High Pressure Phase Behavior of Carbon Dioxide + 2,2,2-Trifluoroethyl Methacrylate and + Poly(2,2,2-trifluoroethyl methacrylate) Systems

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Pressure−composition isotherms for binary mixtures of carbon dioxide (CO_2) + 2,2,2-trifluoroethyl methacrylate (TFEMA) were investigated in a variable volume view cell at temperature from (323.2 to 353.2) K and pressure up to about 12 MPa. Phase behavior of these binary experimental data were correlated with Peng−Robinson equation of state using a van der Waals one fluid mixing rule with two adjustable parameters. The cloud points of CO_2 + poly(2,2,2-trifluoroethyl methacrylate) (poly(TFEMA)) were investigated at temperature up to 450 K and pressure up to 59.4 MPa. The CO_2 + poly(TFEMA) system showed LCST pressure behavior. The Sanchez−Lacombe lattice fluid equation of state is used to correlate the experimental cloud point data.

Introduction

2,2,2-Trifluoroethyl methacrylate (TFEMA) has features of typical methacrylate monomers and a fluorine-containing monomer. The homopolymer of TFEMA is a transparent and amorphous polymer that has excellent water repellency and stain resistance because it contains fluorine in its side chain.[1] Poly(TFEMA) is used in various coating applications because of its excellent heat and chemical resistance, low refractive index, weatherability, non-cohesiveness, water and oil repellency, and electric insulating properties.[1,2] It is easily produced by free radical polymerization using bulk, solution, and emulsion polymerization methods.[2] Recently, supercritical carbon dioxide ($scCO_2$) could be used as the polymerization medium of TFEAM and was studied as a polymerization medium replacing organic solvents.[3] When poly(TFEAM) is synthesized by the solution polymerization method, initial monomer and final polymer must be soluble in CO_2. Then, solution polymerization overcomes many of the disadvantages of the bulk polymerization.[4] CO_2 can act as the diluent and aid transfer of the heat of polymerization. CO_2 also allows easier stirring since the viscosity of the reaction mixture is decreased. Solution polymerization has advantages in thermal control and mass transfer as compared to bulk polymerization.[5] Naturally, these effects show when other organic solvents are used instead of CO_2, but many organic solvents have problems as the radical polymerization medium.[5] The radical chain transfer to solvent can become a disadvantage, and the separation of solvent after the polymerization has a problem in needing a high purity of polymer. CO_2 is an ideal solvent for the polymerization medium because it does not support any detectable chain transfer to solvent during free-radical polymerization, and it is a nonreactive process.[4] CO_2 can be removed by simple depressurization.[4,6] Another important feature of CO_2 as a polymerization medium is the plasticization effect.[3,7] The plasticization effect of ae polymer chain in CO_2 results in lowering viscosity of the polymer melt by increasing free volume between the polymer segments.[7] This plasticizing effect for a polymer can be varied with the density and pressure of CO_2.[3] Therefore, understanding and predicting the phase behavior of CO_2 + TFEMA or poly(TFEMA) are very important.

In this work, we measured pressure−composition isotherms for the binary mixture of CO_2 + 2,2,2-trifluoroethyl methacrylate (TFEMA) at temperatures from (323.2 to 353.2) K, pressure up to 12 MPa, and cloud point curve for CO_2 + poly(2,2,2-trifluoroethyl methacrylate) (poly(TFEMA)) at various temperatures. Phase behavior of the binary experimental data for the CO_2 + monomer system was correlated with the Peng−Robinson equation of state (PR EOS) with two adjustable parameters. $P-T$ isopleth curves for CO_2 + polymer was correlated with the Sanchez−Lacombe lattice fluid equation of state (Sanchez−Lacombe LF EOS).

Experimental Section

Materials. Carbon dioxide (minimum 99.99 %) was purchased from Korea Industrial Gases. 2,2,2-Trifluoroethyl methacrylate (TFEMA, minimum 99 % purity) were obtained from Aldrich and pretreated through an alumina column in order to remove inhibitor (MEHQ). Poly(TFEMA) was synthesized using the bulk polymerization method with 2,2′-azobisisobutyronitrile (AIBN, Junsei Chemical, minimum 98 %) as a initiator at 343.15 K.[3] Molecular weight and distribution of polymer was obtained by gel permeation chromatography (Waters, 600E controller) with a RI detector (Waters, 410) and three columns (Styragel HT2, HT3, HT4). THF was used as the eluent at 40 °C. Narrow MWD PMMA was used as a standard material.[3]

Apparatus and Experimental Method. Figure 1 shows a schematic diagram of a typical variable volume view cell apparatus to obtain phase behavior data at high pressure. The same equipment as our previous work was used.[8,9] The measured amount of TFEMA is loaded first before purging into the assembled cell with a syringe within ± 0.001 g. The assembled cell was purged two or three times with N_2 and CO_2 at room temperature to remove traces of air. CO_2 was then added to the cell to within ± 0.01 g using a high-pressure bomb. The CO_2

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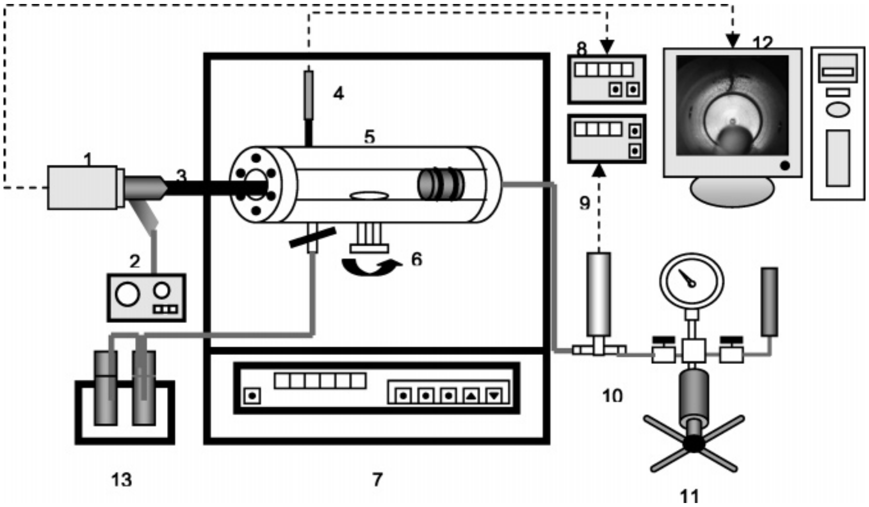

Figure 1. Schematic diagram of the experimental apparatus: 1, camera; 2, light source; 3, borescope; 4, fast response PRT; 5, view cell; 6, magnetic stirrer; 7, air bath; 8, digital thermometer; 9, digital pressure transducer; 10, pressure gauge; 11, hand pump; 12, computer monitor; 13, trap.

+ TFEMA mixture could be compressed to the desired operating pressure by moving a piston fitted within the cell using water compressed with a high-pressure generator (High Pressure Equipment Co., model 62-6-10). A magnetic stirring bar in the cell helped the mixture reach equilibrium rapidly. The pressure of the solution was obtained by measuring the pressure of the water with a digital pressure transducer (Paroscientific, model 43KR-HHT-101) and pressure indicator (Paroscientific, model 730). Temperature was measured with a PRT type thermometer (Hart, model 5622-32SR, accuracy of ± 0.045 K) fixed to surface of the cell and displayed by indicator (Hart, model 1502). At a fixed temperature, the mixture in the cell was compressed to a single phase at high pressures. The pressure was then slowly decreased until a second phase (bubble, mixture critical, or dew point) appeared. This was repeated several times until the fluctuation of pressure at phase transition was minimized (± 0.03 MPa). The inside of the cell was projected onto the computer monitor using a camera (Veltek International Inc., model CVC5520) with a borescope (Olympus Corp., model R100-038-000-50).

The cloud point data of CO_2 + polymer systems were obtained using a device that could be operated at higher pressure.[8] The typical elements of this device were the same that described in Figure 1. In detail, a high-pressure generator (High Pressure Equipment Co., model 37-5.75-60), a Heise gauge (Dresser Industries, Heise model CM-108952, accurate to within ± 0.35 MPa), and a platinum resistance thermal device (RTD) (Thermometrics Corp., Class A accuracy) connected to a digital multimeter (Yokogawa, model 7563, accurate to within ± 0.005 %) were used. The pressure of the polymer solution was determined by measuring the pressure of the water with the Heise gauge. Cloud points were measured at least twice at each temperature and were typically reproducible to within ± 0.5 MPa. A small correction (0.1 MPa) was added for the pressure needed to move the piston.[8] The temperature of the cell was maintained to within ± 0.2 K and measured to within ± 0.2 K with a thermometer placed in a thermowell on the surface of the cell. Cloud points data were measured at a fixed polymer concentration in solution. A typical experimental procedure was same as the case of CO_2 + monomer system. Initially polymer was loaded into the cell, and the cell was purged with inert gas and carbon dioxide carefully. CO_2 was added to the cell using a high-pressure bomb. After finishing the injection, the CO_2 + polymer mixture was compressed to the desired operating pressure using a high-pressure generator. Once the solution reached one phase, pressure was slowly decreased until the cloud point appeared. Cloud point was defined as the pressure at which it was no longer possible to visually observe the stirring bar.[8]

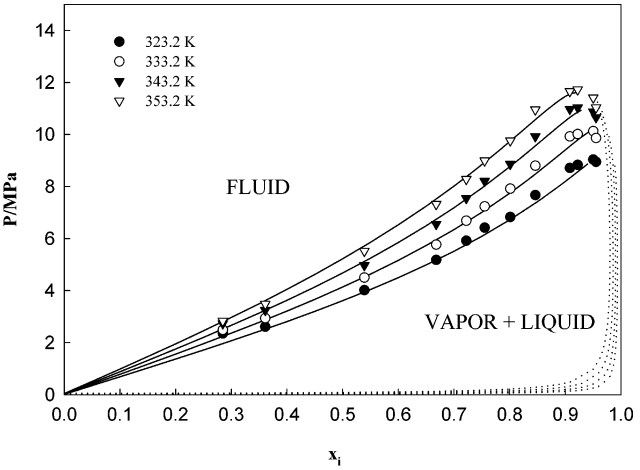

Figure 2. Calculation result for CO_2 + 2,2,2-trifluoroethyl methacrylate system using Peng−Robinson equation of state with $k_{ij} = -0.0258$ and $h_{ij} = -0.0234$: ●, 323.2 K; ○, 333.2 K; ▼, 343.2 K; ▽, 353.2 K.

Results and Discussion

(1) CO_2 + TFEMA System. Figure 2 and Table 1 show pressure−composition isotherms for CO_2 + TFEMA system at (323.2, 333.2, 343.2, and 353.2) K. Experimental data obtained in this study were modeled with PR EOS using van der Waals one fluid mixing rule[10] including two binary interaction parameters:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{1}$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}(1 - k_{ij}) \tag{3}$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{4}$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2}(1 - \eta_{ij}) \tag{5}$$

Table 1. Experimental Data for the CO_2 (1) + 2,2,2-Trifluoroethyl Methacrylate (2) System

T/K	x_1	P/MPa	transition[a]	T/K	x_1	P/MPa	transition[a]
323.2	0.285	2.35	BP	323.2	0.801	6.83	BP
	0.361	2.61	BP		0.846	7.67	BP
	0.539	4.02	BP		0.908	8.71	BP
	0.668	5.18	BP		0.922	8.83	BP
	0.722	5.92	BP		0.950	9.37	BP
	0.755	6.42	BP		0.955	8.95	DP
333.2	0.285	2.49	BP	333.2	0.801	7.92	BP
	0.361	2.94	BP		0.846	8.80	BP
	0.539	4.50	BP		0.908	9.92	BP
	0.668	5.77	BP		0.922	10.02	BP
	0.722	6.68	BP		0.950	10.13	BP
	0.755	7.24	BP		0.955	9.86	DP
343.2	0.285	2.73	BP	343.2	0.801	8.86	BP
	0.361	3.25	BP		0.846	9.93	BP
	0.539	4.97	BP		0.908	10.98	BP
	0.668	6.56	BP		0.922	11.03	BP
	0.722	7.55	BP		0.950	10.88	DP
	0.755	8.21	BP		0.955	10.66	DP
353.2	0.285	2.83	BP	353.2	0.801	9.76	BP
	0.361	3.48	BP		0.846	10.96	BP
	0.539	5.52	BP		0.908	11.66	BP
	0.668	7.32	BP		0.922	11.73	CP
	0.722	8.28	BP		0.950	11.42	DP
	0.755	8.99	BP		0.955	11.03	DP

[a] BP, bubble point; CP, mixture critical point; DP, dew point.

Table 2. Boiling Temperature, Critical Constants, and Acentric Factor[12]

component	T_b/K	T_c/K	P_c/MPa	ω
CO_2		304.10	7.38	0.225
TFEMA	380.2	541.1	2.91	0.477

These two binary interaction parameters were determined by regressing experimental data with PR EOS. The objective function (OBF) and the root mean squared relative deviation (RMSD) of this calculation were defined as follows:

$$\mathrm{OBF} = \sum_{i}^{N} \left(\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right)^2 \tag{6}$$

$$\mathrm{RMSD} = \sqrt{\frac{\mathrm{OBF}}{\mathrm{ND}}} \times 100 \tag{7}$$

ND in eq 7 means the number of data points. We optimized objective function for all isotherms with the Marquardt algorithm.[11] Critical constants (T_c, P_c) and acentric factor for PR EOS are listed in Table 2. Critical temperature (T_c) and pressure (P_c) of TFEMA were estimated with the method of Wilson and Japerson.[12] Then, boiling temperature (T_b) data of TFEMA from F-Tech Inc. were used.[1] Acentric factor (ω) was estimated with the Lee−Kesler method.[12] Figure 2 represents a comparison of experimental data (symbol) and calculated pressure−composition isotherms (solid line) at (323.2, 333.2, 343.2, and 353.2) K. We obtained $k_{ij} = -0.0258$, $\eta_{ij} = -0.0234$, and RMSD = 3.87 % for the CO_2 + TFEMA system. With two binary interaction parameters, good correlation results were obtained.

(2) CO_2 + Poly(TFEMA) System. Figure 3 and Table 3 show the pressure−temperature behavior for poly(TFEMA) + CO_2. The cloud point behavior of the CO_2 + poly(TFEMA) system shows typical LCST curves. Poly(ethyl methacrylate) (PEMA), which has a similar structure in comparison with poly(TFEMA), does not dissolve in CO_2 to temperature of 523 K and pressure of 250 MPa.[13] Poly(TFEMA) with hydrogen in the backbone group of PEMA is substituted with fluorine and dissolves in CO_2 at temperatures under 450 K and pressures under 59.4 MPa.

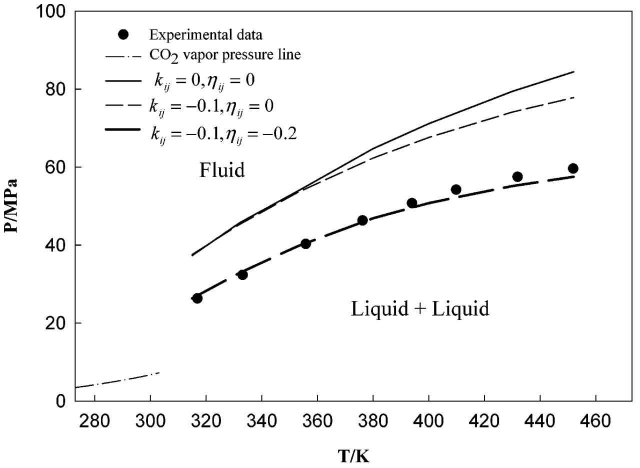

Figure 3. Calculation results for CO_2 + poly(2,2,2-trifluoroethyl methacrylate) system using Sanchez−Lacombe LF EOS with the binary interaction parameters: ●, this work.

Table 3. Experimental Cloud Point Data for the CO_2 (1) + Poly(2,2,2-trifluoroethyl methacrylate) (2) System

poly(TFEMA)/wt %	T/K	P/MPa	transition[a]
3.91	316.9	26.31	CP
	333.2	32.34	CP
	355.8	40.27	CP
	376.2	46.31	CP
	394.0	50.74	CP
	409.8	54.20	CP
	431.9	57.51	CP
	451.9	59.62	CP

[a] CP, cloud point.

The Sanchez−Lacombe LF EOS[14,15] is used to model the experimental cloud point data for the CO_2 + poly(TFEMA) system.

According to the Lattice Fluid (LF) theory, the Sanchez−Lacombe LF EOS is composed of a van der Waals type attractive term and a lattice−gas repulsive term, which can be shown in its reduced form as

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \tilde{\rho}\left(1 - \frac{1}{r}\right)\right] = 0 \tag{8}$$

Then, the reduced temperature, pressure, volume, and density are defined as

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*} = \frac{1}{\tilde{v}} = V^*/V \tag{9}$$

$$T^* = \epsilon^*/R, \quad P^* = \epsilon^*/\nu^*, \quad V^* = N(r\nu^*), \quad \rho^* = M/(r\nu^*) \tag{10}$$

$$\nu^* = \sum_{i=1}\sum_{j=1} \Phi_i \Phi_j v_{ij}^*, \quad v_{ij}^* = \frac{v_{ii}^* + v_{jj}^*}{2}(1 - \eta_{ij}),$$

$$\Phi_i = \frac{m_i}{\rho_i^*\ v_i^*} \Bigg/ \sum_{j=1} \frac{m_j}{\rho_j^*\ v_j^*} \tag{11}$$

$$\epsilon^* = \frac{1}{v^*}\sum_{i=1}\sum_{j=1} \Phi_i \Phi_j \epsilon_{jj}^* v_{ij}^*, \quad \epsilon_{ij}^* = \sqrt{\epsilon_{ii}^*\ \epsilon_{jj}^*}(1 - k_{ij}) \tag{12}$$

where ϵ^* is the mer−mer interaction energy, ν^* is the close-packed molar volume of mer, M is the molecular weight, N is the number of molecules, r is the number of sites (mers) a molecule occupies in the lattice, and R is the universal gas constant.[16]

Table 4. Sanchez−Lacombe LF EOS Characteristic Parameters for CO_2 and Poly(TFEMA)

component	M_w/PDI[a]	T^*/K	P^*/MPa	ρ^*/kg·m^{-3}
CO_2	44.01	305.00	574.50	1510.00
poly(TFEMA)	268 000/1.63	600.03	441.04	1392.63

[a] Molecular weight and distribution of poly(TFEMA) are determined by GPC (gel permeation chromatography).

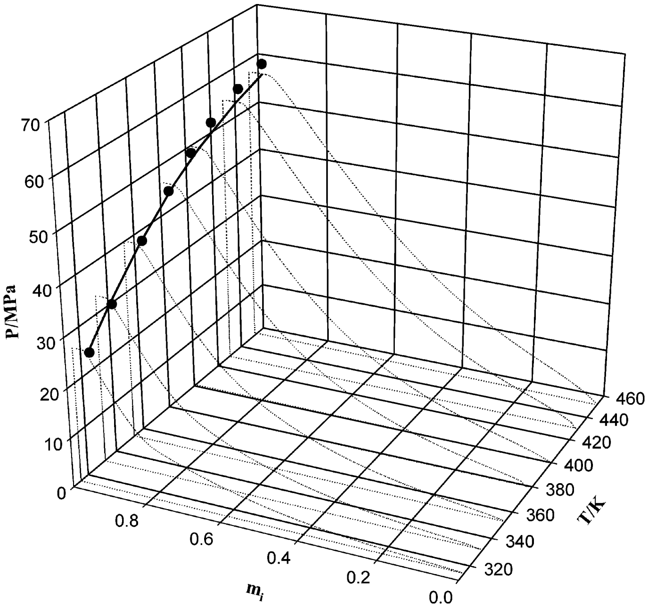

Figure 4. $p-x-T$ diagram for CO_2 + poly(2,2,2-trifluoroethyl methacrylate) system: ●, experimental cloud point data; dotted line, predicted VLE line for CO_2 + poly(TFEMA) system using Sanchez−Lacombe LF EOS with the binary interaction parameters ($k_{ij} = -0.1$ and $h_{ij} = -0.2$); full line, estimated critical line for CO_2 + poly(TFEMA) system, m_i is mass fraction.

For high polymers, eq 8 simplifies to (r(number of segments) = ∞):[17]

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}] = 0 \qquad (13)$$

This equation can be written alternatively as[17]

$$\tilde{\rho} = 1 - \exp\left[-\tilde{\rho} - \frac{\tilde{P}}{\tilde{T}} - \frac{\tilde{\rho}^2}{\tilde{T}}\right] \qquad (14)$$

This equation form can be solved numerically for a given T and P. Then, LF scaling constants (T^*, P^*, and ρ^*) are obtained according to the group contribution method for the polymers.[17]

LF scaling constants for poly(TFEMA) are determined from first-order functional groups, second-order groups, and their contributions for the LF EOS parameters for polymer liquids. Table 4 shows Sanchez−Lacombe LF EOS scaling constants for poly(TFEMA) obtained from group contribution method and CO_2 from reference data.[17,18] Two adjustable binary interaction parameters, k_{ij} and η_{ij}, are used to obtain the better results. k_{ij} is a mixture parameter that accounts for specific binary interactions between components i and j in solution, and η_{ij} corrects for molar volume deviations from the arithmetic mean.[16]

Figure 3 depicts the cloud points of poly(TFEMA) in CO_2 and predicted results with the Sanchez-Lacombe LF EOS using one or two adjustable binary interaction parameters. Figure 4 shows the predicted results of $p-x-T$ diagrams for the CO_2 + poly(TFEMA) system with two binary interaction parameters. Figures 3 and 4 show a good agreement between experimental cloud point and prediction of the Sanchez−Lacombe LF EOS with two binary interaction parameters.

Conclusions

We measured pressure−composition isotherms for CO_2 + TFEMA systems at temperatures from (323.15 to 353.15) K and pressure up to 12 MPa. These results were correlated with PR EOS with two adjustable parameters. We obtained good correlation results. RMSD (%) for the CO_2 + TFEMA system was 3.87 %. We measured cloud point pressures for the system of CO_2 + poly(TFEMA) using the variable volume cell at temperature up to 450 K and pressure up to 59.4 MPa. These experimental results were correlated with the Sanchez−Lacombe LF EOS. The experimental data and predicted results of the CO_2 + monomer or polymer system can be used in the polymerization of TFEMA + CO_2 under the solution state and further processing.

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