

Phase behavior for the poly(alkyl methacrylate)+supercritical CO₂+DME mixture at high pressures

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Abstract—The phase behavior curves of binary and ternary system were measured for poly(alkyl methacrylate) in supercritical CO₂, as well as for the poly(alkyl methacrylate)+dimethyl ether (DME) (or 1-butene) in CO₂. The solubility curves are reported for the poly(alkyl methacrylate)+DME in supercritical CO₂ at temperature from (300 to 465) K and a pressure from (3.66 to 248) MPa. Also, The high-pressure static-type apparatus of cloud-point curve was tested by comparing the measured phase behavior data of the poly(methyl methacrylate) [PMMA]+CO₂+20.0 and 30.4 wt% methyl methacrylate (MMA) system with literature data of 10.4, 28.8 and 48.4 wt% MMA concentration. The phase behavior data for the poly(alkyl methacrylate)+CO₂+DME mixture were measured in changes of the pressure-temperature (p, T) slope and with DME concentrations. Also, the cloud-point pressure for the poly(alkyl methacrylate)+1-butene solution containing supercritical CO₂ shows from upper critical solution temperature (UCST) region to lower critical solution temperature (LCST) region at concentration range from (0.0 to 95) wt% 1-butene at below 455 K and at below 245 MPa.

Keywords: Poly(alkyl methacrylate), Poly(methyl methacrylate), Poly(ethyl methacrylate), Poly(propyl methacrylate), Poly(butyl methacrylate), Cloud-point Pressures, Supercritical CO₂, Dimethyl Ether

INTRODUCTION

Process technology on supercritical fluid is widely used in separations processes, pharmaceuticals, biological materials and chemical reactions, and the phase behavior data of the relevant pure substances and mixtures are an essential part of the technology [1-7]. Particularly, fundamentals and applications knowledge for the binary and ternary mixtures of homopolymers in supercritical solvents is of importance in polymer processes, polymerization condition and related industry. The alkyl methacrylate polymers are widely used in the plastic chemical industry involving a variety of weatherability, scratch and chemical resistance, optical fibers and coating. Therefore, the solubility data of high-pressure and high-temperature for multiple mixtures containing supercritical fluid plus cosolvent mixture and poly(alkyl methacrylate) plays a major role in many industrial and scientific fields. Recently, the phase behavior for binary and ternary mixture containing poly(methacrylate) has been studied at high pressures and temperatures [2,8,9]. In general, several articles and reviews have been published for the phase behavior data [10-14]. The phase behavior for binary and ternary systems consisting of polymers, solvents and cosolvent at high-pressure and high-temperature at earlier work was revealed [8,15-17]. For the phase behavior of solution of poly(methyl methacrylate) [PMMA] in supercritical chlorodifluoromethane (CDFM) the lower critical solution temperature (LCST) curves have been studied at temperature from (339 to 416) K using high-pressure variable volume view

cell [15]. The cloud-point data of ternary mixture for the poly(ethyl methacrylate)+ethyl methacrylate in supercritical carbon dioxide was reported by Byun and McHugh [16]. Maderek et al. [17] measured the phase behavior of pressure-temperature space on the high-temperature demixing of solution for the poly(decyl methacrylate) in supercritical toluene, isooctane, heptane, cyclopentane, hexane and pentane. Also, Rindfleisch et al. [8] reported the cloud-point data for binary mixture of poly(butyl methacrylate)+CO₂ system at temperature up to 523 K and pressure up to 300 MPa. On the other hand, the PMMA and PEMA in CO₂ cannot dissolve over the same range of conditions as above mentioned [16,18]. Also, the cloud-point pressure data for poly(methacrylate)+CO₂+cosolvent system at below temperature of ca. 523 K and at below pressure of ca. 300 MPa were reported by Byun et al. [19,20].

The aim of this research was to determine the impact of DME cosolvent on the phase behavior of poly(alkyl methacrylate) [PMMA, PEMA, PPMA and PBMA]+supercritical CO₂+DME mixture. Cloud-point pressure data were obtained regarding the effect of 1-butene cosolvent for binary system on the PBMA+supercritical CO₂ mixture. Behrenst and Sandler [21] previously thoroughly measured the experimental data for the binary CO₂+1-butene system, which has a critical-mixture curve with the highest pressure of about 7.5 MPa and at temperatures of 310.85 K and 318.15 K. The data for CO₂+1-butene binary system complement the PBMA+CO₂+1-butene data obtained in the present study. Also, experimental data for the binary CO₂+DME system at temperature range from (273.2 to 386.6) K and pressure range from (0.26 to 7.93) MPa was reported by Tsang and Streett [22]. These DME+CO₂ experimental data complement the poly(alkyl methacrylate)+CO₂+DME data obtained in the this study.

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EXPERIMENTAL SECTION

1. Materials

Poly(methyl methacrylate) [PMMA] [$T_g=378$ K, $M_w=102,600$, $M_w/M_n=2.12$], Poly(ethyl methacrylate) [PEMA] [$T_g=336$ K, $M_w=340,000$, $M_w/M_n=2.70$] and Poly(butyl methacrylate) [PBMA] [$T_g=308$ K, $M_w=320,000$, $M_w/M_n=4.35$] were obtained from Sigma-Aldrich Co., and Poly(propyl methacrylate) [PPMA] [$T_g=293$ K, $M_w=250,000$, $M_w/M_n=2.02$] obtained from Scientific Polymer Products, Inc. and used as received. The chemical structure of poly(alkyl methacrylate) is shown in Fig. 1. CO_2 (>0.999 mass fraction purity) was obtained from Daesung Industrial Co., and dimethyl ether (DME) (>0.995 mass fraction purity) were obtained from LG Gas (E1) Co. The specifications of all chemicals used in this work are summarized in Table 1.

2. Apparatus and Procedure

Fig. 2 shows a schematic diagram of a high-pressure variable-volume view cell apparatus used for cloud-point measurement of ternary and binary mixture for the polymer+SCF solvent+cosolvent system, which has already been described [23]. Cloud-point data

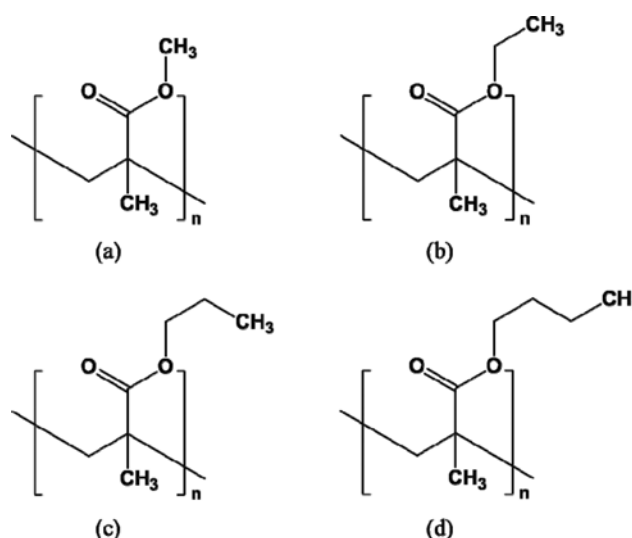


Fig. 1. Chemical structure of (a) poly(methyl methacrylate), (b) poly(ethyl methacrylate) (c) poly(propyl methacrylate) and poly(butyl methacrylate).

Table 1. Specifications of the chemicals used

Chemical name	Mass fraction purity	Source	CAS RN
CO_2	>0.999	Daesung Industrial Gases Co.	124-38-9
Dimethyl ether	>0.995	LG Gas (E1)	115-10-6
Poly(methyl methacrylate)		Sigma-Aldrich Co., Inc. $M_w=102,600$	9011-14-7
Poly(ethyl methacrylate)		Sigma-Aldrich Co., Inc. $M_w=340,000$	9003-42-3
Poly(propyl methacrylate)		Sigma-Aldrich Co., Inc. $M_w=320,000$	25609-74-9
Poly(butyl methacrylate)		Scientific Polymer Products, Inc. $M_w=250,000$	9003-63-8

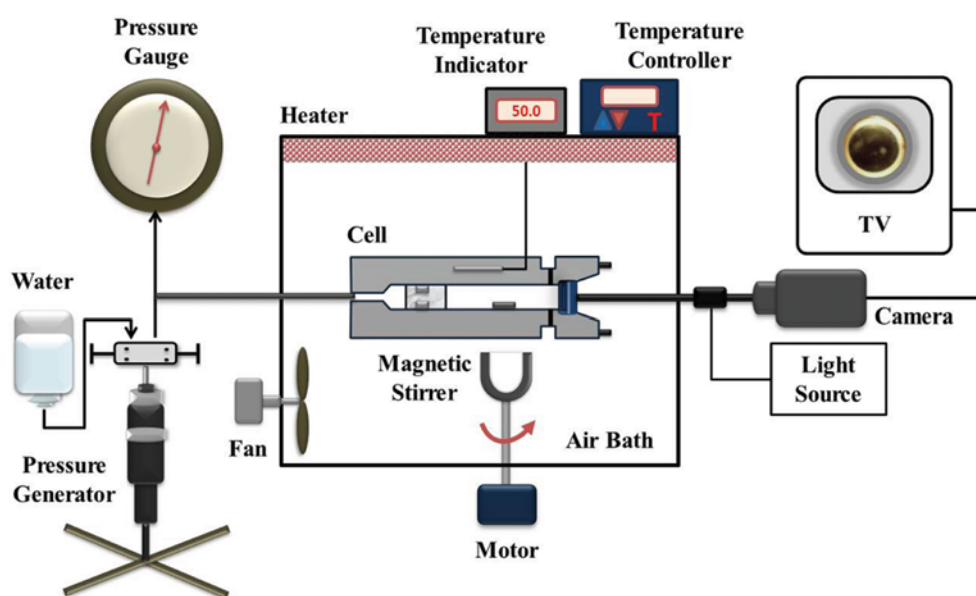


Fig. 2. Schematic diagram of phase behavior measurement apparatus at high-pressure.

for the polymer solutions at a constant poly(alkyl methacrylate) concentration of 5.0 ± 0.5 wt% are measured, which is typical of the concentrations used for the poly(alkyl methacrylate)+supercritical CO₂ or poly(alkyl methacrylate)+supercritical CO₂+DME (or 1-butene) mixture. Poly(alkyl methacrylate) was loaded into the inside of the cell to within ± 0.002 g, and then the cell was purged with nitrogen several times followed by CO₂ to ensure that all of the air and organic matter had been removed. Supercritical CO₂ and cosolvent (DME and 1-butene) were 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, (0-345.0) MPa, accurate to within ± 0.35 MPa]. The system temperature was maintained to within ± 0.2 K. The mixture was compressed to the desired pressure using a high pressure generator (HIP Inc., model 37-5. 75.60), and the inside of the cell was viewed on a video monitor with a camera coupled to a bore-scope (Olympus Corp., model F100-038-000-50).

Phase behavior for the poly(alkyl methacrylate)+CO₂+DME (or 1-butene) mixtures was measured at a fixed polymer concentration. The mixtures in the view cell were heated to the desired temperature and pressurized until a single phase was achieved, and they were maintained in the one-phase region at fixed temperature for 30-40 min. at least to reach thermal equilibrium conditions. The cloud-point is the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar inside the cell. Cloud-points were measured and reproduced at least twice. Phase behavior data for the poly(alkyl methacrylate)+SCF solvents+cosolvent mixtures was obtained, and the combined standard uncertainties of pressure and temperature were estimated to be ± 0.38 MPa and ± 0.16 K for a given loading of the cell [24,25]. Also, uncertainty of measured weight fraction for polymers and DME was predicted to be $\pm 0.08\%$ and $\pm 0.2\%$, respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

The critical properties (T_c , p_c , ρ_c), acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of CO₂ and DME used in this study [26,27] are listed on Table 2. CO₂ has a critical temperature near room temperature and a modest critical pressure, which means that at temperatures slightly above room temperature it is possible to obtain liquid-like and, by implication, liquid-like solvent characteristics. DME has a dipole moment that allows the effect of dipole interactions to be compared with that of quadrupole interactions found with CO₂.

The accuracy of cloud-point curves in the high-pressure apparatus used this work was tested by comparing measured phase behavior data for the PMMA+CO₂+MMA system with those of Lora

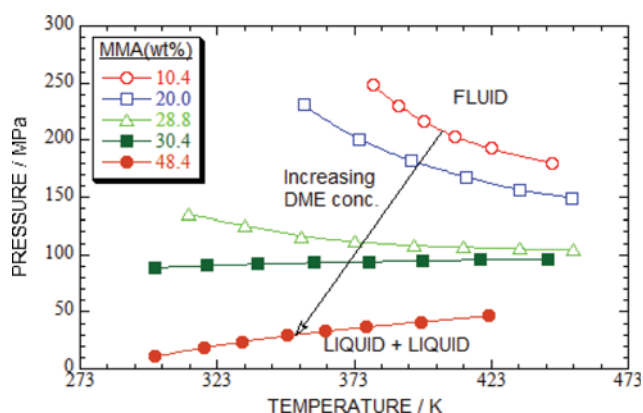


Fig. 3. Impact of MMA on the phase behavior of the PMMA+CO₂+x wt% MMA system. The concentration of polymer is ca. 5 wt% for each solution. Lora and McHugh data: 10.4 wt% (○), 28.8 wt% (△) and 48.4 wt% (●), This work: 20.0 wt% (□) and 30.4 wt% (■).

Table 3. Experimental cloud-point data for the poly(methyl methacrylate) [PMMA]+CO₂+x wt% methyl methacrylate (MMA) system with different MMA content

T^a /K	p^a /MPa
5.1 wt% PMMA+20.0 wt% MMA	
354.7	231.21
374.8	201.03
394.2	181.55
414.0	167.76
433.4	156.38
452.7	149.48
4.9 wt% PMMA+30.4 wt% MMA	
300.2	88.73
319.7	90.66
338.0	91.94
358.8	93.08
378.4	93.97
398.2	94.80
419.3	95.63
443.7	96.59

^aStandard uncertainties are $u(T)=T \pm 0.16$ K and $u(p)=p \pm 0.38$ MPa

and McHugh [18] from 300 to 453 K. The cloud-point curves for the PMMA+CO₂+MMA system are plotted in Fig. 3. As shown in Fig. 3 and Table 3, the solubility curve at temperature in range of 300 to 453 K compares well with those of Lora and McHugh

Table 2. Critical temperatures, critical pressures, critical densities, polarizabilities, dipole moments, and quadrupole moments of solvents used in this study [23,24]

Solvents	T_c /K	p_c /Mpa	ρ_c /kg m ⁻³	ω	$\alpha \cdot 10^{30}$ /m ³	$\mu \cdot 10^{30}$ /C·m	$Q \cdot 10^{40}$ /C·m ²
CO ₂	304.2	7.38	469	0.225	2.65	0.00	-14.34
Dimethyl ether	400.0	5.30	258	0.192	5.22	4.34	4.00
1-Butene	419.6	3.97	234	0.191	8.24	1.13	8.34
Methyl methacrylate	567.2	3.68		0.317		5.57	

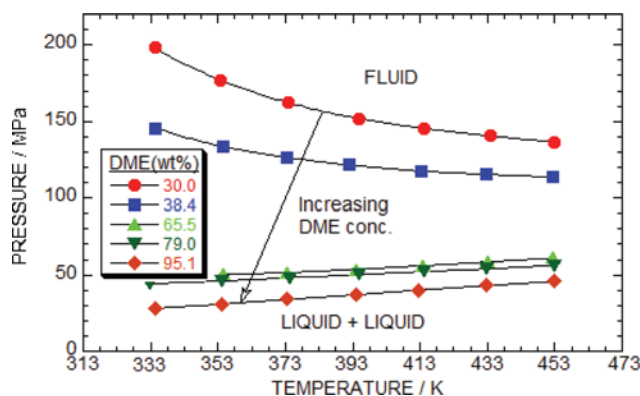


Fig. 4. Impact of DME on the phase behavior of the PMMA+CO₂+x wt% DME system. The concentration of polymer is ca. 5 wt% for each solution.

[18]. Phase behavior data of ternary system for the PMMA+CO₂+20.0 wt% and 30.4 wt% MMA mixture at temperature to 453 K and pressures ranging from 231.21 to 887.30 MPa were measured. The cloud-point curve for PMMA+CO₂+20.0 wt% MMA system exhibits upper critical solution temperature (UCST) region with negative slope. On the other hand, the phase behavior for the PMMA+CO₂+30.4 wt% MMA mixture has slightly positive slope with 0.05 MPa/K at temperature ranging from 300.2 to 443.7 K and pressure up to 96.59 MPa.

Tsang and Streett [22] reported experimental data for the binary CO₂+DME system which has a critical-mixture curve with a highest pressure of about 7.9 MPa. The CO₂+DME phase behavior data complement the poly(alkyl methacrylate)+supercritical CO₂+DME phase behavior curve determined in the present study.

Fig. 4 and Table 4 present the phase behavior of ternary system for the PMMA+DME mixture in supercritical CO₂. PMMA with an $M_w=94,000$ is insoluble in CO₂ to temperatures of 523 K and 273 MPa (Rindfleisch et al. is not soluble until at 528 K and 255 MPa.). A fluid region in the PMMA+DME mixture was obtained at temperatures in the range of 334.4 to 452.1 K and at lower pressures such as 45.69 MPa. As shown in Table 2, DME has a significant dipole moment and quadrupole moment and, reversely, CO₂ has not dipole moment having strong reactivity. When 30.0 wt% DME monomer was added to the solution, the solubility curve for the PMMA+CO₂+30.0 wt% DME system shows UCST behavior of negative gradient at below 453 K and 198.10 MPa. The PMMA+CO₂+38.4 wt% DME phase behavior presents at temperature in the range of 334.5 to 452.6 K and pressure up to 145.69 MPa. At 400 K, the pressure difference of two systems (30.0 and 38.4 wt% DME) are about 30 MPa in accordance with concentration increases due to strong polar DME. With 65.5 and 79.0 wt% DME in solution, the cloud-point pressure remains virtually constant at 557 ± 56 MPa at 65.5 wt% DME and 503 ± 40 MPa (at 79.0 wt% DME) over a temperature in the range of 333.0 to 453.2 K.

Fig. 5 and Table 5 show the impact of DME on the phase behavior for the PEMA+CO₂+(0.0-95.0) wt% DME mixture. The PEMA does dissolve in CO₂ at a temperature below 452.6 K and pressure up to 244.66 MPa. The solubility curve for the PEMA+CO₂ mixture shows -1.58 MPa/K with negative slope at temperature in the

Table 4. Experimental cloud-point data for the poly(methyl methacrylate) [PMMA]+CO₂+x wt% dimethyl ether (DME) system with different DME content

T ^a /K	p ^a /MPa
5.0 wt% PMMA+30.0 wt% DME	
334.4	198.10
353.8	177.07
373.9	162.24
395.1	151.72
414.4	145.34
434.1	140.52
453.1	136.38
5.2 wt% PMMA+38.4 wt% DME	
334.5	145.69
354.6	133.62
373.7	126.38
392.0	121.55
413.5	117.41
432.9	115.34
452.6	113.62
5.0 wt% PMMA+65.5 wt% DME	
354.8	50.17
373.7	51.55
394.3	53.62
413.9	56.03
433.4	58.45
452.6	61.21
5.1 wt% PMMA+79.0 wt% DME	
333.0	44.31
354.4	46.03
374.4	48.10
395.0	50.17
414.3	52.24
432.8	53.97
453.2	56.38
5.1 wt% PMMA+95.1 wt% DME	
334.4	28.10
354.2	30.86
373.8	33.97
394.4	37.07
412.7	40.00
433.0	42.93
453.1	45.69

^aStandard uncertainties are $u(T)=T \pm 0.16$ K and $u(p)=p \pm 0.38$ MPa

range of 422.8 to 452.6 K. The phase behavior for the PEMA+DME system shows a lower pressure curve at pressure from 20 to 48 MPa and at temperature from 334.8 to 452.7 K. The pressure difference between PEMA+CO₂ and PEMA+DME systems is probably due to whether or not the dipole moment in DME and carbon dioxide is as shown in Table 2. When 6.3 wt% DME is added to the solution, high-pressure phase behavior for the PEMA+CO₂+6.3 wt% DME mixture shows UCST curve at temperature from 364

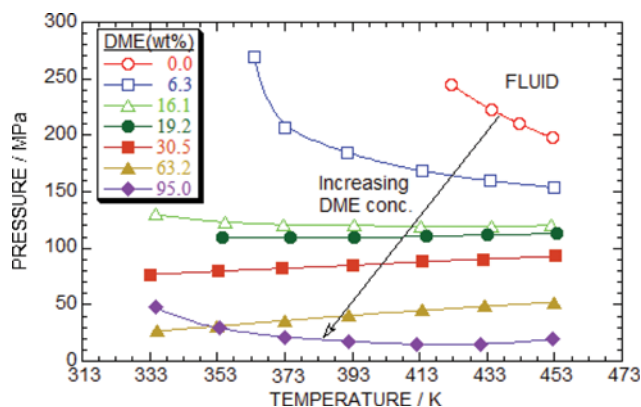


Fig. 5. Impact of DME on the phase behavior of the PEMA+CO₂+x wt% DME system. The concentration of polymer is ca. 5 wt% for each solution.

to 453 K and at pressure from 159.83 to 269.14 MPa. As shown in Fig. 5, the PEMA+CO₂+6.3 wt% DME pressure curve rapidly increases at below 373 K. At the $T < 373$ 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 PEMA polymer precipitates out of the binary and ternary mixtures, probably due to strong polymer+polymer interaction. The cloud-point curve for the PEMA+CO₂+16.1 wt% DME mixture presents U-LCST behavior from a positive slope to a negative slope in the temperature range from 335 to 452 K and pressure from 120 to 130 MPa. With 19.2, 30.5 and 63.2 wt% DME in solution, the solubility curves for the PEMA+CO₂+19.2, 30.5 and 63.2 wt% DME systems show 0.04 MPa/K, 0.14 MPa/K and 0.22 MPa/K a linearly positive gradient with LCST region. At 400 K, the pressure difference between three systems is showed the 15 MPa and 50 MPa, respectively.

Fig. 6 and Table 6 show the impact of DME on the cloud-point curves of the PPMA+CO₂+x wt% DME system obtained in this work. The cloud-point behavior of binary mixture for PPMA in supercritical CO₂ shows a UCST curve at temperature to 452.4 K and pressure up to 248.45 MPa. In contrast, the phase behavior for

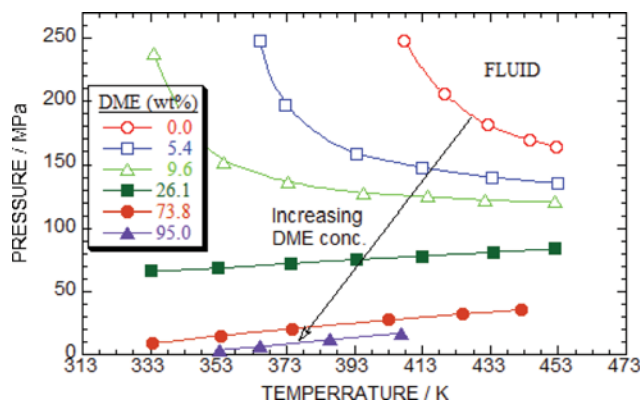


Fig. 6. Impact of DME on the phase behavior of the PPMA+CO₂+x wt% DME system. The concentration of polymer is ca. 5 wt% for each solution.

Table 5. Experimental cloud-point data for the poly(ethyl methacrylate) [PEMA]+CO₂+x wt% dimethyl ether (DME) system with different DME content

T ^a /K	p ^a /MPa
4.9 wt% PEMA+0.0 wt% DME	
422.8	244.66
434.4	222.93
442.8	210.34
452.6	197.59
5.0 wt% PEMA+6.3 wt% DME	
364.0	269.14
373.2	207.07
391.7	184.66
414.0	168.10
434.0	159.83
453.0	153.79
5.1 wt% PEMA+16.1 wt% DME	
335.1	130.00
355.4	123.28
373.0	120.86
394.0	120.17
413.4	119.48
434.4	119.48
452.2	120.17
5.0 wt% PEMA+19.2 wt% DME	
354.8	109.14
375.1	109.14
393.9	109.48
415.2	110.52
433.3	111.90
453.9	112.93
5.1 wt% PEMA+30.5 wt% DME	
333.5	76.55
353.4	79.83
372.5	82.24
393.2	85.00
413.9	88.10
431.9	90.34
453.4	92.93
5.1 wt% PEMA+63.2 wt% DME	
335.4	26.72
352.9	31.03
373.1	36.03
392.3	40.52
413.8	45.00
432.5	48.79
452.8	52.07
5.0 wt% PEMA+95.0 wt% DME	
334.8	48.10
353.7	29.14
373.2	21.55
392.1	17.59
412.3	15.00
431.3	15.34
452.7	20.00

^aStandard uncertainties are $u(T)=T \pm 0.16$ K and $u(p)=p \pm 0.38$ MPa

Table 6. Experimental cloud-point data for the poly(propyl methacrylate) [PPMA]+CO₂+x wt% dimethyl ether (DME) system with different DME content

T ^a /K	p ^a /MPa
5.1 wt% PPMA+0.0 wt% DME	
408.0	248.45
419.8	205.69
432.5	181.21
444.8	169.48
452.4	164.31
5.0 wt% PPMA+5.4 wt% DME	
365.3	248.45
372.7	197.07
393.8	158.45
413.2	147.76
433.7	139.83
452.9	135.34
4.9 wt% PPMA+9.6 wt% DME	
334.2	238.10
354.8	152.24
373.8	136.03
395.9	127.41
414.6	124.66
431.7	121.90
452.4	120.17
5.0 wt% PPMA+26.1 wt% DME	
333.2	66.03
353.3	68.45
374.5	72.24
393.9	75.34
413.2	78.10
434.2	81.21
452.3	83.97
5.0 wt% PPMA+73.8 wt% DME	
333.9	8.79
353.9	15.00
374.9	20.52
403.3	27.41
425.1	32.24
442.2	35.34
5.1 wt% PEMA+95.0 wt% DME	
353.5	3.66
365.4	6.35
385.8	11.79
407.1	17.00

^aStandard uncertainties are $u(T)=T\pm 0.16$ K and $u(p)=p\pm 0.38$ MPa

PPMA in supercritical DME is presented at pressure below 17 MPa and temperature below 407 K. As shown in Table 2, the difference of pressure curves between PPMA+CO₂ and +DME mixtures are due to the presence of a dipole moment in DME [4.34×10^{-30} C·m] and CO₂ [0.0×10^{-30} C·m]. When 5.4 and 9.6 wt% DME are added to the solution, the solubility curves exhibited UCST region with

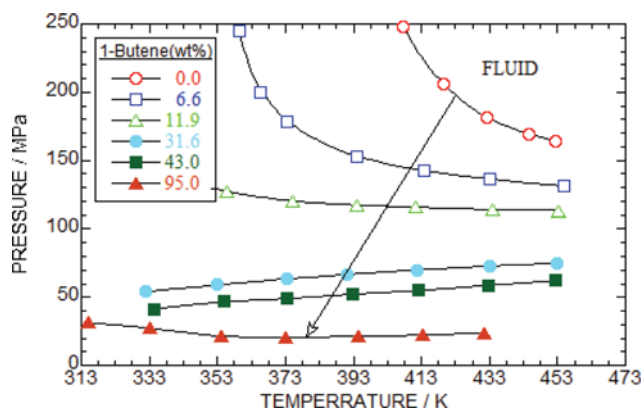


Fig. 7. Impact of 1-butene on the phase behavior of the PPMA+CO₂+x wt% 1-butene system. The concentration of polymer is ca. 5 wt% for each solution.

negative gradient at temperature in the range of 334 to 452 K. The PPMA+CO₂+5.4 wt% DME and PPMA+CO₂+9.6 wt% DME systems did not dissolve below temperatures of 365 K and 334 K, respectively. At the $T<353$ K (9.6 wt%) and $T<373$ K (5.4 wt%), the cloud-point behavior does exhibit a rapid increase in pressure indicated UCST curves, and occurs because of a large increase in energetics between polymer+polymer as compared to polymer+solvent interaction. If the DME concentration is increased to 26.1 wt%, thermodynamic curve for the PPMA+CO₂+26.1 wt% DME mixtures shows LCST behavior of 0.15 MPa/K with linear slope at temperature from 333 to 452 K and pressure below 84 MPa. The phase behavior of the LCST region is mainly due to govern rather polymer+solvent interaction than polymer+polymer and solvent+solvent interaction. With 73.8 wt% DME to the solution, the cloud-point data for this system obtains 0.24 MPa/K slope at temperature to 442 K and at below 35.34 MPa.

Fig. 7 and Table 7 show the effect of 1-butene on the phase behavior of the PPMA+1-butene mixture in supercritical CO₂. When 6.6 wt% 1-butene was added to the solution, the solubility curve exhibited UCST phase behavior with negative slope. The PPMA+CO₂+6.6 wt% 1-butene system does dissolve below pressure of 245 MPa and below temperature of 455 K. At $T<360$ K, the pressure curve increases rapidly as the temperature decreases due to strong impact of PPMA+PPMA interaction. If the 1-butene cosolvent is increased to 11.9 wt%, the phase behavior data for the PPMA+CO₂+11.9 wt% 1-butene system is measured at temperature from 333 to 453 K and pressure from 113 to 145 MPa. At temperatures greater than 373 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. With 31.6 and 43.0 wt% 1-butene to the mixture, the solubility behavior of two systems shows the LCST region with positive slopes. Also, the PPMA+1-butene curve shows U-LCST-type at temperature from 315 to 431 K and pressure to 31.38 MPa. This tendency shows almost same phase behavior for the PPMA+DME mixture.

Fig. 8 and Table 8 show the cloud-point behavior of the PBMA+CO₂+DME systems obtained in this work. PBMA does dissolve in pure CO₂ at 452 K and about 242 MPa. We compared the phase behavior data for binary poly(butyl methacrylate)+supercritical

Table 7. Experimental cloud-point data for the poly(propyl methacrylate) [PPMA]+CO₂+x wt% 1-butene system with different 1-butene content

T ^a /K	p ^a /MPa
5.1 wt% PPMA+6.6 wt% 1-butene	
359.6	245.00
365.7	200.17
373.5	178.45
394.4	152.76
413.8	142.24
433.3	136.27
455.0	131.21
5.0 wt% PPMA+11.9 wt% 1-butene	
333.6	145.17
355.8	127.24
375.4	120.17
394.4	117.07
411.4	115.69
434.0	113.97
453.3	113.28
5.0 wt% PPMA+31.6 wt% 1-butene	
332.2	54.31
353.2	59.14
373.5	63.62
391.4	66.72
412.0	70.17
433.3	72.93
453.0	75.00
5.0 wt% PPMA+43.0 wt% 1-butene	
334.5	41.38
355.2	46.72
373.8	49.14
392.8	52.24
412.4	55.00
432.7	58.79
452.5	62.24
5.1 wt% PPMA+95.0 wt% 1-butene	
315.2	31.38
333.5	27.32
354.4	21.17
373.2	20.86
394.6	21.34
413.5	22.45
431.7	23.79

^aStandard uncertainties are u(T)=T±0.16 K and u(p)=p±0.38 MPa

CO₂ mixture with those measured by Rindfleisch et al. As shown in Fig. 8, the experimental data presented are in good agreement with those of Rindfleisch et al. [8]. When 4.8 wt% DME was added to the solution, the cloud-point curve exhibited UCST-type phase behavior with negative slopes. PBMA+CO₂+4.8 wt% DME system does dissolve below pressure of 248.5 MPa. Thermodynamic behavior for the PBMA+CO₂+14.6 wt% DME mixture shows a

Table 8. Experimental cloud-point data for the poly(butyl methacrylate) [PBMA]+CO₂+x wt% dimethyl ether (DME) system with different DME content

T ^a /K	p ^a /MPa
5.1 wt% PBMA+0.0 wt% DME	
416.3	242.59
418.7	233.27
423.4	215.69
432.5	192.24
452.6	166.72
5.2 wt% PBMA+4.8 wt% DME	
384.2	248.45
394.0	188.28
411.5	159.66
434.7	142.93
451.3	135.69
5.0 wt% PBMA+14.6 wt% DME	
335.4	117.59
354.7	110.86
373.7	106.38
393.4	104.83
411.8	104.31
433.7	102.93
452.5	103.79
5.1 wt% PBMA+32.1 wt% DME	
334.3	51.90
354.8	56.38
373.8	60.52
391.4	63.28
413.9	67.07
432.6	70.17
452.2	72.59
5.0 wt% PBMA+52.4 wt% DME	
332.5	23.28
353.0	28.79
374.0	34.31
394.8	38.79
413.4	42.59
433.5	46.72
452.7	49.83
5.0 wt% PBMA+78.8 wt% DME	
334.9	9.14
352.4	13.97
373.0	19.48
394.5	24.66
413.5	29.31
431.5	32.93
451.2	36.38
465.8	35.34

^aStandard uncertainties are u(T)=T±0.16 K and u(p)=p±0.38 MPa

slight UCST curve at below 452 K and at below 117 MPa, and the cloud-point curve of this system is almost flat at (104.5±1.9) MPa

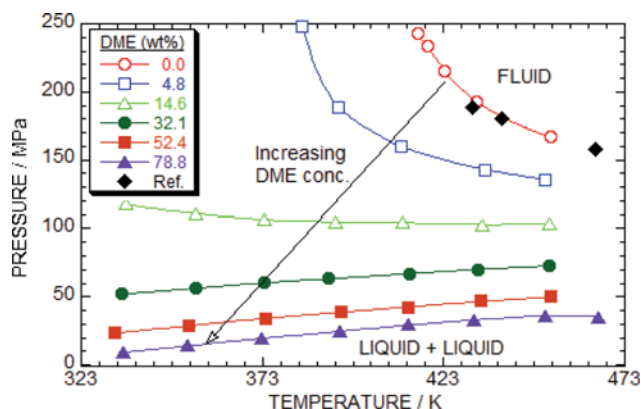


Fig. 8. Effect of DME as a cosolvent for poly(butyl methacrylate) in supercritical CO_2 . The concentration of polymer is ~ 5.0 wt% for each solution. \blacklozenge : Rindfleisch et al. data.

at temperature in the range of 373 to 452 K. The phase behavior curve for the PBMA+ CO_2 +(32.1 to 78.8 wt%) DME system exhibits LCST behavior in which temperature and pressure decreased smoothly from 465 to 332 K and at below pressure of 72.6 MPa. The cloud-point curves for the PBMA+ CO_2 +(32.1, 52.4 and 78.8 wt%) DME are a positive slope at about 0.18 MPa/K (32.1 wt% DME), 0.22 MPa/K (52.4 wt% DME) and 0.21 MPa/K (78.8 wt% DME), respectively. The location in which the curve demonstrates LCST behavior is mainly controlled by entropic contributions, which are sensitive to the changes in pressure. This type of phase behavior is probably due to the difference in free volume among PBMA, CO_2 , and DME [28,29].

CONCLUSIONS

Cloud-point curve for the poly(ethyl methacrylate), poly(propyl methacrylate) and poly(butyl methacrylate) in supercritical CO_2 shows the UCST-type behavior at negative slope. The phase behavior of ternary system for the poly(alkyl methacrylate)+DME (or 1-butene) mixture in supercritical CO_2 shows the (UCST to LCST) region from a negative slope to a positive slope. Also, the cloud-point curves for the poly(alkyl methacrylate)+DME mixtures exhibit the LCST-type phase behavior with a positive slopes.

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