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A Polymer Blend Exhibiting Both Upper and Lower Critical Solution Temperature Behavior: Polystyrene/Poly(o-chlorostyrene)

William MacKnight, *University of Massachusetts Amherst*

Sherrie L. Zacharius

F. E. Karasz

A Polymer Blend Exhibiting Both Upper and Lower Critical Solution Temperature Behavior: Polystyrene/ Poly(*o*-chlorostyrene)

S. L. ZACHARIUS¹, W. J. MACKNIGHT, and F. E. KARASZ

Department of Polymer Science and Engineering, University of Massachusetts,
Amherst, MA 01003

*Polymer-polymer interactions of polystyrene (PS) and poly(*o*-chlorostyrene) (PoClS) blends have been investigated by using a vapor sorption technique. These results, combined with heat of mixing experiments, indicate that both upper and lower critical solution temperature behavior are exhibited by this blend. Previous data showed that the miscibility of the PS/PoClS system is extremely molecular weight sensitive. This sensitivity is shown to be related to the existence of a critical double point in the system. Model calculations using the Flory equation-of-state theory illustrate these points.*

POLYMER-POLYMER INTERACTIONS AND THE GENERAL PHASE BEHAVIOR of the polystyrene/poly(*o*-chlorostyrene) (PS/PoClS) system were investigated with experimental ternary solution methods. Ryan (1) studied PS/PoClS blends as a function of the molecular weight of PS. The phase behavior of the polymer blends was investigated by using differential scanning calorimetry (DSC) to measure the glass transition temperature (T_g) of the blends after the blends were annealed at a series of temperatures between 150 and 400 °C. The enthalpy of mixing was also measured at 35 and 68 °C. Because direct measurement of the enthalpy of mixing is not possible, the required parameters were determined by using differential heats of solution measurements and Hess's law. (1)

¹Present address: The Aerospace Corporation, Los Angeles, CA 90009

The results of the annealing studied showed that, when PoClS of molecular weight 100,000 was blended with PS of molecular weight equal to or greater than 32,400, the blend could be phase separated. When the same PoClS was blended with PS with a molecular weight equal to or less than 26,700, the blend exhibited one T_g and could not be phase separated.

The results of the enthalpy of mixing experiments showed small but nearly always positive values. The molecular weight of the PS did not significantly affect these values.

To explain these experimental results, we postulate that blends with the higher molecular weight PS have an hourglass-type phase diagram; that is, the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST) have merged. The temperature of this merger was determined to be about 550 K. The blends with the lower molecular weight PS are single phase systems. As the molecular weight of the PS decreases, the UCST decreases and the LCST increases to the extent that both critical points are beyond experimental detection. Although a change in the critical points is theoretically predicted, this large a change as a result of such a small change in molecular weight has not been observed before. A change in the molecular weight of less than 4000 results in separation of the UCST and LCST by at least 250 °C.

We combined the experimental results of Ryan with experimental vapor sorption results to conclude that the PS/PoClS blend does exhibit both UCST and LCST behavior. In addition, we present theoretical evidence that the extreme molecular weight sensitivity of the UCST and the LCST is the result of the existence of a critical double point in this system. Sample calculations illustrate this theory.

The familiar Flory-Huggins theory (2-4), which is based on a simple lattice representation for polymer solutions, can only predict the UCST phenomenon. To predict the LCST phenomenon, the differences in the equation-of-state properties of both pure components must be taken into account. Several theories (5, 6), including Flory's equation-of-state theory (7, 8), have been developed to describe both the UCST and LCST behavior.

The equation-of-state theory considers the role of free volume in polymer solution thermodynamics. During the mixing process, the free volume of each component is changed. An intermediate value for the free volume is approached that is characteristic of the mixture. The difference in free volume is particularly significant when the mixture consists of a polymer and a solvent. Polymers typically have very low degrees of thermal expansion and free volume compared to solvents. This difference is reflected in different equation-of-state properties. The difference in free volume between polymers and solvents is independent of any chemical difference between the two components.

The change in free volume results in an overall change in the total

volume of mixing (ΔV_M), the enthalpy of mixing (ΔH_M), the entropy of mixing (ΔS_M), and, therefore, also the free energy of mixing (ΔG_M). In general, the overall volume decreases and results in a negative contribution to both the enthalpy and entropy of mixing. That is,

$$\Delta H_{M, f.v.} < 0 \quad (1)$$

and

$$\Delta S_{M, f.v.} < 0 \quad (2)$$

The total free volume (f.v.) contribution is predicted to be positive (9)

$$\Delta H_{M, f.v.} - T \Delta S_{M, f.v.} > 0 \quad (3)$$

This free volume contribution has an unfavorable effect on mixing. It becomes more significant as the temperature increases. The equation-of-state theory is thus able to predict phase separation as the temperature increases, LCST. The UCST is a result of a positive ΔH_M arising from the breaking of like contacts and the forming of unlike contacts. This positive ΔH_M effect decreases as the temperature increases.

For a mixture of two polymers, the combinatorial entropy of mixing will be very small. Therefore, usually a negative enthalpy of mixing resulting from specific interactions is necessary to attain miscibility. Only if the free volume contribution is very small can a small positive enthalpy of mixing be tolerated. McMaster (10) has shown that in this case the polymer-polymer system can exhibit both UCST and LCST behavior. We believe that the PS/PoClS system is such a system.

Experimental

Polystyrene. Two different molecular weight samples of PS with narrow distributions were used. The lower molecular weight sample and characterization data were obtained from Pressure Chemical Company. The PS is atactic batch 41220, prepared by anionic polymerization. The number average molecular weight ($\bar{M}_n$) as determined by membrane osmometry is $15,000 \pm 6\%$. The polymer was used as received without further purification.

The higher molecular weight sample and characterization data were obtained from Goodyear Chemicals. It is anionically polymerized atactic PS sample CDS-S-6. The $\bar{M}_n$ as determined by membrane osmometry is 80,800, and 75,300 as determined by GPC. The weight average molecular weight ($\bar{M}_w$) as determined by light scattering is 82,900, and 82,100 as determined by GPC. The polymer was dissolved in toluene, filtered through a very fine sintered glass funnel, precipitated into methanol, and then dried under vacuum at 80 °C for several days before being used.

Poly(*o*-chlorostyrene). The polymer was synthesized by free radical polymerization (1). The $\bar{M}_n$ as determined by GPC was 77,700; the $\bar{M}_w$ as determined

by GPC was 169,000. The polymer was then fractionated with a preparative GPC. The fraction used in the vapor sorption measurements had $\bar{M}_n = 100,500$ and $\bar{M}_w = 147,100$, as determined by GPC.

Decahydronaphthalene (Decalin). The decalin, obtained from Fisher Scientific Company, was refluxed over LiAlH for 3.5 h at atmospheric pressure and 180 °C. It was then distilled under partial vacuum at 83 °C.

Film Preparation. Films containing PS, PoClS, and their mixtures were cast from a methylene chloride solution onto aluminum pans. Initial polymer concentration in methylene chloride was approximately 4 %. The ratio of PS to PoClS is on weight basis. This technique provided a sample that was thin, on the order of 0.1 mm. The solvent was allowed to evaporate at room temperature for several hours. The films were then dried under high vacuum (10^{-4} mm Hg) at 80 °C for several days in an abderhalden drying tube. The absence of residual solvent was confirmed by a constant T_g .

Results and Discussion

Vapor Sorption Studies. Vapor sorption technique is used to study the thermodynamic properties of polymer-solvent systems and polymer blends (11). A polymer solvent solution is allowed to come to equilibrium with pure solvent of known partial pressure. As a first approximation, the activity of the solvent is equal to the relative vapor pressure P/P° , where P° is the vapor pressure of the pure solvent. For this study, the approximate activities were corrected for deviation from the perfect gas law by using Equation 4:

$$\ln a_1 - \ln(P/P^\circ) = (P - P^\circ)/\{RT(\alpha/RT - \beta)\} \quad (4)$$

where α and β are the two van der Waals constants. The activity coefficient a_1 of the solvent in a binary or ternary solution is related to the chemical potential $\Delta\mu_1$ by

$$\ln a_1 = \Delta\mu_1/RT \quad (5)$$

For a binary solution

$$\Delta\mu_1/RT = \ln \phi_1 + [1 - 1/r_2]\phi_2 + \chi_{12}\phi_2^2 \quad (6)$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and the polymer, with a degree of polymerization r_2 . The Flory-Huggins parameter is χ_{12} . For a ternary solution (12, 13)

$$\begin{aligned} \Delta\mu_1/RT = & \ln \phi_1 + (1 - 1/r_2)\phi_2 + (1 - 1/r_3)\phi_3 \\ & + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - \chi_{23}\phi_2\phi_3 \end{aligned} \quad (7)$$

where subscript 1 refers to the solvent and subscripts 2 and 3 to the two polymers. The value of χ_{23} of the two polymers can be calculated from three separate vapor sorption experiments, one with each of the polymer components separately and a third with the blend.

Polymer-Solvent Systems. Two different molecular weight PS-decalin systems were investigated, PS 15,000 and PS 80,000. The vapor sorption measurements were made at 80 °C. The T_g is 100 °C for both samples of PS. Once a certain amount of solvent has been absorbed, the PS is sufficiently plasticized so that the experimental temperature is now above T_g and the system is no longer glassy. Equation 6 is used to evaluate the χ_{12} parameter from the equilibrium sorption data of the plasticized systems. Results are shown in Figures 1 and 2 for PS 15,000 and PS 80,000, respectively. The solid lines represent a linear least squares analysis of the data. The results are $\chi_{12} = -1.00 \phi_1 + 0.797$ for PS 15,000, and $\chi_{12} = -0.565 \phi_1 + 0.688$ for PS 80,000. The molecular weight of PS has a considerable influence on the composition dependence of χ_{12} in the investigated composition range.

Vapor sorption measurements were also made on the decalin/PoClS system. The T_g for PoClS is 133 °C. Therefore, the polymer must absorb more solvent before the T_g is depressed below the experimental temperature of 80 °C. The χ_{13} parameter for the plasticized system is shown in Figure 3. The solid line is a linear least squares fit by $\chi_{13} = -1.42 \phi_1 + 1.144$.

Figure 1. The concentration dependence of the χ parameter for the system $C_{10}H_{18}/PS$ 15,000 as measured by vapor sorption experiments.

Figure 2. The concentration dependence of the χ parameter for the system $C_{10}H_{18}/PS$ 80,000 as measured by vapor sorption experiments.

Figure 3. The concentration dependence of the χ parameter for the system $C_{10}H_{18}/PoClS$ as measured by vapor sorption experiments.

Polymer-Polymer-Solvent Systems. Three different ternary systems were investigated: PS 15,000/PoClS/decalin with polymer-polymer ratios of 25:75, 50:50, and 75:25. The blend of the high molecular weight PS is an immiscible system, and Equation 7 does not apply. The values of χ_{23} , calculated by using Equation 7 and the previously determined values of χ_{12} and χ_{13} , are shown in Table I. The χ_{23} values show a considerable scatter. Except for the 25:75 systems the values are small and positive, an indication for a possible absence of specific interactions. Because the χ parameter for the latter systems is negative, it is difficult to draw a definite conclusion regarding the presence or absence of specific interactions. The results are, however, clearly different from those of various other miscible polymer systems where unequivocally negative values are found for the χ parameter (14-17). This difference indicates a much stronger interaction between both components of those blends than between PS and PoClS.

The variation with composition of the χ parameter is generally attributed to a difference in surface-to-volume ratio of the two components (18). This difference might be quite large for polymer-solvent systems. Our results on the polymer-solvent systems are in agreement with this viewpoint. Accordingly, for two polymers that are very much alike, one does not expect a significant composition dependence of the χ parameter as found for the PS 15,000/PoClS system.

A common criticism of mutual solvent techniques in general is that the solvent effect must be "subtracted out." The validity of this approach is questionable. The absolute quantities determined may not be accurate, but these experiments provide a great deal of qualitative information. The only alternative for determining polymer-polymer interactions is to investigate low molecular weight analogs.

Enthalpy of Mixing. According to the equation-of-state theory (7, 8) or the lattice fluid theory (5), the χ parameter consists of two contributions,

Table I. Flory-Huggins Polymer-Polymer Parameter at 80 °C

<i>Percent PS 15,000 in Film</i>	χ_{23}
75	0.31
	0.07
	0.35
	0.14
50	0.04
	0.23
	0.23
	0.08
25	-0.43
	-0.08
	-0.63
	-0.94

an exchange interaction term (X_{23}) and a free volume term. The X_{23} contribution dominates the low temperature behavior. It is positive for dispersive forces and negative when specific interactions like weak hydrogen bonds or charge transfer complexes are present. The free volume contribution is positive and becomes increasingly important at higher temperatures. A well-known schematic representation for χ_{12} as a function of temperature is presented in Figure 4 (19, 20). Curve 1 shows the contribution to χ resulting from contact energy dissimilarities between components 1 and 2. This contribution is considered in both the Flory-Huggins theory and the equation-of-state theory. In the absence of specific interactions, curve 1 decreases with temperature. Curve 2 shows the contribution to χ resulting from equation-of-state parameters for the two components. Curve 3 is the total of these two contributions. Figure 4 illustrates why the Flory-Huggins theory predicts only the UCST and why the equation-of-state theory predicts two critical points: one as the temperature decreases, the UCST; and one as temperature increases, the LCST. Figure 4 also illustrates that two poly-

Figure 4. Schematic representation of the temperature dependence of the χ parameter. See text for explanation of curves.

mers with a specific interaction, that is a negative value for χ_{23} , will exhibit only an LCST. Curve 1 will not be applicable in this situation.

The phase behavior of the system will be determined by the value of the χ parameter. The following is the expression for the critical value of χ_{23} (12, 13)

$$\chi_{cr} = \frac{1}{2}(r_2^{-1/2} + r_3^{-1/2})^2 \quad (8)$$

where r_2 and r_3 are the degree of polymerization for components 2 and 3, respectively. The system is miscible for all temperatures for which $\chi_{23}(T) < \chi_{cr}$ and partially miscible for all temperatures for which $\chi_{23}(T) > \chi_{cr}$.

The equation-of-state expression for the free energy of mixing can be written by using the Flory-Huggins expression where the χ parameter consists of two terms, an interactional term and a free volume term.

$$\Delta G_M/RT = (\phi_2/r_2) \ln \phi_2 + (\phi_3/r_3) \ln \phi_3 + \chi_{23}(T) \phi_2 \phi_3 \quad (9)$$

where ϕ_2 and ϕ_3 are volume fractions of components 2 and 3, respectively.

The enthalpy of mixing is related to the free energy of mixing by

$$\Delta H_m = \Delta G_m - T(\partial \Delta G_m / \partial T)_P \quad (10)$$

Combining Equations 9 and 10 results in

$$\Delta H_m = -RT^2(\partial \chi_{23} / \partial T) \phi_2 \phi_3 \quad (11)$$

The sign of the enthalpy of mixing is determined by the first derivative of the χ parameter. Prigogine and Defay (21) have shown that ΔH_m is negative near an LCST and positive near a UCST, unless an inflection point exists in the composition dependence of ΔH_m .

With this in mind, the implications of Ryan's results become clear. Ryan (1) measured the enthalpy of mixing of PS/PoClS at 35 and 68 °C for various molecular weight samples of PS while keeping the molecular weight of PoClS constant. In nearly all cases a small but positive heat of mixing was found, with no clear dependence on the molecular weight of PS. These results show that 35 and 68 °C are in the temperature range in which a UCST is possible. Consequently, blends of PS and PoClS constitute an example of miscibility without specific interactions. McMaster (10) has already shown that this exceptional situation can occur if the exchange interaction contribution is sufficiently small and if the PVT properties of both components do not differ too much.

Model Calculations. The analysis so far showed that the experimental results for PS/PoClS blends clearly point to the possibility of critical double points in these systems. Although we argued that the enhanced sen-

sitivity of the phase behavior to a change in molar mass is probably a result of this fact, such a small change may not indeed create a miscibility region of over 250 °C. An obvious model to investigate this is given by Flory's equation-of-state theory (7, 8).

The theory is based on the assumption that the degrees of freedom of a molecule in a liquid can be separated into internal and external degrees of freedom. This assumption was first made by Prigogine (22). The external degrees of freedom per polymer segment are less than those for a similar small molecule. This condition is generally denoted as $3c$ ($c \leq 1$) external degrees of freedom. The internal degrees of freedom depend on intramolecular chemical bond forces. The external degrees of freedom depend only on the intermolecular forces. Each pure component is characterized by three equations-of-state parameters: the characteristic temperature (T^*), pressure (p^*), and specific volume (v_{sp}^*). On the basis of these assumptions, the partition function for a system of N r -mers is:

$$Z(T, V) = Z_{\text{int}}(T) Z_{\text{ext}} \quad (12)$$

The partition function associated with the internal degrees of freedom Z_{int} , is assumed to be density independent. It is unaffected by neighboring segments in the liquid and therefore does not contribute to the PVT equation of state. The external contribution is equal to

$$Z_{\text{ext}} = (2\pi mkT/h^2)^{3Ncr/2} Q \quad (13)$$

where

$$Q = Q_{(\text{comb})} (4\pi\gamma/3(v^{1/3} - v^{*1/3})^{3Ncr} \exp(-E_0/kT) \quad (14)$$

In these equations, m is the mass of one segment, k is Boltzmann's constant, h is Planck's constant, V is the total volume, $v = V/rN$ is the volume per mer, v^* is the hard core volume of the mer, Q is the configurational integral, γ is a geometric factor, and E_0 is the mean intermolecular energy.

The first term on the right of Equation 13 is a kinetic contribution that is omitted in Flory's original derivation. It was added by McMaster (10).

The resulting equation of state is

$$\bar{p}\bar{v}/\bar{T} = \bar{v}^{1/3}/(\bar{v}^{1/3} - 1) - 1/\bar{v}\bar{T} \quad (15)$$

where the tilde ($\sim$) represents reduced parameters: $\bar{p} = p/p^*$; $\bar{v} = v/v^*$; and $\bar{T} = T/T^*$. The three characteristic parameters, V^* , p^* , and T^* , can be determined from the experimental values of the thermal expansion coefficient α , the thermal pressure coefficient γ , and the specific volume v_{sp} . With the aid of several combining rules, this theory is easily adapted to mixtures. The mer volumes v_1^* and v_2^* are chosen in such a way that they

have equal hard core volumes. The total number of volume dependent degrees of freedom is $3\bar{r}Nc$, where

$$c = \sum_{i=1}^n \psi_i c_i \quad (16)$$

where ψ_i is the segment fraction of component i . The additional parameter c_{12} introduced by Lin (23), which characterizes the deviation from additivity of the number of external degrees of freedom per segment in the mixture, has been neglected here.

The characteristic pressure of the mixture is defined as

$$p^* = \psi_1 p_1^* + \psi_2 p_2^* - \psi_1 \theta_2 X_{12} \quad (17)$$

where θ_2 is the surface fraction of component 2 and X_{12} is the exchange energy parameter for unlike interactions. The characteristic temperature is obtained from

$$1/T^* = (1/p^*)(\psi_1 \bar{T}_1 p_1^* + \psi_2 \bar{T}_2 p_2^*) \quad (18)$$

Eichinger and Flory (24) have also added an entropic correction parameter Q_{12} to the theory to obtain better agreement between the theory and experimental results. It accounts for the entropy of interaction between unlike segments. This approach is consistent with Guggenheim's contention that intermolecular interactions are not entirely energetic in nature.

By using the above combining rules, the equation of state for the two-component mixture is found to be identical to Equation 15.

The equation for the free energy of mixing for a multicomponent system is

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad (19)$$

$$\begin{aligned} \Delta G_M/kT = & \sum_{i=1}^n N_i \ln \psi_i + \sum_{i=1}^n 3r_i N_i (c_i - c) \ln[(2\pi m_i kT)^{1/2}/h] \\ & + 3 \sum_{i=1}^n r_i N_i c_i \ln[(\bar{v}_i^{1/3} - 1)/(\bar{v}^{1/3} - 1)] \\ & + \bar{r}Nv^*/kT \left[\sum_{i=1}^n \psi_i \theta_i^* (\bar{v}_i^{-1} - \bar{v}^{-1}) \right. \\ & \left. + \sum_{j=2}^n \sum_{i=1}^{j-1} \psi_i \theta_j (X_{ij}/\bar{v} - T\bar{v}_i Q_{ij}) \right] \end{aligned} \quad (20)$$

The enthalpy of mixing is defined in Equation 10. For a binary system this is

$$\Delta H_M = \bar{r}Nv^* [\psi_1 p_1^* (\bar{v}_1^{-1} - \bar{v}^{-1}) + \psi_2 p_2^* (\bar{v}_2^{-1} - \bar{v}^{-1}) + \psi_1 \theta_2 X_{12}/\bar{v}] \quad (21)$$

If the *PVT* data are independent of molar mass then the enthalpy of mixing is also independent of the molar mass of the polymer. Equation 22 is the same for Flory's original formulation without McMaster's modification. The additional term added by McMaster is therefore an entropic contribution.

The chemical potential of each component in a multicomponent system is

$$\Delta\mu_k/kT = (\partial\Delta G_M/\partial N_K) + (\partial\Delta G_M/\partial \bar{v})(\partial \bar{v}/\partial N_K) \quad (22)$$

At low pressures, the last term of Equation 23 is very small and can be neglected. Substitution of Equation 20 into Equation 22 yields

$$\begin{aligned} \Delta\mu_1/kT = & \ln \psi_1 + (1 - r_1/r_2)\psi_2 + 3r_1\psi_2(c_1 - c_2) \ln(m_1/m_2)^{1/2} \\ & + 3r_1c_1 \ln[(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] \\ & + r_1v^*/kT[p_1^*(\bar{v}_1^{-1} - \bar{v}^{-1}) + \theta_2^2(X_{12}/\bar{v} - T\bar{v}_1Q_{12})] \end{aligned} \quad (23)$$

for a binary system.

The relation between the Flory-Huggins interaction parameter χ_{12} and the exchange energy parameter X_{12} is

$$\begin{aligned} \chi_{12} = & 3r_1(c_1 - c_2) \ln(m_1/m_2)^{1/2} + (3r_1c_1/\psi_2^2) \\ & \ln[(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] + (v^*/kT \psi_2^2) \\ & [p_1^*(\bar{v}_1^{-1} - \bar{v}^{-1}) + \theta_2^2(X_{12}/\bar{v} - T\bar{v}_1Q_{12})] \end{aligned} \quad (24)$$

The application of the Flory equation-of-state theory requires the knowledge of the specific volume v_{sp} , the coefficient of thermal expansion α , and the thermal pressure coefficient γ . With these parameters, the characteristic parameters v^* , p^* , and T^* can be evaluated by using the following equations:

$$v_{sp}^* = v_{sp}[(1 + T\alpha)/(1 + 4\alpha T/3)]^3 \quad (25)$$

$$\bar{v} = v_{sp}/v_{sp}^* \quad (26)$$

$$\tilde{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/3} \quad (27)$$

$$\tilde{T} = T/T^* \quad (28)$$

$$p^* = \bar{v}^2 T \gamma \quad (29)$$

$$\tilde{p} = p/p^* \quad (30)$$

The *PVT* properties of PS have been investigated (26–33), but no *PVT* data are available for PoClS. Only the specific volume is available for PoClS (34). The equation-of-state parameters used for PS were those determined by Flory (33). The coefficient of thermal expansion and the thermal pressure coefficient for PoClS were estimated to be 5–6% different from the values for PS. The coefficient of thermal expansion for PoClS was taken to be 6% larger than that of PS, because a survey of literature values for other polymers showed that dense polymers (those with small specific volumes) tended to have larger coefficients of thermal expansion than less dense polymers (35–37). The experimentally determined specific volumes show that PoClS is more dense than PS. The thermal pressure coefficient was taken to be 5% less than the value for PS for the same reason. The *PVT* data and the characteristic parameters for PS and PoClS are shown in Table II.

The last quantity necessary for the full characterization of a mixture of the equation-of-state theory is X_{ij} , the exchange energy parameter. The exchange energy parameter X_{23} is expected to be positive for a nonpolar system (38). On the basis of the chemical similarities of the two components, one would expect that the value of X_{23} would also be very small. The small positive value for the enthalpy of mixing determined by Ryan indicates that a very small but positive value for X_{23} is appropriate for this system. This suggestion is further supported by the small positive values calculated for χ_{23} . With these facts in mind, we calculated spinodal curves for various values of X_{23} .

The simulated spinodals for PS of various molecular weights blended with PoClS (100,000) with $X_{23} = 0.0225$ cal/cm³, $Q_{23} = 0$, and $s_2/s_3 = 1$ are shown in Figure 5. The spinodals are located in the PS-rich region of the phase diagram. This finding is to be expected because the PS is the lower molecular weight component.

As Figure 5 illustrates, the blends with PS of molecular weight 32,000 or greater have an hourglass-shaped spinodal. When the molecular weight of the PS is dropped by only 2000, the blend is now miscible for all compositions between approximately 465 and 530 K. A further reduction of 1000 to

Table II. Pure Component Properties at 200 °C

Property	PS	PoClS
V_{sp} , cm ³ /g	1.033	0.877
$\alpha \times 10^{-4}$, K ⁻¹	5.80	6.30
γ , cal/cm ³ K	0.167	0.157
P^* , cal/cm ³	120	116
T^* , K	8697	8301
V_{sp}^* , cm ³ /g	0.839	0.706
M_w	variable	100,000

Figure 5. Simulated spinodal for the PS/PoClS system for the indicated molecular weights of PS.

PS 29,000 results in a UCST at 380 K and an LCST at 620 K. The LCST is now above the degradation temperature. Figure 5 demonstrates that under the right circumstances the equation-of-state theory is capable of predicting the type of mixing behavior that has been proposed for PS-PoClS system.

The situation is more clearly illustrated in Figure 6. This figure shows the temperature dependence of χ for the PS-PoClS blend with segment fraction equal to 0.5 and $X_{23} = 0.0225$ cal/cm³. This curve is equivalent to curve 3 in Figure 4. The χ is independent of molecular weight, if we assume that the equation-of-state parameters are independent of molecular weight. This assumption is considered reasonable for the molecular weight range under consideration here. Therefore, Figure 6 represents the χ vs T curve for all PS-PoClS blends when $X_{23} = 0.0225$. The critical value of χ is very dependent on molecular weight as shown by Equation 8. The horizontal lines in Figure 6 represent the critical value of χ for PS with the indicated molecular weight. The first intersection of a horizontal line with the curve represents the UCST for that molecular weight system. The second intersection represents the LCST. When the molecular weight of PS is

Figure 6. Calculated temperature dependence of χ parameter for the PS/PoClS system. The horizontal lines represent the critical values of the χ parameter for the indicated molecular weights of PS.

32,000, the LCST and UCST merge at about 490 K. The point at which the LCST and UCST merge is called the critical double point. Any system with a PS molecular weight greater than 32,000 has no UCST or LCST; the blend is immiscible. Clearly, the flatness of the χ vs. T curve in the vicinity of the critical double point is responsible for the large temperature change in the critical temperatures with very small changes in molecular weight.

All predictions of the equation-of-state theory presented here for the PS/PoClS blends have been based on estimated equation-of-state parameters for PoClS. These predictions are intended to give a qualitative picture of the mixing behavior of the polymer blend. The numbers are significant only in terms of their relative magnitudes and signs.

In summary, the experimental observations indicate the existence of both a UCST and an LCST in the PS/PoClS system. The equation-of-state

theory has been used to show the connection between the occurrence of a critical double point and the enhanced sensitivity of the phase behavior to small changes in molecular weight.

Acknowledgments

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