

Phase Behavior on the Binary and Ternary Mixtures of Poly(isooctyl acrylate) + Supercritical Fluid Solvents + Isooctyl Acrylate and CO₂ + Isooctyl Acrylate System

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ABSTRACT: Experimental cloud-point data to the temperature of 180 °C and the pressure up to 2000 bar are presented for ternary mixtures of poly(isooctyl acrylate) + supercritical fluid solvents + isooctyl acrylate systems. Cloud-point pressures of poly(isooctyl acrylate) + CO₂ + isooctyl acrylate system is measured in the temperature range of 60–180 °C and to pressures as high as 2000 bar with isooctyl acrylate concentration of 0–44.5 wt. This system changes the pressure–temperature slope of the phase behavior curves from upper critical solution temperature (UCST) region to lower critical solution temperature (LCST) region as the isooctyl acrylate concentration increases. Poly(isooctyl acrylate) does dissolve in pure CO₂ to the temperature of 180 °C and the pressure of 2000 bar. The phase behavior for poly(isooctyl acrylate) + CO₂ + 9.5, 14.8, 30.6, and 41.9 wt % dimethyl ether (DME) mix-

ture show the curve changes from UCST to LCST as the DME concentration increases. Also, the cloud-point curves are measured for the binary mixtures of poly(isooctyl acrylate) in supercritical propane, propylene, butane, and 1-butene. High pressure phase behaviors are measured for the CO₂ + isooctyl acrylate system at 40, 60, 80, 100, and 120 °C and pressure up to 200 bar. This system exhibits type-I phase behavior with a continuous mixture-critical curve. The experimental results for the CO₂ + isooctyl acrylate system are modeled using the Peng-Robinson equation of state. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1124–1132, 2008

Key words: isooctyl acrylate; high pressure phase behavior; poly(isooctyl acrylate); carbon dioxide; propane; propylene; butane; 1-butene; dimethyl ether; cloud-point

INTRODUCTION

Recently, the phase behavior data of binary and ternary mixture between polymers, cosolvents, and supercritical fluids are needed in polymerization processing, coating, powder formation, and related industrial applications. Also, supercritical fluid solvents have been used as solvents in a variety of polymer synthesis such as extractions, separations, and fractionations.^{1–5} In the binary mixture of small molecules, the information on the high-pressure phase behavior of solvents at supercritical region has been valuable in the design of new separation processes in a wide variety of fields such as food, pharmaceutical, and related industries.²

We have demonstrated that it is possible to dissolve polar acrylate polymers in supercritical fluids

over a large temperature range at lower pressure if acrylate monomer is used.^{6,7} The experiments for acrylate polymer + SCF solution behavior are performed to determine the location of the cloud-point curve in pressure–temperature (*P–T*) space. The location of this curve can be used to generate a qualitative understanding of the relative strength of the different enthalpic of energetic interactions present within the system. The phase behavior for polymers solution in given supercritical fluid solvents is obtained due to several different reasons. If the solvent is highly expanded, the mixture between the polymer and the solvent reduces the free-volume difference by liquid cosolvent.^{6,8} If the cosolvent provides favorable physicochemical interactions, such as polar interactions, the region of miscibility should be increased.⁵ Interpreting the effect of a cosolvent added to an supercritical solvent is slightly more complicated, since increasing the system pressure reduces the free-volume difference between the polymer and the solvent and it increases the probability of interaction between polymer, solvent, and cosolvent segments in solution.⁹

Figure 1 shows the corresponding *P–T* for a polymer + solvent solution, similar to that discussed by

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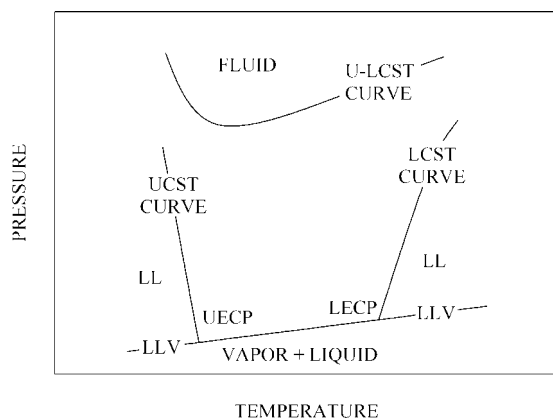


Figure 1 Pressure - temperature diagram for polymer + solvent mixtures exhibiting a UCST, LCST and U-LCST boundary. LL: liquid-liquid, and LLV: liquid + liquid + vapor.

McHugh and Krukoniš² and Folie et al.¹⁰ The boundary at low temperatures with the steep, negative slope describes the pressure dependence of liquid + liquid (LL) to fluid transitions (left part), and is called an upper critical solution temperature (UCST) curve. The location and the slope of the UCST curve are typically controlled by enthalpic interactions between the two components. Enthalpic interactions depend on the density of solvent and on the strength of polymer + polymer, solvent + solvent, and polymer + solvent interactions. The solid curve separating the fluid region from the liquid + vapor region is termed the lower critical solution temperature (LCST) curve (right part). The location of the LCST curve is driven more by entropic effects, as the light component has a much larger coefficient of thermal expansion than the heavy component, particularly in polymer + solvent systems.¹¹ Because of this difference in thermal expansion, pressure has a strong effect on the location of the LCST curve. The point at which the UCST curve intersects this three phases line is termed the upper critical end point (UCEP), and similarly, the LCST curve intersects the three phases [liquid + liquid + vapor (LLV)] line at the lower critical end point (LCEP). Because polymeric molecules do not have pure component critical points, the high temperature end of the mixture-critical curve does not have a distinct endpoint. At high temperatures, the LCST curve is the boundary between the single-phase fluid region and the two phases (liquid + liquid) region. At low temperatures, the UCST curve separates a single phase from two liquid phases.

Experimental phase behavior data of small amount for binary CO₂ + isooctyl acrylate system are obtained to complement the poly(isooctyl acrylate) + CO₂ + isooctyl acrylate studies presented here, since there are no literature phase behavior data

available on this mixture. The phase behavior for the CO₂ + isooctyl acrylate system is presented for the temperature range of 40–120°C and pressure up to 200 bar. The experimental data of CO₂ + isooctyl acrylate system are fitted to the Peng-Robinson equation of state¹² and the phase behavior for this binary solvent mixture is calculated at elevated operating temperatures and pressure.

The focus of this work is to present the determination of the impact of isooctyl acrylate cosolvent on the phase behavior for the poly(isooctyl acrylate) + CO₂ system. The phase behavior for these binary and ternary mixtures of poly(isooctyl acrylate) + supercritical fluids + isooctyl acrylate mixtures provides the information needed on the regions where homogeneous polymerization can occur in the presence of excess monomer.

EXPERIMENTAL SECTION

Apparatus and procedure

Figure 2 shows a schematic diagram of the experimental apparatus used for pressure-composition isotherms for the CO₂ + isooctyl acrylate mixtures¹³ and cloud-point curves obtained for poly(isooctyl acrylate) + CO₂ + isooctyl acrylate ternary mixtures.¹⁴ The bubble-point, dew-point, critical-point, and cloud-point curves are obtained with a high-pressure, variable-volume cell described in detail elsewhere.^{13,14} Cloud-points are measured for the polymer solutions at a fixed poly(isooctyl acrylate) concentration of 5.0 ± 1.0 wt %, which is typical of the concentrations, used for polymer + SCF solvent studies.¹⁴ Polymer is loaded into the cell to within ±0.002 g and then the cell is purged with nitrogen followed by CO₂ to ensure that all of the air and organic matter is removed. Liquid isooctyl acrylate is injected into the cell to within ±0.002 g using a syringe and CO₂ is transferred into the cell gravimetrically to within ±0.004 g using a high-pressure bomb.

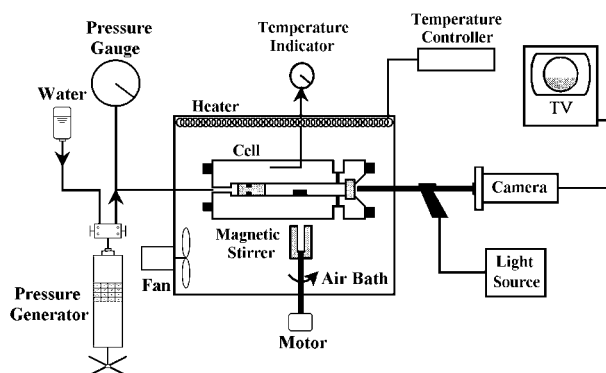


Figure 2 Schematic diagram of the experimental apparatus used for the phase behavior measurements reported in this study.

The mixture in cell is compressed to the desired pressure with an internal piston displaced with water in a high-pressure generator (HIP; model 37-5.75-60) (Erie, PA). The pressure of the mixture is measured with a Heise gauge (Dresser; model CM-108952, 0–3450 bar, accurate to within ± 3.5 bar; model CM-53920, 0–340 bar) (Stratford, CT). The temperature in the cell is measured using a platinum-resistance thermometer (Thermometrics; Class A) connected to a digital multimeter (Yokogawa, model 7563, accurate to within $\pm 0.005\%$). The system temperature is typically maintained to within $\pm 0.2^\circ\text{C}$ below 200°C . The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope (Olympus; model F100-038-000-50) (Tokyo, Japan) placed against the outside of the sapphire window. Light is transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator (Olympus Optical; model ILK-5) and at the other end to a borescope.

Cloud-points are measured and reproduced at least twice to within ± 2.8 bar and $\pm 0.3^\circ\text{C}$. Bubble-, dew-, and critical-point transitions for the CO_2 + isooctyl acrylate mixtures are measured and reproduced at least twice to within ± 0.3 bar and $\pm 0.2^\circ\text{C}$. Mole fraction of isooctyl acrylate are accurate to within ± 0.002 . CO_2 + isooctyl acrylate mole fractions have an estimated accumulation error less than $\pm 0.8\%$ except for the data point at 1.0 mol % isooctyl acrylate.

MATERIALS

CO_2 (99.8% purity) is obtained from Daesung Industrial, Propane (98% purity) is obtained from LG Gas (E1), Propylene (99.6% purity), Butane (97.0% purity), 1-butene (99.5% purity) and dimethyl ether (99.5% purity) are obtained from Yeochun NCC and used as received. Poly(isooctyl acrylate) ($M_w = 60,000$) and the isooctyl acrylate (99.9% purity) were obtained from Scientific Polymer Products and used as received. To prevent isooctyl acrylate polymerization, 2,6-di-tert-butyl-4-methyl phenol (Aldrich, 99% purity) was used as an inhibitor at a concentration of 0.005 times the amount of isooctyl acrylate. Because the poly(isooctyl acrylate) was supplied in a toluene solution, the polymer solution was placed under vacuum for at least 12 h by the Rotary Evaporator (Tamato Scientific; model RE-47) for toluene removal.

RESULTS AND DISCUSSION

Phase behavior of binary CO_2 + isooctyl acrylate mixture

Figure 3 and Table I show the experimental pressure-composition (P - x) isotherms at 40, 60, 80, 100,

and 120°C , and the range of pressures of 38–200 bar for the carbon dioxide + isooctyl acrylate system. As shown in Figure 3, three phases were not observed at any temperatures studied. The carbon dioxide + isooctyl acrylate mixtures for the solubility isotherms at 40 – 120°C are arranged according to the value of at least two independent data points. Bubble, critical, and dew point curves for the carbon dioxide + isooctyl acrylate system were measured and reproduced at least twice to within ± 0.3 bar and $\pm 0.2^\circ\text{C}$, for a given loading of the cell. The mole fractions are accurate to within ± 0.002 .

Experimental P - x isotherm data obtained in this work were correlated with Peng-Robinson equation of state using van der Waals on fluid mixing rule including two binary interaction parameters.¹² The Peng-Robinson equation of state is briefly described here, and defined as the following mixing rules.

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

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

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

$$b_{ij} = 0.5 [(b_{ii} + b_{jj})] (1 - \eta_{ij}) \quad (4)$$

These two binary interaction parameters were determined by regression experimental data with Peng-Robinson equation of state. Objective function¹⁵ (OBF)

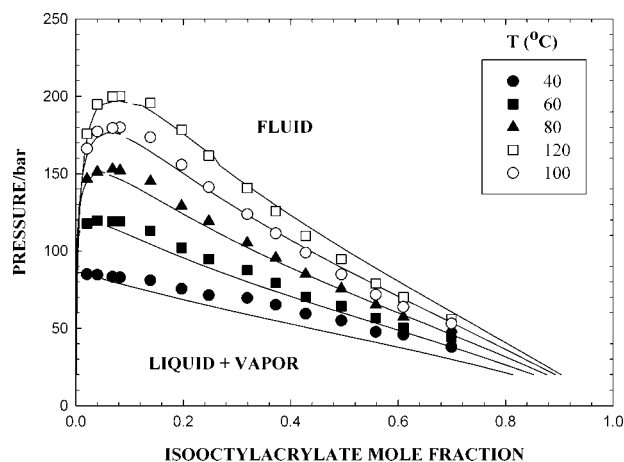


Figure 3 Comparison of the experimental data (symbols) for the CO_2 + isooctyl acrylate system with calculations (solid lines) obtained using the Peng-Robinson equation of state $k_{ij} = 0.023$ and $\eta_{ij} = -0.045$.

TABLE I
Experimental Data for the Carbon Dioxide + Isooctyl Acrylate System Measured in this Study

Mole fraction of the isooctyl acrylate	Pressure (bar)	Transition
<i>T</i> = 40 °C		
0.021	85.0	C.P
0.040	84.7	B.P
0.068	83.3	B.P
0.082	83.0	B.P
0.139	81.0	B.P
0.197	75.5	B.P
0.247	71.4	B.P
0.319	69.7	B.P
0.372	65.2	B.P
0.428	59.5	B.P
0.494	55.0	B.P
0.558	47.8	B.P
0.610	45.9	B.P
0.699	37.9	B.P
<i>T</i> = 60 °C		
0.021	117.8	D.P
0.040	119.7	C.P
0.068	119.3	B.P
0.082	119.2	B.P
0.139	113.1	B.P
0.197	102.1	B.P
0.247	94.8	B.P
0.319	87.6	B.P
0.372	79.3	B.P
0.428	70.3	B.P
0.494	64.3	B.P
0.558	56.7	B.P
0.610	50.5	B.P
0.699	44.5	B.P
<i>T</i> = 80 °C		
0.021	146.6	D.P
0.040	151.2	D.P
0.068	152.9	C.P
0.082	152.1	B.P
0.139	145.2	B.P
0.197	129.1	B.P
0.247	119.3	B.P
0.319	105.3	B.P
0.372	95.5	B.P
0.428	85.0	B.P
0.494	75.5	B.P
0.558	65.2	B.P
0.610	57.4	B.P
0.699	49.7	B.P
<i>T</i> = 100 °C		
0.021	166.2	D.P
0.040	177.2	D.P
0.068	179.5	D.P
0.082	179.8	C.P
0.139	173.5	B.P
0.197	155.7	B.P
0.247	141.7	B.P
0.319	123.8	B.P
0.372	111.4	B.P
0.428	99.0	B.P
0.494	84.8	B.P
0.558	71.7	B.P
0.610	63.8	B.P
0.699	53.1	B.P

TABLE I
Continued

Mole fraction of the isooctyl acrylate	Pressure (bar)	Transition
<i>T</i> = 120 °C		
0.021	175.9	D.P
0.040	194.8	D.P
0.068	199.8	D.P
0.082	200.1	C.P
0.139	195.9	B.P
0.197	178.5	B.P
0.247	161.7	B.P
0.319	140.7	B.P
0.372	125.9	B.P
0.428	109.7	B.P
0.494	94.8	B.P
0.558	79.0	B.P
0.610	70.0	B.P
0.699	55.9	B.P

and root mean squared relative deviation (RMSD) percent of this calculation were defined as follows:

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

$$RMSD(\%) = \sqrt{\frac{OBF}{ND}} \times 100 \tag{6}$$

ND in eq. (6) is the number of data point. Table II lists pure component critical temperatures, critical pressures, and acentric factors for carbon dioxide,¹⁶ isooctyl acrylate that was used with the Peng-Robinson equation of state.¹² The critical property (*T_c*, *P_c*) of isooctyl acrylate was calculated by group-contribution method with Joback method.¹⁷ Also, the vapor pressures and acentric factors were calculated by Lee-Kesler method.¹⁷

Figure 4 shows the comparison of experimental results of carbon dioxide–isooctyl acrylate with calculated value obtained using Peng-Robinson equation at a temperature of 80°C. The optimized values of the binary interaction parameters (bubble-point data = 11; RMSD = 2.44%) of the Peng-Robinson equation of state for the carbon dioxide + isooctyl acrylate system at 80°C are *k_{ij}* = 0.023 and *η_{ij}* = -0.045. A reasonable fit of the data is obtained over most of the composition range even if no mix-

TABLE II
Pure Component Parameters for the Peng-Robinson Equation of State^{16,17}

Compound	<i>M_w</i>	<i>T_c</i> (°C)	<i>P_c</i> (bar)	<i>ω</i>
Carbon dioxide	44.01	31.1	73.8	0.225
Isooctyl acrylate	184.25	386.1	20.3	0.710

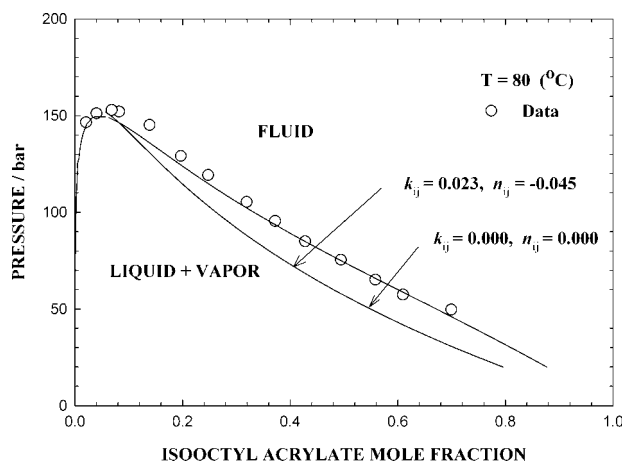


Figure 4 Comparison of the best fit of Peng-Robinson equation of state to the carbon dioxide + isooctyl acrylate system at 80°C.

ture parameters are used. But if two mixture parameters, $k_{ij} = 0.023$ and $\eta_{ij} = -0.045$, are used, the fit of the experimental results is significantly better. The RMSD at five temperatures (40, 60, 80, 100, and 120°C) for carbon dioxide + isooctyl acrylate system was 5.95% of the bubble point number 58. As shown in Figure 3, high pressure phase behavior was compared between experimental results and calculated P - x isotherms at temperatures of 40, 60, 100, and 120°C for the carbon dioxide + isooctyl acrylate system using the optimized values of k_{ij} and η_{ij} determined at 80°C. In the results, a good agreement fit of both data are obtained between experimental data and calculated values by Peng-Robinson equation of state.

Figure 5 shows the comparison between experimental data and the mixture-critical curve for the

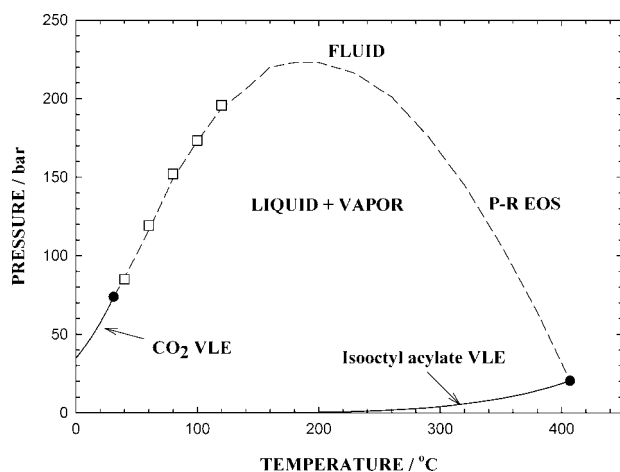


Figure 5 Comparison of the experimental data (symbols) for the CO₂ + isooctyl acrylate system with calculations (solid lines) obtained using the Peng-Robinson equation of state $k_{ij} = 0.023$ and $\eta_{ij} = -0.045$.

carbon dioxide + isooctyl acrylate system with calculated values by the Peng-Robinson equation of state. The experimental data and calculated mixture-critical curve indicates type-I behavior, in agreement with experimental observations. The solid lines represent the vapor pressure for carbon dioxide¹⁶ and isooctyl acrylate.¹⁷ The solid circles represent the critical point for carbon dioxide and isooctyl acrylate. The upper part of the dash line is fluid, and the

TABLE III
Experimental Cloud-Point Data for the Poly(isooctyl acrylate) + CO₂ + Isooctyl Acrylate System Measured in This Study

T (°C)	P (bar)
4.9 wt % poly(isooctyl acrylate) + 0.0 wt % isooctyl acrylate	
120.2	2029.3
126.0	1670.7
140.3	1315.5
156.2	1174.1
171.1	1137.9
181.8	1132.8
5.1 wt % poly(isooctyl acrylate) + 8.9 wt % isooctyl acrylate	
100.7	1925.9
107.7	1386.2
120.0	1124.1
141.3	984.5
161.3	925.9
181.0	898.3
5.5 wt % poly(isooctyl acrylate) + 15.5 wt % isooctyl acrylate	
79.7	1422.4
101.2	922.4
123.1	843.1
140.5	815.5
160.9	801.7
181.4	787.9
5.9 wt % poly(isooctyl acrylate) + 29.7 wt % isooctyl acrylate	
59.9	913.8
78.4	719.0
99.1	677.6
121.7	677.6
142.3	681.0
160.8	691.4
180.6	698.3
5.4 wt % poly(isooctyl acrylate) + 35.8 wt % isooctyl acrylate	
58.4	819.0
78.8	681.0
100.9	656.9
120.7	660.4
141.2	670.7
160.7	681.0
181.0	687.9
6.0 wt % poly(isooctyl acrylate) + 44.5 wt % isooctyl acrylate	
61.0	515.5
79.5	508.6
101.1	525.9
121.0	553.5
140.0	574.1
160.6	594.8
179.7	598.3

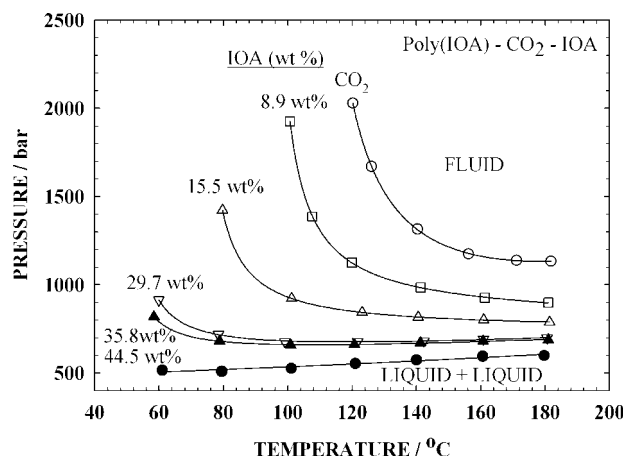


Figure 6 Experimental cloud-point curves for the poly(isooctyl acrylate) + CO₂ + isooctyl acrylate system with different isooctyl acrylate concentration. The concentration of poly(isooctyl acrylate) is ~ 5.0 wt % for these data.

lower part is vapor + liquid (two phases). The open squares are the mixture-critical points determined from isotherms measured in this work. The dash lines represent the calculated value obtained using the Peng-Robinson equation of state.

Phase behavior of poly(isooctyl acrylate) + CO₂ + isooctyl acrylate system

Table III and Figure 6 show the phase behavior of the poly(isooctyl acrylate) + CO₂ + x wt % isooctyl acrylate mixture obtained in this study. The poly(isooctyl acrylate) does dissolve in pure CO₂ to the temperature of 180°C and the pressure of 2000 bar. The poly(isooctyl acrylate) + supercritical CO₂ system shows the UCST-type behavior, a negative slope at the temperature range of 120–180°C. With 8.9 wt %

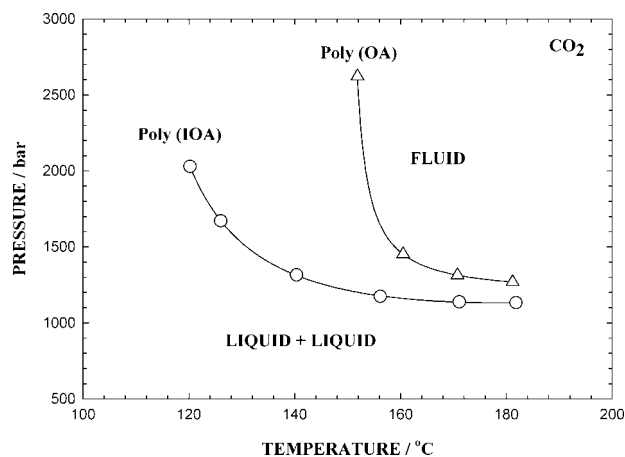


Figure 7 Comparison of cloud-point curves for the poly(*n*-octyl acrylate) (Poly(*n*-OA)) and poly(isooctyl acrylate) (Poly(iso-OA))¹⁹ in supercritical CO₂. The polymer concentration is ~ 5 wt % for both solutions.

TABLE IV
Critical Temperatures, Critical Pressures, Critical Densities, Polarizabilities, and Dipole Moments of the Solvents Used in this Study^{17,21–24}

Solvents	T _c (°C)	P _c (bar)	ρ _c (g/cm ³)	α*10 ²⁵ (cm ³)	μ (D)
CO ₂	31.0	73.8	0.469	26.5	0.0
Propane	96.7	42.5	0.217	62.9	0.1
Propylene	91.9	46.2	0.236	62.6	0.4
<i>n</i> -Butane	152.1	38.0	0.228	81.4	0.0
1-Butene	146.4	39.7	0.234	82.4	0.3
Dimethyl ether	126.8	53.0	0.258	52.2	1.3

isooctyl acrylate added to the solution, the cloud-point curve exhibits UCST type phase behavior with a negative slope. The poly(isooctyl acrylate) + CO₂ + 8.9 wt % isooctyl acrylate system rapidly increases the pressure at the temperature of ~ 100 °C. When 15.5 wt % isooctyl acrylate is added to the solution, the cloud-point pressure curve shows the pressures from ~ 790 bar to 1400 bar and a temperature range of 80–180°C. If 29.7 and 35.8 wt % isooctyl acrylate is added to the solution, the cloud-point curve exhibits U-LCST type phase behavior from positive slope at low pressures to negative slope which increase smooth at 80 and 100°C. Also, the cloud-point pressure remains virtually constant at 700 ± 20 bar over a temperature range from 60 to 180°C. The cloud-point curve for the poly(isooctyl acrylate) + CO₂ + 44.5 wt % isooctyl acrylate system, and it is a continuous curve down to 60°C and ~ 510 bar. The effect of isooctyl acrylate cosolvent on the phase behavior is similar to that observed for the poly(butyl acrylate) + CO₂ + butyl acrylate⁶ and poly(ethyl acrylate) + CO₂ + ethyl acrylate systems.¹⁸ The slope of the 45.6wt % isooctyl acrylate curve is

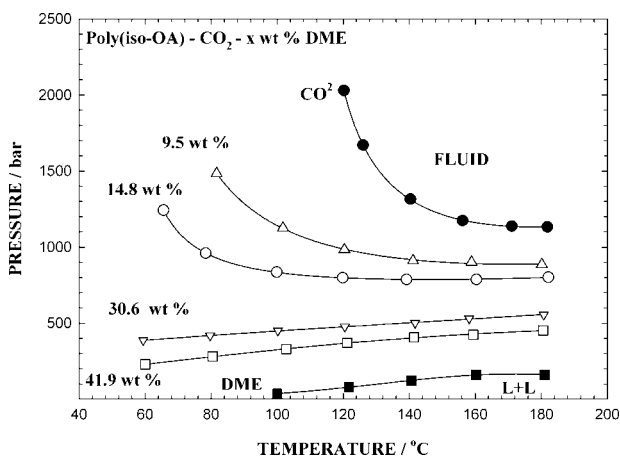


Figure 8 Phase behavior effect on the dimethyl ether concentration for poly(isooctyl acrylate) + CO₂ + x wt % dimethyl ether system. The polymer concentration is ~ 5 wt % for each solution.

TABLE V
Experimental Cloud-Point Data for the Poly(isooctyl acrylate) + CO₂ + DME System Measured in This Study

<i>T</i> (°C)	<i>P</i> (bar)
4.9 wt % poly(isooctyl acrylate) + 0.0 wt % DME	
120.2	2029.3
126.0	1670.7
140.3	1315.5
156.2	1174.1
171.1	1137.9
181.8	1132.8
4.7 wt % poly(isooctyl acrylate) + 9.5 wt % DME	
81.6	1484.5
101.7	1125.9
120.3	982.8
141.2	912.1
158.9	901.7
180.2	886.2
4.9 wt % poly(isooctyl acrylate) + 14.8 wt % DME	
65.5	1243.1
78.4	960.3
99.9	836.2
119.9	798.3
139.2	787.9
160.3	787.9
182.1	801.7
6.2 wt % poly(isooctyl acrylate) + 30.6 wt % DME	
59.4	387.9
79.6	419.0
100.2	450.0
120.4	477.6
141.7	501.7
158.1	531.0
180.7	556.9
5.6 wt % poly(isooctyl acrylate) + 42.0 wt % DME	
60.0	229.3
80.4	281.0
102.8	329.3
121.2	370.7
141.4	407.2
159.4	425.9
180.6	452.8
5.4 wt % poly(isooctyl acrylate) + 94.6 wt % DME	
100.0	36.2
121.7	81.0
140.7	122.4
160.2	160.3
181.0	162.1

~ 0.9 bar/°C, which is very close to the slope found for the poly (butyl acrylate) + CO₂ + 12.6 wt % butyl acrylate curve.⁶ These slopes are ~ 40% greater than those observed for binary poly(isobutylene) + alkane mixtures reported by Zeman and Patterson,¹¹ which is due to the enhanced influence of hydrostatic pressure on the free volume difference between poly(isooctyl acrylate) and the CO₂ – isooctyl acrylate mixture.

Figure 7 compares the cloud-point curves for the poly(*n*-octyl acrylate)¹⁹ and poly(isooctyl acrylate) in

supercritical CO₂. Both the polymers are dissolved in supercritical CO₂. Below 150°C, the pressure difference of cloud-point curve show a big difference as the temperature decrease. Both the curves exhibit LCST region phase behavior with a negative slope. This cloud-point curve shows the same tendency as reported for the poly(isobutyl acrylate) and poly(*n*-butyl acrylate) in supercritical CO₂.²⁰

Phase behavior of poly(isooctyl acrylate) + supercritical fluid solvents and poly(isooctyl acrylate) + CO₂ + DME system

Table IV is list of critical temperature, critical pressure, critical density, polarizability, dipole moment, and quadrupole moment properties of the solvents used in this study.^{17,21–24} For the poly(isooctyl acrylate) + solvents system, CO₂, propylene, propane, butane, 1-butene and DME were used as solvents.

Figure 8 and Table V show the phase behavior of the poly(isooctyl acrylate) + CO₂ – DME mixture obtained in this work. The poly(isooctyl acrylate) + CO₂ mixture was obtained at the range of temperature of 120–180°C and at pressures of 1130–2000 bar, and for poly(isooctyl acrylate) + DME mixture at the range of temperature of 100–180°C and pressures

TABLE VI
Experimental Cloud-Point Data for the Poly(isooctyl acrylate) + Solvents System Measured in This Study

<i>T</i> (°C)	<i>P</i> (bar)
5.5 wt % poly(isooctyl acrylate) + 94.5 wt % propane	
60.1	108.6
82.2	150.0
100.3	174.1
120.4	201.7
140.2	232.8
161.1	256.9
180.3	279.3
5.4 wt % poly(isooctyl acrylate) + 94.6 wt % propylene	
59.8	74.1
80.4	119.0
100.2	153.4
121.1	198.3
139.7	229.3
158.9	250.0
182.7	279.7
6.2 wt % poly(isooctyl acrylate) + 93.8 wt % <i>n</i> -butane	
101.2	25.9
121.4	57.6
140.2	89.0
160.8	119.0
180.7	139.7
6.2 wt % poly(isooctyl acrylate) + 93.8 wt % 1-butene	
120.1	36.2
140.1	70.7
161.8	101.7
180.2	125.9

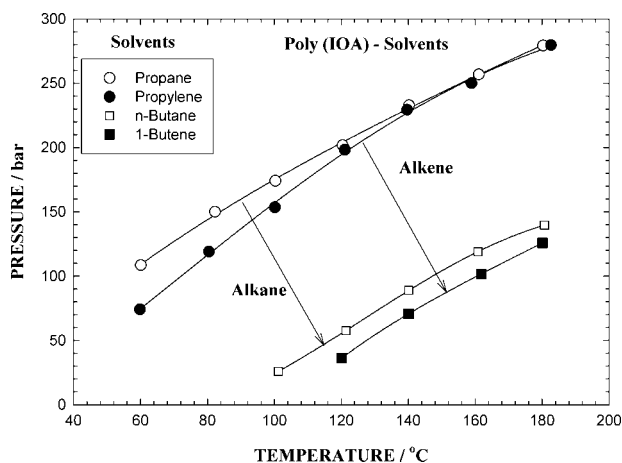


Figure 9 Impact of the phase behavior of poly(isooctyl acrylate) dissolved in supercritical propane, propylene, butane, and 1-butene. The polymer concentration is ~ 5 wt % for each solution.

of 36–162 bar. The pressure difference between two systems is caused due to whether or not dipole moment in DME (1.3 D) and CO_2 (0.0 D) as shown in Table IV. As shown in Figure 8, the poly(isooctyl acrylate) + CO_2 + 9.5 wt % DME mixture shows the UCST-type behavior with the negative slope. With 14.8 wt % DME added to the solution, the cloud-point curve exhibits U-LCST region phase behavior from positive slope to negative slope. The cloud-point pressure remains virtually constant at about 800 bar over a temperature range of 100–180°C. The poly(isooctyl acrylate) + CO_2 + 30.6 and 41.9 wt % DME system show the LCST-type of the positive slope in 1.4 bar/°C (30.6 wt %) and 1.9 bar/°C (41.9 wt %), respectively.

Table VI and Figure 9 show the phase behavior of poly(isooctyl acrylate) dissolved in supercritical propane, propylene, butane, and 1-butene at temperature range of 60–180°C and pressure to 280 bar. The cloud-point behavior for poly(isooctyl acrylate) + propane, + propylene, + butane, and + 1-butene system exhibits LCST curves with positive slope. The poly(isooctyl acrylate) + propane and poly(isooctyl acrylate) + propylene system presented the lower pressure at the temperature range of 60–182°C and pressure range of 74–280 bar. At 150°C, the phase behavior boundary has almost pressure of ~ 240 bar and it is due to the similarity in polarizability propane ($62.9 \times 10^{-25} \text{ cm}^3$) and propylene ($62.6 \times 10^{-25} \text{ cm}^3$), as shown in Table IV. The poly(isooctyl acrylate) + butane, and poly(isooctyl acrylate) + 1-butene system shows a temperature range of 100–180°C and lower pressure of 140 bar. For the temperature at 150°C, the cloud-point curve reduced from ~ 103 bar (butane) to ~ 87 bar (1-butene). As

shown in Table IV, it seems to be due to a little of polarizability for the butane ($81.4 \times 10^{-25} \text{ cm}^3$) and 1-butene ($82.4 \times 10^{-25} \text{ cm}^3$). The pressure difference between poly(isooctyl acrylate) + propane and poly(isooctyl acrylate) + butane system is considered because of the polarity factor.

CONCLUSIONS

We measured P - x isotherms for binary mixture of carbon dioxide + isooctyl acrylate system at temperature from 40 to 120°C and pressure up to 200 bar. The P - x bubble-point curves are convex, which indicates that CO_2 exhibits a high solubility in isooctyl acrylate probably due to the formation of a weak complex between the carboxylic oxygen in isooctyl acrylate and the carbon in CO_2 . The Peng-Robinson equation of state can be used with two adjustable parameters to calculate a reasonable representation of the phase behavior of the CO_2 + isooctyl acrylate system.

Experimental cloud-point data are presented for binary and ternary mixtures of poly(isooctyl acrylate) + CO_2 + x wt % isooctyl acrylate systems. Cloud-point behavior are presented for poly(isooctyl acrylate) + CO_2 + x wt % DME mixtures and with DME concentration of 9.5, 14.8, 30.6, and 41.8 wt %. Poly(isooctyl acrylate) and poly(octyl acrylate) does dissolve in pure CO_2 to 180°C and 2000 bar. Also, the phase behavior is shown for poly(isooctyl acrylate) dissolved in supercritical propane, propylene, butane, and 1-butene at temperature below 180°C and pressure of below 280 bar.

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