*J. Chem. Eng. Data* **2006,** *51,* 1571−1575

# High-Pressure Phase Behavior of Carbon Dioxide + Heptadecafluorodecyl Acrylate + Poly(heptadecafluorodecyl acrylate) System

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Cloud points for binary system of carbon dioxide ($CO_2$) + poly(heptadecafluorodecyl acrylate) (poly(HDFDA)) were measured using a variable volume view cell with polymer concentration up to 10 wt % and at temperature from (303 to 363) K and pressure up to about 30 MPa. Typical lower critical solution temperature phase behavior is observed with a critical concentration between (7.0 and 8.0) wt % poly(HDFDA). In addition, cloud point and bubble point pressures for the ternary system of $CO_2$ + HDFDA + poly(HDFDA) were measured at temperature from (303 to 363) K and pressure up to about 30 MPa. As the weight fraction of HDFDA increased, cloud point pressure dramatically decreased and liquid−liquid−vapor transition was observed at 30.0 wt % monomer.

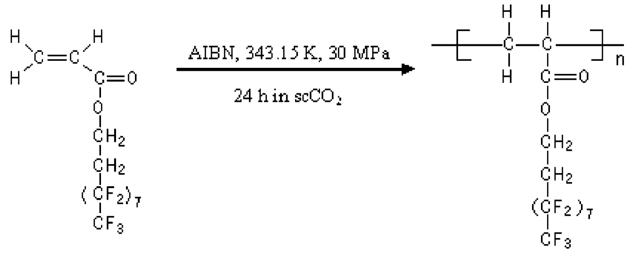
## Introduction

Perfluoroalkyl acrylate polymers are transparent, have a low refractive index, and are low surface tension polymers.[1] Taking advantage of these useful physical properties, several derivatives of the polymers have been industrially used as clad material for optical fibers, high-sensitive resistant polymers for microlithography, moisture-proof coating agents, oil and water repellant agents, etc.[2] In general, a perfluoroalkyl acrylate polymer is insoluble in many traditional organic solvents except for CFCs. However, CFCs have many problems related to the environment.

Recently, a perfluoroalkyl acrylate polymer was synthesized via suspension polymerization in water. In this case, residual water in a perfluoroalkyl acrylate polymer caused a problem during processing. So it is necessary to develop an alternative solvent for synthesis of a perfluoroalkyl acrylate polymer and its processing. Desimone et al.[3] reported the first successful homogeneous free radical polymerization of a perfluoroalkyl acrylate polymer in supercritical carbon dioxide ($scCO_2$).

As a solvent, $scCO_2$ has no dipole moment and has low dielectric constant. Because $scCO_2$ has quadrupole moment, it is a good solvent for nonpolar molecules such as methanol and ethanol. However, solubility for the most commercial polymers in $scCO_2$ is very low. This phenomenon is due to the very low entropy of mixing between polymer and $scCO_2$. For overcoming the low mixing entropy, a specific enthalpic interaction between polymer and $scCO_2$ is demanded. In the case of a perfluoroalkyl acrylate polymer, $scCO_2$ dissolves substantial amounts of the polymer at relatively low pressure. It is due to a specific interaction between fluorine and $scCO_2$.[4]

The phase behavior of polymers in the supercritical fluids is very important in most polymerization processes, polymer production, processing technologies, material development, and industrial application.[5−7] The design and operation of a separation process requires knowledge of phase behavior data. Especially high-pressure phase equilibrium data for binary or ternary mixtures containing $scCO_2$ will be needed to design and operate processing plants.[4,8] Moreover, for homogeneous radical polymerization, monomer and polymer must be dissolved in $scCO_2$ at given conditions. For precipitation polymerization in $scCO_2$, molecular weight and conversion are affected by phase behavior of system.[9] Therefore, measuring, understanding, and predicting phase behavior of the $CO_2$ + monomer + polymer system are very important.



HDFDA

Poly(HDFDA)

**Figure 1.** Chemical structure of HDFDA and poly(HDFDA).

Our group has measured pressure−composition ($P-x$) isotherms for binary systems such as $CO_2$ + heptadecafluorodecyl acrylate (HDFDA), $CO_2$ + heptadecafluorodecyl methacrylate (HDFDMA),[10] $CO_2$ + *N*-vinyl caprolactam (NVCL), and $CO_2$ + *N*-methyl caprolactam (NMCL).[11] High-pressure phase behavior for the ternary system of $CO_2$ + *N*-vinyl-2-pyrrolidone (NVP) + poly(vinyl pyrrolidone) (PVP)[12] was also reported.

In this work, we measured cloud point and bubble point pressures using a variable-volume view cell for the ternary system of $CO_2$ + HDFDA + poly(HDFDA) as a function of polymerization condition and HDFDA contents at temperature from (303 to 363) K.

## Experimental Section

***Materials.*** Carbon dioxide (min. 99.99 %) was purchased from Korea Industrial Gases. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,-

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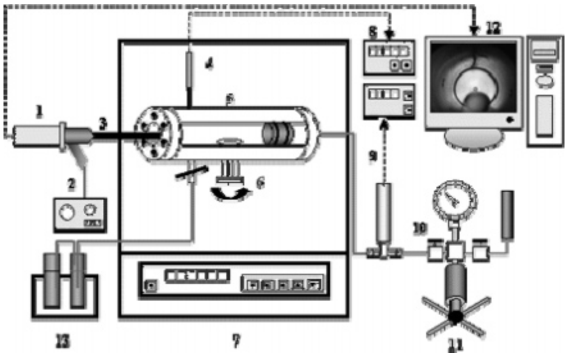

**Figure 2.** Schematic diagram of the experimental apparatus: 1, camera; 2, light source; 3, borescope; 4, fast response PRT; 5, view cell; 6, magnetic stirrer; 7, air bath; 8, digital thermometer; 9, digital pressure transducer; 10, pressure gauge; 11, hand pump; 12, computer monitor; 13 trap.

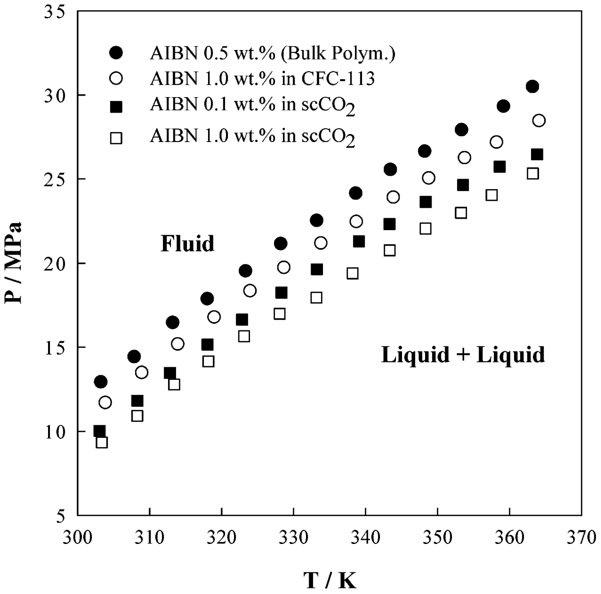

**Figure 3.** Cloud point for $CO_2$ + poly(HDFDA) system with different polymerization conditions.

**Table 1. Inherent Viscosity of Poly(HDFDA)**

| polymerization condition | | |
|---|---|---|
| AIBN/wt % | solvent | $\eta_{inh}{}^{a}$/dL·g$^{-1}$ |
| 0.5 | bulk | 0.649 |
| 1.0 | CFC | 0.099 |
| 0.1 | $CO_2$ | 0.074 |
| 1.0 | $CO_2$ | 0.025 |

[a] Inherent viscosity in HFIP (0.5 g/dL) at 31 °C.

**Table 2. Cloud Point Data for the $CO_2$ + Poly(HDFDA) System with Different Polymerization Conditions**

| polymerization condition | | *T* | *P* | |
|---|---|---|---|---|
| AIBN/wt % | solvent | K | MPa | transition[a] |
| 0.5 | bulk | 303.21 | 12.94 | CP |
| | | 307.85 | 14.44 | CP |
| | | 313.18 | 16.47 | CP |
| | | 317.98 | 17.89 | CP |
| | | 323.32 | 19.54 | CP |
| | | 328.20 | 21.16 | CP |
| | | 333.19 | 22.54 | CP |
| | | 338.61 | 24.16 | CP |
| | | 343.43 | 25.57 | CP |
| | | 348.18 | 26.66 | CP |
| | | 353.31 | 27.93 | CP |
| | | 359.12 | 29.33 | CP |
| | | 363.17 | 30.50 | CP |
| 1.0 | CFC | 303.83 | 11.72 | CP |
| | | 308.90 | 13.50 | CP |
| | | 313.90 | 15.20 | CP |
| | | 318.95 | 16.80 | CP |
| | | 323.92 | 18.36 | CP |
| | | 328.64 | 19.75 | CP |
| | | 333.77 | 21.20 | CP |
| | | 338.68 | 22.47 | CP |
| | | 343.83 | 23.92 | CP |
| | | 348.75 | 25.06 | CP |
| | | 353.72 | 26.27 | CP |
| | | 358.16 | 27.20 | CP |
| | | 364.07 | 28.47 | CP |
| 0.1 | $CO_2$ | 303.05 | 10.03 | CP |
| | | 308.29 | 11.82 | CP |
| | | 312.83 | 13.47 | CP |
| | | 318.05 | 15.16 | CP |
| | | 322.85 | 16.64 | CP |
| | | 328.32 | 18.26 | CP |
| | | 333.23 | 19.64 | CP |
| | | 339.08 | 21.30 | CP |
| | | 343.30 | 22.33 | CP |
| | | 348.35 | 23.64 | CP |
| | | 353.53 | 24.64 | CP |
| | | 358.61 | 25.74 | CP |
| | | 363.82 | 26.47 | CP |
| 1.0 | $CO_2$ | 303.37 | 9.34 | CP |
| | | 308.28 | 10.92 | CP |
| | | 313.41 | 12.79 | CP |
| | | 318.17 | 14.16 | CP |
| | | 323.14 | 15.65 | CP |
| | | 328.07 | 16.99 | CP |
| | | 333.16 | 17.95 | CP |
| | | 338.19 | 19.40 | CP |
| | | 343.34 | 20.76 | CP |
| | | 348.33 | 22.05 | CP |
| | | 353.25 | 22.99 | CP |
| | | 357.50 | 24.05 | CP |
| | | 363.21 | 25.33 | CP |

[a] CP, cloud point.

10,10-Heptadecafluorodecyl acrylate (HDFDA) [min. 97 %, Chemical Abstracts Service Resigry No. (CASRN) 27905-45-9] was obtained from Aldrich and used without further purification. It contained MEHQ as an inhibitor to prevent polymerization. The concentration of MEHQ was 100 ppm of perfluoroalkyl acrylate monomers. Poly(HDFDA) was synthesized by free radical solution polymerization using AIBN as the initiator for 24 h in $scCO_2$. The molecular structures of HDFDA and poly(HDFDA) are shown in Figure 1.

***Viscosity Measurement.*** In case of a perfluoro alkyl acrylate polymer, it is still difficult to determine the molecular weight using GPC, etc. because of the strong interaction between fluorines. Moreover, this polymer has very low solubility in a typical solvent except CFCs, and there is not much difference in the refractive index between polymer and solvent. So we measured inherent viscosity of the polymer to determine the relative order of molecular weight on the polymer. Viscosity of the polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity, we should be able to get an idea about molecular weight. Viscosity techniques are very popular because they are experimentally simple. They are however less accurate, and the determined molecular weight, the viscosity average molecular weight, is less precise. For example, $M_v$ depends on a parameter that depends on the solvent used to measure the viscosity. Therefore, the measured molecular weight depends on the solvent used. Despite these drawbacks, viscosity techniques are very valuable. The inherent viscosity of poly(HDFDA) was measured at a concentration of 0.5 g·dL$^{-1}$ in 1,1,1,3,3,3-hexafluoro 2-propanol (HFIP, CASRN 920-66-1) at 31 °C using a Ubbelohde viscometer with suspending ball-level. Samples were used immediately after preparation.

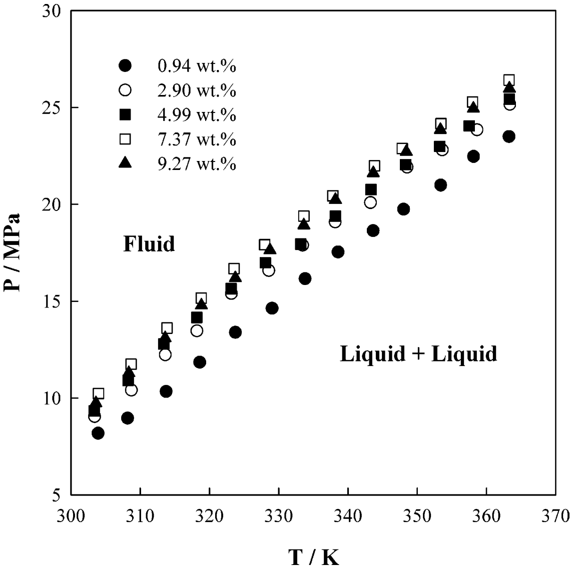

**Figure 4.** Cloud point for $CO_2$ + poly(HDFDA) system with different poly(HDFDA) concentrations.

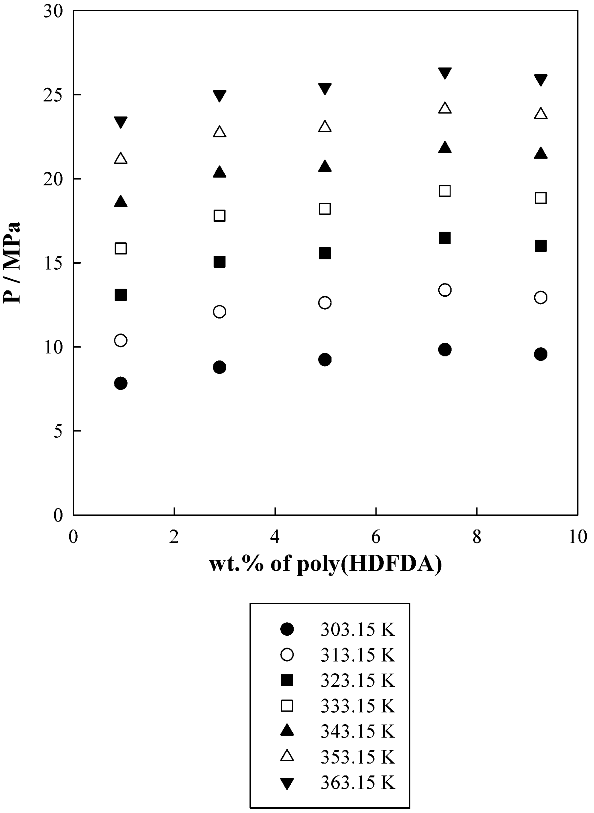

**Figure 5.** Cloud point for $CO_2$ + poly(HDFDA) system: UCSP behavior. ●, 303.15 K; ○, 313.15 K; ■, 323.15 K; □, 333.15 K; ▲, 343.15 K; △, 353.15 K; ▼, 363.15 K.

**Table 3. Cloud Point Data for the $CO_2$ + Poly(HDFDA) System with Different Poly(HDFDA) Concentration**

| wt % of poly(HDFDA) | $P$ / MPa | transition[a] | wt % of poly(HDFDA) | $P$ / MPa | transition[a] |
|---|---|---|---|---|---|
| | $T$ = 303.67 K | | | $T$ = 308.45 K | |
| 0.94 | 8.18 | CP | 0.94 | 8.96 | CP |
| 2.90 | 9.05 | CP | 2.90 | 10.41 | CP |
| 4.99 | 9.34 | CP | 4.99 | 10.92 | CP |
| 7.37 | 10.24 | CP | 7.37 | 11.75 | CP |
| 9.27 | 9.74 | CP | 9.27 | 11.30 | CP |
| | $T$ = 313.65 K | | | $T$ = 318.53 K | |
| 0.94 | 10.34 | CP | 0.94 | 11.85 | CP |
| 2.90 | 12.23 | CP | 2.90 | 13.47 | CP |
| 4.99 | 12.79 | CP | 4.99 | 14.16 | CP |
| 7.37 | 13.61 | CP | 7.37 | 15.16 | CP |
| 9.27 | 13.10 | CP | 9.27 | 14.78 | CP |
| | $T$ = 323.47 K | | | $T$ = 328.48 K | |
| 0.94 | 13.39 | CP | 0.94 | 14.63 | CP |
| 2.90 | 15.40 | CP | 2.90 | 16.58 | CP |
| 4.99 | 15.65 | CP | 4.99 | 16.99 | CP |
| 7.37 | 16.68 | CP | 7.37 | 17.92 | CP |
| 9.27 | 16.20 | CP | 9.27 | 17.63 | CP |
| | $T$ = 333.54 K | | | $T$ = 338.18 K | |
| 0.94 | 16.16 | CP | 0.94 | 17.54 | CP |
| 2.90 | 17.89 | CP | 2.90 | 19.09 | CP |
| 4.99 | 17.95 | CP | 4.99 | 19.40 | CP |
| 7.37 | 19.40 | CP | 7.37 | 20.44 | CP |
| 9.27 | 18.92 | CP | 9.27 | 20.23 | CP |
| | $T$ = 343.54 K | | | $T$ = 348.23 K | |
| 0.94 | 18.64 | CP | 0.94 | 19.75 | CP |
| 2.90 | 20.09 | CP | 2.90 | 21.92 | CP |
| 4.99 | 20.76 | CP | 4.99 | 22.05 | CP |
| 7.37 | 21.99 | CP | 7.37 | 22.88 | CP |
| 9.27 | 21.61 | CP | 9.27 | 22.71 | CP |
| | $T$ = 353.41 K | | | $T$ = 358.07 K | |
| 0.94 | 20.99 | CP | 0.94 | 22.47 | CP |
| 2.90 | 22.81 | CP | 2.90 | 23.85 | CP |
| 4.99 | 22.99 | CP | 4.99 | 24.05 | CP |
| 7.37 | 24.16 | CP | 7.37 | 25.29 | CP |
| 9.27 | 23.85 | CP | 9.27 | 24.94 | CP |
| | $T$ = 363.30 K | | | | |
| 0.94 | 23.50 | CP | | | |
| 2.90 | 25.16 | CP | | | |
| 4.99 | 25.43 | CP | | | |
| 7.37 | 26.41 | CP | | | |
| 9.27 | 25.98 | CP | | | |

[a] CP, cloud point.

***Apparatus and Experimental Method.*** Figure 2 shows a schematic diagram of a typical variable-volume view cell apparatus to obtain phase behavior data at high pressure. The key components of the experimental system are variable-volume view cell, high-pressure generator, and visual apparatus. This view cell is constructed with high nickel-content austenitic steel (5.7 cm o.d., 1.59 cm i.d., ~25 $cm^3$ working volume, fitted with a 1.9 cm o.d., 1.3 cm thick sapphire window).

The cloud point data of $CO_2$ + poly(HDFDA) and $CO_2$ + HDFDA + poly(HDFDA) were obtained by the following procedures and measured for the polymer solution at a fixed polymer concentration of 5.0 ± 0.5 wt %, which is typical of the concentration used for polymer + supercritical solvent studies.[3] At first, poly(HDFDA) was loaded into the cell, and the cell was purged with inert gas and carbon dioxide carefully. HDFDA was injected into the cell with a syringe, and carbon dioxide was added to the cell using a high-pressure bomb. After the injection of the $CO_2$ + HDFDA + poly(HDFDA) mixture was finished, the solution was compressed to the desired operating pressure by replacing a piston fitted within the cell using water pressed with a high-pressure generator (High-Pressure Equipment Co., model 62-2-10). A magnetic stirring bar in the cell helped the mixture to reach equilibrium rapidly. The pressure of the solution was adjusted with measuring the pressure of the water with a digital pressure transducer (Paroscientific Inc., model 43KR-HHT-101, accurate to 0.01 % of reading) and pressure indicator (Paroscientific Inc., model 730). A small correction (0.05 MPa) was added to account for the pressure required to move the piston. The uncertainty in pressure measurements was 0.07 MPa. Temperature was measured with a PRT type thermometer (Hart Scientific Inc., model 5622-32SR, accuracy of ± 0.045 K) fixed to the surface of the cell and displayed by an indicator (Hart Scientific Inc., model 1502). The temperature of the cell was maintained to within ± 0.1 K and measured to within ± 0.1 K. Once the solution is reached

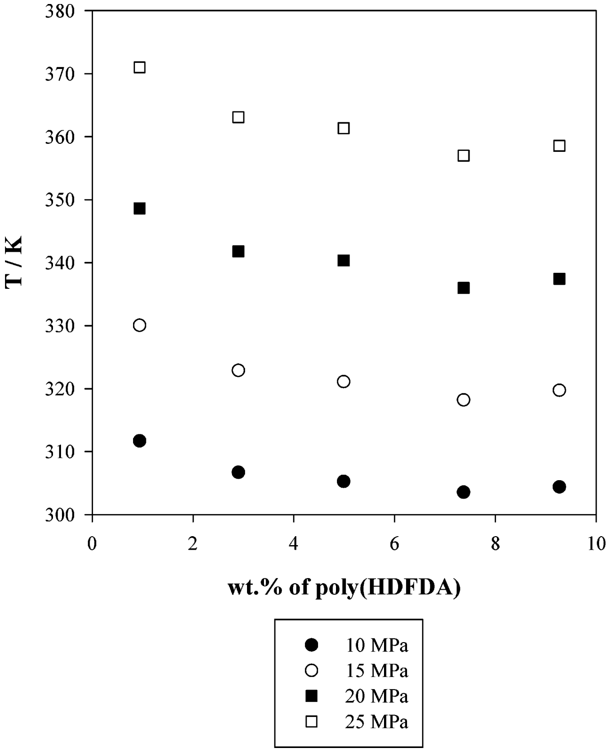

**Figure 6.** Cloud point for $CO_2$ + poly(HDFDA) system: LCST behavior. ●, 10 MPa; ○, 15 MPa; ■, 20 MPa; □, 25 MPa.

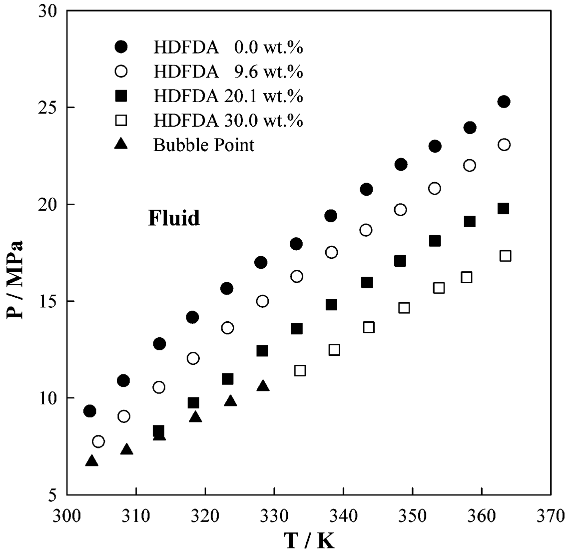

**Figure 7.** Cloud point for $CO_2$ + HDFDA + poly(HDFDA): effect of monomer concentration.

**Table 4. Experimental Data for the $CO_2$ + HDFDA + Poly(HDFDA) System**

| wt % of poly(HDFDA) | wt % of HDFDA | $T$/K | $P$/MPa | transition[a] |
|---|---|---|---|---|
| 4.99 | 0.0 | 303.33 | 9.32 | CP |
| | | 308.20 | 10.89 | CP |
| | | 313.41 | 12.79 | CP |
| | | 318.17 | 14.16 | CP |
| | | 323.14 | 15.65 | CP |
| | | 328.07 | 16.99 | CP |
| | | 333.16 | 17.95 | CP |
| | | 338.19 | 19.40 | CP |
| | | 343.34 | 20.76 | CP |
| | | 348.33 | 22.05 | CP |
| | | 353.25 | 22.99 | CP |
| | | 359.32 | 23.95 | CP |
| | | 363.21 | 25.29 | CP |
| 4.40 | 9.6 | 304.56 | 7.75 | CP |
| | | 308.26 | 9.05 | CP |
| | | 313.34 | 10.55 | CP |
| | | 318.28 | 12.04 | CP |
| | | 323.26 | 13.61 | CP |
| | | 328.30 | 14.99 | CP |
| | | 333.25 | 16.27 | CP |
| | | 338.29 | 17.51 | CP |
| | | 343.24 | 18.66 | CP |
| | | 348.25 | 19.71 | CP |
| | | 353.19 | 20.81 | CP |
| | | 358.25 | 22.00 | CP |
| | | 363.26 | 23.07 | CP |
| 4.87 | 20.1 | 308.26 | 7.58 | CP |
| | | 313.26 | 8.31 | CP |
| | | 318.33 | 9.75 | CP |
| | | 323.26 | 10.99 | CP |
| | | 328.27 | 12.44 | CP |
| | | 333.25 | 13.58 | CP |
| | | 338.29 | 14.82 | CP |
| | | 343.42 | 15.97 | CP |
| | | 348.21 | 17.08 | CP |
| | | 353.23 | 18.11 | CP |
| | | 358.28 | 19.11 | CP |
| | | 363.13 | 19.78 | CP |
| 4.88 | 30.0 | 303.61 | 6.70 | BP |
| | | 308.67 | 7.29 | BP |
| | | 313.40 | 8.01 | BP |
| | | 318.61 | 8.96 | BP |
| | | 323.66 | 9.79 | BP |
| | | 328.36 | 10.56 | BP |
| | | 333.72 | 11.42 | CP |
| | | 338.70 | 12.48 | CP |
| | | 343.67 | 13.65 | CP |
| | | 344.98 | 13.20 | LLV |
| | | 348.79 | 14.65 | CP |
| | | 349.74 | 13.82 | LLV |
| | | 353.81 | 15.68 | CP |
| | | 357.80 | 16.23 | CP |
| | | 363.44 | 17.33 | CP |

[a] CP, cloud point; BP, bubble point; LLV, liquid−liquid−vapor transition.

single phase, pressure was slowly decreased until the cloud point appeared. The cloud point is the point at which the solution becomes so opaque that the stirring bar is no longer visible.[13,14] This procedure was repeated several times until the fluctuation of transition pressure was minimized to within ± 0.03 MPa. The status of the inside was projected onto the monitor using a camera (Veltek International Inc., model CVC5520) with a boroscope (Olympus Corp., model R100-038-000-50).

## Results and Discussion

***Inherent Viscosity of Poly(HDFDA).*** Table 1 shows inherent viscosity of poly(HDFDA) polymerized at different conditions (solvent type, initiator concentration). It is known that the viscosity of the polymer solution increases with increasing molecular weight of polymer. Therefore, we can confirm relative order on molecular weight of polymer from Table 1.

***$CO_2$ + Poly(HDFDA) System.*** Figure 3 and Table 2 represent cloud point data of poly(HDFDA) synthesized at different polymerization conditions and temperatures. Generally, it is known that the molecular weight of a polymer decreases as AIBN concentration increases, and cloud point pressure decreases with decreasing molecular weight. As indicated in Figure 3, cloud point pressure of poly(HDFDA) synthesized by using 1.0 wt % AIBN in $scCO_2$ is the lowest. Figure 4 and Table 3 show cloud point data with concentrations varying from (0.94 to 9.27) wt % of poly(HDFDA) in $scCO_2$. At pressures above or temperatures below the lower critical solution temperature (LCST) curve, one phase is present for all compositions. Figure 5 shows the pressure−concentration ($P$−$x$) isotherms diagram.

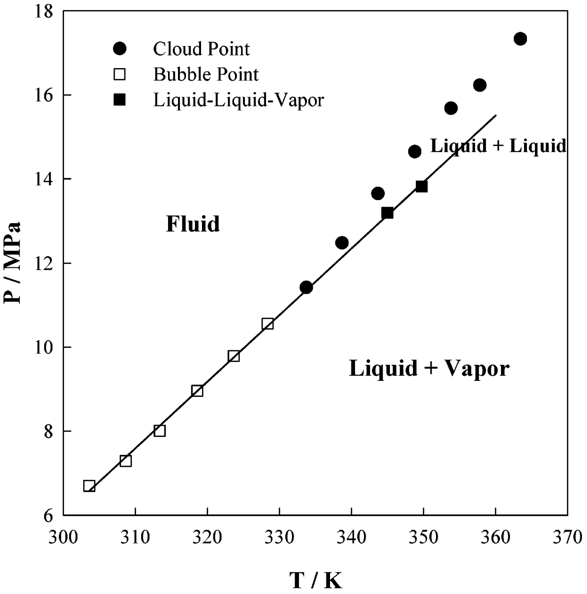

**Figure 8.** Cloud point, bubble point, and liquid−liquid−vapor transition for $CO_2$ + HDFDA + poly(HDFDA).

For a given temperature, one phase is present at a pressure above the cloud point pressure. The maximum pressure is the upper critical solution pressure (UCSP) corresponding to the LCST, where the composition of the two phases become the same. Figure 6 represents the isobaric temperature−concentration ($T-x$) diagram and a typical LCST behavior between (7.0 and 8.0) wt % poly(HDFDA) in $scCO_2$, although determination of an exact critical concentration is difficult due to the flatness of the isotherm.

***$CO_2$ + HDFDA + Poly(HDFDA) System.*** Figure 7 and Table 4 show cloud point data for the $CO_2$ + HDFDA + poly(HDFDA) system as HDFDA contents increased. The cloud point pressure dramatically decreases as monomer contents increased. For adding HDFDA of 30.0 wt %, a bubble point below 330 K and the existence of LLV transition over 335 K were observed in Figure 8. In case of this polymer, the LLV line exists on an extended line of bubble point because vapor pressure of poly(HDFDA) is very low and phase transition dramatically occurred in very narrow range of pressures. In the case of the practical polymerization process, monomer, polymer, and supercritical fluid coexist in the reactor because conversion to the polymer is not completed. In the precipitation polymerization process, the high molecular weight polymer is no longer soluble in SCF as advancing polymerization. Finally, phase separation and precipitation are generated. Therefore, polymerization process can be performed as controlling molecular weight and conversion according to phase behavior of system. Also, at regions of phase 2 (liquid + liquid or liquid + vapor) or phase 3 (liquid + liquid + vapor), compositions of polymer and monomer are different. Using this phase behavior, unreacted residual monomer from polymer can be removed selectively (monomer extraction from polymer). Moreover, for application of supercritical antisolvent (SAS) system or rapid expansion supercritical solution (RESS) process, high-pressure phase behavior data are required.

## Conclusions

We measured cloud point and bubble point pressures for the $CO_2$ + poly(HDFDA) system and the $CO_2$ + HDFDA + poly(HDFDA) system by using a variable-volume view cell as a function of relative molecular weight, weight fraction of poly(HDFDA), and HDFDA contents at temperature up to 363 K. For the binary system of $CO_2$ + poly(HDFDA), typical LCST behavior was observed between (7.0 and 8.0) wt % poly(HDFDA). For the ternary system of $CO_2$ + HDFDA + poly(HDFDA), as the HDFDA content increased, cloud point pressure dramatically decreased and LLV transition was observed at 30.0 wt % HDFDA over 335 K.

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Received for review February 15, 2006. Accepted July 10, 2006. This work was supported by the BK21 Project of the Ministry of Education, and the Ministry of Commerce, Industry & Energy, and the Energy Management Corporation are thanked for financial support.

JE060066V