

Phase Behavior on the Binary and Ternary Mixtures of Poly(cyclohexyl acrylate) and Poly(cyclohexyl methacrylate) in Supercritical CO₂

Hun-Soo Byun

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea

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ABSTRACT: High-pressure phase behavior was measured for the CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate system at 40, 60, 80, 100, and 120°C and pressure up to 206 bar. This system exhibits type I phase behavior with a continuous mixture-critical curve. The experimental results for the CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate system were modeled using the Peng-Robinson equation of state. Experimental cloud-point data, at a temperature of 250°C and pressure of 2800 bar, were presented for ternary mixtures of poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate and poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate systems. Cloud-point pressures of poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate system were measured in the temperature range of 40 to 180°C and at pressures as high as 2200 bar with cyclohexyl acrylate concentrations of 22.5, 27.4, 33.2, and 39.2 wt %. Results showed that adding 45.6 wt % cyclohexyl acrylate to the poly(cyclohexyl acrylate)-CO₂ mixture significantly changes the phase behavior. This sys-

tem changed the pressure-temperature slope of the phase behavior curves from the upper critical solution temperature (UCST) region to the lower critical solution temperature (LCST) region with increasing cyclohexyl acrylate concentration. Poly(cyclohexyl acrylate) did not dissolve in pure CO₂ at a temperature of 250°C and pressure of 2800 bar. Also, the ternary poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate system was measured below 187°C and 2230 bar, and with cosolvent of 27.4-46.7 wt %. Poly(cyclohexyl methacrylate) did not dissolve in pure CO₂ at 240°C and 2500 bar. Also, when 53.5 wt % cyclohexyl methacrylate was added to the poly(cyclohexyl methacrylate)-CO₂ solution, the cloud-point curve showed the typical appearance of the LCST boundary. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1117-1125, 2004

Key words: phase behavior; supercritical fluids; carbon dioxide; monomers; miscibility; poly(cyclohexyl acrylate); poly(cyclohexyl methacrylate)

INTRODUCTION

The experimental data of phase behavior between a polymer and a mixture of supercritical fluids (SCFs) is needed to develop new polymer processing technologies and industrial applications. Also, the binary monomer-SCF is important for a number of applications with SCFs.

Recently we demonstrated that it is possible to dissolve polar (meth)acrylate polymers in supercritical carbon dioxide (SC CO₂) over a large temperature range at modest pressure if (meth)acrylate monomer is used.¹⁻³ For many free-radical polymerization reactions, the time needed to form high molecular weight polymer is on the order of seconds, whereas the residence time in the reactor is typically on the order of minutes. A liquid monomer can greatly enhance high

molecular weight polymer solubility in a given solvent for several different reasons. If the solvent is highly expanded, the addition of a dense, liquid cosolvent reduces the free-volume difference between the polymer and the solvent.^{1,4} Also, 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 a supercritical solvent is slightly more complicated because increasing the system pressure reduces the free-volume difference between the polymer and the solvent and increases the probability of interaction between polymer, solvent, and cosolvent segments in solution.⁶ The polymer-supercritical solvent-cosolvent studies at high pressure 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.^{5,7,8} In these cases, the cosolvency 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 an SCF solvent.

Correspondence to: hsbyun@yosu.ac.kr

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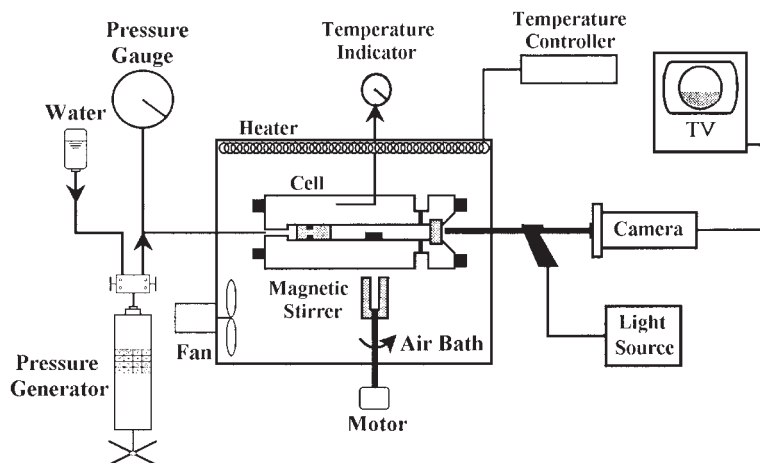


Figure 1 Schematic diagram of the experimental apparatus used in this study.

As a general rule the cloud-point curve of a mixture consisting of a highly polar component, in this case the poly(acrylate), and a much less polar component, here CO_2 , exhibits a negative slope in pressure-temperature space. The interchange that characterizes the balance of polymer segment- CO_2 cross-interactions, relative to polymer segment-segment and CO_2 - CO_2 self-interactions, is extremely temperature sensitive because of the strong polar interactions experienced between polymer segments. At the temperatures where entropic effects are expected to dominate, the location of the cloud-point curve is more a reflection of the free-volume difference between the dense polymer and the expanded CO_2 rather than the balance of intermolecular interactions.

Experimental phase behavior data of small amounts of the binary CO_2 -cyclohexyl acrylate and CO_2 -cyclohexyl methacrylate system were obtained to complement the poly(cyclohexyl acrylate)- CO_2 -cyclohexyl acrylate and poly(cyclohexyl methacrylate)- CO_2 -cyclohexyl methacrylate studies presented here because there are no literature phase behavior data available on this mixture. The primary purpose for obtaining the CO_2 -cyclohexyl acrylate and CO_2 -cyclohexyl methacrylate system was to determine whether CO_2 and cyclohexyl acrylate or cyclohexyl methacrylate form multiple phases in the pressure-temperature-composition regions explored in the poly(cyclohexyl acrylate)- CO_2 -cyclohexyl acrylate and poly(cyclohexyl methacrylate)- CO_2 -cyclohexyl methacrylate studies. The experimental data of CO_2 -cyclohexyl acrylate and CO_2 -cyclohexyl methacrylate system were fitted to the Peng-Robinson equation of state⁹ and the phase behavior for this binary solvent mixture was calculated at elevated operating temperatures and pressures.

The focus of this work is presented in the determination of the impact of cyclohexyl (meth)acrylate cosolvent on the phase behavior of the poly[cyclohexyl

(meth)acrylate]- CO_2 system. Given that CO_2 has been considered a desirable reaction medium for free-radical polymerizations,¹⁰ the phase behavior of these ternary poly(cyclohexyl acrylate)- SCO_2 -cyclohexyl acrylate and poly(cyclohexyl methacrylate)- SCO_2 -cyclohexyl methacrylate mixtures provides the information needed on the regions where homogeneous polymerization can occur in the presence of excess monomer.

EXPERIMENTAL

Apparatus and procedure

Figure 1 shows a schematic diagram of the experimental apparatus used for pressure-composition isotherms for the CO_2 -cyclohexyl acrylate and CO_2 -cyclohexyl methacrylate mixtures^{11,12} and obtained cloud-point curves for poly(cyclohexyl acrylate)- CO_2 -cyclohexyl acrylate and poly(cyclohexyl methacrylate)- CO_2 -cyclohexyl methacrylate ternary mixtures.^{13,14} The bubble-point, dew-point, critical-point, and cloud-point curves were obtained with a high-pressure, variable-volume cell described in detail elsewhere.¹³⁻¹⁶ Cloud-points were measured for the polymer solutions at a fixed poly(cyclohexyl acrylate) and poly(cyclohexyl methacrylate) concentration of 5.0 ± 0.5 wt %, which is typical of the concentrations used for polymer-SCF solvent studies.¹⁷ 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 was removed. Liquid cyclohexyl acrylate and cyclohexyl methacrylate were injected into the cell to within ± 0.002 g, using a syringe, and CO_2 was transferred into the cell gravimetrically to within ± 0.004 g, using a high-pressure bomb.

The mixture was compressed to the desired pressure with an internal piston displaced with water in a high-pressure generator (model 37-5.75-60; HIP Inc.,

Erie, PA). The pressure of the mixture was measured with a Heise gauge (model CM-108952, 0–3450 bar, accurate to within ± 3.5 bar; model CM-53,920, 0–340 bar; Dresser Instruments, Berea, KY). The temperature in the cell was measured using a platinum-resistance thermometer (Class A; Thermometrics Corp., Northridge, CA) connected to a digital multimeter (model 7563, accurate to within $\pm 0.005\%$; Yokogawa, Tokyo, Japan). The system temperature is typically maintained to within $\pm 0.2^\circ\text{C}$ below 200°C . The mixture inside the cell was viewed on a videomonitor using a camera coupled to a borescope (model F100-038-000-50; Olympus Corp., Osaka, 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 (model ILK-5; Olympus Optical Co., Tokyo, Japan) and at the other end to a borescope.

Mole fraction of monomer (cyclohexyl acrylate or cyclohexyl methacrylate) was accurate to within ± 0.002 . Cloud points were 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 CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate mixtures were measured and reproduced at least twice to within ± 0.3 bar and $\pm 0.2^\circ\text{C}$. CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate mole fractions have an estimated accumulation error of less than $\pm 0.8\%$, except for the data point at 1.0 mol % octadecyl acrylate.

Materials

CO₂ (99.8% minimum purity) was obtained from Daesung Oxygen Co. (Yeosu City, South Korea) and used as received. Poly(cyclohexyl acrylate) ($M_w = 150,000$) and poly(cyclohexyl methacrylate) ($M_w = 65,000$) were obtained from Scientific Polymer Products Inc. (Ontario, NY) and used as received.

The cyclohexyl acrylate (99.9% purity) and cyclohexyl methacrylate (98% purity) were obtained from Polysciences Co. (Warrington, PA) and used as received.

To prevent cyclohexyl acrylate or cyclohexyl methacrylate polymerization, 2,6-di-*tert*-butyl-4-methyl phenol (99% purity; Aldrich, Milwaukee, WI) was used as an inhibitor at a concentration of 0.005 times the amount of cyclohexyl acrylate or cyclohexyl methacrylate. Because the poly(cyclohexyl acrylate) was supplied in a toluene solution, the polymer solution was placed under vacuum for at least 10 h by a rotary evaporator (model RE-47; Tamato Scientific Co., Japan) for toluene removal.

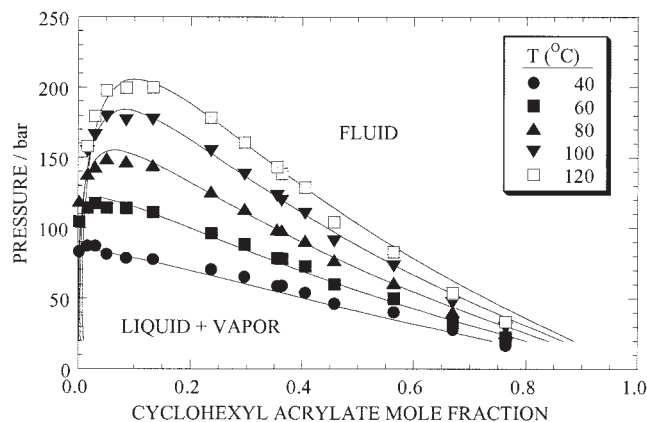


Figure 2 Comparison of the experimental data (symbols) for the CO₂-cyclohexyl acrylate system with calculations (solid lines) obtained with the Peng–Robinson equation of state, where $k_{ij} = 0.031$ and $\eta_{ij} = 0.006$.

RESULTS AND DISCUSSION

Phase behavior of CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate mixture

Bubble-, critical-, and dew-point curves for both the carbon dioxide–cyclohexyl acrylate and carbon dioxide–cyclohexyl methacrylate systems 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 were accurate to within ± 0.002 .

The carbon dioxide–cyclohexyl acrylate and carbon dioxide–cyclohexyl methacrylate mixtures for the solubility isotherms at 40–120°C were arranged according to the value of at least two independent data points having an estimated accumulated error of less than $\pm 1.0\%$.

Figure 2 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 19–200 bar for the carbon dioxide–cyclohexyl acrylate system. As shown in Figure 2, three phases were not observed at any of the five temperatures studied.

Figure 3 and Table II show the experimental phase behavior of $P - x$ isotherms at 40, 60, 80, 100, and 120°C for the carbon dioxide–cyclohexyl methacrylate system. The $P - x$ isotherms shown in Figure 3 are consistent with the characteristics expected for a type I system, where a maximum occurs in the critical mixture curve at 40, 60, 80, 100, and 120°C.

The experimental data obtained in this work were modeled using the Peng–Robinson equation of state. This equation of state is briefly described here. The Peng–Robinson equation⁹ of state is used with the following mixing rules:

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

TABLE I
Experimental Data for the Carbon Dioxide–Cyclohexyl Acrylate System Measured in This Study

Mole fraction of the cyclohexyl acrylate	Pressure (bar)	Transition	Mole fraction of the cyclohexyl acrylate	Pressure (bar)	Transition
$T = 40^\circ\text{C}$					
0.002	83.5	DP	0.237	125.9	BP
0.017	87.4	CP	0.297	113.5	BP
0.030	87.2	BP	0.355	99.1	BP
0.051	81.4	BP	0.363	98.6	BP
0.086	78.6	BP	0.405	91.0	BP
0.133	77.8	BP	0.458	77.4	BP
0.237	70.7	BP	0.564	61.4	BP
0.297	65.5	BP	0.670	40.5	BP
0.355	58.9	BP	0.764	25.9	BP
0.363	59.3	BP	$T = 100^\circ\text{C}$		
0.405	54.1	BP	0.017	154.3	DP
0.458	46.6	BP	0.030	165.5	DP
0.564	40.3	BP	0.051	175.0	DP
0.670	27.8	BP	0.086	176.4	CP
0.764	16.9	BP	0.133	176.7	BP
$T = 60^\circ\text{C}$					
0.002	104.7	DP	0.237	154.7	BP
0.017	114.3	DP	0.297	138.1	BP
0.030	117.6	CP	0.355	122.8	BP
0.051	114.3	BP	0.363	119.5	BP
0.086	114.1	BP	0.405	110.2	BP
0.133	111.3	BP	0.458	90.7	BP
0.237	96.4	BP	0.564	72.9	BP
0.297	88.5	BP	0.670	46.9	BP
0.355	78.6	BP	0.764	29.5	BP
0.363	78.5	BP	$T = 120^\circ\text{C}$		
0.405	73.1	BP	0.017	157.9	DP
0.458	60.2	BP	0.030	179.3	DP
0.564	50.3	BP	0.051	194.6	DP
0.670	33.3	BP	0.086	199.5	CP
0.764	22.6	BP	0.133	199.8	BP
$T = 80^\circ\text{C}$					
0.002	119.0	DP	0.237	178.5	BP
0.017	138.3	DP	0.297	160.9	BP
0.030	143.5	DP	0.355	143.5	BP
0.051	149.3	CP	0.363	138.5	BP
0.086	147.2	BP	0.405	129.0	BP
0.133	144.7	BP	0.458	104.1	BP
			0.564	83.1	BP
			0.670	54.0	BP
			0.764	33.5	BP

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

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

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

where k_{ij} and η_{ij} are interaction binary parameters, determined by fitting pressure–composition data, and a_{ii} and b_{ii} are pure component parameters, as defined by Peng and Robinson.⁹

These two binary interaction parameters were determined by regression experimental data with the Peng–Robinson equation of state. Objection function (OBF) and root mean squared relative deviation

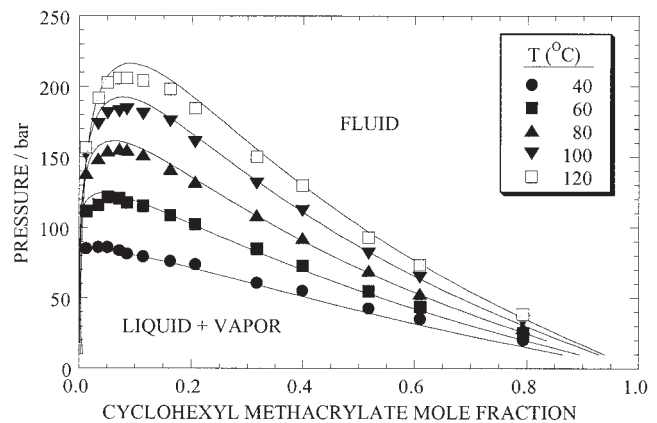


Figure 3 Comparison of the experimental data (symbols) for the CO₂–cyclohexyl methacrylate system with calculations (solid lines) obtained with the Peng–Robinson equation of state, where $k_{ij} = 0.033$ and $\eta_{ij} = -0.013$.

TABLE II
Experimental Data for the Carbon Dioxide–Cyclohexyl Methacrylate System Measured in This Study

Mole fraction of the cyclohexyl methacrylate	Pressure (bar)	Transition	Mole fraction of the cyclohexyl methacrylate	Pressure (bar)	Transition
<i>T</i> = 40°C					
0.012	85.2	DP	0.162	141.7	BP
0.034	86.2	CP	0.206	132.4	BP
0.050	86.4	BP	0.317	108.8	BP
0.071	79.7	BP	0.399	92.6	BP
0.085	81.4	BP	0.518	69.3	BP
0.114	79.7	BP	0.609	53.1	BP
0.162	76.2	BP	0.793	29.0	BP
0.206	74.0	BP	<i>T</i> = 100°C		
0.317	60.7	BP	0.012	152.1	DP
0.399	55.2	BP	0.034	173.3	DP
0.518	42.8	BP	0.050	181.0	DP
0.609	35.2	BP	0.071	182.1	CP
0.793	20.3	BP	0.085	180.7	BP
<i>T</i> = 60°C					
0.012	111.7	DP	0.114	180.5	BP
0.034	116.2	DP	0.162	175.3	BP
0.050	122.1	CP	0.206	160.5	BP
0.071	117.8	BP	0.317	131.2	BP
0.085	117.9	BP	0.399	111.7	BP
0.114	115.7	BP	0.518	81.7	BP
0.162	108.6	BP	0.609	64.7	BP
0.206	102.4	BP	0.793	33.6	BP
0.317	85.2	BP	<i>T</i> = 120°C		
0.399	73.1	BP	0.012	156.6	DP
0.518	55.0	BP	0.034	191.9	DP
0.609	44.0	BP	0.050	202.6	DP
0.793	25.2	BP	0.071	205.7	CP
<i>T</i> = 80°C					
0.012	138.6	DP	0.085	205.9	BP
0.034	148.8	DP	0.114	204.1	BP
0.050	154.5	CP	0.162	197.9	BP
0.071	152.8	BP	0.206	184.5	BP
0.085	153.1	BP	0.317	150.3	BP
0.114	151.9	BP	0.399	129.8	BP
			0.518	92.9	BP
			0.609	73.3	BP
			0.793	38.5	BP

(RMSD) percentage of this calculation were defined as follows:

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

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

where *ND* is the number of data points. We used Marquardt¹⁷ to optimize the objection function. All isotherms were included for calculation.

Table III lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide,¹⁸ cyclohexyl acrylate, and cyclohexyl

methacrylate that are used with the Peng–Robinson equation of state.⁹ The boiling point of cyclohexyl acrylate and cyclohexyl methacrylate were obtained from Polysciences Inc. The properties of cyclohexyl

TABLE III
Pure Component Parameters for the Peng–Robinson Equation of State^a

Compound	<i>M_w</i>	<i>T_c</i> (K)	<i>P_c</i> (bar)	<i>ω</i>
Carbon dioxide	44.01	304.3	73.9	0.225
Cyclohexyl acrylate	154.21	662.46	31.7	0.4226
Cyclohexyl methacrylate	168.24	685.79	27.1	0.4641

^a From Reid et al.¹⁸

acrylate and cyclohexyl methacrylate were calculated by the group-contribution method.¹⁸ Also, the vapor pressures were calculated by the Lee–Kesler method.¹⁸

Figure 2 shows a comparison of experimental results of carbon dioxide–cyclohexyl acrylate with calculated values obtained using the Peng–Robinson equation, at a temperature of 80°C. The binary interaction parameters of the Peng–Robinson equation of state were fitted by the experimental data at 80°C. The values of the optimized parameters (bubble-point data = 11, RMSD = 4.15%) of the Peng–Robinson equation of state for the carbon dioxide–cyclohexyl acrylate system are $k_{ij} = 0.031$ and $\eta_{ij} = 0.006$. A reasonable fit of the data was obtained over most of the composition range, even if no mixture parameters were used. However, if the two mixture parameters, $k_{ij} = 0.031$ and $\eta_{ij} = 0.006$, are used, the fit of the experimental results was significantly better. The RMSD at five temperatures for carbon dioxide–cyclohexyl acrylate system was 5.93% of the bubble-point number 56.

We compared the experimental results with calculated $P - x$ isotherms at temperatures of 40, 60, 100, and 120°C for the carbon dioxide–cyclohexyl acrylate system, using the optimized values of k_{ij} and η_{ij} determined at 80°C. As shown in Figure 2, a good fit of the data was obtained with the Peng–Robinson equation, using adjustable mixture parameters for the carbon dioxide–cyclohexyl acrylate system.

Figure 3 shows a comparison of experimental with calculated $P - x$ isotherms at temperatures of 40, 60, 80, 100, and 120°C for the carbon dioxide–cyclohexyl methacrylate system. These isotherms were calculated using the optimized values (bubble-point data = 10, RMSD = 1.82%) of $k_{ij} = 0.033$ and $\eta_{ij} = -0.013$ determined at 80°C in the same way as above. The RMSD at five temperatures for carbon dioxide–cyclohexyl methacrylate system was 9.29% of the bubble-point number 49.

Phase behavior of poly(cyclohexyl acrylate)–CO₂–cyclohexyl acrylate and poly(cyclohexyl methacrylate)–CO₂–cyclohexyl methacrylate system

Table IV and Figure 4 show the cloud-point behavior of the poly(cyclohexyl acrylate)–CO₂– x wt % cyclohexyl acrylate mixture obtained in this study. The poly(cyclohexyl acrylate) does not dissolve in pure CO₂ at a temperature of 250°C and pressure of 2800 bar. With 22.5 wt % cyclohexyl acrylate added to the solution, the cloud-point curve exhibits upper critical solution temperature (UCST)–type phase behavior with a negative slope. With 27.4 wt % cyclohexyl acrylate in solution, the cloud-point pressure curve shows pressures from about 900 to 2000 bar and a temperature range of 60 to 180°C. If 33.2 wt % cyclohexyl acrylate is added to the solution, the cloud-point curve exhibits upper/lower critical solution tempera-

TABLE IV
Experimental Cloud-Point Data for the Poly(cyclohexyl acrylate) [P(cyHA)]–CO₂–Cyclohexyl Acrylate (cyHA) System Measured in This Study

T (°C)	P (bar)
4.8 wt % P(cyHA) + 22.5 wt % cyHA	
142.7	2192.1
144.2	2146.6
145.5	2105.2
146.1	2065.2
149.2	1946.6
153.3	1819.7
154.3	1802.1
160.4	1621.4
171.8	1522.8
182.9	1401.4
5.4 wt % P(cyHA) + 27.4 wt % cyHA	
59.1	2018.3
69.3	1515.5
79.4	1298.3
99.5	1096.2
119.6	1004.1
139.6	959.0
160.6	934.8
179.9	917.2
5.0 wt % P(cyHA) + 33.2 wt % cyHA	
40.9	1051.7
60.1	892.4
80.2	817.2
100.4	775.2
120.5	768.3
140.8	770.3
159.8	775.2
179.4	777.2
5.0 wt % P(cyHA) + 39.2 wt % cyHA	
39.8	403.1
62.5	438.3
81.9	473.8
101.2	510.0
121.7	536.2
141.6	559.7
162.8	583.1
181.2	579.7

ture (U-LCST)–type phase behavior from a positive slope at low pressures to a negative slope, increasing smoothly at 100°C. The cloud-point curve for the poly(cyclohexyl acrylate)–CO₂–39.2 wt % cyclohexyl acrylate system exhibits LCST-region phase behavior with a positive slope, and is a continuous curve down to 40°C and about 400 bar.

The effect of cyclohexyl acrylate cosolvent on the phase behavior is similar to that observed for the poly(butyl acrylate)–CO₂–butyl acrylate¹ and poly(ethyl methacrylate)–CO₂–ethyl methacrylate systems.³ The slope of the 45.6 wt % cyclohexyl acrylate curve is about 2.9 bar/°C, which is very close to the slope found for the poly(butyl acrylate)–CO₂–32 wt % butyl acrylate curve.¹ These slopes are about 40% greater than those observed for binary poly(isobutylene)–alkane mixtures reported by Zeman and Patter-

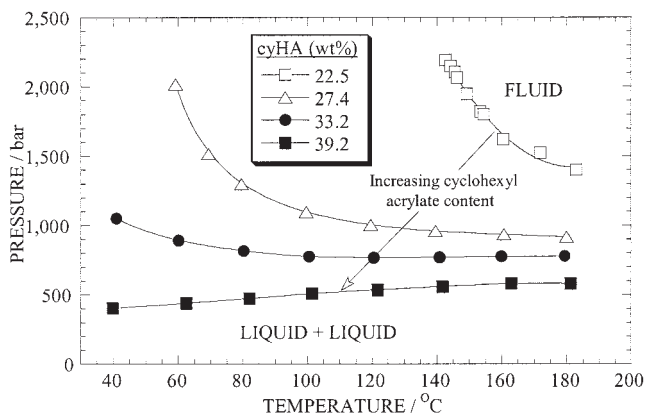


Figure 4 Experimental cloud-point curves for the poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate system with different cyclohexyl acrylate concentrations. The concentration of poly(cyclohexyl acrylate) is 5.0 ± 1.0 wt % for these data.

son,¹⁹ attributed to the enhanced influence of hydrostatic pressure on the free-volume difference between poly(cyclohexyl acrylate) and the CO₂-cyclohexyl acrylate mixture. Even though the poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate curve extends to 30°C, bubble points are observed, which implies that the cloud-point curve will intersect the liquid-liquid-vapor (LLV) curve at a much lower temperature. Finally, it is noted that the effect of cyclohexyl acrylate cosolvent on the location of the cloud-point curve diminishes in a nonlinear fashion as increased amounts of cyclohexyl acrylate are added to the solution. This diminishing returns effect is also seen with the poly-(butyl acrylate)-CO₂-butyl acrylate and poly(ethyl methacrylate)-CO₂-ethyl methacrylate systems. When 45.6 wt % cyclohexyl acrylate is added to the

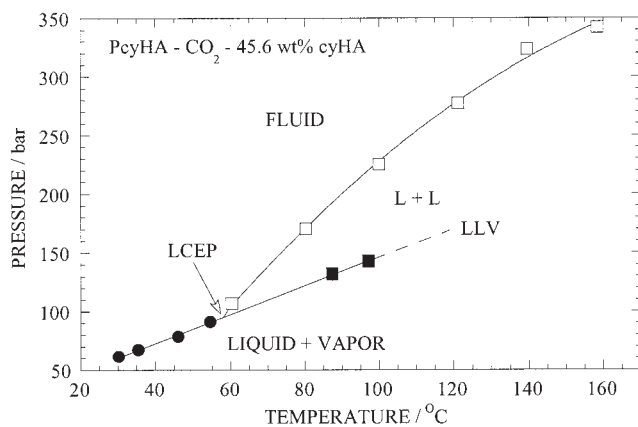


Figure 5 Impact of 45.6 wt % cyclohexyl acrylate monomer (on a polymer-free basis) on the phase behavior of the poly(cyclohexyl acrylate)-CO₂ system. □, fluid → liquid + liquid transition; ●, fluid → liquid + vapor transition; ■, liquid + liquid → liquid₁ + liquid₂ + vapor (LLV) transition; ---, suggested extension of the LLV line.

TABLE V
Experimental Cloud-Point, Bubble-Point, and Liquid-Liquid-Vapor Data for the Poly(cyclohexyl acrylate) [P(cyHA)]-CO₂-Cyclohexyl Acrylate (cyHA) System Measured in This Study

<i>T</i> (°C)	<i>P</i> (bar)	Transition
5.3 wt % P(cyHA) + 45.6 wt % cyHA		
Cloud-point transition		
60.3	106.9	CP
80.3	170.3	CP
100.0	225.2	CP
121.1	277.2	CP
139.5	323.5	CP
158.4	342.1	CP
Bubble-point transition		
30.2	61.7	BP
35.3	67.6	BP
45.9	79.0	BP
54.5	91.4	BP
Liquid-liquid-vapor transition		
87.3	132.0	LLV
97.0	143.1	LLV

poly(cyclohexyl acrylate)-CO₂ solution, the cloud-point curve, shown in Figure 5 and Table V, takes on the typical appearance of an LCST boundary. At 140°C the phase boundary has shifted from 323 to 560 bar as the concentration of cyclohexyl acrylate is increased from 39.2 to 45.6 wt %. The poly(cyclohexyl acrylate)-CO₂-45.6 wt % cyclohexyl acrylate phase behavior curve intersects a liquid → liquid + vapor (LV) curve at about 57°C and about 95 bar. A liquid and vapor phase coexist at pressures below this curve, and the LV curve switches to a liquid₁ + liquid₂ + vapor (LLV) curve at temperatures ≥ 57°C. The initial slope of the poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate LCST curve at the lowest pressures is about 2.9 bar/°C. The results obtained in this study clearly dem-

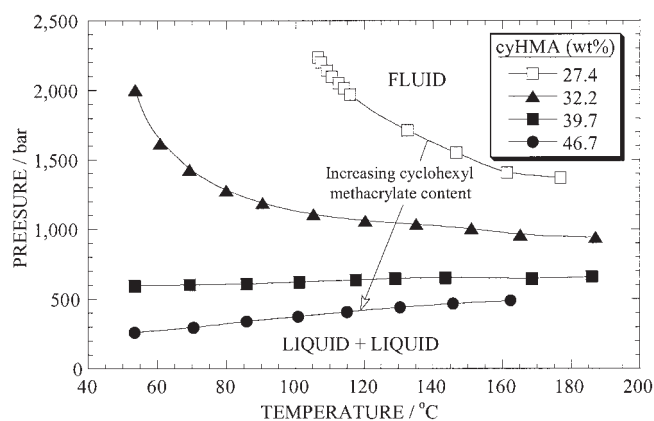


Figure 6 Experimental cloud-point curves for the poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate system with different cyclohexyl methacrylate concentrations. The concentration of poly(cyclohexyl acrylate) is 5.0 ± 0.5 wt % for these data.

TABLE VI
Experimental Cloud-Point Data for the Poly(cyclohexyl methacrylate) [P(cyHMA)]-CO₂-Cyclohexyl Methacrylate (cyHMA) System Measured in This Study

T (°C)	P (bar)
5.4 wt % P(cyHMA) + 27.4 wt % cyHMA	
106.5	2234.1
107.5	2198.3
109.2	2141.7
110.6	2095.5
112.5	2052.1
114.1	2016.2
115.9	1968.6
132.6	1712.1
146.6	1551.0
161.4	1405.2
176.8	1371.0
5.4 wt % P(cyHMA) + 32.2 wt % cyHMA	
53.6	2003.5
60.8	1617.9
69.2	1429.3
79.8	1277.2
90.4	1189.0
105.2	1106.6
120.3	1061.7
135.1	1035.9
151.0	1005.9
165.2	960.7
187.0	940.7
5.4 wt % P(cyHMA) + 39.7 wt % cyHMA	
53.4	595.5
69.4	602.4
85.8	608.3
101.1	622.1
117.5	636.9
129.0	647.6
143.6	653.5
168.4	645.5
185.8	660.0
5.4 wt % P(cyHMA) + 46.7 wt % cyHMA	
53.4	261.0
70.3	297.2
85.7	339.7
100.7	374.1
115.0	409.3
130.6	440.7
145.9	466.2
162.4	487.6

onstrate that it is possible to obtain a single phase that extends over a modest pressures when operating with SC CO₂ as long as sufficient amounts of free cyclohexyl acrylate monomer are present in the solution.

Figure 6 and Table VI show the cloud-point curve of the poly(cyclohexyl methacrylate)-CO₂-27.4, 32.2, 39.7 and 46.7 wt % cyclohexyl methacrylate system. The poly(cyclohexyl methacrylate) does not dissolve in pure CO₂ at a temperature of 240°C and pressure of 2500 bar. With 27.4 and 32.2 wt % cyclohexyl methacrylate added to the solution, the cloud-point curve exhibits UCST-type phase behavior with a negative slope.

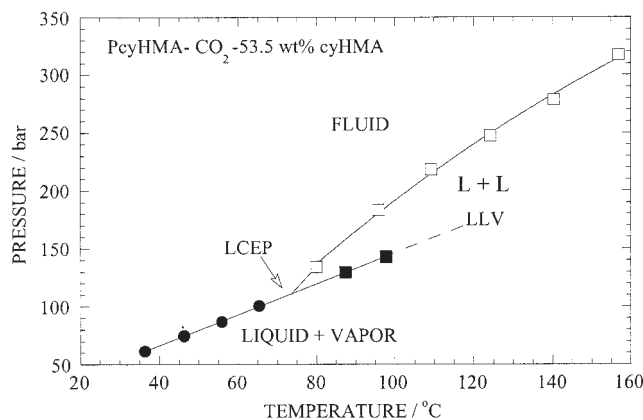


Figure 7 Impact of 53.5 wt % cyclohexyl methacrylate monomer (on a polymer-free basis) on the phase behavior of the poly(cyclohexyl methacrylate)-CO₂ system. □, fluid → liquid + liquid transition; ●, fluid → liquid + vapor transition; ■, liquid + liquid → liquid₁ + liquid₂ + vapor (LLV) transition; ---, suggested extension of the LLV line.

When 39.7 wt % cyclohexyl methacrylate is added to the poly(cyclohexyl methacrylate)-CO₂ solution, the cloud-point curve shown in Figure 6 is virtually flat at about 650 bar and temperature range of 50 to 185°C. Also at 150°C, the cloud-point pressure of the poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate system decreases by about 500 bar, with the first 4.8 wt % cyclohexyl methacrylate (27.4 wt % → 32.2 wt %) added to the solution, and it decreases by another nearly 350 bar with the addition of the next approximately 7.5 wt % (32.2 wt % → 39.7 wt %). With addition of the next 7.0 wt % cyclohexyl methacrylate (39.7 wt % → 46.7 wt %), the cloud-point pressure decreases by 150 bar.

TABLE VII
Experimental Cloud-Point, Bubble-Point, and Liquid-Liquid-Vapor Data for the dPoly(cyclohexyl methacrylate) [P(cyHMA)]-CO₂-Cyclohexyl Methacrylate (cyHMA) System Measured in This Study

T (°C)	P (bar)	Transition
5.4 wt % P(cyHMA) + 53.5 wt % cyHMA		
Cloud-point transition		
79.9	134.1	CP
95.8	183.5	CP
109.2	218.3	CP
124.2	247.6	CP
140.2	278.6	CP
156.8	317.2	CP
Bubble-point transition		
36.3	61.4	BP
46.2	74.8	BP
55.8	86.9	BP
65.3	100.7	BP
Liquid-liquid-vapor transition		
87.3	129.6	LLV
97.7	143.1	LLV

The phase behavior curve with poly(cyclohexyl methacrylate)-CO₂-46.7 wt % cyclohexyl methacrylate 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 cyclohexyl methacrylate cosolvent diminishes as the cyclohexyl methacrylate concentration increases.

Similarities are apparent between the phase behavior of the poly(cyclohexyl methacrylate)-CO₂-53.5 wt % cyclohexyl methacrylate mixtures shown in Figure 7 (Table VII) and that of the poly(cyclohexyl acrylate)-CO₂-45.6 wt % cyclohexyl acrylate mixture shown in Figure 4. When 53.5 wt % cyclohexyl methacrylate is added to the solution, the phase behavior curve exhibits LCST-type cloud-point behavior with a positive slope. The poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate cloud-point (LCST) curve intersects the LV curve at 73°C and 110 bar with 53.5 wt % cyclohexyl methacrylate. A liquid and vapor phase coexist at pressures below this curve. Note that the LV behavior curve switches to a liquid + liquid + vapor (LLV) curve at temperatures > 73°C. The slope of the poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate LCST curve, at about 2.9 bar/°C, is nearly 40% greater than that observed for binary poly-(isobutylene)-alkane mixtures reported by Zeman and Patterson.¹⁹

CONCLUSION

The CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate systems exhibit type I phase behavior. The $P - x$ bubble-point curves are convex, which indicates that CO₂ exhibits high solubility in cyclohexyl acrylate and cyclohexyl methacrylate, likely attributed to the formation of a weak complex between the carboxylic oxygen in cyclohexyl acrylate (cyclohexyl methacrylate) and the carbon in CO₂. The Peng-Robinson equation of state can be used with two adjustable parameters to calculate a reasonable representation of the phase behavior of the CO₂-cyclohexyl acrylate and CO₂-cyclohexyl methacrylate systems.

Cloud-point data are presented for binary and ternary mixtures of poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate and poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate systems. With 45.6 wt % cyclohexyl acrylate added to the poly(cyclohexyl ac-

rylate)-CO₂ mixture, the cloud-point curve shows the typical appearance of an LCST boundary. Cloud-point behavior is presented for poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate mixtures and with cyclohexyl acrylate concentrations of 22.5, 27.4, 33.2, and 39.2 wt %. The ternary poly(cyclohexyl methacrylate)-CO₂-cyclohexyl methacrylate system was measured with cosolvent amounts of 27.4-46.7 wt %. Poly(cyclohexyl acrylate) and poly(cyclohexyl methacrylate) do not dissolve in pure CO₂ at 250°C and 2800 bar. The liquid cyclohexyl acrylate and cyclohexyl methacrylate monomers provide favorable intermolecular interactions between the polymer segments and the solvent molecules, which promote dissolution of the polymer.

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