

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/202178472>

Impact of "Free" Monomer Concentration on the Phase Behavior of Supercritical Carbon Dioxide-Polymer Mixtures

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · DECEMBER 2000

Impact Factor: 2.59 · DOI: 10.1021/ie000516r

CITATIONS

42

READS

13

2 AUTHORS, INCLUDING:



[Mark A Mchugh](#)

Virginia Commonwealth University

194 PUBLICATIONS **4,894** CITATIONS

SEE PROFILE

Impact of “Free” Monomer Concentration on the Phase Behavior of Supercritical Carbon Dioxide–Polymer Mixtures

H.-S. Byun[†] and M. A. McHugh^{*,‡}

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea, and
Department of Chemical Engineering, Virginia Commonwealth University, Richmond, Virginia 23284

Cloud-point data demonstrate that ethyl and butyl methacrylate (EMA and BMA) cosolvents reduce the conditions needed to solubilize poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PBMA) in CO₂. Although PEMA does not dissolve in CO₂ to temperatures of 250 °C and pressures of 2500 bar, PEMA dissolves in CO₂ at temperatures below 150 °C and pressures below 1000 bar if ~10 wt % EMA cosolvent is used. The PEMA–CO₂–EMA and PBMA–CO₂–BMA cloud-point curves are shifted below 40 °C and 600 bar with ~30 wt % methacrylate (MA) cosolvent; however, the impact of the cosolvent diminishes as its concentration increases. BMA and EMA provide favorable polar interactions with the MA groups in the polymer, they increase the solvent density which magnifies the strength of polymer–cosolvent interactions, and they reduce the free-volume difference between the polymer and the solvent. The phase behavior of the binary CO₂–EMA and CO₂–BMA systems is also reported.

Introduction

Recently, it has been demonstrated that it is possible to dissolve polar acrylate polymers in supercritical CO₂ over a large temperature range at modest pressures if acrylate monomer is used as a cosolvent.¹ For many free-radical polymerization reactions, the time needed to form high molecular weight polymer is on the order of seconds, while the polymer residence time in the reactor is typically on the order of minutes. Hence, unreacted monomer, so-called “free” monomer, can be an effective cosolvent for lowering the temperatures and pressures needed to dissolve the parent polymer in supercritical CO₂. In this paper the impact of free monomer is determined for the poly(butyl methacrylate) (PBMA)–CO₂–butyl methacrylate (BMA) and poly(ethyl methacrylate) (PEMA)–CO₂–ethyl methacrylate (EMA) systems. As previously reported, poly(methyl methacrylate) (PMMA), PEMA, and poly(propyl methacrylate) (PPMA) do not dissolve in pure CO₂ at temperatures less than 250 °C and pressures below 2500 bar.^{2–4} Hence, without a cosolvent, it is apparent that homogeneous polymerization of the poly(methacrylate) (PMA) polymers is not viable in supercritical CO₂.

Unreacted liquid monomer is a very attractive cosolvent with supercritical CO₂ for several different reasons. The liquid cosolvent increases the density of the CO₂-rich solvent phase and reduces the free-volume difference between the polymer and the solvent, which enhances polymer solubility.⁵ Also, because unreacted monomer has most of the same physicochemical properties of a repeat unit of the polymer, energetically favorable solvent–polymer interactions are expected to expand the single-phase region.⁶ The high-pressure, polymer–supercritical fluid solvent–cosolvent studies reported in the literature show that cloud points monotonically decrease in pressure and temperature with the

addition of a polar cosolvent as long as the cosolvent does not form a complex with the polar repeat units in the polymer.^{6,7} In these cases, the cosolvency effect is directly related to the polar forces of attraction contributed by the cosolvent and to the increase in solvent density resulting from the addition of a liquid cosolvent to a supercritical fluid solvent. As previously mentioned, PEMA does not dissolve in CO₂. In addition, it takes higher temperatures to dissolve PBMA in CO₂ as compared to poly(butyl acrylate) (PBA).² As a general rule, the cloud-point curve exhibits a negative slope in pressure–temperature space for a mixture consisting of a very polar component, in this case a PMA, and a much less polar component, here CO₂. The interchange energy which characterizes the balance of polymer segment–CO₂ cross-interactions relative to polymer segment–segment and CO₂–CO₂ self-interactions is very temperature sensitive because of the strong polar interactions experienced between polymer segments. At high temperatures, where entropic effects are expected to dominate, the location of the cloud-point curve is more a reflection of the free-volume difference between the dense polymer and the expanded CO₂ rather than the balance of intermolecular interactions. When either BMA or EMA is added to CO₂, the polarity and density of the solvent mixture is expected to increase because both of these cosolvents are dense, polar liquids. Hence, cloud-point pressures at high temperatures should be lower compared to the binary polymer–CO₂ curves, and the temperature where the sharp increase in cloud-point pressure is observed should be reduced. The PBMA used in the present study has a weight-average molecular weight (M_w) of 320 000 and a molecular weight polydispersity of 4.35, and the PEMA has an M_w of 340 000 and a molecular weight polydispersity of 2.70. Although the polydispersities of these two polymers are fairly large, the impact of cosolvent concentration is expected to be much larger than the effect of polydispersity on the resultant phase behavior based on the results from similar studies reported in the literature.⁶

Binary CO₂–BMA and CO₂–EMA data are obtained in this study to complement the ternary studies pre-

* To whom correspondence should be addressed. E-mail: mmchugh@saturn.vcu.edu. Fax: 804-828-4269.

[†] Yosu National University.

[‡] Virginia Commonwealth University.

sented here. The primary purpose for obtaining binary CO₂–monomer data is to determine whether the methacrylate (MA) monomer–CO₂ mixtures form multiple phases in the pressure–temperature–composition regions explored in the ternary studies.

Experimental Section

Phase behavior data are obtained with a high-pressure, variable-volume cell described in detail elsewhere.² For the monomer–CO₂ studies, the empty cell is purged several times with CO₂ to remove traces of air, the liquid monomer is loaded into the cell to within ± 0.002 g using a syringe, and then CO₂ is condensed into the cell to within ± 0.002 g using a high-pressure bomb. Mole fractions are accurate to within ± 0.0025 . For the polymer–CO₂ studies, solid polymer is loaded into the cell that is subsequently purged several times at room temperature with CO₂ at 3–6 bar to remove any entrapped air. CO₂ is then condensed into the cell to within ± 0.002 g. The solution is compressed to the desired pressure with an internal piston displaced with water from a high-pressure generator. The pressure of the mixture is measured to within ± 0.3 bar at pressures below 400 bar and to within ± 3.5 bar at higher pressures. The system temperature is maintained to within ± 0.3 °C. The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope placed against the outside of the sapphire window. The solution in the cell is well mixed using a magnetic stir bar activated by an external magnet beneath the cell. Solution densities are measured for several, but not all, of the PMA–CO₂–MA mixtures reported here. The solution density, with an experimental error of slightly better than $\pm 2\%$,⁸ is determined knowing the amount of material loaded in the cell, and the location of the piston is determined with a transducer coil that tracks the magnetic tip of a steel rod connected to the piston. The reported densities are obtained in the single-phase region at a pressure very close to the phase transition, as noted in the data tables.

Cloud points are obtained at a fixed PBMA or PEMA concentration of ~ 5 wt %. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. There is ~ 5 bar difference between the pressure at the onset of haziness and the cloud-point transition. Cloud points are measured at least twice at each temperature and are typically reproducible to within ± 5 bar. However, the cloud points are reproducible to within ± 10 bar in the region where the cloud-point pressure increases very rapidly for a modest change in temperature.

The monomer–CO₂ mixtures are compressed to a single phase, and the pressure is then slowly decreased until a second phase appears. A bubble point is obtained if small bubbles appear in the cell, while a dew point is obtained if a fine mist appears in the cell. Once the data point is obtained, more CO₂ is added to the cell, and the procedure is repeated at this new concentration. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volumes upon the formation of a second phase.

Materials. PBMA and PEMA were obtained from Aldrich Chemical Co. BMA and EMA (99+% purity), obtained from Aldrich Chemical Co., contain ~ 40 ppm of 2,6-di-*tert*-butyl-4-methylphenol and are used as

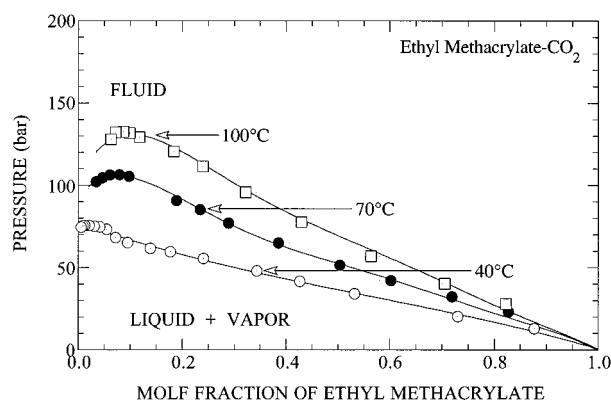


Figure 1. Phase behavior of the EMA–CO₂ system obtained in this study: 40 °C, open circles; 70 °C, closed circles; 100 °C, open squares.

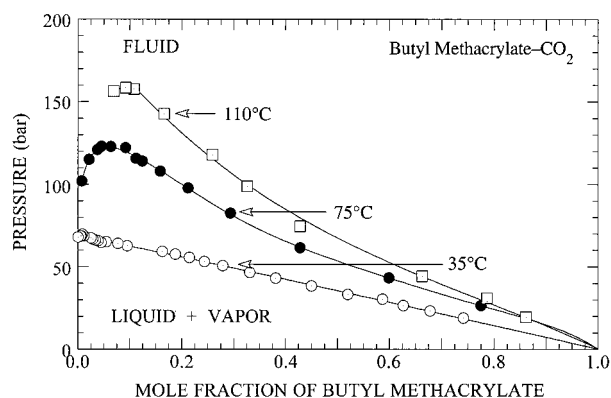


Figure 2. Phase behavior of the BMA–CO₂ system obtained in this study: 35 °C, open circles; 75 °C, closed circles; 110 °C, open squares.

received. CO₂ was obtained from Airgas Corp. (99.8% minimum purity) and used as received.

Results

Monomer–CO₂ Phase Behavior. Figure 1 shows the pressure–composition (P – x) behavior of the EMA–CO₂ system at 40, 70, and 100 °C, and Figure 2 shows the P – x behavior of the BMA–CO₂ system at 35, 75, and 110 °C. Each data point for both MA–CO₂ systems is reproduced to within ± 0.5 bar at least twice, and each isotherm consists of data from several independent loadings of the experimental apparatus. For both systems, three phases are not observed at any of the temperatures studied. The P – x isotherms shown in Figures 1 and 2 are consistent with those expected for a type I system, where a maximum occurs in the critical-mixture curve.^{9,10}

PMA–CO₂–MA Phase Behavior. As previously mentioned, PEMA does not dissolve in pure CO₂ to temperatures of 250 °C and pressures of 2500 bar. Figure 3 shows that it is possible to solubilize PEMA in CO₂ at pressures as low as 900 bar and temperatures as low as 160 °C if 12 wt % EMA monomer is added to the solution. The 12 wt % EMA cloud-point curve does exhibit a rapid increase in pressure at ~ 160 °C, which, more than likely, occurs because of a large increase in the energetics between polymer segments as compared to polymer segment–solvent interactions. If the EMA concentration is increased to 25 wt %, the cloud-point curve exhibits a positive slope, and it is a continuous

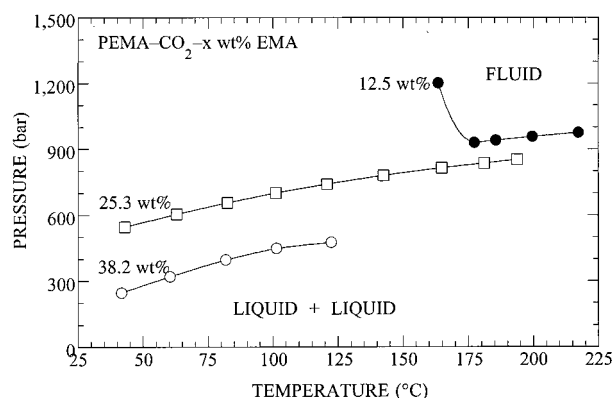


Figure 3. Impact of EMA on the phase behavior of the PEMA-CO₂-*x* wt % EMA system, where *x* equals 12.5 (closed circles), 25.3 (open squares), and 38.2 (open circles).

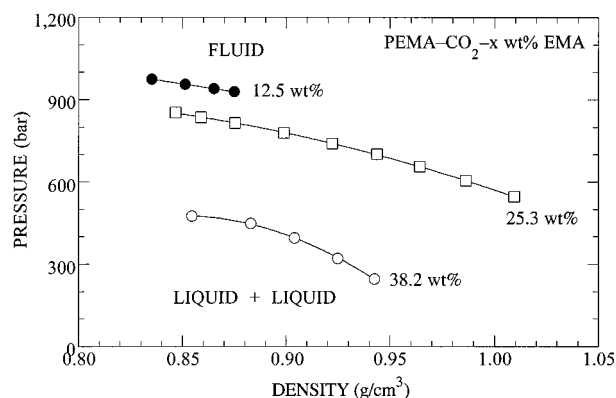


Figure 4. Impact of EMA on the density of the PEMA-CO₂-*x* wt % EMA system, where *x* equals 12.5 (closed circles), 25.3 (closed squares), and 38.2 (closed triangles). Only shown here are density data obtained at the cloud-point pressure while still in the single-phase region. Two phases exist at pressures below each curve.

curve down to 40 °C and ~500 bar. With 38 wt % EMA, the cloud-point curve is parallel to the 25 wt % curve, but the 38 wt % curve is shifted to even lower pressures of ~200 bar at 40 °C. The impact of EMA is quite dramatic considering that PEMA does not dissolve in pure CO₂.

Figure 4 shows the change in PEMA-CO₂-EMA solution density with increasing EMA concentration. Density data for the PEMA-CO₂-EMA system are also listed in Table 1. The density data clearly demonstrate that the energetics of interaction dominate the phase behavior because cloud-point pressures decrease with increasing EMA content at a fixed solution density. However, the density data do show that the cloud-point pressure does decrease with increasing density for solutions with fixed amounts of EMA. Notice that the trends in the density data do not portend the sudden sharp increase in the cloud-point pressure shown in Figure 3 for the PEMA-CO₂-12.5 wt % EMA system.

When 40 wt % EMA is added to the PEMA-CO₂ solution, the cloud-point curve shown in Figure 5 takes on the typical appearance of a lower critical solution temperature (LCST) boundary. At 150 °C the phase boundary has shifted from 800 to 360 bar as the concentration of EMA is increased from 25 to 40 wt %. The PEMA-CO₂-40 wt % EMA cloud-point curve intersects a liquid ⇒ liquid + vapor (LV) curve at ~45 °C and 60 bar. A liquid and vapor phase coexist at pressures below this curve, and the LV curve switches to a liquid₁ + liquid₂ + vapor (LLV) curve at tempera-

Table 1. Density of the PEMA-CO₂-BMA System at ~5 bar into the Single-Phase Region from a Cloud-Point Transition^a

temp (°C)	pressure (bar)	density (g/cm ³)	temp (°C)	pressure (bar)	density (g/cm ³)
12.5 wt % EMA					
163.6	1201		199.6	957	0.851
177.3	929	0.875	217.3	975	0.835
185.5	940	0.865			
25.3 wt % EMA					
42.9	546	1.009	142.5	781	0.899
63.0	605	0.986	164.9	815	0.875
82.5	657	0.964	181.1	836	0.859
101.1	702	0.944	193.6	853	0.847
120.8	742	0.922			
38.2 wt % EMA					
41.7	246	0.943	101.4	448	0.883
60.4	321	0.925	122.4	476	0.854
81.8	396	0.904			

^a For all solutions, the PEMA concentration is ~5.0 wt % and the amount of EMA cosolvent is listed in the heading of each data set.

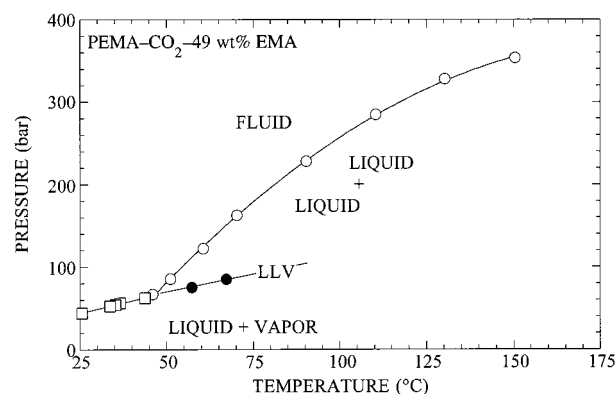


Figure 5. Phase behavior of the PEMA-CO₂-49 wt % EMA system obtained in this study. Open circles represent fluid LL transitions, open squares represent fluid LV transitions, and closed circles represent LLV data.

tures greater than 45 °C. The initial slope of the PEMA-CO₂-EMA LCST curve at the lowest pressures, ~3 bar/°C, is approximately 70% lower than that observed for binary poly(isobutylene)-alkane mixtures reported by Zeman and Patterson.^{11,12} The reason the slopes are different is that the EMA-CO₂ solvent mixture is more compressible than the alkane solvents used in the Zeman study.

Figure 6 shows the cloud-point behavior of the PBMA-CO₂-BMA system. The PBMA-CO₂ data obtained in this study are in excellent agreement with the data of Rindfleisch et al.² The trends observed with the PBMA-CO₂-BMA system shown in Figure 6 are very similar to those observed with the PEMA-CO₂-EMA system shown in Figure 3. For example, at 150 °C, the cloud-point pressure of the PBMA-CO₂-BMA system decreases by ~900 bar with the first 8 wt % BMA added to the solution, and it decreases by another ~200 bar with the addition of the next 8 wt %. However, the decrease in pressure is only 200 bar as the concentration of BMA is almost doubled from 16 to 30 wt %. The temperature where the cloud-point changes slope shifts from 150 to 85 °C with the addition of the first 8 wt % BMA, and it shifts further to ~50 °C with the addition of the next 8 wt % BMA added to the solution. The cloud-point curve with 29.8 wt % BMA has a slight positive slope so that now the remnant of the sharp

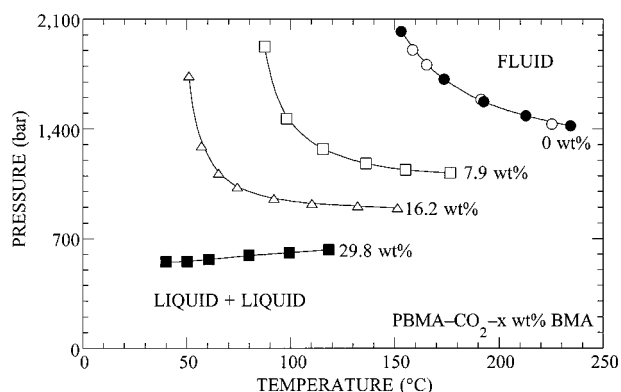


Figure 6. Impact of BMA on the phase behavior of the PBMA-CO₂-*x* wt % butyl methacrylate system, where *x* equals 0 (closed circles, this study; open circles, data of Rindfleisch et al.), 7.9 (open squares), 16.2 (open triangles), and 29.8 (closed squares).

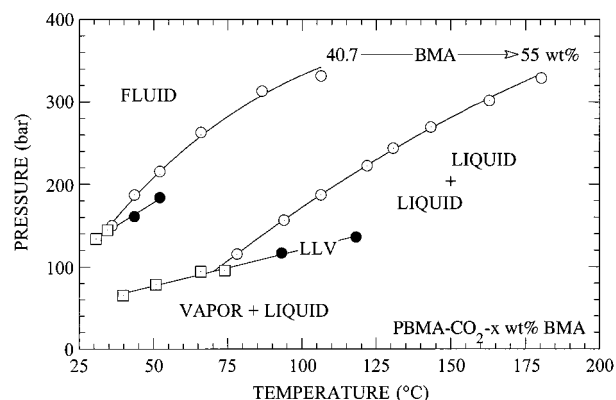


Figure 7. Phase behavior of the PBMA-CO₂-55 wt % BMA system obtained in this study. Open circles represent fluid LL transitions, open squares represent fluid LV transitions, and closed circles represent LLV data.

upturn in the cloud-point pressure is eliminated, which significantly expands the single-phase region. It is evident that the impact of BMA cosolvent diminishes as the BMA concentration increases.

Similarities are also apparent between the phase behavior of the 40.7 and 55.0 wt % PBMA-CO₂-BMA mixtures shown in Figure 7 and the phase behavior of the PEMA-CO₂-49.0 wt % EMA mixture shown in Figure 5. Both of the 40 and 55 wt % BMA curves exhibit LCST behavior. Notice that the slope of the 55 wt % curve is slightly lower than that of the 40 wt % curve, which is a reflection of the higher density of CO₂ at 40 °C relative to the density at 75 °C. The PBMA-CO₂-BMA cloud-point (LCST) curve intersects the LV curve at ~75 °C and 100 bar with 55.0 wt % BMA compared to ~35 °C and 145 bar with 40.7 wt % BMA. The results obtained in this study demonstrate clearly that it is possible to obtain a single phase that extends over a large temperature range at modest pressures when operating with supercritical CO₂ as long as sufficient amounts of free MA monomer are present in the solution.

Figure 8 shows the density behavior of the PBMA-CO₂-BMA system at BMA concentrations ranging from zero to 55 wt %. Density data for the PBMA-CO₂-BMA system are also listed in Table 2. It is readily apparent that increasing the density does not ensure that the cloud-point pressure will decrease. Note that cloud-point pressures increase with increasing density for the solutions with 0, 7.9, and 16.2 wt % BMA. High

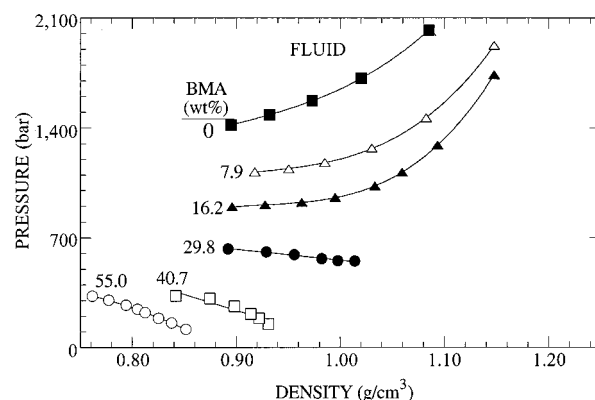


Figure 8. Impact of BMA on the density of the PBMA-CO₂-*x* wt % butyl methacrylate system, where *x* equals 0 (closed squares), 7.9 (open triangles), 16.2 (closed triangles), 29.8 (closed circles), 40.7 (open circles), and 55.0 (open squares). Only shown here are density data obtained at the cloud-point pressure while still in the single-phase region. Two phases exist at pressures below each curve.

Table 2. Density of the PBMA-CO₂-BMA System at ~5 bar into the Single-Phase Region from a Cloud-Point Transition^a

temp (°C)	pressure (bar)	density (g/cm ³)	temp (°C)	pressure (bar)	density (g/cm ³)
0 wt % BMA					
153.2	2021.9	1.085	212.7	1484.1	0.932
173.7	1716.8	1.020	234.3	1419.3	0.895
192.7	1572.3	0.973			
7.9 wt % BMA					
87.4	1924	1.148	136.2	1179	0.985
98.1	1463	1.083	155.3	1138	0.951
115.5	1270	1.031	176.6	1119	0.918
16.2 wt % BMA					
50.9	1739	1.148	92.0	956	0.995
57.0	1291	1.094	110.3	924	0.963
65.2	1116	1.060	132.2	908	0.928
74.2	1029	1.034	151.3	895	0.896
29.8 wt % BMA					
40.0	551	1.014	79.9	591	0.956
50.1	553	0.998	99.3	610	0.929
60.6	565	0.982	118.2	629	0.892
40.7 wt % BMA					
36.0	150	0.931	66.0	263	0.898
43.6	187	0.922	86.5	313	0.874
52.1	216	0.914	106.4	331	0.842
55.0 wt % BMA					
180.3	329	0.762	94.0	156	0.838
162.9	302	0.777	78.1	116	0.852
143.3	270	0.794	65.9	95	0.870*
130.7	244	0.805	50.8	78	0.891*
122.0	223	0.812	39.8	65	0.908*
106.4	187	0.825			

^a The three density data marked with an asterisk are obtained at ~3 bar into the single-phase liquid region from a LV transition point. For all solutions, the PBMA concentration is ~5.0 wt % and the amount of BMA cosolvent is listed in the heading of each data set.

pressures are needed to increase the strength of polymer-solvent interactions relative to polymer-polymer and solvent-solvent interactions. However, as the system temperature is lowered, the energetics favor polar polymer-polymer interactions relative to cross-interactions between the polymer and the solvent, which makes it difficult to keep the polymer in solution with an increase in the hydrostatic pressure alone. However, as the BMA concentration is increased to 30 wt % and higher, the pressure-density curves now exhibit a

negative slope. At these cosolvent concentrations, there is a sufficient amount of polar BMA in solution to maintain a significant amount of polymer–cosolvent interactions so that increasing the system density with increasing pressure promotes the mixing of the polymer in the solution. Notice that the pressures and temperatures needed to obtain a single phase are lowest for the 40 and 55 wt % EMA solutions even though these solutions exhibit the lowest densities relative to the other mixtures.

Conclusions

Very modest pressures and temperatures are needed to dissolve PMAs in supercritical CO₂ if sufficient amounts of “free” MA monomer are present. The liquid MA monomer increases the density of the solvent, which decreases the free-volume difference between the polymer and solvent and, thus, makes the PMA easier to dissolve. In addition, the liquid MA monomer supplies favorable intermolecular interactions between the polymer segments and the solvent, which also favors dissolution of the polymer. Unreacted liquid monomer is the preferred cosolvent when polymerizing in supercritical CO₂ because unreacted monomer can be readily recycled to the reactor.

Acknowledgment

M.A.M. acknowledges the National Science Foundation for partial support of this work under Grant CTS-9729720. H.-S.B. acknowledges the Korea Science and Engineering Foundation for financial support for this project.

Literature Cited

(1) McHugh, M. A.; Rindfleisch, F.; Kuntz, P. T.; Schmaltz, C.; Buback, M. Cosolvent Effect of Alkyl Acrylates on the Phase Behavior of Poly(alkyl acrylates)–Supercritical CO₂ Mixtures. *Polymer* **1998**, *39*, 6049.

(2) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. Solubility of Polymers and Copolymers in Supercritical CO₂. *J. Phys. Chem.* **1996**, *100*, 15581.

(3) Lora, M.; Rindfleisch, F.; McHugh, M. A. Influence of the Alkyl Tail on the Solubility of Poly(alkyl acrylates) in Ethylene and CO₂ at High Pressures: Experiment and Modeling. *J. Appl. Polym. Sci.* **1999**, *73*, 1979.

(4) Lora, M.; McHugh, M. A. Phase Behavior and Modeling of the Poly(methyl methacrylate)–CO₂–Methyl Methacrylate System. *Fluid Phase Equilib.* **1999**, *157*, 285.

(5) Patterson, D. Polymer Compatibility With and Without a Solvent. *Polym. Sci. Eng.* **1982**, *22*, 64.

(6) Kirby, C. F.; McHugh, M. A. Phase Behavior of Polymers in Supercritical Fluid Solvents. *Chem. Rev.* **1999**, *99*, 565.

(7) Wolf, B. A.; Blaum, G. Measured and Calculated Solubility of Polymers in Mixed Solvents: Monotony and Cosolvency. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1975**, *13*, 1115.

(8) Byun, H. S.; DiNoia, T. P.; McHugh, M. A. High-Pressure Density of Ethane, Pentane, Deuterated Pentane, 25.5 wt % Ethane in Deuterated Pentane, 2.4 wt % Deuterated Poly(ethylene-*co*-butene) (PEB) in Ethane, 5.3 wt % Hydrogenated PEB in Pentane, 5.1 wt % Hydrogenated PEB in Deuterated Pentane, and 4.9 wt % Hydrogenated PEB in Deuterated Pentane + 23.1 wt % Ethane. *J. Chem. Eng. Data* **2000**, in press.

(9) Scott, R. L.; van Konynenburg, P. B. Static Properties of Solutions: van der Waals and Related Models for Hydrocarbon Systems. *Discuss. Faraday Soc.* **1970**, *49*, 87.

(10) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth: Stoneham, MA, 1994.

(11) Zeman, L.; Biros, J.; Delams, G.; Patterson, D. Pressure Effects in Polymer Solution Phase Equilibria. I. The Lower Critical Solution Temperature of Polyisobutylene and Poly(dimethylsiloxane) in Lower Alkanes. *J. Phys. Chem.* **1972**, *76*, 1206.

(12) Zeman, L.; Patterson, D. Pressure Effects in Polymer Solution Phase Equilibria. II. Systems Showing Upper and Lower Critical Solution Temperatures. *J. Phys. Chem.* **1972**, *76*, 1214.

Received for review May 23, 2000

Revised manuscript received July 24, 2000

Accepted July 26, 2000

IE000516R