Upper and Lower Critical Solution Temperatures in Polystyrene Solutions. III. Temperature Dependence of the χ_1 Parameter

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ABSTRACT: Upper and lower critical solution temperatures have been determined for solutions of polystyrene in methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, isobutyl acetate, and isoamyl acetate over the molecular weight range of $M_w \times 10^{-4} = 1.0$ to ~270. The temperature dependence of the χ_1 parameter for the polystyrene solutions has been estimated by an application of the Patterson-Delmas theory of corresponding state to the upper and lower critical solution temperatures. The region of complete miscibility between the upper and lower critical solution temperatures increases with the chain length of the solvents for solutions of a series of *n*-acetates and isoacetates. An application of the Flory theory for the polymer solution thermodynamics to the polystyrene-cyclohexane system affords a quantitative agreement with the Patterson theory for the expression of temperature dependence of χ_1. Deviation from linearity in the Shultz-Flory plot is found for solutions of polystyrene in methyl, ethyl, and isopropyl acetate.

Recently much attention has been given to the lower critical solution temperatures (lcst) observed to be of general occurrence in polymer solutions and the negative (exothermic) heats of mixing and the negative volumes of mixing frequently found for nonpolar polymer solutions. Theoretical progress from the viewpoint of the corresponding state law[1] has been made by Patterson *et al.*[2-7] and Flory *et al.*[8-14] The successful prediction of the lcst and the upper critical solution temperature (ucst) and their dependence on the molecular weight of polymer by the recent theories of polymer solution thermodynamics indicated the importance of the role of "free volume" or "equation of state" effects in the solution.[4,7,15-18] The concentration dependence of the χ parameter has been adequately explained by the Flory theory.[12-14] The χ_1-temperature curve, which is represented by a parabolic curve with a minimum, estimated from the experimental critical solution temperatures by adopting the Patterson theory has explained well a correlation with the temperature dependence of polymer chain dimensions.[19] The polymer chain dimension attains a maximum in the vicinity of the minimum of χ_1, while the chain dimensions at the Θ temperatures for the ucst and lcst are almost the same. A similar phase separation behavior of a pair of the ucst and lcst for simple liquid mixtures has been observed by Davenport *et al.*[20] and van Konynenburg[21] in the methane-hydrocarbon systems. It is suggested that the chain connectivity of one component in a binary mixture such as polymer solution plays an important role in causing occurrence of the lcst in the vicinity of the gas-liquid critical temperature of the other component.

Investigations of phase separation behavior of a pair of ucst and lcst in polymer solutions gives useful information on fundamental aspects of solution such as the dependence of the region of immiscibility on temperature and concentration. The temperature dependence of χ_1, which is directly related to the thermodynamic properties of polymer solutions, is also estimated from the critical solution temperatures with the aid of the newer theories. The present work was done to supply phase diagrams for solutions of polystyrene in methyl, ethyl, *n*-propyl, isopropyl, isobutyl, and isoamyl acetate and to examine the effect of the chain length in a series of *n*-acetates and isoacetates on the miscibility region of polymer in solvent with the aid of the Patterson theory. We also apply the Flory theory to the results of the polystyrene-cyclohexane system in previous work.[17]

Experimental Section

The polystyrene samples of this work were obtained from the Pressure Chemical Co. and are characterized by $M_w/M_n < 1.06$ for $M_w \times 10^{-4} = 1.0$ to ~20 and $M_w/M_n < 1.15$ for $M_w \times 10^{-4} = 67$. The sample 14b-2 was obtained by the solution fractionation described elsewhere[17] and is characterized by $M_w \times 10^{-4} = 270$ and $M_w/M_n < 1.10$. Solvents were reagent grade and further purified before use. Methyl acetate was treated with phosphorus pentoxide and then fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with stainless steel helices. The middle fraction was treated again with phosphorus pentoxide and redistilled. Ethyl, *n*-propyl, isopropyl, isobutyl, and isoamyl acetate were treated with phosphorus pentoxide and fractionally distilled in the same column. No cloudiness was observed near the freezing point for these solvents. The solvents were pure according to gas chromatography. Several solutions in a series of *n*-acetates and of isoacetates were prepared from each polymer sample in the concentration range of 0.5 to ~30 wt % and flame sealed under dry nitrogen gas in 7-mm i.d. cylindrical cells.

Cloud points were determined optically[17] to an accuracy of ±0.3° in an ethanol bath for the ucst in the low-temperature range of −30 to ~−90° and ±0.02° in the ethanol bath or a water bath for the ucst of the range of −10 to ~+40°, and ±0.05° in a silicone oil bath for the lcst. The liquid thermometer used for measurements of cloud point temperatures of −30 to ~−90° was calibrated by the freezing point (fp) of nine pure solvents including carbon tetrachloride (fp −23.0°), 1,2-dichloroethane (−35.9°), *n*-nonane (−53.5°), trichloroethylene (−86.4°), and *n*-heptane (−90.6°). The ethanol bath for measurements of cloud points appearing at low temperatures was cooled very slowly by thermal coupling with a liquid-nitrogen bath. The ucst and lcst for the solutions were determined from diagrams of the cloud-point temperature versus concentration plot. Although the maximum and minimum points of the cloud-point curves are not the true critical points, the difference 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.[22] After measurements of the cloud-point temperatures for the lcst, the thermal degradation of polystyrene was examined by reproducibility of the cloud-point temperature for the ucst. Errors caused by thermal degradation for determination of the lcst are estimated to be 0.5 to ~2.5° depending on the molecular weight of the samples for ethyl, *n*-propyl, isobutyl, and isoamyl acetate solutions, while none was observed in methyl and isopropyl acetate solutions.

Results

Typical cloud point curves for the ucst and lcst of polystyrene solutions in *n*-propyl and isopropyl acetate over the low temperature range of −30 to ~−90° are shown in Figures 1 and 2. The cloud-point curves for the ucst in the polystyrene-*n*-propyl acetate system for the sample 7b and in the polystyrene-isopropyl acetate system for the sample 8b were not observed at temperatures higher than the freezing point of the solvents. The values of the ucst and lcst for all systems reported are compiled in Tables I-VI. The cloud-point curves for the lcst of the methyl acetate system are almost the same as those reported by

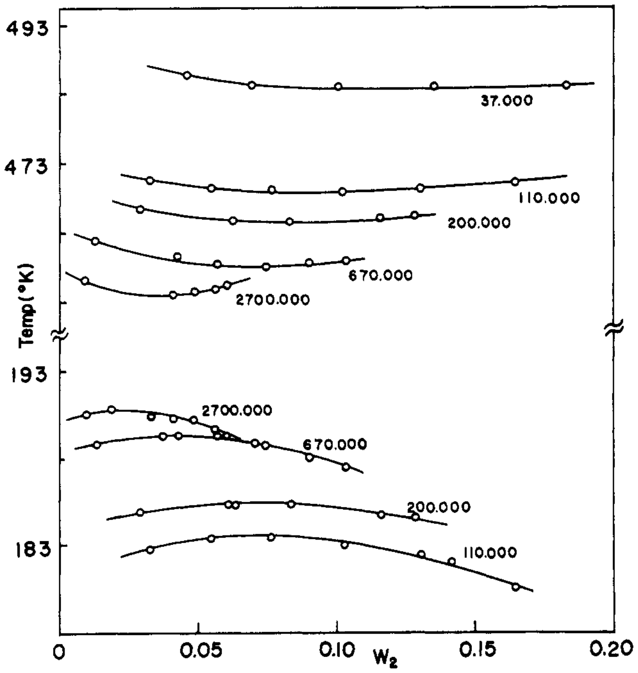

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene-*n*-propyl acetate system for samples of indicated molecular weight.

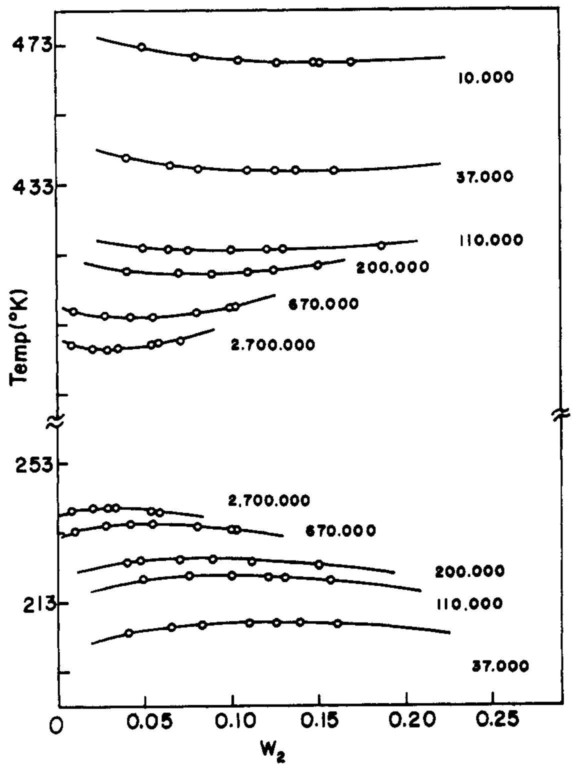

Figure 2. The (temperature, weight fraction) phase diagram for the polystyrene-isopropyl acetate system for samples of indicated molecular weight.

Rowlinson *et al.*[23] and Patterson *et al.*[4] while the maximum temperatures for the ucst are higher than those of Patterson *et al.* by 8°.

The relation proposed by Flory assuming χ independent of concentration is expressed by[24]

$$1/T_c = 1/\theta\{1 + 1/\psi_1(r^{-1/2} + (2r)^{-1})\} \quad (1)$$

where Θ is the Flory temperature and ψ_1 is the entropy parameter. The molecular weight dependence of the ucst and lcst is shown in Figures 3 and 4 in the form of the Shultz-Flory plot. Linearity is observed to the ucst and lcst for the solutions of polystyrene in *n*-propyl acetate, isobutyl acetate, and isoamyl acetate, while the tendency of deviation of experimental points from linearity is ob-

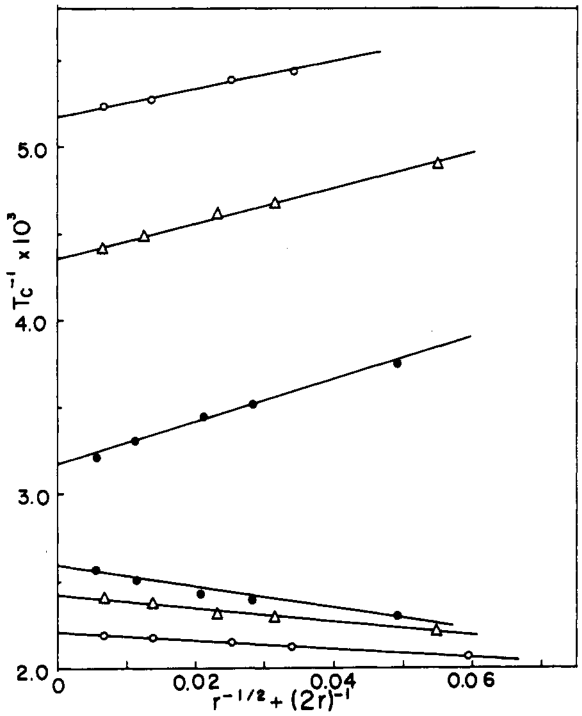

Figure 3. The Shultz-Flory plot of the reciprocal critical solution temperature against $r^{-1/2} + (2r)^{-1}$ for the systems: (a) polystyrene-methyl acetate (●), (b) polystyrene-ethyl acetate (△), (c) polystyrene-*n*-propyl acetate (○).

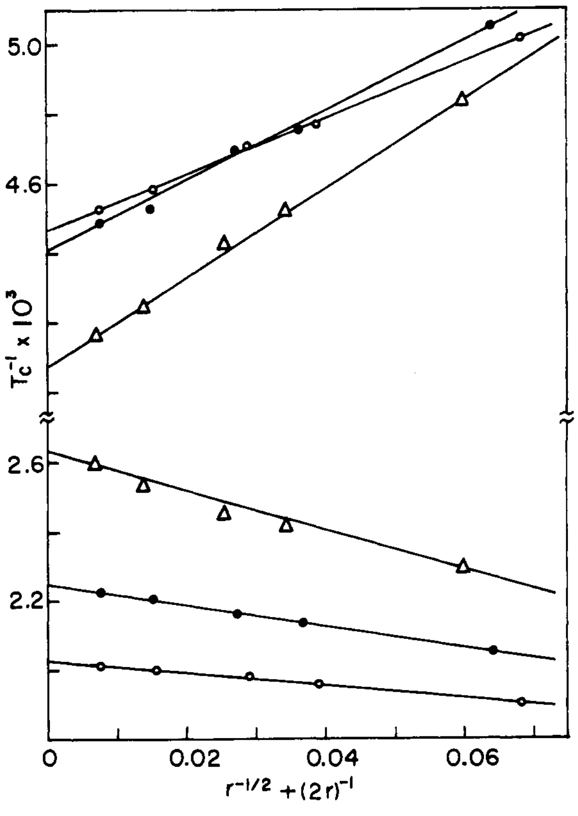

Figure 4. The Shultz-Flory plot of the reciprocal critical solution temperature against $r^{-1/2} + (2r)^{-1}$ for the systems: (a) polystyrene-isopropyl acetate (△), (b) polystyrene-isobutyl acetate (●), (c) polystyrene-isoamyl acetate (○).

Table I
Reduced Critical Temperatures for the Polystyrene–Methyl Acetate System of Various Molecular Weight

Sample	$M_w \times 10^{-4}$	M_w/M_n	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
7b	3.7	<1.06	4.79	266.6	6.049	434.0	9.848
4b	11.0	<1.06	2.78	284.2	6.449	415.7	9.433
1c	20.0	<1.06	2.06	289.7	6.574	409.9	9.301
13a	67.0	<1.15	1.13	301.5	6.841	398.4	9.040
14b-2	270.0	<1.10	0.561	311.0	7.057	389.2	8.831

Table II
Reduced Critical Temperatures for the Polystyrene–Ethyl Acetate System of Various Molecular Weight

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
7b	3.7	5.35	204.1	4.567	451.0	10.09
4b	11.0	3.11	213.9	4.786	435.4	9.743
1c	20.0	2.30	216.5	4.844	430.6	9.635
13a	67.0	1.26	222.9	4.988	421.4	9.429
14b-2	270.0	0.627	226.5	5.068	415.7	9.302

Table III
Reduced Critical Temperatures for the Polystyrene–*n*-Propyl Acetate System of Various Molecular Weight

Sample	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
7b	3.7	5.79			484.1	10.43
4b	11.0	3.36	183.7	3.959	469.0	10.11
1c	20.0	2.49	185.5	3.998	464.8	10.02
13a	67.0	1.36	189.6	4.086	458.2	9.875
14b-2	270.0	0.678	191.0	4.116	454.2	9.789

Table IV
Reduced Critical Temperatures for the Polystyrene–Isopropyl Acetate System of Various Molecular Weight

Sample	$M_w \times 10^{-4}$	M_w/M_n	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
8b	1.0	<1.06	11.2			468.5	9.638
7b	3.7	<1.06	5.83	206.6	4.251	436.7	8.985
4b	11.0	<1.06	3.38	220.9	4.545	414.2	8.522
1c	20.0	<1.06	2.51	225.6	4.642	407.7	8.388
13a	67.0	<1.15	1.37	235.5	4.845	395.2	8.131
14b-2	270.0	<1.10	0.682	240.3	4.944	385.9	7.940

served to the ucst and lcst for the solutions of polystyrene in methyl, ethyl, and to the lcst in isopropyl acetate. The smoothed curves fitted to experimental points are expressed by the convex upward for the ucst and convex downward for the lcst. The maximum quantities of deviation from approximate straight lines for the ucst and lcst in the methyl, ethyl, and isopropyl acetate systems are as large as (1.8°, 3.3°), (1.0°, 2.2°), and (—, 5.5°), which are beyond experimental errors. The Θ and ψ_1 for the methyl, ethyl, and isopropyl acetate systems are estimated by assuming approximate linearity. The Flory parameters are summarized in Table VII, in which the Θ_u and ψ_{1u} are for the ucst and the Θ_l and ψ_{1l} for the lcst. These Flory parameters obtained assuming χ independent of concentration would be somewhat different if the concentration dependence of χ were taken into account.[7,22,25] It is also indicated that the variation of the ucst with chain length of the solvents in a series of *n*-acetates is larger than that of the lcst, while in a series of isoacetates the variation of lcst is much larger than that of the ucst.

Values of the reduced critical solution temperatures $\tilde{T}_1$ are plotted against $r^{-1\ 2}$ in Figures 5 and 6, in which r is defined by the ratio of the molar volumes of the polymer and solvent and is taken to be independent of temperature. In an expression of Flory r is defined by the ratio of the molar volume reduction parameters (core volume), *i.e.*, V_2^*/V_1^*.[26] $\tilde{T}_1$ is calculated from the reduced volume $\tilde{V}_1$ by use of the equations[8]

$$\tilde{T}_1 = \tilde{V}_1^{-1}(1 - \tilde{V}_1^{-1/3}) = T/T_1^* \tag{2}$$

and

$$\tilde{V}_1 = \{\alpha_1 T/3(1 + \alpha_1 T) + 1\}^3 = V_1/V_1^* \tag{3}$$

T_1^* and V_1^* are the characteristic temperature and volume reduction parameters of the solvent and α_1 is the thermal expansion coefficient of the solvent. A theoretical analysis of the reduced critical solution temperature is described elsewhere.[17] The subscripts u and l for $\tilde{T}_1$ in Tables I-VI are for the ucst and lcst, respectively.

The departure from linearity in the Shultz-Flory plot observed for solutions of polystyrene in methyl, ethyl, and isopropyl acetate is beyond experimental error. In previous work similar nonlinearity was found for the lcst in the polystyrene-methyl ethyl ketone system.[18] Large deviations are observed for the polystyrene–isopropyl acetate system as compared to the polystyrene-methyl acetate system. The deviation from linearity in the Shultz-Flory plot is larger for the lcst than for the ucst for solutions of polystyrene in methyl acetate, ethyl acetate, isopropyl acetate, acetone,[7] methyl ethyl ketone,[18] and diethyl ether.[7] Exceptions are solutions of polystyrene in cyclopentane[18] and dimethoxymethane[7] with the gas–liquid critical temperature lower than 270°.

Discussions

The Patterson[2-4] and Flory[10-12] theories of polymer so-

Table V
Reduced Critical Temperatures for the Polystyrene–Isobutyl Acetate System of Various Molecular Weight

System	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
7b	3.7	6.21	197.9	4.188	487.4	10.32
4b	11.0	3.60	210.4	4.453	468.5	9.915
1c	20.0	2.67	212.9	4.506	463.3	9.805
13a	67.0	1.46	220.9	4.675	453.9	9.606
14b-2	270.0	0.727	223.1	4.722	449.0	9.502

Table VI
Reduced Critical Temperatures for the Polystyrene–Isoamyl Acetate System of Various Molecular Weight

System	$M_w \times 10^{-4}$	$r^{-1/2} \times 10^2$	Ucst (°K)	$\tilde{T}_{1,u} \times 10^2$	Lcst (°K)	$\tilde{T}_{1,l} \times 10^2$
7b	3.7	6.59	199.4	4.667	526.2	12.31
4b	11.0	3.82	210.1	4.917	510.1	11.94
1c	20.0	2.83	212.3	4.969	505.1	11.82
13a	67.0	1.55	218.2	5.106	499.2	11.68
14b-2	270.0	0.771	220.8	5.167	497.0	11.62

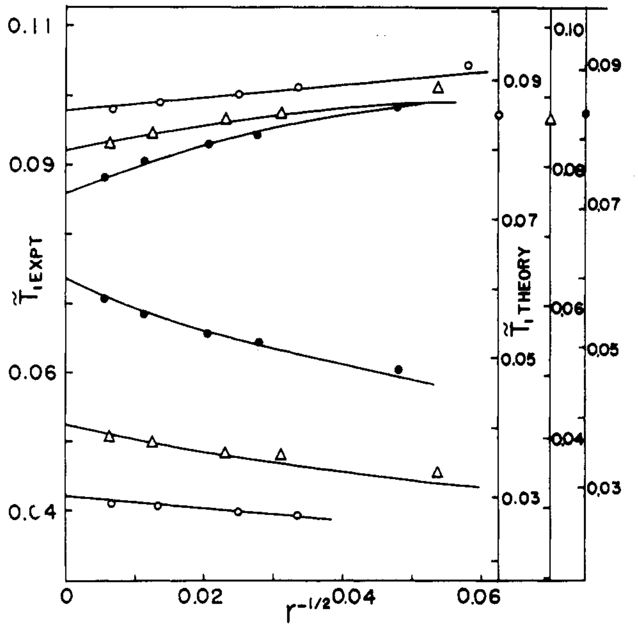

Figure 5. Comparison of experimental reduced temperatures $\tilde{T}_1$ with theoretical curves of eq 10 for the systems: (a) polystyrene-methyl acetate (●), (b) polystyrene-ethyl acetate (△), (c) polystyrene-*n*-propyl acetate (○).

lution thermodynamics lead to expressions for χ_1 as a function of temperature. The Patterson theory is by

$$\chi_1 = -(U_1/RT)\nu^2 + (C_{p,1}/2R)\tau^2 \qquad (4)$$

and that of Flory by

$$\chi_1 = (p_1^*V_1^*/\tilde{V}_1RT)(A^2\alpha_1T/2 + Y_{12}) - V_1^*Q_{12}/R(s_1/s_2)^2 \qquad (5)$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)(X_{12}/p_1^*) \qquad (6)$$

and

$$Y_{12} = (X_{12}/p_1^*)(s_2/s_1)^2 \qquad (7)$$

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

Table VII
Flory's Parameter of the Systems

System	θ_u (°K)	θ_l (°K)	ψ_{1u}	ψ_{1l}
Polystyrene–methyl acetate	316	387	0.253	−0.424
Polystyrene–ethyl acetate	229	412	0.452	−0.622
Polystyrene–*n*-propyl acetate	193	451	0.631	−0.853
Polystyrene–isopropyl acetate	246	380	0.319	−0.464
Polystyrene–isobutyl acetate	227	445	0.438	−0.704
Polystyrene–isoamyl acetate	224	493	0.554	−1.09

$$\tau = 1 - T_1^*/T_2^* \qquad (8)$$

where T_i^* is the characteristic temperature reduction parameter of the solvent (1) and polymer (2). In the Flory equation the parameter X_{12} measures the interchange energy upon formation of contacts between unlike molecules, Q_{12} is analogously defined to represent the entropy arising from interchange of neighboring molecules, and s_1 and s_2 denote the numbers of surface sites (or surface area) for segments of the respective species, segments being of equal core volumes (V^*). P_i^* is defined as the characteristic pressure reduction parameter of the solvent (1) and polymer (2) and p_1^* is obtained by the relation[8]

$$p_1^* = \gamma_1T\tilde{V}_1^2 = (\alpha_1T/\beta_T)\tilde{V}_1^2 \qquad (9)$$

where γ_1 and β_T are the thermal pressure coefficient and the isothermal compressibility of the solvent.

A van der Waals model for the volume dependence of the configurational energy of the liquid emphasized by Flory *et al.* is used to obtain eq 4 and 5 for χ_1, which are essentially the same expression,[7,15] although definitions of the molecular parameters are different. At zero pressure χ_1(crit) for eq 4 is given as a function of the reduced volume $\tilde{V}_1$ of the solvent by[4,7]

$$\chi_1(\text{crit}) = c_1\nu^2/(1 - \tilde{V}_1^{-1/3}) + c_1\tau^2/2\{(4/3)\tilde{V}_1^{-1/3} - 1\}$$
$$= (1/2)(1 + r^{-1/2})^2 \qquad (10)$$

where $3c_1$ is the number of external degrees of freedom of the solvent and calculated from the relation

$$c_1 = p_1^*V_1^*/RT_1^* \qquad (11)$$

Table VIII
Patterson's Parameter and Equation of State Parameter of the Systems

System	$c_1\nu^2$	$c_1\tau^2$	c_1	τ^2	$10^3\nu^2$	T_1^* (°K)	p_1^* (J/cm^3)	V_1^* (cm^3/mol)	c_1 (cal)
Polystyrene–methyl acetate	0.0152	0.140	0.928	0.151	16.4	4407[a]	649[a]	60.3[a]	1.07
Polystyrene–ethyl acetate	0.0115	0.140	0.971	0.144	11.8	4469[a]	612[a]	74.7[a]	1.23
Polystyrene–*n*-propyl acetate	0.0086	0.140	1.11	0.127	7.78	4640[b]		89.1[b]	
Polystyrene–isopropyl acetate	0.0140	0.140	1.32	0.106	10.6	4861[c]		92.4[c]	
Polystyrene–isobutyl acetate	0.0140	0.120	1.00	0.120	14.0	4711[b]		104.0[b]	
Polystyrene–isoamyl acetate	0.0100	0.110	0.664	0.165	15.0	4274[d]		112.0[d]	

[a] From ref 27. [b] From International Critical Tables. [c] From The Merck Index. [d] From Organic Solvents.

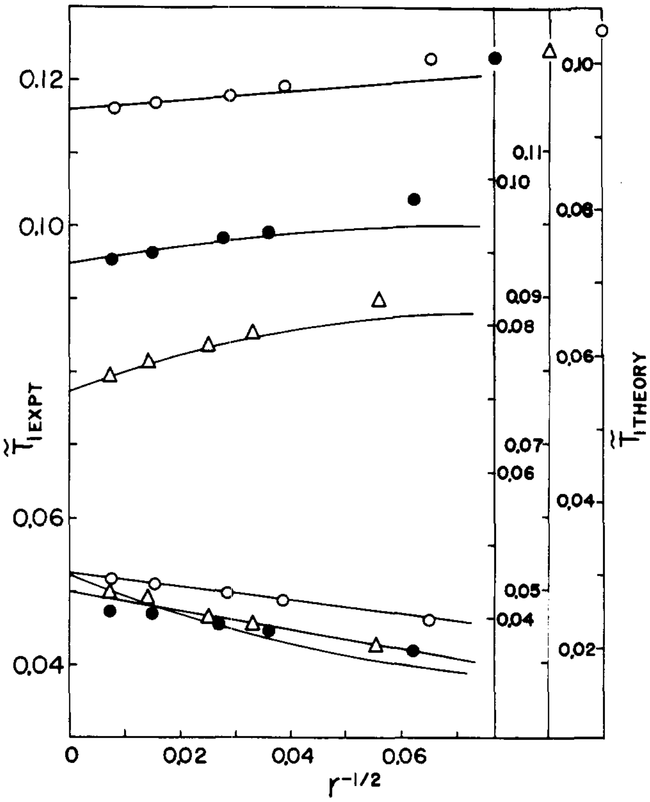

Figure 6. Comparison of experimental reduced temperatures $\tilde{T}_1$ with theoretical curves of eq 10 for the systems: (a) polystyrene-isopropyl acetate (△), (b) polystyrene-isobutyl acetate (●), (c) polystyrene-isoamyl acetate (○).

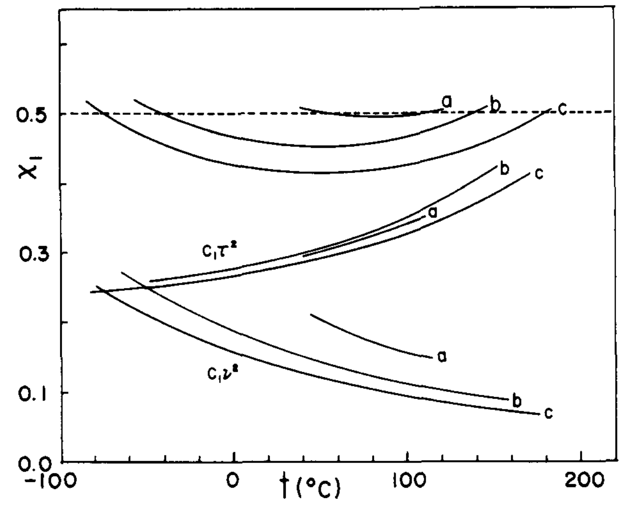

Figure 7. The temperature dependence of the χ_1 parameter estimated from eq 10 with the parameters of $c_1\nu^2$ and $c_1\tau^2$: (a) polystyrene-methyl acetate, (b) polystyrene-ethyl acetate, (c) polystyrene-*n*-propyl acetate.

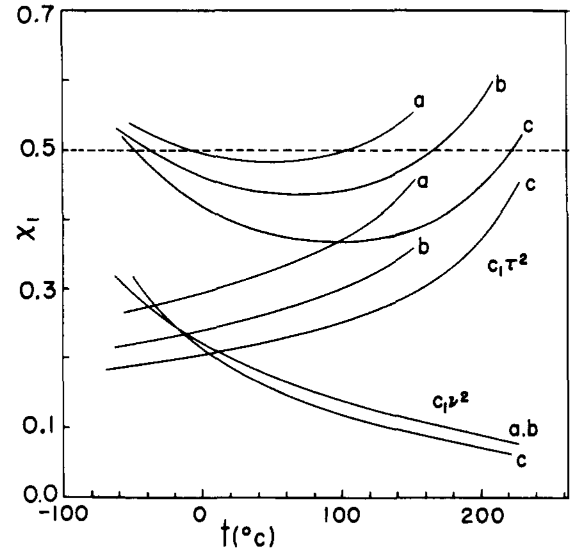

Figure 8. The temperature dependence of the χ_1 parameter estimated from eq 10 with the parameters of $c_1\nu^2$ and $c_1\tau^2$: (a) polystyrene-isopropyl acetate, (b) polystyrene-isobutyl acetate, (c) polystyrene-isoamyl acetate.

Theoretical curves of $\tilde{T}_1$ *vs.* $r^{-1/2}$ for solutions of polystyrene in methyl, ethyl, *n*-propyl, isopropyl, isobutyl, and isoamyl acetate derived from eq 10 with suitable molecular parameters are shown in Figures 5 and 6. Shifts of temperature to fit the experimental critical temperatures with the calculated curves are 60° for the methyl acetate, 47° for the ethyl acetate, 58° for the *n*-propyl acetate, 1° for the isopropyl acetate, 30° for the isobutyl acetate, and 97° for the isoamyl acetate systems. The temperature dependence of the χ_1 parameter calculated from eq 10 with the molecular parameters such as $c_1\nu^2$ and $c_1\tau^2$ are shown in Figures 7 and 8, in which the temperature dependence of the $c_1\nu^2$ and $c_1\tau^2$ terms is also included. Values of $c_1\nu^2$, $c_1\tau^2$, c_1, and ν^2 estimated with use of the procedure described elsewhere[17] and calculated values of τ^2 from T_1^* and T_2^* = 7205 are collected in Table VIII, in which the calculated values of c_1, p_1^*, and V_1^* are also included.

The effect of the chain length on the miscibility region of polystyrene in a series of *n*-acetates appears in the $c_1\nu^2$ term rather than in the $c_1\tau^2$ term, as is shown in Figure 7. In a series of isoacetates in Figure 8 the $c_1\tau^2$ term plays an important role in the miscibility region suggesting significance of the free-volume term. Separation of χ_1 into the $c_1\nu^2$ and $c_1\tau^2$ terms is of great importance in the understanding of the miscibility of polymer solutions. A decrease of the $c_1\nu^2$ term with an increase of the chain length in a series of *n*-acetates is related to the decrease of ν^2 reflecting the difference of cohesive energy and size between the solvent molecules and polymer segments, while a decrease of the $c_1\tau^2$ term with an increase of the chain length in a series of isoacetates is related to the decrease of c_1 representing the external degrees of freedom of the solvents, as is shown in Table VIII. The estimated values of c_1 for the methyl acetate and ethyl acetate systems are smaller than the calculated values listed in Table VIII. The complete miscibility region in the *n*-propyl acetate system is much larger than that in the isopropyl acetate system, as is shown by comparison of the χ_1 *vs.* temperature plot between the two systems. The characteristic difference in the molecular structure between the two solvents appears in the values of $c_1\nu^2$, not in $c_1\tau^2$. It should be also noted that the free-volume contribution to χ_1 is large over the temperature range of the ucst to the lcst in the polystyrene solutions.

An application of eq 5 to the experimental critical solution temperatures is possible through the parameters of X_{12} and Q_{12}, which are determined from the data of the concentration dependence of χ. The direct prediction for the lcst of infinite molecular weight in the polystyrene–cyclohexane system made by Flory *et al.*[13] is 474°K as compared to our experimental value of 486°K.[17] The temperature dependence of χ_1 in the Flory theory is separated into two terms characterized by decreasing and increasing functions of temperature. The calculated values of the temperature coefficient of the two terms, which correspond to $c_1\nu^2$ and $c_1\tau^2$ in the Patterson theory, determined by use of the equation of state parameters, X_{12}, and s_1/s_2 are 0.0235 and 0.128 for the polystyrene–cyclohexane system. These values are in satisfactory agreement with 0.016 and 0.120 determined from the experimental critical temperatures of the polystyrene–cyclohexane system[17] by the aid of the Patterson theory. Direct application of eq 4 and 5 to experimental critical solution temperatures of polymer solutions is carried out by use of available data for the equation of state parameters over a wide temperature region containing the ucst and lcst.

It is also interesting that new expression for χ_1 in the Patterson and Flory theories predicts deviation from linearity in the Shultz–Flory plot. In the newer theories, χ_1 is simply not a reciprocal linear function of temperature and consists of two terms; one is a reciprocal linear function of temperature and the other an increasing function with respect to temperature. The curvature of a parabolic curve in the χ_1 *vs.* temperature plot is emphasized in solvents of poor quality having the narrow temperature region of complete miscibility such as the solutions of polystyrene in isopropyl acetate, ethyl acetate, and methyl acetate, while in solvents of good quality such as *n*-propyl, isobutyl, and isoamyl acetate the curvature is not appreciably emphasized. In a solvent of good quality the χ_1 parameter for the lcst is mainly determined by the free-volume term which is approximated by a linear function of temperature over the narrow range of temperature in the vicinity of the Θ temperature for the lcst, in contrast to the χ_1 parameter for the ucst being approximately a reciprocal linear function of temperature. As a result deviation from linearity in the Shultz–Flory plot would apparently disappear. The Shultz–Flory plot for the ucst as well as the lcst in a solvent of poor quality having the narrow temperature region of complete miscibility should be a rough approximation to speculate the Θ temperature and ψ_1 parameter.

In this work it is emphasized that the phase separation behavior of the ucst and lcst is of general occurrence in nonpolar polymer solutions and is adequately described by the temperature dependence of χ_1 of the Patterson and Flory theories with the van der Waals model for the volume dependence of the configurational energy of the liquid. For solutions of polystyrene in a series of *n*-acetates the contact interaction term (or $c_1\nu^2$ term) is more important than the free-volume term (or $c_1\tau^2$ term) in the contribution to the miscibility region with an increase of the chain length of the solvents, while in a series of isoacetates the free-volume term is more important than the contact interaction term.

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