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High-Pressure Phase Behavior of Polymer−Solvent Systems with Addition of Supercritical CO_2 at Temperatures from 323.15 K to 503.15 K

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The effect of carbon dioxide on the lower critical solution temperature (LCST) behaviors of binary polyisobutylene−*n*-heptane, polyethylene−*n*-heptane, polybutadiene−cyclohexane, and polybutadiene−toluene solutions was measured with a variable-volume view cell at temperatures from 323.15 to 503.15 K and pressures from ambient to 34 MPa. After addition of supercritical carbon dioxide, the LCEPs of these binary polymer solutions were lowered by 40 to 100 K, and the phase-transition pressures in the region of the LCST for these solutions tended to increase.

Introduction

In recent decades, considerable attention has been given to the utilization of supercritical fluid medium in various process industries. The unique physicochemical properties of supercritical fluids made them applicable to polymer separation processes such as fractionation and the recovery of monomers from polymer solutions.[1] In the early 1960s, Freeman and Rowlinson[2] reported that a homogeneous polymer solution can be separated into a polymer-rich phase and a solvent-rich phase when the solution temperature approaches the critical temperature of the solvent. This principle can be directly applied to the recovery process design of polymeric substances from solution.

The large difference of physical properties between polymer and solvent induces the complicated physicochemical interactions in polymer solutions. Thus, polymer solutions show extremely complex phase-equilibrium behaviors. For example, a polymer−solvent solution can show various phase behaviors such as homogeneous liquid phase (L), liquid−vapor phase (LV), liquid−liquid phase (LL), and liquid−liquid−vapor phase (LLV). Among these possible phases, a knowledge of critical solution temperature as a function of temperature and pressure is essential to speculate possible phase separation of a single liquid phase into two liquid−liquid phases. Published data for critical solution temperatures of polymer solutions are available in the literature.[3−7]

In a polymer solution, a lower critical solution temperature (LCST) behavior occurs in the vicinity of the critical temperature of the solvent. To date, low-molecular-weight hydrocarbon solvents have been widely used for polymer recovery processes. Thus, there are few data for the high-pressure phase behavior of polymer solutions containing high-critical-temperature solvents because of possible thermal degradation of a polymer. In the 1980s, Irani et al.[8] reported that the LCST of a polymer solution with a high-molecular-weight organic solvent could be significantly lowered by the addition of a small-molecular-weight supercritical fluid. Since then, much attention has been given to the investigation of phase-equilibrium behavior of ternary solutions that contain a polymer, organic solvent, and supercritical fluid. Because of density-tunable properties of supercritical fluids, the supercritical fluids have a much larger effect on the variation of the free volume of the solvent. Hence, the existence of a supercritical fluid in a binary polymer solution can induce phase separation at low temperature. In recent years, many investigators reported on the effect of the addition of supercritical fluids such as ethylene, propane, ethane, or carbon dioxide on the phase behavior of various polymer solutions. These include McHugh and Guckes,[9] Seckner et al.,[10] Bungert et al.,[11] Kiamos and Donohue,[12] and Li and Han.[13]

In this work, interest has been focused on the investigation of the effect of adding supercritical CO_2 to the polymer solutions containing a high-molecular-weight solvent (high critical temperature) such as *n*-heptane ($T_c = 540.3$ K), toluene (591.8 K), and cyclohexane (553.5 K). The systems investigated are polyisobutylene (PIB)−*n*-heptane−CO_2, polyethylene (PE)−*n*-heptane−CO_2, polybutadiene (PB)−toluene−CO_2, and polybutadiene (PB)−cyclohexane−CO_2.

Experimental Section

Materials. The polymers, PIB ($M_w = 1\,000\,000$, $M_v = 1\,200\,000$, $M_n = 600\,000$), PE ($M_w = 125\,000$), and PB ($M_w = 420\,000$), and the solvents, *n*-pentane (HPLC grade, 99.5% purity) and cyclohexane (HPLC grade, 99.5% purity), were purchased from Aldrich Co. (Milwaukee, WI) and used directly without further purification. *n*-Heptane (HPLC grade, 99.4% purity) was from J. T. Baker Inc. (Phillipsburg, NJ), and toluene (HPLC grade, 99.5% purity) was from Mallinckrodt Baker Inc. (Paris, KY). CO_2 (99.9% purity) was purchased from Seoul Gas Co. (Seoul, Korea). These solvents were also used directly without further purification.

Apparatus. A schematic diagram of the experimental apparatus used in the present study is shown in Figure 1. The high-pressure valves and tubes are stainless steel (316) and were obtained from HIP Co. (Erie, PA) and Autoclave Co. (Erie, PA). The internal volume of the equilibrium view cell was 33 mL. Sample polymer and solvent in the cell can be mixed well with a magnetic stirrer. System temperature was controlled with a Pt-thermocouple and PID controller within ±0.1 K. Pressure in the cell was measured

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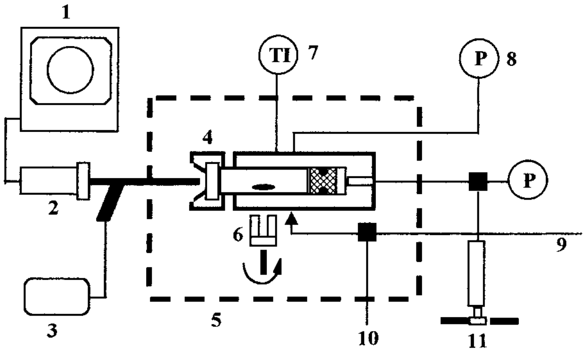

Figure 1. Schematics of the high-pressure variable-volume view cell: 1, monitor; 2, CCD camera; 3, halogen light source; 4, variable-volume view cell; 5, air oven; 6, magnetic stirrer; 7, temperature indicator; 8, pressure transducer and indicator; 9, input line of CO_2 and solvent; 10, vacuum pump; 11, pressure generator.

with a pressure transducer that was purchased from Varcom Co. (Winchester, USA) within ±0.02 MPa. The pressure generator was purchased from NOVASWISS Co. (Vogelsangstrasse, Switzerland). Organic solvent and CO_2 were accurately fed into the cell within ±0.02 g with a syringe pump (ISCO Model-260D, Lincoln, NE). Phase behaviors in the cell were observed through the view window with a CCD (charge coupled device) camera (Toshiba IK-C41MF, Toshiba, Japan) with a halogen light source and a real time frame grabber (RTFG) purchased from DATA TRANSLATION Co. (MASH Series DT3155, USA).

Experimental Procedure. The weight of the polymer sample was measured with an electronic balance (OHAUS Corp., Florham Park, NJ) with a resolution of 1 mg. After a polymer sample was introduced into the cell, the equipment was evacuated with a vacuum pump (Anelva Corp., Japan). A precalculated amount of an organic solvent was fed into the cell with the syringe pump. Then, a known amount of supercritical CO_2 at 20 MPa and 313.15 K was fed into the polymer−solvent solution. The sample polymer solution in the cell was mixed with the magnetic stirrer until the solution reached a homogeneous phase. When the cell reached an equilibrium temperature, the solution was pressurized with the pressure generator until the solution became a single liquid phase.

In the present study, two types of phase behaviors were observed. They were the L−LV coexistence curves and the L−LL coexistence curves. The L−LV coexistence curves indicate the liquid → liquid + vapor transition points, and the L−LL coexistence indicates the liquid → liquid_1 + liquid_2 transition points. The L−LL curve actually represents the LCST curve, that is, the cloud point curve. These phase-transition points were visually observed by lowering pressure at the isotherm.

To investigate the L−LV curves, the pressure of the single-liquid phase in the cell is decreased at a constant temperature until the first bubble of vapor appears visually. The pressure at which the vapor bubble occurs is taken as the phase-transition pressure. For the L−LL curves, the system pressure is isothermally increased until the $L_1 + L_2 + V$ mixture in the cell turns into a single-liquid phase. Then, the pressure is slowly decreased until the single-liquid phase begins to become cloudy. Because of the cloudy phenomena, the halogen light intensity reflecting from the cell is greatly decreased. The RTFG used in this study can easily measure a deviation of light intensity between a single clear phase and a cloudy opaque phase. When the deviation is around 90%, the pressure is taken as the phase-transition pressure.

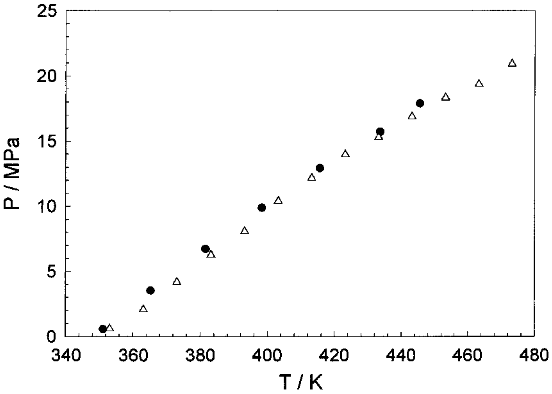

Figure 2. Comparison of measured and literature data for the phase behavior of the PIB−*n*-pentane system: △, data obtained in this work; ●, data reported by Zeman et al. (1972).

Results and Discussion

1. LCST of the Polyisobutylene−n-Pentane Mixture. In this work, the LCST data of the PIB−*n*-pentane solution reported by Zeman et al.[4] were reproduced to confirm the reliability of the apparatus and experimental procedures. The concentration of PIB (M_v = 1 660 000) was 2.43 wt % in the data source mentioned above. In the present work, the concentration of PIB (M_v = 1 200 000) was 2.24 wt %. The LCST data measured in this work were compared with published data in Figure 2. Although there was a slight difference of molecular weight distribution of PIB, the LCST data obtained from both sources agreed well with each other. These are the results averaged for three repeated runs. Thus, we assumed that the apparatus and experimental procedure adopted in this work are reliable.

2. Effect of CO_2 on the Phase Behavior of Polymer−Solvent Systems. In the present study, three different polymers (PIB, PE, and PB) and three kinds of organic solvents (*n*-heptane, cyclohexane, and toluene) were used to make binary solvent−polymer solutions. The solvents tested in the present study have high critical temperatures. For each binary solvent−polymer solution, a known amount of supercritical CO_2 was added and the LCST behavior was observed.

2-1. PIB−n-Heptane−CO_2 and PE−n-Heptane−CO_2 System. For PIB−*n*-heptane solutions, the measured phase-transition pressures at various concentrations of CO_2 were summarized in Table 1 and depicted in Figure 3. The concentration of PIB was fixed as 2.5 wt % in this system. In Figure 3, the L−LV curve denotes the phase-transition points of the polymer solution from single-liquid phase to L + V phases, and the LCST curve represents the phase-transition points (cloud point) from a single-liquid phase to L + L phases with reduced pressure. In the present study, it was not possible to measure accurately the LCEP (lower critical end point) where the LV, LLV, and LL loci converge. However, the existence of a LCEP can be predicted in the region where the L−LV and LCST curves coexist together.

From Table 1 and Figure 3, the existence of a LCEP in the absence of CO_2 can be predicted in the temperature regions from 433.15 to 443.15 K. When CO_2 was added up to 8.8 wt % to the solution, the LCEP shifted to lower temperature regions from 393.15 to 403.15 K. Also, when the concentration of CO_2 was increased up to 26.0 wt %, only the LCST locus was observed within experimental

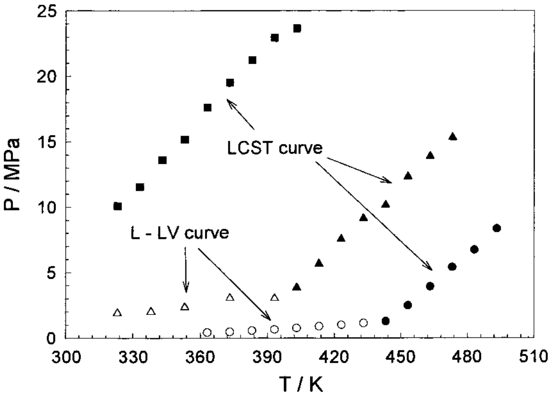

Figure 3. Pressure and temperature phase diagram for the PIB–*n*-heptane–CO_2 system: ●○, 0 wt % CO_2; ▲△, 8.8 wt % CO_2; ■, 26.0 wt % CO_2.

Table 1. Measured Phase Transition Pressures with the Addition of CO_2 to the Polyisobutylene (2.5 wt %)–*n*-Heptane System

	P/MPa		
T/K	0 wt %	8.8 wt %	26.0 wt %
323.15		1.9^{L-LV}	10.1^{LCST}
333.15			11.6
338.15		2.0	
343.15			13.6
353.15		2.3	15.2
363.15	0.4^{L-LV}	17.6	
373.15	0.5	3.0	19.5
383.15	0.5		21.2
393.15	0.6	3.0	22.9
403.15	0.7	3.8^{LCST}	23.7
413.15	0.9	5.7	
423.15	1.0	7.6	
433.15	1.1	9.1	
443.15	1.3^{LCST}	10.2	
453.15	2.5	12.3	
463.15	3.9	13.9	
473.15	5.4	15.3	
483.15	6.7		
493.15	8.3		

Table 2. Measured Phase Transition Pressures with the Addition of CO_2 to the Polyethylene (2.4 wt %)–*n*-Heptane System

	P/MPa		
T/K	0 wt %	12.5 wt %	27.3 wt %
383.15		6.2^{LCST}	28.0^{LCST}
393.15	0.6^{L-LV}	8.0	29.7
403.15		9.3	30.8
408.15	0.7		
413.15		10.8	32.0
423.15	0.9	12.0	32.9
433.15		13.2	33.5
438.15	1.1		
443.15	1.2	14.3	
453.15	1.2	15.4	
463.15	2.0^{LCST}	16.5	
473.15	3.2	17.7	
483.15	4.6		
493.15	5.7		
503.15	7.1		

temperatures. Also, the phase-transition pressure was increased significantly when increasing amounts of CO_2 were added to the system. The slope of the LCST, ($\partial P/\partial T$), was 0.14 MPa·K^{-1} at 0.0 CO_2 wt %, 0.16 at 8.8 wt %, and 0.17 at 26.0 wt %, respectively.

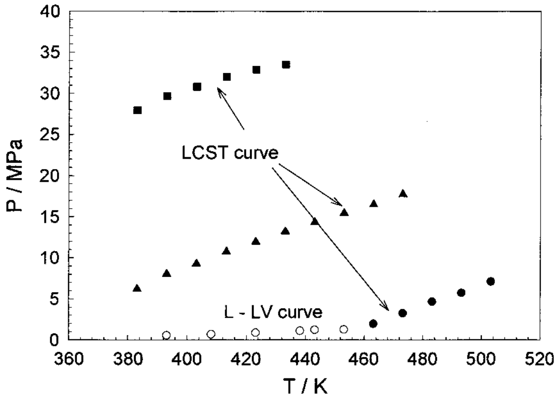

Figure 4. Pressure and temperature phase diagram for the PE-*n*-Heptane-CO_2 system: ● and ○, 0 wt % CO_2; ▲, 12.5 wt % CO_2; ■, 27.3 wt % CO_2.

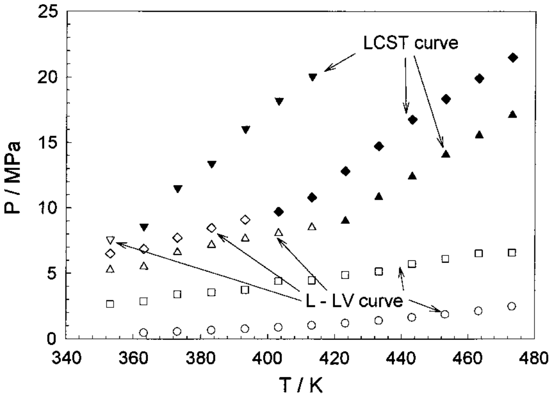

Figure 5. Pressure and temperature phase diagram for the PB–cyclohexane–CO_2 system: ○, 0 wt % CO_2; □, 8.1 wt % CO_2; ▲ and △, 17.2 wt % CO_2; ◆ and ◇, 24.0 wt % CO_2; ▼, 30.0 wt % CO_2.

Measured data for the PE–*n*-heptane–CO_2 system are summarized in Table 2, and the phase behavior of this system is shown in Figure 4. In this system, the concentration of PE was 2.4 wt %. The general phase-equilibrium behavior of this ternary system was similar to that of the PIB–*n*-heptane–CO_2 system. In the case of the binary PE–*n*-heptane system in the absence of CO_2, the LCEP was detected in the high-temperature regions from 453.15 to 463.15 K. However, when the added amount of CO_2 reached up to 12.5 wt % and 27.3 wt %, the LCST loci shifted to the low-temperature region. When the concentration of CO_2 was 27.3 wt %, the phase-transition pressure was elevated to 33.5 MPa. As shown in Figure 4, the slopes of the LCST were 0.13 MPa·K^{-1} at 0.0 CO_2 wt %, 0.13 at 12.5 wt %, and 0.11 at 27.3 wt %.

2-2. PB–Cyclohexane–CO_2 and PB–Toluene–CO_2 Systems. The measured phase-equilibrium behavior of the PB–cyclohexane–CO_2 system over a wide range of temperature and pressure is shown in Figure 5 and presented in Table 3. In Table 3, the concentration of PB was fixed to 5.0 wt %. As shown in Figure 5, only L–LV coexistence points were observed in low concentrations of CO_2 below 8.1 wt %. However, the LCST loci were observed at the high addition amount of CO_2 above 17.2 wt %. When the concentration of CO_2 was 30.0 wt %, the LCEP shift was investigated within lower temperature ranges from 353.15 to 363.16 K. The slopes of LCST loci were 0.16 MPa·K^{-1} at 17.2 CO_2 wt %, 0.17 at 24.0 wt %, and 0.21 at 30.0 wt %, respectively.

The phase behavior of the PB–toluene–CO_2 system is shown in Figure 6, and the data are summarized in Table 4. In this system, the concentration of PB was fixed to 5.9 wt % and the concentration of CO_2 was fixed at 10.8, 18.6, 27.8, and 33.7 wt %, respectively. At the concentration of

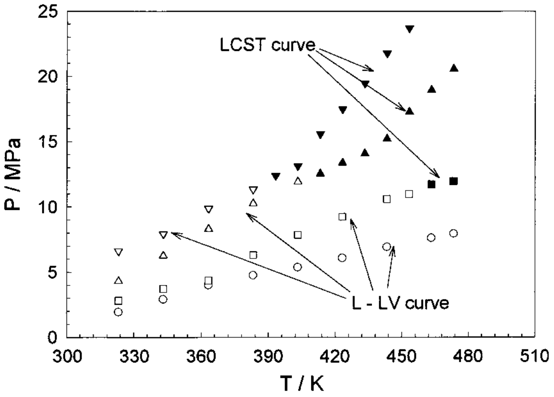

Figure 6. Pressure and temperature phase diagram for the PB−toluene−CO_2 system: ○, 10.8 wt % CO_2; ■ and □, 18.6 wt % CO_2; ▲ and △, 27.8 wt % CO_2; ▼ and ▽, 33.7 wt % CO_2.

Table 3. Measured Phase Transition Pressures with the Addition of CO_2 to the Polybutadiene (5 wt %)−Cyclohexane System

	P/MPa				
T/K	0 wt %	8.1 wt %	17.2 wt %	24.0 wt %	30.0 wt %
353.15		$2.6^{\text{L−LV}}$	$5.3^{\text{L−LV}}$	$6.5^{\text{L−LV}}$	$7.6^{\text{L−LV}}$
363.15	$0.5^{\text{L−LV}}$	2.9	5.5	6.9	8.6^{LCST}
373.15	0.6	3.4	6.6	7.7	11.5
383.15	0.6	3.6	7.2	8.5	13.4
393.15	0.8	3.7	7.7	9.1	16.1
403.15	0.9	4.4	8.1	9.7^{LCST}	18.2
413.15	1.0	4.5	8.5	10.8	20.0
423.15	1.2	4.9	9.0^{LCST}	12.8	
433.15	1.4	5.2	10.8	14.7	
443.15	1.6	5.7	12.4	16.8	
453.15	1.9	6.1	14.1	18.3	
463.15	2.1	6.5	15.6	19.9	
473.15	2.5	6.6	17.1	21.5	

Table 4. Measured Phase-Transition Pressures with the Addition of CO_2 to the Polybutadiene (5.9 wt %)−Toluene System

	P/MPa			
T/K	10.8 wt %	18.6 wt %	27.8 wt %	33.7 wt %
323.15	$1.9^{\text{L−LV}}$	$2.8^{\text{L−LV}}$	$4.3^{\text{L−LV}}$	$6.6^{\text{L−LV}}$
343.15	2.9	3.7	6.3	7.9
363.15	4.0	4.4	8.3	9.9
383.15	4.8	6.3	10.3	11.4
393.15				12.4^{LCST}
403.15	5.4	7.9	11.9	13.1
413.15			12.5^{LCST}	15.6
423.15	6.1	9.2	13.4	17.5
433.15			14.1	19.5
443.15	6.9	10.6	15.2	21.8
453.15		11.0	17.3	23.7
463.15	7.6	11.7^{LCST}	19.0	
473.15	8.0	12.0	20.6	

10.8 wt % CO_2, the LCST locus was not observed because of the high critical temperature of toluene, and only the L−LV boundary points were detected. However, when the concentration of CO_2 was 18.6, 27.8, and 33.7 wt %, the LCST loci were observed. In Figures 5 and 6, the PB−toluene−CO_2 system showed a smaller LCST shift than that for the PB−cyclohexane−CO_2 system. Finally, the slope of the LCST of the PB−toluene−CO_2 mixture was 0.14 $MPa\cdot K^{-1}$ at 27.8 CO_2 wt % and 0.19 at 33.7 wt %, respectively.

Conclusions

The phase behaviors of polymer and solvent with a high critical temperature were investigated by adding CO_2 over a wide range of temperatures (from 323.15 to 503.15 K). The systems of PIB−*n*-heptane, PE−*n*-heptane, PB−cyclohexane, and PB−toluene were examined.

It has been observed that, with the increase of the amount of CO_2 in the polymer−solvent solutions, the pseudocritical temperatures are significantly decreased. In increasing the amount of CO_2, the LCEP shifts of the PIB−*n*-heptane system and the PE−*n*-heptane system were around 120 K and 80 K, respectively. The LCEP shift for both the PB−cyclohexane system and the PB−toluene system was around 70 K. The addition of compressible supercritical solvent into the polymer solutions makes the phase behaviors pressure-dependent.

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