High-Pressure Solution Behavior of the Polystyrene-Toluene-Ethane System

The effect of supercritical ethane on the high-pressure phase behavior of the polystyrene-toluene system is experimentally investigated. Adding 17.8 wt. % ethane to the polystyrene-toluene solution lowers the temperature of the lower critical solution temperature (LCST) curve by 162°C, 22.5 wt. % lowers the temperature of the curve by 231°C, and with 24.9 wt. % the curve is shifted to such low temperatures that it merges with the upper critical solution temperature curve. In practice this means that polymer solutions can be separated at lower temperatures where thermal degradation of the polymer is less. Also, more than 99 wt. % of the polystyrene is recovered in the polymer-rich phase after the solution phase splits. Patterson's corresponding states treatment is used to model the LCST data.

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Introduction

One method of separating a polymer solution is to use a lower critical solution temperature (LCST) phase split (Anolick and Goffinet, 1971; Anolick and Slocum, 1973; Caywood, 1970; Gutowski et al., 1983; Irani et al., 1982). In the early 1960's Freeman and Rowlinson (1960) showed that a miscible polymer solution will separate into a polymer-rich phase and a solvent-rich phase if the system temperature approaches the critical temperature of the solvent. The LCST is controlled by the chemical nature of the components, their molecular sizes, especially the molecular weight of the polymer, and the critical temperature and pressure of the solvent (Allen and Baker, 1965). As the system temperature increases, the free volume or thermal expansivity of the solvent increases at a much faster rate than that of the polymer. Eventually the solution phase-separates due to the difference in free volumes of the components. The drawback to separating a polymer solution at the LCST is that the solution must be heated to temperatures close to the critical temperature of the solvent, which for good polymer solvents, such as cyclohexane, can be very high (T_c = 287.2°C). Energy costs increase at these high temperatures along with the probability of degrading the polymer.

The motivation of this research was to decrease the LCST to moderate temperatures by adding a low molecular weight supercritical fluid (SCF) to the solution (Irani et al. 1982; McHugh and Guckes, 1985; McClellan and McHugh, 1985; Irani and Cozewith, 1986). A liquid anti-solvent could also be added to the polymer solution to shift the LCST to lower temperatures (Cowie and McEwen, 1974). However, unlike a liquid additive, which has a relatively fixed density, an SCF additive is a variable-density additive, which has a much larger effect on the free volume of the solvent and hence induces the polymer solution to phase-separate at much lower temperatures. Increasing the system pressure increases the density of the SCF additive and decreases the difference in the free volumes of the polymer and solvent, which is now a binary solvent. Eventually, at a high enough pressure, the two-phase system will coalesce into a single phase. Therefore, pressure can be used to control the phase separation.

In this paper we present the phase behavior of the polystyrene-toluene-ethane system. In particular, the experimental investigation has focused on determining the shift of the LCST phase-border curve as a function of ethane, the composition of the polymer-rich and solvent-rich phases in the two-phase region, and the fractionation of polystyrene in the two-phase region. The resultant phase behavior is modeled using the corresponding states approach of Patterson and Delmas (1969).

Polymer Phase Diagrams

If the molecular weight of the polymer is reasonably narrow, the polymer-solvent mixture can be considered as a pseudobinary mixture whose behavior can be described using P-T phase diagrams (Scott and van Konynenburg, 1970; McHugh and Krukonis, 1986). Figure 1a shows the phase behavior for a binary mixture where the vapor-liquid equilibrium curves for the two pure components end in their respective critical points,

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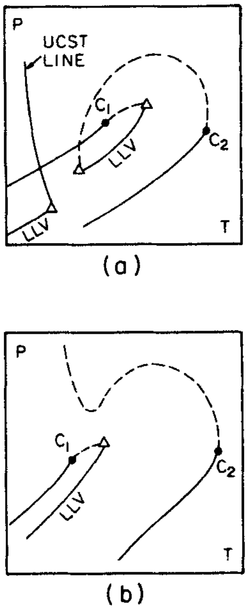

Figure 1. Pressure-temperature diagrams for binary mixtures.

C_1 and C_2. This mixture exhibits a discontinuous critical mixture curve with two branches (broken lines) that intersect a liquid-liquid-vapor (LLV) line at an LCST point and at an upper critical endpoint (UCEP). At low temperatures there is a region of liquid-liquid immiscibility bounded by another LLV line and a UCST line. Many binary polymer-solvent mixtures exhibit the phase behavior depicted in Figure 1a (Allen and Baker, 1965; Baker et al., 1966; Zeman et al., 1972; Zeman and Patterson, 1972; Siow et al., 1972; Saeki et al., 1973).

Figure 1b, also typical of polymer-solvent mixtures, shows an LLV line intersected by only one branch of the critical-mixture curve. This is the *P-T* diagram which is associated with pressure-composition and temperature-composition solubility curves that exhibit the so-called hourglass shape (McHugh and Krukonis, 1986). By comparing Figures 1a and 1b it is apparent that the branch of the critical mixture curve, which starts at C_2, has merged with the UCST curve, and thus exhibits a pressure minimum with decreasing temperature.

Although the phase behavior of polymer-solvent mixtures can be represented on *P-T* diagrams similar to those of Figures 1a and 1b, there are certain features of polymer phase diagrams that need to be described. A schematic representation of the phase behavior of a polymer-solvent mixture is shown in the insert in Figure 2. The phase diagram in this insert is similar to that in Figure 1a. Since a polymer normally degrades before it exhibits a critical point, only the phase behavior in the broken-line box in the insert is expanded in Figure 2. For polymer-solvent mixtures the *P-T* projections of the LLV lines are virtually indistinguishable from that of the vapor pressure curve of the solvent. The section of the critical mixture curve that is closest to the critical point of the solvent is termed an LCST curve since the transitions along the curve are more physically representative of L → L + L transitions rather than F → L + V transitions where *F* designates a fluid phase. Also, the intersection of the LCST curve with the LLV line is termed the lower critical end point (LCEP).

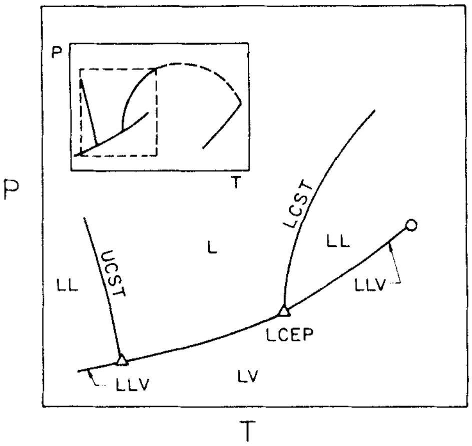

Figure 2. Pressure-temperature diagram for a polymer-solvent mixture.

If the polymer solution is heated, the free volume of the solvent will increase at a much faster rate than the free volume of the polymer. When the free volume difference between the polymer and solvent becomes large enough, the solution will separate into a polymer-rich and a solvent-rich phase at the LCST (Somcynsky, 1982). Figure 3 shows that the location of the LCST curve can be shifted to lower temperatures if an SCF additive is introduced into the polymer solution. Increasing the concentration of the SCF additive, which increases the free volume of the solvent, is equivalent to heating the polymer-solvent mixture without the adverse effect of polymer degradation.

Figure 2 shows that the polymer solution can also be separated by decreasing the temperature and crossing the UCST curve. Oftentimes, though, the UCST can be at such low temperatures that the solution will solidify before it phase-separates. An SCF additive will raise the temperature of the UCST curve, but the effect will not be very large. However, if enough SCF additive is introduced into the solution, the UCST and LCST curves will merge, as shown schematically in Figure 3. When the curves merge there is a large region in *P-T* space in which the solution can be effectively separated.

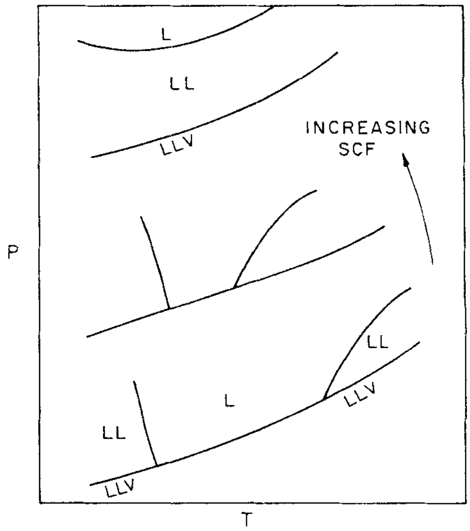

Figure 3. Effect of a supercritical fluid additive on pressure-temperature behavior of a polymer solution (McHugh and Krukonis, 1986).

Allen and Baker (1965) and, more recently, Irani and Coseworth (1986) have shown that if the concentration of polymer in solution is less than about 6 wt. %, a good representation of the *P-T* trace of the LCST curve can be obtained by measuring a constant-composition, cloud-point curve. Therefore, the amount experimental work needed to develop a *P-T* diagram is reduced. The experimental apparatus and techniques used to determine cloud-point curves for polymer-solvent-SCF additive mixtures is described in the following section.

Experimental Method

Phase-behavior determination

The experimental apparatus and procedures used in this study are described in detail elsewhere (Occhiogrosso et al., 1986; McHugh and Guckes, 1985). The major features of the apparatus are a gas-metering system and a variable-volume view cell. Ethane is quantitatively transferred from the gas-metering system to the high-pressure view cell, which has been previously charged with a measured amount of a 5.0 wt. % solution of polystyrene in toluene. The polystyrene-toluene-ethane solution, viewed through a boroscope (Olympus model D100-048-000-90) placed against a Pyrex window secured at one end of the cell, is mixed by a glass-encased stirring bar activated by a magnet located below the cell. The contents of the cell can also be projected onto a video monitor (Panasonic model BT-S1900N) using a video camera (Panasonic model WV-3240) linked to the boroscope. The advantages of using the video equipment are that the operator is not directly in front of the window, which may break, and that the image of the cell contents is enlarged several times and hence is easier to analyze and interpret.

The polymer solution can be compressed to the desired operating pressure by a movable piston fitted within the cell. System pressure is measured with a pressure transducer (Heise Co. model 715TA), accurate to within ±0.67 bar; and the system temperature is measured with a platinum RTD (resistance thermal device) connected to a digital multimeter (Keithly Co. model 195T DMM), accurate to within ±0.1°C. Phase-boundary curves (LL → L, LV → L, and LLV → LL) are visually obtained at a fixed overall composition as described by McHugh and Guckes (1985).

Hystereses in the cloud-point pressures were observed at certain times during the phase behavior studies. If, after obtaining a cloud point, the solution is quickly repressurized back into the one-phase region and again slowly decompressed, a different cloud-point pressure is observed. The cloud-point pressure could vary by as much as 7 bar, depending on the length of the time the solution remained in the one-phase region prior to determining the cloud point. The hysteresis in cloud-point pressure is a consequence of the time it takes for polystyrene to entangle and disentangle in solution (Laufer et al., 1973; Peterlin et al., 1965). The degree of entanglement is expected to be very different in the liquid-liquid region as compared to the single-phase region since the concentration of polystyrene in the polymer-rich phase in the liquid-liquid region is about 20 wt. %, while in the single-phase region it is less than 5 wt. %. A finite time is expected for polystyrene molecules to disentangle or to entangle in solution, hence, spurious LCST transitions will be obtained if sufficient time is not allowed for these processes to occur.

Within the liquid-liquid (LL) region it generally takes about 1 to 2 h for the solution to phase-separate completely. These separation times are as much as one order of magnitude greater than those found in an earlier study (McHugh and Guckes, 1985). Once the solution phase-separates, samples are obtained by displacing approximately 8 to 12 g of each phase into sample bombs connected to the top and bottom ports of the view cell. While a phase is sampled the piston is moved forward to maintain the pressure constant to within ±1.7 bar. It is assumed that without mixing, this small variation in the pressure will have no effect on the compositions in the two phases.

The compositions of the solvent-rich and polymer-rich phases are determined gravimetrically. The loaded sample bomb is weighed (Arbor Laboratories, Inc., model 1207, accurate to within ±0.02 g) and then cooled in a dry ice-acetone bath for approximately 30 min. At dry ice-acetone conditions, ethane is slowly vented to the atmosphere. The bomb is then allowed to equilibrate thermally to room temperature and again is slowly vented to remove any residual ethane. The amount of ethane in the sample is simply determined by reweighing the bomb. The remaining polystyrene-toluene mixture is flushed from the bomb with an excess amount of toluene. The resultant solution is transfered to a flask of known weight that is then connected to a Rotovap system (Bushi Rotovapor model R110) where the toluene is stripped from solution with gentle heating while under vacuum. The amount of polystyrene in the sample is determined by reweighing the flask; the amount of toluene in the original sample is determined as the difference between the original sample weight and the weights of polystyrene and ethane.

The molecular weight distribution of the polymer recovered from the sample bombs is determined using gel permeation chromatography (GPC) (Waters model 481 with an ultraviolet variable-wavelength detector). Tetrahydrofuron (THF) is used as the chromatographic mobile phase. Three columns are used to ensure an effective separation of the molecular weights (Waters, Ultrastyragel pore sizes 500, 1,000, and 5,000 Å). The molecular weight distribution of the polystyrene is determined using calibration curves made from ten polystyrene standards of narrow molecular weight distribution (Pressure Chemical Co., Pittsburgh, PA).

Materials

The polystyrene, donated by Dow Chemical Co. had M_w = 150,000, M_n = 68,000, and M_w/M_n = 2.21. Toluene (HPLC grade, 99.9% purity) and THF (HPLC grade, 99.9% purity) were supplied by Aldrich Chemical Co., Ethane, (CP grade, 99.0% purity) was purchased from Linde Co.

Results and Discussion

The phase behavior of the polystyrene-toluene system with overall ethane concentrations of 17.8, 22.5, and 24.9 wt. % is shown in Figure 4. Since we are dealing with the *P-T* projection of a multicomponent mixture, the LLV line depicted schematically in Figure 2 appears as an area in Figure 4. As expected, the *P-T* slope of the LCST curves is positive since hydrostatic pressure decreases the free volume difference between the polymer and solvent and hence makes them more compatible.

Table 1 shows the dramatic shift of the LCEP with the addition of ethane to the polystyrene-toluene mixture. Without any ethane, the LCEP for the polystyrene-toluene system occurs at 284°C (Saeki et al., 1973). With the addition of 17.8 wt. % ethane the LCEP is lowered to 122°C, a decrease of 162°C. If

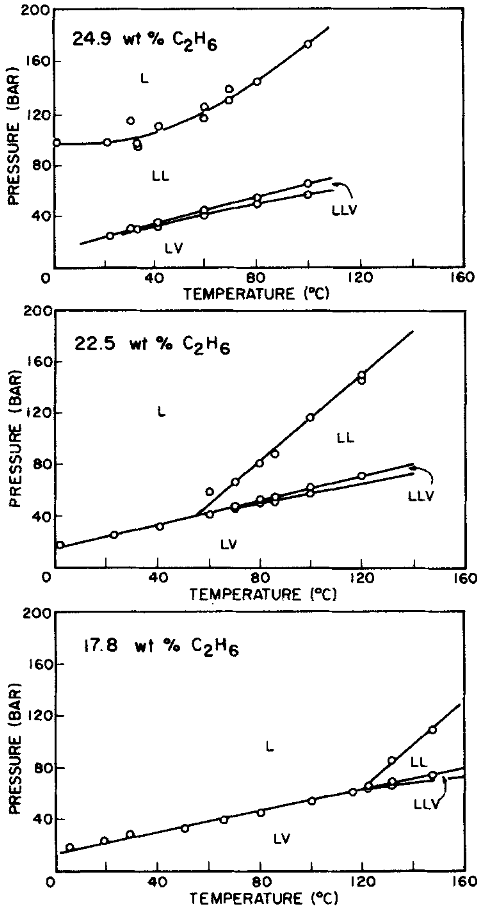

Figure 4. Experimental data from this study for polystyrene-toluene-ethane system.

the ethane concentration is increased to 22.5 wt. % the LCEP occurs at 53°C. Finally, if the ethane concentration is increased just slightly, to 24.9 wt. %, the LCST and UCST curves merge as shown schematically in Figure 3. Since the location of the LCST curve becomes very sensitive to ethane concentration at levels of 20 wt. % or greater, the slight discrepancy between the data reported here and those reported by McClellan et al. (1985) could be due to an error in their concentration measurements.

The UCST curve is also shifted to higher temperatures with the addition of ethane to the solution. Saeki et al (1973) were unable to detect the UCST curve for the polystyrene-toluene system at temperatures as low as −70°C. Although the UCST curve merges with the LCST curve at loadings of 24.9 wt. % ethane, we are unable to detect the UCST curve at 17.8 and 22.5 wt. % ethane at temperatures as low as 0°C.

Table 1. Effect of Ethane on LCEP of Polystyrene-Toluene-Ethane System

C_2H_6 wt. %	LCEP °C
0.0	284 (Saeki et al., 1973)
17.8	122
22.0	53
24.9	UCST and LCST merge

For these mixtures the concentration of polystyrene in toluene (on an ethane-free basis) remains fixed at 5.0 wt. %

By adjusting the amount of ethane in solution the LCST curve can be shifted by more than 200°C to moderate temperatures. This means that the polystyrene-toluene solution can be separated at temperatures where the polymer is less likely to degrade. Also, recovering the polymer from a dilute solution using an LCST phase-split at moderate operating temperatures should be a less energy-intensive recovery technique as compared to solvent-evaporation techniques (Irani and Cozewith, 1986).

The amount of polystyrene recoverable from solution can be determined by sampling the equilibrium phases within the LL region of the phase diagram. Solvent-rich and polymer-rich phases were obtained at one specific temperature, 70°C, and two different pressures, 62.0 and 117.2 bar. These sampling results are shown in Figure 5. The triangular symbols in these figures represent the overall mixture composition in the view cell. Sampling the polymer-rich phase containing polystyrene concentrations greater than 35 wt. % became experimentally untenable since this phase became extremely viscous. Attempts to sample this highly viscous phase proved futile as the sample lines clogged and unclogged in an uncontrollable manner, leading to large pressure fluctuations in the cell that disrupted the equilibrium state of the two-phase system.

Figure 5a shows the phase behavior for the ternary polystyrene-toluene-ethane system at 117.2 bar and 70°C. Note that toluene and ethane are totally miscible at this condition (Seckner, 1987). Hence, the binodal curve in Figure 5a does not intersect the toluene-ethane binary axis. Figure 5a also shows that an addition of at least 22.5 wt. % ethane is required to phase-split the original polystyrene-toluene solution. For overall ethane loadings between 22.5 and 30 wt. % the concentration of polystyrene in the solvent-rich phase is less than 1 wt. %, and most often near 0.2 wt. %.

Figure 5b shows the phase behavior for the ternary system at 62.0 bar and 70°C. At this condition toluene and ethane are no longer totally miscible (Seckner, 1987). Hence, the binodal curve of Figure 5b intersects the toluene-ethane binary axis, and as the overall mixture concentration of ethane is increased above 40 wt. %, a three-phase region is observed. Based on the slopes of the tie lines and the point of intersection of the binodal curve with the toluene-ethane binary axis, broken lines are drawn in Figure 5b to suggest the boundaries of the LLV region.

The tie lines in Figure 5a and 5b that pass through approximately equivalent overall mixture compositions have the same slope and similar solvent-rich and polymer-rich phase compositions. Thus, the data from these figures suggest that a separation process should operate at the lower pressure of 62.0 bar since the separation of polystyrene from solution is not improved at the higher pressure.

The molecular weight distribution of polystyrene in the parent polystyrene-toluene solution and in the solvent-rich and polymer-rich phases was determined. Typical molecular weight distribution chromatograms, shown in Figure 6, indicate that the low molecular weight fraction of the polymer is recoverd in the solvent-rich phase while the higher molecular weight fraction is recovered in the polymer-rich phase. The difference in the molecular weight distributions of the two phases is significant, particularly for molecular weights that are less than 1,800 (i.e., molecular weights less than 1,800 correspond to retention times

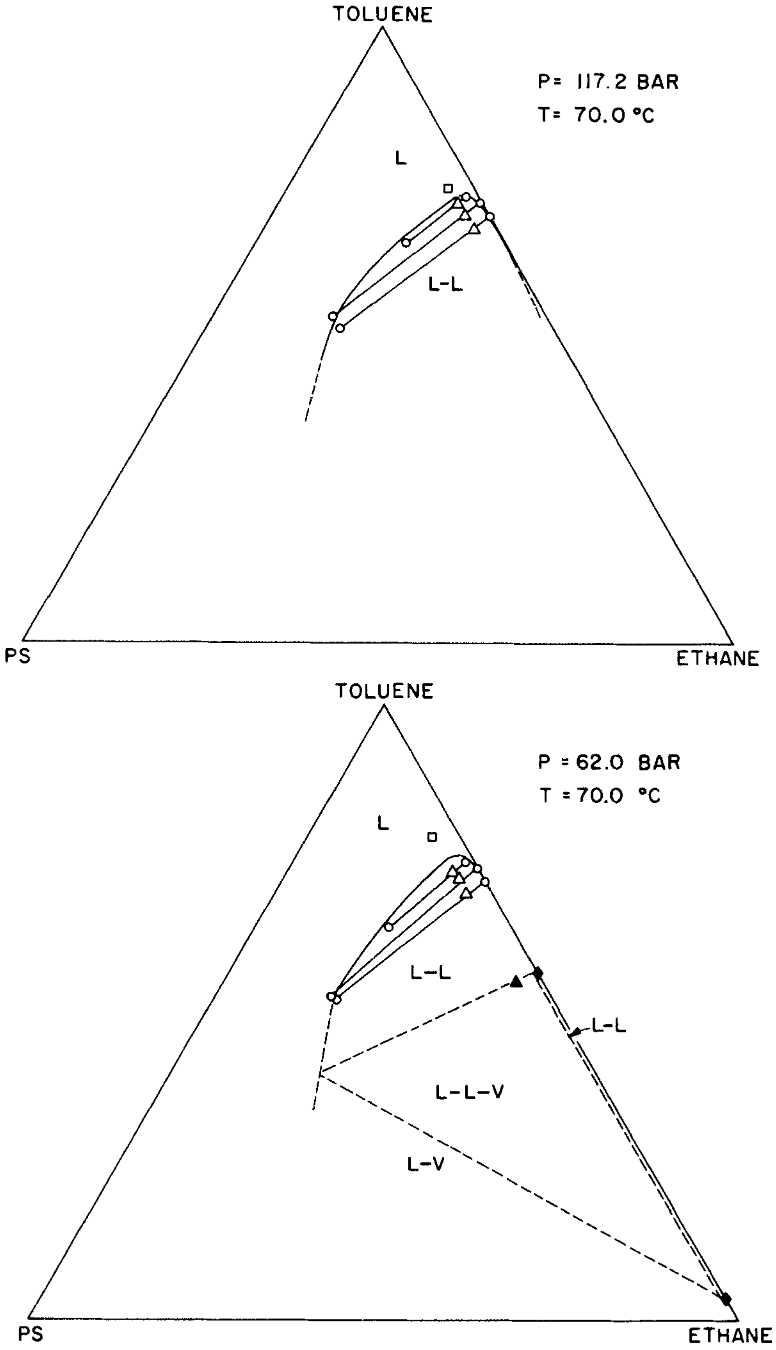

Figure 5. Experimentally determined ternary phase diagrams for polystyrene-toluene-ethane system.

Δ overall mixture composition; □ one-phase region; ■ composition of equilibrium phases for binary toluene-ethane system
▲ overall mixture composition where three phases are first observed

greater than 26 min). Note that the polydispersity [i.e., the ratio of weight-average to number-average molecular weights) of the polystyrene is 4.63 in the solvent-rich phase, 2.06 in the polymer-rich phase, and 2.21 in the parent solution. Hence, not only is the polymer recovered from solution at mild temperatures when an SCF additive is used, it is also fractionated in a beneficial manner.

Data Reduction

Our objective in this section is to employ a straightforward method for calculating the concentration of ethane needed to merge the UCST and LCST curves. No attempt is made to calculate the composition of the polymer-rich and solvent-rich phases in the liquid-liquid region of the phase diagram.

Along the LCST and UCST curves the Flory-Huggins free energy parameter is

$$\chi = \tfrac{1}{2}(1 + r^{-1/2})^2 \qquad (1)$$

where $r = V_p^*/V_s^*$, subscripts s and p represent the solvent and polymer, respectively, and the asterisks represent reduction parameters as determined from pure-component P-V-T data. Pat-

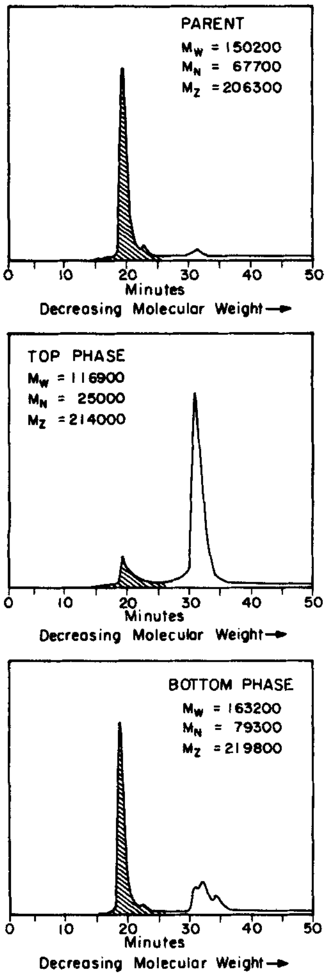

Figure 6. Typical molecular weight distribution chromatograms.

Parent: polystyrene-toluene parent solution
Top phase: solvent-rich phase sample
Bottom phase: polymer-rich phase sample
Samples obtained at 70°C and 117.2 bar

terson and Delmas (1969) show that χ can be derived as a function of reduced properties,

$$\chi/c = (1/\tilde{T}\tilde{V})\nu^2 + \tfrac{1}{2}\tilde{C}_p\{\tau + [\pi\tilde{P}\tilde{V}^2/(\tilde{P}\tilde{V}^2 + 1)]\}^2 \qquad (2)$$

where $\tilde{T}$, $\tilde{V}$, $\tilde{P}$ represent reduced temperature, volume, and pressure, and $\tilde{C}_p$ represents the reduced heat capacity. The parameter c, which is the familiar Prigogine parameter representing the number of external degrees of freedom, is given by

$$c = P_s^* V_s^* / RT_s^* \qquad (3)$$

The parameter ν^2 is a fitted parameter that is a measure of the chemical difference of the components, τ is a measure of the free volume difference between the polymer and solvent, and π is a measure of the pressure difference between the polymer and solvent. The parameters π and τ are defined as

$$\pi = P_s^*/P_p^* - 1 \qquad (4)$$

$$\tau = 1 - T_s^*/T_p^* \qquad (5)$$

Patterson uses Flory's equation of state to derive an expression for the reduced heat capacity

$$\tilde{T} = (\tilde{P}\tilde{V} + \tilde{V}^{-1})(1 - \tilde{V}^{-1/3}) \qquad (6)$$

$$\tilde{C}_p^{-1} = (1 - \tfrac{2}{3}\tilde{V}^{-1/3}) - 2(1 - \tilde{V}^{-1/3})/(\tilde{P}\tilde{V}^2 + 1) \qquad (7)$$

To obtain a reasonable fit of the experimental data over wide ranges of temperatures and pressures, it was necessary to allow the toluene parameters T_{tol}^*, P_{tol}^*, and V_{tol}^*, to vary with temperature. Ethane parameters T_{eth}^* and V_{eth}^* were made functions of both temperature and pressure, while P_{eth}^* was a function only of temperature. The pure-component parameters for toluene and ethane were obtained by fitting pure-component P-V-T data (Albert et al., 1985; Din, 1961) to Eq. 6. The equations used to determine the pure-component parameters for toluene and ethane are given in the Appendix. The pure-component parameters for polystyrene, which are constants, are also given in the Appendix.

To obtain the reduction parameters needed for solvent mixtures of toluene and ethane, the following mixing rules are used (Flory, 1965).

$$V_s^* = \Sigma x_i V_i^* \qquad (7)$$

where x_i is the mole fraction of component i on a polymer-free basis.

$$P_s^* = \Sigma\Sigma x_i x_j V_i^* V_j^* (P_i^* P_j^*)^{1/2}/(V_s^*)^2 \qquad (8)$$

$$1/T_s^* = \Sigma x_i P_i^* V_i^* / (T_i^* P_s^* V_s^*) \qquad (9)$$

For these mixing rules we assumed that site and segment fractions are equal for the solvent mixture.

For each set of data the value for ν^2 is adjusted until a reasonable fit of the data is obtained. Calculated LCST and UCST curves are shown in Figure 7. The general trends of the data are reproduced with reasonably small values for ν^2. As the concentration of ethane increases, ν^2 also increases. At low concentrations of ethane, Figure 7a, the predicted slope of the LCST curve is in poor agreement with the experimental data. However, at higher ethane concentrations, Figures 7b and 7c, the calculations show much better agreement with the slope of the experimental LCST curves. Also, the model successfully predicts the merging of the UCST and LCST curves as shown in Figure 7c. Therefore, with only a small amount of mixture data, the model of Patterson can be used to estimate the effect of a supercritical fluid additive on the location of the LCST and UCST curves. A more rigorous model is needed to calculate the compositions of the polymer-rich and solvent-rich phases in the liquid-liquid region of the phase diagram.

Conclusions

Adding supercritical ethane as an antisolvent to a polystyrene-toluene solution effectively changes the temperature required to achieve a phase split of the solution. The addition of ethane shifts both the UCST and LCST phase-border curves to temperatures where a separation process becomes viable. The

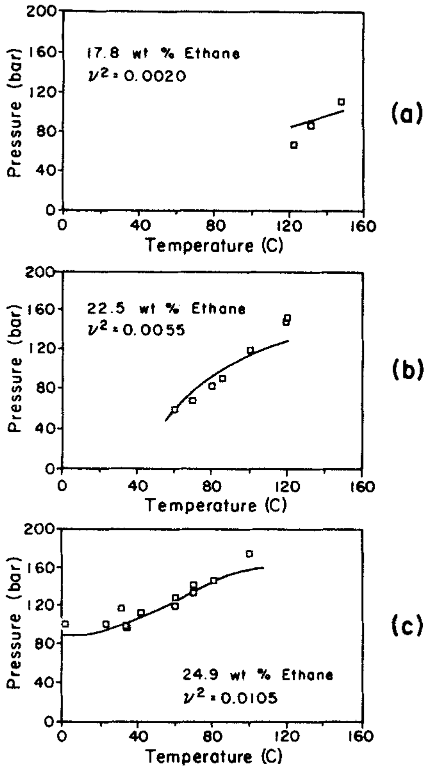

Figure 7. Calculated pressure-temperature diagram for polystyrene-toluene-ethane system using the model of Patternson.

—— calculated results; ☐ experimental data.

composition of the polymer-rich and solvent-rich phases within the liquid-liquid region show that virtually all of the polymer is recovered from the solvent and that some beneficial fractionation of polystyrene has occurred. The effect of ethane on the UCST and LCST phase-border curves of the polystyrene-toluene-ethane system can be modeled using the theory of Patterson and Delmas. This model, along with a minimum amount of mixture information, reasonably predicts the location of the LCST and UCST curves as a function of ethane concentration.

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Notation

c = one-third the number of external degrees of freedom
$\tilde{C}_p$ = reduced heat capacity
F = fluid phase
L = liquid phase
M_n = number-average molecular weight
M_w = weight-average molecular weight
P = pressure
$\tilde{P} = P/P^*$ = reduced pressure
$r = \tilde{V}_s/\tilde{V}_p$ = measure of polymer-solvent size difference
T = temperature
$\tilde{T} = T/T^*$ = reduced temperature
V = volume
$\tilde{V} = V/V^*$ = reduced volume
V = vapor phase
x_i = mole fraction of component i

Greek letters

π = measure of pressure difference between polymer and solvent
ν^2 = measure of chemical difference between polymer and solvent
τ = measure of free volume difference between polymer and solvent
χ = Flory-Huggins free energy parameter

Subscripts

c = critical
eth = ethane
i = component i
p = polymer
$psty$ = polystyrene
s = solvent
tol = toluene

Superscripts

$*$ = characteristic variable
$\sim$ = reduced variable

Appendix: Pure-Component Characteristic Parameters of Polystyrene, Toluene, and Ethane

The pure-component characteristic parameters for toluene were calculated with the following equations

$$P^*_{tol} = 7{,}410 - 6.07 \times T(\mathrm{K}) \tag{A1}$$

$$T^*_{tol} = 4{,}141 + 2.78 \times T(\mathrm{K}) \tag{A2}$$

$$V^*_{tol} = 0.854 + 2.018 \times 10^{-4} \times T(\mathrm{K}) \tag{A3}$$

The pure-component characteristic parameters for ethane were calculated with the following equations

$$P^*_{eth} = 2{,}006 + 4.50 \times T(\mathrm{K}) \tag{A4}$$

The characteristic volume and temperature were determined as a function of both temperature and pressure by interpolating between the following equations

$$T^*_{eth} = 3{,}740 - 0.83 \times P(\mathrm{bar}) \quad \text{at } T = 325\ \mathrm{K} \tag{A5}$$

$$T^*_{eth} = 2{,}750 - 0.85 \times P(\mathrm{bar}) \quad \text{at } T = 355\ \mathrm{K} \tag{A6}$$

$$T^*_{eth} = 2{,}780 - 0.90 \times P(\mathrm{bar}) \quad \text{at } T = 380\ \mathrm{K} \tag{A7}$$

$$V^*_{eth} = 1.325 + 8.29/P(\mathrm{bar}) \quad \text{at } T = 325\ \mathrm{K} \tag{A8}$$

$$V^*_{eth} = 1.124 + 35.9/P(\mathrm{bar}) \text{at } T = 355\ \mathrm{K} \tag{A9}$$

$$V^*_{eth} = 0.974 + 60.6/P(\mathrm{bar}) \quad \text{at } T = 380\ \mathrm{K} \tag{A10}$$

If the temperature was greater than 380 K the characteristic parameters for ethane were obtained from Eq. A4, A7, and A10. Although it was possible to fit pure-component ethane data at higher temperatures, the fit of the LCST curve at 17.9 wt.% could not be improved over that shown in Figure 7a.

The pure-component characteristic parameters for polystyrene were assumed to be constant.

$$P^*_{psty} = 5{,}450 \text{ bar} \tag{A11}$$

$$T^*_{psty} = 7{,}400 \text{ K} \tag{A12}$$

$$V^*_{psty} = 0.81 \text{ cm}^2/\text{g} \tag{A13}$$

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