Cloud Points of Biodegradable Polymers in Compressed Liquid and Supercritical Chlorodifluoromethane

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Experimental cloud point curves were measured using a variable-volume view cell apparatus for poly(L-lactide) (L-PLA), poly(D,L-lactide) (D,L-PLA), and poly(D,L-lactide-*co*-glycolide) (D,L-PLG) in high-pressure chlorodifluoromethane (HCFC-22) solvent. All the biodegradable polymers studied in this work exhibited a lower critical solution temperature (LCST) phase behavior in HCFC-22. The L-PLA (MW = 2000 g·mol^{-1}) was soluble in HCFC-22 over the temperature range of 343.15 to 393.15 K and at pressures of less than 16 MPa. The $P-x$ isotherms and $T-x$ isobars showed a very broad critical region. The L-PLA was observed to become less soluble in HCFC-22 as its molecular weight increased. No differences in the cloud points were observed between the L-PLA and D,L-PLA polymers. When the D,L-lactide content in the D,L-PLG copolymers was decreased, the single-phase region shrunk in size.

Introduction

Supercritical fluids (SCFs) have been used in polymer processes such as fractionation and swelling. SCF technology has recently gained great attention in the particle formation of biodegradable polymers for sustained delivery devices in pharmaceutical industries (Bodmeier et al., 1995; Kim et al., 1996; Benedetti et al., 1997). SCF solvents are an attractive alternative to incompressible organic liquid solvents, since they can have liquidlike dissolving power while exhibiting transport properties of a gas. Phase behavior data for polymer−SCF systems are required for efficient operation and design of SCF polymer processes.

The selection of SCF solvents to dissolve polymers is often challenging for processing applications because it is difficult to find a good SCF solvent that will dissolve the polymer at relatively moderate conditions. Carbon dioxide (CO_2) is the favorite solvent in SCF processes because it has a relatively low critical temperature and pressure and because it is inexpensive, nonflammable, nontoxic, and readily available. However, it is generally not a good solvent for dissolving high molecular weight polymers with the exception of fluoropolymers (Mawson et al., 1995) and siloxane polymers (McHugh and Krukonis, 1994; Xiong and Kiran, 1995). On the other hand, hydrocarbon solvents and hydrochlorofluorocarbons (HCFCs) have been known to be good solvents for a variety of high molecular weight polymers. Meilchen et al. (1991) observed that poly(methyl acrylate) and poly(ethylene-*co*-methyl acrylate) were soluble in chlorodifluoromethane (HCFC-22). Haschets and Shine (1993) reported the phase behavior of poly(methyl methacrylate) and polycaprolactone in HCFC-22 at temperatures up to 423.15 K and pressures up to 35 MPa. Such polymers were believed to be soluble in HCFC-22 due to the specific interaction between the hydrogen atom in the HCFC-22 and the ester group in the polymers.

Debenedetti et al. (1993) and Kim et al. (1996) measured the solubilities of poly(L-lactide) (MW = 5500 g·mol^{-1}), a biodegradable polymer, in CO_2 using a flow-type apparatus, and reported extremely low solubilities of less than 0.08 wt % at temperatures of 318.15 to 338.15 K and pressures of 20 to 30 MPa. From our preliminary cloud point experiments, however, poly(L-lactide) (MW = 2000) polymer was observed to be not completely soluble in CO_2 even for very low polymer concentrations of less than 0.03 wt % at conditions of 318.15 to 338.15 K and 45 MPa. Thus, no further study was considered with CO_2, but our work was focused on HCFC-22 solvent.

In this study the phase behavior of several biodegradable polymers in compressed liquid and supercritical HCFC-22 was measured through the cloud point experiments. The cloud point measuring technique has been generally used to determine the location of the phase boundary between single-phase and two-phase regions (McHugh and Krukonis, 1994). The cloud points of the biodegradable polymers in HCFC-22 were characterized as functions of pressure, temperature, and polymer concentration and molecular weight. The phase behavior data produced in this work would be useful for establishing operating conditions in the particle formation of biodegradable polymers using SCF processing.

Experimental Section

Materials. The biodegradable polymers used in this study were poly(L-lactide) (L-PLA), poly(D,L-lactide) (D,L-PLA), and poly(D,L-lactide-*co*-glycolide) (D,L-PLG). They are nontoxic, biodegradable polymers that are currently being used as a reservoir device for controlled drug delivery in pharmaceutical industries. The D,L-PLA is a racemic

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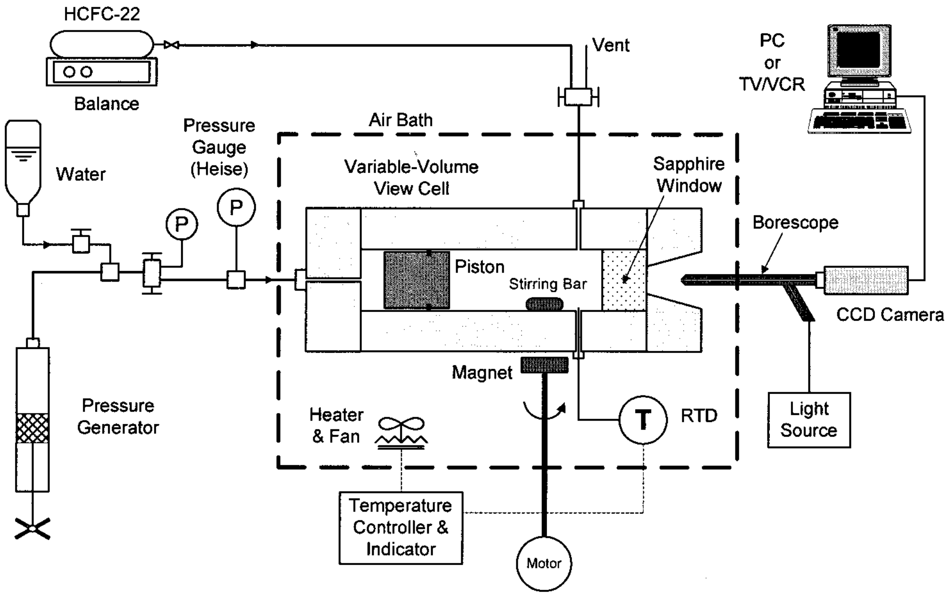

Figure 1. A schematic diagram of the experimental apparatus for measuring cloud points.

mixture of L-PLA and D-PLA. The L-PLAs of four different average molecular weights (MW = 2000, 50 000, 100 000, 300 000) were examined to characterize the molecular weight dependence on the cloud points. The D,L-PLG copolymers of four different average D,L-lactide:glycolide weight ratios (90:10, MW = 5000; 80:20, MW = 5000; 70:30, MW = 10 000; 55:45, MW = 14 500) were used to show the effect of the D,L-lactide content on the cloud points. The D,L-PLA (MW = 2000) and D,L-PLG (55:45, MW = 14 500) were purchased from Boehringer Ingelheim Co., and all the other polymers from Polysciences Inc. The polymer molecular weights described above, provided by the suppliers, are the viscosity average molecular weights derived from the intrinsic viscosity and Mark−Houwink equation. HCFC-22 was obtained from Solvey Gas Co. (USA), and its certified purity was 99.99 wt %. It was used as received without further purification.

Apparatus. Figure 1 shows a schematic diagram of the experimental high-pressure apparatus for measuring the cloud point behavior of the biodegradable polymers in HCFC-22, which is similar to that used by Haschets and Shine (1993) and Lee et al. (1996). The heart of the system is the high-pressure variable-volume view cell. The cell has dimensions of 16 mm i.d. by 70 mm o.d., and an internal working volume of about 31 cm^3. A movable piston is placed inside the cell to change the cell volume. A pressure generator (High-Pressure Equipment Co. model 50-6-15) is used to pressurize water and therefrom displace the piston. A change in the cell volume causes a change of the system pressure. A sapphire window ($^3/_4$ in. diameter by $^3/_4$ in. thick) is inserted into the view cell for visual observation of the interior of the cell. An advantage of using the variable-volume cell is that the concentration of the system, is kept constant during experiment. On the other side, using a constant-volume cell often requires venting off solution to decrease the pressure of the system, causing unknown changes in the concentration of the cell contents.

The system pressure is measured using a high-precision pressure gauge (Dresser Heise model CC-12-G-A-02B, ±0.05 MPa accuracy) installed on the pressurizing fluid (water) side between the pressure generator and the cell. Connecting the pressure gauge directly to the solvent side of the cell can cause an uncertainty in the exact concentration of the solution due to dead volume and can plug the line due to high viscosity in the case of a high polymer concentration solution. The pressure drop was observed to be about 0.05 MPa across the piston, and thus in each experiment the cloud point pressure was increased by 0.05 MPa to account for the pressure drop. The system temperature is measured by an RTD (Pt-100 Ω) inserted into the cell and is read by a high-precision digital thermometer (ASL model F250, ±0.01 °C accuracy).

A visual observation of the cell inside through the sapphire window is made by a borescope (Olympus model R080-044-000-50) and a CCD camera (WAT-202B) connected to a VCR/TV monitor and a computer. A cold light source (Olympus model ILK-5) is used to provide illumination inside the view cell. A magnetic stirring system is equipped under the cell body to agitate the polymer solution. A stirring bar in the cell is rotated by a samarium−cobalt magnet located below the cell, and the magnet is driven by an electric motor and an RPM controller.

Method. The experiment for measuring the cloud points was performed by the following procedure. First, the cell was charged with a certain amount of polymer measured within ±0.1 mg, and then the stirring bar was placed inside the cell. After a piston, O-rings, and a sapphire window into the view cell were assembled, the cell was placed inside the air bath in a horizontal position. To remove any entrapped air present in the cell, the cell was purged at least three times with low-pressure HCFC-22 gas of less than 0.3 MPa at a very slow rate so that the polymer in the cell was not disturbed and loss of polymer was avoided. A certain amount of liquid HCFC-22 was charged into the cell through the inlet line. The amount of HCFC-22 charged was determined by weighing the HCFC-22 sample cylinder before and after HCFC-22 was charged into the cell. Approximately 7 to 12 g of HCFC-22 was charged into the cell for each run.

The solution in the cell was continuously pressurized using the pressure generator. As the pressure generator pressurizes water, the compressed water displaces the piston to the window side to decrease the cell volume and thus raise the pressure in the cell. As the pressure increases, the solution in the cell finally becomes a single homogeneous phase. At the same time the solution was well agitated by a stirring bar.

Table 1. Experimental Cloud Point Results for the Biodegradable Polymers in HCFC-22

polym	polym MW	polym concn wt %	temp K	pressure MPa
poly(L-lactide)	2 000	0.09	346.95	3.85
			354.65	6.05
			364.55	8.65
			373.35	10.80
			383.75	13.45
			393.55	15.20
poly(L-lactide)	2 000	1.06	344.35	3.35
			353.55	5.80
			363.45	8.55
			373.45	11.05
			383.55	13.25
			392.85	15.20
poly(L-lactide)	2 000	2.88	344.35	3.60
			353.05	5.95
			363.35	8.72
			372.75	10.90
			382.05	13.05
			392.65	15.62
poly(L-lactide)	2 000	3.71	345.85	4.10
			352.85	5.96
			363.35	8.66
			372.85	11.00
			382.95	13.35
			392.45	15.42
poly(L-lactide)	2 000	5.77	347.35	4.55
			353.75	6.23
			363.25	8.85
			373.95	11.30
			383.15	13.50
			392.75	15.85
poly(L-lactide)	2 000	10.29	352.65	6.20
			362.95	8.95
			372.05	11.05
			383.05	13.50
			393.65	15.70
poly(L-lactide)	2 000	13.91	345.35	3.68
			355.85	6.60
			364.55	8.94
			373.95	11.25
			383.65	13.53
			393.95	15.87
poly(L-lactide)	2 000	17.98	346.55	3.40
			355.25	5.77
			366.45	8.87
			374.55	10.95
			383.05	12.95
			393.35	15.22
poly(L-lactide)	50 000	3.59	334.85	3.25
			339.45	4.78
			353.25	9.10
			362.35	11.90
			372.05	14.68
			382.45	17.48
			392.05	20.00
poly(L-lactide)	100 000	3.82	333.55	3.15
			342.95	6.25
			353.45	9.55
			362.15	12.13
			372.25	15.00
			383.35	18.00
			392.55	20.25
poly(L-lactide)	300 000	3.36	334.55	4.05
			343.25	7.15
			363.05	13.46
			384.05	19.50
poly(D,L-lactide)	2 000	5.68	346.95	4.25
			355.15	6.40
			364.75	8.85
			373.05	11.05
			382.45	13.43
			392.75	15.72
poly(D,L-lactide-*co*-glycolide) (90:10 wt %)	5 000	3.70	331.85	3.73
			343.05	7.70
			352.75	11.06
			362.85	14.05
			372.85	16.95
			383.15	19.67
poly(D,L-lactide-*co*-glycolide) (80:20 wt %)	5 000	3.99	325.05	3.45
			334.55	7.10
			344.05	10.65
			352.95	13.60
			362.95	16.85
			374.05	20.15
			382.55	22.60
poly(D,L-lactide-*co*-glycolide) (70:30 wt %)	10 000	3.14	314.65	3.80
			324.85	8.35
			334.75	12.50
			344.55	16.50
			352.45	19.45
			362.85	23.25
			372.75	26.62
			382.55	29.65
poly(D,L-lactide-*co*-glycolide) (55:45 wt %)	14 500	3.24	313.65	7.55
			335.25	17.35
			353.15	24.75
			373.15	31.45

The system was heated to a desired temperature. Once the system reached thermal equilibrium and the solution was maintained at a single phase, the pressure was then slowly reduced until the solution became cloudy, by displacing the piston back to the water side using the pressure generator. Enough time was allowed to ensure thermal equilibrium during the pressure reduction. The pressure was reduced at a rate of about 0.05 MPa/min when the cloud point pressure was approached. At a fixed polymer concentration and temperature, the cloud point indicating the single to liquid−liquid phase transition was defined as the pressure at which it was no longer possible to visually observe the stirring bar (Meilchen et al., 1991). For obtaining consistent measurements, every measurement was repeated at least twice at each temperature.

The temperature of the system was raised in about 10 K increments, and the above procedure was repeated, thus creating a pressure−temperature ($P-T$) cloud point curve at a fixed polymer concentration. The maximum temperature was set to about 393.15 K to avoid thermal degradation of O-rings and polymers.

Results and Discussion

The cloud points of several types of the biodegradable polymers in HCFC-22 solvent were investigated as functions of pressure, temperature, and polymer concentration and molecular weight. All the results for the experimental cloud points of the biodegradable polymers in HCFC-22 are shown in Table 1. Figure 2 shows the $P-T$ isopleths of the cloud points of L-PLA (MW = 2000) in HCFC-22 at various polymer concentrations of about 0.09 to 18 wt %. The saturation curve of pure HCFC-22, which is obtained from Daubert and Danner (1994), is also shown along with the cloud point data. Above each cloud point is the single-phase region, and below the point is the two-phase region. For all the polymer concentrations studied, the L-PLA (MW = 2000) was soluble in HCFC-22 over the temperature range of 343.15 to 393.15 K and at pressures of less than 16 MPa. The cloud point curves had similar slopes for all the polymer concentrations.

The cloud point pressure increased as the temperature increased, indicating that the L-PLA/HCFC-22 system

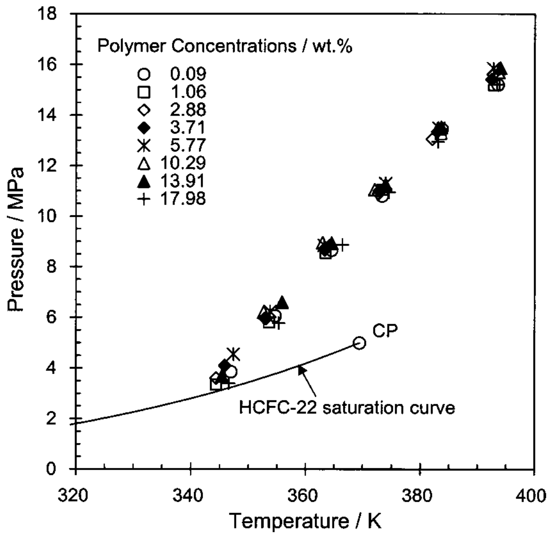

Figure 2. $P-T$ isopleths of cloud points of L-PLA (MW = 2000) in HCFC-22 at various polymer concentrations.

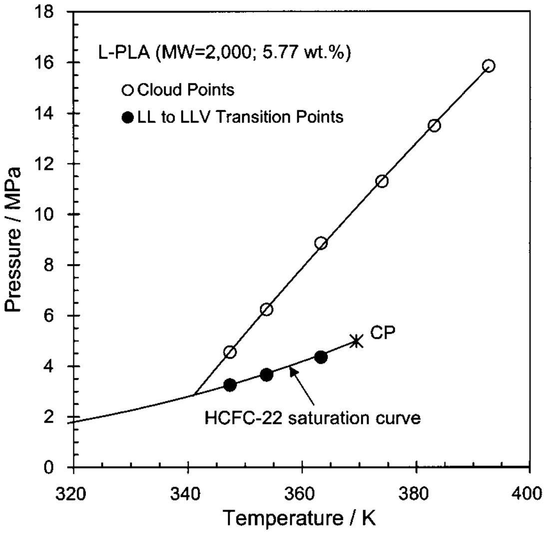

Figure 3. LL to LLV phase transitions along with the cloud points for a 5.77 wt % L-PLA (MW = 2000)/HCFC-22 solution.

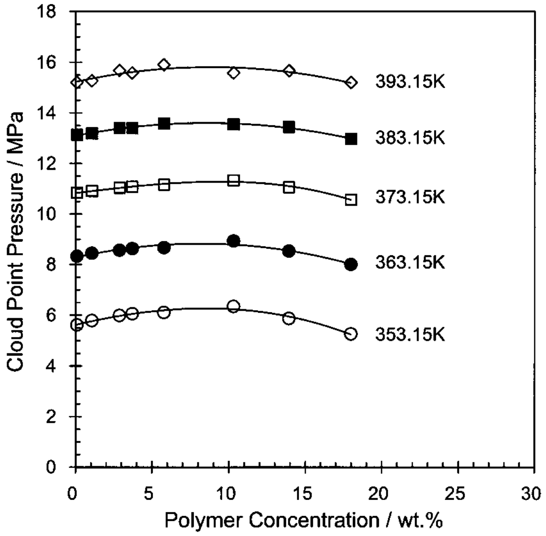

Figure 4. $P-x$ isotherms for L-PLA (MW = 2000)/HCFC-22 system.

exhibited a typical lower critical solution temperature (LCST) behavior. The dissolving power of HCFC-22 decreased as the temperature increased. In other words, as the temperature increased, a higher pressure was needed to obtain a single-phase solution from a two-phase solution. For a polymer–solvent solution the LCST behavior is believed to occur as a result of strong polar interaction such as hydrogen bonding, and a large difference in free volume between the polymer and solvent molecules (Somcynsky, 1982; McHugh and Krukonis, 1994). We have previously found that the L-PLA (MW = 2000) is not completely soluble in CO_2 even for polymer concentrations of less than 0.03 wt % at pressures as high as 45 MPa and at temperatures of 318.15 to 338.15 K. The enhanced solubility of the L-PLA in HCFC-22 can be attributed to the hydrogen bonding of the hydrogen atom in HCFC-22 with the ester group in the L-PLA.

The LCST-type cloud point curves intersected the HCFC-22 saturation curve at the lower critical end points (LCEPs), at which the fluid to liquid–liquid (LL) phase transition ended. The LCEPs for the L-PLA (MW = 2000)/HCFC-22 system were observed around 343.15 K and 3 MPa, as shown in Figure 2. The LCEP was not measured experimentally, but it was estimated as the intersection point of the cloud point curve with the solvent saturation curve using extrapolation of the polynomial fit to the cloud point curve. A second-order polynomial-type equation was found to be enough to fit the experimental values of the cloud points.

The liquid–vapor (LV) equilibrium occurs on the HCFC-22 saturation curve at temperatures below the LCEP. The liquid–liquid–vapor (LLV) equilibrium occurs on the HCFC-22 saturation curve at temperatures above the LCEP and below the HCFC-22 critical point (369.3 K, 4.97 MPa) (Daubert and Danner, 1994), since the LLV line is projected onto the solvent saturation curve at temperatures above the LCEP for polymer–SCF systems. The LL to LLV phase transition for our system was experimentally measured. After the cloud point was measured, the pressure was further reduced to measure the LLV boundary at a constant temperature until vapor bubbles started to form. The transition to the LLV was defined as the initial pressure at which the first vapor bubble was observed. Figure 3 illustrates the LL to LLV transition points along with the cloud points of 5.77 wt % L-PLA (MW = 2000) in HCFC-22. The transition points were in excellent agreement with the HCFC-22 saturation curve, as expected.

The $P-T$ isopleths of the cloud points given in Figure 2 were further characterized by drawing pressure–composition ($P-x$) and temperature–composition ($T-x$) diagrams. The $P-x$ profile was obtained by fitting the cloud point curve with a second-order polynomial equation, and then by determining the pressure from the curve fit at a desired temperature and composition. Several $P-x$ isotherms are shown in Figure 4 for the L-PLA (MW = 2000)/ HCFC-22 system. The pressure necessary to maintain the polymer solution in the single-phase region increased with the temperature. The $P-x$ isotherms exhibited a very broad critical region, and the maxima indicated the upper critical solution pressures (UCSPs) at the given temperatures. The critical concentrations for different temperatures were between 8 and 11 wt %, although their exact values were difficult to determine due to the flatness of the isotherms. Although a lower cloud point pressure was obtained at a higher polymer concentration, a longer time was required to dissolve the polymer in HCFC-22 solvent.

Similarly, the $T-x$ profile was obtained by fitting the cloud point curve with a second-order polynomial equation

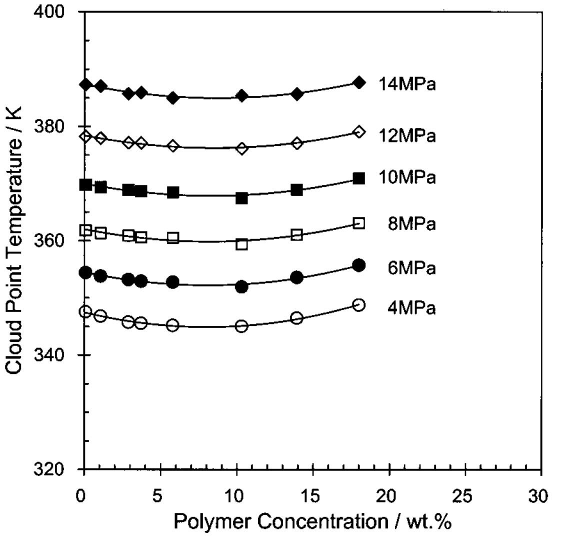

Figure 5. $T-x$ isobars for the L-PLA (MW = 2000)/HCFC-22 system.

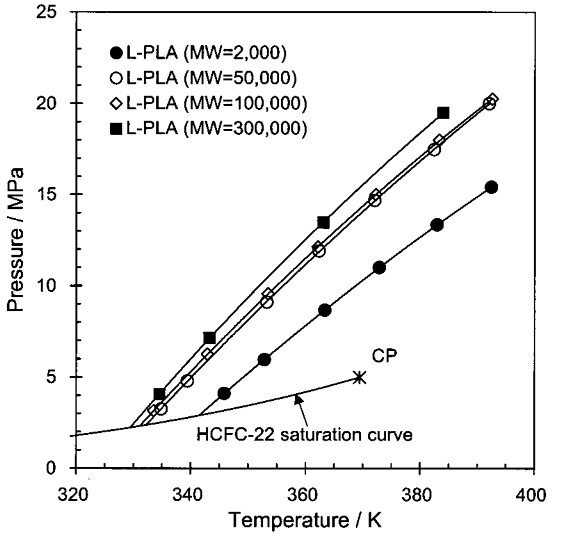

Figure 6. Effect of polymer molecular weight on $P-T$ isopleths of the cloud points for the L-PLA/HCFC-22 system. L-PLA concentrations in solutions are given in Table 1.

and then by interpolating the temperature from the curve fit at a desired pressure and concentration. Figure 5 shows the $T-x$ isobars for the same system as in Figure 4. The isobars also exhibited a very broad critical region, as observed in the isotherms. In Figures 4 and 5, the lines through data points are shown only for revealing changes of the isotherms and isobars with polymer concentrations.

Figure 6 shows the effect of the polymer molecular weight on the cloud points for the L-PLA/HCFC-22 system. The polymer concentration was kept at (3.62 ± 0.14) wt % to eliminate the concentration dependence on the cloud points. As the polymer molecular weight increased, the cloud point pressures increased. Increasing the polymer molecular weight reduced the single-phase region. This indicates that the L-PLA becomes less soluble in HCFC-22 as its molecular weight increases, which is consistent with the results of other polymer−SCF systems (Haschets and Shine, 1993; McHugh and Krukonis, 1994; Xiong and Kiran, 1995; Han et al., 1997). As the polymer molecular weight increased, the slopes of the isopleths increased slightly as well.

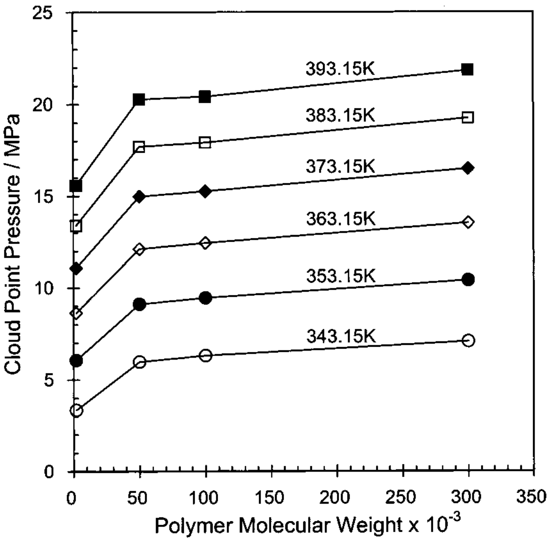

Figure 7. Effect of the polymer molecular weight on the cloud point pressures at various temperatures for the L-PLA/HCFC-22 system.

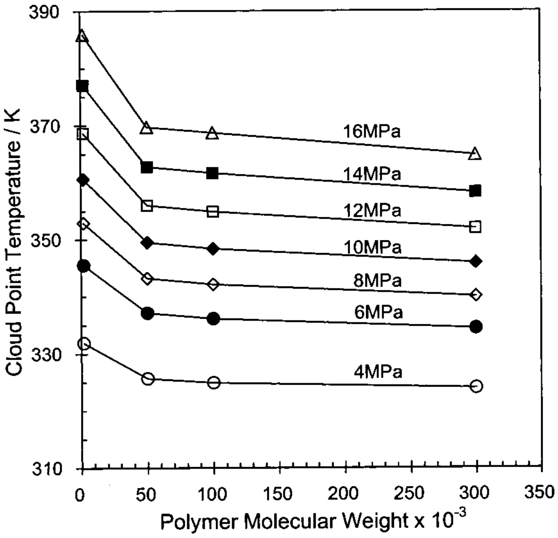

Figure 8. Effect of the polymer molecular weight on the cloud point temperatures at various pressures for the L-PLA/HCFC-22 system.

The cloud point pressures and temperatures were plotted as a function of the L-PLA molecular weight. Figure 7 shows the effect of the molecular weight on the cloud point pressures at various temperatures, while Figure 8 exhibits the molecular weight dependence on the cloud point temperatures at different pressures. The estimation of the cloud point pressures and temperatures at different molecular weights was performed by the second-order polynomial fittings of Figure 6, as described above when the $P-x$ isotherms and the $T-x$ isobars were obtained. The effect of the polymer molecular weight on the cloud points was weakened at molecular weights greater than 50 000.

Figure 9 illustrates the comparison of the cloud points for the L-PLA and D,L-PLA polymers in HCFC-22. No differences in the cloud points were observed between two isomeric forms of the PLA polymer. The HCFC-22 is such a good solvent for the PLA that it could not have any influence on the cloud points between the isomeric forms of the PLA. Figure 10 shows the cloud point results of D,L-PLG copolymers in HCFC-22. The D,L-PLG concentration in the solution was between 3.1 and 4.0 wt %. As the D,L-lactide:glycolide weight ratios in the copolymers decreased

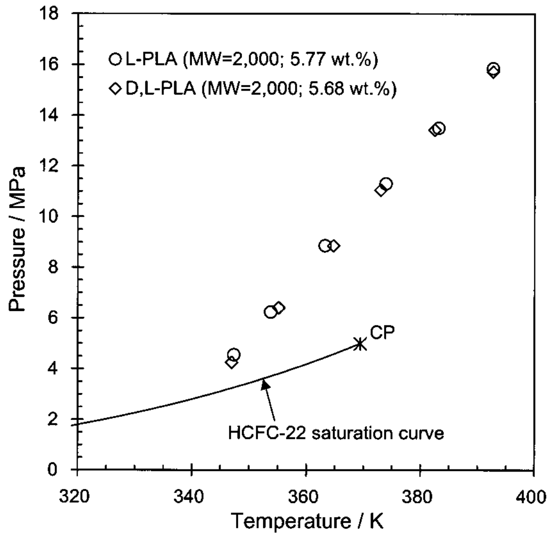

Figure 9. Comparison of the cloud points for L-PLA (MW = 2000) and D,L-PLA (MW = 2000) in HCFC-22.

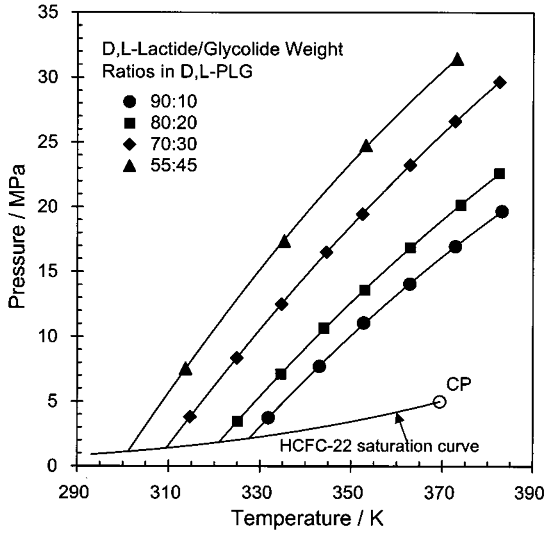

Figure 10. Effect of D,L-lactide content on the cloud points of D,L-PLG copolymers in HCFC-22. Average molecular weights of the copolymers and their concentrations in solution are given in Table 1.

from 90:10 to 55:45, the cloud point pressures increased at a given temperature. Decreasing the D,L-lactide content in the D,L-PLG caused the single-phase region to shrink. Thus, the single-phase region where poly(glycolide) (PGA) is soluble in HCFC-22 is also assumed to shrink. We tried to dissolve the PGA (MW = 33 000) in HCFC-22 solvent at temperatures of 353.15 to 373.15 K and pressures up to 50 MPa. The PGA was found to be not completely soluble in HCFC-22 at those conditions.

Conclusions

The cloud points of L-PLA, D,L-PLA, and D,L-PLG polymers in compressed liquid and supercritical HCFC-22 were measured using the high-pressure equilibrium apparatus equipped with a variable-volume view cell. The location of the phase boundary between single and liquid−liquid phases was mapped out as functions of pressure, temperature, and polymer concentration and molecular weight.

All the biodegradable polymers studied in this work exhibited an LCST phase behavior in HCFC-22 solvent, due to the hydrogen bonding of the hydrogen atom in HCFC-22 with the ester group in the polymers. The dissolving power of HCFC-22 decreased as the temperature increased. The L-PLA (MW = 2000) polymer was soluble in HCFC-22 over the temperature range of 343.15 to 393.15 K and at pressures of less than 16 MPa. The $P-x$ isotherms and $T-x$ isobars showed a very broad critical region for the L-PLA (MW = 2000)/HCFC-22 system. The L-PLA became less soluble in HCFC-22 as its molecular weight increased. No differences in the cloud points were observed between the L- and D,L-forms of the PLA. When the D,L-lactide content in the D,L-PLG copolymers was decreased, the single-phase region shrunk.

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