Phase Behavior for Mixtures of Poly(2-ethylhexyl acrylate) + 2-Ethylhexyl Acrylate and Poly(2-ethylhexyl methacrylate) + 2-Ethylhexyl Methacrylate with Supercritical Fluid Solvents

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Experimental cloud-point data up to 478 K and 248.0 MPa are reported for binary and ternary mixtures of poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) + 2-ethylhexyl methacrylate (3) and poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + 2-ethylhexyl acrylate (3) systems. High-pressure cloud-point data are also reported for poly(2-ethylhexyl methacrylate) and poly(2-ethylhexyl acrylate) in supercritical propane, propylene, butane, 1-butene, and dimethyl ether. Cloud-point behavior for the poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) + 2-ethylhexyl methacrylate (3) system were measured in changes of the pressure, temperature (p, T) slope and with 2-ethylhexyl methacrylate mass fraction of $w_3 = 0.0$, 0.201, 0.303, and 0.564. With $w_3 = 0.666$ 2-ethylhexyl methacrylate to the poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) solution, the cloud-point curves take on the appearance of a typical lower critical solution temperature boundary. The poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + $w_3 = 0.0$, 0.097, 0.206, 0.409, 0.552, and 0.604 2-ethylhexyl acrylate (3) systems change the (p, T) curve from upper critical solution temperature region to lower critical solution temperature region as the 2-ethylhexyl acrylate mass fraction increases. For $w_3 = 0.709$ 2-ethylhexyl acrylate, the poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) solution significantly changes the phase behavior. Also, the impact by dimethyl ether mass fraction for the poly(2-ethylhexyl methacrylate) (1) and poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + dimethyl ether (3) system is measured at temperatures to 455 K and a pressure range of (4.3 to 248.0) MPa. Pressure, composition (p, x) isotherms are obtained for the carbon dioxide (1) + 2-ethylhexyl methacrylate (2) systems at (313.15, 333.15, 353.15, 373.15, and 393.15) K and pressure up to 20.5 MPa. The carbon dioxide (1) + 2-ethylhexyl methacrylate (2) systems exhibit type-I phase behavior with a continuous mixture critical curve. The experimental results for carbon dioxide (1) + 2-ethylhexyl methacrylate (2) mixtures are modeled using the Peng−Robinson equation of state with two adjustable parameters.

Introduction

The interest in supercritical fluid (SCF) has increased over the past decades. Knowledge of phase behavior for the polymers, monomers, and polymers + monomers in supercritical fluid solvents is of importance in related industrial processes. SCF technology has been widely applied to several industrial processes including the processing of pharmaceuticals, biological material, and polymers.[1−3] In more recent years, SCF solvents have appeared in a much more diverse array of processes such as environmentally preferable solvents for liquefaction and mixing of crystalline materials, powder formation, particle and surface impregnation, and antisolvent precipitation.[4,5] The acrylate and methacrylate components are widely used in modern plastic technology. The acrylate and methacrylate monomers and polymers are used mainly for a variety of applications such as prostheses, contact lenses, photopolymer printing plates, adhesives, and coating.[6]

Recently, we have demonstrated that it is possible to dissolve poly(acrylate) and poly(methacrylate) in SCF solvents over a wide range of temperatures at high pressure if an acrylate and methacrylate monomer are used as cosolvent.[7,8] The cosolvent can enhance high molecular weight polymer solubility in a given solvent due to several reasons. If the supercritical solvent is expanded, the addition of a dense, cosolvent reduces the density difference between the polymer and the solvent.[9,10]

The objective of this work is to determine the phase behavior of poly(2-ethylhexyl acrylate) [P(EHA)] and poly(2-ethylhexyl methacrylate) [P(EHMA)] in low molecular weight SCF solvents. The cloud-point behavior for the P(EHA) + carbon dioxide + 2-ethylhexyl acrylate (EHA) and P(EHMA) + carbon dioxide + 2-ethylhexyl methacrylate (EHMA) systems show the curves changing from a positive slope to a negative slope. The interchange that characterizes the balance of polymer segment + solvent cross interactions relative to polymer segment + polymer segment and solvent + solvent self-interactions is very temperature sensitive due to the strong polar interactions experienced between polymer segments.[11]

The focus of this work is the experimental determination of the phase equilibria of EHMA in supercritical carbon dioxide. The (p, x) isotherm data are obtained at the temperature range of (313.15 to 393.15) K and at the pressure range of (3.3 to 20.5) MPa. The experimental data obtained in this work were correlated with the Peng−Robinson equation of state[12] (PR EOS) using a van der Waals one-fluid mixing rule including two adjustable parameters.

Experimental Section

Materials. Poly(2-ethylhexyl methacrylate) [P(EHMA)] (M_w = 100 000; T_g = 263.15 K; CASRN 25719-51-1), poly(2-

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10.1021/je060349n CCC: $37.00

Table 1. Properties of Critical Temperatures, Critical Pressures, Critical Densities, Polarizabilities, Dipole Moments, and Quadrupole Moments of the Solvents[17−20]

	T_c	p_c	ρ_c	$\alpha \times 10^{18}$	$\mu \times 10^{25}$	$Q \times 10^{35}$
solvents	K	MPa	$kg\cdot m^{-3}$	m^3	$(J\cdot m^3)^{1/2}$	$J^{1/2}\cdot m^{5/2}$
carbon dioxide	304.15	7.38	469	2.65	0.00	−13.60
propane	369.85	4.25	217	6.29	0.32	3.79
propylene	365.05	4.62	236	6.26	1.27	7.91
butane	425.25	3.80	228	8.14	0.00	
1-butene	419.55	3.97	234	8.24	1.95	7.91
dimethyl ether	399.95	5.30	258	5.22	4.11	
$CHClF_2$	369.35	4.97	525	4.44	4.43	

ethylhexyl acrylate) [P(EHA)] ($M_w = 90\,000$; $T_g = 223.15$ K; CASRN 9003-77-4), 2-ethylhexyl methacrylate (EHMA) (> 98 % purity; CASRN 688-84-6), and 2-ethylhexyl acrylate (EHA) (> 99 % purity; CASRN 103−11-7) used in this work were obtained from Scientific Polymer Products, Inc. and used as received. To prevent EHMA and EHA 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 EHMA and EHA. Carbon dioxide (99.8 % minimum purity) was obtained from Daesung Industrial Co., propane (98 % purity) was obtained from LG Gas (E1). Propylene (99.6 % purity), butane (97.0 % purity), 1-butene (99.5 % purity), and dimethyl ether (99.5 % purity) were obtained from Yeochun NCC Co. and used as received. Since the P(EHMA) (with toluene (65 to 70) %) and P(EHA) (with toluene (65 to 70) %) were 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 removal.

Apparatus and Procedure. The phase behavior measurements were carried out using the static type of variable-volume view cell that has already been described in detail elsewhere.[13−16] Cloud-point curves were obtained for P(EHA) + carbon dioxide + EHA, P(EHMA) + carbon dioxide + EHMA, P(EHA) + carbon dioxide + dimethyl ether (DME), P(EHMA) + carbon dioxide + DME mixtures, and P(EHA) (or P(EHMA)) + supercritical solvents mixture using high-pressure experimental apparatus.[13,14] p, x isotherms were also obtained for the carbon dioxide + EHMA mixtures.[15,16]

Polymer was loaded into the cell to within ± 0.002 g, and then the cell was purged with nitrogen followed by SCF fluid solvents to ensure that all of the organic matters are removed. Liquid cosolvent was injected into the cell to within ± 0.002 g using a syringe, and supercritical solvent and cosolvent are transferred into the cell gravimetrically to within ± 0.004 g using a high-pressure bomb. The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-108952, (0 to 345.0) MPa, accurate to within ± 0.35 MPa) and high-pressure generator (HIP Inc., model 37-5.75-60). The temperature in the cell was measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, model 7563, accurate to within ± 0.005 %). The system temperature was typically maintained to within ± 0.20 K below 473 K. The cell inside was viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. Light was transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator (Olympus Optical Co., model ILK-5) and at the other end to a borescope.

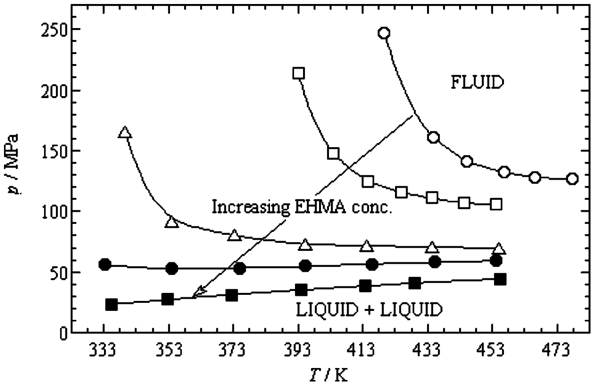

Figure 1. Experimental cloud-point curves for the poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) + 2-ethylhexyl methacrylate (EHMA) (3) system with different EHMA concentration. The concentration of poly(2-ethylhexyl methacrylate) is w_1 = ca. 0.050 for each solution. ○, $w_3 = 0.0$; □, $w_3 = 0.087$; △, $w_3 = 0.201$; ●, $w_3 = 0.303$; ■, $w_3 = 0.564$.

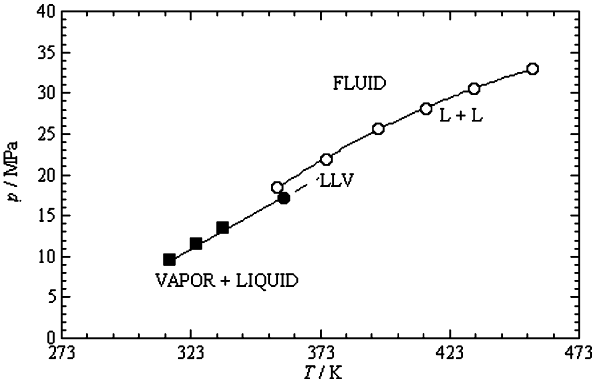

Figure 2. Impact of $w_3 = 0.666$ monomer (on a polymer-free basis) on the phase behavior of the poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) + 2-ethylhexyl methacrylate (3) system. ○, fluid → liquid + liquid transition; ●, liquid + liquid + vapor (LLV) transition; ■, fliud → liquid + vapor transition. The concentration of poly(2-ethylhexyl methacrylate) is w_1 = ca. 0.050 for the solution.

Polymer + solvent + monomer mixture in the cell was heated to the desired temperature and pressurized until a single phase was achieved. The binary and ternary mixtures were maintained in the one-phase region at designed temperature for at least (30 to 40) min so that the cell could reach thermal equilibrium. Pressure was then slowly decreased until the solution became cloudy. Cloud-point pressure was defined as the point at which the solution became so opaque that it was no longer possible to see the stir bar in solution. After a cloud-point was obtained, the solution was recompressed into a single phase, and the process was repeated. Cloud-points were measured for the polymer solutions at a fixed P(EHA) (1) and P(EHMA) (1) mass fraction of w_1 = ca. 0.050. The uncertainty of cloud points was less than ± 0.28 MPa and ± 0.3 K. The uncertainty of bubble-, dew-, and critical-point transitions for the carbon dioxide + EHMA mixture was less than ± 0.03 MPa and ± 0.20 K.

Results and Discussion

Table 1 lists the critical properties, polarizability, dipole moment, and quadrupole moment of the solvents used in this study.[17−20] For the P(EHA) + and P(EHMA) + solvents system, carbon dioxide, propylene, propane, butane, 1-butene, and DME were used as solvents. Propane and propylene have similarity in critical properties and polarizabilities, but propylene, different from propane, possesses both dipole and quadrupole moments that favorably interact with the EHA and EHMA groups in the polymer. Like propane, butane does not possess an appreciable dipole moment; therefore, it interacts with the polymer only through dispersion and induction forces. 1-Butene, like propylene, interacts with EHA and EHMA segments through quadrupolar and dipolar forces. DME has a significant dipole

Table 2. Experimental Cloud-Point Data for the Poly(2-ethylhexyl methacrylate) (1) + Carbon Dioxide (2) + 2-Ethylhexyl Methacrylate (3) System

T/K	p/MPa	T/K	p/MPa
	$w_1 = 0.059$, $w_3 = 0.0$		
419.9	247.07	456.7	132.24
434.8	161.38	466.2	127.90
445.3	141.21	477.7	126.48
	$w_1 = 0.047$, $w_3 = 0.087$		
393.2	213.97	434.5	110.86
404.0	147.59	444.6	106.62
414.6	125.00	454.5	105.86
425.2	115.31		
	$w_1 = 0.050$, $w_3 = 0.201$		
339.8	165.69	414.3	71.59
354.3	91.69	434.5	70.62
373.5	80.00	455.2	69.35
395.2	72.93		
	$w_1 = 0.074$, $w_3 = 0.303$		
333.6	56.38	415.8	56.52
354.3	52.83	435.4	58.00
375.0	53.48	454.3	59.35
395.5	54.72		
	$w_1 = 0.051$, $w_3 = 0.564$		
335.8	23.14	413.9	38.45
352.8	27.28	429.2	41.07
372.7	31.41	455.5	44.10
394.3	35.35		

Table 3. Phase Behavior for Poly(2-ethylhexyl methacrylate) (1) + Carbon Dioxide (2) + 2-Ethylhexyl Methacrylate (3) System

	$w_1 = 0.052$, $w_3 = 0.666$	
T/K	p/MPa	transition
	Cloud-Point Transition	
356.5	18.45	CP
375.4	21.90	CP
395.4	25.69	CP
414.0	28.10	CP
432.5	30.52	CP
455.0	32.93	CP
	Bubble-Point Transition	
314.7	9.68	BP
325.0	11.55	BP
335.5	13.62	BP
	Liquid−Liquid−Vapor Transition	
359.0	17.20	LLV

moment that provides an opportunity to compare the impact of dipole interactions with that of quadrupole interactions found in alkenes and carbon dioxide.

Phase Behavior for the P(EHMA) + Carbon Dioxide + Cosolvents (EHMA and DME) Mixtures. The phase behavior of binary and ternary systems for P(EHA) + supercritical solvents + EHA and P(EHMA) + supercritical solvents + EHMA mixture are measured to within ± 0.28 MPa and ± 0.3 K.

Figure 1 and Table 2 show the phase behavior of the P(EHMA) (1) + carbon dioxide (2) + EHMA (3) system obtained in this work. The phase behavior of P(EHMA) + carbon dioxide + EHMA with $w_3 = 0.0$ shows a negative slope in the temperature range of (419 to 478) K and pressure up to 247.0 MPa. The phase behavior curve shows the upper critical solution temperature (UCST) type. At temperatures greater than 453 K, the cloud-point curve is shifted to moderately lower pressures, more than likely due to the decrease in the free volume difference between polymer and mixed solvent. For instance, at $T = 453$ K, the addition of $w_3 = 0.201$ to a P(EHMA) (1) + carbon dioxide (2) mixture lowers the cloud-point pressure from (134.0 to 69.0) MPa. Note that the sharp increase in the P(EHMA) cloud-point curve shifts from (418 to 338) K with $w_3 = 0.201$. The solubility curve exhibits the phase behavior with a negative slope at (339 to 455) K and below 165.6 MPa. If the EHMA mass fraction is increased to $w_3 = 0.303$, the cloud-point pressure remains virtually constant at about 55.0 MPa over a temperature range of (333 to 454) K. The phase behavior of P(EHMA) (1) + carbon dioxide (2) + EHMA (3) with $w_3 = 0.564$ exhibits the LCST type phase behavior with a positive slope (1.8 MPa/K) at low pressures. As shown in Figure 2 and Table 3, the cloud-point curve with $w_3 = 0.666$ takes on the typical appearance of a LCST boundary. At $T = 423$ K, the phase boundary has shifted from (ca. 39.6 to ca. 29.5) MPa as the mass fraction of EHMA is increased from $w_3 = 0.564$ to 0.666. The P(EHMA) (1) + carbon dioxide (2) + EHMA(3) with $w_3 = 0.666$ phase behavior curve intersects a liquid → liquid + vapor (LV) curve at ca. 340 K and ca. 14.0 MPa. 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 about

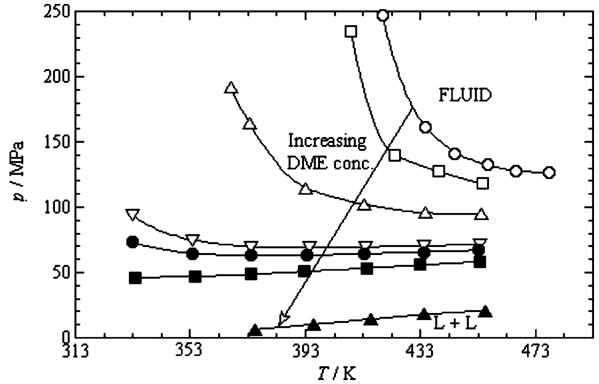

Figure 3. Impact of dimethyl ether (DME) concentration on the phase behavior of the poly(2-ethylhexyl methacrylate) (1) + carbon dioxide (2) + dimethyl ether (3) system. The concentration of polymers is w_1 = ca. 0.050 for each solution. ○, $w_3 = 0.0$; □, $w_3 = 0.053$; △, $w_3 = 0.192$; ▽, $w_3 = 0.261$; ●, $w_3 = 0.303$; ■, $w_3 = 0.398$; ▲, $w_3 = 0.957$.

Table 4. Experimental Cloud-Point Data for the Poly(2-ethylhexyl methacrylate) (1) + Carbon Dioxide (2) + Dimethyl Ether (3) System

T/K	p/MPa	T/K	p/MPa
	$w_1 = 0.051$, $w_3 = 0.053$		
408.9	234.66	439.6	127.24
424.2	139.48	454.7	118.03
	$w_1 = 0.051$, $w_3 = 0.192$		
367.5	191.90	413.7	102.10
373.6	164.31	434.7	95.59
393.2	113.97	454.3	94.79
	$w_1 = 0.050$, $w_3 = 0.261$		
333.1	93.97	414.3	69.83
353.8	74.66	434.7	70.52
374.1	69.83	454.0	71.90
394.8	69.14		
	$w_1 = 0.051$, $w_3 = 0.303$		
333.3	73.28	413.8	64.51
353.9	64.69	434.2	65.90
374.3	62.93	453.2	67.07
393.6	63.31		
	$w_1 = 0.050$, $w_3 = 0.398$		
333.8	46.38	414.6	53.41
354.9	46.86	433.0	55.90
374.4	48.69	453.7	58.35
392.8	50.86		
	$w_1 = 0.043$, $w_3 = 0.957$		
375.5	6.38	434.5	18.10
395.9	10.35	455.9	20.69
415.8	14.31		

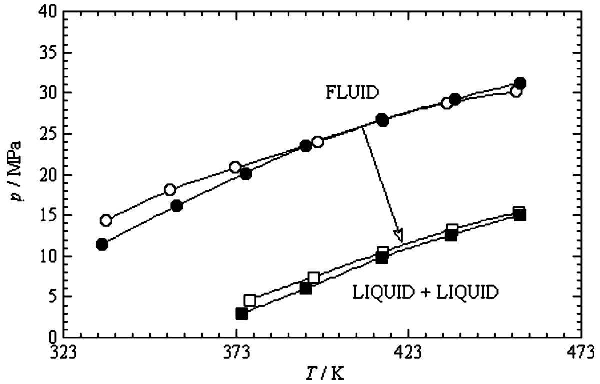

Figure 4. Effect of the phase behavior of poly(2-ethylhexyl methacrylate) dissolved in supercritical propane, propylene, butane, and 1-butene. The concentration of polymers is w_1 = ca. 0.050 for each solution. ○, propane; ●, propylene; □, butane; ■, 1-butene.

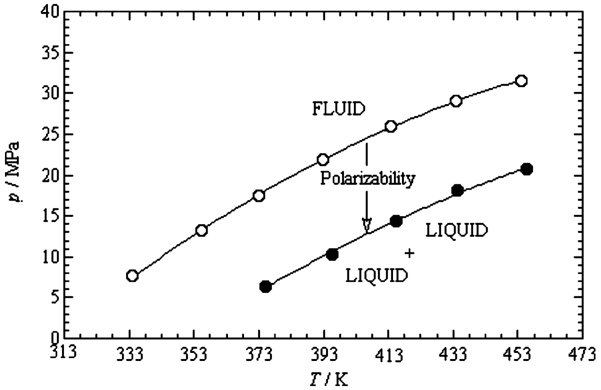

Figure 5. Effect of the phase behavior of poly(2-ethylhexyl methacrylate) dissolved in supercritical DME and $CHClF_2$. The concentration of polymers is w_1 = ca. 0.050 for each solution. ○, $CHClF_2$; ●, DME.

Table 5. Experimental Cloud-Point Data for the Poly(2-ethylhexyl methacrylate) (1) + Solvents (2) System

T/K	p/MPa	T/K	p/MPa
$w_1 = 0.052$, $w_2 = 0.948$ (Propane)			
335.6	14.31	415.5	26.72
354.2	18.10	434.2	28.79
372.9	20.86	454.3	30.17
396.8	23.97		
$w_1 = 0.051$, $w_2 = 0.949$ (Propylene)			
334.5	11.48	415.6	26.69
356.0	16.17	436.8	29.31
375.9	20.17	453.4	31.21
393.2	23.55		
$w_1 = 0.049$, $w_2 = 0.951$ (Butane)			
377.1	4.66	435.7	13.28
395.6	7.41	455.1	15.35
415.9	10.52		
$w_1 = 0.054$, $w_2 = 0.946$ (1-Butene)			
374.7	2.93	435.4	12.59
393.6	6.03	455.4	15.00
415.4	9.83		

340 K. The initial slope of the P(EHMA) + carbon dioxide + EHMA LCST curve at the lowest pressures is ca. 1.5 MPa/K.

Figure 3 and Table 4 show the cloud-point behavior of P(EHMA) (1) + carbon dioxide (2) + DME (3) mixture obtained in this work. The P(EHMA) (1) + carbon dioxide (2) mixture was obtained at a temperature range of (419 to 477) K and at pressures of (126.5 to 247.0) MPa and for the P(EHMA) (1) + DME (3) mixture at a temperature range of (375 to 455) K and pressures of (6.3 to 20.6) MPa. The pressure difference between two systems is probably due to whether or not the dipole moment in DME and carbon dioxide is as shown in Table 1. As shown in Figure 3, for the P(EHMA) (1) + carbon dioxide (2) + DME (3) system, $w_3 = 0.053$ shows the UCST-type behavior with a negative slope, and then the pressure increases rapidly at T = ca. 418 K. At the $T < 418$ K, the cloud-point curve increases sharply with pressure, suggesting that either polymer + polymer or cosolvent + cosolvent polar interactions dominate the interchange energy and induce the system to phase separately. Hence, the EHMA polymer precipitates out of the binary and ternary mixtures, probably due to strong polymer + polymer interaction. If the EHMA mass fraction is increased to $w_3 = 0.192$, the phase behavior exhibits a negative slope in the temperature of (368 to 453) K. The $w_3 = 0.192$ EHMA cloud-point curve does exhibit a rapid increase in pressure at $T = 383$ K and occurs because of a large increase in energetics between polymer segment + polymer segment as compared to polymer segment + solvent interaction. With $w_3 = 0.261$ and 0.303, the cloud-point curve exhibits a upper-lower critical solution temperature (U-LCST) region from a positive slope to a negative slope in the temperature range from (453 to 333) K and pressures to 93.9 MPa. Cloud-point pressure remains virtually constant at 64.7 MPa ($w_3 = 0.303$) and 70.0 MPa ($w_3 = 0.261$) over a temperature range from (373 to 453) K. The P(EHMA) (1) + carbon dioxide (2) + DME (3) with $w_3 = 0.398$ system shows the LCST type cloud-point of a positive slope of 1.0 MPa/K at the temperature range of (333 to 453) K and pressure range of (46.3 to 58.3) MPa. The location of the LCST curve is probably governed by entropic interactions, which are more sensitive to changes in pressure. In cosolvent effect of DME, DME decreases the free volume of solvent, while increasing the solvent density since DME is more than twice as dense as carbon dioxide. Increasing cosolvent content increases the density of the mixed solvent and favorable interactions between polymer and (co)solvent, leading to decreasing temperature and pressure.[21,22]

Phase Behavior for the P(EHMA) + Supercritical Solvents System. Figure 4 and Table 5 show the results for phase behavior of P(EHMA) dissolved in supercritical propane, propylene, butane, and 1-butene. The cloud-point behavior for P(EHMA) + propane, + propylene, + butane, and + 1-butene system exhibits LCST curves with a positive slope. The cloud-point curve for the P(EHMA) + propane and + propylene system presents almost the same pressure at the temperature range of (333 to 455) K and pressure range of (11.5 to 31.0) MPa. It is probably due to the same polarizability of propane (6.29×10^{-18} m^3) and propylene (6.26×10^{-18} m^3) as shown in Table 1. Cloud-point curves for the P(EHMA) + butane and + 1-butene systems were obtained at the temperature range of (373 to 453) K and low pressure of 15.3 MPa. For $T = 413$ °C, the cloud-point curve reduces from 9.1 MPa for butane to 8.0 MPa for 1-butene. As shown in Table 1, it is probably due to polarizability of the butane (8.14×10^{-18} m^3) and 1-butene (8.24×10^{-18} m^3). The pressure difference between the P(EHMA) + propane system and the P(EHMA) + butane system could be attributed to their differing polarity.

Figure 5 shows the cloud-point behavior for the P(EHMA) dissolved in supercritical DME and $CHClF_2$. The phase behavior for the P(EHMA) + $CHClF_2$ system shows the LCST curve in the temperature range of (334 to 454) K and pressure range of (7.6 to 31.5) MPa. At $T = 413$ K, the pressure difference is almost 12.0 MPa. It is more probably due to different reduced states.

Figure 6 compares the cloud-point curves of the poly(butyl methacrylate) [P(BMA): $M_w = 320\ 000$, $T_g = 293$ K] + butyl methacrylate;[16] poly(hexyl methacrylate) [P(HMA): M_w =

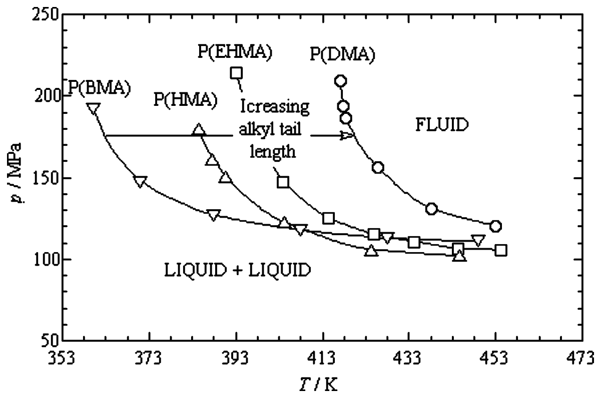

Figure 6. Impact of the straight chain alkyl tail of the methacrylate group on the cloud-point curves of poly(butyl methacrylate) [P(BMA), M_w = 320 000, T_g = 293 K], poly(hexyl methacrylate) [P(HMA), M_w = 90 000, T_g = 268 K], poly(2-ethylhexyl methacrylate) [P(EHMA), M_w = 100 000, T_g = 263 K], and poly(decyl methacrylate) [P(DMA), M_w = 100 000, T_g = 203 K] in supercritical carbon dioxide. The concentration of polymer is ~ 5 wt % for each solution. The cosolvent concentration is ~ 9 wt % for each solution except for the P(DMA) + carbon dioxide + 6.7 wt % DMA solution.

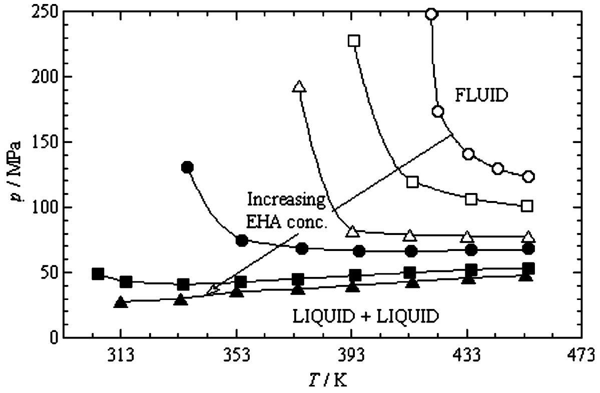

Figure 7. Experimental cloud-point curves for the poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + 2-ethylhexyl acrylate (EHA) (3) system with different EHA concentration. The concentration of poly(2-ethylhexyl acrylate) is w_1 = ca. 0.050 for each solution. ○, w_3 = 0.0; □, w_3 = 0.097; △, w_3 = 0.206; ●, w_3 = 0.409; ■, w_3 = 0.552; ▲, w_3 = 0.604.

90 000, T_g = 268 K] + hexyl methacrylate;[23] P(EHMA) (M_w = 100 000, T_g = 263 K) + EHMA; and poly(decyl methacrylate) [P(DMA): M_w = 100 000, T_g = 203 K] + decyl methacrylate[7] in supercritical carbon dioxide. As the alkyl tail on the methacrylate increases, T_g decreases, leading to increasing the cloud-point pressure. The cloud-point curves are expected to be decreased by free volume of the polymer in the high temperatures.[24]

Phase Behavior for the P(EHA) + Carbon Dioxide + Cosolvents (EHA and DME) Mixtures. Figure 7 and Table 6 present the phase behavior for the P(EHA) (1) + carbon dioxide (2) + EHA (3) mixture. The P(EHA) does dissolve in pure carbon dioxide to temperature below 454 K and pressure up to 248.0 MPa. The binary P(EHA) + carbon dioxide system shows the UCST region with a negative slope. The sharp rise of the cloud-point pressure with decreasing temperature is attributed to the increase of solvent + solvent interactions over polymer + solvent interactions. At temperatures below 418 K, carbon dioxide possibly enhances self-interactions, due to its quadrupole moment, that outweigh P(EHA) + carbon dioxide cross-interaction. However, increased pressure in this temperature range does not dissolve P(EHA) in quadrupolar carbon dioxide leading to phase separation of the polymer + solvent system. When w_3 = 0.097 and w_3 = 0.206, the cloud-point curve exhibits UCST-type phase behavior with a negative slope at temperature range from (373 to 454) K and pressure to 227.7 MPa. The P(EHA) (1) + carbon dioxide (2) + w_3 = 0.097 and 0.206 EHA (3) systems reveal that it is not enough to prevent carbon dioxide + carbon dioxide interactions from dominating favorable polymer + solvent interactions at temperature below (373 and 393) K, respectively. If w_3 = 0.409 EHA and w_3 = 0.552 EHA are added to the solution, both cloud-point pressure curves slowly increased at 323 K (w_3 = 0.552) and 353 K (w_3 = 0.409) as temperature decreased from (453 to 303) K. The phase behavior curve exhibits U-LCST-type from a positive slope to a negative slope. In the case of w_3 = 0.604, the cloud-point pressure curve exhibits typical LCST type with a positive slope (1.5 MPa/K) in the temperature range of (313 to 453) K and pressure range of (27.7 to 47.8) MPa. At T > 343 K, the cloud-point curve is shifted to moderately lower pressure of 50.0 MPa (w_3 = 0.552) and 68.0 MPa (w_3 = 0.409), more than likely due to the decrease in the free volume difference between polymer and mixed solvent. At T = 423 K, w_3 = 0.409 and w_3 = 0.552 lower the cloud-point pressure from (67.0 to 51.0) MPa. Note that the sharp increase in the P(EHA) cloud-point curve shifts from (333 to 303) K with w_3 = 0.409 and w_3 = 0.552.

Table 6. Experimental Cloud-Point Data for the Poly(2-ethylhexyl acrylate) (1) + Carbon Dioxide (2) + 2-Ethylhexyl Acrylate (3) System

T/K	p/MPa	T/K	p/MPa
	w_1 = 0.048, w_3 = 0.0		
420.9	248.45	443.8	129.69
423.3	173.41	454.8	123.10
434.0	141.31		
	w_1 = 0.056, w_3 = 0.097		
393.9	227.76	434.7	106.55
414.7	119.28	454.2	100.69
	w_1 = 0.056, w_3 = 0.206		
375.0	193.28	433.6	78.10
393.8	81.69	454.7	78.10
413.7	79.00		
	w_1 = 0.046, w_3 = 0.409		
336.3	131.21	414.1	66.66
355.0	74.72	434.7	67.17
376.0	68.79	454.7	67.97
396.0	66.83		
	w_1 = 0.050, w_3 = 0.552		
305.0	49.38	394.6	47.83
315.1	43.14	413.5	49.97
335.1	41.07	434.8	52.31
354.8	42.76	454.9	53.66
374.7	45.31		
	w_1 = 0.057, w_3 = 0.604		
313.1	27.76	393.7	40.17
334.0	30.14	414.2	43.21
353.5	35.55	433.7	46.03
374.7	37.35	453.6	47.83

Figure 8 and Table 7 represent experimentally measured cloud-point data for P(EHA) + carbon dioxide + EHA with w_3 = 0.709 mixture. As shown in Figure 8, the phase behavior curve exhibits LCST-type cloud-point behavior with a positive slope (ca. 1.7 MPa/K). This curve intersects the LV curve at ca. 307 K and ca. 8.1 MPa. The positive slope of the P(EHA) + carbon dioxide + EHA LCST curve is ca. 1.7 MPa/K.

Figure 9 shows the comparison between experimental data (M_w = 90 000) and McHugh data (M_w = 112 800)[25] for the P(EHA) + carbon dioxide mixture. At 448 K, the phase boundary has shifted from (140.0 to 126.0) MPa as the weight average molecular weight (M_w) of P(EHA) decreases from 112 800 to 90 000. The pressure difference of the two curves is probably due to M_w.

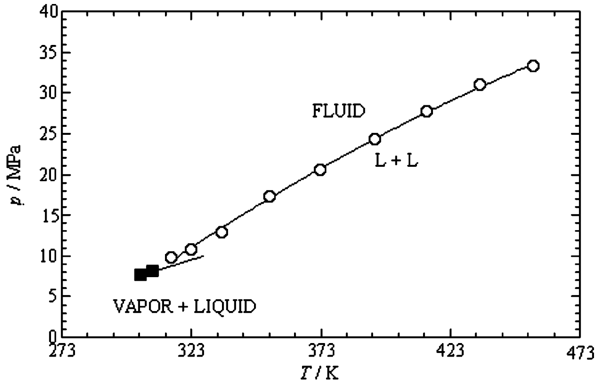

Figure 8. Impact of $w_3 = 0.709$ monomer (on a polymer-free basis) on the phase behavior of the poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + 2-ethylhexyl acrylate (3) system. ○, fluid → liquid + liquid transition; ■, fliud → liquid + vapor transition.

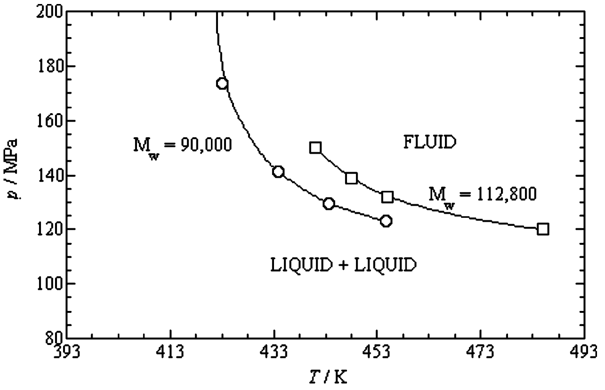

Figure 9. Comparison of cloud-point behavior for the poly(2-ethylhexyl acrylate) [M_w = 90 000 and 112 800] in supercritical carbon dioxide. ○, this work; □, ref 25.

Table 7. Experimental Cloud-Point, Bubble-Point, and Liquid−Liquid−Vapor Data for the Poly(2-ethylhexyl acrylate) (1) + Carbon Dioxide (2) + 2-Ethylhexyl Acrylate (3) System

$w_1 = 0.056$, $w_3 = 0.709$		
T/K	p/MPa	transition
	Cloud-Point Transition	
315.5	9.83	CP
323.3	10.86	CP
334.7	12.86	CP
353.4	17.31	CP
373.0	20.59	CP
394.3	24.38	CP
414.2	27.69	CP
434.6	31.07	CP
455.4	33.28	CP
	Bubble-Point Transition	
303.4	7.76	BP
308.2	8.11	BP

Figure 10 shows the cloud-point curves of the poly(butyl acrylate) [P(BA): M_w = 61 800, T_g = 219 K],[25] poly(hexyl acrylate) [P(HA): M_w = 90 000, T_g = 216 K],[23] P(EHA) (M_w = 90 000, T_g = 223 K), and poly(decyl acrylate) [P(DA): M_w = 130 000, T_g = unknown][7] in supercritical carbon dioxide. As the alkyl tail on the acrylate increases, the effective polarity decreases since the reduced dipole moment scales inversely with the square root of the molar volume.[20] At high temperatures, where polar interactions are decreased, the free volume of the polymer is expected to have a influence on the location of cloud-point curves.[24]

Figure 11 and Table 8 show the cloud-point behavior of DME effect for the P(EHA) (1) + carbon dioxide (2) mixture obtained in this work. The phase behavior is presented for P(EHA)(1) + carbon dioxide (2) + w_3 = (0.061 to 0.161) DME (3) system at temperature range of (373 to 455) K and pressure range of (88.0 to 179.4) MPa. Also, the cloud-point curve of three (w_3 = 0.061, 0.099, and 0.161) systems exhibit UCST-type curves with negative slopes. As the temperature is decreased, the strength of polar interaction increases, and since cloud-point pressure decrease, it can be surmised that the ester linkage in

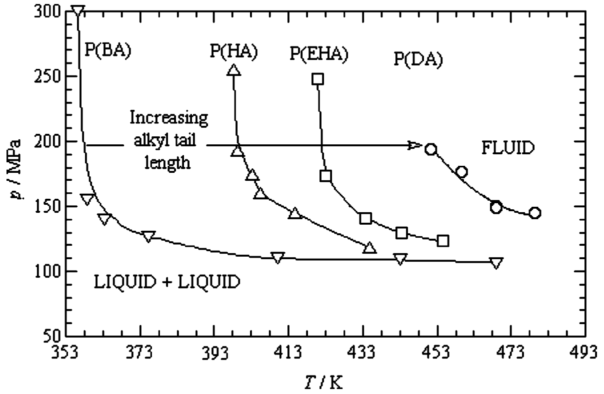

Figure 10. Impact of the alkyl tail of the acrylate group on the cloud-point curves of poly(butyl acrylate) [P(BA), M_w = 61 800, T_g = 219 K], poly(hexyl acrylate) [P(HA), M_w = 90 000, T_g = 216 K], poly(2-ethylhexyl acrylate) [P(EHA), M_w = 90 000, T_g = 223 K], poly(decyl acrylate) [P(DA), M_w = 130 000, T_g = unknown] and in supercritical carbon dioxide. T_g is the glass transition temperature, and M_w is the weight-average molecular weight.

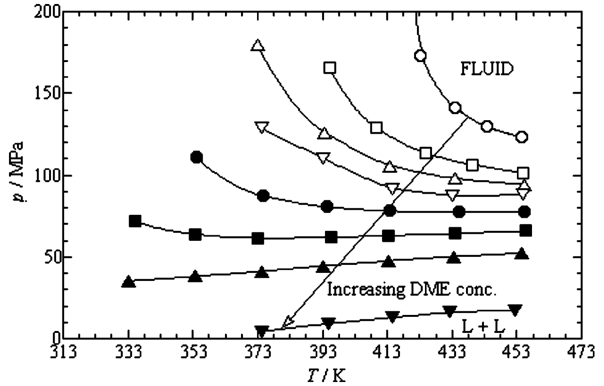

Figure 11. Impact of dimethyl ether (DME) concentration on the phase behavior of the poly(2-ethylhexyl acrylate) (1) + carbon dioxide (2) + dimethyl ether (3) system. The concentration of polymers is w_1 = ca. 0.050 for each solution. ○, w_3 = 0.0; □, w_3 = 0.061; Δ, w_3 = 0.099; ▽, w_3 = 0.161; ●, w_3 = 0.207; ■, w_3 = 0.297; ▲, w_3 = 0.404; ▼, w_3 = 0.932.

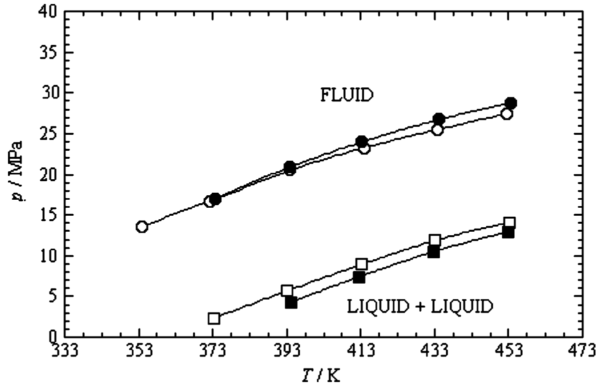

Figure 12. Effect of the phase behavior of poly(2-ethylhexyl acrylate) dissolved in supercritical propane, propylene, butane, and 1-butene. The concentration of polymers is w_1 = ca. 0.050 for each solution. ○, propane; ●, propylene; □, butane; ■, 1-butene.

Table 8. Experimental Cloud-Point Data for the Poly(2-ethylhexyl acrylate) (1) + Carbon Dioxide (2) + Dimethyl Ether (3) System

T/K	p/MPa	T/K	p/MPa
	$w_1 = 0.052$, $w_3 = 0.061$		
395.4	165.69	439.4	106.38
409.7	128.97	455.0	101.65
424.9	113.45		
	$w_1 = 0.051$, $w_3 = 0.099$		
373.2	179.48	434.1	97.90
393.8	126.14	455.6	94.28
414.2	105.76		
	$w_1 = 0.054$, $w_3 = 0.161$		
274.6	128.69	433.1	87.76
393.3	110.17	455.0	88.10
414.9	91.55		
	$w_1 = 0.050$, $w_3 = 0.207$		
354.4	111.17	414.1	78.10
374.8	87.07	435.2	77.59
394.6	80.48	455.5	77.59
	$w_1 = 0.051$, $w_3 = 0.296$		
335.5	72.17	413.5	63.03
354.0	63.55	434.2	64.31
373.3	61.52	455.8	65.93
395.7	62.10		
	$w_1 = 0.053$, $w_3 = 0.404$		
333.4	35.35	413.6	47.59
354.1	38.10	433.9	50.21
374.5	41.28	454.9	52.52
393.5	44.45		
	$w_1 = 0.068$, $w_3 = 0.932$		
374.3	4.31	432.4	16.03
394.9	9.19	452.5	17.59
414.8	12.93		

DME is able to strongly interact with the resin by hydrogen bonding, dramatically enhancing solubility.[5] If $w_3 = 0.207$ and 0.296 DME is added to the P(EHA) (1) + carbon dioxide (2) solution, the cloud-point behavior was presented at temperature range of (335 to 455) K and pressure to 111.1 MPa. The cloud-point curves increase smoothly at temperature of 373 K ($w_3 = 0.207$) with a negative slope and 353 K ($w_3 = 0.296$) from a negative slope to a positive slope as the temperature decreases. By increasing the DME mass fraction to $w_3 = 0.404$, the cloud-point curves are altered. Not only does the pressure drop by 50.0 MPa at 433 K, but also the slope of the curve changes, producing a line with a positive slope of nearly 1.5 MPa/K, until the temperature near 333 K and pressure of 35.3 MPa. Pure DME is an even better solvent, reducing the cloud-point pressure to about 4.3 MPa at 373 K.

Phase Bhevior for the P(EHA) + Supercritical Solvents System. Figure 12 and Table 9 show the results for phase behavior of P(EHA) dissolved in supercritical propane, propylene, butane, and 1-butene. The cloud-point curves for P(EHA) + supercritical solvents (propane, propylene, butane, and 1-butene) systems show LCST-type with a positive slope. The cloud-point behavior for P(EHA) in supercritical propane and propylene appeared at (353 to 453) K and (13.6 to 28.7) MPa. At 413 K, the phase behavior boundary has almost the same pressure of ca. 24.0 MPa, and it is probably due to the almost same polarizability of propane (6.29×10^{-18} m^3) and propylene (6.26×10^{-18} m^3) from Table 1. The phase behavior for P(EHA) with butane and 1-butene appeared at (373 to 453) K and pressure to about 14.0 MPa. For the temperature at 413 K, the cloud-point curve showed some pressure difference. As shown in Table 1, it is probably due to polarizability of butane (8.14×10^{-18} m^3) and 1-butene (8.24×10^{-18} m^3).

Phase Behavior for P(EHA) and P(EHMA) in Supercritical Carbon Dioxide without and with DME. Figure 13 provides an interesting comparison between the cloud-point curves for the P(EHA) and P(EHMA) in supercritical carbon dioxide. The P(EHA) + carbon dioxide cloud-point curve was at (100 to 200) MPa pressures lower than the P(EHMA) + carbon dioxide curve, and these two curves were crossed at 421 K and 240 MPa. The pressure difference resulted from T_g [P(EHA): 223.15 K, P(EHMA): 263.15 K] and M_w [P(EHA): 90 000, P(EHMA): 100 000], and this result looked similar to the one discussed by Rindfleisch et al.[24]

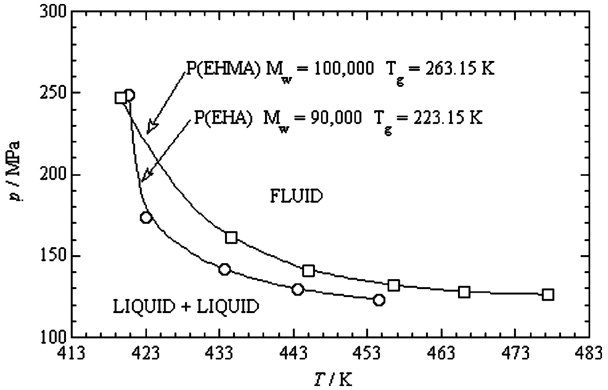

Figure 13. Comparison of cloud-point curves of poly(2-ethylhexyl acrylate) [P(EHA)] and poly(2-ethylhexyl methacrylate) [P(EHMA)] in supercritical carbon dioxide. T_g is the glass transition temperature, and M_w is the weight-average molecular weight. The polymer concentration is w_1 = ca. 0.050 for both solutions.

Table 9. Experimental Cloud-Point Data for the Poly(2-ethylhexyl acrylate) (1) + Solvents (2) System

T/K	p/MPa	T/K	p/MPa
	$w_1 = 0.053$, $w_2 = 0.947$ (Propane)		
354.1	13.62	414.2	23.28
372.3	16.72	433.8	25.48
394.2	20.52	452.5	27.41
	$w_1 = 0.065$, $w_2 = 0.935$ (Propylene)		
373.9	17.07	434.4	26.72
394.0	20.86	453.9	28.79
413.5	23.97		
	$w_1 = 0.052$, $w_2 = 0.948$ (Butane)		
373.7	2.35	433.4	11.90
393.3	5.69	453.4	14.10
413.5	8.93		
	$w_1 = 0.050$, $w_2 = 0.950$ (1-Butene)		
394.4	4.31	432.9	10.52
412.8	7.41	353.1	12.93

Figure 14 presented the comparison between cloud-point curves for the P(EHA) + DME ($w_3 = \approx 0.30$) and P(EHMA) + DME ($w_3 = \approx 0.30$) in supercritical carbon dioxide. The P(EHA) (or P(EHMA)) + carbon dioxide cloud-point curve shifted to lower temperatures (below 453 K) and pressures (below 73 MPa) when DME was added, and both systems exhibited U-LCST phase behavior curves.

High Pressure Vapor−Liquid Equilibria for Carbon Dioxide + EHMA System. The experimental data of phase behavior for the carbon dioxide (1) + 2-ethylhexyl methacrylate (EHMA) (2) systems are measured to within ± 0.03 MPa and ± 0.20 K for a loading of the cell. The mole fractions are measured to within ± 0.002. The carbon dioxide (1) + EHMA (2) mole fraction for the solubility isotherms at (313.15 to 393.15) K have an estimated accumulated error of less than ± 1.0 %.

Figure 15 and Table 10 present the results for the carbon dioxide (1) + EHMA (2) system obtained in this study. Figure 15 shows the (p, x) isotherms at (313.15, 333.15, 353.15, 373.15, and 393.15) K and pressure up to 18.2 MPa. The (p, x) isotherms

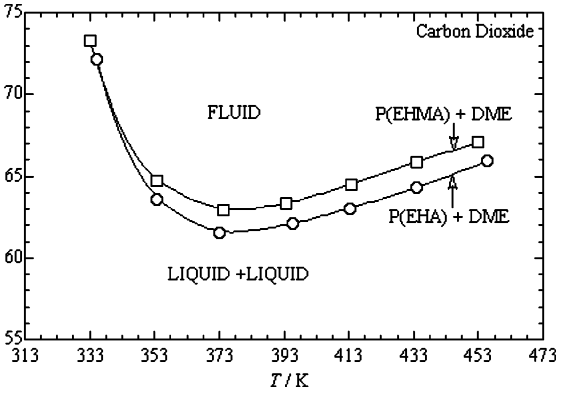

Figure 14. Comparison of experimental cloud-point curves for poly(2-ethylhexyl acrylate) [P(EHA)] (1) + dimethyl ether (DME) (3) and poly-(2-ethylhexyl methacrylate) [P(EHMA)] (1) + DME (3) in supercritical carbon dioxide. The polymer concentration is w_1 = ca. 0.050, and the cosolvent concentrations are also w_3 = ca. 0.300 for both solutions.

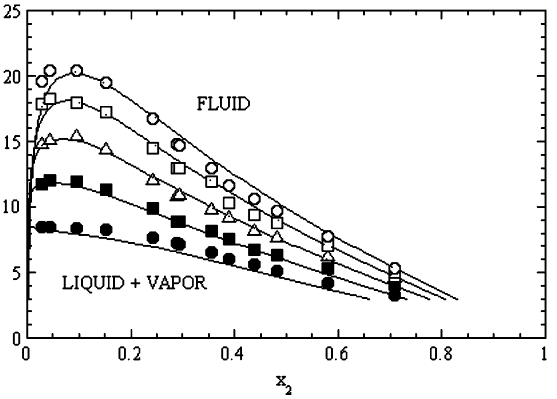

Figure 15. Comparison of the experimental data (symbols) for the carbon dioxide (1) + 2-ethylhexyl methacrylate (2) system with calculations (solid lines) obtained using the Peng−Robinson equation of state with k_{ij} equal to 0.060 and η_{ij} equal to −0.015: ●, 40 °C; ■, 60 °C; △, 80 °C; □, 100 °C; ○, 120 °C.

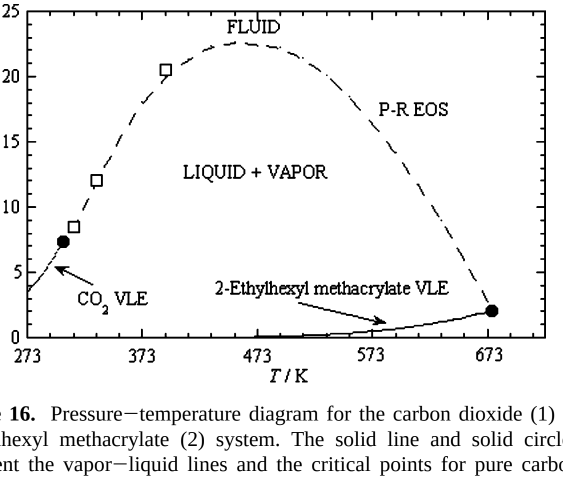

Figure 16. Pressure−temperature diagram for the carbon dioxide (1) + 2-ethylhexyl methacrylate (2) system. The solid line and solid circles represent the vapor−liquid lines and the critical points for pure carbon dioxide and 2-ethylhexyl methacrylate. The open squares are mixtures of critical points determined from isotherms measured in this study. The dashed lines represent calculation obtained using the Peng−Robinson equation of state with $k_{ij} = 0.060$ and $\eta_{ij} = -0.015$.

shown in Figure 13 is consistent with those expected for type-I system,[4,26] and liquid + liquid + vapor (LLV) equilibrium was not observed at these conditions. The phase behaviors exhibited by the carbon dioxide (1) + EHMA (2) systems are consistent with that of the carbon dioxide + alkyl methacrylate system.[7−9,13,15,16,23,27]

Table 10. Experimental Data for the Carbon Dioxide (1) + 2-Ethylhexyl Methacrylate (2) System

x_2	p/MPa	transition	x_2	p/MPa	transition
T = 313.15 K					
0.028	8.49	CP	0.355	6.57	BP
0.044	8.45	BP	0.390	6.06	BP
0.094	8.38	BP	0.438	5.66	BP
0.152	8.32	BP	0.483	5.12	BP
0.243	7.70	BP	0.581	4.18	BP
0.288	7.22	BP	0.710	3.26	BP
0.295	7.16	BP			
T = 333.15 K					
0.028	11.76	DP	0.355	8.17	BP
0.044	12.07	CP	0.390	7.52	BP
0.094	11.97	BP	0.438	6.79	BP
0.152	11.34	BP	0.483	6.32	BP
0.243	9.91	BP	0.581	5.32	BP
0.288	8.86	BP	0.710	4.09	BP
0.295	8.90	BP			
T = 353.15 K					
0.028	14.93	DP	0.355	9.93	BP
0.044	15.24	DP	0.390	9.34	BP
0.094	15.48	BP	0.438	8.24	BP
0.152	14.48	BP	0.483	7.76	BP
0.243	12.10	BP	0.581	6.31	BP
0.288	10.93	BP	0.710	4.72	BP
0.295	11.00	BP			
T = 373.15 K					
0.028	17.86	DP	0.355	11.90	BP
0.044	18.24	DP	0.390	10.34	BP
0.094	17.93	BP	0.438	9.38	BP
0.152	17.24	BP	0.483	8.76	BP
0.243	14.48	BP	0.581	7.07	BP
0.288	12.93	BP	0.710	5.00	BP
0.295	12.93	BP			
T = 393.15 K					
0.028	19.59	DP	0.355	13.00	BP
0.044	20.41	DP	0.390	11.69	BP
0.094	20.48	CP	0.438	10.59	BP
0.152	19.45	BP	0.483	9.69	BP
0.243	16.79	BP	0.581	7.72	BP
0.288	14.76	BP	0.710	5.34	BP
0.295	14.66	BP			

Table 11. Properties of Critical Pressure, Critical Temperature, and Acentric Factor Using the Peng−Robinson Equation of State in This Work

components	M_w	T/K	p_c/MPa	ω
carbon dioxide	44.01	304.15	7.38	0.225
2-ethylhexyl methacrylate	198.3	673.76	2.09	0.4928

The experimental data obtained in this work are modeled using the PR EOS.[12] Table 11 lists the pure component critical temperatures, critical pressures, and acentric factors for carbon dioxide and EHMA used with the PR EOS. The critical properties of EHMA are obtained by the Joback method.[17] The acentric factor was estimated with the Lee−Kesler method. The vapor pressures were calculated by the Lee−Kesler method.[17] Boiling point of EHMA was listed in the Scientific Polymer Products Catalog.[28]

First, Figure 15 shows the comparison of carbon dioxide (1) + EHMA (2) experimental results with calculations obtained using the Peng−Robinson equation at the temperature of 353.15 K. The binary interaction parameters of the PR EOS are fitted by the experimental data at 353.15 K. The values of the adjusted parameters of the PR EOS for the carbon dioxide + EHMA system are $k_{ij} = 0.060$ and $\eta_{ij} = -0.015$. As shown in Figure 15, we show the comparison of experimental data (symbol) with (p, x) isotherms (solid line) data calculated by the PR EOS at (313.15, 333.15, 373.15, and 393.15) K using adjusted parameters ($k_{ij} = 0.060$ and $\eta_{ij} = -0.015$). The data are satisfactorily correlated with the PR EOS.

Figure 16 shows the mixture-critical curve for the carbon dioxide + EHMA system calculated by the PR EOS. The calculated mixture−critical curve is type-I, in agreement with experimental observations. As shown Figure 14, the solid lines represent the vapor pressure for pure carbon dioxide[17] and EHMA.[17] The solid circles represent the critical point for pure carbon dioxide and EHMA. The upper part of the dash line means single phase (fluid); the lower part of the dash line two phases (vapor−liquid). The open squares represent the mixture−critical points determined by isotherms measured in this experiment. The dash lines represent the calculated value obtained using the PR EOS. The binary mixture parameters are then obtained from the PR equation, with k_{ij} equal to 0.060 and η_{ij} equal to −0.015.

Conclusions

Experimental data of cloud-point are presented for the P(EHMA) (1) + carbon dioxide (2) + EHMA (3) system at temperature below 478 K and pressure up to 247.0 MPa. With $w_3 = 0.666$, the cloud-point curve shows the typical appearance of a LCST boundary. Cloud-point behaviors are presented for P(EHMA) (1) + carbon dioxide (2) + EHMA (3) mixtures with $w_3 = (0.0 \text{ to } 0.564)$. The EHMA monomers induce favorable intermolecular interactions between the polymer segments and the solvent molecules, which help dissolution of the polymer.

The phase behavior for the P(EHA) (1) + carbon dioxide (2) + EHA (3) system exhibit U-LCST-type from a positive slope to a negative slope at temperature below 453 K and pressure up to 248.0 MPa. The cloud-point for the P(EHA) (1) + carbon dioxide (2) + EHA (3) with $w_3 = 0.709$ mixture exhibits LCST type with a positive slope. The cloud-point curves are shown for the binary mixtures for poly[2-ethylhexyl (meth)-acrylate] in supercritical propane, propylene, butane, 1-butene, $CHClF_2$, and DME at temperatures below 453 K and a pressure range of (3.0 to 31.5) MPa. Also, the impact of DME for the poly[2-ethylhexyl (meth)acrylate] + carbon dioxide + $w_3 = (0.053 \text{ to } 0.404)$ DME system is measured at temperatures to 453 K and a pressure range of (50.0 to 235.0) MPa. The carbon dioxide + EHMA system exhibits type-I phase behavior. The (p, x) bubble-point curves are convex, which indicates that carbon dioxide exhibits a high solubility in EHMA, probably due to the formation of a weak complex between the carboxylic oxygen in EHMA and the carbon in carbon dioxide. Phase behavior of the binary experimental data for the carbon dioxide + EHMA system was correlated with two adjustable parameters of the PR EOS.

Literature Cited

(1) Jung, J.; Perrut, M. Particle design using supercritical fluids: literature and patent survey. *J. Supercrit. Fluids* **2001**, *20*, 179−219.

(2) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. Polymerizations in supercritical carbon dioxide. *Chem. Rev.* **1999**, *99*, 543−564.

(3) Kompella, U. B.; Koushik, K. Preparation of drug delivery systems using supercritical fluid technology. *Crit. Rev. Ther. Durg Carrier Syst.* **2001**, *18*, 173−199.

(4) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*; Butterworth: Boston, 1994.

(5) Conway, S. Application of supercritical fluid solvents to new technologies: development of a high-pressure surface plasmon resonance spectroscopy sensor to monitor polymer adsorption. Ph.D. Thesis, Johns Hopkins University, Baltimore, MD, 2000.

(6) Waegemaekers, T. H. J.; Bensink, M. M. P. M. Non-mutagenicity of 27 aliphatic acrylate esters in the salmonella-microsome test. *Mutat. Res.* **1984**, *137*, 95−102.

(7) Byun, H. S.; Lee, D. H. Phase behavior of binary and ternary mixtures of poly(decyl acrylate)−supercritical solvents−decyl acrylate and poly(decyl methacrylate)−CO_2−decyl methacrylate systems. *Ind. Chem. Eng. Res.* **2006**, *45*, 3373−3380.

(8) Byun, H. S. Phase behavior on the binary and ternary mixtures of poly(cyclohexyl acrylate) and poly(cyclohexyl methacrylate) in supercritical CO_2. *J. Appl. Polym. Sci*. **2004**, *94*, 1117−1125.

(9) Lora, M.; McHugh, M. A. Phase behavior and modeling of the poly(methyl methacrylate)−CO_2−methyl methacrylate system. *Fluid Phase Equilib.* **1999**, *157*, 285−297.

(10) Wolf, B. A.; Blaum, G. J. Measured and calculated solubility of polymers in mixed solvents: monotony and cosolvency. *Polym. Sci., Polym. Phys. Ed*. **1975**, *13*, 1115−1132.

(11) Kirby, C. F.; McHugh, M. A. Phase behavior of polymers in supercritical fluid solvents. *Chem. Rev.* **1999**, *99*, 565−602.

(12) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Res. Fundam*. **1976**, *15*, 59−63.

(13) Byun, H. S.; Choi, M. Y.; Lim, J. S. High pressure phase behavior and modeling of binary mixtures for alkyl acetate in supercritical carbon dioxide. *J. Supercrit. Fluids* **2006**, *37*, 323−332.

(14) Byun, H. S.; Shin, J. S. Bubble-point measurement for CO_2 + vinyl acetate and CO_2 + vinyl acrylate system at high pressure. *J. Chem. Eng. Data* **2003**, *48*, 97−101.

(15) Byun, H. S.; Lee, D. H. Cosolvent effect and solubility measurement for butyl (meth)acrylate polymers in benign environmental supercritical solvents. *Ind. Chem. Eng. Res*. **2006**, *45*, 3354−3365.

(16) Byun, H. S.; McHugh, M. A. Impact of “free” monomer concentration on the phase behavior of supercritical carbon dioxide−polymer mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 4658−4662.

(17) Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(18) Benson, R. C.; Flygare, W. H. The molecular zeeman effect in propane and comparison of the magnetic susceptibility anisotropies with cyclopropene and other small ring compounds. *Chem. Phys. Lett*. **1969**, *4*, 141−143.

(19) Meyer, G.; Toennies, J. P. Determination of quadrupole moments of light hydrocarbon molecules from rotationally inelastic state scattering cross sections. *Chem. Phys.* **1980**, *52*, 39−46.

(20) Prausniz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.

(21) Tuminello, W. H.; Dee, G. T. Thermodynamics of poly(tetrafluoroethylene) solubility. *Macromolecules* **1994**, *27*, 669−676.

(22) Smith, P.; Gardner, K. H. Dissolution of poly(tetrafluoroethylene). *Macromolecules* **1985**, *18*, 1222−1228.

(23) Byun, H. S.; Kim, J. G.; Yang, J. S. Phase behavior on the poly[hexyl (meth)acrylate]−supercritical solvents−monomer mixtures at high pressures. *Ind. Chem. Eng. Res*. **2004**, *43*, 1543−1552.

(24) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. Solubility of polymers and copolymers in supercritical CO_2. *J. Phys. Chem.* **1996**, *100*, 15581−15587.

(25) McHugh, M. A.; Rindfleisch, F.; Kuntz, T.; Schmaltz, C.; Buback, M. Cosolvent effect of alkyl acrylates on the phase behavior of poly(alkyl acrylates)−supercritical CO_2 mixtures. *Polymer* **1998**, *39*, 6049−6052.

(26) Scott, R. L.; van Konynenburg, P. B. Static properties of solutions: van der Waals and related models for hydrocarbon system. *Discuss. Faraday Soc.* **1970**, *49*, 87−97.

(27) Byun, H. S. Monomer concentration effect on the poly(propyl acrylate) and poly(propyl methacrylate) solution phase behavior in supercritical CO_2 and C_2H_4. *Korean J. Chem. Eng*. **2002**, *19*, 126−131.

(28) Scientific Polymer Products, Inc. *Product Catalog 2003*; Scientific Polymer Products, Inc.: Ontario, NY, 2003.

Received for review August 7, 2006. Accepted December 10, 2006. The authors gratefully acknowledge the financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation.

JE060349N