

High pressure phase behavior for the binary mixture of pentafluoropropyl methacrylate and poly(pentafluoropropyl methacrylate) in supercritical carbon dioxide and dimethyl ether

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Abstract—Pressure-composition isotherm is obtained for the carbon dioxide+2,2,3,3,3-pentafluoropropyl methacrylate (PFPPMA) using static apparatus with a variable volume view cell at temperature range from 40 °C to 120 °C and pressure up to 130 bar. This system exhibits type-I phase behavior with a continuous mixture-critical curve. The experimental result for carbon dioxide+PFPPMA mixture was modeled using the Peng-Robinson (P-R) and multi-fluid nonrandom lattice fluid (MF-NLF) equation of state. Experimental cloud-point data of pressure up 470 bar and temperature to 182 °C were reported for the binary mixture of poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPPMA)] in supercritical carbon dioxide and dimethyl ether (DME). The Poly(PFPPMA)+carbon dioxide and Poly(PFPPMA)+DME systems showed LCST behavior.

Key words: High Pressure Phase Behavior, Carbon Dioxide, Dimethyl Ether, Poly(2,2,3,3,3-Pentafluoropropyl Methacrylate), 2,2,3,3,3-Pentafluoropropyl Methacrylate, Peng-Robinson Equation of State, MF-NLF Equation of State

INTRODUCTION

Perfluoroalkyl methacrylate monomer and polymer have a low refractive index, low surface tension, chemical resistance, and high transparency. These monomers and polymers have been industrially used as clad material for optical fibers, high-sensitive resistant for microlithography, moisture-proof coating agents, antifouling property, oil and water repellent agents, etc. due to specific nature of fluorine atoms contained in the molecules or as a starting compound for surfactants [1,2].

Recently, a perfluoroalkyl methacrylate polymer was synthesized via suspension polymerization in water. DeSimone et al. reported the free radical polymerization of a perfluoroalkyl methacrylate polymer in supercritical carbon dioxide [3]. Carbon dioxide has quadrupole moment, no dipole moment, and low dielectric constant. It is a good solvent for such nonpolar molecules as methane and ethane.

The phase behavior of polymers and monomers in the supercritical fluids is very important in most polymerization processes, polymer production, processing technologies, material development, and industrial application [4-6]. Also, high-pressure phase equilibrium data for binary or ternary mixtures containing supercritical carbon dioxide will be needed to design and operate processing plants [7,8].

The phase behavior experimental data for the heptafluorodecyl methacrylate in supercritical carbon dioxide was reported at temperature of 50 °C to 80 °C and pressure up to 140 bar by Bae et al. [9]. The solubility of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in supercritical carbon dioxide and halogenated supercritical solvents were reported at temperature from (118 to 250) °C and pressure up to 2,700 bar performed by Mertdogan et al. [10].

Also, cloud-point phase behavior of fluoropolymer mixtures with supercritical fluid solvents was measured at pressure and temperature up to 2,500 bar and 260 °C by Byun and Yoo [11]. Recently, the phase behavior of poly(heptafluorodecyl methacrylate) in supercritical carbon dioxide was studied at temperature from (30 to 92) °C and pressure up to 260 bar by Shin et al. [12].

The objective of this work is to obtain experimental data of the high pressure, phase behavior information for the systems of carbon dioxide+2,2,3,3,3-pentafluoropropyl methacrylate (PFPPMA) and poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPPMA)] +carbon dioxide and Poly(PFPPMA)+dimethyl ether (DME) mixtures. The experimental data of pressure-composition isotherms are presented for the carbon dioxide+PFPPMA system. The pressure-temperature trace of the mixture-critical points is presented in the vicinity of pure DME between the critical point of pure DME and that of PFPPMA. The other objective is to compare the calculated result by the Peng-Robinson equation of state (P-R EOS) [13] and multi-fluid nonrandom lattice fluid (MF-NLF) [14,15] equation with the experimental result for carbon dioxide+PFPPMA system.

EXPERIMENTAL SECTION

1. Materials

Carbon dioxide (99.8% minimum purity) was obtained from Dae-sung Industrial Co., and dimethyl ether (99.5% purity) obtained from Yeochun NCC Co. and used as received. PFPPMA (>97% purity, CAS RN 45115-53-5, $C_7H_7F_5O_2/H_2C=C(CH_3)CO_2CH_2CF_2CF_3$) was obtained from Alfa Aesar Co. and used without further purification. It contained MEHQ as an inhibitor to prevent polymerization. The concentration of MEHQ was 100 ppm of PFPPMA monomers.

PFPPMA was used and purified by distillation under atmospheric pressure. Tetrahydrofuran [THF] (min. 99.9% purity with HPLC

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grade; J. T. Baker; CAS RN 109-99-9, $M_w=72.11$, $(CH_2)_4O$) and α , α' -Azobis(isobutronitrile) [AIBN] (98% purity; Junsei Chemical Co; CAS RN 78-67-1, $M_w=164.21$, $(CH_3)_2C(CN)N:N(CN)C(CH_3)_2$) were used without further purification. Poly(PFPMA) [$M_w=5,500$, $M_w/M_n=1.95$, CAS RN 95243-53-1] was purchased from Aldrich Co. and used as received.

2. Sample Preparation

Poly(PFPMA) was synthesized by solution polymerization using AIBN as the initiator and THF as the solvent. The preparation procedure was as follows. PFPMA (2.0 g, 9.17 mmol) and AIBN (0.05, 0.1, 0.2, or 0.5 wt%, monomer weight bases) were dissolved in THF (30 ml), respectively. Dissolved oxygen was removed from the solutions by purging with dry nitrogen for 10 min. Polymerization was carried out at 65 °C for 48 hr. After concentration by evaporation of the solvent under reduced pressure, the resulting polymer was isolated by precipitation into methanol. All resultant polymers were dried in vacuum oven at 30 °C. The chemical structures of PFPMA and Poly(PFPMA) are shown in Fig. 1.

3. Determination of M_w and T_g

Molecular weight of polymer was obtained by gel permeation chromatography (GPC) system (Waters M77251, M510, USA). The mobile phase was HPLC grade THF. Polymer solutions were 0.2 w/v% in THF and were syringe-filtered through a 0.2 μ m Teflon

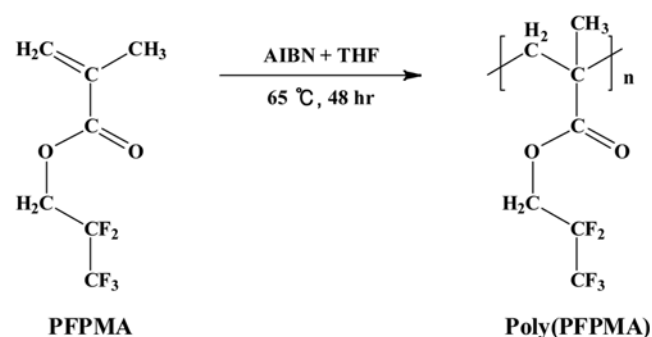


Fig. 1. Chemical structure of 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMA) and poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)].

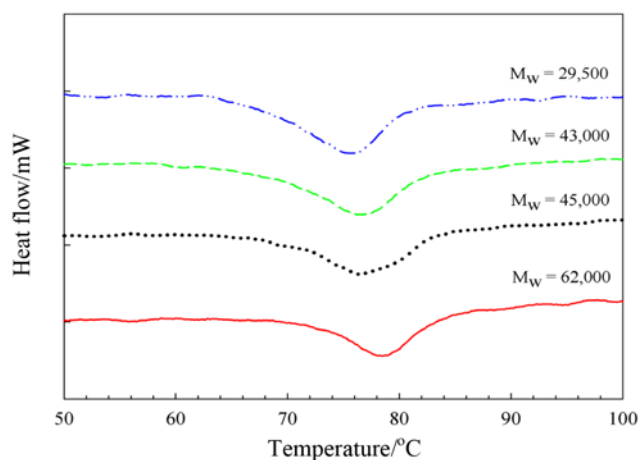


Fig. 2. Glass transition temperature with weight-average molecular weight [$M_w=62,000$, 45,000, 43,000 and 29,500] for the poly(2,2,3,3,3-pentafluoropropyl methacrylate).

Table 1. Effect of molecular weight and α , α' -azobis(isobutronitrile) [AIBN] concentration by solution polymerization of 2,2,3,3,3-pentafluoropropyl methacrylate

AIBN (wt%)	M_w	M_w/M_n	Appearance
0.05	62,000	1.13	White powder
0.10	45,000	1.35	White powder
0.20	43,000	1.36	White powder
0.50	29,500	1.78	White powder
Aldrich Co.	5,500	1.95	

* M_n : Number-average molecular weight

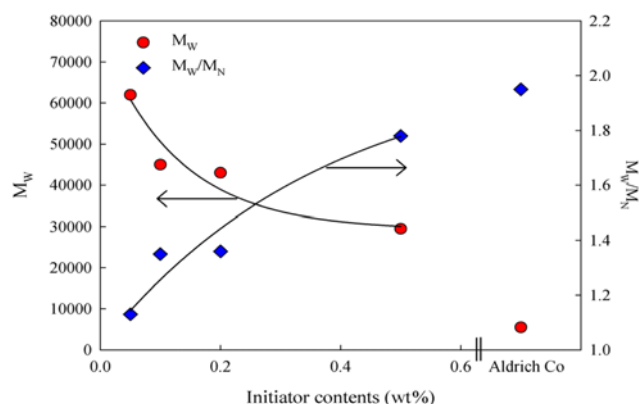


Fig. 3. Weight-average molecular weight (M_w) and polydispersity index (PDI, M_w/M_n) with initiator content (AIBN=0.05 wt%, 0.10 wt%, 0.20 wt% and 0.50 wt%) by solution polymerization of poly(2,2,3,3,3-pentafluoropropyl methacrylate).

membrane filter. One milliliter of the filtered solution was injected into the chromatograph. The flow rate of the eluent was 1.0 ml/min. From calibration curves of the injected polystyrene standard samples, the number-average molecular weight (M_n) and molecular weight distribution (MWD) of the synthesized polymers were determined. Signals from the samples were detected with differences in the refractive index. Also, samples of the Poly(PFPMA) were analyzed by using a differential scanning calorimeter (DSC, DSC-50, Shimadzu, Kyoto, Japan) to determine the glass transition temperatures (T_g). (Fig. 2) The samples (5 mg) were placed in hermetically sealed aluminum pans and determined from 30 to 200 °C at a heating rate 5 °C/min under helium. An empty pan was used as reference. Therefore, analysis for the weight-average molecular weight and appearance of AIBN concentration by solution polymerization of PFPMA are shown Table 1 and Fig. 3.

4. Experimental Apparatus and Method

Fig. 4 shows a schematic diagram of a variable-volume view cell apparatus to obtain phase behavior data at experimental high pressure [16,17]. The main components of experimental apparatus are variable-volume view cell, high-pressure generator, air bath, and borescope apparatus. This view cell is constructed with high nickel-content austenitic steel (6.2 cm O.D. \times 1.59 cm I.D., 28 cm³ working volume, fitted with a 1.3 cm thick \times 1.9 cm O.D. sapphire window) capable of operating to pressures of 2,000 bar. Typically, PFPMA monomer is loaded into the cell to within 0.002 grams using a syringe after the empty cell is purged several times with carbon dioxide and

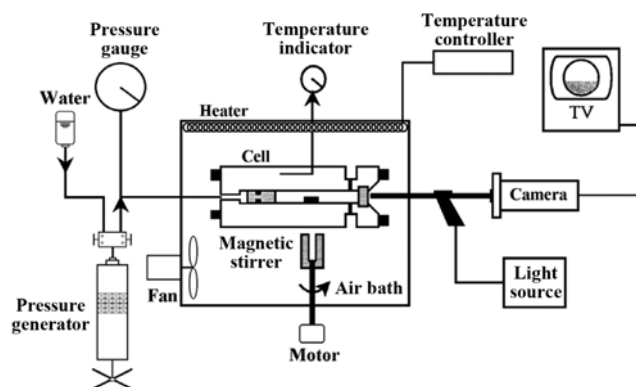


Fig. 4. Experimental apparatus of high-pressure phase behavior.

nitrogen to remove traces of air and organic matter. Carbon dioxide was added to the cell to within 0.002 gram using a high pressure cylinder.

The cloud-point data of Poly(PFPMA) in supercritical carbon dioxide and DME were obtained by the following procedures and measured for the polymer solution at a fixed polymer concentration of about 3.0 gram (about 0.3 wt%). At first, Poly(PFPMA) was loaded into the cell, and the cell was purged carefully with inert gas and carbon dioxide. Carbon dioxide was added to the cell from a high-pressure cylinder. After the carbon dioxide+Poly(PFPMA) mixture was finished, the solution was compressed to the desired operating pressure by replacing a piston fitted within the cell by using water pressed with a high pressure generator (HIP Co., model 37-5.75-60). The pressure of the mixture is measured with a Heise gauge (Dresser Ind., polymer+solvents mixture: model CM-108952, 0 to 3,450 bar, accurate to within ± 3.5 bar; carbon dioxide+monomer mixture: model CM-53920, 0 to 340 bar, accurate to within ± 0.2 bar) and high pressure generator. A magnetic bar in the cell helped the mixture to reach equilibrium rapidly.

A small correction (0.5 bar) was added to account for the pressure required to move the piston. The uncertainty in pressure measurements was 0.7 bar. The temperature of the cell was measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) accuracy of (± 0.05 °C) fixed to the inside of the cell port and displayed by a digital multimeter (Yokogawa, model 7563, accurate to $\pm 0.005\%$). The temperature of the cell was maintained to within ± 0.1 °C and measured to within ± 0.2 °C. Once the solution reached single phase, pressure was slowly decreased until the cloud point appeared. At the cloud point the solution becomes so opaque that the stirring bar is no longer visible. This procedure was repeated several times until the fluctuation of transition pressure was minimized to within 0.3 bar. The status of the inside was projected onto the monitor (Fujilink, model HT-1900WT) with a camera (Watec Corp., model WAT-202B) coupled to a boroscope (Olympus Corp., model R100-038-000-50). Light is transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator (Olympus Optical Co., model ILK-5) and at the other end to a bore-scope.

RESULTS AND DISCUSSION

1. Phase Equilibrium for the Carbon Dioxide+PFPMA Mixture

Phase behavior data for the CO₂+PFPMA system is measured

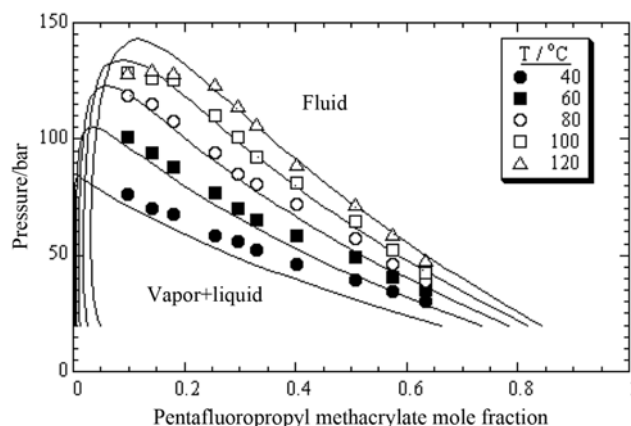


Fig. 5. Comparison of experimental data (symbol) for the carbon dioxide+2,2,3,3,3-pentafluoropropyl methacrylate system with calculated result (solid lines) obtained using the Peng-Robinson equation of state with k_{ij} and η_{ij} equal to 0.0.

and reproduced at least twice to within ± 0.2 bar and ± 0.2 °C for a given loading of the cell. The mole fractions are accurate to within ± 0.002 . The carbon dioxide+PFPMA mole fraction for the solubility isotherms at (40–120) °C have an estimated accumulated error of less than $\pm 1.0\%$.

Fig. 5 and Table 2 show the experimental pressure-composition (P–x) isotherms for carbon dioxide+PFPMA system at (40, 60, 80, 100 and 120) °C, and the range of pressures of 30–129.7 bar.

Table 2. Experimental data for carbon dioxide+2,2,3,3,3-pentafluoropropyl methacrylate [PFPMA] system. BP is a bubble point, CP is a critical point and DP is a dew point

PFPMA mole fraction	P/bar	Transition
T=40 °C		
0.097	80.0	BP
0.143	72.2	BP
0.182	67.6	BP
0.255	61.4	BP
0.298	55.9	BP
0.330	52.4	BP
0.401	49.0	BP
0.508	41.4	BP
0.575	34.3	BP
0.634	30.0	BP
0.255	61.4	BP
T=60 °C		
0.097	105.2	BP
0.143	96.4	BP
0.182	87.9	BP
0.255	78.8	BP
0.298	70.0	BP
0.330	65.3	BP
0.401	58.7	BP
0.508	49.0	BP
0.575	40.3	BP
0.634	34.4	BP

Table 2. Continued

PFPMa mole fraction	P/bar	Transition
T=80 °C		
0.097	118.5	BP
0.143	117.8	BP
0.182	107.8	BP
0.255	94.8	BP
0.298	83.1	BP
0.330	78.6	BP
0.401	71.7	BP
0.508	57.2	BP
0.575	46.2	BP
0.634	39.0	BP
T=100 °C		
0.097	128.3	CP
0.143	125.2	BP
0.182	125.5	BP
0.255	112.1	BP
0.298	100.7	BP
0.330	92.2	BP
0.401	81.2	BP
0.508	64.8	BP
0.575	52.6	BP
0.634	42.8	BP
T=120 °C		
0.097	128.6	DP
0.143	129.7	CP
0.182	128.6	BP
0.255	127.8	BP
0.298	114.5	BP
0.330	106.2	BP
0.401	89.3	BP
0.508	72.2	BP
0.575	58.8	BP
0.634	47.8	BP

The P–x isotherms shown in Fig. 5 are consistent with those expected for a type-I system [18] where a maximum occurs in the critical mixture curve. The solubility of carbon dioxide in the liquid phase decreases as temperatures shift higher under constant pressure.

Experimental results obtained in this study were correlated with the P-R EOS and MF-NLF equation. First, experimental data were modeled with P-R EOS by using mixing rule including two binary interaction parameters:

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (1)$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \quad (2)$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (3)$$

$$b_{ij} = \frac{(b_i + b_j)}{2} (1 - \eta_{ij}) \quad (4)$$

Table 3. The properties of pure components used with Peng-Robinson and multi-fluid nonrandom lattice fluid equation of state

Component	M _w	T _c /°C	P _c /bar	ω
Carbon dioxide	44.01	31.0	73.8	0.225
2,2,3,3,3-Pentafluoropropyl methacrylate	218.12	287.5	24.4	0.561

where k_{ij} and η_{ij} are binary interaction parameters that are determined by fitting P–x isotherms curves and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson [13]. These two binary interaction parameters were determined by regressing experimental data with P-R EOS. Objective function [19] (OF) of this calculation was defined by,

$$OF = \sum_i^N \left(\frac{P_{exp} - P_{cal}}{P_{exp}} \right)^2 \quad (5)$$

P_{exp} and P_{cal} are the experimental and calculated pressures, respectively. We optimized the objective function for all isotherms with the Marquardt algorithm [19]. The property of pure component for critical constants (T_c , P_c) and acentric factor for P-R EOS are listed in Table 3.

Critical temperature (T_c) and pressure (P_c) of PFPMa were estimated by using Joback method. [20] Then, boiling temperature (T_b) data of PFPMa from Joback group contribution were used [20]. Acentric factor (ω) was estimated with the Lee-Kesler method [20].

Fig. 5 represents the comparison of experimental data (symbol) and calculated P–x isotherms (solid line) at temperature of (40, 60, 80, 100 and 120) °C. We obtained $k_{ij}=0.0$ and $\eta_{ij}=0.0$ for the carbon dioxide+PFPMa system. As a result, good agreement is obtained without changing two interaction parameters.

Also, Yoo et al. [14,15] reported on a equation of state based on the two-liquid approximation of lattice-hole theory. The phase behavior experimental data in this work are modeled using the MF-NLF equation of state. [14,15] The detailed MF-NLF equation of state is not reproduced here. The process to determine the two molecular parameters for the MF-NLF equation of state is briefly described here. The two molecular parameters in the equation of state for pure component, that is, V_1^* and ε_{11} , are determined from the following two equations:

$$\varepsilon_{11}/k = E_a + E_b(T - T_0) + E_c[T \ln(T_0/T) + T - T_0] \quad (6)$$

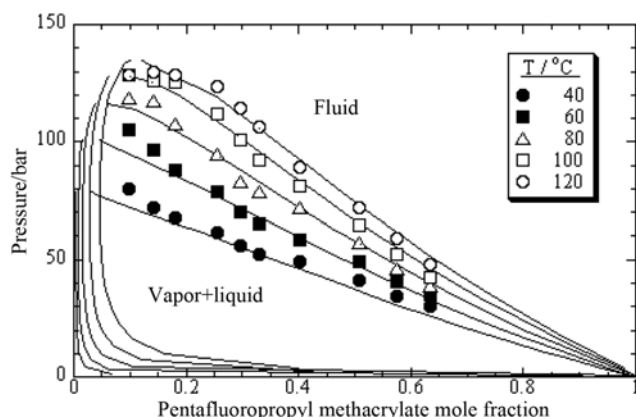
and

$$V_1^* = V_a + V_b(T - T_0) + V_c[T \ln(T_0/T) + T - T_0] \quad (7)$$

where, $T_0=25$ °C. T is the desired temperature of interest, E_a , E_b , E_c and V_a , V_b , V_c are fitted parameters. The liquid density and vapor pressure of PFPMa were obtained from Yamada & Gunn's method [20] and Antoine method [20], respectively. Table 3 lists the physical properties of carbon dioxide and PFPMa used in this work. The property of PFPMa was calculated by Joback group contribution method. [20] Thus, for pure fluids, two molecular parameters, V_1^* and ε_{11} , are determined using the calculated vapor pressure and liquid density data. The estimated coefficients for Eq. (6) and Eq. (7) are presented in Table 4 for PFPMa. For binary mixture, a temperature-independent binary interaction energy parameter, λ_{12} , is needed and

Table 4. Coefficient of energy and volume parameter for carbon dioxide and 2,2,3,3,3-pentafluoropropyl methacrylate

Component	E_a	E_b	E_c	V_a	V_b	V_c
Carbon dioxide	85.91302	-0.10298	-0.36562	34.28608	0.01428	-0.01304
2,2,3,3,3-Pentafluoropropyl methacrylate	28.75381	0.01423	10.83160	-212.1083	-0.26026	76.24109

**Fig. 6.** Comparison of experimental data (symbol) for the carbon dioxide+2,2,3,3,3-pentafluoropropyl methacrylate system with calculated result (solid lines) obtained using the MF-NLF equation of state with λ_{12} equal to 0.082.

is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{0.5}(1 - \lambda_{12}) \quad (8)$$

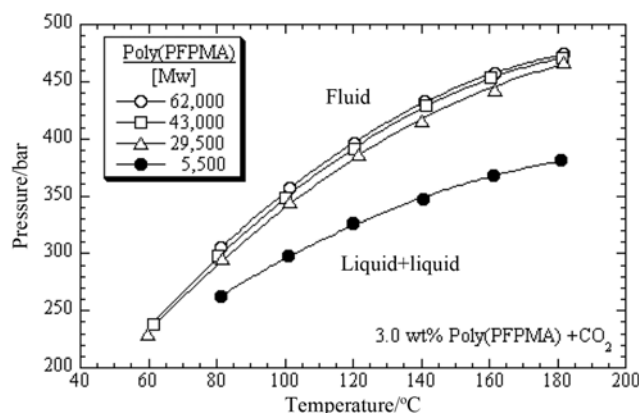
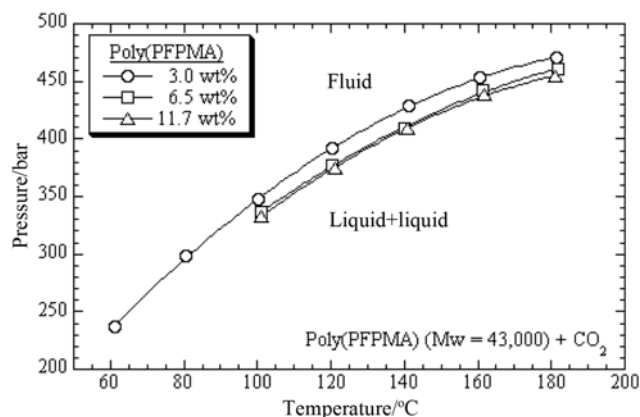
The optimum values (λ_{12}) are obtained for binary systems. We present here a calculated result of phase equilibrium of mixtures using the MF-NLF equation of state. Therefore, the optimum binary interaction energy parameter, λ_{12} , for the carbon dioxide+PFPMA system is determined from a fit of a single isotherm at 80 °C. Optimum values of λ_{12} for the carbon dioxide + PFPMA system is 0.082.

Fig. 6 shows the experimental and calculated high-pressure phase behavior of a carbon dioxide+PFPMA system at various isotherms with calculations using as optimized value of λ_{12} equal to 0.082 obtained from a fit of the 80 °C isotherm. The fit between experimental data and calculated results shows a good agreement on the whole range of PFPMA concentrations. The critical pressures predicted by MF-NLF equation of state are also in reasonable agreement at all five temperatures. The MF-NLF model reasonably predicts the transition pressures; however, the fit is satisfactory with one temperature-independent parameter.

2. Phase Behavior for the Poly(PFPMA)+Carbon Dioxide or DME System

Cloud points are measured and reproduced at least twice to within ± 2.8 bar and ± 0.2 °C. Cloud point transitions for the carbon dioxide + PFPMA mixture are measured and reproduced at least twice to within ± 0.2 bar and ± 0.2 °C.

Fig. 7 shows the pressure-temperature behavior of weight-average molecular weight (M_w) for about 3.0 wt% Poly(PFPMA) [M_w = 62,000, 45,000, 43,000, and 5,500 (Aldrich Product)]+carbon dioxide mixture. The cloud point behavior of the Poly(PFPMA)+carbon dioxide system shows typical lower critical solution temperature (LCST) curves. The phase behavior for Poly(PFPMA)+carbon dioxide system shows almost the same tendency with four pressure

**Fig. 7.** Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [M_w = 62,000, 43,000, 29,500 and 5,500]+carbon dioxide mixture. The mass fraction of polymer is about 3 wt% for each solution.**Fig. 8.** Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [M_w = 43,000]+carbon dioxide mixture. The mass fraction of polymer is about 3 wt% for each solution.

curves at a temperature range of 60–180 °C. The pressure difference of this phase behavior is probably due to M_w and glass transition temperature (T_g).

Fig. 8 shows the cloud point behavior for the binary mixture of carbon dioxide with Poly(PFPMA) content [3.0 wt%, 6.5 wt% and 11.7 wt%] for the Poly(PFPMA) [M_w = 43,000]. The cloud point curve for the Poly(PFPMA)+carbon dioxide mixture exhibits LCST-type behavior with positive slope at a pressure range of 240–470 bar and at a temperature range of 61–181 °C.

Fig. 9 shows the cloud point curves on the weight-average molecular weight (M_w = 62,000, 43,000 and 5,500) for ca. 3.0 wt% Poly(PFPMA)+DME mixture. DME has a dipole moment and polarizability. Therefore, DME is expected to be a better solvent than car-

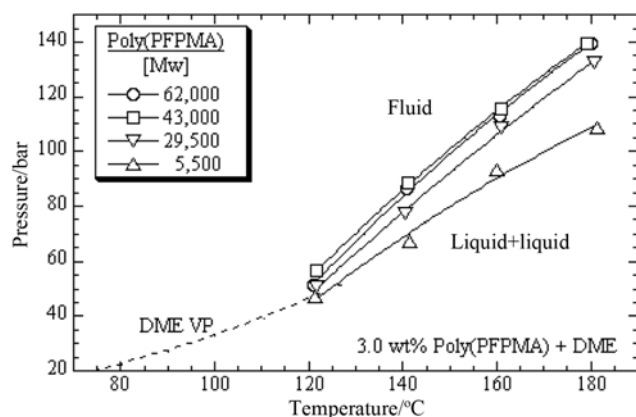


Fig. 9. Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [$M_w=62,000$, 43,000, 29,500 and 5,500]+dimethyl ether (DME) mixture. The mass fraction of polymer is about 3 wt% for each solution.

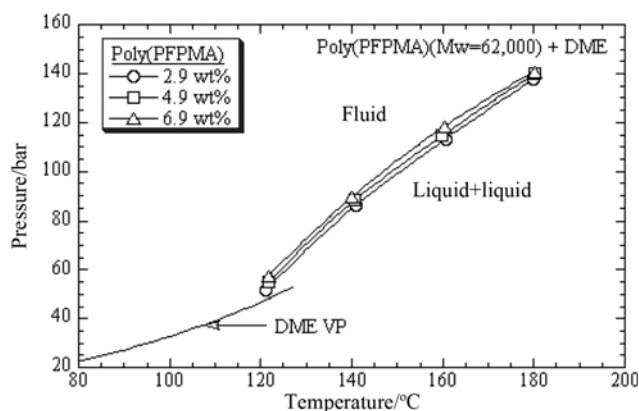


Fig. 10. Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [$M_w=62,000$]+dimethyl ether (DME) mixture. The mass fraction of polymer is about 3 wt% for each solution.

bon dioxide for Poly(PFPMA). The pressure-temperature curves in Fig. 9 are indeed at much lower pressures than those for Poly(PFPMA) in carbon dioxide. As shown in Fig. 9, phase behavior curves exhibit the LCST type a positive slope at temperatures below about 180 °C.

Fig. 10 represents the phase behavior with Poly(PFPMA) content [2.9 wt%, 4.9 wt% and 6.9 wt%] for the Poly(PFPMA) [$M_w=62,000$]+DME mixture. The cloud-point behavior of this system shows the LCST behavior with positive slope at a temperature range of 121–180 °C. Also, the pressure behavior decreases as the temperature decreases. A fluid phase (single) region exists at pressures and temperatures to the left of the LCST line, while a liquid+liquid region exists at pressures and temperatures to the right of the LCST line.

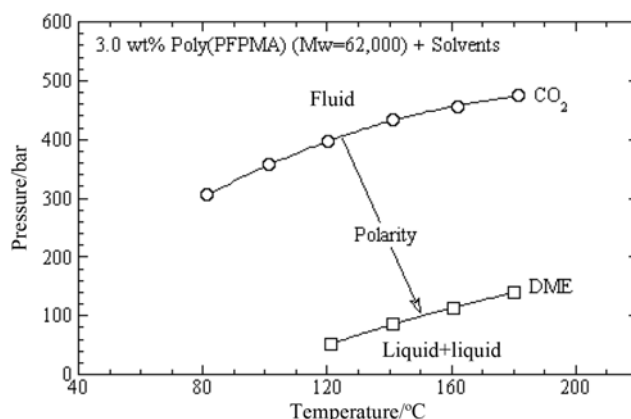


Fig. 11. Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [$M_w=62,000$] in supercritical carbon dioxide and dimethyl ether (DME). The mass fraction of polymer is about 3 wt% for each solution.

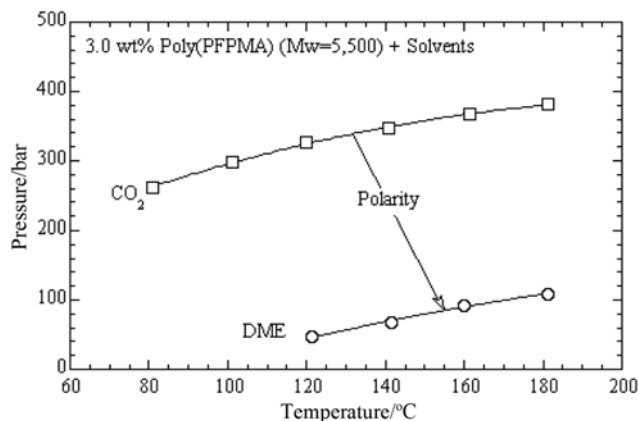


Fig. 12. Phase behavior for the poly(2,2,3,3,3-pentafluoropropyl methacrylate) [Poly(PFPMA)] [$M_w=5,500$] in supercritical carbon dioxide and dimethyl ether (DME). The mass fraction of polymer is about 3 wt% for each solution.

3. Comparison of Phase Behavior for Poly(PFPMA)+Solvents Mixture

Binary cloud-point curves are obtained for Poly(PFPMA) in supercritical carbon dioxide and DME. These data show the effect of solvent polarity on the location of the cloud-point curves. Table 5 lists the critical temperature, critical pressure, critical density, polarizability, dipole moment, and quadrupole moment for the solvents used in this study [20–22]. DME has a significant dipole moment that provides an opportunity to compare the impact of dipole interactions with quadrupole interactions found with carbon dioxide.

Fig. 11 represents cloud point curves of Poly(PFPMA) [$M_w=62,000$] synthesized in supercritical carbon dioxide and DME. The

Table 5. Critical temperatures (T_c), critical pressures (P_c), critical densities (ρ_c), polarizabilities (α), dipole moments (μ), and quadrupole moments (Q) of the solvents used in this study [20–22]

Solvents	T_c (°C)	P_c (bar)	ρ_c (g/cm ³)	$\alpha \times 10^{25}$ (cm ³)	μ (Debye)	$Q \times 10^{26}$ (erg ^{1/2} cm ^{5/2})
Carbon dioxide	31.0	73.8	0.469	26.5	0.0	–4.3
Dimethyl ether	126.8	53.0	0.258	52.2	1.3	1.2

cloud point behavior for Poly(PFPMA)+carbon dioxide and Poly(PFPMA)+DME systems exhibits LCST-type curves with a positive slope. The pressure difference between two systems is probably due to whether or not the dipole moment was in DME and carbon dioxide as shown in Table 5.

Fig. 12 shows the phase behavior for Poly(PFPMA) [$M_w=5,500$: Aldrich Co.] in supercritical carbon dioxide and DME. The phase behavior for Poly(PFPMA)+carbon dioxide and Poly(PFPMA)+DME systems represents LCST-type with a positive slope at temperature from 80 °C to 182 °C and at pressure range of 40-380 bar. Poly(PFPMA)+carbon dioxide curve is higher than Poly(PFPMA)+DME curve because carbon dioxide does not have a dipole moment, but has a quadrupole moment that is a result of the strong electronegative character of oxygen relative to carbon.

CONCLUSIONS

We measured cloud-point and bubble-point pressures for the carbon dioxide (or DME)+Poly(PFPMA) system and the carbon dioxide+PFPMA system by using a variable-volume view cell. For the carbon dioxide+PFPMA mixture, the experimental results are correlated with P-R EOS and MF-NLF equation.

For the binary system of Poly(PFPMA)+carbon dioxide, typical LCST behavior was observed between (62,000 and 5,500) with weight-average molecular weight of Poly(PFPMA). Also, phase behavior for the Poly(PFPMA) [$M_w=43,000$]+carbon dioxide mixture shows LCST behavior with positive slope between (3.0 and 11.7) wt% Poly(PFPMA). For the binary system of Poly(PFPMA)+DME, as the Poly(PFPMA) [$M_w=62,000, 43,000, \text{ and } 5,500$] molecular weight increased, cloud point pressure dramatically decreased and LCST behavior was observed at over 120 °C.

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