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Upper and Lower Critical Solution Temperatures in Polystyrene Solutions. IV. Role of Configurational Heat Capacity

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ABSTRACT: Temperature dependence of the polymer–solvent interaction parameter χ_1 has been estimated by use of the critical χ_1 values $\chi_{1,c}$ and the upper and lower critical solution temperatures in solutions of polystyrene ($M_w \times 10^{-4} = 0.22$–$345$) in methyl acetate, *sec*-butyl acetate, *tert*-butyl acetate, ethyl formate, ethyl *n*-butyrate, diethyl malonate, and *trans*-decalin. The critical solution temperatures are characterized by the T_c^{-1} dependence of $(\chi_{1,c} - 0.5)$ for the ucst and of $-(\chi_{1,c} - 0.5)$ for the lcst in the diethyl malonate and *sec*-butyl acetate solutions, for the ucst in the *trans*-decalin solution and for the lcst in the ethyl *n*-butyrate solution, while the $T_c^{-4/3}$ dependence of $(\chi_{1,c} - 0.5)$ for the ucst and the T_c^{-2} dependence of $-(\chi_{1,c} - 0.5)$ for the lcst in the *tert*-butyl acetate and methyl acetate solutions. Temperature dependence of the $(\chi_{1,c} - 0.5)$ in the polystyrene–ethyl formate system exhibiting the hour glass phase diagram is approximately expressed by a parabolic-like curve with a minimum. Temperature dependence of the polymer chain dimension estimated by the limiting viscosity number in the polystyrene–*tert*-butyl acetate system over the temperature range including the Θ_u (23°C) and Θ_l (84°C) indicates the continuous change with a maximum value at 55°C, which is consistent with the behavior of temperature dependence of the χ_1. An application of the method derived by Eichinger for the evaluation of the heat capacity term in the dilute polymer solution to the polystyrene–*tert*-butyl acetate system leads to a parabolic-like function of temperature with a minimum at 52°C for the reduced excess chemical potential at infinite dilution $-B(T)$ or $\chi_1 - 0.5$. Temperature dependence of the unperturbed mean-square end-to-end distance of polystyrene in *tert*-butyl acetate, which is determined from viscosity measurements at the Θ_u and the Θ_l, is $\mathrm{d} \ln \langle r_0^2 \rangle / \mathrm{d}T \times 10^3 = 0.34 \pm 0.07$ deg^{-1} for $M_w \times 10^{-4} = 345$ and 0.07 ± 0.07 deg^{-1} for $M_w \times 10^{-4} = 67$.

Evaluation of the polymer–solvent interaction parameter such as the χ_1 parameter or the second virial coefficient A_2, of the first derivative of χ_1 or A_2 on temperature (the excess partial molar entropy and enthalpy), and of the second derivative of χ_1 or A_2 on temperature (the excess partial molar heat capacity) over a wide range of temperature including the Θ_u and Θ_l, where the Θ_u and Θ_l are respectively the Flory or Θ temperatures for the upper critical solution temperature (ucst) and lower critical solution temperature (lcst), is of great interest to examine the thermodynamic properties of the polymer solution. The contribution to χ_1 originating from differences of the characteristics of pure components such as the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient should be taken into account in addition to the enthalpic contribution of the contact interaction between the polymer segment and solvent molecule. Introduction of "the equation of state of the liquid" in the thermodynamic theory of the polymer solution by Patterson[1–7] and by Flory,[8–12] which is based on the Prigogine theory of corresponding state,[13,14] has led to the semiquantitative prediction of the lcst[15–25] and the other properties such as the excess volume of mixing,[26–28] pressure dependence of the ucst and lcst,[29–31] and concentration dependence of χ.[12,16,26–28,32] The increase of χ_1 with an increase of temperature is characterized by the configurational heat capacity or equation of state term. The division of the χ_1 parameter into the contact interaction term of a decreasing function of temperature and the configurational heat capacity term of an increasing function of temperature is of great importance in understanding of fundamental aspects of the polymer–solvent interaction over the temperature range of Θ_u–Θ_l.[23] Investigation of temperature dependence of the polymer chain dimension in the dilute polymer solution over Θ_u–Θ_l is also of great importance in obtaining useful information on the excluded volume effect in the dilute polymer solution.

In this work we have determined the ucst and lcst in the solutions of polystyrene in *sec*- and *tert*-butyl acetate, methyl acetate, ethyl ester (ethyl formate, ethyl *n*-butyrate), and diethyl malonate and the ucst for the polystyrene–*trans*-decalin system. We also determined the limiting viscosity number in the polystyrene–*tert*-butyl acetate over the temperature range including the Θ_u and Θ_l.

Experimental Section

The polystyrene samples were obtained from the Pressure Chemical Co. The samples are characterized by $M_w/M_n < 1.10$ for $M_w \times 10^{-4} = 0.22$ and 0.4, $M_w/M_n < 1.06$ for $M_w \times 10^{-4} = 1.0$ and 2.04. Characterizations for the other samples of $M_w \times 10^{-4} = 3.7$–270 have been described elsewhere.[21] A sample designated by 14b-1 for measurements of the limiting viscosity number was obtained from the solution fractionation described in detail elsewhere[21] and is characterized by $M_w \times 10^{-4} = 345$, $M_w/M_n < 1.10$. Solvents were reagent grade and were further purified before use. *tert*-Butyl acetate (500 g) refluxed for 2 hr over about 15 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. Ethyl formate was treated with phosphorus pentoxide and *sec*-butyl acetate, ethyl *n*-butyrate, diethyl malonate, and *trans*-decalin were dried over anhydrous potassium carbonate. The dried solvents were fractionally distilled by the same column. Purification of methyl acetate has been described in detail elsewhere.[23]

Table I
Parameters Obtained from Viscosity for the Polystyrene-*tert*-Butyl Acetate System

	Sample 13a	Sample 14b-1
$M_w \times 10^{-4}$	67.0	345.0
M_w/M_n	<1.15	<1.10
$[\eta]_{\theta_u}$, dl/g	0.623 ± 0.002	1.420 ± 0.005
$[\eta]_{\theta_l}$, dl/g	0.627 ± 0.002	1.465 ± 0.005
$K_{\theta_u} \times 10^4$, (dl/g)(g mol wt)$^{-1/2}$	7.61 ± 0.03	7.65 ± 0.03
$K_{\theta_l} \times 10^4$, (dl/g)(g mol wt)$^{-1/2}$	7.66 ± 0.02	7.89 ± 0.03
d ln $\langle r_0^2 \rangle/\mathrm{d}T \times 10^3$, deg^{-1}	0.07 ± 0.07	0.34 ± 0.07

The density of *tert*-butyl acetate over the temperature range of 20–95°C was determined by use of a mercury-sealed pycnometer placed in an ethylene-glycol bath controlled to ±0.05°C. The density ρ as a function of temperature is given by

$$\rho^{-1} = 1.1302 + 1.429 \times 10^{-3}t + 0.7376 \times 10^{-6}t^2 + 17.6 \times 10^{-9}t^3$$

where ρ is expressed in g/cm^3 and t is the temperature in °C.

Viscosity measurements were carried out with use of an Ubbelohde type viscometer having negligible kinetic energy corrections. The viscometer was placed in an ethylene-glycol bath controlled to ±0.05°C. The solution viscosities in the polystyrene-*tert*-butyl acetate system were measured over the temperature range of 20–95°C including the Θ_u and Θ_l and no thermal degradation of polystyrene in *tert*-butyl acetate was found.

Several solutions for determinations of cloud-point curves were prepared from each polymer sample and flame sealed under dry nitrogen gas in 7-mm i.d. cylindrical cells. Cloud points were optically determined[21] with an accuracy of ±0.3° in an ethanol bath for the ucst in the low-temperature range of 0 to −90°C and ±0.02° in an ethanol or a water bath for the ucst of temperature 0–60°C and ±0.05° in a silicon oil bath for the lcst. The liquid thermometer used for measurements of low-temperature range (−90 to ca. −95°C) was calibrated by the freezing point (fp) of three solvents: *n*-heptane (fp −90.7°C), cyclopentane (−93.9°C), and *n*-hexane (−95.3°C). Calibrations for the temperature range of −40 to ca. −90°C have been described elsewhere.[23] The ethanol bath for the measurements of cloud points appearing at low temperatures was cooled very slowly by thermal coupling with a liquid-nitrogen bath. Errors caused by thermal degradation for determinations of the lcst are estimated to be 0.5 to ~1.5°C depending on the molecular weight of the samples for *sec*-butyl acetate, ethyl *n*-butyrate, and diethyl malonate solutions, while none was observed in the *tert*-butyl acetate solution.

Results

Typical cloud-point curves for the ucst and lcst in the polystyrene–ethyl formate system are shown in Figure 1, in which immiscibility occurs if the temperature of the solutions is raised above the lcst or lowered below the ucst. An "hour glass" shape of phase diagram is observed for the solution of polystyrene ($M_w \times 10^{-4} = 9.7$) in ethyl formate. The critical points for the ucst and lcst would be given by respectively the maximum and minimum points of cloud-point curves if the polymer were completely monodisperse. Polydispersity tends to displace the critical point to the lower temperature and higher concentration for the ucst and higher temperature and higher concentration for the lcst depending on the polydispersity[33,34] of the polymer sample. The difference of the maximum and minimum temperatures from their critical temperatures should be small because of the small value of M_w/M_n for 12 samples in this work. The values of the ucst and lcst for all systems in this work are determined under the saturated vapor pressure.[35] The collected lcst to zero pressure for the polystyrene solutions should be lower than the observed lcst by 0.5–0.7 deg atm^{-1}.[30,36]

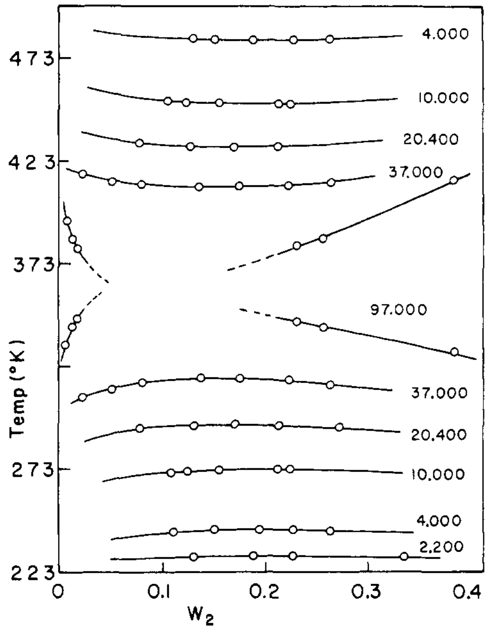

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene–ethyl formate system for samples of indicated molecular weight.

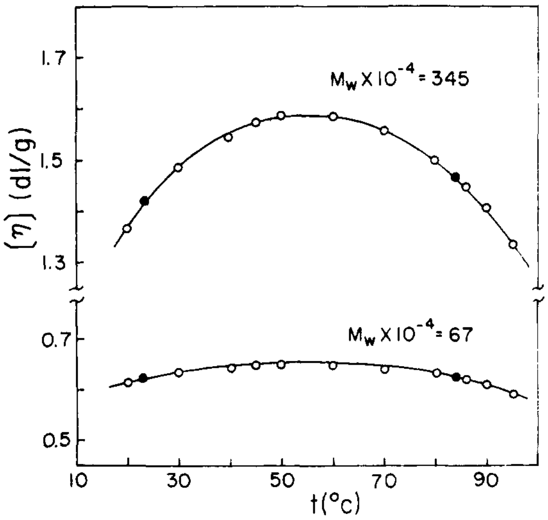

Figure 2. The limiting viscosity number vs. temperature plot for the polystyrene-*tert*-butyl acetate system for samples of indicated molecular weight. The symbol ● indicates $[\eta]_{\Theta_u}$ and $[\eta]_{\Theta_l}$.

Viscosity data were treated by double extrapolation of η_{sp}/c and ln η_{rel}/c against c to determine the limiting viscosity number $[\eta]$, in which η_{sp} and η_{rel} are respectively the specific and relative viscosity and c is the concentration expressed by g/dl. The values of $[\eta]_\Theta$ for the polystyrene-*tert*-butyl acetate are given in Table I and temperature dependence of the $[\eta]$ over the temperature range including the Θ_u and Θ_l is shown in Figure 2. For solutions of polystyrene in *tert*-butyl acetate there is no trace of the discontuinity

Table II
Corrected Values of θ_u and θ_l of the Systems

	From Flory–Shultz plot		From modified Flory–Shultz plot	
System	θ_u, °K	θ_l, °K	θ_u, °K	θ_l, °K
Polystyrene–*tert*-butyl acetate	288	374	296[c]	357[d]
Polystyrene–isopropyl acetate	246[a]	380[a]	250[c]	365[d]
Polystyrene–methyl acetate	316[a]	387[a]	324[c]	370[d]
Polystyrene–ethyl acetate		412[a]		399[d]
Polystyrene–methyl ethyl ketone		422[b]		417[c]

[a] From ref 23. [b] From ref 21. [c] From plot of T_c^{-1} vs. $(\chi_{1,c} - 0.5)^{3/4}$. [d] From plot of T_c^{-1} vs. $(\chi_{1,c} - 0.5)^{1/2}$.

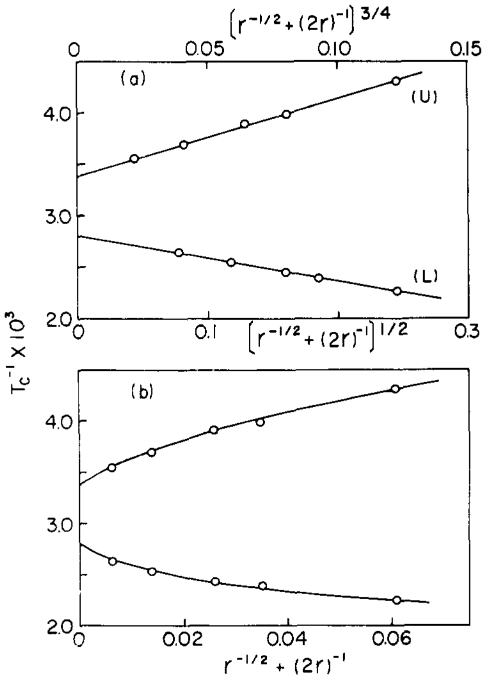

Figure 3. The determination of Θ temperature for the polystyrene–*tert*-butyl acetate system: (a) the modified Flory–Shultz plot $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}^{1/2}]$ for the lcst (L) and $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}^{3/4}]$ for the ucst (U); (b) open circle represents the original Flory–Shultz plot $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}]$ and the solid curve represents the recalculated one from the modified Flory–Shultz plot of (a).

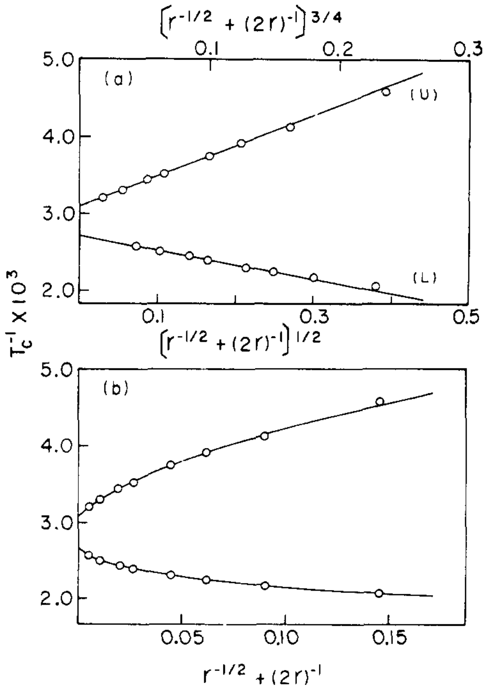

Figure 4. The determination of Θ temperature for the polystyrene–methyl acetate system: (a) the modified Flory–Shultz plot $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}^{1/2}]$ for the lcst (L), and $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}^{3/4}]$ for the ucst (U); (b) open circle represents the original Flory–Shultz plot $[T_c^{-1}$ vs. $\{r^{-1/2} + (2r)^{-1}\}]$ and the solid curve represents the recalculated one from the modified Flory–Shultz plot of (a).

in $[\eta]$ in the neighborhood of 80°C found by Reiss and Benoit.[37] The values of $\mathrm{d} \ln \langle r_0^2 \rangle / \mathrm{d}T$ for the polystyrene–*tert*-butyl acetate given in the last column of Table I were calculated by[38]

$$\mathrm{d} \ln \langle r_0^2 \rangle / \mathrm{d}T = \tfrac{2}{3} \, \mathrm{d} \ln K_\Theta / \mathrm{d}T$$

where $\langle r_0^2 \rangle$ is the unperturbed mean-square end-to-end distance of the polymer and K_Θ is equivalent to $[\eta]_\Theta / M_w^{1/2}$. The $\mathrm{d} \ln \langle r_0^2 \rangle / \mathrm{d}T$ obtained from K_{Θ_u} and K_{Θ_l} in the polystyrene–*tert*-butyl acetate is $(0.34 \pm 0.07) \times 10^{-3}$ deg^{-1} for $M_w \times 10^{-4} = 345$ and $(0.07 \pm 0.07) \times 10^{-3}$ deg^{-1} for $M_w \times 10^{-4} = 67$ as compared with -0.1×10^{-3} deg^{-1} obtained in the polystyrene–cyclopentane system.[39] The reliability of the $\mathrm{d} \ln \langle r_0^2 \rangle / \mathrm{d}T$ is higher in the *tert*-butyl acetate solutions than in the cyclopentane solutions because of the Θ_l (84°C) for the *tert*-butyl acetate solutions and viscosity measurements under the low solution vapor pressure without the thermal degradation of polystyrene.

The Flory or Θ temperatures have been determined by a linear extrapolation in the Flory–Shultz plot of T_c^{-1} vs. $\chi_{1,c} - 0.5$ for the ucst and lcst in the solutions of polystyrene in diethyl malonate and *sec*-butyl acetate, for the ucst in the *trans*-decalin solution, and for the lcst in the ethyl *n*-butyrate solution, while in the solutions of polystyrene in *tert*-butyl acetate and methyl acetate the departure from linearity in the Flory–Shultz plot is remarkably large. As is shown in Figures 3 and 4 the Θ_u for the solutions of polystyrene in *tert*-butyl acetate and methyl acetate can be determined by a linear extrapolation in the plot of T_c^{-1} vs. $(\chi_{1,c} - 0.5)^{3/4}$, while the Θ_l for both the systems can be determined by the plot of T_c^{-1} vs. $(\chi_{1,c} - 0.5)^{1/2}$. The Θ_u and the Θ_l determined by the modified Flory–Shultz plot for the polystyrene solutions, in which nonlinearity in the original Flory–Shultz plot is observed, are listed in Table II.

Discussion

The original relation of the critical solution temperature at constant pressure proposed by Flory[38] assuming χ independent of concentration and a linear function of T^{-1} can be written as

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

$$1/T_c = (1/\Theta)\,[1 + (1/\psi_1)\{r^{-1/2} + (2r)^{-1}\}] \quad (2)$$

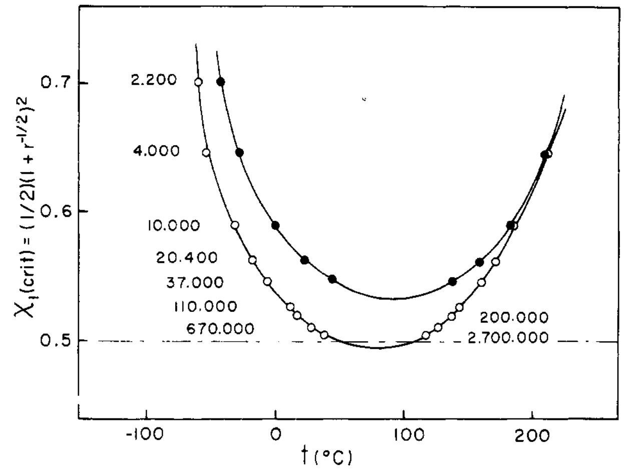

Figure 5. $\chi_1(\text{crit}) = \frac{1}{2}(1 + r^{-1/2})^2$ vs. critical temperature obtained from experiment for samples of indicated molecular weight: (a) polystyrene–ethyl formate (●), (b) polystyrene–methyl acetate (○). The ucst and lcst of polystyrene ($M_w \times 10^{-4}$ = 3.7–270) in methyl acetate is described elsewhere.[23]

where r is the ratio of the molar volumes of the polymer and solvent or the ratio of the characteristic molar volume reduction parameters V_i^* of polymer (2) and solvent (1). The value of $\chi_{1,c}$ obtained by use of eq 1 and $r = V_2^*/V_1^*$ for polystyrene ($M_w \times 10^{-4}$ = 20) in cyclohexane is 0.5231, while the value of $\chi_{1,c}$ evaluated by critical miscibility data for the polystyrene solution ($M_w \times 10^{-4}$ = 20) is 0.5071.[34] On the other hand, the experimental value at the critical point by the critical miscibility data is concentration dependent and gives 0.5326 for the polystyrene ($M_w \times 10^{-4}$ = 20) in cyclohexane.[34] Considerations of concentration dependence of the χ parameter observed by the osmotic pressure and vapor pressure measurements over the wide concentration range lead to the platter shape of the cloud-point curves or the coexistence curves for the ucst and lcst and the displacement of the critical concentrations to higher concentrations for the ucst and lcst than those of the original Flory–Huggins prediction.[19,40] The value of $\chi_{1,c} - 0.5 = 0.0231$ by eq 1 is about three times larger than the experimental value of $\chi_{1,c} - 0.5 = 0.0071$ by the critical miscibility data. Therefore, the value of χ_1 based on eq 1 is not available as a parameter of the polymer–solvent interaction in the dilute solution without further consideration of the concentration dependence of χ. However, it should be still very useful for qualitative examination of temperature dependence of the polymer–solvent interaction.

The typical temperature dependence of $\chi_{1,c}$ determined by eq 1 for solutions of polystyrene in methyl acetate and ethyl formate is shown in Figure 5. On the other hand, the χ_1–temperature curve derived from the critical miscibility data by taking account of the concentration dependence of χ can be expressed by a parabolic curve with a smaller absolute value of $d\chi_1/dT$ by about one third than that of the $\chi_{1,c}$–temperature curve based on eq 1. In either case the χ_1–temperature relation observed in the nonpolar polymer solutions suggests the continuous change from endothermic to exothermic conditions passing through an athermal-like condition at a temperature with a minimum value of χ_1. It should be also noted that the excess entropy of dilution for the noncombinatorial part changes from positive to negative with an increase of temperature.

The original method for determination of the Θ temperature by eq 2 in the plot of T_c^{-1} vs. $(\chi_{1,c} - 0.5)$ is useful for the ucst and lcst in the systems with a relatively large interval of temperature between the ucst and the lcst such as the solutions of polystyrene in diethyl malonate, *sec*-butyl acetate, and *trans*-decalin, while in the systems with a small temperature interval between the ucst and the lcst such as the solutions of polystyrene in methyl acetate and *tert*-butyl acetate the deviation from linearity in the Flory–Shultz plot is considerably large beyond the experimental errors. The $\chi_{1,c}$–temperature curve for the polystyrene–ethyl formate system is a typical example of the parabolic dependence of $\chi_{1,c}$ against temperature. The division of the χ_1 into the contact interaction term ($c_1\nu^2$ term) and the configurational heat capacity term ($c_1\tau^2$ term) according to the Patterson theory is shown in Figure 6 for the solutions of polystyrene in isobutyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate, in which the contribution of two terms to χ_1 strongly depends on the molecular structure of the solvent. The aspect of temperature dependence of the χ_1 parameter at the critical condition depends on the behavior in the vicinity of the critical line of $\chi_{1,c} = 0.5$ in the parabolic-like curve of $\chi_{1,c}$ against temperature, which is peculiarly determined by a pair of polymer and solvent through the contribution of the two terms to χ_1. The characteristic difference of the thermodynamic properties at the Θ_u and the Θ_l should be reflected in pressure dependence of the critical solution temperatures for the ucst and lcst,[36] which are closely related to the excess volume of mixing in the solution. Determinations of the molecular parameters such as $c_1\nu^2$ and $c_1\tau^2$ in the Patterson theory by use of the experimental critical solution temperatures for the ucst and lcst have been made through the procedure described elsewhere[21] and values of the parameters are listed in Table III.

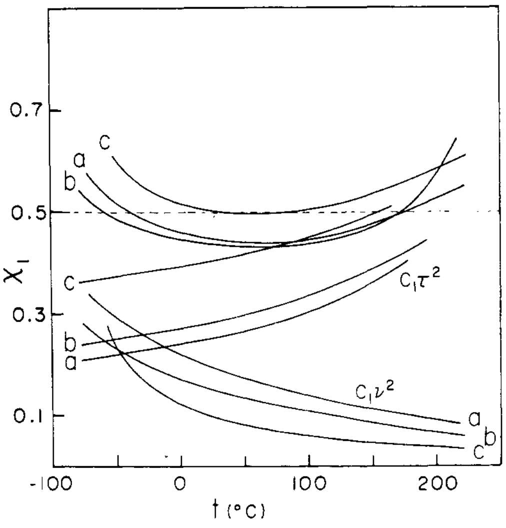

Figure 6. Temperature dependence of the χ_1 parameter calculated by the procedure described elsewhere:[21,23] (a) polystyrene–isobutyl acetate,[23] (b) polystyrene–*sec*-butyl acetate, (c) polystyrene–*tert*-butyl acetate.

It is of particular interest to compare the temperature dependence of $[\eta]$ with the temperature dependence of χ_1 for the polystyrene–*tert*-butyl acetate system shown in Figure 6. The dimension of polystyrene in *tert*-butyl acetate attains a maximum at 55°C, while χ_1 becomes a minimum in the neighborhood of 55°C. The maximum value of $[\eta]$ and of the expansion factor $\alpha_\eta^3 = [\eta]/[\eta]_\Theta$ in the polystyrene ($M_w \times 10^{-4}$ = 67) -*tert*-butyl acetate are respectively 0.651 dl/g and 1.04, which are much smaller than those of polystyrene ($M_w \times 10^{-4}$ = 67) –cyclopentane system,[39] i.e. 0.91 dl/g and 1.41 at 90°C. The difference of $[\eta]$ and α_η^3 between both systems is closely related to the minimum value of χ_1 in that the *tert*-butyl acetate solution is larger than that in the cyclopentane solution. These excellent agreements of $[\eta]$ with χ_1 suggests that we have to take account

Table III
Parameters of the Systems

System	θ_u, °K	θ_l, °K	$c_1\nu^2$	$c_1\tau^2$	T_1^*, °K	V_1^*, cm^3/mol
Polystyrene–diethyl malonate	309	578	0.0150	0.100	5289[a]	122.0[a]
Polystyrene–*trans*-decalin	294	>360			5758[b]	127.0[b]
Polystyrene–ethyl formate	"hour glass"		0.0085	0.200	4382[a]	60.9[a]
Polystyrene–ethyl *n*-butyrate		471	0.0100	0.115	4741[a]	103.0[a]
Polystyrene–*sec*-butyl acetate	210	442	0.0100	0.140	4830[a]	105.0[a]
Polystyrene–*tert*-butyl acetate	296	357	0.0031	0.235	4598[c]	105.0[c]

[a] From International Critical Tables. [b] From organic solvents. [c] From experimental result of density measurement. $T_2^* = 7420$ and $v_2^* = 0.8098$ cm^3 g^{-1} for polystyrene were taken from ref 44.

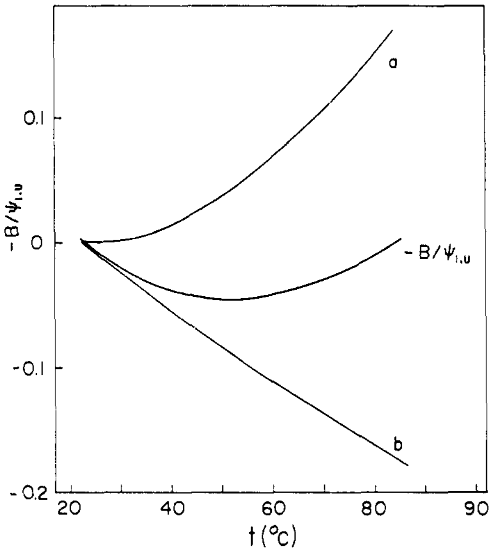

Figure 7. Temperature dependence of the thermodynamic parameter $-B(T)/\psi_{1,u}$ for the dilute solution of polystyrene in *tert*-butyl acetate. The plotted function of $-B(T)/\psi_{1,u}$ is calculated by eq 3. (a) and (b) correspond to the second and the first term in $-B(T)/\psi_{1,u}$, respectively.

of the noncombinatrial free-energy parameter with a parabolic-like temperature dependence for studies of the excluded volume effect in dilute polymer solutions. The traditional assumption for the segmental excluded volume integral is justified only in a limited temperature range or a limited system indicating the T^{-1} dependence of the integral, but cannot be valid over the temperature range of Θ_u–Θ_l.

Eichinger[41] has extended the Flory's treatment of the excluded volume integral for a pair of polymer segments by taking account of temperature dependence of the enthalpy and the entropy of mixing. The reduced excess chemical potential at infinite dilution $-B$ or $\chi_1 - 0.5$ is approximately obtained by

$$B(T) = \psi_{1,u}(1 - \Theta_u/T) - \xi_1\,[(1 - \Theta_u/T) + \ln(\Theta_u/T)] \tag{3}$$

where $\psi_{1,u}$ is the entropy parameter at the Θ_u and ξ_1 is an average quantity independent of temperature and corresponds to the value of the reduced excess partial molar heat capacity of dilution $\bar{C}_{p,1}{}^E/R\varphi_2{}^2$ at infinite dilution. The quantity ξ_1 is defined by

$$\xi_1 = T(\mathrm{d}\psi_1/\mathrm{d}T) = \mathrm{d}(T\kappa_1)/\mathrm{d}T \tag{4}$$

where κ_1 is the enthalpy parameter. The value of $\bar{C}_{p,1}{}^E/\bar{S}_1{}^E$ at infinite dilution or $\xi_1/\psi_{1,u}$ in the polystyrene–*tert*-butyl acetate evaluated from the Θ_u and the Θ_l in eq 3 is −10.4, which is much larger as compared with −4.1 in the polystyrene–cyclohexane and −2.6 to −2.0 in the polystyrene–decalin (56% cis) reported by Eichinger. As is shown in Figure 7 temperature dependence of the $-B(T)/\psi_{1,u}$ is represented by a parabolic-like function of temperature with a minimum at 52°C. The temperature dependence of $-B(T)/\psi_{1,u}$ is consistent with the temperature dependence of $[\eta]$ in the polystyrene–*tert*-butyl acetate.

The values of d ln $\langle r_0{}^2\rangle/\mathrm{d}T$ evaluated from the limiting viscosity numbers at the Θ_u and the Θ_l in the polystyrene–*tert*-butyl acetate are to be compared to the value of 0.44×10^{-3} deg^{-1} obtained by use of different Θ solvent systems[42,43] and of 0.37×10^{-3} deg^{-1} by measurements of the stress-temperature coefficient for the amorphous polystyrene converted to a network by cross-linking.[42,43] Viscosity or light-scattering measurements at the Θ_u and Θ_l in the same solvent should be an attractive way for the determinations of d ln $\langle r_0{}^2\rangle/\mathrm{d}T$ without a small variation of the unperturbed dimensions at different Θ solvents.

In this work it is emphasized that temperature dependence of the χ_1 parameter is characterized by a parabolic curve with a minimum contrary to the prediction of the regular solution and the polymer chain dimension in the dilute solution over the Θ_u to ca. the Θ_l has a maximum value at the minimum value of χ_1. It is also suggested that the configurational heat capacity term in the χ_1 parameter plays an important role in the determination of the polymer–solvent interaction over the temperature range including the Θ_u and Θ_l.

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Solutions of Flexible Polymers. Neutron Experiments and Interpretation

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ABSTRACT: We present small angle neutron scattering data on polystyrene (normal or deuterated) in a good solvent (carbon disulfide). All data are taken in the *semidilute* regime where the chains overlap strongly, but the solvent fraction is still large. We have measured the following. (a) The radius of gyration $R_G(c)$ for one deuterated chain in a solution of normal chains with concentration c. We find that $R_G^2(c)$ is proportional to the molecular weight and that R_G^2 decreases with concentration like c^{-x} where $x = 0.25 \pm 0.02$. (b) The screening length $\xi(c)$ (introduced, but not quite correctly calculated by Edwards) giving the range of the $\langle c(\mathbf{r})c(\mathbf{r}')\rangle$ correlations. We find $\xi \sim c^{-z}$, with $z = 0.72 \pm 0.06$. (c) The osmotic compressibility $\chi(c)$ (through the scattering intensity of identical chains in the small angle limit). From an earlier light-scattering experiment, we find $\chi \sim c^{-y}$ with $y = 1.25 \pm 0.04$. These results are to be compared with the predictions of the mean field (Flory–Huggins–Edwards) theory which are: R_G independent of c, $\chi \sim c^{-1}$, and $\xi \sim c^{-1/2}$ in the semidilute range. We show in the present paper that the measured exponents can all be interpreted in terms of a simple physical picture. The underlying basis is the analogy, recently found by Des Cloizeaux, between the semidilute system and a ferromagnet under an external field. However, in this paper, we emphasize mainly the polymer aspects. At short distances ($r < \xi$) the correlations are determined by excluded volume effects. At large distances ($\xi < r < R_G$) the chains are gaussian and the effective interaction between subunits of the same chain are weak.

I. Introduction

1. General Aims. For a long time, the main experiments on polymer solutions measured *macroscopic* parameters such as the osmotic pressure, or the heat of dilution. The resulting data for good solvents are rather well systematized by a mean field theory analysis due to Flory[2a] and Huggins.[2b] A precise description of the method and some of the data can be found in chapter 12 of Flory's book.[3] Recently, however, it has become possible to probe solutions more *locally* (i.e., at distances of order 20 to 500 Å) by small-angle neutron scattering.[4] Using the large difference between the scattering amplitude of protons and deuterons, many different measurements become feasible. For instance it is possible to study one *single-labeled chain* among other chains which are chemically identical, but not labeled.[5] In the present report we present two distinct series of neutron studies on polymer solutions: one with identical chains, and another one with a few labeled chains. These experiments prove that the mean field theory must be refined, and that a number of anomalous exponents occur; fortunately the theory of polymer solutions in good solvents has progressed remarkably in the last year mainly through the work of Des Cloizeaux.[6] In his original article, Des Cloizeaux was concerned mainly with thermodynamic properties. In the theoretical part of the present paper, we show that (a) his results can be derived directly from certain scaling assumptions and (b) his arguments can be extended to discuss local correlation properties. Our discussion is only qualitative, but it does account for the anomalous exponents, without the heavy theoretical background which is needed to read ref 6. (A simplified version of ref 6, requiring only a modest knowledge of magnetism and phase transitions, is given in the Appendix.) To reach a (hopefully) coherent presentation, we shall not separate the theory from the experiments, but rather insert the latter at the right point in the discussion.

2. Organization. This paper is organized as follows. Section II describes the experimental method. Section III contains a general presentation of the three concentration domains for polymer solutions, corresponding respectively to