Cloud-Point Curves in Polymer Solutions with Adjacent Upper and Lower Critical Solution Temperatures

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ABSTRACT: Phase diagrams have been obtained for different molecular weight fractions of polystyrene in acetone, diethyl ether, and dimethoxymethane. The first two systems show upper and lower critical solution temperatures which approach each other as the molecular weight of the polymer is increased until the regions of limited miscibility merge. It is suggested that this behavior occurs generally for polymer-poor solvent systems. The phase diagrams are predicted semiquantitatively by the Prigogine and Flory theories of polymer solution thermodynamics using a concentration-dependent χ parameter.

The phase diagram of a polymer solution shows two regions of limited miscibility[1] in the temperature–composition plot. One is found below the upper critical solution temperature (UCST) associated with the Flory Θ point, the other above the less well-known lower critical solution temperature (LCST). This type of LCST should be distinguished from that occurring in some highly polar systems, such as polyoxyethylene–water,[2] where a closed solubility loop is found. The present type of LCST and the UCST are predicted by recent theories of polymer solution thermodynamics. Values of the pairs of UCST and LCST have been given for a few systems, *e.g.*, polystyrene–cyclohexane (33,[3] 210°[4]) and polyisobutylene–benzene (24,[5] 260°[6]). Cloud-point curves (CPC) at one or the other of the critical solution temperatures have been published for various systems. It is surprising, however, that there has been little work showing CPC around both critical solution temperatures in a single polymer–solvent system, *i.e.*, showing the supposedly typical phase diagram. One purpose of this work is to supply two examples of such phase diagrams in the systems low molecular weight polystyrene–acetone and –diethyl ether.

By increasing the molecular weight of the polymer, the UCST is raised and the LCST lowered, thus shrinking the temperature region of complete polymer–solvent miscibility. If a solvent of poor quality is chosen, it is predicted that the increase of molecular weight could cause the UCST and LCST to "coalesce" so that the two regions of limited miscibility merge to give an "hourglass" shape (*cf.* Figure 1). This behavior should be typical of polymer-poor solvent systems and be of common occurrence. Baker and Allen[7] indicate that the poly(propylene oxide)–isobutane system should show this behavior. The most extensive study of polymer-poor solvent systems has been made by Cowie and coworkers[8] on cellulose acetate–acetone systems. Both the UCST and LCST occur for cellulose triacetate. However, they have coalesced in the case of the diacetate of high molecular weight, and in this system the CPC would have the hourglass shape. We show such a phase diagram here, for polystyrene of molecular weight 19,800 + acetone.[9] Qualitative theoretical considerations had indicated that the hourglass CPC would be conveniently observable near room temperature using a solvent which had a large thermal expansion coefficient and which was moderately different in solubility parameter from the polymer.

It should be noted that LCST does not require the presence of a polymer, but occurs when there is a sufficiently large difference of thermal expansions or free volumes between the two components. Cloud-point curves around the UCST and LCST have been given for the methane + 1-hexene system[10] and a number of other systems composed of methane and hexene isomers or branched alkanes.[11] Furthermore, the hourglass CPC has been observed for the methylcyclopentane–methane system under a pressure of 170 bars.[12] With an increase of pressure, the difference of free volumes between the components is decreased so that their compatibility is improved and the UCST and LCST appear. Similar behavior is found on applying pressure to the polystyrene–acetone solution and other polymer systems.[13]

Experimental Section

The polystyrene fractions were obtained from the Pressure Chemical Co., who report M_w/M_n values less than 1.06. The acetone, diethyl ether, and dimethoxymethane were Aldrich Spectranalyzed and "pure" grades of purity >99%. The CPC were determined optically at the saturated vapor pressure essentially as described in ref 14.

Results

Figure 1 shows the CPC obtained at solution vapor pressure for three molecular weights of polystyrene in acetone: 4800, 10,300, and 19,800. If the samples had been completely monodisperse, the critical temperatures would be represented by the maxima (UCST) or minima (LCST) of the CPC. Polydispersity displaces[15] the critical point to higher concentration.

(1) D. Patterson, *Macromolecules*, **2**, 672 (1969).
(2) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).
(3) A. R. Schultz and P. J. Flory, *J. Amer. Chem. Soc.*, **74**, 4760 (1952).
(4) G. Delmas and D. Patterson, *Polymer*, **7**, 513 (1966).
(5) T. G. Fox and P. J. Flory, *J. Amer. Chem. Soc.*, **73**, 1909 (1951).
(6) A. H. Liddell and F. L. Swinton, *Discuss. Faraday Soc.*, **No. 49**, 115 (1970).
(7) G. Allen and C. H. Baker, *Polymer*, **6**, 181 (1965).
(8) J. M. G. Cowie, A. Maconnachie, and R. J. Ranson, *Macromolecules*, **4**, 57 (1971).
(9) After submission of the present article, our attention was called to the work of B. A. Wolf, J. W. Breitenbach, and H. Senftl, *J. Polym. Sci., Part C*, **No. 31**, 345 (1970), on the ternary system polystyrene–acetone–methyl ethyl ketone. The CPC are similar in shape to those in the binary systems and will be discussed below.
(10) J. A. Davenport, J. S. Rowlinson, and G. Saville, *Trans. Faraday Soc.*, **62**, 322 (1966).
(11) P. H. van Konynenburg, Ph.D. Dissertation, U.C.L.A., 1968; R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.*, **No. 49**, 87 (1970).
(12) D. Oeder and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, **73**, 229 (1969).
(13) L. Zeman and D. Patterson, *J. Phys. Chem.*, in press.
(14) D. Patterson, G. Delmas, and T. Somcynsky, *Polymer*, **8**, 503 (1967).
(15) R. Koningsveld, *Discuss. Faraday Soc.*, **No. 49**, 180 (1970).

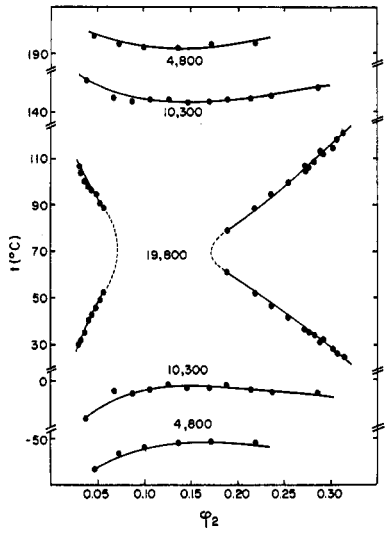

Figure 1. The (temperature, volume fraction) phase diagram for the polystyrene–acetone system, for fractions of indicated molecular weight, showing UCST and LCST for low molecular weights and the "hourglass" cloud-point curve for the 19,800 fraction.

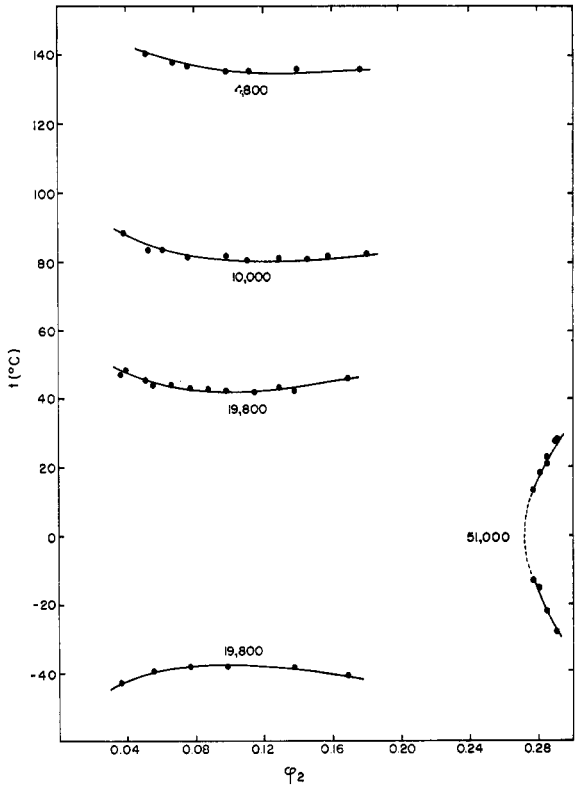

Figure 2. The (temperature, volume fraction) phase diagram for the polystyrene–diethyl ether system for fractions of indicated molecular weight, showing a UCST and the LCST. In the case of the 51,000 fraction, the two-phase region extends from virtually zero concentration (unmeasured) to the cloud-point curve at the right of the diagram.

The maxima and minima are termed upper precipitation threshold (UPT) and lower precipitation threshold (LPT), respectively. Koningsveld, Kleintjens, and Shultz[16] have measured M_n, M_w, and M_z for seven of the Pressure Chemical Co. fractions. These include the 19,800 and 51,000 M_w samples used in the present work but not the 4800 and 10,300 molecular weights. However, the M_w/M_n and M_z/M_w ratios are quite uniform for the fractions, being respectively 1.05 and 1.07. Assuming the same ratios for the 4800 and 10,300 fractions, one can calculate the displacement of the critical concentration from the concentration at the precipitation threshold using eq 8 of ref 16. The displacement for these two fractions corresponds to $\Delta\phi_2 \simeq 0.003$. The uncertainty in estimating the concentration at the precipitation threshold is greater than this due to the flat shape of the CPC. The difference between the threshold temperature and the critical temperature would be a small fraction of a degree and is impossible to estimate from our experiments. We assume the curvature of the CPC to be about the same as that of the CPC for a monodisperse polymer. Then, calculated CPC may be used, and the difference between threshold and critical temperatures is $\sim 0.01°$. In the present work, we are mainly interested in qualitative features of the phase separation. We believe therefore that we are justified in equating the critical solution point and the precipitation threshold, ignoring effects of polydispersity, but we return to this point in the Discussion. Finally then, for the polystyrene fractions in acetone, the UCST and LCST values are 4800 (−51, 192°) and 10,300 (−2, 144°). For the 19,800 fraction, the two regions of limited miscibility have merged. Quantities of polystyrene of molecular weight 19,800 and acetone corresponding to $\phi_2 = 0.13$ were brought to the neighborhood of 70°. Complete miscibility was not achieved. This system thus gives the hourglass phase diagram but is obviously very close to showing both the UCST and LCST. This is confirmed by experiments with polystyrene of molecular weight 20,400 in acetone under pressure.[13] A pressure of only 10 atm suffices to separate the UCST and LCST. In Figure 1, the dotted lines are estimates only. It was found impracticable to obtain experimental points in this region since changing the temperature gave no sharp change in the optical density of the solution.

Figure 2 shows the CPC for the polystyrene–diethyl ether system using fractions of molecular weights 4.8, 10.0, 19.8, and 51.0 × 10^3. The UCST for the 4800 and 10,000 fractions lay too low to be measured conveniently. The 19,800 fraction still shows the UCST and LCST, but they have coalesced when the next fraction of the Pressure Chemical Co. series, of molecular weight 51,000, is used. The low-concentration half of the hourglass CPC was too low to be found experimentally. Theory indicates the value of ϕ_2 to be $\sim 10^{-4}$. However, Figure 2 shows the high-concentration half of the hourglass, $\phi_2 \simeq 0.27$. It is clear that the phase diagram changes rapidly on raising the molecular weight of the polymer from 19,800 to 51,000. Apparently, the low-concentration half of the hourglass CPC can be observed in practice for a very limited range of molecular weights.

Figure 3 shows CPC for polystyrene–dimethoxymethane systems with molecular weight fractions 5.10, 9.72, 16.0, 41.1, and 86 × 10^4. The curves have similar, regular shapes and their minima lie at concentrations which decrease regularly with increasing molecular weight. No UCST's were observed with this system; that for the highest molecular weight apparently lies below −78°.

Discussion

Qualitative Features of the Cloud-Point Curves. The CPC around the UCST and LCST are essentially mirror images of one another, and the average of the UCST and LCST is almost independent of mol. wt. The CPC show little variation of

(16) R. Koningsveld, L. A. Kleintjens, and A. R. Shultz, *J. Polym. Sci., Part A-2*, **8**, 1261 (1970).

temperature with composition, a feature which has been found for other polystyrene systems,[17] and which has been associated[17] with a concentration-dependent value of the χ parameter.

The dependence of the UCST and LCST on molecular weight is much larger when these temperatures are close together, as for polystyrene–acetone or polystyrene–diethyl ether, than when they are far apart, as for polystyrene–dimethoxymethane. This is seen in Figure 4, showing the Shultz–Flory plot of T_c^{-1} against $r^{-1/2} + (2r)^{-1}$ for the three systems. The plot is expected[3] to be a straight line of slope $(\psi_1\theta)^{-1}$. The curvature of the plot for the first two systems corresponds to a decrease of the entropy parameter, ψ_1, with temperature through the region of the UCST's followed by increasingly negative values in the region of the LCST's. Shultz and Epstein[18] found this curvature of the plot in 1955 with UCST values for three fractions of polystyrene in acetone, and also observed that a 20,000 mol. wt. fraction was never completely miscible with acetone. Our results are in good agreement with theirs, as shown in Figure 4.

Prediction of the Cloud-Point Curves. The Flory–Huggins theory extended to allow for higher χ_i, $i > 1$, gives,[19] for the free energy of mixing

$$\Delta G_M/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + rn_2 \sum_{i=1} (\chi_i/i)(1 - \phi_2^i) \quad (1)$$

where the n's designate number of moles and r is given by the ratio of molar volumes of the components, or as more recently suggested,[20] the ratio of the molar volume reduction parameters (core volumes), *i.e.*, V_2^*/V_1^*. Correspondingly, ϕ_2 may be either the volume fractions or the closely related segment fractions.[20] Using eq 1, the chemical potentials are found to be

$$\Delta\mu_1/RT = \ln \phi_1 + (1 - r^{-1})\phi_2 + \sum_{i=1} \chi_i \phi_2^{i+1} \quad (2)$$

$$\Delta\mu_2/RT = \ln \phi_2 + (1 - r)\phi_1 + r \sum_{i=1} \chi_i \left(\frac{1 - \phi_2^i}{i} - \phi_1 \phi_2^i \right) \quad (3)$$

(The most extensive treatment of phase equilibria has been made by Koningsveld,[16] who uses equations identical with 1–3 but with a change of nomenclature.) We first discuss the CPC in terms of the usual Flory–Huggins equations, *i.e.*, eq 1–3, retaining only χ_1. The well-known result for the critical value of χ_1 is

$$\chi_{1c} = (1/2)(1 + r^{-1/2})^2 \quad (4)$$

The theories of Prigogine[21] and of Flory[20] and their coworkers give essentially the same expressions for χ_1 as a function of temperature, as discussed in ref 21c. The former gives[21b]

$$\chi_1 = -(U_1/RT)\nu^2 + (C_{p,1}/2R)\tau^2 \quad (5)$$

(17) H. Tompa, "Polymer Solutions," Butterworths, London, 1956, Chapter 7.
(18) A. R. Shultz and B. N. Epstein, unpublished results, 1955.
(19) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).
(20) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).
(21) (a) I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam, 1957; (b) D. Patterson, *J. Polym. Sci., Part C*, **No. 16**, 3379 (1969); (c) J. Biroš, L. Zeman, and D. Patterson, *Macromolecules*, **4**, 30 (1971).

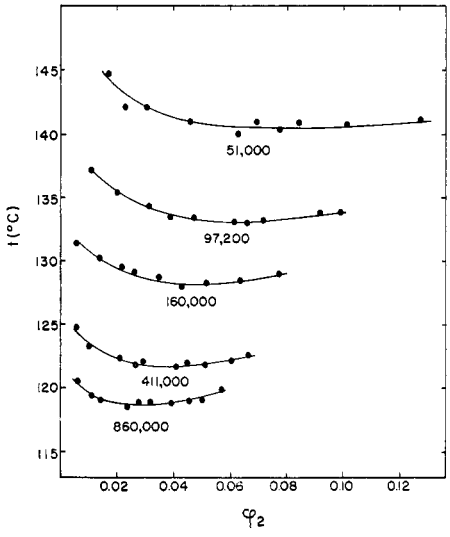

Figure 3. The (temperature, volume fraction) phase diagram for the polystyrene–dimethoxymethane system, showing LCST for the fractions of indicated molecular weight.

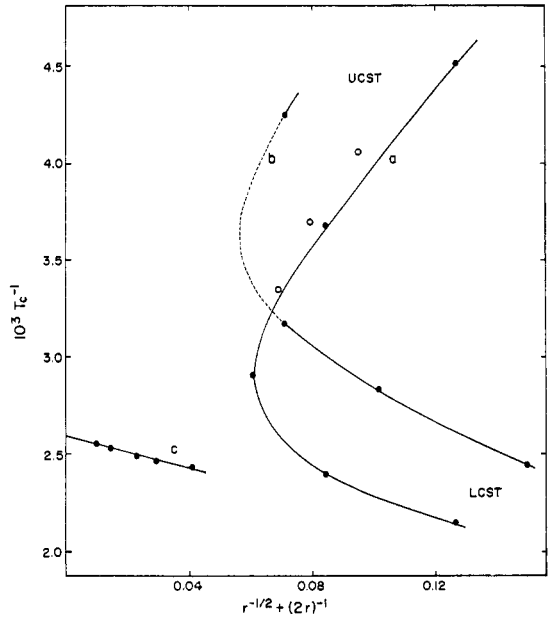

Figure 4. The Shultz–Flory plot of reciprocal critical solution temperature against $r^{-1/2} + (2r)^{-1}$ for: (a) polystyrene–acetone, (b) polystyrene–diethyl ether, and (c) polystyrene–dimethoxymethane. The open circles correspond to polystyrene–acetone data of Shultz and Epstein.[18] The dotted line represents an estimated section of the curve.

The τ parameter is a measure of the difference of free volumes or thermal expansions of the two components

$$\tau = 1 - T_1^*/T_2^* \quad (6)$$

and the ν^2 parameter expresses the difference of chemical nature of the components which results in a weakness of the (1–2) contacts relative to the (1–1) and (2–2). It is identical with the ratio X_{12}/P_1^* of the Flory theory. The quantity U_1 is the configurational energy of the solvent and $C_{p,1}$ its temperature derivative, *i.e.*, the configurational heat capacity. The Flory theory[20] essentially predicts U_1 and $C_{p,1}$ using a van der Waals model of the liquid and the Hirschfelder–Eyring cell

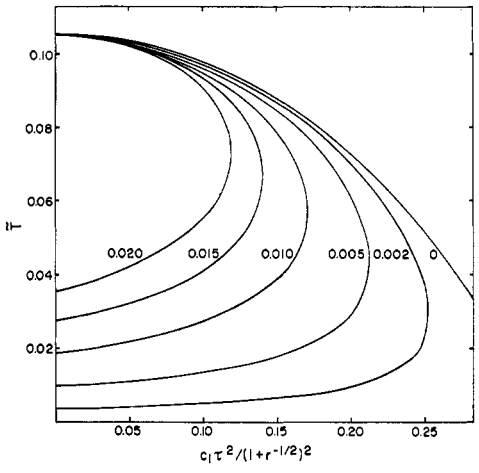

Figure 5. Prediction of the UCST and LCST: the reduced critical solution temperature, $\tilde{T}$, which satisfies eq 7 as a function of $c_1\tau^2/[1 + r^{-1/2}]^2$ for the indicated values of $c_1\nu^2/[1 + r^{-1/2}]^2$. Zero pressure conditions apply. Values of $\tilde{T}$ less than about 0.04 would be inaccessible due to freezing of the solution.

TABLE I
PARAMETERS OF THE SYSTEMS

	T_1^*, deg	c_1	τ^2	$10^3\nu^2$	χ_2
Polystyrene–acetone	4349	0.91	0.171	19.5[b]	0.33[b]
Polystyrene–diethyl ether	4056	1.11	0.206	5.0[b]	0.20[b]
Polystyrene–dimethoxymethane	4278	1.10[a]	0.179	5.1[b]	0.29[b]

[a] Estimated. [b] Fitted as described in text.

partition function. Using this model, eq 5 gives χ_1 at a critical point under zero or negligible pressure

$$\chi_{1c} = \frac{c_1\nu^2}{1 - \tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2[(4/3)\tilde{V}_1^{-1/3} - 1]} = (1/2)(1 + r^{-1/2})^2 \quad (7)$$

where

$$\tilde{T} = \tilde{V}^{-1}(1 - \tilde{V}^{-1/3}) = T/T^* \quad (8)$$

Here $3c_1$ is the number of external degrees of freedom of the solvent molecule, related to the reduction parameters through $c_1 = P_1^*V_1^*/RT_1^*$.

Figure 5 shows the reduced critical solution temperatures which are roots of eq 7 as a function of $c_1\tau^2/(1 + r^{-1/2})^2$ for various values of $c_1\nu^2/(1 + r^{-1/2})^2$. If the system is composed of a pair of homologs, $\nu^2 = 0$, and Figure 5 shows only single roots for $\tilde{T}$, corresponding to LCST's. As $\tau^2 \to 0$, the LCST increases, approaching the vapor–liquid critical temperature of the solvent. (In Figure 5 the system is held at zero pressure instead of following the saturated vapor pressure. The LCST in the figure tends to a value corresponding to $C_p \to \infty$ at $P = 0$. This is a slightly lower temperature than the vapor–liquid critical temperature of the solvent, where $C_p \to \infty$ for $P = P_c$.) When $\nu^2 \neq 0$, the curve of $\tilde{T}$ in Figure 5 passes through a point of infinite slope. To the left of this point, there are two roots for $\tilde{T}$ corresponding to the UCST and LCST. To the right of the point, there is no root of eq 7, indicating that the UCST and LCST have coalesced as in the high molecular weight polystyrene–acetone and –diethyl ether cases. The condition for the existence of two roots corresponds to a low value of τ^2 or of ν^2, whereas that for no root corresponds to high values of either or both of these parameters. Figure 5 also shows the effect of molecular weight on the critical solution temperatures. A decrease of r moves the system to the left in Figure 5, and also onto curves of lower $c_1\nu^2/(1 + r^{-1/2})^2$. Both of these displacements decrease the predicted UCST and increase the LCST. When the UCST and LCST are close together, their molecular weight dependence becomes very large and at the point of coalescence becomes infinite. This is associated with $\chi_1(T)$ being a minimum at this point, whereas it varies rapidly when the critical solution temperatures are far apart. The theory thus accounts qualitatively for the observed phase behavior.

Quantitative Comparison of Theory and Experiment. Table I shows values of the c_1, T_1^*, and τ^2 parameters used in applying the theory. They were obtained from equation of state data using the Flory and Eichinger prescription.[20]

In the polystyrene–acetone system, the UCST and LCST coalesce for a mol. wt. of 19,800 corresponding to a point of infinite slope on a curve such as shown in Figure 5. The value of ν^2 has been adjusted so that coalescence takes place at this mol. wt. with the values of c_1 and τ^2 which correspond to the polystyrene–acetone system. This procedure has been used and described by Cowie, *et al.*,[8] in treating their similar phase data. The CPC for all of the fractions were calculated[22] using eq 2 and 3, retaining only χ_1. The values of the chemical potentials of the two components in one phase were set equal to those in the other phase, giving the CPC in terms of $\chi_1(\phi_2)$. These are transformed into $T(\phi_2)$ using the $\chi_1(T)$ relationship of eq 7 with the fitted value of $c_1\nu^2$. It is interesting to compare the relative sizes of the first (ν^2) and second (τ^2) terms in eq 7 for χ_{1c} at the UCST and LCST. For the 19,800 molecular weight sample at the temperature of coalescence of the UCST and LCST, the term in ν^2 contributes 0.174 and that in τ^2 0.350 to χ_{1c}. For the 4800 molecular weight sample at the LCST, the terms are ν^2 0.125 and τ^2 0.435, whereas at the UCST they are ν^2 0.260 and τ^2 0.300. Thus, although the UCST is associated with the ν^2 term and the LCST with that in τ^2, the latter term is the larger at both temperatures in this system.

Figure 6 shows the results, which may be compared with the experimental CPC in Figure 1. The temperatures of the cloud points are ~50° too low and the molecular weight dependence of the critical solution temperatures is too small, *i.e.*, the CPC are too close together. This corresponds to a $\chi_1(T)$ function which is too large and too steep around the minimum. Furthermore, the CPC are "narrower" than found experimentally and the critical concentrations about half those found.

Equation 7 predicts the χ_1 parameter at zero pressure, while the LCST's are obtained under the solution vapor pressure, which may be as high as 10 atm. The value of the LCST corrected to the zero-pressure condition[13] would lie up to 6° lower than observed. This difference has been ignored in comparing prediction with experiment.

Experimental CPC are often[17] found, as here, to be flatter than given by the Flory–Huggins theory, and the predicted shape may be improved[17] by including the χ_2 parameter in eq 1–3. The critical value of χ_1 is now lower than given in eq 4. The calculation of the CPC is essentially the same as for $\chi_2 = 0$. A value of $\chi_2 = 0.33$ is chosen to fit the polystyrene–acetone system. Vapor pressure measurements on

(22) The calculation of the CPC for zero or nonzero χ_2 was run on an IBM 360 computer. The program is available on request.

polystyrene of 15,000 mol. wt. + acetone indicate[23] a somewhat larger value of χ_2, about 0.5. The shapes of the curves and the critical concentrations now agree with experiment, as shown by a comparison of Figures 1 and 6 drawn on the same scale. We have also calculated the CPC for a fraction of 50,000 molecular weight to show how the two-phase region expands when the molecular weight is increased. However, the absolute values of the cloud-point temperatures are still too low, as in the case when $\chi_2 = 0$. The situation does not change on taking account of the small polydispersity of the present polymer samples. In the calculation, the value of χ_2 is fixed, using a value of the critical concentration taken equal to the threshold concentration. If the critical concentration is increased by $\Delta\phi_2 \simeq 0.003$, as required by the polydispersity correction, a higher value of χ_2 would be obtained. However, the difference is only $\Delta\chi_2 \simeq 0.007$ and has a negligible effect on the calculated cloud-point curves.

The presence of χ_2 in the free energy expression may be justified by theory,[20,21b] and is due to a combination of effects. A large positive value seems to be associated with a molecular surface/volume ratio for the polymer which is considerably less than that of the solvent, *i.e.*, $s_2/s_1 \ll 1$ in the Flory nomenclature. This effect was neglected in our presentation of the Prigogine theory and an introduction of it would cause the ν^2 parameter in eq 5 and 7 to be replaced by $(s_2/s_1)^2\nu^2$. Since the parameter is fitted to experiment, no change would occur in the present treatment.

It is of interest to note that CPC similar to those in Figure 1 can be obtained with a single molecular weight of polymer, but adding a solvent of lower thermal expansion to form a ternary system. Wolf, Breitenbach, and Senftl[9] have illustrated this with the polystyrene–acetone–methyl ethyl ketone system. The methyl ethyl ketone ($\alpha = 1.29 \times 10^{-3}$ K^{-1} at 20°), having a lower degree of thermal expansion than the acetone ($\alpha = 1.42 \times 10^{-3}$ K^{-1} at 20°), lowers the free volume contribution to χ throughout the temperature range. The effect is therefore similar to applying pressure[13] to the polystyrene–acetone system. The LCST is raised and the UCST lowered, so that qualitatively one has the same effect as obtained by decreasing the molecular weight of the polymer. By adding a less expanded solvent or applying pressure, the χ parameter is decreased, while by decreasing the molecular weight the critical value of χ is increased.

The polystyrene–diethyl ether system was treated similarly to polystyrene–acetone. A value of $\chi_2 = 0.20$ gave the correct critical concentration (assumed to be the CPC show a minimum or maximum) for the 19,800 molecular weight fraction. The critical value of χ_1 is now lower than given by eq 4. The value of ν^2 was fitted so that eq 7 predicted the correct temperature interval between the critical solution temperatures for the 19,800 molecular weight fraction. The cloud-point curves for all the fractions could then be predicted, as in the polystyrene–acetone case. The critical concentrations and the shapes of the curves were in excellent agreement with experiment, except for the 51,000 fraction. However, the critical solution temperatures were uniformly too low and their dependence on the molecular weight was too small, *i.e.*, the CPC were too close together. Consistent with this, the 51,000 fraction was predicted to be more soluble than found, *i.e.*, the two-phase region occupies too small a concentration interval.

A value of 0.29 for χ_2 was found to give the critical concentrations and shapes of the CPC for all fractions in the polystyrene–dimethoxymethane system. Here, the dependence of the LCST on molecular weight was used to fit ν^2 in eq 7. Again the values of the LCST were predicted much too low. The small molecular weight dependence of the LCST in this system indicates that there should be a wide gap between the LCST and UCST of even the highest fraction. The theoretical treatment predicts the gap to be 120°, whereas experimentally it is considerably greater, since the UCST could not be found above −78°.

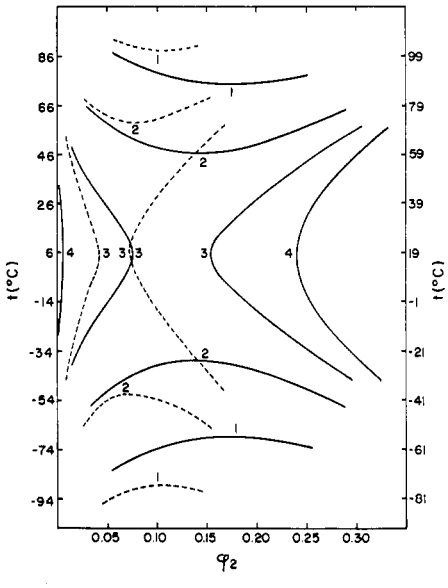

Figure 6. Calculated phase diagram for polystyrene–acetone. Two choices of the χ_2 parameter are made in calculating the cloud-point curves: dotted curves with temperature scale at right, $\chi = 0$; solid curves with temperature scale at left, $\chi_2 = 0.33$. The numbers refer to the polystyrene molecular weights (1) 4800, (2) 10,300, (3) 19,800, and (4) 50,000.

Predictions by Other Models. We have investigated the possibility of obtaining better agreement with experiment through the use of other models for the liquid state. The Hirschfelder–Eyring cell partition function may be retained with a dependence of the configurational energy on volume inspired by the Lennard-Jones (m–n) potential between point centers[21a]

$$\tilde{U} = (-n\tilde{V}^{-m/3} + m\tilde{V}^{-n/3})/(n - m) \qquad (9)$$

The results with the Flory model may be obtained by putting $m = 3$, $n \to \infty$. We have used the (m–∞) potential but with $m \neq 3$. The choice of $m = 2$ gives the correct molecular weight dependence of the cloud-point temperatures in the polystyrene–acetone system. However, the absolute values of the temperatures are further displaced below those found experimentally. When $m > 3$, the agreement between the absolute values is improved but their molecular weight dependence is worse than with $m = 3$, *i.e.*, $\chi(T)$ has an even steeper minimum. The effect of varying the n parameter was not explored. It appears that the (3–∞) choice is a reasonable compromise if the Flory–Huggins combinatorial approximation, *i.e.*, eq 1–3, is used to give the critical value of χ_1, as in the present work. This assumes a random mixture (Bragg–Williams approximation), which may not be appropriate at temperatures approaching the critical solution point. An approximation such as the Guggenheim quasichemical which allows for nonrandomness would give a higher critical value

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for χ_1 than given in eq 4. If the calculations are made as before, but with the higher value of χ_1, the CPC are displaced to higher temperatures, in better agreement with experiment. We conclude that the Flory model with the Flory–Huggins critical value of χ_1 predicts the phase behavior semiquantitatively, but that further experiments may show a modification of the theory to be warranted.

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Appendix. Correspondence of the Prigogine and Flory Expressions for χ_1

The theory of Flory and collaborators gives (*cf.* eq 49–51 of ref 20)

$$\chi_1 = \frac{P_1^* V_1^*}{RT\tilde{V}_1}\left[\left(\frac{s_2}{s_1}\right)^2 \frac{X_{12}}{P_1^*} + \frac{\alpha_1 T}{2}\left\{\frac{P_2^*}{P_1^*}\tau - \frac{s_2}{s_1}\frac{X_{12}}{P_1^*}\right\}^2\right] \quad (10)$$

If one neglects the third order of differences in the starred reduction parameters

$$\chi_1 = \frac{P_1^* V_1^*}{RT\tilde{V}_1}\left[\left(\frac{s_2}{s_1}\right)^2 \frac{X_{12}}{P_1^*} + \frac{\alpha_1 T}{2}\tau^2\right] \quad (11)$$

In the model used by the theory, $-U_1 = P_1^* V_1^*/\tilde{V}_1$ and $TC_{p,1} = P_1^* V_1^* \alpha_1 T/\tilde{V}_1$, whence eq 11 and the Prigogine eq 5 are identical if ν_2 is replaced by $(s_2/s_1)^2(X_{12}/P^*)$. The (s_2/s_1) parameter is the ratio of the surface to volume ratios for polymer and solvent. In deriving[21b] eq 5, this was set equal to unity, surface and segment fractions being made equal, and so does not appear in eq 5.

Kinetic Study of Ring-Opening Polymerization of Oxepane

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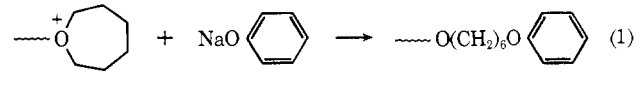
ABSTRACT: Kinetics of the cationic polymerization of oxepane, a seven-membered cyclic ether, by the initiator system BF_3·THF–epichlorohydrin (promoter) in CH_2Cl_2 was examined. The kinetic analysis was based on the determination of the concentration of propagating species, [P*], by the phenoxyl end-capping method. On the basis of SN2 reaction mechanism, the rate constant of propagation reaction, k_p, was calculated from the integrated equation, $\ln [([M]_{t_1} - [M]_e)/([M]_{t_2} - [M]_e)] = k_p \int_{t_1}^{t_2} [P^*]dt$, where the $[M]_t$'s and $[M]_e$ are respectively the instantaneous and equilibrium concentrations of monomer, and the $\int_{t_1}^{t_2} [P^*]dt$ value is obtained by graphical integration on the time–[P*] curve. From the k_p values at five temperatures in a range from −10 to 30°, the activation parameters of this polymerization were determined: $\Delta E_p^{\ddagger} = 18$ kcal/mol, $A_p^{\ddagger} = \times 10^9$ l./(mol sec).

In ring-opening polymerization, the relationship between the ring sizes and the polymerization reactivities of a series of cyclic monomers is one of the most fundamental problems. As to cyclic ethers, the propagation rate constants, k_p, of the polymerizations of four- (oxetane)[1] and five- (THF)[2–5] membered cyclic ethers have been determined by us on the basis of the determination of the concentration of propagating species, [P*]. This paper is concerned with a seven-membered cyclic ether, oxepane.

Previously we reported general features of the oxepane polymerization and characterization of the oxepane polymer as well as the monomer–polymer equilibrium.[6] In the present study, the kinetic studies of the oxepane polymerization by the BF_3·THF–epichlorohydrin (ECH) system were performed on the basis of the concentration of propagating species determined by means of the phenoxyl end-capping method.[2] BF_3·THF–ECH catalyst is among the most suitable systems for the analysis of our phenoxyl end-capping method because of the stability of BF_3·THF complex and the absence of side reactions such as phenetole formation in the case of the oxonium ion salt system.[5] Our studies on polymerizations of other cyclic ethers have systematically been performed with the same counterion derived from the BF_3·THF–ECH system. The k_p values were successfully determined in a temperature range between −10 and 30°, and the activation parameters were obtained. The kinetic data of the oxepane polymerization were interestingly compared with the corresponding data of four- and five-membered cyclic ethers.

Results and Discussion

Determination of [P*] by the Phenoxyl End-Capping Method. The [P*] determination by the phenoxyl end-capping method has been established in the polymerizations of oxetane[1] and THF.[2] In the present study, the same method was applied to the oxepane polymerization, *i.e.*, the active species at the propagating chain end was converted into the corresponding phenyl ether (eq 1) and its concentration was analyzed by uv absorption at 272 mμ. As to the phenoxyl end capping, the molar extinction coefficient value



(1)

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