Phase Behavior of Binary and Ternary Carbon Dioxide + Heptadecafluorodecyl Methacrylate + Poly(heptadecafluorodecyl methacrylate) Systems

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Experimental cloud point data for a binary system composed of carbon dioxide (CO_2) + poly(heptadecafluorodecyl methacrylate) (poly(HDFDMA)) were obtained using a variable volume view cell with a polymer concentration of up to ~9.1 wt %, a temperature between (303 and 363) K, and a pressure of up to 33 MPa. The cloud point and bubble point pressures for a ternary system comprised of CO_2 + HDFDMA + poly(HDFDMA) were determined for HDFDMA concentrations of (0, 10.9, 20.3, and 28.6) wt % at temperatures ranging from (303 to 363) K and pressures up to approximately 27 MPa. The results of this evaluation indicated that as the HDFDMA concentration increased the cloud point pressure decreased and that the liquid−liquid−vapor (LLV) transition occurred when the system was comprised of 28.6 wt % HDFDMA.

Introduction

Fluorine is a highly reactive element; however, when it bonds with other elements, it creates highly stable compounds that are heat resistant and highly impermeable to chemicals and solvents. These compounds exhibit unique traits, such as repellency to water and oil, excellent sliding properties, low refraction indexes, superior electrical characteristics, and non-stick surfaces. Because of their unique traits, fluorine compounds are used in a wide range of products, including household appliances, semiconductors, and automobiles.[1]

Perfluoroalkyl acrylate polymers have many industrial functions and are used as the clad material for optical fibers, highly sensitive resistant polymers for microlithography, and moisture-proof coating agents.[2] Although perfluoroalkyl acrylate polymers are generally insoluble in organic solvents, they are soluble in CFCs. However, because CFCs are associated with many environmental problems, it is necessary to use an alternative solvent when working with perfluoroalkyl acrylate. One such solvent is supercritical carbon dioxide ($scCO_2$), which can dissolve substantial amounts of perfluoroalkyl polymer at relatively low pressure due to specific interactions between fluorine and $scCO_2$.[3]

The study of phase behavior in polymer/supercritical fluid systems began with the development of the high-pressure polyethylene process, which involved dissolving LDPE (low density polyethylene) in supercritical ethylene. However, the phase behavior of polymers in other supercritical solvents, such as carbon dioxide, has only attracted attention in the last few decades. This lack of interest is primarily a result of polymers being soluble only to a very limited extent in supercritical gases unless tremendous pressures are applied. Therefore, the use of the unique solvent properties of supercritical fluids under mild conditions in polymer processing still remains a challenge for polymer chemists and engineers.[4]

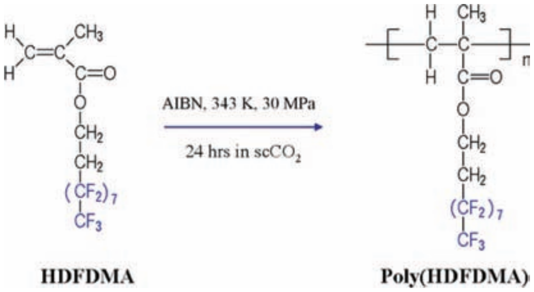

Figure 1. Chemical structures of HDFDMA and poly(HDFDMA).

Table 1. Inherent Viscosity of Poly(HDFDMA)

polymerization condition		η_{inh}[a]
AIBN/wt %	solvent	$g \cdot dL^{-1}$
0.5	bulk	1.217[a]
1.0	CFC	0.130[b]
0.1	CO_2	0.111[b]
0.5	CO_2	0.071[b]
1.0	CO_2	0.049[b]

[a] Inherent viscosity in HFIP (0.227 $g \cdot dL^{-1}$) at 307.2 K. [b] Inherent viscosity in HFIP (0.5 $g \cdot dL^{-1}$) at 307.2 K.

Meantime, thermodynamic information regarding the monomers and polymers that the supercritical fluids are comprised of indicates that they play an important role in the chemical design and operation of separation processes, fine chemical processes, supercritical fluid extraction, and polymerization processes.[5–7] Additionally, information generated by conducting high pressure experiments can provide a powerful tool for understanding the fundamental mechanisms involved in these processes and therefore help develop a firm basis for the successful purification and application of supercritical solvents as polymer reaction media, as well as for the modification of the mechanical properties and morphology of polymers.[4]

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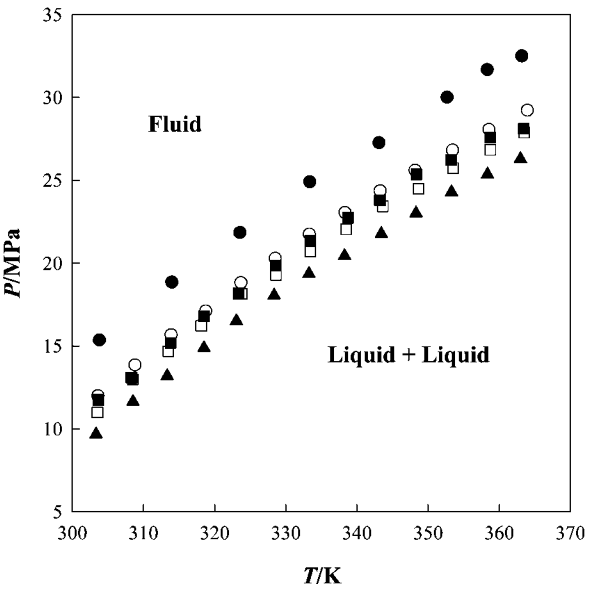

Figure 2. Experimental cloud point curve for the CO_2 + poly(HDFDMA) system with different polymerization conditions. ●, AIBN 0.5 wt % (bulk polymerization); ○, AIBN 1.0 wt % in CFC-113; ■, AIBN 0.1 wt % in $scCO_2$; □, AIBN 0.5 wt % in $scCO_2$; ▲, AIBN 1.0 wt % in $scCO_2$.

Our group previously measured pressure−composition (P-w) isotherms for binary systems of CO_2 + perfluoro materials, including CO_2 + perfluoroalkyl acrylate monomer,[8] CO_2 + perfluoroalkyl acrylate monomer + perfluoroalkyl acrylate polymer,[9] and CO_2 + perfluoroalkyl alcohol.[10]

In this study, we measured the cloud point pressures for a binary system comprised of CO_2 + poly(HDFDMA) and bubble point pressures for a ternary system comprised of CO_2 + HDFDMA + poly(HDFDMA) as a function of the relative molecular weight and weight fraction of HDFDMA at temperatures ranging from (303 to 363) K.

Experimental Section

Materials. Carbon dioxide (min. 99.99 %) was obtained from Korea Industrial Gases. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate (HDFDMA) [min. 97 %, CAS No. 1996-88-9] that contained 100 ppm of MEHQ as an inhibitor to prevent polymerization was purchased from Aldrich and used without further purification. Poly(HDFDMA) was prepared by solution free-radical polymerization using AIBN as the initiator at 30 MPa and 343 K for 24 h in $scCO_2$.[11] The molecular structures of HDFDMA and poly(HDFDMA) are shown in Figure 1.

Viscosity Measurement. The only common liquid solvents that poly(HDFDMA) is soluble in are CFCs, and there is very little difference in the refractive index of poly(HDFDMA) and CFCs. Moreover, because of the strong interaction between fluorines, it is difficult to determine the molecular weight of poly(HDFDMA) using methods such as GPC (gel permeation chromatography) and DLS (dynamic light scattering). Therefore, we measured the inherent viscosity of the poly(HDFDMA) to determine the relative order of the molecular weight of the polymer. The viscosity of a polymer solution depends on the concentration and size (i.e., molecular weight) of the dissolved polymer; therefore, by measuring the viscosity of the solution, it should be possible to estimate its molecular weight. Methods that use viscosity to determine molecular weight are very popular because they are experimentally simple; however, although viscosity techniques are very valuable, it should be noted that they are less accurate than other methods.[9] The inherent viscosity of the poly(HDFDMA) was measured at a concentration of (0.227 and 0.5) $g \cdot dL^{-1}$ in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, CAS No. 920-66-1) at 307.2 K using a Ubbelohde viscometer with suspending ball-level. Samples were used immediately after preparation.

Table 2. Experimental Cloud Point Data for the CO_2 + Poly(HDFDMA) System with Different Molecular Weight Poly(HDFDMA)[a]

polymerization condition		T	P	
AIBN/wt %	solvent	K	MPa	transition
0.5	bulk	303.8	15.37	CP
		314.0	18.86	CP
		323.6	21.85	CP
		333.4	24.92	CP
		343.1	27.27	CP
		352.8	30.02	CP
		358.3	31.68	CP
		363.2	32.51	CP
1.0	CFC	303.6	12.00	CP
		308.8	13.86	CP
		313.9	15.68	CP
		318.8	17.12	CP
		323.7	18.82	CP
		328.5	20.30	CP
		333.3	21.75	CP
		338.3	23.06	CP
		343.3	24.37	CP
		348.2	25.61	CP
		353.4	26.82	CP
		358.6	28.06	CP
		364.0	29.23	CP
0.1	$scCO_2$	303.7	11.75	CP
		308.3	13.10	CP
		313.8	15.20	CP
		318.5	16.82	CP
		323.4	18.18	CP
		328.6	19.85	CP
		333.5	21.37	CP
		338.8	22.74	CP
		343.3	23.81	CP
		348.4	25.36	CP
		353.2	26.22	CP
		358.8	27.57	CP
		363.4	28.12	CP
0.5	$scCO_2$	303.5	10.99	CP
		308.5	12.99	CP
		313.5	14.68	CP
		318.2	16.23	CP
		323.8	18.16	CP
		328.6	19.30	CP
		333.5	20.71	CP
		338.5	22.05	CP
		343.7	23.43	CP
		348.6	24.50	CP
		353.5	25.74	CP
		358.8	26.84	CP
		363.5	27.88	CP
1.0	$scCO_2$	303.4	9.68	CP
		308.5	11.65	CP
		313.4	13.20	CP
		318.5	14.89	CP
		323.1	16.51	CP
		328.4	18.06	CP
		333.3	19.37	CP
		338.3	20.44	CP
		343.4	21.78	CP
		348.3	23.02	CP
		353.3	24.29	CP
		358.4	25.36	CP
		363.0	26.29	CP

[a] CP = cloud point.

Apparatus and Experimental Method. The bubble point and cloud point pressures were obtained using a variable volume

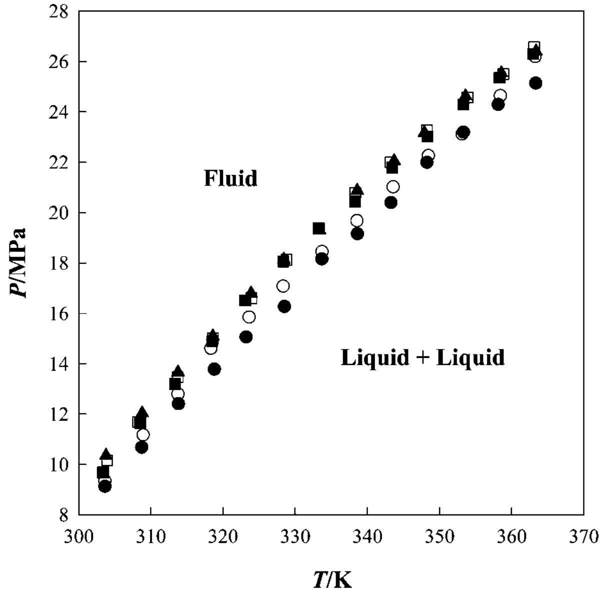

Figure 3. Experimental cloud point curve for the CO_2 + poly(HDFDMA) system with different concentrations of poly(HDFDMA). ●, 0.95 wt %; ○, 2.85 wt %; ■, 4.88 wt %; □, 6.95 wt %; ▲, 9.04 wt %.

Table 3. Experimental Cloud Point Data for the CO_2 + Poly(HDFDMA) System with Different Concentrations of Poly(HDFDMA)

poly(HDFDMA) wt %	*P* MPa	transition	poly(HDFDMA) wt %	*P* MPa	transition
	T = 303.7 K			*T* = 338.5 K	
0.95	9.13	CP[a]	0.95	19.16	CP
2.85	9.34	CP	2.85	19.68	CP
4.88	9.68	CP	4.88	20.44	CP
6.95	10.15	CP	6.95	20.78	CP
9.04	10.36	CP	9.04	20.88	CP
	T = 308.6 K			*T* = 343.4 K	
0.95	10.68	CP	0.95	20.40	CP
2.85	11.17	CP	2.85	21.02	CP
4.88	11.65	CP	4.88	21.78	CP
6.95	11.68	CP	6.95	22.00	CP
9.04	12.04	CP	9.04	22.05	CP
	T = 313.7 K			*T* = 348.2 K	
0.95	12.41	CP	0.95	21.99	CP
2.85	12.79	CP	2.85	22.26	CP
4.88	13.20	CP	4.88	23.02	CP
6.95	13.47	CP	6.95	23.26	CP
9.04	13.66	CP	9.04	23.17	CP
	T = 318.6 K			*T* = 353.5 K	
0.95	13.78	CP	0.95	23.19	CP
2.85	14.61	CP	2.85	23.12	CP
4.88	14.89	CP	4.88	24.29	CP
6.95	15.01	CP	6.95	24.57	CP
9.04	15.09	CP	9.04	24.62	CP
	T = 323.5 K				
0.95	15.06	CP	0.95	24.29	CP
2.85	15.85	CP	2.85	24.64	CP
4.88	16.51	CP	4.88	25.36	CP
6.95	16.61	CP	6.95	25.50	CP
9.04	16.80	CP	9.04	25.56	CP
	T = 328.5 K			*T* = 363.2 K	
0.95	16.27	CP	0.95	25.14	CP
2.85	17.08	CP	2.85	26319	CP
4.88	18.06	CP	4.88	26.29	CP
6.95	18.13	CP	6.95	26.57	CP
9.04	18.14	CP	9.04	26.41	CP
	T = 333.5 K				
0.95	18.16	CP			
2.85	18.45	CP			
4.88	19.37	CP			
6.95	19.37	CP			
9.04	19.30	CP			

[a] CP = cloud point.

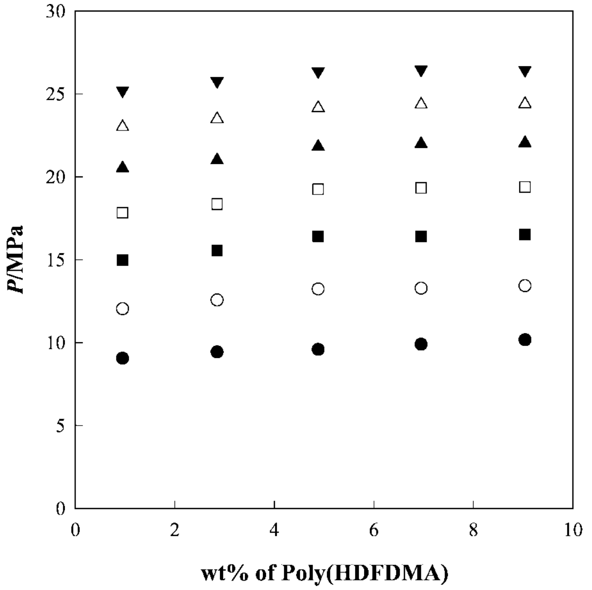

Figure 4. Experimental cloud point curve for the CO_2 + poly(HDFDMA) system: $P-w$ isotherm diagram. ●, 303.2 K; ○, 313.2 K; ■, 323.2 K; □, 333.2 K; ▲, 343.2 K; Δ, 353.2 K; ▼, 363.2 K.

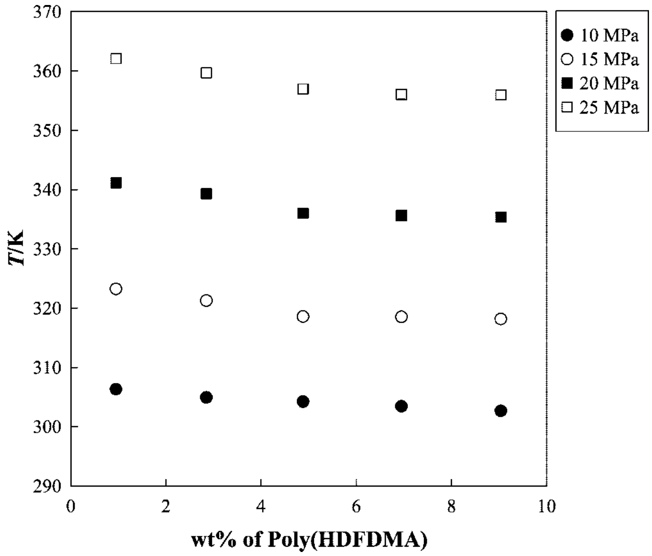

Figure 5. Experimental cloud point curve for the CO_2 + poly(HDFDMA) system: $T-w$ isobaric diagram. ●, 10 MPa; ○, 15 MPa; ■, 20 MPa; □, 25 MPa.

view cell apparatus, which is described in detail elsewhere.[8–10] The cloud point data of CO_2 + poly(HDFDMA) and CO_2 + HDFDMA + poly(HDFDMA) were obtained using the following experimental procedures. Cloud point data were 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.[12] First, poly(HDFDMA) was loaded into the cell, and the cell was then purged carefully with inert gas and carbon dioxide. Next, HDFDMA was injected into the cell using a syringe to within ± 0.001 g, and then carbon dioxide was added to the cell to within ± 0.01 g using a high-pressure bomb. After injection of the CO_2 + HDFDMA + poly(HDFDMA), the solution was compressed to the desired operating pressure by replacing a piston fitted within the cell and then applying water with a high-pressure generator (High Pressure Equipment Co., model 62-2-10). A magnetic stirring bar in the cell was then used to help the mixture reach equilibrium rapidly, and the pressure of the solution was determined by measuring the pressure of the water applied to the piston using a digital pressure transducer (Paroscientific Inc., model 43KR-HHT-101, accurate to 0.01 % of reading) and pressure indicator (Paroscientific Inc., model

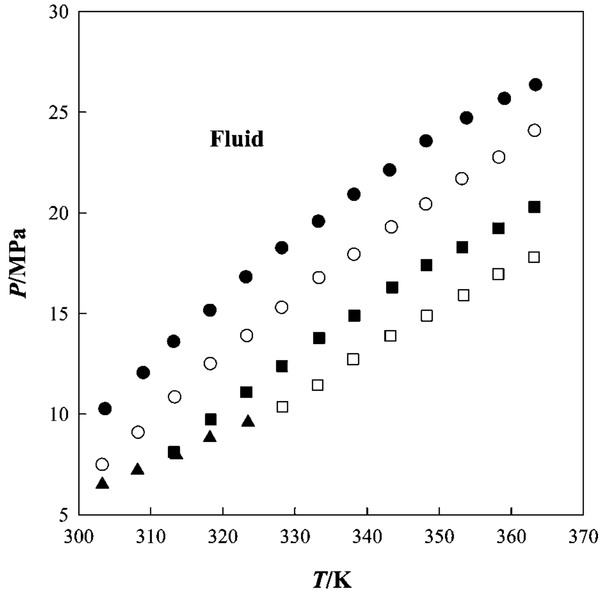

Figure 6. Experimental cloud point for CO_2 + HDFDMA + poly(HDFDMA). Effect of monomer concentration. ●, HDFDMA 0.0 wt %; ○, 10.9 wt %; ■, 20.3 wt %; □, 28.6 wt %; ▲, bubble point.

No. 730). A small correction (0.05 MPa) was added to account for the pressure required to move the piston, and the uncertainty of the pressure measurements was 0.07 MPa. The temperature was measured using a PRT type thermometer (Hart Scientific Inc., model 5622-32SR, accuracy of ± 0.045 K) that was fixed to the surface of the cell and displayed the temperature on an indicator (Hart Scientific Inc., model 1502). The temperature of the cell was maintained within ± 0.1 K of the desired temperature and measured to within ± 0.1 K. Once the solution reached the single phase, the pressure was slowly decreased until the cloud point, which is the point at which the solution becomes so opaque that the stirring bar is no longer visible, was reached. This procedure was repeated several times until the fluctuation of the transition pressure was minimized to within ± 0.03 MPa. The status of the inside of the cell was observed on a computer 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(HDFDMA). Table 1 represents the inherent viscosity of poly(HDFDMA) when it was polymerized under different conditions. In general, the molecular weight of a polymer increases as the AIBN concentration decreases. Also, it is known that the viscosity of a polymer solution increases as the molecular weight of the polymer increases. Therefore, we can verify the relative order of the molecular weights of the polymer using Table 1.

CO_2 + Poly(HDFDMA) System. It is difficult to determine the molecular weight of perfluoroalkyl acrylate polymers using methods such as GPC and DLS because of the strong interaction between fluorines. Additionally, the perfluoroalkyl acrylate polymer has very low solubility in typical solvents, and although it is soluble in CFCs, CFCs have very high vapor pressure and are very volatile at room temperature. Therefore, we used the cloud point to determine the relative order of the molecular weights in the polymer from the general fact that the cloud point increases as the molecular weight of the polymer increases. In addition to being a relatively simple method for comparing the molecular weights of perfluoroalkyl acetate polymers, the cloud point data can be used as a reference when determining design conditions for polymer synthesis and processing in $scCO_2$.

Table 4. Experimental Data for the CO_2 + HDFDMA + Poly(HDFDMA) System[a]

poly(HDFDMA) wt %	HDFDA wt %	T K	P MPa	transition
>5.03	0.00	303.6	10.27	CP
		308.9	12.06	CP
		313.2	13.61	CP
		318.2	15.16	CP
		323.2	16.82	CP
		328.17	18.26	CP
		333.2	19.57	CP
		338.2	20.92	CP
		343.1	22.12	CP
		348.2	23.57	CP
		353.8	24.71	CP
		359.1	25.67	CP
		363.4	26.36	CP
5.06	10.88	303.3	7.50	CP
		308.2	9.10	CP
		313.3	10.86	CP
		318.3	12.51	CP
		323.3	13.91	CP
		328.2	15.30	CP
		333.3	16.78	CP
		338.1	17.94	CP
		343.4	19.30	CP
		348.1	20.44	CP
		353.1	21.69	CP
		358.1	22.76	CP
		363.2	24.06	CP
5.11	20.34	308.2	7.31	CP
		313.2	8.12	CP
		318.3	9.74	CP
		323.2	11.10	CP
		328.2	12.39	CP
		333.3	13.78	CP
		338.2	14.89	CP
		343.5	16.30	CP
		348.2	17.40	CP
		353.2	18.30	CP
		358.2	19.23	CP
		363.2	20.30	CP
4.61	28.61	303.3	6.51	BP
		308.2	7.20	BP
		313.6	7.96	BP
		318.2	8.82	BP
		323.5	9.60	BP
		328.3	10.36	CP
		333.1	11.44	CP
		338.1	12.73	CP
		338.6	12.10	LLV
		343.2	13.89	CP
		347.3	13.45	LLV
		348.3	14.89	CP
		353.4	15.92	CP
		353.2	16.95	CP
		363.2	17.80	CP

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

Figure 2 and Table 2 show cloud point data obtained from poly(HDFDMA) synthesized under different conditions. Generally, the molecular weight of a polymer increases as the AIBN concentration decreases and cloud point pressure increases as the molecular weight of a polymer increases. As shown in Figure 2, the cloud point pressure of poly(HDFDMA) that was bulk-polymerized using 0.5 wt % AIBN as an initiator was the highest. Figure 3 and Table 3 show the cloud point data obtained when concentrations of poly(HDFDMA) polymerized using 1.0 wt % AIBN as an initiator in $scCO_2$ varying from (0.95 to 9.04) wt % were used. At pressures above or temperatures below the

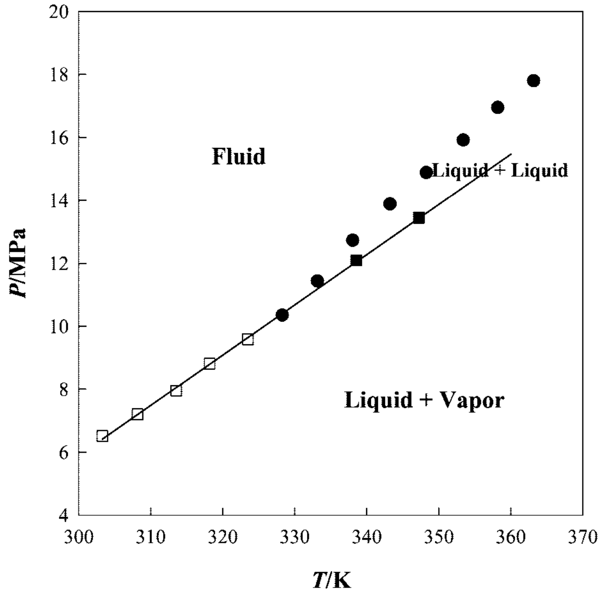

Figure 7. Experimental cloud point, bubble point, and liquid−liquid−vapor transition for the CO_2 + HDFDMA + poly(HDFDMA) system: HDFDMA 28.6 wt %. ●, cloud point; □, bubble point; ■, liquid−liquid−vapor.

cloud point pressure curve, only one phase is present for all compositions. Figure 4 shows the pressure−concentration ($P-w$) isotherms diagram. For a given temperature, one phase is present at a pressure above the cloud point pressure. Figure 5 shows the temperature−concentration ($T-w$) isobaric diagram and like low critical solution temperature (LCST) curve when behavior between (7.0 and 9.0) wt % poly(HDFDMA) in $scCO_2$ was used; however, determination of an exact critical concentration was difficult because the isotherm was relatively flat.

CO_2 + HDFDMA + Poly(HDFDMA) System. Figure 6 and Table 4 show the cloud point data for the CO_2 + HDFDMA + poly(HDFDMA) system as the HDFDMA contents increased. The cloud point pressure decreased as the monomer contents increased. As shown in Figure 7, when a 28.6 wt % HDFDMA was added, a bubble point below 325 K and an LLV transition over 330 K were observed. In the case of poly(HDFDMA), the LLV line exists on the extended line of the bubble point because the vapor pressure of poly(HDFDMA) is very low and the phase transition occurred in a very narrow range of pressures. In practical polymerization processes, the monomer, polymer, and supercritical fluid coexist in the reactor because 100 % conversion to the polymer does not occur. However, in the precipitation polymerization process, as polymerization advances, the amount of created high molecular weight polymer that is no longer soluble in the SCF increases until phase separation and precipitation occur. Therefore, the polymerization process can be performed by controlling the molecular weight and conversion according to the phase behavior of system. Additionally, when there are two phases (liquid + liquid or liquid + vapor) or three phases (liquid + liquid + vapor), the compositions of the polymer and monomer are different. Therefore, this phase behavior can be used to selectively remove unreacted residual monomers from the polymer (monomer extraction from polymer). Thus, it is essential that the high pressure phase behavior is determined for application of the supercritical antisolvent (SAS) system or the rapid expansion supercritical solution process (RESS) to be successful.

Conclusion

Cloud point and bubble point pressures for the CO_2 + poly(HDFDMA) binary system and the CO_2 + HDFDMA + poly(HDFDMA) ternary system were measured using a variable volume view cell apparatus to determine the relative molecular weight, poly(HDFDMA) weight fraction, and HDFDMA contents. For the binary system of CO_2 + poly(HDFDMA), LCST like behavior was observed between (7.0 and 9.0) wt % poly(HDFDMA). However, determination of an exact critical concentration was difficult because the isotherm was relatively flat.

For the ternary system of CO_2 + HDFDMA + poly(HDFDMA), as the HDFDMA content increased, the cloud point pressure decreased and the LLV transition appeared at 28.6 wt % HDFDMA over 335 K. The experimental results of the CO_2 + poly(HDFDMA) system and the CO_2 + HDFDMA + poly(HDFDMA) system were similar to those of the poly(HDFDA) system.[9]

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