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Monomer Concentration Effect on the Phase Behavior of Poly(propyl acrylate) and Poly(propyl methacrylate) with Supercritical CO_2 and C_2H_4

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Abstract−Experimental cloud-point data to temperature of 186 °C and pressure of ~2,500 bar are presented for ternary mixtures of poly(propyl acrylate)(PPA)-CO_2-propyl acrylate (PA) PPA-C_2H_4-PA and poly(propyl methacrylate) (PPMA)-CO_2-propyl methacrylate (PMA) systems. Cloud-point pressures of PPA-CO_2-PA system were measured in the temperature range of 32 °C to 175 °C and to pressures as high as 2,070 bar with PA concentrations of 0.0, 5.0, 11.7 and 30.4 wt%. Adding 34.1 wt% PA to the PPA-CO_2 mixture significantly changes the phase behavior. This system changes the pressure-temperature slope of the phase behavior curves from U-LCST region to LCST region as the PA concentration increases. Cloud-point data to 170 °C and 1,400 bar are presented for PPA-C_2H_4-PA mixtures and with PA concentration of 0.0, 5.7, 15.5 and 22.2 wt%. The cloud-point curve of PPA-C_2H_4 system shows relatively flat at 730 bar for temperatures between 41 and 150 °C. With 15.5 and 22.2 wt% PA the cloud-point curve exhibits a positive slope that extends to 35 °C and ~180 bar. Also, the ternary PPMA-CO_2-PMA system was measured below 186 °C and 2,484 bar, and with cosolvent of 5.2-20.1 wt%. PPMA does not dissolve in pure CO_2 to 233 °C and 2,500 bar. Also, when 41.5 wt% PMA is added to the PPMA-CO_2 solution, the cloud-point curve shows the typical appearance of a lower critical solution temperature (LCST) boundary.

Key words: Carbon Dioxide, Ethylene, Phase Behavior, PPA-CO_2-PA, PPA-C_2H_4-PA, PPMA-CO_2-PMA, Cosolvent

INTRODUCTION

Carbon dioxide has been touted as a solvent of choice for many industrial applications because of its attractive attributes: it is environmentally benign, nonhazardous, and very inexpensive. Ethylene is expected to exhibit some of the solvent characteristics of CO_2 since ethylene also has a quadrupole moment. Byun et al. [1996] reported that the cloud point curve for the PBA-ethylene system is relatively flat at ~800 bar and temperatures from 65 to 190 °C. The behavior of the PBA-ethylene system is similar to that of the PBA-CO_2 system, where the curve is flat at ~1,000 bar and temperature from 130 to 200 °C [Rindfleisch et al., 1996]. However, as previously mentioned, the PBA-CO_2 curve has a sharp increase in pressure at ~80 °C, whereas the PBA-ethylene curve is still flat at this temperature [Lora et al., 1999]. PBA remains dissolved in ethylene to lower temperatures because ethylene has a much higher polarizability than CO_2, 42.5 cm^3 versus 27.5 cm^3, and, therefore, PBA-ethylene dispersion interactions are much stronger. Dispersion interaction energy scales with polarizability divided by molar volume, which explains why high pressures are needed for ethylene and CO_2 to dissolve PBA since these solvents are expanded gases at elevated temperatures and ambient pressure.

A liquid cosolvent can greatly enhance polymer solubility in a supercritical fluid solvent if it has an intermolecular potential that matches closely with that of a polymer repeat unit [Wolf and Blaum, 1975]. In addition, a cosolvent that has a much higher density than that of the supercritical fluid solvent reduces the free volume difference between the polymer and the solvent [Cowie and McEwen, 1974]. However, it is not easy to decouple the effect of a cosolvent from that of hydrostatic pressure since increasing the pressure also reduces the free volume difference between the solvent and the polymer and it increases the probability of interaction between polymer, solvent, and cosolvent segments [LoStracco et al., 1994; Lora et al., 1999].

The objective of this study was the determination of the impact of propyl acrylate (PA) cosolvent on the phase behavior of the poly(propyl acrylate)(PPA)-supercritical CO_2 and C_2H_4 system and of propyl methacrylate (PMA) cosolvent on the phase behavior of the poly(propyl methacrylate) (PPMA)-supercritical CO_2 system. Given that CO_2 has been considered a desirable reaction medium for free radical polymerizations [DeSimone et al., 1992], the phase behavior for these ternary poly(propyl acrylate)-CO_2-propyl acrylate, poly(propyl acrylate)-CO_2-propyl acrylate, and poly(propyl methacrylate)-CO_2-propyl methacrylate mixtures provides needed information on the regions where homogeneous polymerization can occur in the presence of excess monomer. McHugh et al. [1998] have demonstrated that the Poly(butyl acrylate) (PBA)-CO_2 and poly(ethylhexyl acrylate) (PEHA)-CO_2 cloud point curves are horizontal at ~1,100 bar at high temperatures. However, as the temperature is lowered the PEHA-CO_2 curve increases sharply in pressure at ~155 °C and the PBA-CO_2 curve increases in pressure at ~80 °C. This sharp pressure increase reflects a significant change in the interchange energy which characterizes the balance of polymer segment-CO_2 cross-interactions relative to polymer segment-segment and CO_2-CO_2 self-interactions. At high temperatures, where entropic effects are expected to dominate, the location of the cloud-point curves is fixed by the free volume difference between PBA and CO_2 and PEHA and CO_2. When BA and EHA are added to CO_2 the polarity and the density of the solvent mixture are expected to increase

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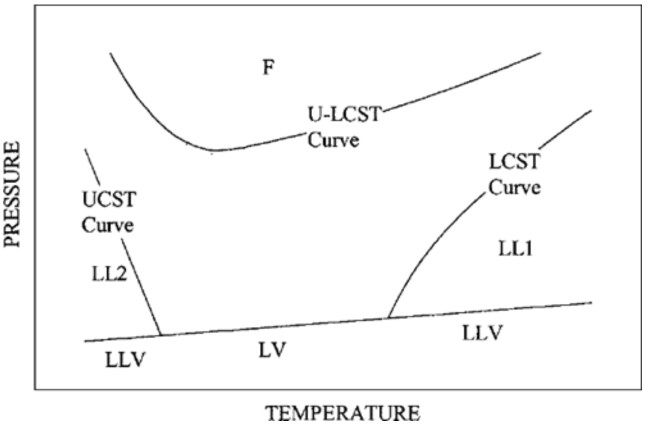

Fig. 1. Generalized P-T phase diagram for polymer-solvent mixtures exhibiting a U-LCST boundary.
F: Fluid, LL: liquid-liquid, LV: liquid-vapor, and LLV: liquid-liquid vapor.

since both of these cosolvents are dense, polar liquids. Hence, cloud-point pressures at high temperatures should be lower compared to the binary polymer-CO_2 curves and the temperature where the sharp increase in cloud-point pressure is observed should be reduced.

Fig. 1 shows a qualitative pressure-temperature (P-T) phase diagram of a polymer-solvent system, similar to that discussed by Folie and Radosz [1996]. As usual, the liquid-liquid (LL_1 and LL_2) phase boundary curves are labeled as being of the upper critical solution temperature (UCST) type and the lower critical solution temperature (LCST) type. The phase behavior of polymer-solvent mixtures is quite different from that of conventional binary small molecule mixtures. Fig. 1 shows a generalized pressure-temperature (P-T) phase diagram for a mixture of two components. The upper-critical-solution-temperature (UCST) line has a large, negative slope and separates a single phase, dense fluid region from a two-phase liquid +liquid region. Typically, UCST behavior is governed by enthalpic (i.e., energetic) interactions between the two components [Bardin and Patterson, 1969]. Enthalpic interactions are the result of intermolecular forces between the components in the mixture which are not strongly dependent on the pressure because the density of the phase containing the components is rather high [Prausnitz et al., 1986; McHugh et al., 1993]. Since the UCST curve separates a single dense fluid phase from two dense liquid phases, the density of the mixture is not strongly dependent on the pressure. As a result, pressure does not have a significant effect on the location of the UCST curve in binary polymer-solvent mixtures. The solid curve separating the fluid region from the liquid+vapor region is termed the lower-critical-solution-temperature (LCST) curve. 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 [Zeman and Patterson, 1972]. 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-phase line is termed the upper-critical-end-point (UCEP), and similarly, the LCST curve intersects the three-phase 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 from the two phase liquid+liquid region. At low temperatures, the UCST curve separates a single phase from two liquid phases. Because polymers are usually polydisperse, these "binary" phase diagrams actually represent multicomponent phase behavior in which the polymer is treated as a pseudo-pure component.

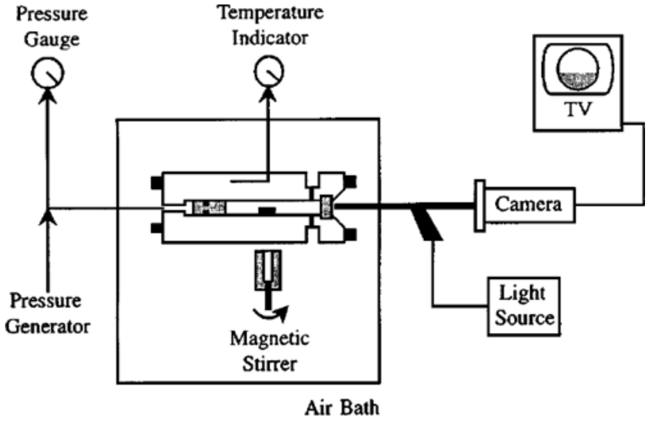

Fig. 2. Schematic diagram of the experimental apparatus used in this study.

As the degree of molecular asymmetry between the polymer and solvent increases, e.g. as the molecular weight and density differences increase, the UCST and LCST curves approach each other. Eventually, the two curves merge to become a single curve, labeled U-LCST in Fig. 1, as suggested by Chen and Radosz [1992].

EXPERIMENTAL SECTION

1. Apparatus and Procedure

Fig. 2 shows a schematic diagram of a cloud-point, liquid-liquid-vapor, and bubble-point transition in a typical polymer-supercritical solvent-cosolvent system. The details of the experimental apparatus and procedure used in this work are described elsewhere [Byun and McHugh, 2000; Byun and Kim, 1996], so only a brief overview is given here. All cloud-points are determined isothermally in a variable-volume view cell capable of operating at pressures to 3,000 bar and temperature as high as 250 °C. The body of the cell is constructed of a high nickel content steel (Nitroic 50) that has a 5.7 cm o.d. by 1.59 cm i.d. and a 28 cm^3 working volume. A 1.9 cm o.d. by 1.9 cm thick sapphire window is fitted to one end of the cell and is sealed with an elastomeric O-ring. The cell contents are compressed to the desired operating pressure by displacing a piston in the cell by using water pressurized with a high-pressure generator (High Pressure Equipment Co., model 37-5.75-60). The pressure of system is the water pressure measured with a Heise gauge (Dresser Industries, Heise model CM-108952, accurate to within ±3.5 bar) plus the 1 bar of pressure needed to move the piston toward the back of the cell. The temperature of the cell is measured with a platinum resistance thermal device (RTD) (Thermometrics Corp., Class A accuracy) and maintained to within ±0.1 °C and measured to within ±0.2 °C with a thermometer placed in a thermowell on the surface of the cell. The RTD is connected to a digital multimeter (Yokogawa, model 7563, accurate to within ±0.005%). The mixture in the cell is stirred by a magnetic stir bar, which is activated by an external magnet beneath the cell. The mixture inside the cell is viewed on a video monitor by using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window.

Cloud-points are measured for the polymer solutions at a fixed polymers (PPA and PPMA) concentration of 5.0±0.5 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 point are taken does not influence the results. Polymer is loaded into the cell to within ±0.002 g and then the cell is purged with nitrogen followed by CO_2 (or ethylene) to ensure that all of the air is removed. Liquid monomer (propyl acrylate and propyl methacrylate) injected into the cell to within ±0.002 g by using a syringe and CO_2 is transferred into the cell gravimetrically to within ±0.05 g using a high pressure bomb. Cloud points are measured and reproduced at least twice to within ±2.8 bar and ±0.4 °C.

2. Materials

CO_2 (99.8% minimum purity) was obtained from Deasung Oxygen Co. and Ethylene (99.9% minimum purity) was obtained from Yeochun NCC. Both solvents are used without futher purification in the experiments. Poly(propyl acrylate) (M_w=140,000) and poly (propyl methacrylate) (M_w=250,000) were obtained from Scientific Polymer Products, Inc. Propyl acrylate (99.9% purity) and propyl methacrylate (99.9% purity) used in this work were obtained from Polysciences, Inc. To prevent propyl acrylate and propyl methacrylate polymerization, 4-methoxyphenol (Aldrich Co., 99% purity) were used as an inhibitor at a concentration of 0.005 times the amount of monomers.

Since the poly(propyl acrylate) was supplied in a toluene solution, the polymer solution was placed under vacuum for at least 10 h by the Rotary Evaporator (Tamato Scientific Co., model RE-47) for toluene (solvent) removal.

Table 1. Experimental cloud-point data for the poly(propyl acrylate)-CO_2-propyl acrylate system measured in this study

T (°C)	P (bar)
5.1 wt% PPA+0.0 wt% PA	
88.7	2070.7
90.1	1932.8
93.1	1794.8
97.1	1656.9
101.0	1556.9
110.5	1474.5
130.5	1332.1
150.8	1263.8
175.3	1215.5
5.0 wt% PPA+5.0 wt% PA	
45.9	1794.8
46.8	1519.0
49.8	1381.0
55.9	1241.7
75.3	1092.1
95.9	1039.7
115.3	1023.8
135.5	1015.5
155.8	1015.5
5.0 wt% PPA+11.7 wt% PA	
34.9	645.9
50.7	669.3
71.6	698.4
91.0	737.6
112.0	789.7
133.8	798.8
5.1 wt% PPA+30.4 wt% PA	
32.4	84.5
40.9	118.3
60.4	199.0
81.4	268.3
100.1	330.3
121.6	396.6

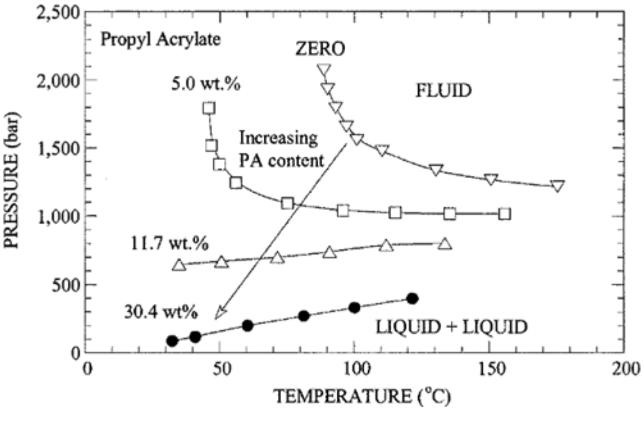

Fig. 3. Impact of free propyl acrylate monomer (on a polymer-free basis) on the phase behavior of the poly(propyl acrylate)-CO_2 system.

RESULTS AND DISCUSSION

1. PPA-CO_2 (or C_2H_4)-PA Phase Behavior

Fig. 3 and Table 1 presents the PPA-CO_2-PA data obtained in this study. PPA does dissolve in pure CO_2 to temperature of 175 °C and pressure of 2,070 bar. With 5.0 wt% PA added to the solution, the cloud-point curve exhibits upper critical solution temperature (UCST) type phase behavior from positive slope to negative slope. Also, it is possible to solubilize PPA in CO_2 at pressures as low as 1,000 bar and temperatures as low as 80 °C. The 5.0 wt% PA cloud-point curve does exhibit a rapid increase in pressure at ~50 °C, which, more than likely, occurs because of a large increase in the energetics between polymer segments as compared to polymer segment-

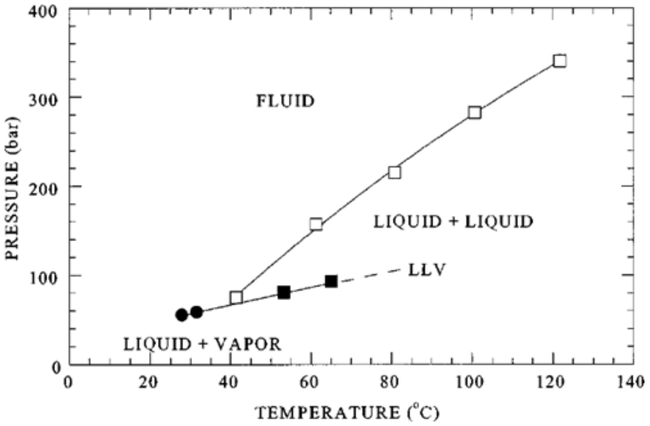

Fig. 4. Phase behavior of the poly(propyl acrylate)-CO_2-34.1 wt% propyl acrylate system obtained in this study. □, fluid → liquid+liquid transitions; ●, fluid → liquid+vapor transition; ■, liquid+liquid → liquid1+liquid2+vapor (LLV) transitions; ---, suggested extension of the LLV line.

solvent interactions. If the PA concentration is increased to 11.7 wt%, the cloud-point curve exhibits lower critical solution temperature (LCST) type phase behavior with a positive slope, and it is a continuous curve down to 40 °C and ~650 bar. With 30.4 wt% PA, the phase behavior curve is almost parallel to the 11.7 wt% cloud-point curve, but the 30.4 wt% cloud-point curve is shifted to even lower pressures of ~84 bar at 32 °C. The 30.4 wt% curve exhibits LCST-type cloud-point curve with a positive slope.

When 40 wt% PA is added to the PPA-CO_2 solution, the cloud-point curve shown in Fig. 4 and Table 2 takes on the typical appearance of an LCST boundary. At 120 °C the phase boundary has shifted from 1,035 to 340 bar as the concentration of PA is increased from 5.0 to 34.1 wt%. The PPA-CO_2-34.1 wt% PA cloud-point curve intersects a fluid→liquid+vapor (LV) curve at ~40 °C and 60 bar. A liquid and vapor phase coexist at pressures below this curve, and the LV curve switches to a liquid$_1$+liquid$_2$+vapor (LLV) curve at temperatures greater than 40 °C. The initial slope of the PPA-CO_2-49 wt% PA LCST curve at the lowest pressures, ~3.2 bar/°C, is approximately 70% lower than that observed for binary poly(isobutylene)-alkane mixtures reported by Zeman and Patterson [1972].

Table 2. Experimental cloud-point, bubble-point and liquid-liquid-vapor data for the poly(propyl acrylate)-CO_2-propyl acrylate system measured in this study

T (°C)	P (bar)	Transition
5.2 wt% PPA+34.1 wt% PA		
Cloud-point transition		
41.3	74.8	CP
61.3	157.2	CP
80.8	215.2	CP
100.7	282.4	CP
121.7	340.3	CP
Bubble-point transition		
27.8	55.5	BP
31.4	59.0	BP
Liquid-liquid-vapor transition		
53.2	81.0	LLV
65.0	93.2	LLV

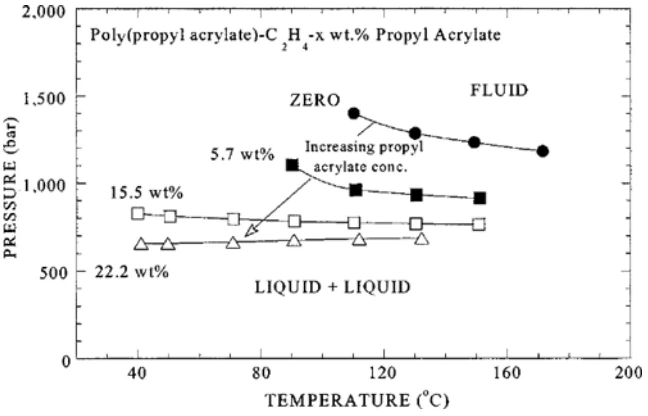

Fig. 5. Impact of free propyl acrylate monomer (on a polymer-free basis) on the phase behavior of the poly(propyl acrylate)-C_2H_4 system.

Fig. 5 and Table 3 show the cloud-point curve of the PPA-C_2H_4-0.0, 5.7, 15.5, and 22.2 wt% PA system. With 0.0-5.7 wt% PA added to the solution, the cloud-point curve exhibits UCST (upper critical solution temperature)-type phase behavior with a negative slope. With 15.5 wt% PA in solution the cloud-point pressure remains vir-

Table 3. Experimental cloud-point data for the poly(propyl acrylate)-C_2H_4-propyl acrylate system measured in this study

T (°C)	P (bar)
5.4 wt% PPA+0.0 wt% PA	
110.2	1401.0
130.2	1285.2
149.4	1232.1
171.5	1183.1
5.1 wt% PPA+5.7 wt% PA	
90.0	1104.2
110.7	961.7
130.6	933.5
151.1	913.8
4.7 wt% PPA+15.5 wt% PA	
39.8	826.9
50.3	811.0
70.9	795.5
90.8	781.0
110.2	774.8
130.5	767.9
150.8	763.8
4.6 wt% PPA+22.2 wt% PA	
41.0	656.9
49.6	657.6
70.8	664.5
90.7	675.2
112.0	682.1
132.4	686.2

tually constant at ~800 bar over a temperature range of 40 to 150 °C. If 22.2 wt% PA is added to the solution, the cloud-point curve exhibits slightly LCST-type phase behavior with a positive slope at low pressures.

Table 4. Experimental cloud-point data for the poly(propyl methacrylate)-CO_2-propyl methacrylate system measured in this study

T (°C)	P (bar)
4.8 wt% PPMA+5.2 wt% PMA	
90.5	2484.5
91.5	2263.8
93.1	2099.7
95.5	1959.0
100.2	1776.2
100.8	1754.1
119.5	1520.3
140.2	1390.0
160.4	1326.6
186.2	1281.0
4.7 wt% PPMA+13.2 wt% PMA	
34.9	1505.2
53.0	1081.7
71.0	978.3
90.8	942.1
109.7	933.5
131.8	936.2
150.9	941.4
169.2	949.0
5.1 wt% PPMA+20.1 wt% PMA	
38.3	547.9
55.5	575.5
70.2	600.4
90.7	641.0
110.3	681.0
130.6	716.6
153.3	744.8

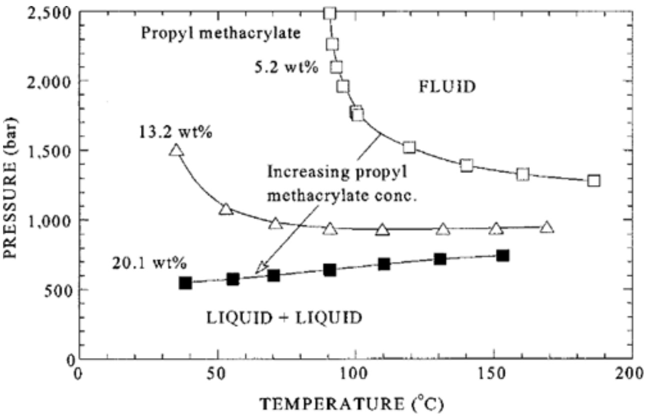

Fig. 6. Impact of free propyl methacrylate monomer (on a polymer-free basis) on the phase behavior of the poly(propyl methacrylate)-CO_2 system.

2. PPMA-CO_2-PMA Phase Behavior

Table 4 and Fig. 6 present the cloud-point behavior of the PPMA-CO_2-PMA system data obtained in this study. The PPMA does not dissolve in pure CO_2 to temperature of 232 °C and pressure of 2,500 bar. When 5.2 wt% PMA is added to the PPMA-CO_2 solution, the cloud-point curve exhibits UCST-type phase behavior of the negative slope. With 13.2 wt% PMA added to the solution, the cloud-point curve exhibits U-LCST-type phase from positive slope to a negative. The cloud-point behavior shows virtually flat at ~950 bar, a temperature range of 70 to 170 °C. Also at 150 °C, the cloud-point pressure of the PPMA-CO_2-PMA system decreases by ~500 bar with the first 8.0 wt% PMA added to the solution, and it decreases by another ~200 bar with the addition of next ~7 wt%. The temperature where the cloud-point changes the slope shifts from 150 to 90 °C with the addition of the first 5.2 wt% PMA, and it shifts

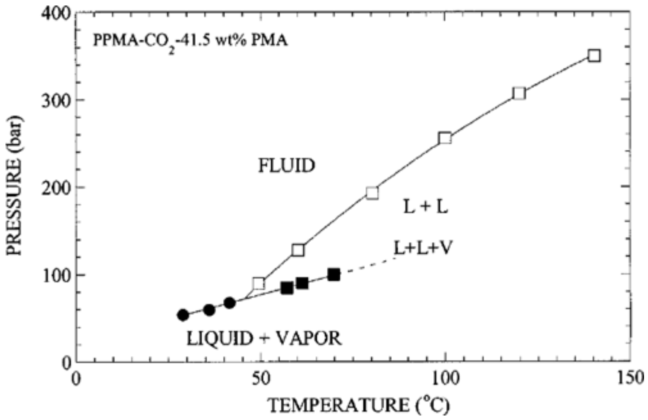

Fig. 7. Phase behavior of the poly(propyl methacrylate)-CO_2-41.5 wt% propyl methacrylate system obtained in this study. □, fluid → liquid+liquid transitions; ●, fluid → liquid+vapor transition; ■, liquid+liquid → liquid1+liquid2+vapor (LLV) transitions; ---, suggested extension of the LLV line.

Table 5. Experimental cloud-point, bubble-point and liquid-liquid-vapor data for the poly(propyl methacrylate)-CO_2-propyl methacrylate system measured in this study

T (°C)	P (bar)	Transition
5.1 wt% PPMA+41.5 wt% PMA		
Cloud-point transition		
49.4	89.3	CP
60.1	127.6	CP
80.4	192.4	CP
99.9	255.5	CP
120.0	306.9	CP
140.4	350.0	CP
Bubble-point transition		
41.5	67.2	BP
36.0	59.7	BP
28.9	53.5	BP
Liquid-liquid-vapor transition		
57.1	84.9	LLV
61.3	89.7	LLV
69.8	99.6	LLV

further to ~500 bar with the addition of the next ~8 wt% PMA to the solution. The phase behavior curve with 20.1 wt% PMA has a slightly positive slope so that now the remnant of the sharp upturn in the cloud-point pressure is eliminated, which significantly expands the single-phase region. It is evident that the impact of PMA cosolvent diminishes as the PMA concentration increases.

Similarities are apparent between the phase behavior of the PPMA-CO_2-41.5 wt% PMA mixtures shown in Fig. 7 (Table 5) and the phase behavior of the PPA-CO_2-34.1 wt% PA mixture shown in Fig. 4. When 41.5 wt% PMA is added to the solution, the phase behavior curve exhibits LCST-type cloud-point behavior with a positive slope. The PPMA-CO_2-PMA cloud-point (LCST) curve intersects the LV curve at 45 °C and 70 bar with 41.5 wt% PMA. A liquid and a vapor phase coexist at pressures below this curve. Note that the LV behavior curve switches to a liquid+liquid+vapor (LLV) curve at greater than 45 °C. The slope of the PPMA-CO_2-PMA LCST curve, ~2.9 bar/°C, is approximately 40% greater than that observed for binary poly(isobutylene)-alkane mixtures reported Zeman and Patterson [1972].

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 pressures when operating with supercritical carbon dioxide as long as sufficient amounts of free PMA monomer are present in the solution.

CONCLUSIONS

Very modest pressures and temperatures are needed to dissolve poly(propyl acrylate) and poly(propyl methacrylate) in supercritical carbon dioxide if sufficient amounts of "free" propyl acrylate and propyl methacrylate monomer are present.

Cloud-point data are presented for binary and ternary mixtures of poly(propyl acrylate)-CO_2-propyl acrylate, poly(propyl acrylate)-C_2H_4-propyl acrylate and poly(propyl methacrylate)-CO_2-propyl methacrylate systems. With 34.1 wt% propyl acrylate added to the poly(propyl acrylate)-CO_2 mixture, the cloud-point curve is shown on the typical appearance of an LCST boundary. Cloud-point behavior is presented for PPA-C_2H_4-PA mixtures and with PA concentration of 0.0, 5.7, 15.5 and 22.2 wt%. The ternary PPMA-CO_2-PMA system is measured with cosolvent of 5.2-20.1 wt%. PPMA does not dissolve in pure CO_2 to 233 °C and 2,500 bar. The liquid PA and PMA monomers provide favorable intermolecular interactions between the polymer segments and the solvent molecules, which help dissolution of the polymer. Unreacted liquid monomer is the preferred cosolvent when polymerizing in supercritical CO_2 because unreacted monomer can be readily recycled to the reactor.

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