

Solubility in the Binary and Ternary System for Poly(alkyl acrylate)-Supercritical Solvent Mixtures

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Abstract—Experimental cloud-point data to 210 °C and 2,200 bar are presented for binary and ternary mixtures of poly(methyl acrylate)-CO₂-methyl acrylate and poly(ethyl acrylate)-CO₂, propylene, and 1-butene-ethyl acrylate systems. The accuracy of the experimental apparatus was tested by comparing the measured pressure-temperature phase behavior data of the poly(ethyl acrylate)-CO₂ system obtained in this study with those of Rindfleisch et al. [1995]. The phase behaviors for the system poly(methyl acrylate)-CO₂-methyl acrylate were measured in changes of pressure-temperature slope, and with cosolvent concentrations of 0, 5.0, 13.7, 25.3, and 43.3 wt%, respectively. With 48.3 wt% methyl acrylate to the poly(methyl acrylate)-CO₂ solution significantly changes, the phase behavior curve takes on the appearance of a typical lower critical solution temperature (LCST) boundary. The impact of ethyl acrylate on the cloud-point for the poly(ethyl acrylate)-CO₂ system shows the change of slope of the phase behavior curves from negative to positive with ethyl acrylate concentration of 0, 8.2, and 25.0 wt%. The cloud-point behavior for the poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate system shows an LCST curve. The solubility curve to ~150 °C and 1,650 bar for poly(ethyl acrylate)-propylene-ethyl acrylate system shows the change of pressure-temperature diagram and with ethyl acrylate concentration of 0, 7.2 and 21.0 wt%. Also, when 41.1 wt% ethyl acrylate was added to the poly(ethyl acrylate)-propylene solution, the phase behavior curve showed the LCST region. The high pressure phase behavior of poly(ethyl acrylate)-1-butene-0, 3.1, 8.1, 18.5 and 30.7 wt% ethyl acrylate system presented the change of pressure-temperature curve from the UCST region to U-LCST region as the ethyl acrylate concentration increased.

Key words: Phase Behavior, Poly(methyl acrylate), Poly(ethyl acrylate), Supercritical CO₂, Propylene, 1-Butene, High Pressure

INTRODUCTION

The phase behavior of high molecular weight polymer-supercritical fluid solvents mixture is needed in developing new polymer processing technologies and industrial application. Also, supercritical fluid solvents have been used as solvents in a variety of polymer processes [DeSimone et al., 1992; Lee and Kim, 2002] such as extractions [McHugh and Krukonic, 1993], separations [Rindfleisch et al., 1996; Lee and McHugh, 2002], fractionations [Pratt and McHugh, 1996; Mertdogan et al., 1997], and reactions [Kajimoto, 2002]. Supercritical fluid technology has recently gained considerable attention in the particle formation of polymers [Shiho and DeSimone, 2001; Christian et al., 2000].

We have reported in many studies that a polar cosolvent can shift a polymer-supercritical fluid solvent cloud-point curve to much lower pressures and temperatures [McHugh et al., 1998; Byun and Park, 2002; Byun and Choi, 2002; Kiran and Liu, 2002]. The work presented herein demonstrates the impact of a polar cosolvent, methyl acrylate and ethyl acrylate, on the phase behavior of a polar polymer, poly(methyl acrylate) and poly(ethyl acrylate), in three supercritical solvents, CO₂, propylene, and 1-butene.

Unreacted liquid cosolvent is a very attractive monomer with supercritical carbon dioxide for several factors. The liquid cosolvent increases the density of the supercritical solvent-rich solvent phase and reduces the free-volume difference between the polymer and

the solvent, which enhances polymer solubility [Patterson, 1982]. Also, if the cosolvent provides favourable physical interactions, such as polar interactions, the region of miscibility should expand [Wolf and Blaum, 1975]. The high-pressure, polymer-supercritical fluid solvent-cosolvent studies reported in the literature show that cloud points monotonically decrease in pressure and temperature with the addition of a polar cosolvent as long as the cosolvent does not form a complex with the polar repeat units in the polymer [Kirby and McHugh, 1999; Wolf and Blaum, 1975]. In these cases, the cosolvent effect is directly related to the polar forces of attraction contributed by the cosolvent and to the increase in solvent density resulting from the addition of a liquid cosolvent to a supercritical fluid solvent.

The focus of the work presented here is the determination of the impact of methyl acrylate cosolvent on the phase behavior of the poly(methyl acrylate)-CO₂ system and of the ethyl acrylate cosolvent on the phase behavior of the poly(ethyl acrylate)-CO₂, propylene, and 1-butene system. Given that CO₂ has been considered a desirable reaction medium for free-radical polymerizations [DeSimone et al., 1992], the phase behavior for these ternary poly(alkyl acrylate)-CO₂-monomer mixtures provides needed information on the regions where homogeneous polymerization can occur in the presence of excess monomer.

EXPERIMENTAL SECTION

Fig. 1 shows a schematic diagram of the experimental apparatus used for obtaining the pressure-temperature relation of the poly-

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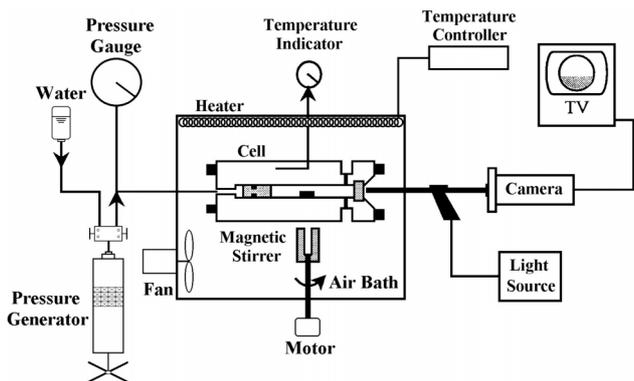


Fig. 1. Apparatus diagram of cloud-point measurement for the polymer-solvent-cosolvent mixtures.

mer-solvent mixtures at high pressure [Byun and Lee, 2002]. Phase behavior data were obtained with a high-pressure, variable-volume cell that has a 1.59 cm inner diameter, 7.0 cm outer diameter, and a working volume of $\sim 28 \text{ cm}^3$. A 1.9 cm thick sapphire window is fitted in the front part of the cell for observation of the phases. Polymer is loaded into the cell, which is subsequently purged several times at room temperature with CO_2 at 3–6 bar to remove any entrapped air. Methyl acrylate or ethyl acrylate monomer is quantitatively transferred into the cell with a syringe and CO_2 is then transferred into the cell gravimetrically with a high-pressure bomb. The solution is compressed to the desired pressure with an internal piston displaced with water in a high-pressure generator (HIP, model 37-5.75-60). The pressure of the mixture is measured with a Heise gauge (Dresser Ind., Model CM-108952, 0-3450 bar, accurate within ± 3.5 bar). The temperature of the cell is measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, Model 7563, accurate within $\pm 0.005\%$). The system temperature is typically maintained within $\pm 0.2^\circ\text{C}$ below $\pm 200^\circ\text{C}$ and within $\pm 0.4^\circ\text{C}$ above $\pm 200^\circ\text{C}$. The mixture inside the cell is viewed on a video monitor by using a camera coupled to a borescope (Olympus Corp., Model F100-034-000-50) 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 and at the other end to a borescope. The solution in the cell is well mixed by using a magnetic stir bar activated by an external magnet beneath the cell.

Cloud points are obtained for the polymer mixtures at a fixed poly(methyl acrylate) or poly(ethyl acrylate) concentration of $5.0 \pm 0.5 \text{ wt}\%$, which is typical of the concentrations, used for polymer-supercritical solvent studies [Byun and McHugh, 2000; Conway et al., 2001]. The pressure is slowly decreased until the cloud point is reached. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. After a cloud point is obtained, the solution is recompressed into a single phase, and the process repeated. Typically, cloud point pressures are determined first at the highest temperature desired; however, the order in which the cloud points are taken does not influence the results. Polymer is loaded into the cell to within $\pm 0.002 \text{ g}$ and then the cell is purged with nitrogen followed by CO_2 to ensure that all of the air is removed. Liquid methyl acrylate or ethyl acrylate monomer is injected into the cell with-

in $\pm 0.002 \text{ g}$ using a syringe and CO_2 is transferred into the cell gravimetrically within $\pm 0.004 \text{ g}$ using a high pressure bomb. Cloud points obtained by both methods are identical within the reproducibility of the data. Cloud points are measured and reproduced at least twice to within $\pm 2.8 \text{ bar}$ and $\pm 0.4^\circ\text{C}$.

MATERIALS

Both polymers are obtained from Polysciences Inc. The poly(methyl acrylate) has a average molecular weight, M_w , of $\sim 40,000$ (GPC) and the poly(ethyl acrylate) has a M_w of $\sim 70,000$ (GPC) obtained from Polysciences Co. Methyl acrylate (99.5% purity) and ethyl acrylate (99.5% purity), obtained from Junsei Chemical Company, contain approximately 300 ppm of hydroquinone and are used as received. CO_2 is obtained from Daesung Oxygen Co. (99.9% minimum purity), Propylene (99.8% purity) and 1-butene (99.8% purity) obtained from Yeochun NCC Co. and used as received.

Since the poly(methyl acrylate) and poly(ethyl acrylate) were supplied in a toluene solution, the polymer solution was placed under vacuum for at least 10 h by the Rotary Evaporator (Tamato Scien-

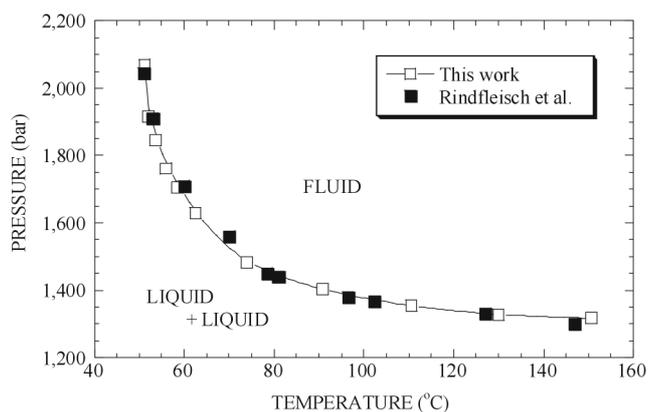


Fig. 2. Comparison of pressure-temperature cloud-point for the poly(ethyl acrylate)- CO_2 system obtained in this study and Rindfleisch et al. data.³

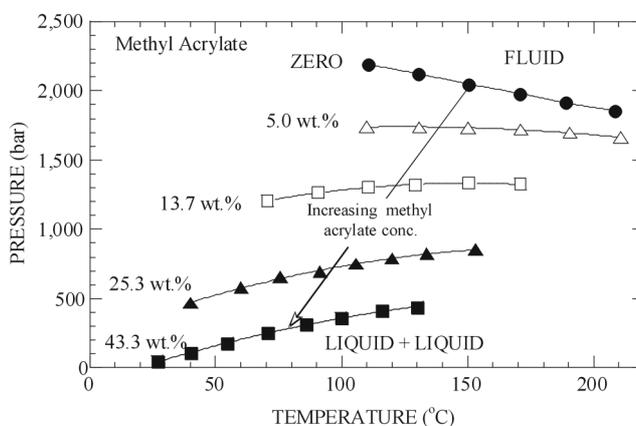


Fig. 3. Impact of methyl acrylate on the phase behavior of the poly(methyl acrylate)- CO_2 -x wt% methyl acrylate system, where x equal 0.0 (●), 5.0 (△), 13.7 (□), 25.3 (▲), and 43.3 (■).

tific Co., model RE-47) for toluene solvent removal.

EXPERIMENTAL RESULTS

Fig. 2 shows the experimental pressure-temperature cloud-point, the range of temperature at 50-150 °C, and the range of pressure of 1,300-2,070 bar for the poly(ethyl acrylate)-CO₂ system. In order to check the accuracy and reproducibility of the experimental apparatus, we compared the phase behavior data for binary poly(ethyl acrylate)-supercritical CO₂ mixture with those measured by Rindfleisch et al. [1996].

Table 1. Experimental cloud-point data for the poly(methyl acrylate)-CO₂-methyl acrylate system measured in this study

T (°C)	P (bar)
4.2 wt% PMA+0.0 wt% MA	
110.6	2191.4
130.6	2122.8
150.3	2050.0
170.7	1979.7
188.7	1912.8
208.2	1856.9
4.8 wt% PMA+5.0 wt% MA	
109.8	1740.3
130.8	1734.5
150.2	1733.4
171.0	1719.0
190.4	1697.6
210.7	1662.1
5.1 wt% PMA+13.7 wt% MA	
70.6	1206.6
90.6	1267.2
110.5	1304.5
129.3	1322.4
150.5	1333.4
170.8	1325.9
4.8 wt% PMA+25.3 wt% MA	
40.0	468.6
60.1	582.4
75.6	652.8
91.3	694.5
105.7	749.3
119.9	787.9
133.8	820.7
153.1	853.5
5.0 wt% PMA+43.3 wt% MA	
26.8	50.0
40.4	104.8
54.7	179.7
70.8	250.0
85.9	311.4
99.7	363.8
115.9	413.5
130.0	439.7

As shown in Fig. 2, the experimental data presented are in good agreement with those of Rindfleisch et al. [1996].

Fig. 3 and Table 1 show the effects of modest amounts of methyl acrylate on the cloud-point behavior of the poly(methyl acrylate)-CO₂ system. At temperatures below 150 °C, the cloud-point curve is shifted to moderately lower pressures, due to the decrease in the free volume difference between poly(methyl acrylate) and the mixed solvent. Poly(methyl acrylate) is dissolved in pure supercritical CO₂ to the temperature of 208 °C and pressure of 2,190 bar. The phase behavior for the poly(methyl acrylate)-CO₂ mixture exhibits upper critical solution temperature (UCST) curve with a negative slope. At 150 °C, the addition of 5.0 wt% methyl acrylate to a poly(methyl acrylate)-CO₂ mixture lowers the cloud-point pressure from 2,050 bar to 1,750 bar. Note that the sharp plate in the poly(methyl acrylate) cloud-point curve shifts from 210 to ~110 °C with 5.0 wt%

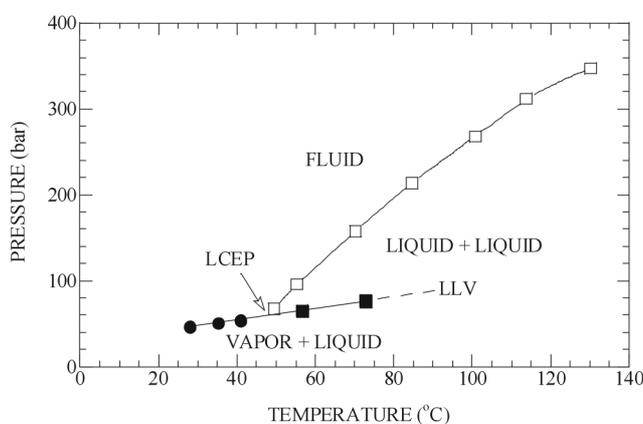


Fig. 4. Phase behavior of the poly(methyl acrylate)-CO₂-48.3 wt% methyl acrylate system obtained in this study. □, fluid → liquid+liquid transitions; ●, fluid → liquid+vapor transitions; ■, liquid+liquid → liquid+liquid+vapor transitions; ---, suggested extension of the LLV line.

Table 2. Experimental cloud-point, bubble-point, and liquid-liquid-vapor data for the poly(methyl acrylate)-CO₂-methyl acrylate system measured in this study

T (°C)	P (bar)	Transition
5.6 wt% PMA+48.3 wt% MA		
Cloud-point transition		
49.5	66.9	CP
55.3	95.9	CP
70.2	157.6	CP
84.6	214.1	CP
100.8	267.9	CP
113.8	312.1	CP
130.1	347.2	CP
Bubble-point transition		
40.9	54.1	BP
35.2	50.7	BP
27.9	46.9	BP
Liquid-liquid-vapor transition		
56.5	65.3	LLV
72.7	76.7	LLV

methyl acrylate added to the solution. When 13.7 wt% methyl acrylate is added to the solution, in fact, the poly(methyl acrylate)-CO₂-13.7 wt% methyl acrylate curve exhibits a negative slope over the range of 70-170 °C. With 25.3 and 43.3 wt% methyl acrylate added to the solution, the phase behavior curve is almost parallel to 25.3 and 43.3 wt% methyl acrylate in two cloud-point curve. Also, 43.3 wt% cloud-point curve is shifted to even lower pressures of 50 bar at 27 °C, but the cloud-point curve exhibits lower critical solution temperature (LCST) with a positive slope.

Fig. 4 and Table 2 show that adding 48.3 wt% methyl acrylate to the poly(methyl acrylate)-CO₂ solution significantly changes the phase behavior. Now the cloud-point curve takes on the appearance of a typical LCST boundary [McHugh and Krukoni, 1993]. The phase transition has shifted from 2,200 bar in supercritical pure CO₂ to ~320 bar in a CO₂+48.3 wt% methyl acrylate mixture at 120 °C. The cloud-points curve intersects a fluid→liquid+vapor curve at ~50 °C and ~60 bar. The liquid and vapor phase coexist at pressure below this curve. Note that the LV curve switches to a liquid₁+liquid₂+vapor (LLV) curve at higher temperatures than 50 °C.

Table 3 and Fig. 5 present the cloud-point behavior of the poly(ethyl acrylate)-CO₂-ethyl acrylate system data obtained in this work. The cloud-point behavior of the poly(ethyl acrylate)-CO₂-ethyl acrylate system shown in Fig. 5 exhibits many of the same trends as that reported for the poly(butyl acrylate)-CO₂-butyl acrylate system¹⁰.

Table 3. Experimental cloud-point data for the poly(ethyl acrylate)-CO₂-ethyl acrylate system measured in this study

T (°C)	P (bar)
5.4 wt% PEA+0.0 wt% EA	
51.2	2070.7
52.1	1915.5
53.7	1846.6
55.9	1762.4
58.5	1706.6
62.5	1630.0
74.0	1482.8
90.8	1403.1
110.6	1354.5
129.9	1327.9
150.6	1317.2
5.5 wt% PEA+8.2 wt% EA	
37.9	719.7
50.6	768.6
71.1	822.4
90.9	846.2
110.1	902.4
129.8	935.3
150.6	947.2
4.8 wt% PEA+25.0 wt% EA	
39.8	239.0
34.3	214.1
51.3	285.9
65.7	348.9
81.6	404.8
101.2	477.6

The cloud-point pressure decreases by ~500 bar at 100 °C with the first 8.2 wt% ethyl acrylate added to solution and it does by ~400 bar with the addition of the next 16.8 wt%. Nevertheless, the cloud-point pressure at 100 decreases from 1,350 bar (0.0 wt% ethyl acrylate) to 450 bar with 25.0 wt% ethyl acrylate added to solution. The impact of methyl acrylate as a cosolvent is perhaps more impressively relative to that of ethyl acrylate since it is much more difficult to dissolve poly(methyl acrylate) in pure CO₂ than it is to dissolve poly(ethyl acrylate).

When 39.5 wt% ethyl acrylate is added to the poly(ethyl acrylate)-CO₂ solution, the phase behavior shown in Fig. 6 and Table 4 takes on the typical appearance of an LCST boundary. At 100 °C, the phase boundary has shifted from ~480 to 200 bar as the concentration of ethyl acrylate is increased from 25 to 39.5 wt%. The poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate LCST curve intersects an LV curve at 60 °C and 75 bar. The LV curve switches to a liquid₁+liquid₂+vapor (LLV) curve at higher temperatures than 60 °C.

Similarities are also apparent between the phase behavior of the poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate system shown in

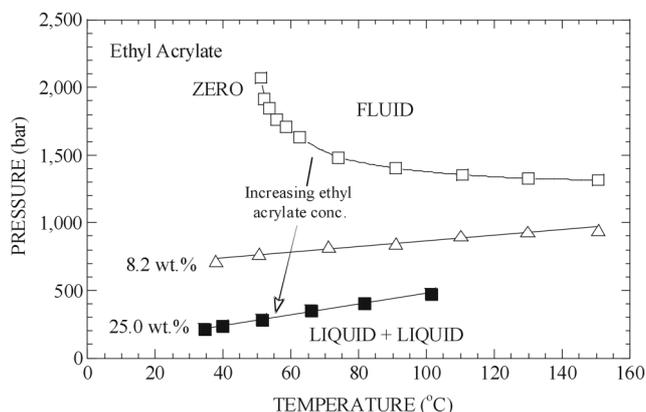


Fig. 5. Impact of ethyl acrylate on the phase behavior of the poly(ethyl acrylate)-CO₂-x wt% ethyl acrylate system, where x equal 0.0 (□), 8.2 (△), and 25.0 (■).

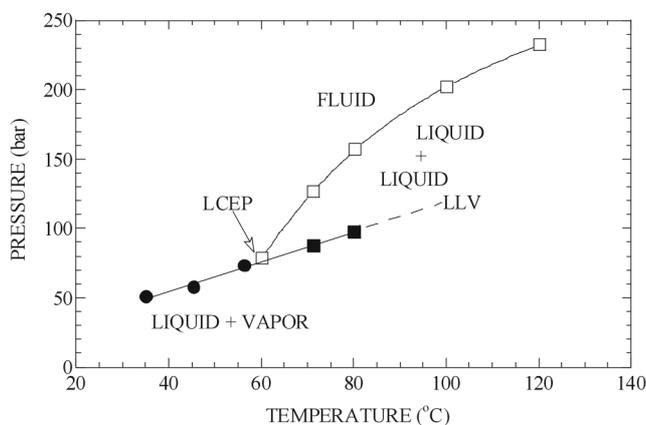


Fig. 6. Phase behavior of the poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate system obtained in this study. □, fluid→liquid+liquid transitions; ●, fluid→liquid+vapor transitions; ■, liquid+liquid→liquid+liquid+vapor transitions; ---, suggested extension of the LLV line.

Table 4. Experimental cloud-point, bubble-point, and liquid-liquid-vapor data for the poly(ethyl acrylate)-CO₂-ethyl acrylate system measured in this study

T (°C)	P (bar)	Transition
5.5 wt% PEA+39.5 wt% EA		
Cloud-point transition		
60.3	78.6	CP
71.2	126.6	CP
80.3	156.9	CP
100.1	202.4	CP
120.3	232.8	CP
Bubble-point transition		
56.2	73.8	BP
45.3	58.3	BP
35.0	51.4	BP
Liquid-liquid-vapor transition		
71.2	87.7	LLV
80.0	97.9	LLV

Table 5. Experimental cloud-point data for the poly(ethyl acrylate)-propylene-ethyl acrylate system measured in this study

T (°C)	P (bar)
5.4 wt% PEA+0.0 wt% EA	
38.6	1647.2
43.4	1498.3
47.6	1354.8
51.2	1233.4
57.5	1119.7
71.4	903.1
91.4	736.9
111.3	667.2
132.1	621.7
150.6	599.0
5.5 wt% PEA+7.2 wt% EA	
37.6	920.3
44.1	836.2
51.6	745.9
66.5	656.2
81.5	601.7
101.7	545.9
120.4	523.1
5.3 wt% PEA+21.0 wt% EA	
25.5	448.6
26.5	445.5
29.5	425.9
36.1	409.3
45.6	383.1
60.4	356.2
81.4	349.3
101.3	351.0
120.2	354.8

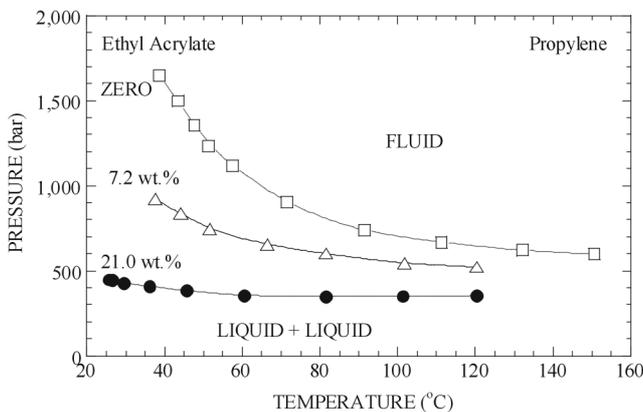
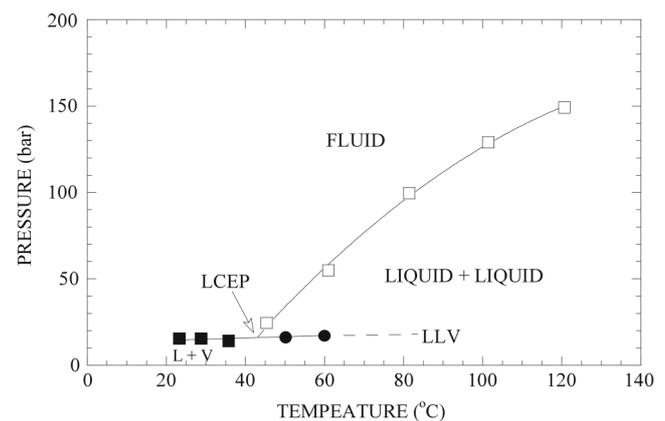
**Fig. 7. Impact of ethyl acrylate on the phase behavior of the poly(ethyl acrylate)-propylene-x wt% ethyl acrylate system, where x equals 0.0 (□), 7.2 (△), and 21.0 (●).**

Fig. 6 and the poly(methyl acrylate)-CO₂-48.3 wt% methyl acrylate system shown in Fig. 4. The poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate cloud-point curve in the LCST region intersects the LV curve at 60 °C and 75 bar compared to ~50 °C and 60 bar for the poly(methyl acrylate)-CO₂-48.3 wt% methyl acrylate curve. The slope of the poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate LCST curve shows ~3.0 bar/°C.

Fig. 7 and Table 5 show the impact of ethyl acrylate on the phase behavior of the poly(ethyl acrylate)-propylene-0.0, 7.2 and 21.0 wt% ethyl acrylate system. The cloud-point behavior for the poly(ethyl acrylate)-propylene-ethyl acrylate mixture measured in the temperature range of 25 °C to 150 °C, to pressures as high as ~1,650 bar. Poly(ethyl acrylate) is dissolved in pure propylene to 150 °C and ~1,650 bar. As shown in Fig. 7, the cloud-point curve exhibits UCST curve phase behavior with a negative slope for the poly(ethyl acrylate)-propylene system. The phase behavior for the poly(ethyl acrylate)-propylene-7.2 wt% ethyl acrylate system exhibits a negative slope that reaches 920 bar at 37 °C. With 21.0 wt% ethyl acrylate added to the solution, the cloud-point curve remains relatively

**Fig. 8. Phase behavior of the poly(ethyl acrylate)-propylene-41.1 wt% ethyl acrylate system obtained in this study. □, fluid → liquid+liquid transitions; ■, fluid → liquid+vapor transitions; ●, liquid+liquid → liquid+liquid+vapor transitions; ---, suggested extension of the LLV line.**

flat at 400-500 bar and temperatures between 25 and 120 °C.

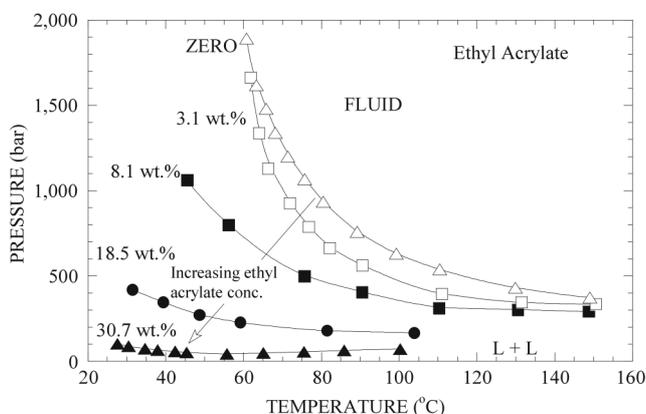
Fig. 8 and Table 6 show the phase behavior of an LCST bound-

Table 6. Experimental cloud-point, bubble-point, and liquid-liquid-vapor data for the poly(ethyl acrylate)-propylene-ethyl acrylate system measured in this study

T (°C)	P (bar)	Transition
5.9 wt% PEA+41.1 wt% EA		
Cloud-point transition		
45.4	24.5	CP
61.0	54.8	CP
81.4	99.7	CP
101.4	129.0	CP
120.7	149.3	CP
Bubble-point transition		
35.8	14.4	BP
28.7	15.5	BP
23.2	15.5	BP
Liquid-liquid-vapor transition		
50.1	16.3	LLV
59.9	17.1	LLV

ary for the poly(ethyl acrylate)-propylene-41.1 wt% ethyl acrylate system obtained in this work. At 120 °C, the phase boundary has shifted from 350 to 150 bar as the concentration of ethyl acrylate is increased from 21.0 wt% to 41.1 wt%. The poly(ethyl acrylate)-propylene-41.1 wt% ethyl acrylate cloud-point curve intersects a fluid→liquid+vapor (LV) curve at very low ~43 °C and 15 bar. A liquid and vapor phase coexist at pressures below this curve, and the LV curve switches to a liquid₁+liquid₂+vapor (LLV) curve temperature greater than 43 °C.

Fig. 9 and Table 7 show the cloud-point behavior of the poly(ethyl acrylate)-1-butene-ethyl acrylate system obtained in this study. Poly(ethyl acrylate) is dissolved in pure 1-butene at temperatures of 60–150 °C and pressures of 1,900 bar. With 3.1 wt% ethyl acrylate added to the solution, the cloud-point curve exhibits UCST phase behavior with a negative slope. When 8.1 and 18.5 wt% ethyl acrylate is added to the poly(ethyl acrylate)-1-butene solution, the cloud-point curve exhibits the typical appearance of a UCST boundary. If 30.7 wt% ethyl acrylate is added to the solution, the cloud-point curve

**Fig. 9. Impact of ethyl acrylate on the phase behavior of the poly(ethyl acrylate)-C₄H₈-x wt% ethyl acrylate system, where x equals 0.0 (△), 3.1 (□), 8.1 (■), 18.5 (●), and 30.7 (▲).****Table 7. Experimental cloud-point data for the poly(ethyl acrylate)-1-butene-ethyl acrylate system measured in this study**

T (°C)	P (bar)
5.4 wt% PEA+0.0 wt% EA	
60.8	1892.8
63.3	1619.7
65.8	1479.7
68.2	1338.3
71.4	1200.3
75.7	1068.6
80.5	934.8
89.2	759.0
99.3	631.0
110.4	538.3
129.9	431.4
149.0	372.8
5.4 wt% PEA+3.1 wt% EA	
61.9	1663.8
64.1	1336.2
66.4	1127.9
71.9	925.9
76.8	787.9
82.2	664.1
90.6	561.7
111.0	394.8
131.5	344.5
150.6	334.1
6.6 wt% PEA+8.1 wt% EA	
45.5	1063.8
56.1	800.0
75.6	500.4
90.5	406.6
110.3	313.5
130.5	303.1
148.7	291.4
5.2 wt% PEA+18.5 wt% EA	
31.5	420.7
39.3	347.2
48.7	272.4
59.2	227.9
81.6	179.7
103.9	167.9
5.2 wt% PEA+30.7 wt% EA	
27.6	101.7
30.5	87.9
34.6	74.1
37.9	66.6
42.5	56.9
45.4	51.7
55.8	43.1
65.1	48.6
75.5	55.5
85.9	63.8
100.2	71.4

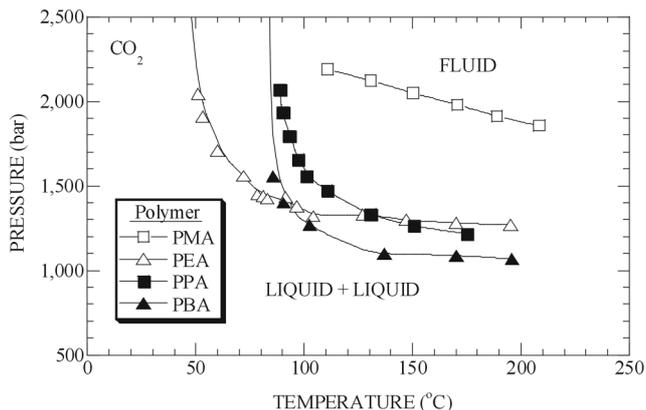


Fig. 10. Impact of the alkyl acrylate group on the cloud-point curves of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(propyl acrylate) (PPA)¹¹, and poly(butyl acrylate) (PBA)¹⁰ in supercritical CO₂.

exhibits U-LCST-type phase behavior to negative slope from positive slope at very low pressures.

Fig. 10 compared the impact of the alkyl acrylate group on the cloud-point curves of poly(methyl acrylate), poly(ethyl acrylate), poly(propyl acrylate) [Byun and Park, 2002] and poly(butyl acrylate) [McHugh et al., 1998] in supercritical CO₂. As shown in Fig. 10, the phase behavior curves presented the poly(methyl acrylate) > poly(ethyl acrylate) > poly(propyl acrylate) > poly(butyl acrylate) of pressure sequence at above 130 °C.

Below 130 °C, the cloud-point pressure shows higher in poly(ethyl acrylate) than in poly(propyl acrylate), and at about 90 °C, the phase behavior pressure in poly(butyl acrylate) and in poly(ethyl acrylate) cross each other.

Also, Fig. 11 shows the cloud-point curves for the supercritical CO₂, propylene and 1-butene with the poly(ethyl acrylate). As shown in Fig. 11, the cloud-point curves presented the CO₂ > propylene > 1-butene of pressure sequence at about 90 °C.

At below 90 °C, the poly(ethyl acrylate)-propylene and poly(ethyl acrylate)-1-butene system cross each other and this is due to a dipole moment.

The results obtained in this study demonstrate clearly that it is

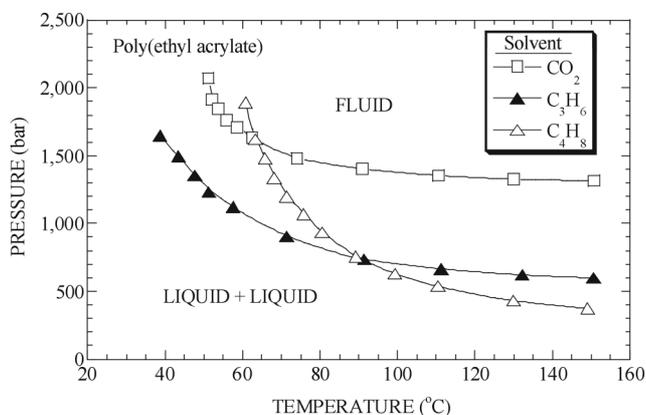


Fig. 11. Impact of the poly(ethyl acrylate)-supercritical CO₂, propylene and 1-butene system.

possible to obtain a single phase that extends over a large temperature range at modest pressures if sufficient amounts of free acrylate monomer are added to the solution.

CONCLUSIONS

The phase behavior for the system poly(methyl acrylate)-CO₂-methyl acrylate was measured in changes of the pressure-temperature slope, and with cosolvent concentrations of 0-43.3 wt%. The poly(methyl acrylate)-CO₂-48.3 wt% methyl acrylate solution shows the appearance of a typical LCST region.

The cloud-point for the poly(ethyl acrylate)-CO₂-0, 8.2, and 25.0 wt% ethyl acrylate system shows a change of slope of the phase behavior curves from negative to positive. The cloud-point behavior for the poly(ethyl acrylate)-CO₂-39.5 wt% ethyl acrylate system shows the LCST curve.

The solubility curve to ~150 °C and 1,650 bar for poly(ethyl acrylate)-propylene-ethyl acrylate system shows a change of pressure-temperature and with ethyl acrylate concentration of 0, 7.2 and 22.2 wt%. The high pressure phase behavior of poly(ethyl acrylate)-1-butene-0, 3.1, 8.1, 18.5 and 30.7 wt% ethyl acrylate system presented the change of pressure-temperature curve from UCST region to U-LCST region as the ethyl acrylate concentration increased.

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