structure and composition is not very pronounced, we have proposed a procedure to determine the molecular weight of a block copolymer from measurements of its limiting viscosity number and its sedimentation coefficient (or translational diffusion coefficient) together with the interpolated value of $\Phi^{1/3}P^{-1}$.

References and Notes

(1) W. F. Hall and R. E. DeWames, *Macromolecules*, **8**, 349 (1975).
(2) D. R. Hansen and M. Shen, *Macromolecules*, **8**, 343 (1975).
(3) W. H. Stockmayer and J. W. Kennedy, *Macromolecules*, **8**, 351 (1975).
(4) F. W. Wang and E. A. DiMarzio, *Macromolecules*, **8**, 356 (1975)..
(5) F. W. Wang, *Macromolecules*, **8**, 364 (1975).
(6) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(7) L. Mandelkern and P. J. Flory, *J. Chem. Phys.*, **20**, 212 (1952).
(8) H. A. Scheraga and L. Mandelkern, *J. Am. Chem. Soc.*, **75**, 179 (1953).
(9) H. Yamakawa and M. Fujii, *Macromolecules*, **6**, 407 (1973).
(10) "BUMP2: Basic Unified Matrix Package Reference Manual for the 1108", Madison Academic Computer Center, University of Wisconsin, 1969, p 8–3.
(11) F. W. Wang, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1215 (1975).
(12) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128, (1974).
(13) J. Eigner and P. Doty, *J. Mol. Biol.*, **12**, 549 (1965).
(14) L. Mandelkern, W. R. Krigbaum, H. A. Scheraga, and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).
(15) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 628.
(16) T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami, and H. Inagaki, *Polym. J.*, **1**, 245 (1970).
(17) J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).
(18) W. B. Gratzer and P. Doty, *J. Am. Chem. Soc.*, **85**, 1193 (1963).
(19) B. Chu, *Annu. Rev. Phys. Chem.*, **21**, 145 (1970).
(20) F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1619 (1974).

Pressure Dependence of Upper and Lower Critical Solution Temperatures in Polystyrene Solutions

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ABSTRACT: The pressure dependence of the upper critical solution temperature (ucst) and the lower critical solution temperature (lcst) in solutions of polystyrene in *tert*-butyl acetate and diethyl ether has been determined over the pressure range 0 to ~50 atm. The values of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the ucst and lcst over the molecular weight range of $M_\mathrm{w} \times 10^{-4} = 67$ to ~345 in the polystyrene–*tert*-butyl acetate system depend on the molecular weight of the polymer and are negative (−0.110 to −0.175 deg atm^{-1}) for the ucst and positive (0.65–0.68 deg atm^{-1}) for the lcst, while the values of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the solution of polystyrene of $M_\mathrm{w} \times 10^{-4} = 2.04$ in diethyl ether are negative (−0.24 deg atm^{-1}) for the ucst and positive (0.62 deg atm^{-1}) for the lcst. The pressure dependence of the Flory or theta temperatures in the polystyrene–*tert*-butyl acetate system evaluated in the neighborhood of 0 atm are −0.30 deg atm^{-1} for θ_u and 0.70 deg atm^{-1} for θ_l, where the θ_u and θ_l are the θ temperature for the ucst and lcst. The observed behavior of the pressure dependence of the ucst and lcst in polystyrene solutions is qualitatively predicted by the Patterson–Delmas theory of corresponding states and the newer Flory theory of polymer solution thermodynamics through the expression for the χ_1 parameter.

The importance of the phase diagram (P, T, composition) over a wide range of temperature and pressure[1-3] has been recognized for nonpolar polymer solutions[4-11] after the discovery of the lcst in nonpolar polymer solutions.[12] As is well known, the cloud point curves characterized by the ucst and lcst for the (T, composition) phase diagram under the saturated vapor pressure behave like mirror images across the temperature axis of the intermediate region between the ucst and lcst.[13-18] In the (P, composition) phase diagram at constant temperature the cloud point curves in the polymer solution are classified into two types by the shape of the cloud point curve on the pressure–composition plot. One is characterized by the existence of a maximum pressure, the other by a minimum one. For solutions of polymers with a very narrow molecular weight distribution, the maximum pressure corresponds to the upper critical solution pressure (ucsp) and the minimum pressure to a lower critical solution pressure (lcsp), as discussed by Ehrlich and Kurpen[5,8] for solutions of polyethylene in n-alkanes. A critical condition in the (P, T, composition) phase diagram is completely determined by the critical solution temperature and critical solution pressure, i.e., the (P, T) critical line of the polymer solution.[2,3,5-11] The thermodynamic conditions for the ucsp observed in either system with a positive value of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the lcst and a negative value of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the ucst is a negative excess volume of mixing and corresponds to an increase of the polymer–solvent compatibility with an increase of pressure at constant temperature. The condition for the lcsp observed in either system with a negative value of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the lcst or a positive value of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ for the ucst is a positive excess volume of mixing and corresponds to the decrease of the polymer–solvent compatibility with an increase of pressure.[1-3]

Investigation of the excess volume of mixing[19-27] and the pressure effect on the thermodynamic properties of polymer solutions, such as the second virial coefficient[28-30] or the χ_1 parameter, the mean square end-to-end distance of polymer in the dilute solution,[28-30] and the ucst and lcst,[4-11] are of importance in the characterization of polymer solutions. The determination of the (P, T) critical line is also of great importance in connection with the pressure and temperature coefficients of the unperturbed mean-square end-to-end distance of polymer chains in dilute solution.[31]

In this work we supply the (P, T, composition) phase diagram over the middle pressure range of 0 to ~50 atm in the vicinity of the ucst and lcst for solutions of polystyrene in *tert*-butyl acetate and diethyl ether. We also examine the experimental values of $(\mathrm{d}T/\mathrm{d}P)_\mathrm{c}$ in the light of the recent theories of polymer solution thermodynamics of Patterson and Flory.

Experimental Section

Polystyrene samples were obtained from the Pressure Chemical Co. Samples designated by 14b-1, 14b-2, and 14b-3 were obtained

Table I
Patterson's Parameter and Equation of State Parameter of the System

System	$c_1\nu^2$	$c_1\tau^2$	T^*_1, deg	P^*_1, atm	V_1^*, cm^3 mol^{-1}	γ_V, atm deg^{-1}
PS–*tert*-butyl acetate	0.0031_0[a]	0.235_0[a]	4598[a]	5038[b]	105.0[a]	9.95[b]
PS–diethyl ether	0.0055_5[c]	0.228_7[c]	4056[c]	4858[d]	76.1[d]	8.88[d]

[a] From ref 18. [b] From this work. [c] From ref 14. [d] From ref 46.

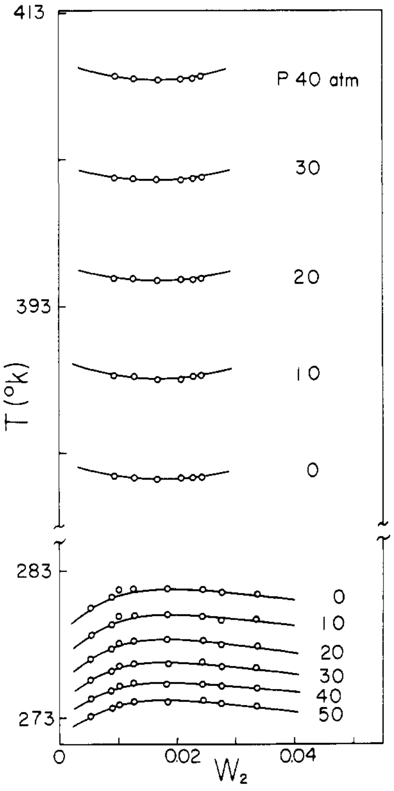

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene ($M_w \times 10^{-4} = 345$)–*tert*-butyl acetate system at pressures indicated in atm.

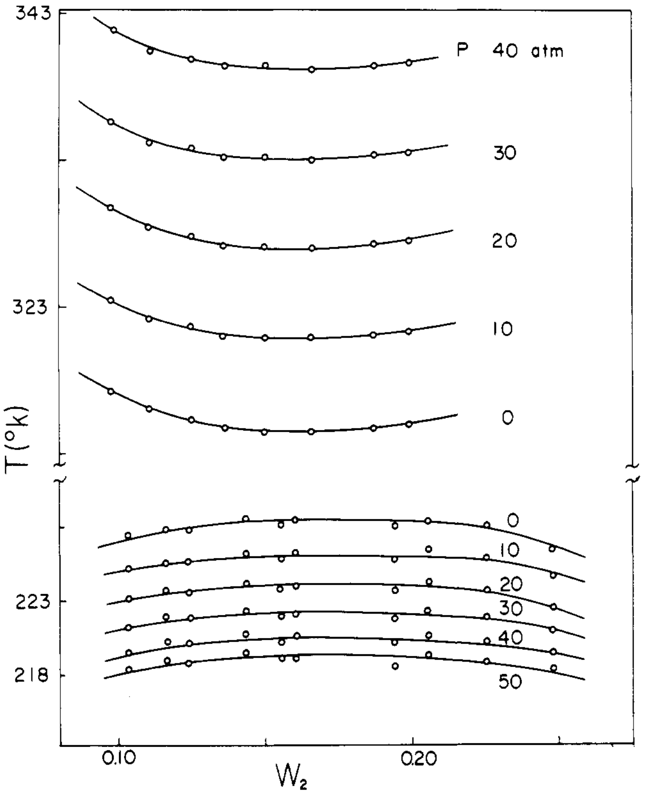

Figure 2. The (temperature, weight fraction) phase diagram for the polystyrene ($M_w \times 10^{-4} = 2.04$)–diethyl ether system at pressures indicated in atm.

by solution fractionation of a sample ($M_w \times 10^{-4} = 200$, $M_w/M_n < 1.30$) described in detail elsewhere.[15] The solvents were reagent grade and were purified further before use. A sample of 500 g of *tert*-butyl acetate, refluxed for 3 hr over about 20 g of acetic anhydride, was dried over anhydrous potassium carbonate and fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with stainless-steel helices. Diethyl ether was dried over anhydrous potassium carbonate and fractionally distilled in the same column. A pressure apparatus for determinations of the cloud point temperatures under pressure has been described in detail elsewhere.[11] Several solutions in *tert*-butyl acetate and diethyl ether prepared from each sample in the concentration range of 0.5 to ~38 wt % were stirred for about 3 hr and then sealed inside the solution cells by mercury seals. In the determination of $(dT/dP)_c$ for the ucst (−44.8°C atm) in the polystyrene–diethyl ether system the solution was not sealed by mercury. The cloud-point temperatures for the ucst and lcst were determined with an accuracy of ±0.05° for the temperature range of −10° to ~10°C, ±0.3° for −40° to ~−60°C for the ucst and ±0.05° for the lcst by the aid of the pattern of the He–Ne laser beam, as described elsewhere.[15] The cloud point temperatures under pressure are obtained by cooling slowly at 0.04 to ~0.09 deg min^{-1} in a water or ethanol bath for the ucst in the polystyrene–*tert*-butyl acetate system, 0.09 to ~0.12 deg min^{-1} for the ucst in the diethyl ether solution, and by heating at 0.07 to ~0.10 deg min^{-1} in a silicon oil bath for the lcst in the *tert*-butyl acetate and diethyl ether solutions. Upper and lower critical solution temperatures were estimated from the cloud-point curves. The thermal pressure coefficient of *tert*-butyl acetate has been measured by means of a constant volume thermometer. The stainless-steel vessel of high pressure holding a constant volume thermometer of Pyrex glass was immersed into a water bath controlled within ±0.002° and then pressure was raised very slowly (0.03 to ~0.05 kg cm^{-2} min^{-1}) until a pilot lit. The pilot in series with the mercury and the platinum wire sealed into the cell indicated that the solvent in the cell was contracted with an increase of pressure and separation of the tip of the wire from the mercury was established at an applied pressure. The pressure at which the pilot lights with a slight increase of pressure and vanishes with a slight decrease of pressure was determined with an accuracy of ±0.01 kg cm^{-2} at a constant temperature (±0.002°) by use of a calibrated Bourdon type pressure gauge of 45 cm diameter (Heise Co., to 50 kg cm^{-2}). The constant volume thermometer used in this work will be described in detail elsewhere.[32] The plot of the applied pressure against temperature was linear within experimental error and gave the uncorrected value of γ_v, i.e., γ_{obsd}. An accurate value for γ_v was obtained by correcting for the thermal expansion and isothermal compressibility of the glass cell and mercury by the relation[33]

$$\gamma_v = \gamma_{obsd}(1 + (V_{Hg}\beta_{Hg} - V_g\beta_g)/V_s\beta_s) + (V_g\alpha_g - V_{Hg}\alpha_{Hg})/V_s\beta_s$$

where $V_g = V_s + V_{Hg}$ = the volume of the cell; β_{Hg} = the coefficient of isothermal compressibility of mercury = 4.09×10^{-6} atm^{-1} at 25°C; β_g = the coefficient of isothermal compressibility of Pyrex glass = 3.00×10^{-6} atm^{-1}; β_s = the coefficient of isothermal compressibility of solvent; α_g = the coefficient of thermal expansion of Pyrex glass = 9.9×10^{-6} deg^{-1}; α_{Hg} = the coefficient of thermal expansion of mercury = 1.82×10^{-4} deg^{-1}. For the value of α_s it was determined in other experiments[18] that an approximate value of β_s ($= \alpha_s/\gamma_{obsd}$) could be used without altering the value of γ_v by a significant amount. The value found for γ_v of *tert*-butyl acetate is given in Table I.

Results

Typical cloud-point curves at different pressures from 0 to ~50 atm for solutions of polystyrene ($M_w \times 10^{-4} = 345$)

Table II
Critical Solution Temperatures for Polystyrene Solutions of Various Molecular Weights and Pressures

			ucst (°K) at pressure, atm						lcst (°K) at pressure, atm				
Sample	$M_w \times 10^{-4}$	M_w/M_n	0	10	20	30	40	50	0	10	20	30	40
					Polystyrene–*tert*-Butyl Acetate								
13a	67.0	<1.15	270.8	269.7	268.6	267.5	266.4	265.5	393.7	400.2	407.1	413.7	420.2
14b-3	145.0	<1.10	276.7	275.3	273.8	272.4	271.1	270.0	387.1	393.8	400.6	407.3	414.0
14b-2	270.0	<1.10	280.7	278.8	277.2	275.8	274.4	273.3	382.5	388.8			
14b-1	345.0	<1.10	281.8	280.0	278.3	276.8	275.4	274.2	381.2	388.1	394.9	401.7	408.4
	∞		296.1	293.1	290.7	288.5	286.8	285.5	359.3	366.3	372.7	380.4	387.0
					Polystyrene–Diethyl Ether								
2b	2.04	<1.06	228.4	226.2	224.0	222.2	220.6	219.2	314.5	320.8	327.0	333.2	339.4

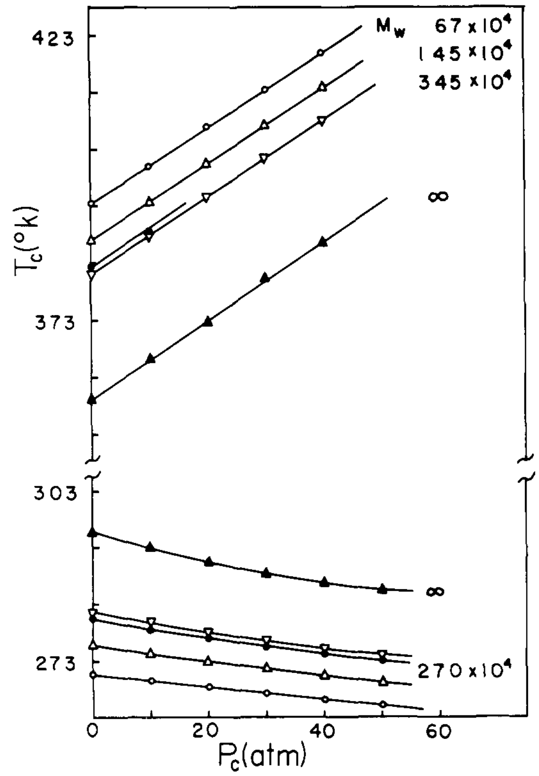

Figure 3. Projection on the (*P*, *T*) plane of the critical lines corresponding to the ucst and lcst in the polystyrene–*tert*-butyl acetate system for the samples of indicated molecular weight. The critical line for the sign ∞ is that of the infinite molecular weight of the polymer corresponding to the θ condition.

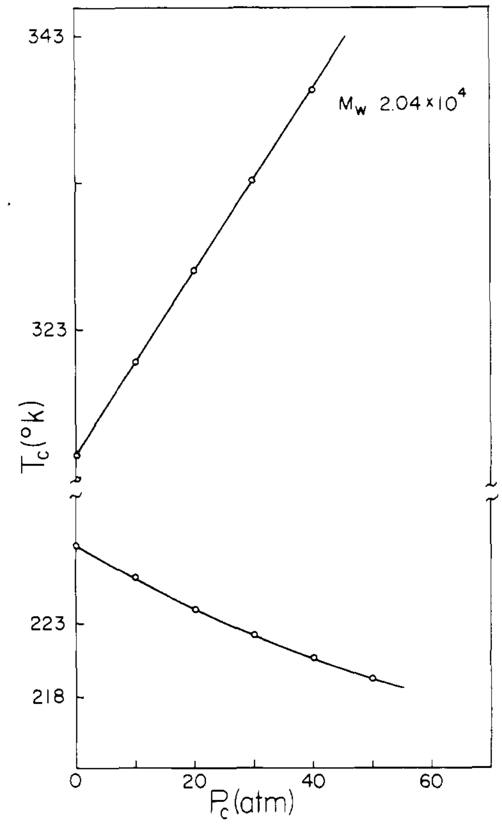

Figure 4. Projection on the (*P*, *T*) plane of the critical line corresponding to the ucst and lcst in the polystyrene ($M_w \times 10^{-4}$ = 2.04)–diethyl ether system.

in *tert*-butyl acetate and of polystyrene ($M_w \times 10^{-4}$ = 2.04) in diethyl ether are shown in Figures 1 and 2. The value of the lcst at the saturated vapor pressure in the polystyrene ($M_w \times 10^{-4}$ = 2.04)–diethyl ether system is lower by 1° and that of the ucst is lower by 7° than that of the polystyrene ($M_w \times 10^{-4}$ = 1.98)–diethyl ether system reported by Siow et al.[14] The hour-glass-shaped phase diagram, in which the complete miscibility region exists at concentrations less than 3.0 wt % and higher than 34.5 wt % of polymer, was observed for solutions of polystyrene of $M_w \times 10^{-4}$ = 3.7 in diethyl ether. The pressure derivative of the cloud-point temperatures in the polystyrene ($M_w \times 10^{-4}$ = 3.7)–diethyl ether system is 0.79 deg atm^{-1} at a concentration of 2.1 wt % and 0.64 deg atm^{-1} at a concentration of 37.8 wt %. Although the maximum and minimum points of the cloud-point curves are not the critical points, the difference of the maximum or minimum points from the critical points for the ucst or lcst should be quite small because of the small deviation from unity of M_w/M_n for the five samples in this work.[34,35] The critical solution temperatures at pressure from 0 to ~50 atm for polystyrene of various molecular weights are listed in Table II. The pressure dependence of the ucst and lcst for polystyrene in *tert*-butyl acetate and diethyl ether is shown in Figures 3 and 4, as well as the pressure dependence of the θ temperature for the polystyrene–*tert*-butyl acetate system. The θ temperature at different pressures in the polystyrene–*tert*-butyl acetate system was determined by linear extrapolation of the plot of T_c^{-1} vs. $(\chi_{1,\mathrm{crit}} - 0.5)^{1/2}$ for the lcst and $(\chi_{1,\mathrm{crit}} - 0.5)^{3/4}$ for the ucst in Figure 5. The method of determination of the θ temperature has been described in detail elsewhere.[18] The values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the *tert*-butyl acetate solutions and the diethyl ether solutions are collected in Table III. Linearity in the plot of the critical solution temperature versus pressure is observed for the lcst in the *tert*-butyl acetate and diethyl ether solutions and for the ucst in the polystyrene ($M_w \times 10^{-4}$ = 67)–*tert*-butyl acetate system within experimental error, while nonlinearity characterized by convex downward curves is observed for the ucst in solutions of polystyrene ($M_w \times 10^{-4}$ = 145 to ~345) in

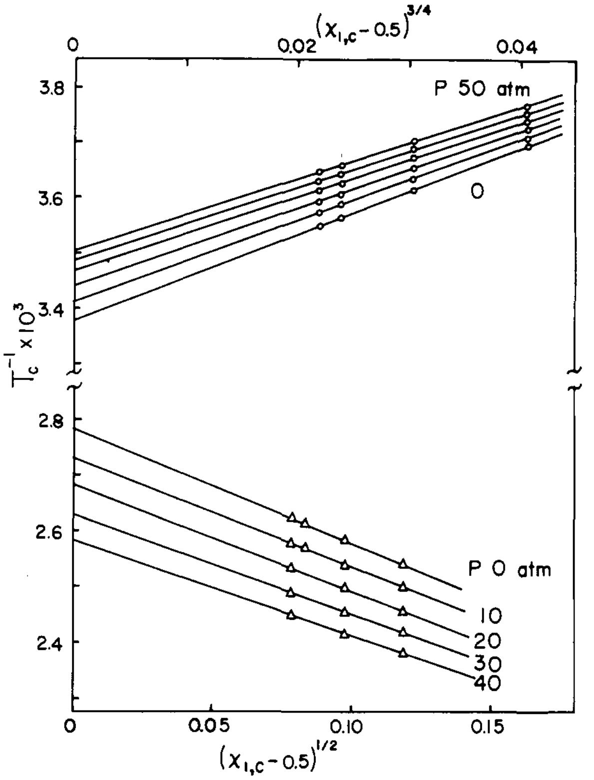

Figure 5. The determination of the θ temperatures by the modified Flory–Shultz plot [T_c^{-1} vs. $(\chi_{1,\mathrm{crit}} - 0.5)^{1/2}$] for the lcst and [$T_c^{-1}$ vs. $(\chi_{1,\mathrm{crit}} - 0.5)^{3/4}$] for the ucst in the polystyrene–*tert*-butyl acetate system at the pressures indicated.

Table III
Pressure Dependence of Critical Solution Temperatures for Polystyrene Solutions at 0 atm

System	$M_w \times 10^{-4}$	$(\mathrm{d}T/\mathrm{d}P)_{c,\mathrm{ucst}}$ at 0 atm, deg atm^{-1} Obsd	$(\mathrm{d}T/\mathrm{d}P)_{c,\mathrm{ucst}}$ at 0 atm, deg atm^{-1} Calcd	$(\mathrm{d}T/\mathrm{d}P)_{c,\mathrm{lcst}}$ at 0 atm, deg atm^{-1} Obsd	$(\mathrm{d}T/\mathrm{d}P)_{c,\mathrm{lcst}}$ at 0 atm, deg atm^{-1} Calcd
PS–*tert*-butyl acetate	67.0	−0.110	−0.027	0.65	0.20
	145.0	−0.140	−0.039	0.67	0.20
	270.0	−0.170	−0.051	0.67	0.22
	345.0	−0.175	−0.059	0.68	0.22
	∞	−0.30	−0.13	0.70	0.31
PS–diethyl ether	2.04	−0.24	−0.026	0.62	0.23

tert-butyl acetate and of polystyrene ($M_w \times 10^{-4} = 2.04$) in diethyl ether. A maximum deviation from linearity in the *tert*-butyl acetate and diethyl ether solutions is estimated as 0.3–0.4°. The tendency of the deviation from linearity in the plot of the ucst vs. pressure is emphasized in the plot of the θ_u vs. pressure, as shown in Figure 3. The listed values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst in Table III are determined from the initial slope at 0 atm. The molecular weight dependence of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst and lcst in the polystyrene–*tert*-butyl acetate system is characterized by the increasing absolute values of $(\mathrm{d}T/\mathrm{d}P)_c$ with an increase of the molecular weight of the polymer or with an approach to the θ temperature for the ucst and lcst, as shown in Table III. After measurement of the cloud-point temperatures in the region of the lcst, the thermal degradation of polystyrene was examined for the polystyrene–*tert*-butyl acetate system by the reproducibility of the cloud-point temperatures for the ucst. Errors caused by thermal degradation in the determinations of the lcst over the pressure range of 0 to 50 atm are estimated as 0.2 to 0.7° depending on the molecular weight of the polymer.

Discussion

In previous work[11] we have determined the pressure dependence of the ucst in the polystyrene-cyclohexane system and found that the value of $(\mathrm{d}T/\mathrm{d}P)_c$ changes from positive (3.14×10^{-3} deg atm^{-1}) for polystyrene of $M_w \times 10^{-4} = 3.7$ in cyclohexane to negative (-4.40×10^{-3} to -5.64×10^{-3} deg atm^{-1}) for $M_w \times 10^{-4} = 67$ and 145 passing through the negligibly small negative value (-0.52×10^{-3} deg atm^{-1}) for $M_w \times 10^{-4} = 11$. The values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst in solutions of the polystyrene ($M_w \times 10^{-4} = 67$ to ∼345) in *tert*-butyl acetate and of polystyrene ($M_w \times 10^{-4} = 2.04$) in diethyl ether are greatly different in magnitude and sign of $(\mathrm{d}T/\mathrm{d}P)_c$ from those of the polystyrene–cyclohexane system. The values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the lcst in *tert*-butyl acetate and diethyl ether are larger than the values reported in such systems as polyethylene–pentane (0.59 deg atm^{-1}),[5] polystyrene–methyl acetate (0.45 deg atm^{-1}),[6] and polyisobutene–isopentane (0.46 deg atm^{-1}).[7]

According to the thermodynamic analysis in the vicinity of the critical point the pressure dependence of the critical solution temperature is related to the ratio of the second derivatives of volume and enthalpy per mole of mixture with respect to composition[1–3]

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_c = \lim_{\substack{T\to T_c \\ \varphi_2\to\varphi_c}} \frac{T(\partial^2 V/\partial\varphi_2^2)_{T,P}}{(\partial^2 H/\partial\varphi_2^2)_{T,P}} \tag{1}$$

In the Flory theory the polymer–solvent interaction parameter χ is identified as the residual chemical potential $(\mu_1 - \mu_1^0)^R/RT\varphi_2^2$ and represented as a series in powers of φ_2[20,25]

$$\chi = \chi_1 + \chi_2\varphi_2 + \chi_3\varphi_2^2 + \ldots \tag{2}$$

The value of $(\mathrm{d}T/\mathrm{d}P)_c$ is dominated by the ratio of the first derivatives of χ_1 with respect to pressure and temperature. By neglecting $\chi_2\varphi_2$ and higher terms in eq 2 we obtain

$$(\mathrm{d}T/\mathrm{d}P)_c = -(\partial\chi_1/\partial P)_{T_c}/(\partial\chi_1/\partial T)_{P_c} \tag{3}$$

and χ_1 at the critical point is given by

$$\chi_{1,\mathrm{crit}} = (1/2)(1 + r^{-1/2})^2 \tag{4}$$

The values of $(\partial^2 H/\partial\varphi_2^2)_c$ or $(\partial\chi_1/\partial T)_{P_c}$ are negative for the ucst corresponding to the endothermic condition and positive for the lcst corresponding to the exothermic condition, while the $(\partial^2 V/\partial\varphi_2^2)_c$ or $-(\partial\chi_1/\partial P)_{T_c}$ are positive for the ucsp corresponding to the negative excess volume of mixing and negative for the lcsp corresponding to the positive excess volume of mixing. The observed negative value of $(\mathrm{d}T/\mathrm{d}P)_{c,\mathrm{ucst}}$ and positive value of $(dT/dP)_{c,\mathrm{lcst}}$ for polystyrene in *tert*-butyl acetate and diethyl ether corresponds to the negative excess volume of mixing in the vicinity of the critical point and to the existence of ucsp in the pressure–composition phase diagram at a constant temperature.

The sign and magnitude of $(\mathrm{d}T/\mathrm{d}P)_c$ are qualitatively predicted by the Patterson[36–41] and Flory[42–45] theories of polymer solution thermodynamics through the pressure and temperature dependence of the χ_1 parameter. The estimation of the pressure dependence of the critical solution temperatures for the ucst and lcst has been carried out according to the Patterson theory by a procedure described elsewhere.[11] The values of $(\mathrm{d}T/\mathrm{d}P)_c$ given in Table III were calculated with use of molecular parameters such as $c_1\nu^2$ and $c_1\tau^2$ listed in Table I determined from the molecular weight dependence of the ucst and lcst.[18] The values of characteristic reduction parameters (P^*, V^*, T^*) for *tert*-butyl acetate and diethyl ether were determined from the thermal pressure coefficient and thermal expansion coefficient.[25,46] A qualitative prediction of the sign of $(\mathrm{d}T/\mathrm{d}P)_c$

and molecular weight dependence $(\mathrm{d}T/\mathrm{d}P)_c$ is obtained from the theory. The calculated values of $(\mathrm{d}T/\mathrm{d}P)_c$ are about one-third the experimental values for polystyrene in *tert*-butyl acetate and diethyl ether. The values of $(\mathrm{d}T/\mathrm{d}P)_c$ calculated from the experimental values of χ_1 modified by taking into account the concentration dependence of χ and the expression for χ_1 in the Patterson theory should be larger through the $(\partial\chi_1/\partial T)$ in eq 3 than that of $(\mathrm{d}T/\mathrm{d}P)_c$ based on $\chi_{1,c}$ in eq 4. It is found in the polystyrene–cyclohexane system that the value of $\chi_{1,c} - 0.5$ calculated from eq 4 is about three times larger than the experimental value of $\chi_{1,c} - 0.5$ from the critical miscibility data,[18,35] while θ_u is 34°C from eq 4[15] and 33.2°C from the critical miscibility data.[35] It is suggested that the value of $(\partial\chi_1/\partial T)$ based on eq 4 is larger by about three times than that of the critical miscibility data when account is taken of the concentration dependence of χ. In the light of this fact the discrepancy between the observed and calculated values of $(\mathrm{d}T/\mathrm{d}P)_c$ in Table III should be attributed to the overestimate of $(\partial\chi_1/\partial T)$ by eq 4. The large absolute value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the lcst reflects the large positive value of $(\partial^2 V/\partial\varphi_2{}^2)_c$ or the large negative value of $(\partial\chi_1/\partial P)_{T_c}$ and is caused by the large contribution of the configurational heat capacity term (or $c_1\tau^2$ term) to χ_1 and a rapid decrease of the $c_1\tau^2$ term with increase of pressure as compared to a small contribution of the configurational energy term ($c_1\nu^2$ term) to χ_1 and a slow increase of the $c_1\nu^2$ term with increase of pressure at constant temperature. Linearity in the lcst vs. pressure plot is attributed to the dominant negative contribution of the configurational heat capacity term to $(\partial\chi_1/\partial P)_{T_c}$. In the vicinity of the ucst for the polystyrene solutions the $c_1\tau^2$ term contributes to χ_1 by almost the same amount as the $c_1\nu^2$ term, as expected from comparison of the experimental values of the ucst and lcst with the theoretical expressions for χ_1 in the Patterson theory, in which the expression of χ_1 at constant pressure consists of two terms characterized by a decreasing function of temperature ($c_1\nu^2$ term) and an increasing function of temperature ($c_1\tau^2$ term).[16,18] The value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst which is mainly determined by the magnitude of $(\partial\chi_1/\partial P)_{T_c}$ is expected to be smaller than that at the lcst because of the small negative value of $(\partial\chi_1/\partial P)_{T_c}$. The latter is due to the decreasing absolute value of the negative contribution of the $c_1\tau^2$ term and to partial compensation by the positive contribution of the $c_1\nu^2$ term of the negative contribution of the $c_1\tau^2$ term. The positive value of $(\partial\chi_1/\partial P)_{T_c}$ or the positive excess volume of mixing is also predicted by the theories at sufficiently low temperature, at which the $c_1\nu^2$ term is dominant and the value of $(\partial\chi_1/\partial P)_{T_c}$ is determined by the positive contribution of the $c_1\nu^2$ term. The change from negative $(\mathrm{d}T/\mathrm{d}P)_c$ value to a positive one for the ucst has been observed in the polystyrene–cyclohexane system[11] and this change of signs is expected to occur generally in polymer solutions, as predicted theoretically. The tendency of deviation from linearity in the ucst vs. pressure plot characterized by the convex downward curve and the molecular weight dependence of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst and lcst in the *tert*-butyl acetate solutions are well explained by two effects: one is the increasing positive contribution of the $c_1\nu^2$ term to $(\partial\chi_1/\partial P)_{T_c}$ with decrease of temperature accompanying the decreasing absolute value of the negative contribution of the $c_1\tau^2$ term; the other is the decreasing absolute value of $(\partial\chi_1/\partial T)_{P_c}$ with an increase of the molecular weight of the polymer or with an approach to the θ_u or θ_l brought about by the parabola-like dependence of χ_1 with a minimum at a given temperature. The latter affects the value of $(\mathrm{d}T/\mathrm{d}P)_c$ through the denominator in eq 3. The calculated and experimental values for the pressure derivative of θ_u and θ_l in the *tert*-butyl acetate solutions at 0 atm are listed in Table III.

The pressure dependence of critical composition along the critical locus is related to the third derivatives of chemical potential, volume, and enthalpy with respect to composition.[1] It is of great interest to determine the value of $(\mathrm{d}\varphi_2/\mathrm{d}P)_c$ along the critical locus to define roughly the thermodynamic functions of partially miscible liquids with respect to composition of the mixture near the critical point.[47] The pressure dependence of the critical composition in the solution of polymer with a very narrow molecular weight distribution should be observed as the displacement of the composition corresponding to the maximum or minimum point of the cloud-point curves for the ucst and lcst with an increase of pressure. The displacement of composition of the maximum or minimum point was not detected over the pressure range of 0 to ~50 atm in solutions of polystyrene in *tert*-butyl acetate and diethyl ether. In this work it is emphasized that the behavior of the pressure dependence of the ucst and lcst in polystyrene solutions over the pressure range of 0 to ~50 atm is qualitatively predicted by the Patterson or the Flory theories of polymer solution thermodynamics through the expressions for χ_1. It is also suggested that the pressure effect on the thermodynamic properties of the polymer solution such as the phase separation behavior at the ucsp and lcsp at constant temperature is determined in the region of high temperature or pressure by the excess volume of mixing in the polymer solution.

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References and Notes

(1) I. Prigogine and R. Defay, "Chemical Thermodynamics", Longmans, Green and Co., London, 1954.
(2) J. S. Rowlinson, "Liquid and Liquid Mixtures", 2nd ed, Butterworths, London, 1969.
(3) G. M. Schneider, *Adv. Chem. Phys.*, **16**, 1 (1970).
(4) J. Ham, M. C. Bolen, and J. K. Hughes, *J. Polym. Sci.*, **57**, 25 (1962).
(5) P. Ehrlich and J. J. Kurpen, *J. Polym. Sci., Part A-1*, 3217 (1963).
(6) C. D. Myrat and J. S. Rowlinson, *Polymer*, **6**, 645 (1965).
(7) G. Allen and C. H. Baker, *Polymer*, **6**, 181 (1965).
(8) P. Ehrlich, *J. Polym. Sci., Part A-1*, 131 (1965).
(9) L. Zeman, J. Biros, G. Delmas, and D. Patterson, *J. Phys. Chem.*, **76**, 1206 (1972).
(10) L. Zeman and D. Patterson, *J. Phys. Chem.*, **76**, 1214 (1972).
(11) S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **16**, 445 (1975).
(12) P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).
(13) J. M. G. Cowie, A. Maconnachie, and R. J. Ranson, *Macromolecules*, **4**, 57 (1971).
(14) K. S. Siow, G. Delmas, and D. Patterson, *Macromolecules*, **5**, 29 (1972).
(15) S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 246, 589 (1973).
(16) S. Saeki, S. Konno, N. Kuwahara, M. Nakata, and M. Kaneko, *Macromolecules*, **7**, 521 (1974).
(17) N. Kuwahara, S. Saeki, T. Chiba, and M. Kaneko, *Polymer*, **15**, 777 (1974).
(18) S. Konno, S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Macromolecules*, in press.
(19) C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubeey, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).
(20) P. J. Flory and H. Hocker, *Trans. Faraday Soc.*, **67**, 2258 (1971).
(21) H. Hocker and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2270 (1971).
(22) H. Hocker, H. Shih, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2275 (1971).
(23) P. J. Flory and H. Shih, *Macromolecules*, **5**, 761 (1972).
(24) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968).
(25) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035, 2053, 2061, 2066 (1968).
(26) R. A. Orwoll and J. A. Small, *Macromolecules*, **6**, 755 (1973).
(27) Y. Baba, H. Katayama, and A. Kagemoto, *Makromol. Chem.*, **175**, 209 (1974).

(28) G. V. Schulz and M. Lechner, *J. Polym. Sci., Part A-2*, **8**, 1885 (1970).
(29) G. V. Schulz and M. Lechner in "Light Scattering from Polymer Solutions", M. B. Huglin, Ed., Academic Press, New York, N.Y., 1971.
(30) D. Gaeckle and D. Patterson, *Macromolecules*, **5**, 136 (1972).
(31) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley, New York, N.Y., 1969.
(32) M. Nakata, S. Higashida, N. Kuwahara, S. Saeki, and M. Kaneko, *J. Chem. Phys.*, in press.
(33) G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, **1**, 467 (1960).
(34) R. Koningsveld, L. A. Kleitjens, and A. R. Shultz, *J. Polym. Sci., Part A-2*, **8**, 1261 (1970).
(35) N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **14**, 415 (1973).
(36) G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **57**, 79 (1962).
(37) D. Patterson, *J. Polym. Sci., Part C*, **16**, 3379 (1968).
(38) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).
(39) D. Patterson, *Macromolecules*, **2**, 672 (1969).
(40) D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, **49**, 98 (1970).
(41) J. Biros, L. Zeman, and D. Patterson, *Macromolecules*, **4**, 30 (1971).
(42) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).
(43) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3515 (1964).
(44) P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(45) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).
(46) G. Allen, G. Gee, and G. J. Wilson, *Polymer*, **1**, 456 (1960).
(47) R. D. Dunlap and S. D. Furrow, *J. Phys. Chem.*, **70**, 1331 (1966).

Thermal Diffusion of Polystyrene in Eight Solvents by an Improved Thermal Field-Flow Fractionation Methodology[1]

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ABSTRACT: The characteristics and advantages of the thermal field-flow fractionation methodology for measuring thermal diffusion parameters in polymer solutions is discussed. The theory of the method is presented and is extended to include the effect of variable thermal conductivity. This in combination with experimental retention data yield values for thermal diffusion factors, α. To get thermal diffusion coefficient D_T, ordinary diffusion coefficient D is needed; Flory's method is used for this purpose. These parameters are acquired from experimental data obtained with polystyrene samples of molecular weight 20 000, 51 000, 97 000, and 160 000, dissolved in eight organic solvents. Trends occurring with changes in molecular weight, solvent, and temperature are investigated. Some aqueous solutions of macromolecules are shown to exhibit much weaker thermal diffusion effects.

Thermal field-flow fractionation (TFFF) comprises a methodological subclass of field-flow fractionation (FFF), a macromolecular separation technique.[2-5] In TFFF, a thermal gradient, applied across a channel through which solvent is flowing, retards the downstream progress of macromolecular solutes.[6-10] This retardation, or retention, is caused by thermal diffusion, which forces macromolecules into the low-velocity region next to the channel wall. Retention among assorted macromolecules is differential, hinging on the magnitude of the thermal diffusion effect for each species.

Differential retention causes separation and thus leads to the realization of the primary goal of TFFF: chemical fractionation. Differential retention also makes it possible to discern the magnitude of the underlying thermal diffusion effect, thus making it possible to measure thermal diffusion parameters for various macromolecules. This is an important secondary goal for TFFF, especially in view of the fact that existing data on thermal diffusion for macromolecules are scarce and inconsistent. In an earlier work it was shown that TFFF has certain advantages in making such measurements compared to other techniques, including those using thermogravitational columns, static cells, and moving boundaries.[11] These advantages include relative speed, simultaneous fractionation, and minute sample requirements (on the order of 1 mg).

In this paper we present an improved methodology for TFFF measurements and analyze the faults of the previous TFFF system. We introduce an important theoretical correction, accounting for the variation with temperature of solvent thermal conductivity. We report thermal diffusion parameters for a variety of chemical systems not yet characterized with respect to thermal diffusion. We analyze the results in an attempt to isolate the effects of temperature, molecular weight, and other chemical factors. Systems included in this study are polystyrene polymers of molecular weights 20 000, 51 000, 97 000, and 160 000, and solvents that include toluene, ethyl benzene, methyl ethyl ketone, chloroform, ethyl acetate, cyclohexane, dioxane, and dimethyl formamide. We also include some preliminary remarks on thermal diffusion (or the lack of it) in aqueous solutions and in binary mixtures of water with DMSO, urea, and guanidine hydrochloride.

Theory

The theory of TFFF has been developed and refined in several publications.[2b,3,8,9] The essential equations are based on the existence of an exponential steady-state solute cloud at the cold wall of the channel

$$c^* = c_0 \exp(-x/l) \tag{1}$$

In this equation, c^* is the steady-state concentration, c_0 the concentration at the cold wall, $x = 0$, and l is the characteristic thickness of the solute layer. Parameter l is most conveniently expressed in dimensionless form

$$\lambda = l/w \tag{2}$$

where w is the distance between hot and cold walls. In dilute solutions, which we assume here, quantity λ is related to thermal diffusion by[8]

$$\lambda = 1/\left(\frac{\alpha}{T} + \gamma\right)\frac{\mathrm{d}T}{\mathrm{d}x}\,w \tag{3}$$

where α is the thermal diffusion factor, γ is the (cubical) coefficient of thermal expansion of the solution, and $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient.