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(14) See ref 2, pp 576–581. See also pp 511–514 and pp 520–523.
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Pressure Dependence of Upper Critical Solution Temperatures in Polymer Solutions

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ABSTRACT: The pressure dependence of the upper critical solution temperature (UCST) in solutions of polystyrene (PS) in diethyl oxalate (DEO) has been determined over the pressure range 1–1000 atm (1 atm = 0.1011 MPa). The UCST–pressure curves show a minimum when polystyrene has molecular weight $M_w \times 10^{-4}$ = 5.0, 11, and 60, but there is no minimum when $M_w = 1.67 \times 10^4$. The UCSTs increase with increasing pressure over 1–50 atm. The pressure indicating the minimum UCST tends to decrease with decreasing molecular weight of PS. The behavior of the UCST against pressure in PS/DEO has been explained semiquantitatively by the corresponding-states theories by Patterson and Flory, which give a parabolic-like pressure dependence of the χ_1 parameter with a minimum at higher constant temperature and a monotonically increasing function of pressure for χ_1 at lower constant temperature.

Introduction

Investigations of phase separation behavior in polymer solutions over a wide range of temperature up to the vapor–liquid critical point of the solvent[1] have drawn much attention to the theory of polymer solution thermodynamics.[2-4] It is recognized that both upper and lower critical solution temperatures are general phenomena in liquid mixtures and are observed in polymer solutions,[1,5-7] simple liquid mixtures,[8,9] and polymer mixtures.[10] Systematic works have been carried out by introducing pressure as a thermodynamic variable on the critical solution phenomena.[11-19] Over a moderate pressure range, it is observed that the upper critical solution temperature (UCST) for polymer solutions decreases or increases with increasing pressure,[13,15-19] while the lower critical solution temperature (LCST) increases with increasing pressure[11,13,14,16] except for the poly(ethylene glycol)/water system, where LCSTs are almost constant over 1–50 atm.[17] A parabolic-like pressure dependence of the UCST with a minimum is also reported for a few polymer solutions.[19]

The corresponding-states theories derived by Patterson[4] and Flory[2,3] are able to explain the LCST, excess volume of mixing, concentration dependence of the χ parameter, and so on. In this work we have determined the pressure dependence of the UCST in the polystyrene (PS)/diethyl oxalate (DEO) system over the pressure range 1–1000 atm and tried to explain the data with the aid of the corresponding-states theory.

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Table I
Experimental and Calculated Values of T_c and (dT_c/dP) at 1 atm and Experimental Values of ϕ_c for PS/DEO Systems

$M_w \times 10^{-4}$	$T_{c,exptl}$, °C	$(dT_c/dP)_{exptl}$, °C/atm	$T_{c,calcd}$, °C	$(dT_c/dP)_{calcd}$,[a] °C/atm	$\phi_{2,c}$	$\chi_{1,c}$[b]
1.67	-11.19	+0.00126	19.98	-0.0024	0.1578	0.5931
5.0	6.90	-0.0045	45.8	-0.0080	0.1302	0.5529
11.0	19.44	-0.0105	58.4	-0.015	0.0927	0.5353
60.0	36.81	-0.019	75.7	-0.040	0.0427	0.5150

[a] The values are obtained from the theoretical P-T critical lines shown in Figure 1. [b] Values of $v^*_{i,sp}$ used to calculate $r = M_{w,PS}v^*_{PS,sp}/M_{w,DEO}v^*_{DEO,sp}$ are 0.7364 cm³/g for DEO and 0.8098 cm³/g for PS.

Experimental Section

Polystyrene samples were obtained from Pressure Chemical Co. and values of M_w and M_w/M_n are given by 1.67×10^4 and ≤1.06, 5.0×10^4 and ≤1.06, 11×10^4 and ≤1.10, and 60×10^4 and ≤1.10. DEO was obtained from Wako Pure Chemicals and was distilled before use after removal of trace water by potassium carbonate anhydride. The apparatus for measuring UCSTs under high pressure consists of three parts: a He–Ne gas laser (Spectra-Physics 155) used as a light source, a pressure cell in which the solution is sealed by mercury, connected to a Heise pressure gauge (12 in., maximum 4000 atm) and pressure generator (Nikkiso HPO oil pump), and a CdS photosensor, which detects the intensity of light passed through the solution. The phase separation temperature is determined as the temperature at which the resistance of the CdS photosensor indicates a discontinuous change. Measurements of the phase separation temperature are carried out by decreasing the temperature of the solution slowly (0.001–0.002 °C/min) under constant pressure, and the phase separation temperatures are determined to an accuracy of 0.001 °C in a bath controlled within 0.001 °C, in which a quartz thermometer (Hewlett-Packard 2804A, 18116A) calibrated by the triple point of water is set. The coexisting curves were determined by a differential refractometer in the bath controlled within ±0.001 °C. A detailed description of the refractometer and experimental procedures are described elsewhere.[20] The critical solution temperatures T_c and concentrations $\phi_{2,c}$ in the PS/DEO system evaluated from coexisting curves at 1 atm are given in Table I, where ϕ_2 is the volume fraction of polymer and is calculated from the weight fraction of polymer w_2 by

$$\phi_2 = \{(\rho_{PS}/\rho_{DEO})(w_2^{-1} - 1) + 1\}^{-1}$$

where ρ_{PS} and ρ_{DEO} are the density of PS and DEO, respectively. The density of DEO was measured with an Anton Paar Co. densitometer, and the density is given by

$$\rho_{DEO}\ (g/cm^3) = 1.10000 \pm 1.8 \times 10^{-5} - (9.864 \pm 2.2 \times 10^{-2}) \times 10^{-4}t - (3.801 \pm 7.9 \times 10^{-2}) \times 10^{-6}t^2 + (1.482 \pm 8.7 \times 10^{-2}) \times 10^{-8}t^3 \qquad 10 \le t \le 50\ °C$$

where t is in °C. The density for PS was obtained from ref 22.

All solutions were prepared in a drybox filled with dry nitrogen gas. Measurement of the pressure dependence of the UCST in the PS/DEO system is carried out by using the sample of critical concentration.

Theory

Phase separation behaviors in polymer solutions are often analyzed by using the Flory–Huggins formulation for the activity coefficients[21]

$$a_1/\phi_1 = \exp\{(1 - r^{-1})\phi_2 + \chi\phi_2^2\} \quad (1)$$

where the ϕ's represent the volume fraction of solvent (ϕ_1) and polymer (ϕ_2) and r is the ratio of the molar volume of the polymer to that of the solvent. Following the corresponding-states theory,[2-4] the volume fractions in eq 1 are replaced by the segment fractions (ψ), and the polymer–solvent interaction parameter χ_1 is given as a function of temperature and pressure[4]

$$\chi_1/c_1 = (-\tilde{U}_1/\tilde{T}_1)\nu^2 + \tilde{C}_{p,1}(\tau + \pi\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1)^2/2 \quad (2)$$

and

$$\psi_1 = w_1v^*_{1,sp}/(w_1v^*_{1,sp} + w_2v^*_{2,sp}) \quad (3)$$

where $\tilde{T}_1 = T/T^*_1$ and $\tilde{P}_1 = P/P^*_1$ are reduced variables of solvent molecules, ν, τ, and π are molecular parameters, and $3c_1$ is the external degrees of freedom of the solvent molecules. The ν^2 parameter is related to the difference of cohesive energy and size between the solvent and the polymer segment and $-\tilde{U}_1$ is the reduced vaporization energy of the solvent. The τ parameter reflects the free volume change, which occurs in mixing the dense polymer (small $\tilde{T}_2$) with the relatively expanded solvent (large $\tilde{T}_1$) and is defined by

$$\tau = 1 - \tilde{T}_2/\tilde{T}_1 = 1 - T^*_1/T^*_2 \quad (4)$$

while $\tilde{C}_{p,1}$ is the reduced configurational heat capacity of the solvent and reflects the variation of the quantity $-\tilde{U}_1$ due to temperature change. The two terms in the second term in eq 2 expressed by $\tilde{C}_{p,1}(2\tau\pi\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1)$ and $\tilde{C}_{p,1}(\pi\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1)^2$ correspond to $\tilde{P}_1\tilde{V}_1\alpha_1\tau\pi$ and $\tilde{P}_1^2\tilde{V}_1\tilde{\beta}_1\pi^2/\tilde{T}_1$, respectively, in the Patterson theory[4] and are explained as the terms from $(\partial^2\tilde{G}/\tilde{P}_1\tilde{T}_1)(\tilde{P} - \tilde{P}_1)(\tilde{T} - \tilde{T}_1)$ and $(\partial^2\tilde{G}/\partial\tilde{P}_1^2)(\tilde{P} - \tilde{P}_1)^2$, respectively, where $\tilde{P}$ and $\tilde{T}$ are values for solution. By using the van der Waals model for the configurational energy, the quantities $-\tilde{U}_1$ and $\tilde{C}_{p,1}$ are given by[4]

$$\tilde{U}_1 = -\tilde{V}_1 \quad (5)$$

and

$$\tilde{C}_{p,1} = [1 - 2/(3\tilde{V}_1^{1/3}) - 2(1 - \tilde{V}_1^{-1/3})/(\tilde{P}_1\tilde{V}_1^2 + 1)]^{-1} \quad (6)$$

where

$$\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1 = \tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2 + 1) \quad (7)$$

Values of $\tilde{\alpha}_1$ and $\tilde{\beta}_1$ in eq 7 are the reduced thermal expansion coefficient and compressibility of the solvent and are calculated by the reduced equation of states proposed by Flory et al.[3]

$$\tilde{P}\tilde{V}/\tilde{T} = 1/(1 - \tilde{V}^{-1/3}) - (\tilde{V}\tilde{T})^{-1} \quad (8)$$

The corresponding-states theory of Flory[3] also gives essentially the same expression for the χ_1 parameter given in eq 2.

We have adopted two approximations in the calculations: (1) the term $(\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1)$ in eq 2 is negligibly small compared to τ and (2) the χ parameter is independent of concentration and is a function of temperature and pressure as given by eq 2. From approximation 2, the critical condition is expressed by

$$\chi_1(crit) = (1/2)(1 + r^{-1/2})^2 \quad (9)$$

where r is the ratio of molar volume reduction parameters (see Table I).

Results

Experimental values of the UCST as a function of pressure in solutions of PS in DEO are shown in Figure 1, in which the critical lines calculated by eq 2 and 9 are also included. Values of the molecular parameters $\nu^2 = 0.052$ and $c_1 = 0.652$ used in the calculation are adjustable parameters, while $\tau^2 = 0.10$ is estimated from the value

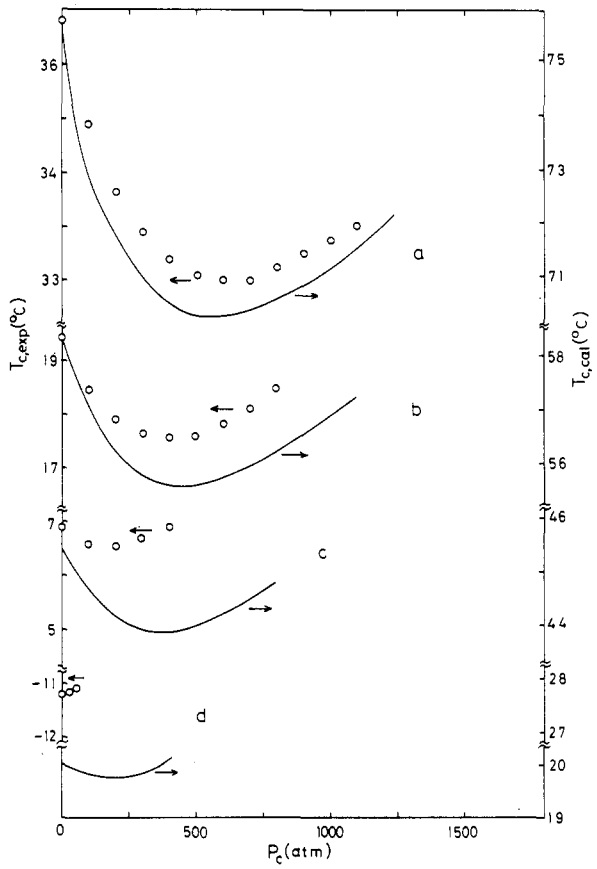

Figure 1. Projection on the (P,T) plane of the critical lines corresponding to the UCST in the polystyrene (PS)/diethyl oxalate (DEO) system for samples of various molecular weight: (a) $M_w = 60 \times 10^4$; (b) 11.0×10^4; (c) 5.0×10^4; (d) 1.67×10^4. The solid lines are calculated by using eq 2 with $\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1 = 0$, $c_1\nu^2 = 0.0339$ and $c_1\tau^2 = 0.0652$.

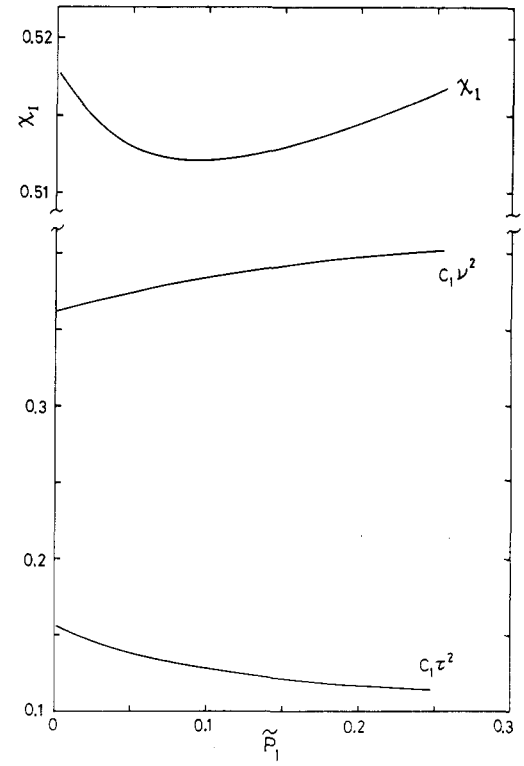

Figure 2. Reduced pressure $\tilde{P}_1$ dependence of χ_1 calculated by eq 2 and the same parameters as in Figure 1 at constant reduced temperature $\tilde{T}_1 = 0.06975$. The lines indicated by $c_1\nu^2$ and $c_1\tau^2$ correspond to the $c_1\nu^2$ and $c_1\tau^2$ terms, respectively, and therefore χ_1 = the $c_1\nu^2$ term + the $c_1\tau^2$ term.

calculated by eq 4, which gives $\tau^2 = (1 - 4944/7420)^2 = 0.11$. The value of T^*_1 for DEO is calculated from the thermal expansion coefficient $\alpha = 1.092_4 \times 10^{-3}$ deg^{-1} at 20 °C and eq 8 with $P = 0$, while that of PS, $T^*_2 = 7420$ K, is taken from ref 22. Although the absolute values of the UCST in various PS/DEO systems are not predicted (see Table I), the theory predicts the pressure dependence of the UCST semiquantitatively. A main difference between the theory and the experimental result is that the observed pressure dependence of the UCST, $(dT_c/dP)_{UCST}$, is positive in PS ($M_w = 1.67 \times 10^4$)/DEO over the pressure range 1–50 atm, while a negative $(dT_c/dP)_{UCST}$ was obtained from the calculation (see Table I). Experimental and calculated values of T_c and $(dT_c/dP)_{UCST}$ for PS/DEO systems are given in Table I. A positive $(dT_c/dP)_{UCST}$ is predicted by eq 2 for solutions of lower molecular weight PS ($M_w = 7430$) in DEO where χ_1 increases with increasing pressure.

It is interesting to analyze the pressure dependence of the UCST through eq 2, which consists of two important terms, the $(-\tilde{U}_1/\tilde{T}_1)\nu^2$ or ν^2 term and the $\tilde{C}_{p,1}\tau^2/2$ or τ^2 term. Typical values of the $c_1\nu^2$ and $c_1\tau^2$ terms as a function of reduced pressure at constant reduced temperature calculated by eq 2 with $(\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1) = 0$ are plotted in Figure 2, where the $c_1\nu^2$ and $c_1\tau^2$ terms mean the ν^2 and τ^2 terms multiplied by c_1, respectively. It is shown that the pressure dependence of χ_1 is determined by the increasing function of pressure ($c_1\nu^2$ term) and the decreasing function ($c_1\tau^2$ term). Determination of the theoretical critical line is carried out by using the χ_1–reduced pressure of solvent $\tilde{P}_1$ curve at a constant reduced temperature $\tilde{T}_1$, which is calculated by eq 2 with two adjustable parameters, ν^2 and c_1. The procedure is as follows: (1) Values of the adjustable parameter ν^2 ($\ll 1$) and τ^2 calculated by eq 4 are set into eq 2 to calculate χ_1/c_1 at various reduced pressures $\tilde{P}_1$ under a constant reduced temperature $\tilde{T}_1$. From the calculation, the χ_1/c_1–$\tilde{P}_1$ curves at various $\tilde{T}_1$ are determined. (2) Values of χ_1(crit) are calculated by eq 9. (3) With the use of an adjustable parameter c_1 (≤ 1), χ_1–P curves are obtained for various temperatures T, where $\tilde{P}_1$ and $\tilde{T}_1$ are converted into P and T through $P = \tilde{P}_1P^*_1$ and $T = \tilde{T}_1T^*_1$. The value of P^*_1 for DEO is 6103 atm, which is calculated from values of the thermal expansion and thermal pressure coefficients of DEO and eq 8 with $P = 0$. The value of the thermal pressure coefficient of DEO used in this work is 13.06 atm/°C at 20 °C. (4) From the χ_1–P curves at various temperatures, P–T pairs satisfying the χ_1(crit) are determined, which are the theoretical P–T critical lines shown in Figure 1.

It has been found from the study of the UCST and LCST in polymer solutions[7] that contributions of the $c_1\nu^2$ term to χ_1 in eq 2 vicinity of the UCST are comparable with those of the $c_1\tau^2$ term. It is suggested from the fact that the parabolic-like pressure dependence of χ_1 with a minimum at constant temperature in the vicinity of the UCST is one of important behaviors characterizing polymer solutions, and that means the pressure dependence of the UCST is parabolic-like with a minimum in most polymer solutions. It is also interesting to analyze the pressure dependence of the UCST from the viewpoint of the excess volume of mixing. The thermodynamic equation for the pressure dependence of the critical solution temperature derived by Prigogine[23] is given by

$$(dT_c/dP) = (\partial^2\Delta V_M/\partial\phi_2^2)_c/(\partial^2\Delta S_M/\partial\phi_2^2)_c \quad (10)$$

where ΔV_M and ΔS_M are the excess volume of mixing and entropy of mixing, respectively. In the vicinity of the UCST the denominator $(\partial^2\Delta S_M/\partial\phi_2^2)_c$ is negative.

Therefore, if (dT_c/dP) is negative, $(\partial^2\Delta V_M/\partial\phi_2^2)_c$ is positive or ΔV_M is negative, while a positive (dT_c/dP) corresponds to positive ΔV_M. It is speculated that the value of excess volume of mixing ΔV_M in PS/DEO changes from negative to positive with increasing pressure over 1–1000 atm for solutions with $M_w > 5.0 \times 10^4$, while in solutions with $M_w = 1.67 \times 10^4$, values of ΔV_M are positive over 1–50 atm.

Since eq 2 with values of $c_1\nu^2 = 0.0339$ and $c_1\tau^2 = 0.0652$ also predicts the upper and lower critical solution temperatures in PS/DEO, eq 2 is very useful for predicting the phase separation behaviors in polymer solutions over wide temperature and pressure ranges.

Discussion

In this calculation we have adopted two approximations. The first is neglect of the $\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1$ term in eq 2, which means that a direct contribution of the $\tilde{P}_1\tilde{V}_1$ term to the χ_1 parameter is negligibly small compared to that of the $\tilde{C}_{p,1}\tau^2$ term. The former is related to $(\partial^2\tilde{G}/\partial\tilde{P}_1\tilde{T}_1)$ and $(\partial^2\tilde{G}/\partial\tilde{P}_1^2)$, while the latter is originally related to $(\partial^2\tilde{G}/\partial\tilde{T}_1^2)$. In this work we have obtained that the experimental behavior of the UCST against pressure in PS/DEO can be predicted through the two terms, $(-\tilde{U}_1/\tilde{T}_1)\nu^2$ and $\tilde{C}_{p,1}\tau^2/2$ without the $\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1$ term in eq 2. It is also found from the calculation that the term $\tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2 + 1)$ corresponding to $\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1$ in eq 6 is an increasing function of pressure, and therefore the term may cause a poor prediction of the experimental results because the second term in eq 2 changes to an increasing function of pressure from a decreasing one with the introduction of $\tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2 + 1)$ term. However, the large difference between the calculated values and experimental ones observed in low molecular weight PS may be improved by introducing the contribution of the $\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1$ term to χ_1. The other approximation is related in that the χ_1 parameter is independent of concentration. Although the approximation is not accepted experimentally, we can obtain useful information on the general aspect of phase separation behavior under pressure for dilute polymer solutions near the critical concentration through eq 9.

It is interesting to refer to theoretical works on the polymer–solvent interaction parameter. A closed expression for χ as a function of concentration has been derived by Koningsveld and Kleintjens[24] by taking account of the distinction between the site fraction and volume fraction. Sanchez and co-workers[25,26] have applied the lattice-fluid theory to polymer solutions. Whether these theories can explain the pressure dependence of the UCST obtained in this work depends on whether the pressure dependence of the χ parameter in these theories is expressed by the parabolic-like function of pressure with a minimum.

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Static Structure Factor of Charged Reptating Polymer Chains

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ABSTRACT: Using the biased reptation model that we have introduced recently to understand DNA gel electrophoresis, we study here the static structure factor of highly entangled charged polymer chains in an electric field. The relevant time and length scales are found and interpreted in terms of the dynamics of the chains. The exact structure factor is given for some examples. The possibility of studying such systems by small-angle neutron scattering and computer simulations is discussed.

1. Introduction

One of the most popular models for highly entangled polymer systems is the so-called reptation model.[1-3] Conceptually easy to understand, it leads to relatively simple calculations of various rheological parameters.[3] The nonequilibrium correlation function of a reptating chain has also been calculated with this model;[4,5] the time-dependence of the static structure factor of a uniaxially stretched coil has been obtained from these results and compared with available data from small-angle neutron scattering (SANS) experiments.[6]

Recently, we introduced a biased reptation model (BRM) to study the problem of DNA gel electrophoresis.[7] This model predicts that the electric forces together with

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