Cloud point behavior for poly(isodecyl methacrylate)+supercritical solvents+cosolvent and vapor-liquid behavior for CO_2+isodecyl methacrylate systems at high pressure

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Abstract−Experimental cloud-point data of binary and ternary mixtures for poly(isodecyl methacrylate) [P(IDMA)] in supercritical carbon dioxide, dimethyl ether (DME), propane, propylene, butane and 1-butene have been studied experimentally using a high pressure variable volume view cell. These systems show the phase behavior at temperature of 308 K to 473 K and pressure up to 255 MPa. The cloud-point curves for the P(IDMA)+CO_2+isodecyl methacrylate (IDMA) are measured in changes of the pressure-temperature (P-T) slope, and with cosolvent concentrations of 0-60.1 wt%. Also, experimental data of phase behaviors for IDMA in supercritical carbon dioxide is obtained at temperature range of 313.2-393.2 K and pressure range of 5.8-22.03 MPa. The experimental results were modeled with the Peng-Robinson equation of state. The location of the P(IDMA)+CO_2 cloud-point curve shifts to lower temperatures and pressures when DME is added to P(IDMA)+CO_2 solution. The P(IDMA)+C_4 hydrocarbons cloud-point curves are ca. 16.0 MPa lower pressures than the P(IDMA)+C_3 hydrocarbons curves at constant temperature.

Key words: High Pressure Phase Behavior, Poly(isodecyl methacrylate), Isodecyl Methacrylate, Supercritical Fluid Solvents, Cloud-point

INTRODUCTION

Methacrylate-based polymers are widely used in modern plastic technology [1]. Methacrylate monomers and polymers are used mainly for a variety of applications such as prostheses, contact lenses, photopolymer printing plates, adhesives, coatings, contact lenses, dentistry and other industrial applications [2,3].

Phase behavior data of binary and ternary mixture for polymers in supercritical fluid (SCF) solvents have played an important role in most polymerization process development, chemical separation processes and related industrials [4-6]. These phase behavior measurements require an understanding of the chemistry and physics that control the location and the shape of the phase behavior [7]. Also, thermodynamic behavior of phase equilibrium for small molecules hydrocarbon+SCF solvents is required for practical use in separation processes, polymerization conditions and chemical reactions [8,9].

The phase behavior experimental data of binary and ternary mixtures for poly(butyl methacrylate) and poly(ethyl methacrylate) in supercritical carbon dioxide+cosolvent were reported by Byun and McHugh [10]. Lora and McHugh [11] studied the phase behavior of poly(methyl methacrylate)+CO_2+methyl methacrylate system at the temperature range of 293.2 to 443.2 K and pressure up to 250.0 MPa. Recently, Byun and McHugh [12] reported the phase behavior experimental data for poly(isopropyl methacrylate)+supercritical solvents+isopropyl methacrylate system at below 443.2 K and pres-

sure up to 250.0 MPa using static phase behavior apparatus. Also, the high pressure phase behavior of binary system for CO_2+(straight alkyl and branch isoalkyl) methacrylate mixture is reported at several temperatures [10,12]. However, the phase behavior of CO_2+monomer system is very important for determining initial polymerization condition because particle formation and particle size distribution of polymer are directly affected.

The primary focus of this work is to determine the impact of IDMA and dimethyl ether (DME) cosolvent on the phase behavior of P(IDMA) in supercritical CO_2, and of solubility of binary mixture for P(IDMA) in supercritical propane, propylene, butane, 1-butene and DME. The P(IDMA)+solvents cloud-point curves are located at the pressure-temperature (P-T) space by effect of solvent polarity. Table 1 lists the critical temperature (T_c), critical pressure (P_c), polarizability (α), dipole moment (μ), and quadrupole moment (Q) for the solvents and cosolvents used in this study [13-16]. Propane and propylene have similarity in critical properties and polarizabilities, but propylene, with a double bond, has a significant quadrupole moment. Hence, it is possible to determine the impact of quadrupole interactions, essentially independent of dispersion interactions by

Table 1. The properties of critical temperature, critical pressure, polarizability, dipole moment, and quadrupole moment of the SCFs solvents used in this study [13-16]

Solvents	T_c/K	P_c/MPa	$\alpha \times 10^{25}$/cm³	μ/D	Q/esu-cm²
CO_2	304.1	7.38	26.5	0.0	−4.3
Propane	369.85	4.25	62.9	0.1	1.2
Propylene	365.05	4.62	62.6	0.4	2.5
Butane	425.25	3.80	81.4	0.0	
1-Butene	419.55	3.97	82.4	0.3	2.5
Dimethyl ether	399.95	5.30	52.2	1.3	

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comparing the cloud-point curves for each of these pairs of C_3 hydrocarbons and C_4 hydrocarbons solvents. Likewise, the comparison of propane and propylene, or butane and 1-butene yields information on the effect of solvent size, and hence, polarizability effect on the phase behavior. DME has a significant dipole moment that provides an opportunity to compare the impact of dipole interactions with quadrupole interactions found with the alkenes and with CO_2.

However, P(IDMA) is a weak polar; the addition of IDMA to CO_2 provides enhanced polar interaction between P(IDMA) and the mixed solvent that is expected to lead to a decrease in cloud-point temperature and pressure [10,12]. This study complements the work presented in previous several papers [6,10,11,17,18], which describe the effect of cosolvent on the solubility of polymers in supercritical CO_2. Given that CO_2 has been considered a desirable reaction medium for free radical polymerization [19], the phase behavior for ternary mixture of P(IDMA)+CO_2+IDMA system provides information needed on the region where homogeneous IDMA polymerization can occur in the presence of excess monomer. The second focus of this work is to determine the high pressure phase behavior of the CO_2+IDMA system since these data are not available in the literature. The experimental knowledge for obtaining CO_2+IDMA data is to present whether CO_2 and IDMA form multiple phase in the pressure-temperature-composition regions explored in the P(IDMA)+CO_2+IDMA mixtures. The experiment results for CO_2+IDMA mixture are modeled with the Peng-Robinson equation of state.

EXPERIMENTAL SECTION

1. Materials

Poly(isodecyl methacrylate) [P(IDMA)] (M_w=165,000; T_g=232.2 K; CAS RN 37200-12-7) and isodecyl methacrylate (IDMA) (>95% purity; CAS RN 29964-84-9) used in this work were obtained from Scientific Polymer Products, Inc. and used as received. Since the P(IDMA) was supplied in a toluene solution, the polymer solution was placed under vacuum for at least 10 hrs by the Rotary Evaporator (Tamato Scientific Co., model RE-47) to remove toluene in it. Carbon dioxide (99.8% min. purity) was obtained from Daesung Industrial Co., Propane (98% purity) from LG Gas (E1), Propylene (99.6% purity), Butane (97.0% purity), 1-butene (99.5% purity) and dimethyl ether (DME) (99.5% purity) from Yeochun NCC Co. and used as received.

2. Equipment and Procedure

The cloud-point curves and vapor-liquid phase equilibria data were obtained with a high-pressure, variable-volume cell described in detail elsewhere [12,20]. Cloud-points are measured for the polymer solutions at a fixed P(IDMA) concentration of 5.0±1.0 wt%, which is typical of the concentrations, used for polymer+SCF solvents studies [18]. Polymer was loaded into the cell to within ±0.002 g and then the cell was purged with nitrogen followed by CO_2 to ensure that all of the air and organic matter was removed. The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-108952, 0-345.0 MPa, accurate to ±0.35 MPa; model CM-53920, 0-34.0 MPa, accurate to ±0.03 MPa) and with an internal piston displaced with water in a high-pressure generator (HIP Inc., model 37-5.75-60). The temperature in the cell was measured with a platinum-resistance thermometer (Thermometrics Corp., Class

A) connected to a digital multimeter (Yokogawa, model 7563, accurate to within ±0.005%). The system temperature was typically maintained to within ±0.20 K below 473 K. The mixture inside the cell was viewed on a video monitor with a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. The solution within the cell was contained between a sapphire window (1.9 cm thick×1.9 cm O.D) and a floating steel piston, both sealed with elastomeric o-rings.

Liquid IDMA was injected into the cell to within ±0.002 g by using a syringe and CO_2 was transferred into the cell gravimetrically to within ±0.004 g by using a high-pressure bomb. Cloud points were measured and reproduced at least twice to within ±0.28 MPa

Table 2. Experimental cloud-point data for the poly(isodecyl methacrylate) [P(IDMA)]+CO_2+isodecyl methacrylate (IDMA) system

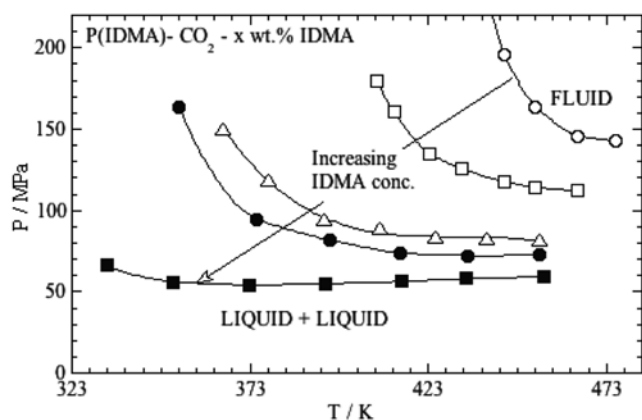| T/K	P/MPa
5.4 wt% P(IDMA)+0.0 wt% IDMA	
438.2	255.15
444.3	195.52
453.3	163.62
465.0	145.69
475.7	142.76
6.2 wt% P(IDMA)+6.0 wt% IDMA	
408.6	179.48
413.4	160.52
423.5	134.66
432.5	125.69
444.6	117.76
453.1	114.31
465.0	112.24
6.5 wt% P(IDMA)+16.3 wt% IDMA	
365.6	150.17
378.2	118.28
393.8	93.93
409.5	89.14
425.0	83.62
439.5	82.41
454.3	81.55
6.6 wt% P(IDMA)+28.0 wt% IDMA	
353.2	163.62
375.0	94.31
395.4	81.90
415.4	73.62
434.2	72.24
454.5	72.93
6.5 wt% P(IDMA)+45.5 wt% IDMA	
332.8	66.21
351.6	56.04
372.7	54.07
394.2	55.00
415.6	56.38
433.8	58.10
455.4	59.24

Fig. 1. Experimental cloud-point curves for the poly(isodecyl methacrylate) [P(IDMA)]+CO_2+isodecyl methacrylate (IDMA) system with different IDMA concentrations. The polymer concentration is ca. 5 wt% for each solution. ○, 0.0 wt%; □, 6.0 wt%; △, 16.3 wt%; ●, 28.0 wt%; ■, 45.5 wt%.

Table 3. Experimental Cloud-point, Bubble-point and Liquid-liquid-vapor Data for the poly(isodecyl methacrylate) [P(IDMA)] +CO_2+isodecyl methacrylate (IDMA) system

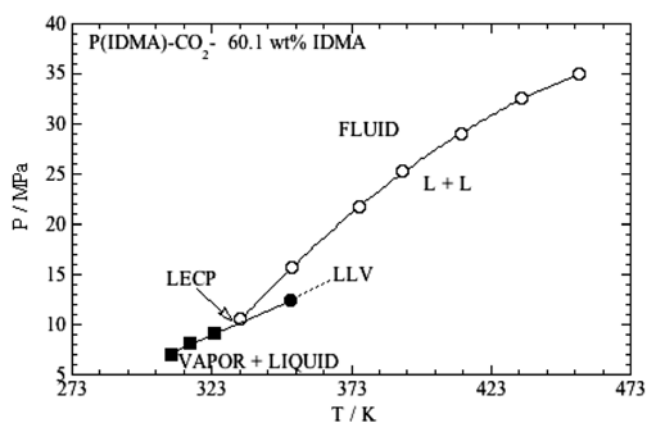| T/K	P/MPa	Transition
5.0 wt% P(IDMA)+60.1 wt% IDMA		
Cloud-point transition		
333.3	10.52	CP
351.9	15.69	CP
376.0	21.72	CP
391.6	25.35	CP
412.2	29.00	CP
434.2	32.59	CP
454.6	35.00	CP
Bubble-point transition		
308.6	7.07	BP
415.3	8.10	BP
323.8	9.14	BP
Liquid-liquid-vapor transition		
351.1	12.40	LLV

Fig. 2. Impact of 60.1 wt% isodecyl methacrylate[IDMA] monomer (on a polymer-free basis) on the phase behavior of the poly(isodecyl methacrylate) [P(IDMA)]+CO_2 system. ○, fluid→liquid+liquid transition; ■, fliud→liquid+vapor transition; ●, liquid+liquid→liquid₁+liquid₂+vapor (LLV) transition; ------, suggested extension of the LLV line.

and ±0.30 K. Bubble-, dew-, and critical-point transitions for the IDMA+CO_2 mixtures were measured and reproduced at least twice to within ±0.03 MPa and ±0.20 K. Mole fractions were accurate to ±0.002.

The polymer+solvent+monomer mixture in the cell was heated to the desired temperature, and pressurized until a single phase was achieved. The mixtures were maintained in the one-phase region at the designed temperature for at least 30-40 min so that the cell could reach thermal equilibrium. The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution.

EXPERIMENTAL RESULTS

1. Phase Behavior of P(IDMA)+CO₂+IDMA System

Table 2 and Fig. 1 show the phase behavior of the P(IDMA)+ CO_2+x wt% IDMA mixture. The P(IDMA) does dissolve in pure CO_2 at a temperature of 475 K and pressure of 255 MPa. The cloud-point curve of the P(IDMA)+CO_2 mixture had a upper critical solution temperature (UCST) type behavior with negative slope at pressure up to 255 MPa and at temperatures between 438 and 475 K. The sharp rise of the cloud-point pressure with decreasing temperatures is attributed to the increase of solvent+solvent interactions over polymer+solvent interactions. At temperature below 433 K, CO_2 exhibits the enhanced self-interactions, due to its quadrupole moment, that outweigh P(IDMA)+CO_2 cross interaction. However, increasing pressure in this temperature range does not help P(IDMA) dissolve in quadrupole CO_2 leading to phase separation of the polymer+solvent system. [21] With 6.0 wt% IDMA added to the solution, the cloud-point curve exhibits UCST type phase behavior with negative slope. At temperatures greater than 433 K, the cloud-point curve is shifted to moderately lower pressures, more likely than due to the decrease in the free volume difference between polymer and mixed solvent. With 16.3 and 28.0 wt% IDMA in solution, the cloud-point pressure curve shows the negative slope at pressures from 73 MPa to 163 MPa as the temperature decreases from 453 K to 353 K. If 45.5 wt% IDMA is added to the solution, the cloud-point curve

shows a change from positive slope to negative slope. The cloud-point pressure remains virtually constant at ca. 58 MPa at low pressures over a temperature range from 333 to 455 K. When 60.1 wt% IDMA is added to the P(IDMA)+CO_2 solution, the cloud-point curve shown in Table 3 and Fig. 2 takes on the appearance of a positive slope. At 423 K, the phase boundary has shifted to lower pressure as the concentration of IDMA increases. The P(IDMA)+CO_2+60.1 wt% IDMA phase behavior curve intersects a liquid→liquid+vapor (LV) curve at ca. 333 K and ca. 10.0 MPa. A liquid and vapor phase coexist at pressures below this curve, and the LV curve is expected to switch to a liquid₁+liquid₂+vapor (LLV) curve at temperatures greater than ca. 333 K. The initial slope of the P(IDMA)+CO_2+IDMA curve at the lowest pressures is ca. 2.6 MPa/K. The results obtained in this study demonstrate clearly that it is possible to obtain a single phase that extends over a large temperature range at modest pres-

sures if sufficient amounts of free methacrylate monomer are added to the solution.

Fig. 3 shows the comparison of experimental cloud-point curves for mixtures of P(IDMA)+ca. 6 wt% IDMA and poly(decyl methacrylate) (P(DMA))+ca. 6 wt% decyl methacrylate [18], both in supercritical CO_2. Although the addition of cosolvent in each of these mixtures makes it difficult to definitively rationalize the ordering of the two cloud-point curves, the trends exhibited by these curves are similar to those described for the poly(isodecyl acrylate)+CO_2 and poly(decyl acrylate)+CO_2 curves discussed by Byun et al. [22]. The cloud-point curve for P(DMA) with a straight chain alkyl tail is located at higher temperatures than the curve for P(IDMA) with a branched isoalkyl tail, but, in this case, only by ca. 10 K at a fixed pressure of 160 MPa. We suspect that P(DMA) dissolves at higher temperatures because the decyl side groups shield CO_2 from the methacrylate group more than an isodecyl group does.

Fig. 4 shows the comparison of cloud-point curves for P(IDMA) and poly(isopropyl methacrylate) [P(IPMA)] [12] in supercritical
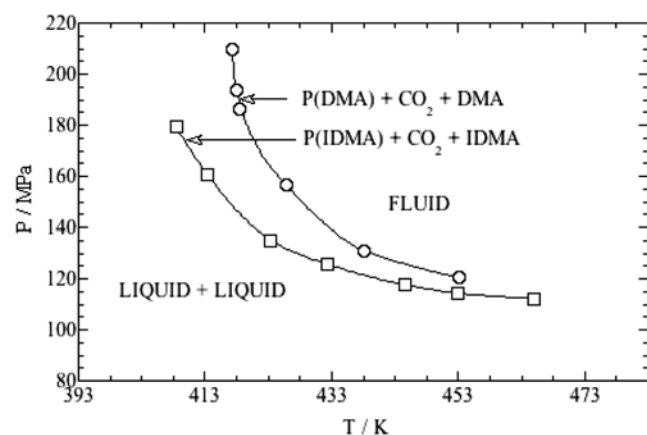

Fig. 3. Comparison of experimental cloud-point curves for poly(isodecyl methacrylate) [P(IDMA)] and poly(decyl methacrylate) [P(DMA)] [18] in supercritical CO_2. The polymer concentrations is ca. 5 wt% and the cosolvent concentrations are also at ca. 6 wt% for both solutions.
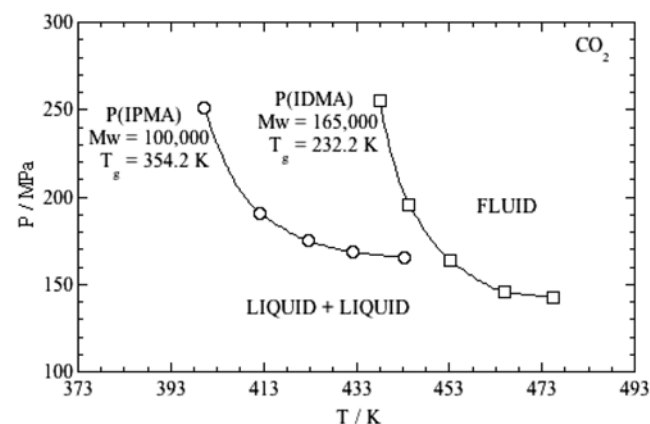

Fig. 4. Comparison of experimental cloud-point curves for poly(isodecyl methacrylate) [P(IDMA)] and poly(isopropyl methacrylate) [P(IPMA)] [12] in supercritical CO_2. The polymer concentration is ca. 5 wt% for each solution.

CO_2. As shown in Fig. 4, we presented the weight-average molecular weight (M_w) and glass transition temperature (T_g) of the poly-

Table 4. Experimental data for the CO_2+isodecyl methacrylate system

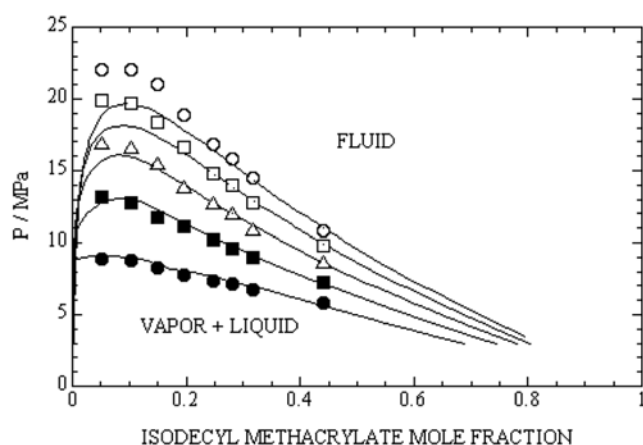| Mole fraction of the isodecyl methacrylate	P/MPa	Transition
T=313.2 K		
0.051	8.86	B.P
0.103	8.73	B.P
0.149	8.28	B.P
0.195	7.81	B.P
0.248	7.31	B.P
0.281	7.19	B.P
0.317	6.70	B.P
0.442	5.84	B.P
T=333.2 K		
0.051	13.21	B.P
0.103	12.80	B.P
0.149	11.76	B.P
0.195	11.14	B.P
0.248	10.21	B.P
0.281	9.56	B.P
0.317	8.96	B.P
0.442	7.20	B.P
T=353.2 K		
0.051	16.91	C.P
0.103	16.62	B.P
0.149	15.50	B.P
0.195	13.86	B.P
0.248	12.77	B.P
0.281	12.00	B.P
0.317	10.90	B.P
0.442	8.69	B.P
T=373.2 K		
0.051	19.88	D.P
0.103	19.69	B.P
0.149	18.40	B.P
0.195	16.69	B.P
0.248	14.79	B.P
0.281	13.97	B.P
0.317	12.72	B.P
0.442	9.83	B.P
T=393.2 K		
0.051	22.02	D.P
0.103	22.03	C.P
0.149	21.00	B.P
0.195	18.93	B.P
0.248	16.84	B.P
0.281	15.83	B.P
0.317	14.45	B.P
0.442	10.86	B.P

Fig. 5. Comparison of CO₂+isodecyl methacrylate experimental data (symbols) with calculations (solid lines) obtained using the Peng-Robinson equation of state with k_{ij}=0.093 and η_{ij}= −0.015. ●, 313.2 K; ■, 333.2 K; ○, 353.2 K; □, 373.2 K; △, 393.2 K.

mers. The M_w of P(IDMA) is 1.6 times greater than that of P(IPMA) which should cause the P(IDMA) cloud-point curve to be at higher pressures than the P(IPMA) curve. Also, comparing the cloud-point curves of P(IDMA) and P(IPMA) shows that the cloud-point pressure increases smoothly with decreasing T_g, and this result looks similar to the one discussed by Rindfleisch et al. [5] As the isoalkyl tail on the acrylate is decreased, the polymers remain in solution at lower temperature at a fixed pressure, suggesting that quadrupole-dipole interactions between the acrylate group and CO₂ are favorable for solubility.

2. Phase Behavior of CO₂+IDMA Mixture

Table 4 and Fig. 5 show the experimental pressure-composition (P-x) isotherms at 313.2, 333.2, 353.2, 373.2 and 393.2 K, and pressures range of 5.8-22.03 MPa for CO₂+IDMA system. As shown in Fig. 5, three phases were not observed at any of the five temperatures studied. The phase behavior of experimental results obtained in this work is modeled with the Peng-Robinson equation of state [23,24]. These two binary interaction parameters were determined by regressing experimental data with the Peng-Robinson equation of state. Objection function (OBF) [25] of this calculation was defined as follows.

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

Table 5 lists pure component critical temperatures, critical pressures, and acentric factors for CO₂ [13], IDMA that are used with the Peng-Robinson equation of state [23]. The boiling point of IDMA was obtained by Rohm and Haas Co. [26] The property of IDMA was calculated by group-contribution method [13]. The CO₂+IDMA mixture is fitted by experimental results with calculated value obtained by using the Peng-Robinson equation at 353.2 K. The values of the optimized interaction parameters of the Peng-Robinson equation of state for the CO₂+IDMA system are k_{ij}=0.093 and η_{ij}= −0.015. We compared experimental results with calculated P-x isotherms at temperatures of 313.2, 333.2, 373.2, and 393.2 K for the CO₂+IDMA system using the optimized values of k_{ij} and η_{ij} deter-

Table 5. Pure component parameters for the Peng-Robinson equation of state [13]

Compounds	M_w	T_c, K	P_c, MPa	ω
Carbon dioxide	44.01	304.1	7.38	0.225
Isodecyl methacrylate	226.36	641.9	1.60	0.701

Table 6. Experimental cloud-point data for the poly(isodecyl methacrylate) [P(IDMA)]+CO₂+dimethyl ether (DME) system

T/K	P/MPa
5.3 wt% P(IDMA)+8.6 wt% DME	
398.8	191.90
403.7	163.62
414.4	134.31
434.1	118.10
454.5	111.21
5.2 wt% P(IDMA)+21.1 wt% DME	
335.8	150.17
354.6	94.66
373.5	83.28
394.1	78.79
414.1	77.76
434.1	77.07
453.8	77.59
3.6 wt% P(IDMA)+47.7 wt% DME	
333.6	31.55
352.1	33.97
373.5	37.59
393.7	40.86
412.6	43.97
432.5	46.03
453.1	48.10
4.6 wt% P(IDMA)+95.4 wt% DME	
375.6	5.00
392.8	8.79
412.4	13.28
432.7	17.00
453.7	19.31

mined at 353.2 K. As shown in Fig. 5, a good fit of the liquid-phase (bubble-point) curves is obtained with the Peng-Robinson equation using an optimized mixture parameters for the CO₂+IDMA system; however, mixture-critical curves show big difference as the temperature increases.

3. Phase behavior of P(IDMA)+CO₂+dimethyl Ether and P (IDMA)+supercritical Fluid Solvens Systems

Table 6 and Fig. 6 show the phase behavior of the P(IDMA)+ CO₂+DME mixture. The P(IDMA)+CO₂ mixture was obtained in the temperature range of 438-475 K and pressures of 142-255 MPa, and for P(IDMA)+DME mixture at the range of temperature of 375-453 K and pressures of 5-19 MPa. The pressure difference between two systems is due to whether or not dipole moment in DME (1.3 D) and CO₂ (0.0 D) as shown in Table 1. For the P(IDMA)+CO₂ system, the rapid rise in the cloud-point pressure with decreasing tem-
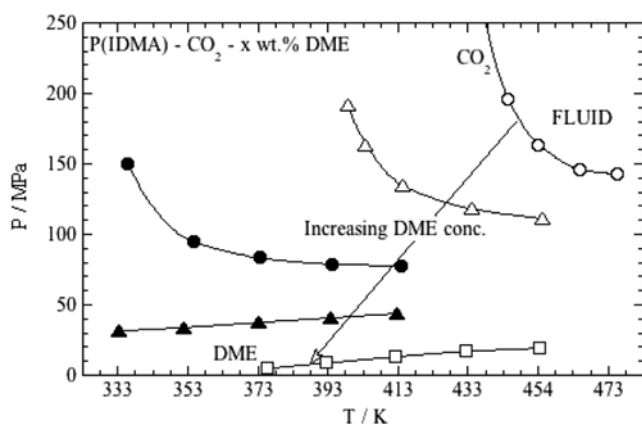
Fig. 6. Phase behavior of the dimethyl ether [DME] concentration for P(IDMA)+CO₂+DME system. The polymer concentration is ca. 5.0 wt% for each solution. ○, 0.0 wt%; △, 8.6 wt%; ●, 21.1 wt%; ▲, 47.7 wt%; □, 100 wt%.
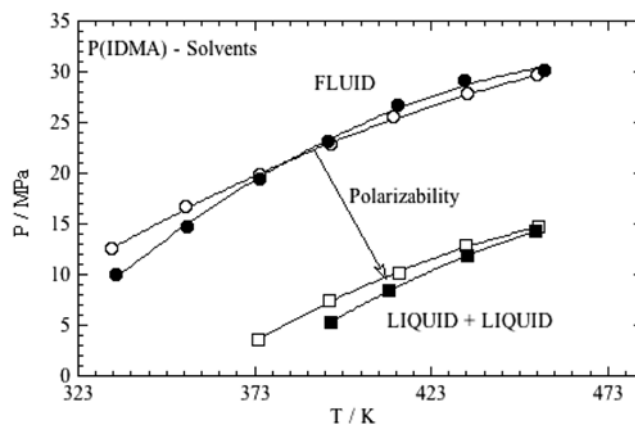

Fig. 7. Effect of the phase behavior of P(IDMA) dissolved in supercritical propane, propylene, butane, and 1-butene. The polymer concentration is ca. 5 wt% for each solution. ○, propane; ●, propylene; □, butane; ■, 1-butene.

Table 7. Experimental cloud-point data for the poly(isodecyl methacrylate) [P(IDMA)]+solvents system

T/K	P/MPa
7.0 wt% P(IDMA)+93.0 wt% Propane	
332.6	12.59
353.4	16.72
374.6	19.83
394.7	22.93
412.5	25.52
433.5	27.93
453.3	29.66
4.6 wt% P(IDMA)+95.4 wt% Propylene	
333.7	10.04
353.9	14.66
374.6	19.48
393.9	23.14
413.6	26.72
432.3	29.14
455.0	30.17
5.3 wt% P(IDMA)+94.7 wt% n-Butane	
374.1	3.62
394.4	7.41
414.1	10.17
433.1	12.93
453.5	14.66
5.6 wt% P(IDMA)+94.4 wt% 1-Butene	
394.6	5.35
411.2	8.45
433.4	11.90
452.8	14.31

perature is attributed to the increase of CO_2+CO_2 interactions over P(IDMA)+CO₂ interactions. The phase behavior of low pressure for P(IDMA)+DME system is due to ester polar with a large dipole moment of DME.

As shown in Fig. 6, the P(IDMA)+CO₂+8.6 wt% DME mix-

ture shows the UCST-type behavior with negative slope, and then the pressure increases slowly at ca. 413 K. With 21.1 wt% IDMA added to the solution, the cloud-point curve shows a negative slope. The cloud-point curve for P(IDMA)+CO₂ with 21.1 wt% DME is located at lower temperatures than the curve for P(IDMA)+CO₂ with 8.6 wt% DME, in this case, because DME has a significant dipole moment, which has resulted in the large temperature difference by ca. 70 K at a fixed pressure of 150 MPa. The P(IDMA)+CO₂+47.7 wt% DME system show the LCST-type with the positive slope in ca. 1.6 MPa/K. At 373 K, the pressure difference between the P(IDMA)+CO₂+21.1 and 47.7 wt% DME system shows ca. 50 MPa, caused by the impact of free volume and dipole moment as DME concentration increases.

Table 7 and Fig. 7 show the cloud-point of P(IDMA) dissolved in supercritical propane, propylene, butane and 1-butene obtained in this work. The phase behavior for P(IDMA)+propane, +propylene, +butane and +1-butene system exhibits LCST curves with positive slope in ca. 1.4 MPa/K (propane), ca. 1.7 MPa/K (propylene), ca. 1.4 MPa/K (butane) and ca. 1.5 MPa/K (1-butene), respectively. The P(IDMA)+C₃ hydrocarbons system presented the lower pressure at the temperature range of 333-453 K. At 383 K, the phase behavior boundary has almost similar pressure to ca. 20 MPa and it is due to the almost same polarizability of propane and propylene from Table 1. The P(IDMA)+C₄ hydrocarbon system is located at temperature range of 373-453 K and lower pressure of 3.6-14.7 MPa. As shown in Table 1, it seems to be due to about the same polarizability for the butane (81.4×10⁻²⁵ cm³) and 1-butene (82.4×10⁻²⁵ cm³). The pressure difference between P(IDMA)+C₃ hydrocarbons and P(IDMA)+C₄ hydrocarbons system is considered due to polarity factor reduced from ca. 27 MPa to ca. 11 MPa at temperature of ca. 423 K.

CONCLUSION

High pressure phase behavior of poly(isodecyl methacrylate), poly(isodecyl acrylate) and poly(isopropyl methacrylate) in SCF solvents and SCF solvent+cosolvent mixtures presents the impact of SCF solvent polarity and steric effect of a decyl group relative

to isodecyl group. The SCF Solvents with a large dipole moment (C_3, C_4 and DME) dissolve at lower pressure than methacrylate polymers. P(IDMA) does dissolve in pure CO_2 to 473 K and 255 MPa. The location of the P(IDMA)+CO_2 phase behavior curve shifts to lower temperatures and pressures when IDMA or DME is added to the P(IDMA)+CO_2 solution. The C_4 hydrocarbon cloud-point curves shift to lower pressures than the C_3 hydrocarbons curves at fixed temperature. Vapor-liquid phase behavior for CO_2+IDMA system is presented at temperatures of 313.2-393.2 K and pressure to 22.03 MPa. The CO_2+IDMA system is obtained a good fit with the Peng-Robinson equation of state using adjustable interaction parameters.

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REFERENCES

1. A. Z. Husain, G. Zwolak and F. P. Lucien, *J. Chem. Eng. Data*, **51**, 718 (2006).
2. T. H. J. M. Waegemaekers and M. P. M. Bensink, *Mutation Research/Genetic Toxicology*, **137**, 95 (1984).
3. A. R. Singh, W. H. Lawrence and J. Autian, *J. Dent. Res*., **51**, 1632 (1972).
4. S. D. Yeo and E. Kiran, *Macromolecules*, **37**, 8239 (2004).
5. F. Rindfleisch, T. P. DiNoia and M. A. McHugh, *J. Phys. Chem.*, **100**, 15581 (1996).
6. C. Pan and M. Radosz, *Ind. Eng. Chem. Res*., **38**, 2842 (1999).
7. I. Wichterle, *Pure & Appl. Chem*., **65**, 1003 (1993).
8. S. Chio, K. Lee, S. Kwon and H. Kim, *J. Supercrit. Fluids*, **37**, 287 (2006).
9. J. Jung and M. Perrut, *J. Supercrit. Fluids*, **20**, 179 (2001).
10. H. S. Byun and M. A. McHugh, *Ind. Eng. Chem. Res*., **39**, 4658 (2000).
11. M. Lora and M. A. McHugh, *Fluid Phase Equilibria*, **157**, 285 (1999).
12. H. S. Byun and M. A. McHugh, *J. Supercrit. Fluids*, **41**, 482 (2007).
13. R. C. Reid, J. M. Prausnitz and B. E. Polling, *The properties of gases and liquid*, 5th ed., McGraw-Hill, New York (1987).
14. R. C. Benson and W. H. Flygare, *Chem. Phys. Lett*., **4**, 141 (1969).
15. G. Meyer and J. P. Toennies, *Chem. Phys*., **52**, 39 (1980).
16. J. M. Prausniz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular thermodynamics of fluid-phase equilibria*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1986).
17. C. F. Kirby and M. A. McHugh, *Chem. Rev*., **99**, 565 (1999).
18. H. S. Byun and D. H. Lee, *Ind. Chem. Eng. Res*., **45**, 3373 (2006).
19. M. DeSimone, G. Zihibin and C. S. Elsebernd, *Science*, **257**, 945 (1992).
20. H. S. Byun, M. Y. Choi and J. S. Lim, *J. Supercrit. Fluids*, **37**, 323 (2006).
21. S. Conway, *Doctor of philosophy in chemical engineering*, Johns Hopkins University, Baltimore, MD (2000).
22. H. S. Byun, C. H. Bang and J. S. Lim, *J. Macromolecular Science, Part B: Physics*, *submitted* (2007).
23. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Res. Fundam*., **15**, 59 (1976).
24. M. A. McHugh and V. J. Krukonis, *Supercritical fluid extraction: principles and practice*, Butterworth, Boston, MA (1994).
25. J. L. Kuester and J. H. Mize, *Optimization techniques with fortran*, McGraw-Hill (1973).
26. Rohm and Haas Company, Methacrylic/Acrylic Monomers, Form 18297 Rev. II, Philadelphia, PA (2002).