Polymer–cosolvent systems: 5. Upper and lower critical solution temperatures of polystyrene in n-alkanes

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The demixing behaviour of low molecular weight polystyrene in three n-alkanes (hexane, heptane and octane) has been established. Critical solution behaviour is a function of alkane chain length, and application of free volume theory shows this to be an entropic effect. The quality of n-alkanes, up to twenty carbons in length, as solvents for polystyrene has been estimated.

Keywords Critical solution temperatures; polystyrene; n-alkanes; cloud pount curves; free volume theory

INTRODUCTION

The formation of ternary, solvent(1)solvent(2)polymer(3), systems may be effected by using binary solvent combinations prepared from good, poor, or non-solvents. In the absence of strong specific interactions, the resulting mixtures normally exhibit smooth monotonic changes in properties as a function of composition[1]. Rather more unusual is the situation where the mixture may behave as a cosolvent[2–5], where a cosolvent mixture is defined as one in which the polymer coil is more effectively solvated than in either of the two separate component liquids. Cosolvency will then be most obvious when such synergistic mixtures are formed from poor or non-solvents.

The extent of interaction between a polymer and the solvating medium can be established quantitatively in a number of ways. Coil sizes can be estimated from viscosity or light scattering measurements[6,7] and in a mixed solvent observation of a maximum value of the coil size or a positive deviation from an 'ideal' average value[8] may be taken as evidence of cosolvent action. Information on the phenomenon of preferential adsorption (or solvation)[3,4,6] in mixed solvent systems, which results in changes in the local solvent composition around the polymer coil, can be used to indicate the optimum solvent mixture required for maximum coil expansion. However, these methods tend to be limited by the fact that temperature effects cannot be studied conveniently over a wide range, either in mixtures or in single liquids. Such measurements are desirable as solvent–polymer interactions are temperature dependent and cosolvency may not always be obvious at ambient temperatures.

An alternative method of establishing polymer–solvent interactions and miscibility as a function of temperature is to study polymer solvent demixing equilibria. In the absence of effects such as degradation and polymer or solvent crystallization, phase boundaries can be established marking the limits of miscibility of the system as a function of temperature. Normally, two such boundaries can be established, characterized by either an upper critical solution temperature (*UCST*) or a lower critical solution temperature (*LCST*)[9,10]. These critical temperatures vary with the molecular weight of the polymer, but in the limit of infinite molecular weight can be identified as upper and lower Flory (θ) temperatures, viz. θ_u and θ_L. Between θ_u and θ_L, the limiting viscosity number and the second virial coefficient both pass through maxima while the interaction parameter χ_1 passes through a minimum[9,11–14]. The quality of a solvent or the extent of polymer solvent interaction can thus be judged more accurately and conveniently from the magnitude of the miscibility range $\Delta\theta = \theta_L - \theta_u$ rather than from the value of a particular solution parameter at or near room temperature.

The extent of any cosolvent action exhibited by a pair of liquids can also be quantified by establishing the miscibility ranges at intermediate liquid(1)–liquid(2) compositions, and comparing these with the ranges obtained in each of the pure liquids. In the case where one or both of these are poor solvents, i.e. only capable of dissolving medium to high molecular weight polymer so that $\Delta\theta = 0$, then comparison may be made with respect to the phase behaviour of any convenient molecular weight.

A classic example of true cosolvency is exhibited by the system acetone(1)–diethyl ether(2)–polystyrene(3)[2]. Neither acetone nor ether alone will dissolve polymer $\bar{M}_n > 3.7 \times 10^4\,\mathrm{g\,mol^{-1}}$, but for this same molecular weight a miscibility range of up to 170K is obtained in mixtures of acetone and ether of various compositions. The same system shows that the conventional viewpoint of considering behaviour mainly at ambient temperatures can be inappropriate when discussing cosolvency, since the maximum cosolvent effect for polystyrene $\bar{M}_n > 1.0 \times 10^6\,\mathrm{g\,mol^{-1}}$ is to be found at 260K with volume fraction of acetone $= 0.35$.

A similar study of phase behaviour[15] has been carried out on the system methylcyclohexane(1)–diethyl ether(2)–polystyrene(3) where the mixed solvent is a combination of a good ($\Delta\theta = 140$K) and a poor solvent. A maximum in A_2 as a function of solvent composition was found, indicating considerable cosolvency. However, the phase boundaries constructed from the demixing behaviour

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revealed that this effect is predominantly a consequence of the widely differing temperatures at which each of the solvents exhibit their maximum compatibility with polystyrene (ether at *ca.* 270K, methylcyclohexane at *ca.* 415K). Isothermal measurements on this system, which has a decidedly 'skewed' phase diagram, will of necessity pass through compositions with a changing polymer–solvent interaction. The ability to gain a fuller picture of mixed solvent–polymer behaviour from demixing studies has prompted us to establish the phase diagrams for a number of potential cosolvent systems, but in doing so it is necessary to take account of the polymer interactions with the component liquids as a function of temperature. This paper examines the phase behaviour of polystyrene in n-hexane, n-heptane and n-octane, as a necessary prerequisite to a study of cosolvent systems involving these compounds, and an analysis of these in terms of the corresponding states theory. A companion paper describes the phase behaviour in cosolvent systems formed from a series of n-alkanes and acetone.

EXPERIMENTAL

The polystyrene samples used were narrow molecular weight distribution fractions obtained from the Pressure Chemical Co., with $\bar{M}_w/\bar{M}_n$ ratios quoted at less than 1.06. The solvents used were best grade, dried and fractionally distilled prior to use.

Polymer solutions were made up in thick-walled Pyrex tubes by weighing known amounts of polymer into the tubes and adding the required volume of solvent from a microsyringe to give concentrations in which the volume fraction of polymer (ϕ_2) varied in the range 0–0.4. The air in the tubes was displaced by dry N_2, the tubes evacuated and sealed at 0.05 torr. Dissolution was achieved by agitating the contents at an appropriate temperature until a homogeneous system was obtained.

Precipitation temperatures (T_p) were obtained as described in previous publications[2,15]. In the cases where phase separation was observed at temperatures above ~520K some polymer degradation was present as evidenced by non-reproducibility of T_p. Apart from this, T_p values are believed accurate to ±0.5K.

RESULTS AND DISCUSSION

Cloud point curves were constructed for low molecular weight polystyrene fractions in n-hexane, n-heptane and n-octane from determinations of the T_p in the volume fraction range polystyrene (ϕ_2) of 0–0.4, and the results are shown in *Figure 1* (*a–c*). For monodisperse samples, the maxima and minima of each pair of curves represent the critical temperatures for that molecular weight. In the case of the narrow fractions used here no appreciable error is introduced if the maxima and minima are identified with the *UCST* and *LCST* respectively[16]. It can be seen that, for an increase in n-alkane chain length, there is a corresponding increase in the miscibility range of any particular fraction. This is most evident in the case of polystyrene $\bar{M}_n = 4800$ g mol^{-1}. In n-hexane the *UCST* and *LCST* have coalesced to give an 'hour-glass'[2] phase diagram where, for $\phi_2 = 0.07$–0.32, demixing occurs over the whole temperature range. On changing the solvent to n-heptane and n-octane the hour-glass opens up to give increasing separation of the critical temperatures.

The three systems are more conveniently compared if the critical temperatures are plotted as a function of $r^{-1/2}$, where r is given by the ratio of the 'hard core' volumes (V_1^* and V_2^*, see later), and this is shown in *Figure 2*. The turning points of the three parabolic curves drawn through the data give the limiting molecular weights in each solvent at which the *LCST* and the *UCST* just coalesce. These are, respectively, 3700, 7400 and 9100 g mol^{-1} for n-hexane, n-heptane and n-octane. For molecular weights just above these limiting values, hourglass phase behaviour will be exhibited, as shown in *Figure 1a*. Note that only the low concentration side of the

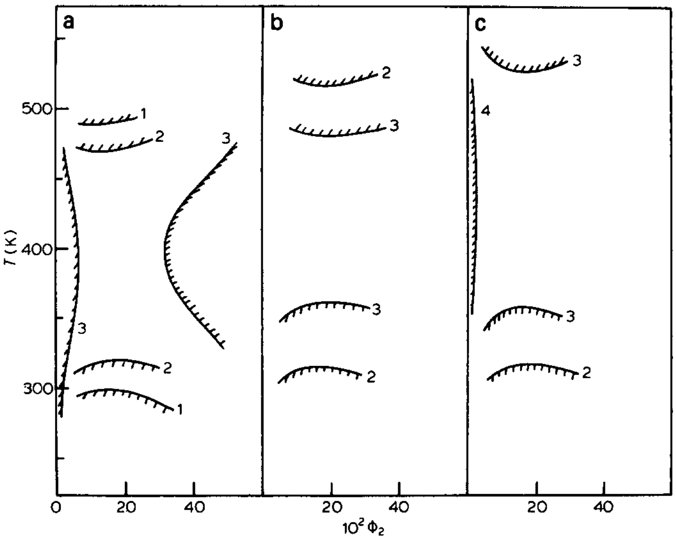

Figure 1 Cloud point curves for polystyrene fractions in (a) n-hexane, (b) n-heptane and (c) n-octane. Fraction molecular weights (g mol^{-1}) are:– 1 = 900, 2 = 2030, 3 = 4800 and 4 = 10300

One phase

Two phases

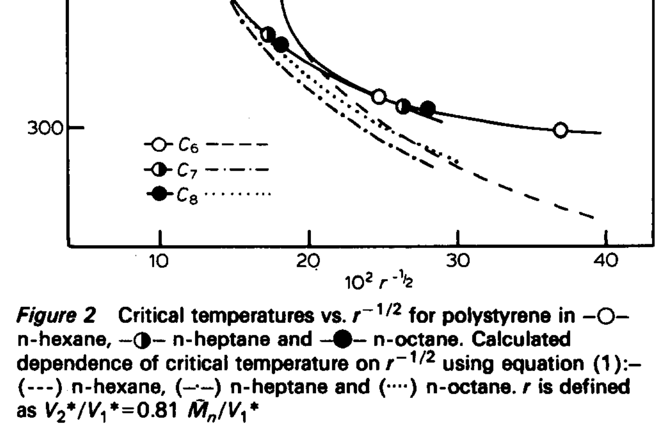

Figure 2 Critical temperatures vs. $r^{-1/2}$ for polystyrene in –O– n-hexane, –◐– n-heptane and –●– n-octane. Calculated dependence of critical temperature on $r^{-1/2}$ using equation (1):– (---) n-hexane, (–·–) n-heptane and (····) n-octane. r is defined as $V_2^*/V_1^* = 0.81\ \bar{M}_n/V_1^*$

hour-glass is easily detected for polystyrene 10 300 g mol^{-1} in n-octane (*Figure 1c*).

Although at room temperature the three alkanes exhibit an almost identical compatibility with polystyrene, the increasing *LCST* values result in an overall improvement in solvent quality with increasing alkane chain length, as judged from the miscibility ranges. The occurrence of both a *UCST* and an *LCST* is predicted by modern theories of polymer solutions which take into account the increasing free volume difference between solvent and solute as the temperature is raised. The Prigogine theory of corresponding states[17], in the form developed by Patterson and his co-workers, and the essentially equivalent approach of Flory[18], provide a basis for the treatment of critical temperature data. According to Patterson[19], the equation relating to critical conditions is

$$\chi_1^{\mathrm{crit}} = \frac{T_1^* C_1 \nu^2}{T \tilde{V}_1} + \frac{C_1 \tau^2}{2(\frac{4}{3}\tilde{V}_1^{-1/3} - 1)} = \tfrac{1}{2}(1 + r^{-1/2})^2 \qquad (1)$$

The reduced volume of the solvent $\tilde{V}_1$ may be calculated from

$$\tilde{V}_1^{1/3} = \frac{\alpha_1 T}{3(1 + \alpha_1 T)} + 1 \qquad (2)$$

where α_1 is the thermal expression coefficient. The temperature reduction parameter T_1^* is in turn calculated from

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

The parameter $C_1 = \frac{p_1^* V_1^*}{R T_1^*}$ is one-third of the external degrees of freedom of the solvent molecule. The other reduction parameters are given by

$$\tilde{V}_1 = \frac{V_1}{V_1^*} \qquad (4)$$

and

$$p_1^* = \gamma_1 T \tilde{V}_1^2 \qquad (5)$$

where V_1 is the molar volume of the solvent (with 'hard-core' volume V_1^*) and γ_1 is the thermal pressure coefficient.

The free volume or thermal expansion difference between solvent and polymer is characterized by the τ parameter

$$\tau = 1 - T_1^*/T_2^* \qquad (6)$$

where the temperature reduction parameter for the polymer T_2^* is also evaluated *via* equations (2) and (3). ν^2 expresses the difference between the 1–2 contacts of the mixture and the 1–1 and 2–2 contacts of the pure components.

It is convenient to think of the ν^2 and the τ^2 containing terms of equation (1) as enthalpic and entropic components of χ_1 and to recast equation (1) as

$$\chi_1 = \chi_1^{\mathrm{H}} + \chi_1^{\mathrm{S}} = \tfrac{1}{2}(1 + r^{-1/2})^2 \qquad (7)$$

Because of the paucity of primary data in the literature which would allow us to calculate ν^2 it must be treated as an adjustable parameter, and the best fitting theoretical curves of $r^{-1/2}$ *versus* T can then be drawn for polystyrene plus n-hexane, n-heptane and n-octane in *Figure 2* using equation (1). The equation of state terms used for the three systems are those given by Flory[20,21] and are listed in *Table 1*. It can be seen that the observed curvature in the $r^{-1/2}$-critical temperature data for polymer–poor solvent systems is predicted by the theory, although not precisely, as in the systems examined earlier[2,15]. One major weakness of the corresponding states theory is its inability to predict the absolute values of the critical temperatures and it should be noted that the theoretical curves of *Figure 2* have been shifted along the temperature axes to coincide with the data. The reason for this lies, in part, with the fact that the reduction parameters are temperature dependent[15] whereas the theory requires them to be constant. In the three systems reported here the temperature shifts are essentially the same, as are the values of ν^2 required to obtain the fits shown. This latter finding is in accord with the predictions of corresponding states theory which requires ν^2 to be zero for a mixture of two homologues[22] and consequently constant for mixtures of homologues with a dissimilar component, where the contact energy differences remain the same.

The variation of χ_1 with temperature, calculated using equations (1) and (7), and the $C_1\nu^2$ values obtained from the fits shown in *Figure 2*, are shown for the three systems in *Figure 3*. The minima (χ_1^{min}) in each curve are the predicted temperatures of maximum compatibility of the three n-alkanes with polystyrene. The curves for χ_1^{H} and χ_1^{S} are also shown and reveal that the improvement in solvent quality in this series of n-alkanes is, in terms of the theory, due to a more favourable χ_1^{S}-temperature behaviour where the parameter increases less slowly with lengthening of the alkane chain. Since the χ_1^{S} term reflects the difference in expansion between polymer and solvent (through τ^2), this entropic component of χ_1 will continue to decrease on going to longer alkanes and, in the absence of any other effects, will bring about an enhancement of solvent quality as the chain lengths increase. On the basis of an assumed constant solvent–polymer interaction, quantified by $\nu^2 \simeq 0.017$, and Flory's reduction parameters for the n-alkanes[21], equation (1) was used to predict χ_1^{min} for n-alkanes up to 20 carbon atoms. The result is shown in

Table 1 Equation of state terms for the three binary systems n-hexane n-heptane and n-octane with polystyrene

	T^*/K	p^*/J cm^{-3}	V^*/cm^3 mol^{-1}	C_1	$10^3\ \nu^2$	$10^2\ C_1\tau^2$	ΔT/K†
n-hexane	4420	448	99.48	1.21	17.5_2	19.7_8	105
n-heptane	4670	431	113.65	1.26	17.3_0	17.3_1	100
n-octane	4850	431	127.89	1.37	16.8_6	16.4_4	100
polystyrene	7420	–	84.33	–	–	–	–

† Temperature shift applied to obtain coincidence of experimental data and theoretical curves in *Figure 2*

Figure 4 where it can be seen that the entropic contribution does not lead to ever smaller χ_1^{min} values with increasing solvent chain length, these pass through a minimum then increase again. The reason for the predicted deterioration in solvent quality after n-nonane is the eventual dominance of the χ_1^H term which becomes increasingly unfavourable. The temperature at which χ_1 attains its minimum value for each polystyrene–n-alkane combination can also be deduced from *Figure 4*, and these indicate that the region of miscibility for low molecular weight polymer in n-alkanes moves rapidly to higher, and experimentally inconvenient, temperatures with increasing solvent chain length. By considering the solvent (at long chain lengths) and the solute to constitute a mixture of oligomeric pairs, the analysis predicts a rapid rise in the oligomer/oligomer *UCST* with molecular weight. This behaviour has been observed experimentally in a number of similar systems[23].

Examination of the three binary systems has shown that n-hexane, n-heptane and n-octane are poor solvents for polystyrene, dissolving low molecular weight polymer only, and that the temperature range over which solution occurs varies with solvent size. Analysis of the critical data using corresponding states theory reveals the temperature dependence of χ_1 in the systems and indicates, as expected for poor solvents, that χ_1 is always $>> 0.5$. Extrapolation to longer chain length alkanes suggests that there will be no improvement in solvent quality and, additionally, that the range of limited polymer–solvent compatibility lies at increasingly higher temperatures. The behaviour of n-alkanes, each as one member of a cosolvent pair, is thus expected to vary with alkane chain length, and this is examined in a companion paper[24] where the phase behaviour of polystyrene in alkane–acetone mixtures is presented.

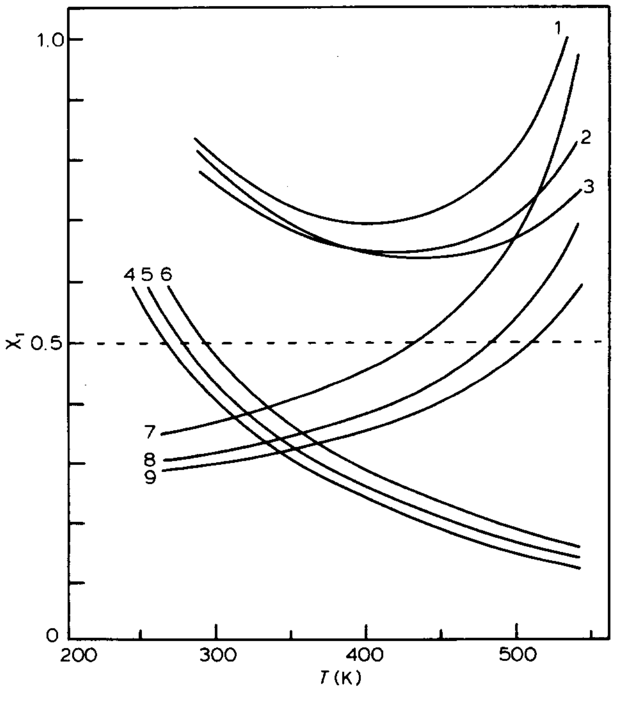

Figure 3 χ_1 vs. temperature behaviour for n-hexane, n-heptane and n-octane (curves 1, 2 and 3 respectively). χ_1^H, (curves 4, 5 and 6) and χ_1^S (curves 7, 8 and 9) vs. temperature behaviour for n-hexane, n-heptane and n-octane respectively. All curves calculated from equations (1) and (8) using data in *Table 1*

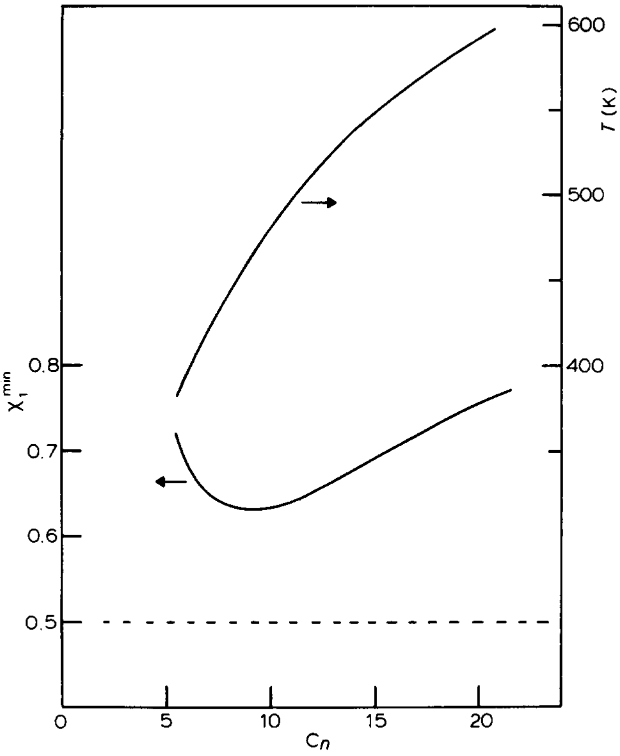

Figure 4 Minimum value of χ_1 (χ_1^{min}) calculated from equation (1) as a function of n-alkane chain length (C_n = number of carbon atoms per alkane), and the temperature corresponding to χ_1^{min} for the same n-alkanes. A temperature shift (100 K) has been applied to both curves

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