order of  $\text{CHF}_3 > \text{CHClF}_2 > \text{DME} > \text{CO}_2$ . The polarizability has a  $\text{CO}_2$  ( $2.71 \times 10^{-25} \text{ cm}^3$ ),  $\text{CHF}_3$  ( $2.65 \times 10^{-25} \text{ cm}^3$ ),  $\text{CHClF}_2$  (no literature) and DME ( $52.2 \times 10^{-25} \text{ cm}^3$ ).

The critical temperatures for 1-propanol and 1-pentanol increase as the molecular weight increases, while the critical pressure and critical density for them decrease. The dipole moment has similar 1-propanol and 1-pentanol.

### 1. Phase Behavior of Binary System

The impact of polymer backbone architecture on fluoropolymer solubility in supercritical fluid solvents is studied by systematically varying the chemical type of the repeat units in the main chain. A variable-volume view cell, capable of operating to high temperatures and high pressures, was designed and implemented to meet these extreme operating conditions.

Fig. 2 shows the comparison between the phase behavior of  $\sim 5$

**Table 1. Properties of the solvent and cosolvent used in this study**

Solvents	$M_w$	$T_c$ ( $^\circ\text{C}$ )	$P_c$ (bar)	$\rho_c$ ( $\text{g}/\text{cm}^3$ )	Polarizability ( $\text{cm}^3 \times 10^{25}$ )	Dipole moment (D)	$\omega$
$\text{CO}_2$	44.0	31.0	73.8	0.469	26.5	0.0	0.225
$\text{CHF}_3$	70.	26.2	48.6	0.528	26.5	1.6	0.260
$\text{CHClF}_2$	86.5	96.1	49.7	0.525		1.4	0.221
DME	46.1	126.8	52.4	0.271	52.2	1.3	0.200
1-Propanol	60.1	263.6	51.7	0.274		1.7	0.623
1-Pentanol	88.1	315.0	39.1	0.270		1.7	0.579

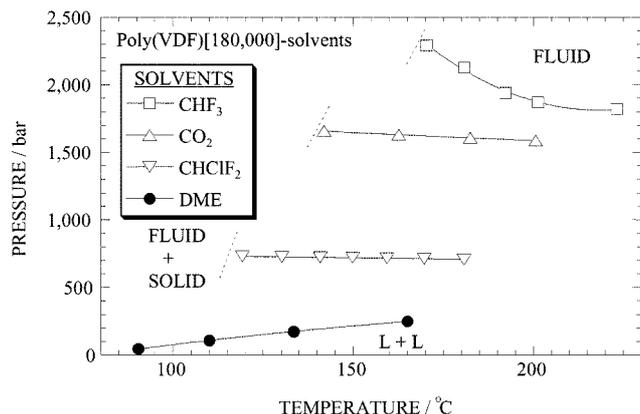


Fig. 2. Comparison of the cloud-point curve of poly(vinylidene fluoride) [ $M_w=180,000$ ] in  $\text{CO}_2$ ,  $\text{CHF}_3$ ,  $\text{CHClF}_2$  and DME. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

wt% PVDF [ $M_w=180,000$ ] in  $\text{CO}_2$ , DME,  $\text{CHF}_3$  and  $\text{CHClF}_2$ . As shown in Fig. 2, the phase behavior of the  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CHF}_3$  mixture presents a negative slope with dissolution at a temperature of  $\sim 225$  °C and a pressure of  $\sim 2,300$  bar. The cloud-point of the  $\sim 5$  wt% PVDF [ $M_w=180,000$ ] in  $\text{CO}_2$  shows a plate slope at a temperature range of 140–200 °C and a pressure of  $\sim 1,600$  bar. Also, the solubility of the  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CHClF}_2$  and -DME mixture presents a positive slope in lower pressure at a range of temperature of 90 to 180 °C and a range of pressure of 45 to 730 bar. At 170 °C, the phase behavior boundary has shifted from 2,100 bar ( $\text{CHF}_3$ ), 1,600 bar ( $\text{CO}_2$ ), 700 bar ( $\text{CHClF}_2$ ) to 300 bar (DME).

Fig. 3 shows the phase behavior curve of PVDF [ $M_w=275,000$ ] dissolved in supercritical  $\text{CO}_2$ , DME,  $\text{CHF}_3$  and  $\text{CHClF}_2$ . The cloud-point behavior for PVDF [ $M_w=275,000$ ]- $\text{CO}_2$ ,  $\text{CHF}_3$  and  $\text{CHClF}_2$  system exhibits UCST curves with a negative slope. The phase behavior of PVDF [ $M_w=275,000$ ]-DME mixture exhibits LCST curve

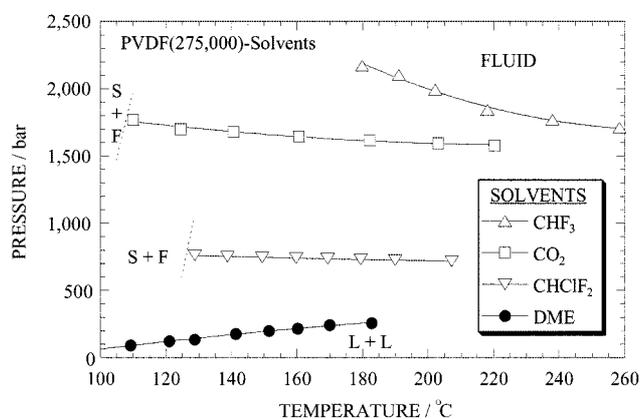


Fig. 3. Comparison of the cloud-point curve of poly(vinylidene fluoride) [ $M_w=275,000$ ] in  $\text{CO}_2$ ,  $\text{CHF}_3$ ,  $\text{CHClF}_2$  and DME. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

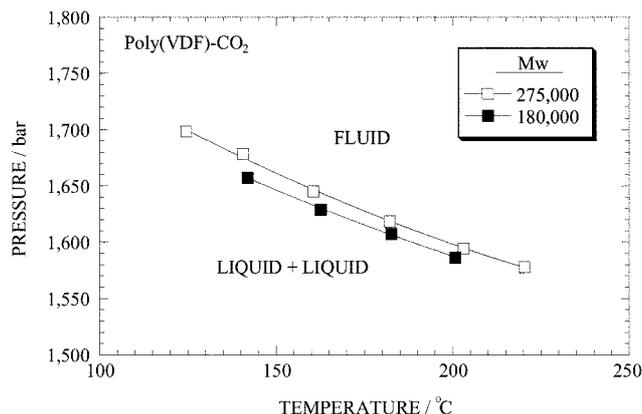


Fig. 4. Comparison the cloud-point curve of poly(vinylidene fluoride) [ $M_w=180,000$  and 275,000] in  $\text{CO}_2$ . The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

with a positive slope. The PVDF [ $M_w=275,000$ ]- $\text{CO}_2$ ,  $\text{CHF}_3$  and  $\text{CHClF}_2$  system is present at the temperature range of 90–260 °C and pressure to 2,170 bar. At 180 °C the phase behavior boundary has shifted from 2,200 bar ( $\text{CHF}_3$ ) to 300 bar (DME) and it is due to the polarizability difference of  $\text{CHF}_3$  ( $2.65 \times 10^{-25} \text{ cm}^3$ ) and DME ( $52.2 \times 10^{-25} \text{ cm}^3$ ).

Fig. 4 shows a comparison between the cloud-point of  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CO}_2$  and  $\sim 5$  wt% PVDF [ $M_w=275,000$ ]- $\text{CO}_2$  mixture. At 170 °C, the pressure difference of solubility curve for  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CO}_2$  and  $\sim 5$  wt% PVDF [ $M_w=275,000$ ]- $\text{CO}_2$  system has shifted from 1,620 bar to 1,630 bar, and this is due to the molecular weight difference.

Fig. 5 shows the comparison between the phase behavior of  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CHClF}_2$  and  $\sim 5$  wt% PVDF [ $M_w=275,000$ ]- $\text{CHClF}_2$  system at a temperature range of 120–215 °C and a pressure range of 706–760 bar. The pressure difference of the solubility curve for two systems has about 25 bar at 170 °C.

## 2. Phase Behavior of Ternary System

Fig. 6 shows the effect of  $\text{CHClF}_2$  on the cloud-point curves of the  $\sim 5$  wt% PVDF [ $M_w=180,000$ ]- $\text{CHF}_3$  system obtained in this study. The PVDF [ $M_w=180,000$ ] does dissolve in pure  $\text{CHF}_3$  to tem-

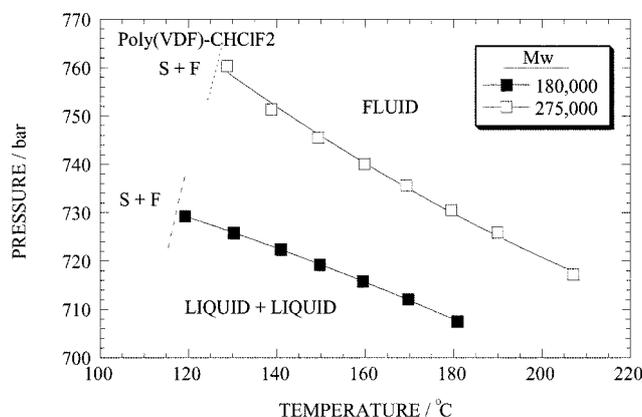


Fig. 5. Comparison the cloud-point curve of poly(vinylidene fluoride) [ $M_w=180,000$  and 275,000] in  $\text{CHClF}_2$ . The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

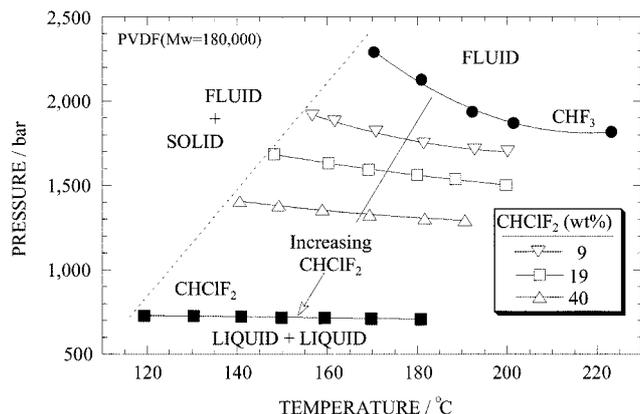


Fig. 6. Effect of  $\text{CHClF}_2$  on the phase behavior of the poly(vinylidene fluoride) [ $M_w=180,000$ ] in  $\text{CHF}_3$  system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

perature of  $225^\circ\text{C}$  and pressure of  $2,300$  bar. When  $9$  wt%  $\text{CHClF}_2$  is added to the PVDF [ $M_w=180,000$ ]- $\text{CHF}_3$  solution, the cloud-point curve exhibits UCST-type phase behavior of the negative slope at temperature range from  $157$  to  $200^\circ\text{C}$ . With  $19$  wt%  $\text{CHClF}_2$  added to the solution, the cloud-point curve exhibits UCST-type phase behavior of a negative slope. The cloud-point curve shows a slight slope at  $1,500$ - $1,680$  bar and at a temperature range of  $148$  to  $200^\circ\text{C}$ . Also at  $170^\circ\text{C}$ , the cloud-point pressure of the PVDF [ $M_w=180,000$ ]- $\text{CHF}_3$ - $\text{CHClF}_2$  system decreases by  $\sim 200$  bar with the first  $9$  wt%  $\text{CHClF}_2$  addition to the solution, and it decreases by another  $\sim 400$  bar with the addition of  $18$  wt%  $\text{CHClF}_2$ . The phase behavior curve with  $40$  wt%  $\text{CHClF}_2$  has a slightly negative slope at a temperature range from  $140$  to  $190^\circ\text{C}$  and pressure to  $1,400$  bar.

Fig. 7 presents the cloud-point experimental behavior of the PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ - $x$  wt% DME system data obtained in this study. The PVDF [ $M_w=180,000$ ] does dissolve in pure  $\text{CO}_2$  to a temperature of  $200^\circ\text{C}$  and pressure of  $1,658$  bar. When  $11$  wt% DME is added to the PVDF [ $M_w=180,000$ ]- $\text{CO}_2$  solution, the phase behavior exhibits UCST-type phase behavior of the slightly negative slope

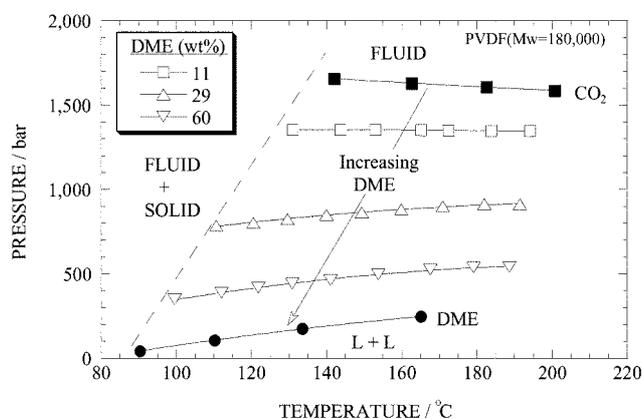


Fig. 7. Effect of DME on the phase behavior of the poly(vinylidene fluoride) [ $M_w=180,000$ ] in  $\text{CO}_2$  system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

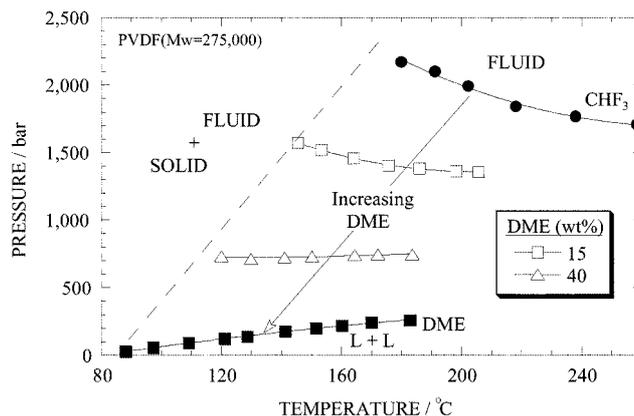


Fig. 8. Effect of DME on the phase behavior of the poly(vinylidene fluoride) [ $M_w=275,000$ ] in  $\text{CHF}_3$  system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

at temperature range from  $130$  to  $195^\circ\text{C}$ . Also with  $29$  wt% DME added to the solution, the cloud-point curve exhibits LCST-type phase behavior of the positive slope. At  $160^\circ\text{C}$ , the cloud-point pressure of the PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ -DME system decreases by  $\sim 450$  bar with the first  $11$  wt% DME addition to the solution, and it decreases by another  $\sim 350$  bar with the addition of  $31$  wt%. When  $60$  wt% DME is added to the solution, the phase behavior curve exhibits LCST-type cloud-point behavior with a positive slope. The phase behavior curve with  $60$  wt% DME shows at a temperature range of  $100$  to  $190^\circ\text{C}$  and a pressure range from  $350$  to  $540$  bar.

Fig. 8 shows the impact of the phase behavior of PVDF [ $M_w=275,000$ ]- $\text{CHF}_3$ - $x$  wt% DME mixture obtained in this work. With  $15$  wt% DME added to the solution, the cloud-point curve exhibits UCST type phase behavior with a negative slope. With  $40$  wt% DME in solution the cloud-point pressure remains virtually flat at  $700$  bar over a temperature range of  $120$  to  $185^\circ\text{C}$ . As shown in Fig. 8, the PVDF [ $M_w=275,000$ ]- $\text{CHF}_3$ - $15$  and  $40$  wt% DME system has lower cloud-point pressure as the DME increases.

Fig. 9 shows the effect of  $\text{CHClF}_2$  on the phase behavior of the

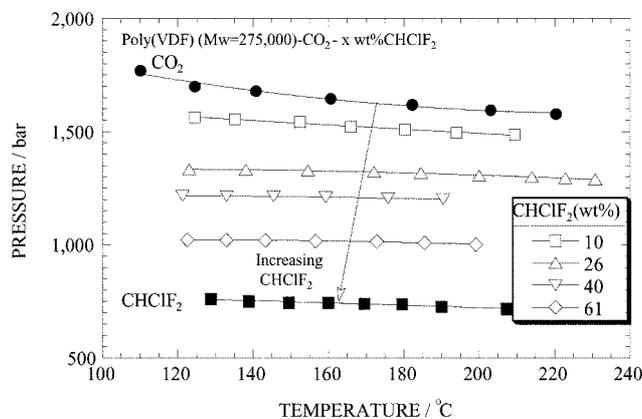
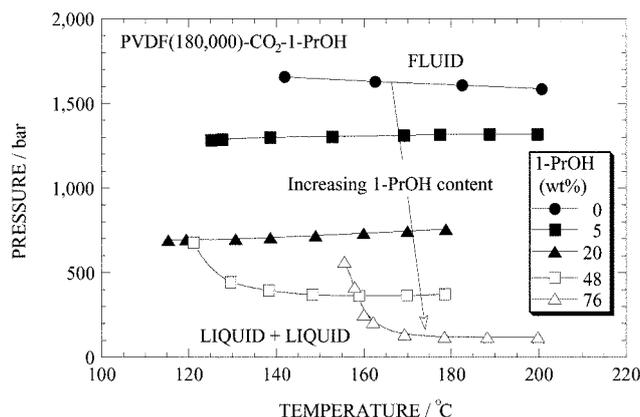


Fig. 9. Effect of  $\text{CHClF}_2$  on the phase behavior of the poly(vinylidene fluoride) [ $M_w=275,000$ ] in  $\text{CO}_2$  system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

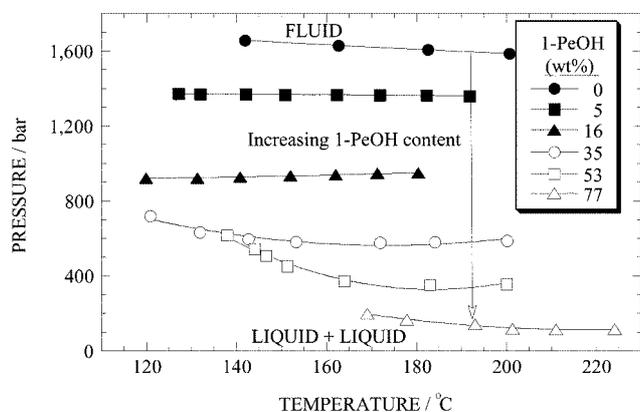


**Fig. 10.** Effect of 1-propanol on the phase behavior of the poly(vinylidene fluoride) [ $M_w=180,000$ ] in  $\text{CO}_2$  system. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

PVDF [ $M_w=275,000$ ]- $\text{CO}_2$  mixture. The PVDF [ $M_w=275,000$ ]- $\text{CO}_2$ -10, 26, 40, and 61 wt%  $\text{CHClF}_2$  system presents a virtually flat pressure of 1,500 bar, 1,300 bar, 1,200 bar and 1,000 bar at constant temperature of 170 °C, respectively.

### 3. Phase Behavior of PVDF-Supercritical Solvents-1-Alkanol System

Fig. 10 shows the effect of 1-propanol on the cloud-point of the PVDF [ $M_w=180,000$ ]- $\text{CO}_2$  system obtained in this work. The PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ -5 wt% 1-propanol mixture shows a virtually flat curve at a temperature range of 125-200 °C and pressure up to  $\sim 1,300$  bar. When 20 wt% 1-propanol is added to the solution, the phase behavior exhibits LCST region cloud-point behavior with slightly positive slope. With 48 wt% 1-propanol in solution, the cloud-point curve is presented as almost virtually flat at a temperature range from 130 °C to 180 °C, and the phase behavior pressure increases rapidly at below 130 °C which suggests that the interchange energy favors 1-propanol 1-propanol interactions relative to 1-propanol PVDF interactions at these lower temperatures. If 76 wt% 1-propanol is added to the solution, the cloud point curve increases in pressure at the higher temperature of 165 °C in agreement with the expectation that 1-propanol 1-propanol hydrogen bonding should



**Fig. 11.** Effect of 1-pentanol on the phase behavior of the poly(vinylidene fluoride) [ $M_w=180,000$ ] in  $\text{CO}_2$  system. The poly(vinylidene fluoride) concentration is  $\sim 5$  wt% in each case.

increase with decreasing temperature.

Fig. 11 shows the impact of 1-pentanol on the phase behavior of the PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ -x wt% 1-pentanol system obtained in this work. With 5 and 16.7 wt% 1-pentanol in solution, the phase behavior shows virtually flat at a temperature range from 120 °C to 195 °C and pressure to  $\sim 1,400$  bar and  $\sim 950$  bar, respectively. The PVDF [ $M_w=180,000$ ]- $\text{CO}_2$ -35, 53 and 77 wt% 1-pentanol mixtures shows the phase behavior curves of slowly increase at below 140 °C (35 wt%), 160 °C (53 wt%) and 180 °C (77 wt%).

## CONCLUSION

A supercritical fluid solvent was used to solubilize polar PVDF. The cloud point pressures of these two poly(vinylidene fluoride) [ $M_w=180,000$ ,  $M_w/M_n=2.53$  and  $M_w=275,000$ ,  $M_w/M_n=2.57$ ] are lower in DME than those in  $\text{CO}_2$  since DME is a very dense solvent and has a significant dipole moment.

The phase behavior for the systems supercritical  $\text{CO}_2$ ,  $\text{CHF}_3$ ,  $\text{CHClF}_2$  and DME in PVDF is measured in changes of the pressure-temperature slope, and with cosolvent concentrations. The PVDF- $\text{CO}_2$ -DME (11, 29 and 60 wt%) and  $\text{CHClF}_2$  (10, 26, 40 and 61 wt%) solution shows the appearance of a typical LCST and UCST region. The DME (15 and 40 wt%) and  $\text{CHClF}_2$  (9, 19 and 40 wt%) for the PVDF- $\text{CHF}_3$  mixture shows a typical UCST region.

The solubility curve up to  $\sim 200$  °C and 1,320 bar for PVDF ( $M_w=180,000$ )- $\text{CO}_2$ -1-propanol system shows the change of pressure-temperature and with 1-propanol concentration of 0, 5, 20, 48 and 76 wt%. The high pressure phase behavior for PVDF ( $M_w=180,000$ )- $\text{CO}_2$ -0, 5, 17, 35, 53 and 77 wt% 1-pentanol system shows the change of pressure-temperature curve from LCST region to U-LCST region as the 1-pentanol concentration increases.

## ACKNOWLEDGMENTS

This work was supported by Korea Research Foundation Grant (KRF-2002-041- D00105).

## REFERENCES

- Byun, H.-S. and Choi, T.-H., "Effect of Octadecyl Acrylate Concentration on the Phase Behavior of Poly(octadecyl acrylate)-Supercritical  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  at High Pressure," *J. App. Polym. Sci.*, **86**, 372 (2002).
- Byun, H.-S., "Monomer Concentration Effect on the Poly(propyl acrylate) and Poly(propyl methacrylate) Solution Phase Behavior in Supercritical  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ ," *Korean J. Chem. Eng.*, **19**, 126 (2002).
- Chang, C. J., Chang, Y. F., Lee, H. Z., Lin, J. Q. and Arai, Y., "Supercritical Carbon Dioxide Extraction of High-Value Substances from Soybean Distillate," *Ind. Eng. Chem. Res.*, **39**, 4521 (2000).
- Chun, S. W. and Kim, J. D., "Swelling and Deswelling Transition of Water-Soluble Poly(N-isopropylacrylamide) by a Method of Blob Rescaling," *Korean J. Chem. Eng.*, **19**, 803 (2002).
- Daubert, T. E. and Danner, R. P., "Physical and Thermodynamic Properties of Pure Chemicals," Hemisphere Publishing, NY (1989).
- DeSimone, J. M., Guan, Z. and Elsbernd, C. S., "Synthesis of Fluoropolymer in Supercritical Carbon Dioxide," *Science*, **257**, 945 (1992).
- Hsu, C. C. and Geil, P. H., "Morphology-Structure-Property Relationships in Ultraquenched Poly(vinylidene fluoride)," *J. Appl. Phys.*,

- 56, 2404 (1984).
- Lora, M., Lim, J. S. and McHugh, M. A., "Comparison of the Solubility of PVF and PVDF in Supercritical  $\text{CH}_2\text{F}_2$  and  $\text{CO}_2$  and in  $\text{CO}_2$  with Acetone, Dimethyl Ether, and Ethanol," *J. Phys., Chem. B*, **103**, 2818 (1999).
- Mertdogan, C. A., Byun, H.-S., McHugh, M. A. and Tuminello, W. H., "Solubility of Poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in Supercritical  $\text{CO}_2$  and Halogenated Supercritical Solvents," *Macromolecules*, **29**, 6548 (1996).
- Mertdogan, C. A., DiNoia, T. P. and McHugh, M. A., "Impact of Backbone on the Solubility of Fluorocopolymers in Supercritical  $\text{CO}_2$  and Halogenated Supercritical Solvents: Comparison of Poly(vinylidene fluoride-co-22 mol% hexafluoropropylene) and Poly(tetrafluoroethylene-co-19 mol% hexafluoro-propylene)," *Macromolecules*, **30**, 7511 (1997).
- Mertdogan, C. A., McHugh, M. A., Barth, H. G., Walls, D. J. and Tuminello, W. H., "Supercritical Fractionation of a Perfluorinated Copolymer," *Int. J. Polymer Analysis & Characterization*, **4**, 231 (1997).
- Newman, B. A., Yoon, K. D., Pae, K. D. and Scheinbeim, J. I., "Piezoelectric Activity and Field-Induced Crystal Structure Transition in Poled Poly(vinylidene fluoride) Films," *J. Appl. Phys.*, **50**, 6095 (1979).
- Perrut, M., "Supercritical Fluid Applications: Industrial Developments and Economic Issues," *Ind. Eng. Chem. Res.*, **39**, 4531 (2000).
- Reid, R. C., Prausnitz, J. M. and Polling, B. E., "The Properties of Gases and Liquids," 4th ed., McGraw-Hill, New York, NY (1987).
- Sarbu, T., Styrane, T. J. and Beckman, E. J., "Design and Synthesis of Low Cost, Sustainable  $\text{CO}_2$ -philes," *Ind. Eng. Chem. Res.*, **39**, 4678 (2000).