Upper and Lower Critical Solution Temperatures in Polystyrene Solutions

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ABSTRACT: Upper and lower critical solution temperatures have been determined for solutions of polystyrene in cyclohexane and methylcyclohexane and lower critical solution temperatures for the polystyrene–toluene system over the molecular weight range of $M_w \times 10^{-4} = 3.7$ to ~270. The Patterson–Delmas theory of corresponding states, based on the Prigogine theory, has been applied to the polystyrene solutions and found to afford semiquantitatively good prediction of the molecular weight dependence of their critical temperatures. Polystyrene solution in methylcyclohexane displays a smaller miscibility region than that of the polystyrene–cyclohexane system, as indicated by the relative positions of their upper and lower critical solution temperatures. The entropy parameter ψ_1 and Flory temperature Θ obtained from lower critical solution temperatures for the polystyrene–toluene system are -1.92 and 277°, respectively.

The role of free volumes or thermal expansions in explaining the lower critical solution temperature (lcst) of nonpolar polymer solutions has recently attracted considerable attention. The most interesting aspect of these results had been discovered by Freeman and Rowlinson.[1] Phase diagrams of polymer solutions are classified into two types by the shape of the cloud-point curve in the temperature–concentration plot. One is characterized by the existence of a maximum, which tends to move toward higher temperature and lower concentration with increasing molecular weight of the polymer. The upper critical solution temperature (ucst) for the solution of the polymer with very narrow molecular weight distribution is almost equivalent to the maximum temperature as a function of concentration. As is well known, the temperature of the maximum corresponding to the infinite molecular weight is the Θ or Flory temperature.[2] The other type of cloud-point curve, which lies at temperatures in the vicinity of the gas-liquid critical temperature of solvent, has a concave shape with a minimum. The minimum point tends to be displaced to lower temperature and lower concentration with an increase of the molecular weight of the polymer. The temperature of its minimum point is called the lower critical solution temperature.

Immiscibility occurs if the temperature of the polymer solution is raised above the lcst or lowered below the ucst. By increasing the molecular weight of the polymer, the ucst is raised and the lcst is lowered, thus shrinking the temperature region of complete miscibility. The two regions of miscibility are merged to give an "hourglass" shape in the polymer-poor solvent system in which the solvent has a much larger thermal expansion coefficient than that of the polymer, *e.g.*, polystyrene–acetone.[3] The present type of lcst should be distinguished from that of polar systems which are attributed to the existence of a special interaction, for example, the polyethylene glycol–water system.[4] Recently values of pairs of ucst and lcst have been reported for polystyrene,[5-7] primary and secondary cellulose acetate,[8] and polyisobutene solutions.[9,10] Since the existence of the ucst and lcst is a very widespread phenomenon in polymer solutions, the lcst should be generally expected in systems along with the ucst.[11,12] It is interesting that the ucst and lcst for polymer solutions are systematized by the recent theories of polymer solution thermodynamics, from which a new parameter namely the number of external degrees of freedom of the solvent molecule is derived.

The Prigogine[13,14] and Flory[15,16] theories of the polymer solution thermodynamics lead to essentially the same expression for χ_1 as a function of temperature

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

The ν^2 parameter is related to the difference of the cohesive energy and size between the solvent molecule (1) and the polymer segment (2). 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 reflects the free volume change, which occurs in mixing the dense polymer with the relatively expanded solvent, and is defined by

$$\tau = 1 - T_1^*/T_2^* \qquad (2)$$

where T_i^* is the characteristic temperature reduction parameter of the solvent (1) and polymer (2). The first term in eq 1 is positive and increases with a decrease of temperature. The second term, which is the structual contribution to χ_1, increases without limit as the temperature increases and brings about the phase separation at the lcst. This relation allows χ_1 to vary in parabolic curve with a minimum in a plot of χ_1 against temperature.

Patterson and Delmas[7] have derived an expression for χ_1 at the critical miscibility point by adopting a van der Waals model for the volume dependence of the configurational energy of the liquids. The use of this model is emphasized by Flory and collaborators.[15] In using a van der Waals model the configurational energy and heat capacity

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can be expressed in terms of the reduced volume $\tilde{V}_1$ of the solvent. At zero pressure χ_1(crit) is given by[7]

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

where $3c_1$ is the number of external degrees of freedom of the solvent molecule. χ_1(crit) can also be related to the molecular weight of the polymer through r, which is the ratio of the molar volumes of the polymer and solvent and is taken to be independent of temperature. The free volume of the component (1) is related to its reduced temperature $\tilde{T}$, which is derived from $\tilde{V}_1$ through

$$\tilde{T} = \tilde{V}_1^{-1}(1 - \tilde{V}_1^{-1/3}) = T/T_1^* \quad (4)$$

If the critical solution temperatures have been determined in a given polymer-solvent system over a wide range of molecular weight and the reduction parameters for the polymer and solvent are known, the reduced volume is calculated through the reduced temperature $\tilde{T}$. The variation of the critical solution temperatures with the molecular weight can be predicted from a suitable pair of parameters $c_1\nu^2$ and $c_1\tau^2$. As τ is calculated from the reduction parameters only in eq 2, the values of c_1 and ν^2 are estimated. The procedure is detailed later. The present work was done to supply three examples of phase diagrams for the solutions of polystyrene in cyclohexane, methylcyclohexane, and toluene.

We took into special account the molecular weight distribution of the polymer samples. If the polymer were completely monodisperse, the true ucst and lcst should correspond to the temperatures of the maximum and minimum points of the cloud-point curves, respectively. It was shown that polydispersity tends to displace the critical point to higher concentration depending on the polydispersity of the polymer sample.[17] Although the maximum or minimum points are not the critical points, the differences of the maximum and minimum points from the critical points should be quite small because of the small values of M_w/M_n for the six samples in this work.

Experimental Section

Polystyrene samples except for 14b-2 were obtained from the Pressure Chemical Co., Pittsburgh, Pa. The samples are characterized by $M_w/M_n < 1.06$ for $M_w \times 10^{-4} = 3.7$ to $\sim$40 and $M_w/M_n < 1.10$ for $M_w \times 10^{-4} = 67$. The sample designated by 14b-2 was obtained by the solution fractionation technique called coacervation fractionation. Batch 14b ($M_w \times 10^{-4} = 200$; $M_w/M_n < 1.30$) was fractionated into four fractions by keeping solution more dilute than 0.3 g/100 cm^3 of polystyrene in cyclohexane at a temperature a little lower than its cloud-point temperature. A fraction of $M_w \times 10^{-4} = 270$; $M_w/M_n < 1.10$ was used in this work. Solvents were reagent grade and were further purified before use. Cyclohexane was dried over anhydrous calcium chloride and then over silica gel. Methylcyclohexane and toluene were dried over anhydrous calcium chloride. The dried solvents were fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with stainless-steel helices.

Upper and lower critical solution temperatures were estimated from cloud-point curves. Several solutions in cyclohexane, methylcyclohexane, and toluene were prepared from each sample in the concentration range 1 to $\sim$25 wt % and flame sealed under dry nitrogen gas in 7-mm i.d. cylindrical cells. A glass sphere was inserted in each cell to stir the solution. The solutions were slowly cooled in a water bath controlled to ±0.01° for measurements of the ucst and cloud-point temperatures were determined as the temperature at which the pattern of a He-Ne laser beam passed through the cell gave a dramatic change,[18] which was observed at the cloud-point temperature for all of the solutions. The cloud-point temperature for the ucst was determined with an accuracy of ±0.01° by the aid of the pattern of the He-Ne laser beam. Determinations of the cloud-point curves for the lcst were carried out in a silicone oil bath with an accuracy of ±0.05°. Near the cloud point for the lcst the temperature of the bath was raised by 0.02 to $\sim$0.05° per min. After measurements of the precipitation temperature for the lcst, the thermal degradation of polystyrene was examined by the reproducibility of the precipitation temperature for the ucst. The thermal degradation of polystyrene in solvent was minimized by flame sealing after keeping polystyrene solutions under dry nitrogen gas. Errors caused by the thermal degradation are estimated as 0.2 to $\sim$1.0° depending on the molecular weight of the sample.

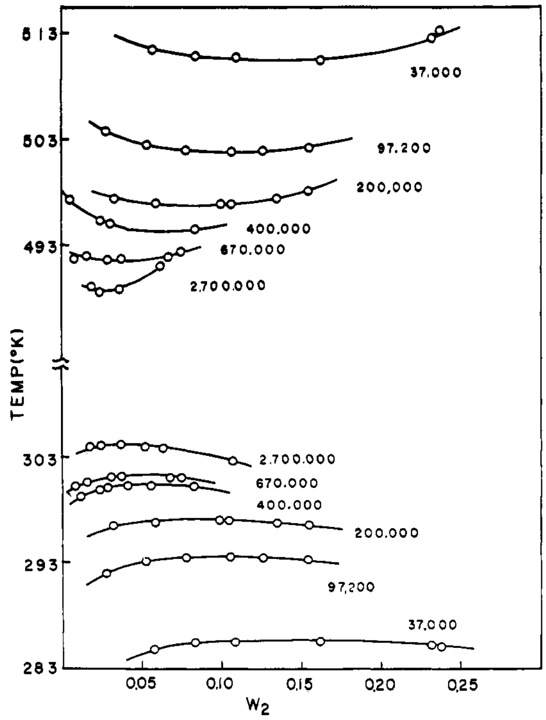

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene–cyclohexane system for samples of indicated molecular weight.

Results

Figure 1, 2, and 3 show the cloud-point curves for solutions of polystyrene in cyclohexane, methylcyclohexane, and toluene. The ucst is raised and the lcst lowered by increasing the molecular weight, although the hourglass phase diagram does not appear in the present work. Values of the ucst and lcst for these systems are compiled in Tables I to III. Values of the reduced critical temperature $\tilde{T}$ are calculated from T/T_1^*. T is the measured critical temperature and T_1^* is calculated from the reduced volume $\tilde{V}_1$ by an use of eq 4, in which $\tilde{V}_1$ is derived from the expression

$$\tilde{V}_1 = \left[\frac{\alpha_1 T}{3(1 + \alpha_1 T)} + 1\right]^3 \quad (5)$$

where α_1 is the thermal expansion coefficient of the solvent. A value $T_2^* = 7205$ for polystyrene[7] was used, while the values of T_1^* for solvents were taken from the litera-

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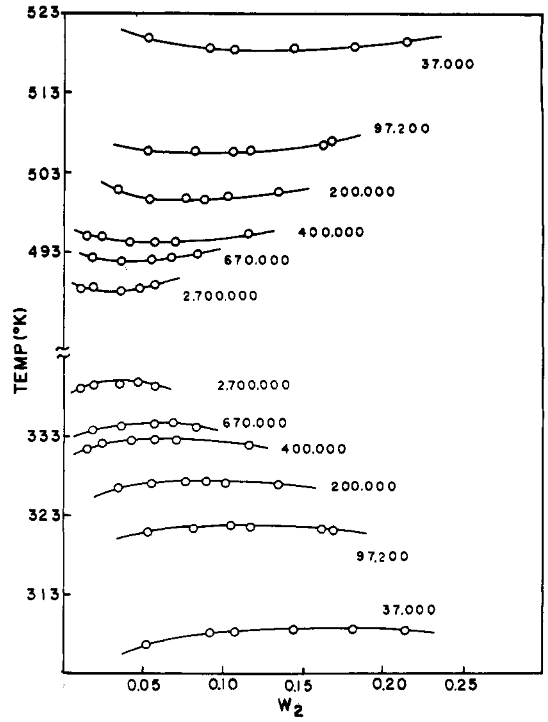

Figure 2. The (temperature, weight fraction) phase diagram for the polystyrene-methylcyclohexane system for samples of indicated molecular weight.

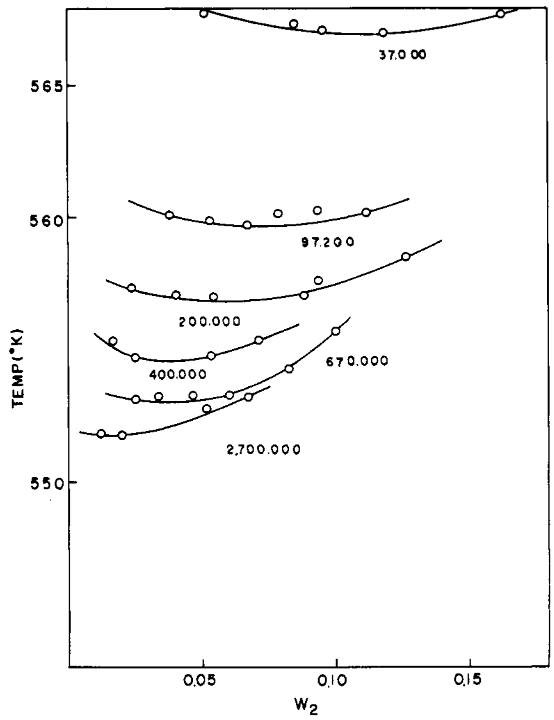

Figure 3. The (temperature, weight fraction) phase diagram for the polystyrene-toluene system for samples of indicated molecular weight.

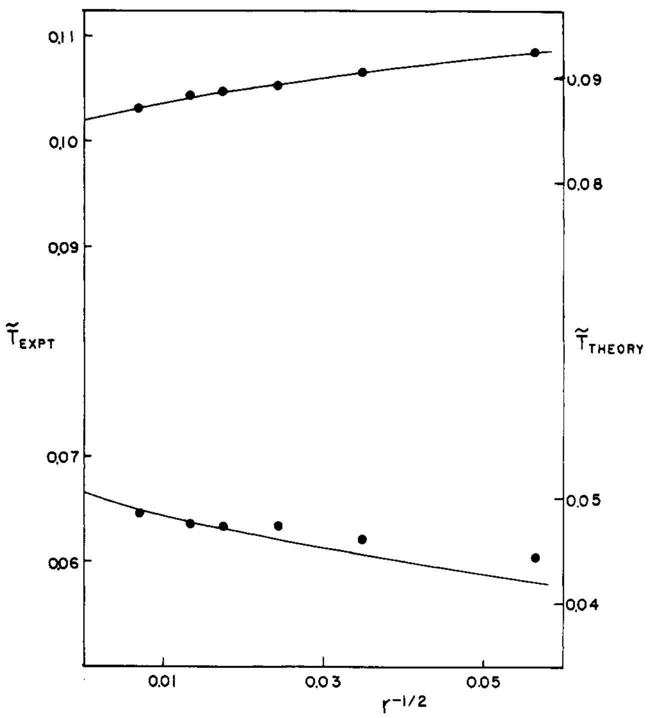

Figure 4. Comparison of experimental reduced temperatures $\tilde{T}$ with theoretical curves of eq 3 for the polystyrene-cyclohexane system.

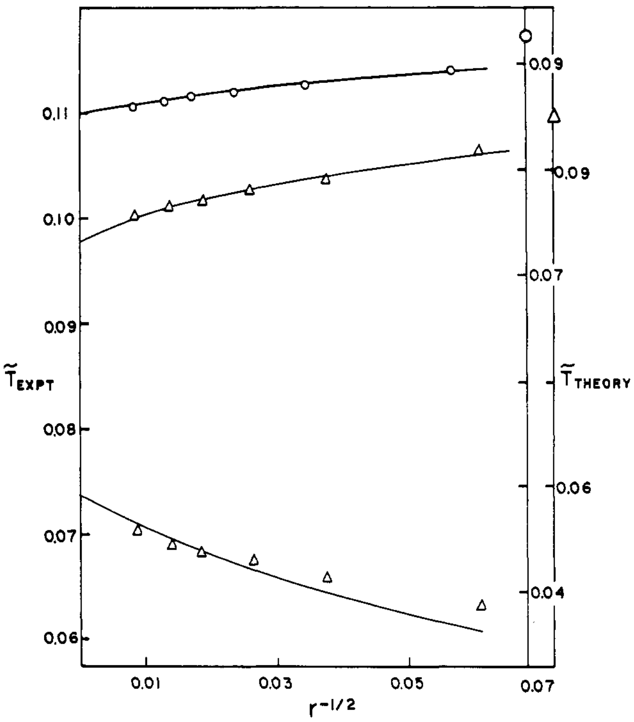

Figure 5. Comparison of experimental reduced temperatures $\tilde{T}$ with theoretical curves of eq 3 for the polystyrene-methylcyclohexane system (△), and polystyrene-toluene system (○).

ture.[7,19,20] Values of the experimental reduced temperature $\tilde{T}$ are plotted against $r^{-1/2}$ in Figures 4 and 5.

The theoretical curves in Figures 4 and 5 are derived using a suitable pairs of the parameters $c_1\nu^2$ and $c_1\tau^2$. For evaluation of these parameters we resort to two graphs, one being a $\tilde{T}$ *vs.* $\tilde{V}_1^{-1/3}$ plot in accord with eq 4 and the other being plots of the ν^2 and τ^2 terms in eq 3 against the same variable $\tilde{V}_1^{-1/3}$. The variable ranges for $\tilde{V}_1^{-1/3}$, $c_1\nu^2$, and $c_1\tau^2$ are obtained from the literature.[7] In the latter graph the sum of the two terms at an arbitrary pair of $c_1\nu^2$ and $c_1\tau^2$ is equal to χ_1 and also to the right side of eq 3. The χ_1 *vs.* $\tilde{V}_1^{-1/3}$ plot determines the value of $\tilde{V}_1^{-1/3}$ for an arbitrary r, in other words the point at which the curve for χ_1 intersects the horizontal line determined by a given r value on the right-hand side of eq 3 gives the value

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Table I
Reduced Critical Temperatures for Polystyrene–Cyclohexane System of Various Molecular Weights

Sample	$M_w \times 10^{-4}$	M_w/M_n	$r^{-1/2} \times 10^2$	ucst (°K)	$\tilde{T}_U$	lcst (°K)	$\tilde{T}_L$
7b	3.7	<1.06	5.64	285.6	0.06050	510.9	0.1082
4a	9.72	<1.06	3.49	293.5	0.06218	502.1	0.1064
1c	20.0	<1.06	2.43	297.0	0.06292	496.9	0.1053
3a	40.0	<1.06	1.72	300.3	0.06361	494.7	0.1048
13a	67.0	<1.10	1.33	301.1	0.06379	491.7	0.1042
14b-2	270.0	<1.10	0.66	304.2	0.06444	488.6	0.1035

Table II
Reduced Critical Temperatures for Polystyrene–Methylcyclohexane System of Various Molecular Weights

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	ucst (°K)	$\tilde{T}_U$	lcst (°K)	$\tilde{T}_L$
7b	3.7	6.11	309.7	0.06359	518.8	0.1065
4a	9.72	3.77	321.8	0.06607	505.9	0.1039
1c	20.0	2.63	327.4	0.06723	499.9	0.1027
3a	40.0	1.86	332.7	0.06831	494.6	0.1016
13a	67.0	1.44	334.5	0.06868	492.3	0.1011
14b-2	270.0	0.72	339.6	0.06972	488.4	0.1003

Table III
Reduced Critical Temperatures for Polystyrene–Toluene System of Various Molecular Weights

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	lcst (°K)	$\tilde{T}_L$
7b	3.7	5.59	567.2	0.1139
4a	9.72	3.45	559.9	0.1125
1c	20.0	2.41	557.2	0.1119
3a	40.0	1.70	554.9	0.1114
13a	67.0	1.31	553.1	0.1111
14b-2	270.0	0.65	552.0	0.1109

of $\tilde{V}_1^{-1/3}$ corresponding to r. In the $\tilde{T}$ vs. $\tilde{V}_1^{-1/3}$ plot $\tilde{T}$ is directly determined from $\tilde{V}_1^{-1/3}$. The curves shown fitted to the experimental results were obtained through the procedure just described.

Discussion

The molecular weight dependence of the ucst and lcst is usually described by a relation such as that proposed by Flory, which can be written as[2]

$$\frac{1}{T_c} = \frac{1}{\Theta}\left\{1 + \frac{1}{\psi_1}\left(\frac{1}{r^{1/2}} + \frac{1}{2r}\right)\right\} \tag{6}$$

where ψ_1 is the entropy parameter. Figure 6 shows that the data for solutions of polystyrene in cyclohexane, methylcyclohexane, and toluene are adequately represented by eq 6 within experimental error. Here we denote the Θ temperature and the ψ_1 parameter with the subscript U for the ucst to distinguish them from the parameters determined in the lower critical region, which shall be designated by Θ_L and ψ_{1L}. Values of Θ_U, Θ_L, ψ_{1U}, and ψ_{1L} are summarized in Table IV. It is recognized that the values of ψ_{1U} and ψ_{1L} listed therein would be different if the variation of the polymer–solvent interaction parameter with concentration were taken into account.[3,17] The thermodynamic conditions for the lcst are that the heat of dilution is exothermic and the excess entropy of dilution is negative. It was confirmed that the Θ_L point, like the Θ_U point, confers unperturbed dimensions on the polymer.[6] The difference of the Θ_L point from the vapor–liquid critical point of the solvent is 44° in the toluene, 67° in cyclohexane, and 88° in methylcyclohexane. The complete miscibility region of the polymer solution systems is given by the region between pairs of lines in Figure 6 or pairs of curves in Figures 4 and 5. The difference between Θ_U and Θ_L is about 180° in the polystyrene–cyclohexane system, and 140° in the polystyrene–methylcyclohexane system. On the other hand, the miscibility region is very large in the polystyrene–toluene system, which is the mixture of homologous polymer and solvent, $\nu^2 = 0$.

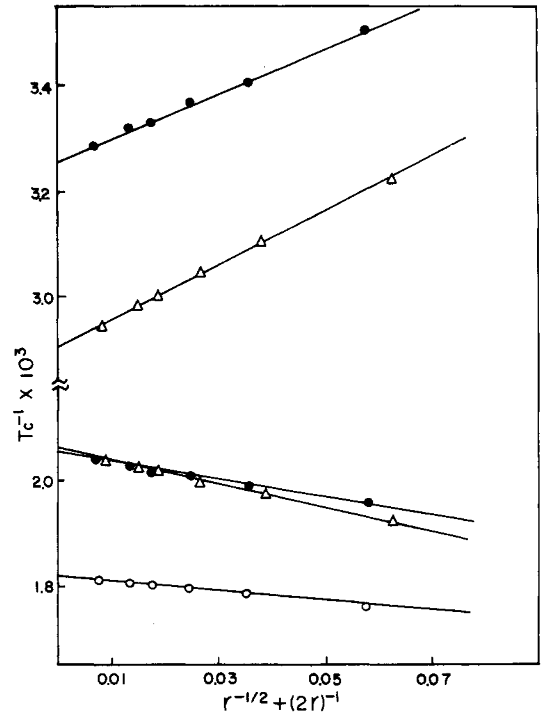

Figure 6. The Schultz–Flory plot of the reciprocal critical solution temperature against $r^{-1/2} + (2r)^{-1}$ for the systems: (a) polystyrene–cyclohexane (●), (b) polystyrene–methylcyclohexane (△), (c) polystyrene–toluene (○).

As shown in Figures 4 and 5, the variation of $\tilde{T}$ with $r^{-1/2}$ may be expressed linearly within experimental error. The slopes of $\tilde{T}$ against $r^{-1/2}$ are 0.093 and −0.076 in cyclohexane, 0.116 and −0.109 in methylcyclohexane, and 0.065 in toluene. Our values are considerably lower than the value of 0.173 for the polystyrene–toluene system and values of 0.105 and −0.065 for the polystyrene–cyclohexane system obtained by Delmas and Patterson.[7] Negative

Table IV
Parameters of the Systems

System	Flory's Parameter				Rel Values of the (ν^2) and (τ^2) Terms in Eq 3 at Θ Temp			
					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–cyclohexane	307	486	0.79	−1.19	0.255	0.245	0.125	0.375
Polystyrene–methylcyclohexane	344	484	0.56	−0.94	0.250	0.250	0.145	0.355
Polystyrene–toluene		550		−1.92			0[a]	0.50

[a] Assumed value.

Table V
Parameters of the Systems

System	T_1^* (deg)	c_1	τ^2	$10^3\,\nu^2$
Polystyrene–cyclohexane	4720	1.01	0.119	15.9
Polystyrene–methylcyclohexane	4870	1.14	0.105	15.8
Polystyrene–toluene	4979	1.57	0.095	0[a]

[a] Assumed value.

values of ($d\tilde{T}/dr^{-1/2}$) correspond to the ucst and positive values to the lcst. As the absolute value of the critical temperature or $\tilde{T}$ cannot be predicted by the theory, a shift of the temperature is necessary to fit the theoretical curve to the experimental points. For the polystyrene–toluene system this temperature shift is 110°, while shifts of 76 and 71° are required for cyclohexane and methylcyclohexane solutions, respectively. The experimental points for the ucst deviate slightly from the theoretical curves in the region of low molecular weight, while those for the lcst agree well with the theoretical curves over the molecular weight range covered in this work. Equation 3 predicts the χ_1 parameter at zero pressure, while the lcst's are obtained under the solution vapor pressure estimated as 3 to ~5 atm. As the effect of pressure on the lcst of the polyethvlene–pentane and polyisobutene–isopentane systems has been found to be 0.5 deg/atm, the values of the lcst corrected to the zero-pressure condition would be 1 to ~3° lower than those observed.[21,22] The thermal degradation of the polymer due to temperatures such as high as 200 to ~300° raised the precipitation temperature for the lcst by 0.2 to ~1.0° depending on the molecular weight. Since we are mainly interested in semiquantitative features of the phase separation, the somewhat compensating displacements of the critical temperatures by the pressure and thermal degradation should be of minor importance.

Values of T_1^*, c_1, τ^2, and ν^2 parameters adopted in fitting the theoretical curves to the experimental points are given in Table V. Values of pairs of $c_1\nu^2$ and $c_1\tau^2$ are (0.016, 0.120) for polystyrene–cyclohexane, (0.018, 0.120) for polystyrene–methylcyclohexane, and (0, 0.150) for polystyrene–toluene. In the polystyrene–toluene system $c_1\tau^2$ is determined from the reasonable assumed value of $\nu^2 = 0$. The experimental values of $c_1\nu^2$ are lower than the limiting values calculated from the equation[7]

$$c_1\nu^2 = 3/8[1/3 - (4/3\,c_1\tau^2)^{1/2} + c_1\tau^2] \qquad (7)$$

The unique feature of the system is that χ_1(crit) is formed by the structural term in $c_1\tau^2$ only. A value of $c_1\tau^2 = 0.151$ obtained from the data at 20° for the polyisobutene–methylcyclohexane system[20] is almost equal to the value for the polystyrene–toluene system. The τ^2 value, which reflects directly the difference of the structure factor (c/q) of the polymer and the solvent due principally to the polymer chain connectivity, is smallest for the toluene solution. The parameter q is related to the number of external intermolecular contacts. The value of $c_1\nu^2$ for the polystyrene–methylcyclohexane system is a little larger than that for the polystyrene–cyclohexane system, while the values of $c_1\tau^2$ are almost the same. The difference in the $c_1\nu^2$ is attributed to c_1, not ν^2. The contribution of c_1 is dominant for comparison of the $c_1\tau^2$ values and the τ^2 value for the methylcyclohexane solution is smaller than that for the cyclohexane solution.

Useful information is derived from a comparison of the relative values of the first (ν^2) and second (τ^2) terms expressing χ_1(crit) at Θ_U and Θ_L, where the entropy parameter ψ_1 is equal to the enthalpy parameter κ_1 in the Flory theory.[2] The relative values at Θ_U and Θ_L are given in Table IV. Those relative values suggest that the term (τ^2) contributes more to χ_1(crit) as compared with the term (ν^2) at temperatures higher than Θ_U, while at Θ_U the two terms makes almost equal contributions to χ_1(crit). We may emphasize that phase separation appears in the region of the ucst and lcst in any nonpolar polymer solution and that the free volume or the thermal expansion plays an important role in the case of polymer solutions. We conclude that the Prigogine corresponding state theory and the Flory model with the Flory–Huggins critical value of χ_1 give a semiquantitative prediction of the phase separation behavior in the nonpolar polymer solution.

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