

초임계 이산화탄소내에서 폴리(싸이클로헥실 아크레이트)와 폴리(싸이클로헥실 메타크레이트)에 대한 삼성분 혼합물의 상거동에 관한 모노머 영향

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Monomer Effect on the Phase Behavior of Ternary Mixture for Poly(cyclohexyl acrylate) and Poly(cyclohexyl methacrylate) in Supercritical Carbon Dioxide

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Introduction

Recently, we have 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.[1] For many free radical polymerization reactions the time to form a polymer is on the order of seconds, while the 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. 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 Patterson has shown enhances the solubility.[2] Also, since unreacted monomer has most of the same physico-chemical properties of a repeat unit of the polymer, solvent-polymer interactions are favorable which results in an expansion of the single-phase region.[3] The high-pressure, polymer-SCF 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.[3,4] A liquid cosolvent can greatly enhance polymer solubility in a supercritical fluid (SCF) solvent if it has an intermolecular potential that matches closely with that of a polymer repeat unit. In addition, a cosolvent that has a much higher density than that of the SCF solvent reduces the free volume difference between the polymer and the solvent[4].

However, it is not easy to decouple the effect of a cosolvent from that of hydrostatic pressure since increasing the pressure also reduces the free volume difference between the solvent and the polymer and it increases the probability of interaction between polymer, solvent, and cosolvent segment[6].

The focus of this work is the determination of the impact of cyclohexyl (meth)acrylate cosolvent on the solubility of poly[cyclohexyl (meth)acrylate] in supercritical CO₂. Since poly[cyclohexyl (meth)acrylate] is a polar polymer, the addition of polar cyclohexyl (meth)acrylate to CO₂ provides enhanced polar interactions between poly[cyclohexyl (meth)acrylate] and the mixed solvent that is expected to lead to a decrease in cloud-point temperature and pressure. This study complements the work presented in a previous paper[1], which describes the effect of butyl-acrylate and 2-ethyl hexyl acrylate cosolvents on the solubility of poly(butyl acrylate) and poly(ethyl hexyl acrylate) in CO₂, respectively.

Experimental section

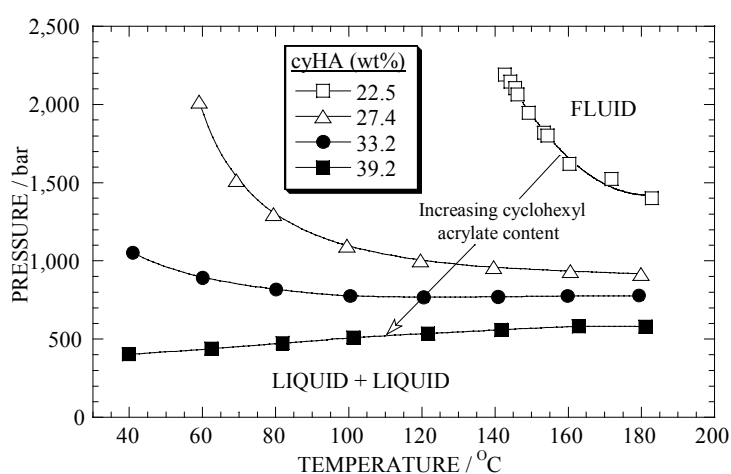
Cloud-point behavior data are obtained with a high-pressure, variable-volume cell described in detail elsewhere.[7] For the polymer-CO₂ studies, liquid or solid polymer is loaded into the cell that is subsequently purged several times at room temperature with CO₂ at three to six bar to remove any entrapped air. The solution is compressed to the desired pressure with an internal piston displaced with water in 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 $\pm 0.2^\circ\text{C}$. 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.

Phase behavior data are obtained at a fixed poly(cyclohexyl acrylate) or poly(cyclohexyl methacrylate) 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. Cloud points are measured at least twice at each temperature, and are typically reproducible to within ± 5 bar at the highest temperatures. In the region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within ± 10 bar.

Both (meth)acrylate polymers are obtained from Scientific Polymer Product Inc. The poly(cyclohexyl acrylate) has a weight average molecular weight, M_w , of 150,000. The poly(cyclohexyl methacrylate) has an M_w of 65,000. Cyclohexyl acrylate (99.9 % purity) and cyclohexyl methacrylate (99.9 % purity), obtained from Polysciences Inc. and are used as received. CO₂ is obtained from Daesung Oxygen Co. (99.9% minimum purity) and used as received.

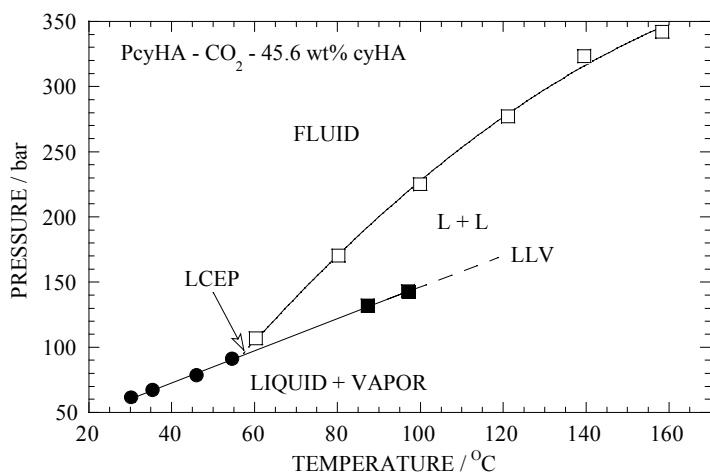
Experimental results and discussion

Poly(cyclohexyl acrylate) does not dissolve in pure CO₂ to temperatures of 250°C and pressures of 2,800 bar. Figure 1 shows that it is possible to solubilize poly(cyclohexyl acrylate) in CO₂ at pressures as high as 2100 bar and temperatures down to 180°C if 22.5 wt% cyclohexyl acrylate monomer is added to the solution. The 22.5 wt% cyclohexyl acrylate cloud-point curve does exhibit a rapid increase in pressure at ~160 °C which, more than likely, occurs due to a large increase in the energetics between polymer segments as compared to polymer segment-solvent interactions. If the cyclohexyl acrylate concentration is increased to 27.4 wt% the cloud-point curve exhibits a negative slope and it is a continuous curve up to 60°C and 2000 bar. With 33.2 wt% cyclohexyl acrylate, the cloud-point curve is UCST region to the 25 wt% curve, but the 33.2 wt% curve is shifted to even lower pressures of ~800 bar at 80-180°C.



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Figure 1. Experiment cloud-point curves for the poly(cyclohexyl acrylate) in supercritical carbon dioxide-monomer system.



When 45.6 wt% cyclohexyl acrylate is added to the poly(cyclohexyl acrylate)-CO₂ solution, the cloud-point curve takes on the appearance of a typical lower critical solution temperature (LCST) boundary as shown in Figure 2.

Figure 2. Impact of poly(cyclohexyl acrylate)-CO₂-45.6 wt% monomer system.

At 150°C the phase boundary has shifted from 600 to 330 bar as the concentration of cyclohexyl acrylate is increased from 39.2 to 45.6 wt%. The poly(cyclohexyl acrylate)-CO₂-45.6 wt% cyclohexyl acrylate cloud-point curve intersects a liquid→ liquid + vapor (LV) curve at ~57°C and 90 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 temperatures greater than 57°C. The initial slope of the poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate 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.[8,9] The reason the slopes are different is that the cyclohexyl acrylate-CO₂ solvent mixture is more compressible than the alkane solvents used in the Zeman study.

Conclusions

Cloud-point pressures of poly(cyclohexyl acrylate)-CO₂-cyclohexyl acrylate system is measured in the temperature range of 40 °C to 180 °C and to pressures as high as 2200 bar with cyclohexyl acrylate concentration of 22.5, 27.4, 33.2, and 39.2 wt.%. This system changes the pressure-temperature slope of the phase behavior curves from UCST region to LCST region as the cyclohexyl acrylate concentration increases. poly(cyclohexyl acrylate) does not dissolve in pure CO₂ to temperature of 250 °C and pressure of 2,800 bar. Also, the ternary poly(cyclohexyl methacrylate)-CO₂- cyclohexyl methacrylate system is measured below 185 °C and 2300 bar, and with cosolvent of 27.4 ~ 46.7 wt%. Poly(cyclohexyl methacrylate) does not dissolve in pure CO₂ to 240 °C and 2500 bar.

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