Upper and Lower Critical Solution Temperatures in Polystyrene Solutions. II

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ABSTRACT: Phase equilibria have been examined for solutions of narrow-distribution polystyrene ($3.7 \leq 10^{-4}M_w \leq 270$) in benzene, methyl ethyl ketone, and cyclopentane. Lower critical solution temperatures have been determined for polystyrene solutions in benzene and methyl ethyl ketone and upper and lower critical solution temperatures for the polystyrene-cyclopentane system. The Patterson-Delmas corresponding states theory has been applied to the experimental results through the χ_1 parameter and found to afford semiquantitatively good prediction of the molecular weight dependence of their critical temperatures. The one-third of external degrees of freedom of the solvents estimated by the aid of the theory are 1.23 for benzene, 1.76 for methyl ethyl ketone, and 0.706 for cyclopentane.

The importance of free volumes in explaining the lower critical solution temperatures (lcst) in nonpolar polymer solutions has been recognized during the last decade. It is well known that the cloud point curve associated with the upper critical solution temperatures (ucst) is convex upward and its maximum point gradually shifts to a higher temperature and a lower concentration with increasing molecular weight of the polymer. The maximum point for a solution of polymer having a very narrow molecular weight distribution is almost equivalent to the ucst.[1] This maximum temperature extrapolated to infinite molecular weight of the polymer affords the θ or Flory temperature.[2] Phase separation again occurs if the temperature of the solution is raised to the vicinity of the vapor-liquid critical temperature of the solvent.[3-7] The cloud point curve in this region is convex downward and its minimum point tends to move toward lower temperature and lower concentration with an increase of the molecular weight of the polymer.[5-7] The temperature of this minimum point is called the lower critical solution temperature and the minimum temperature for the infinite molecular weight of the polymer also gives a θ or Flory temperature.[8] The two types of cloud point curves behave like mirror images across the temperature axis of the intermediate region of the ucst and lcst. This behavior suggests that both ucst and lcst may generally appear in nonpolar polymer solutions. Unfortunately, polymer solution are not realizable at a temperature below the freezing point of the solvent. This makes observations of the ucst possible for only the polymer-solvent systems with the ucst at temperatures above the freezing point of the solvent. It has been found that the Patterson-Delmas theory[5] of corresponding states adequately describes the dependence of the ucst and lcst on the molecular weight of the polymer.[6,7] The theory may be used as a basis for satisfactorily deriving empirical parameters to characterize the thermodynamic properties of the polymer solution. Investigation[5-12] of the ucst and lcst in the polymer solutions has been of great interest as a practical means of characterizing polymer solutions and of elucidating thermodynamic and conformational properties of macromolecules.

The Patterson[13-16] and Flory[17-19] theories of polymer solution thermodynamics lead to essentially the same expression for χ_1 as a function of temperature

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

The ν^2 parameter is related to the cohesive energy and segment size of the solution components, while the τ parameter reflects the free volume change, which occurs in mixing the dense polymer with the relatively expanded solvent. The quantity $-U_1$ is the energy of vaporization of the solvent $C_{p,1}$ is its configurational heat capacity, and R is the gas constant. The τ parameter is related to the reduced temperatures $\tilde{T}_i$ by

$$\tau = 1 - \tilde{T}_2/\tilde{T}_1 = 1 - T_1^*/T_2^* \quad (2)$$

where T_i^* is the characteristic temperature reduction parameter of the solvent(1) and polymer(2). The reduced temperature $\tilde{T}_i$ is defined by

$$\tilde{T}_i = T/T_i^* = \frac{c_i kT}{q_i \epsilon_i^*} \quad (3)$$

where q_i is the effective number of the contacts between individual components, ϵ_i^* is the cohesive energy between neighboring nonbonded segments and k is the Boltzmann constant. The new parameter (c_i/q_i), which is called a structural factor, is one-third the total number $(3c_i)$ of external degrees of freedom per segment.

Patterson and Delmas[5] have derived an expression for χ_1 at the critical miscibility point by adopting a van der Waals model for volume dependence of the configurational energy of the liquid. At zero pressure it is given as a function of the reduced volume $\tilde{V}_1$ of the solvent by

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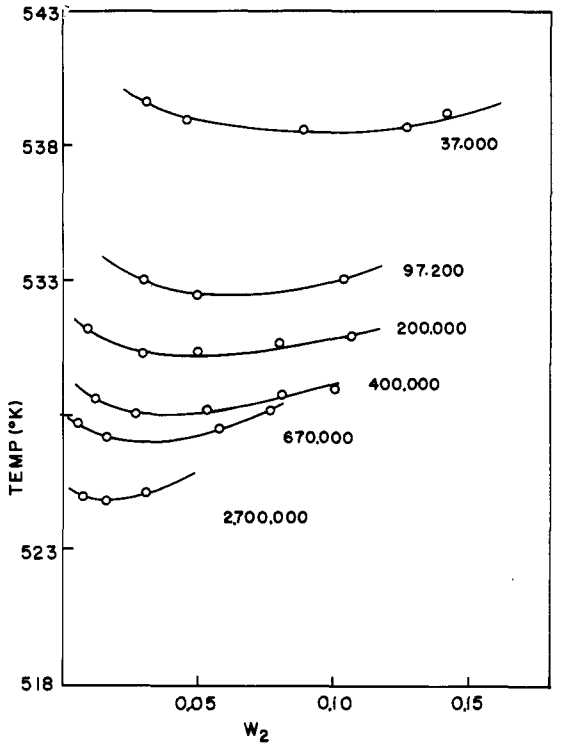

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene-benzene system for samples of indicated molecular weight.

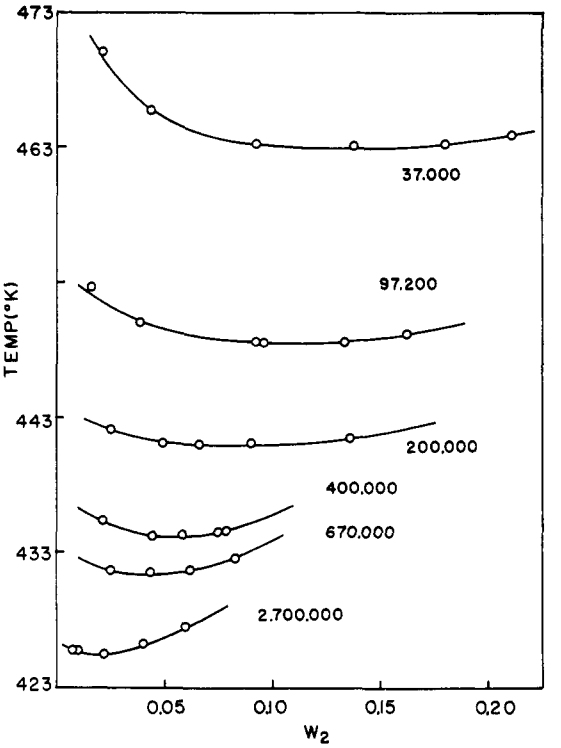

Figure 2. The (temperature, weight fraction) phase diagram for the polystyrene-methyl ethyl ketone system for samples of indicated molecular weight.

$$\chi_1(\text{crit}) = \frac{c_1\nu^2}{1 - \tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2[(4/3)\tilde{V}_1^{-1/3} - 1]} = (1/2)(1 + r^{-1/2})^2 \quad (4)$$

where r is the ratio of the molar volumes of the polymer and solvent and is taken to be independent of temperature. The present work was done to supply the phase diagram for polystyrene solutions in benzene, methyl ethyl ketone, and cyclopentane and also to evaluate solvent effects from the view point of the free volume in these polymer solutions. Benzene, which is well known as a good solvent for polystyrene,[2] and methyl ethyl ketone which has a low entropy and enthalpy of dilution at the ucst[2,20] were chosen because of a further indication of the general appearance of the lcst in good solvents.[3-5,7] Cyclopentane was selected from the view point of the appearance of the ucst in the neighborhood of room temperature and the lcst at temperatures less than 190°. In this temperature region the thermal degradation of polystyrene is not appreciable. The polystyrene-cyclopentane system will be one of the polymer-solvent systems which make it possible to investigate the excluded-volume effect in dilute polymer solutions over the temperature range containing the ucst and lcst.

Experimental Section

The polystyrene samples, except for 14b-2, were obtained from the Pressure Chemical Co. The samples are characterized by $M_w/M_n < 1.06$ for $M_w \times 10^{-4} = 3.7 \sim 40$ and $M_w/M_n < 1.10$ for $M_w \times 10^{-4} = 67$. The sample 14b-2 ($M_w \times 10^{-4} = 270$, $M_w/M_n < 1.10$) was obtained by solution fractionation[7] of the Pressure Chemical Co. Batch 14b ($M_w \times 10^{-4} = 200$, $M_w/M_n < 1.30$). Solvents were reagent grade and were further purified before use. Benzene, methyl ethyl ketone, and cyclopentane were dried over anhydrous potassium carbonate. The dried solvents were fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with stainless-steel helices. Several solutions in benzene, methyl ethyl ketone, and cyclopentane were prepared from each sample in the concentration range 1–25 wt % and flame sealed under dry nitrogen gas in 7-mm i.d. cylindrical cells.

Cloud points were optically determined with an accuracy ±0.01° in a water bath for the ucst and ±0.05° in a silicone oil bath for the lcst, as described in detail elsewhere.[7] For measurements at temperatures below 0°, cloud points were measured with

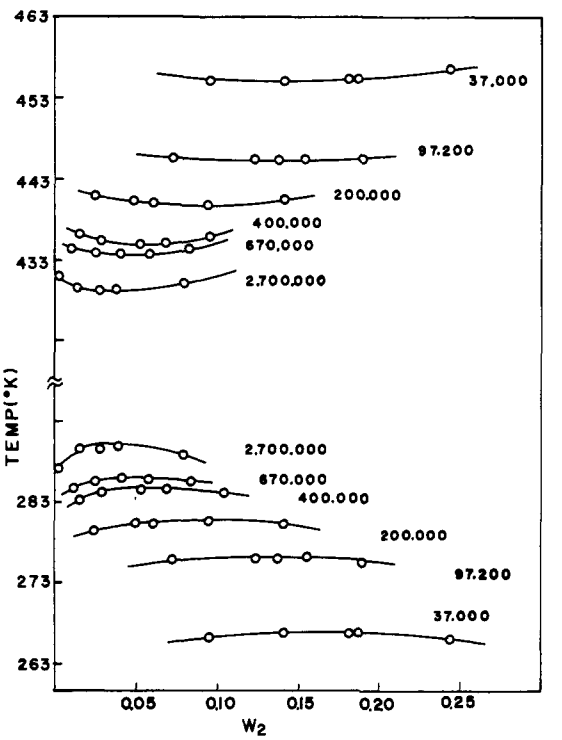

Figure 3. The (temperature, weight fraction) phase diagram for the polystyrene-cyclopentane system for samples of indicated molecular weight.

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Table I
Reduced Critical Temperatures for Polystyrene-Benzene System of Various Molecular Weight

Sample	$M_w \times 10^{-4}$	M_w/M_n	$r^{-1/2} \times 10^2$	lcst (°K)	$\tilde{T}_{1,l}$
7b	3.7	<1.06	5.10	538.7	0.1150
4a	9.72	<1.06	3.15	532.5	0.1137
1c	20.0	<1.06	2.19	530.5	0.1132
3a	40.0	<1.06	1.55	528.3	0.1128
13a	67.0	<1.10	1.19	527.0	0.1125
14b-2	270.0	<1.10	0.597	525.0	0.1121

Table II
Reduced Critical Temperatures for Polystyrene-Methyl Ethyl Ketone System of Various Molecular Weights

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	lcst (°K)	$\tilde{T}_{1,l}$
7b	3.7	5.12	463.2	0.1019
4a	9.72	3.16	448.8	0.09872
1c	20.0	2.20	441.1	0.09703
3a	40.0	1.56	434.5	0.09558
13a	67.0	1.20	431.8	0.09498
14b-2	270.0	0.600	425.7	0.09364

Table III
Reduced Critical Temperatures for Polystyrene-Cyclopentane System of Various Molecular Weights

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	ucst (°K)	$\tilde{T}_{1,u}$	lcst (°K)	$\tilde{T}_{1,l}$
7b	3.7	5.25	267.0	0.05940	455.3	0.1013
4a	9.72	3.24	276.2	0.06147	445.5	0.09912
1c	20.9	2.26	280.9	0.06249	440.0	0.09790
3a	40.0	1.60	284.7	0.06334	435.4	0.09687
13a	67.0	1.23	285.9	0.06361	433.8	0.09652
14b-2	270.0	0.615	289.9	0.06451	429.5	0.09556

an accuracy ±0.03° by the aid of the water-methanol-ice system. Upper and lower critical solution temperatures were estimated from the cloud-point curves.

Results

Figures 1-3 show the cloud point curves for the solutions of polystyrene in benzene, methyl ethyl ketone, and cyclopentane. The values of the ucst and lcst for these systems are compiled in Tables I-III. Errors in the lcst caused by the thermal degradation of the polystyrenes are +0.2-0.7° for benzene solutions, +0.2-0.8° for methyl ethyl ketone solutions, and +0.2-0.4° for cyclopentane solutions depending on the molecular weight of the samples. The displacement of the critical temperature for the lcst by the pressure was estimated to be as low as −0.1 to −0.3°.[4,21]

Figures 4 and 5 show the molecular weight dependence of the reduced temperatures $\tilde{T}_1$ for the systems of polystyrene in benzene, methyl ethyl ketone, and cyclopentane. The $\tilde{T}_1$ is related to $\tilde{V}_1$ through

$$\tilde{T}_1 = \tilde{V}_1^{-1}(1 - \tilde{V}_1^{-1/3}) \quad (5)$$

The reduced volume $\tilde{V}_1$ is associated with the thermal expansion coefficient α_1 of the solvent and defined by

$$\tilde{V}_1 = \left[\frac{\alpha_1 T}{3(1 + \alpha_1 T)} + 1\right]^3 \quad (6)$$

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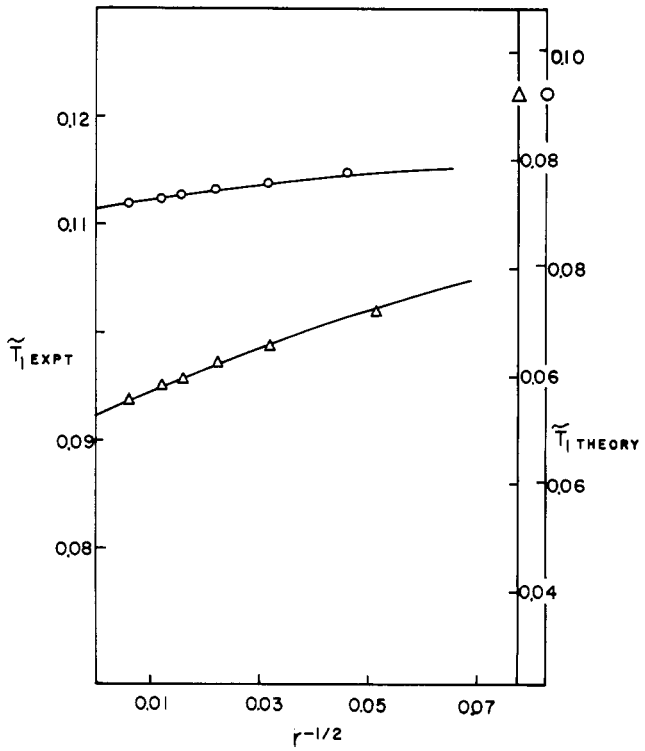

Figure 4. Comparison of experimental reduced temperatures $\tilde{T}_1$ with theoretical curves of eq 4 for the polystyrene-benzene system (○) and polystyrene-methyl ethyl ketone system (△).

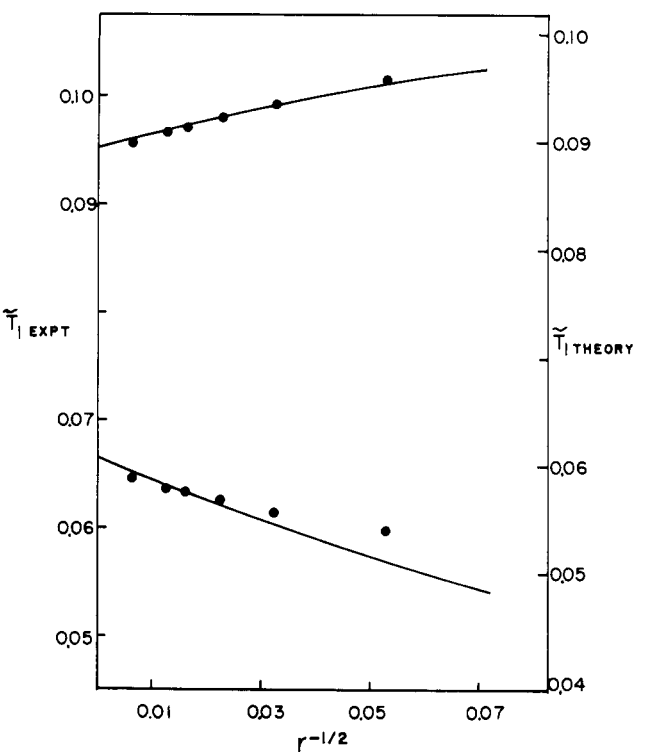

Figure 5. Comparison of experimental reduced temperatures $\tilde{T}_1$ with theoretical curves of eq 4 for the polystyrene-cyclopentane system.

Values of the characteristic temperature reduction parameter for the polystyrene and solvents were taken from literature.[5] The procedure of the analysis for $\tilde{T}_1$ was described elsewhere.[7]

Discussion

The cloud-point curves for the ucst and lcst in the poly-

Table IV
Parameters of the Systems

System	Flory's Parameters				Relative Values of the ν^2 and τ^2 (eq 4)			
					At θ_u		At θ_l	
	θ_u (°K)	θ_l (°K)	ψ_{1u}	ψ_{1l}	ν^2	τ^2	ν^2	τ^2
Polystyrene–benzene		523		−1.79			0[a]	0.50
Polystyrene–methyl ethyl ketone		422		−0.592			0[a]	0.50
Polystyrene–cyclopentane	293	427	0.548	−0.858	0.285	0.215	0.155	0.345

[a] Assumed value.

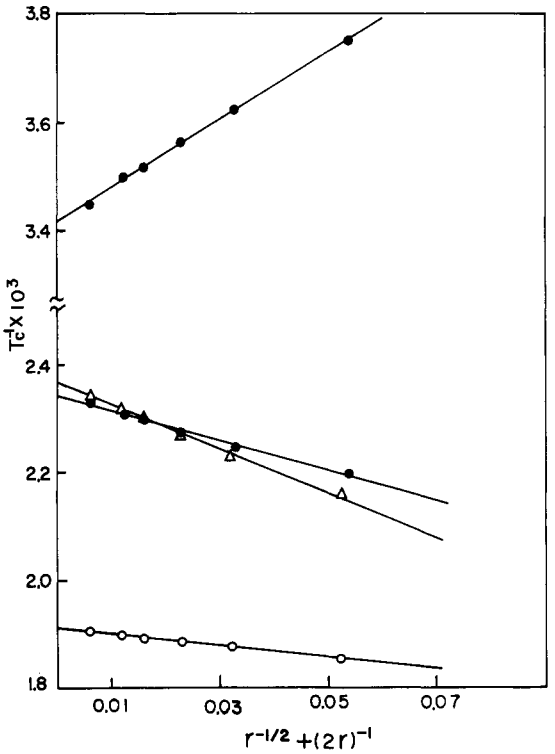

Figure 6. The Shultz-Flory plot of the reciprocal critical solution temperature against $r^{-1/2} + (2r)^{-1}$ for the systems: (a) polystyrene-benzene (○), (b) polystyrene-methyl ethyl ketone (△), and (c) polystyrene-cyclopentane (●).

styrene-cyclopentane system appear essentially in the form of mirror images. The shapes of the cloud-point curves for the ucst and lcst gradually sharpen and become more asymmetric with increasing molecular weight of the polymer, while the cloud-point curves are relatively flat in the neighborhood of their maximum or minimum points. The difference in temperature of the maximum or minimum point from the critical temperature should be quite small for solutions of polystyrene with narrow molecular weight distribution.[1]

The relation proposed by Flory assuming χ independent of concentration can be written as[2]

$$1/T_c = 1/\theta[1 + 1/\psi_1(r^{-1/2} + (2r)^{-1})] \qquad (7)$$

where ψ_1 is the entropy parameter. The molecular weight dependence of the ucst and lcst is shown in Figure 6 expressing the Shultz-Flory plot. Linearity is observed for polystyrene in benzene and in cyclopentane within experimental error, while nonlinearity is observed for polystyrene in methyl ethyl ketone. The maximum deviation from an approximate straight line for the polystyrene-methyl ethyl ketone system is estimated as large as 2° and is beyond experimental error. Values of θ and ψ_1 are summarized in Table IV. The θ and ψ_1 with the subscript u are for the ucst with subscript l for the lcst. The values of θ_l and ψ_{1l} for polystyrene in methyl ethyl ketone are estimated by assuming approximate linearity. There has been no consideration of a concentration dependence of χ. It is recognized that these ψ_{1u} and ψ_{1l} would be different if the concentration dependence of the χ parameter were taken into account.[1,9,12] The flat shape of the cloud-point curves in these systems indicates that there is some concentration dependence of this parameter,[9] and the predicted molecular weight dependence of the critical solution temperatures would be somewhat different if it were taken into account.

The variation of $\tilde{T}_1$ with $r^{-1/2}$, which reflects the dependence of the free volume of the solvent liquid on the molecular weight of the polymer, are 0.080 for solutions of polystyrene in benzene, 0.188 in methyl ethyl ketone, and 0.120 and −0.106 in cyclopentane. Positive values of $(d\tilde{T}_1/dr^{-1/2})$ correspond to the lcst and the negative value to the ucst. Our value for the polystyrene-benzene system is considerably lower than the value of 0.197 reported by Delmas-Patterson.[5] Theoretical curves for the molecular weight dependence of the $\tilde{T}_1$ in Figures 4 and 5 were determined through the procedure described elsewhere.[7] Parameters c_1 and ν^2 estimated from this work and previous work[7] and the parameters τ^2 and T_1^* are collected in Table V. A shift of temperature is required to fit the theoretical curves to the experimental points in each system. The temperature shifts are 109° for solutions of polystyrene in benzene, 164° in methyl ethyl ketone, and 27° in cyclopentane. The effect of free volume on the χ_1(crit) is estimated from a comparison of the relative values of the first (ν^2) and second (τ^2) terms in eq 4 at the θ_u and θ_l. In the polystyrene-benzene and polystyrene-methyl ethyl ketone systems the first term of χ_1(crit) is assumed to be negligibly small compared to the second free volume term. These values are listed in Table IV. Values of $\tilde{T}_1$ at infinite molecular weight of the polymer are 0.1115 for the lcst in benzene, 0.0925 for the lcst in methyl ethyl ketone, and 0.0950 and 0.0650 for the lcst and ucst in cyclopentane, respectively.

In the Prigogine theory,[5,13] ν^2 and τ are characterized by three parameters, which reflect the difference between polymer and solvent from the viewpoint, respectively, of segmental cohesive energies (ϵ^*), and of segmental sizes (r^*), and structural factors (c/q)

$$\begin{aligned} \delta &= \epsilon_{22}^*/\epsilon_{11}^* - 1 \\ \rho &= r_{22}^*/r_{11}^* - 1 \\ -\lambda &= \frac{c_2/q_2}{c_1/q_1} - 1 \end{aligned} \qquad (8)$$

Table V
Parameters of the Systems

System	T_1* (deg)	c_1	τ^2	$10^3\,\nu^2$	$c_1\tau^2$	$c_1\nu^2$
Polystyrene-benzene	4685	1.23	0.122	0[a]	0.150	0[a]
Polystyrene-toluene[b]	4979	1.57	0.095	0[a]	0.150	0[a]
Polystyrene-methyl ethyl ketone	4546	1.76	0.136	0[a]	0.240	0[a]
Polystyrene-cyclopentane	4494	0.706	0.142	31.2	0.100	0.022
Polystyrene-cyclohexane[b]	4720	1.01	0.119	15.9	0.120	0.016
Polystyrene-methylcyclohexane[b]	4870	1.14	0.105	15.8	0.120	0.018

[a] Assumed value. [b] From ref 7.

Assuming the geometric mean rule for the contact energy

$$\tau \simeq \delta + \lambda$$
$$\nu^2 \simeq \delta^2/4 + 9\rho^2 \qquad (9)$$

The τ and ν^2 are correlated through the δ parameter. In mixtures of polymer and solvent for which the ν^2 parameter is assumed to be zero, the τ parameter directly reflects the structural factor. Values of pairs of $c_1\nu^2$ and $c_1\tau^2$ used to fit the theoretical curves to the experimental points in Figures 4 and 5 are given in Table V. Values obtained from the previous work[7] are also included. One-third of the external degrees of freedom of the solvent expressed by c_1 seems to be the controlling factor for the χ_1(crit) through $c_1\tau^2$ irrespective of τ^2 in the six polystyrene solutions. The value of c_1 is largest in the polystyrene-methyl ethyl ketone system and smallest in the polystyrene-cyclopentane system in these polystyrene solutions. The value of the ν^2 parameter for polystyrene in cyclohexane is almost equal to the value in methylcyclohexane and is about one half the value in cyclopentane.

In this work we conclude that the phase separation behavior of the nonpolar polymer solutions and also the solvent effects on the ucst and lcst are adequately described by Patterson-Delmas theory of corresponding states and the Flory model with the Flory-Huggins critical value of χ_1. The polystyrene-cyclopentane system with the ucst and lcst in a convenient temperature range is one of the most suitable ones for studying the excluded-volume effect in dilute polymer solutions.

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Inelastic Light Scattering Study of Macromolecular Reaction Kinetics. II. The Association Reaction $mA + nB \rightleftarrows pC$

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ABSTRACT: We present a study of the effect of chemical reactions on the spectrum of light scattered from macromolecular solutions. We employ the general formalism developed in paper I of this series using the matrix eigenvalue technique of Salsburg and coworkers and considering only diffusion and chemical reaction as processes perturbing local equilibrium. This paper considers the general reaction $mA + nB \rightleftarrows pC$, focusing on the special case where at least two of the diffusion coefficients of reactants and products are different, while their polarizabilities are identical. Numerical calculations have been made using plausible values of diffusion coefficients and reaction rates for macromolecular solutions for two special cases, $A + B \rightleftarrows C$ and $A + 144B \rightleftarrows C$. These indicate that macromolecular assembly reactions should measurably perturb inelastic light scattering spectra of polydisperse solutions due to differences in diffusion coefficients alone, providing a means of determining both equilibrium constants and kinetic rate constants for the reaction under investigation. Particularly favorable systems are those in which both of the reactants are small while the product is large. For the reaction $A + B \rightleftarrows C$, a system in which one of the reactants is large, while both the other reactant and the product are small, constitutes another favorable combination. And for the reaction $A + 144B \rightleftarrows C$, a large reactant combining with 144 smaller reactants to form a relatively small product would be a favorable system. In any case the ratio of the reciprocal reaction half-life to the spectral half-width due to diffusion should be ≥ 1.

A major theme in biophysical chemistry over the past few years has been the development of new methods for the study of structure and macromolecular assembly of subunit aggregates such as viruses, multimeric proteins, and enzyme-substrate complexes.[1-4] Inelastic light scattering has proven to be an accurate and rapid tool for the determination of diffusion coefficients of macromolecules, thereby yielding valuable information on biopolymer size

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