Upper and lower critical solution temperatures for polystyrene in methyl cyclopentane and in dimethyl cyclohexane

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The demixing of polystyrene in methyl cyclopentane, and in dimethyl cyclohexane has been investigated, and the upper and lower critical solution temperatures established for several polymer molecular weights. In the former solvent both upper and lower θ temperatures can be defined, but not in the latter where cloud point curves for the upper and lower critical temperatures coalesce for high molecular weights. The Patterson theory of polymer solutions has been applied to the data, and the characteristic free volume and exchange energy parameters have been evaluated. The lower critical solution temperatures are nearly the same in cyclopentane and methyl cyclopentane due to a compensation between the free volume and contact interaction terms. Solvent size effects are considered in order to explain the differences in the interaction of solvent with polymer.

(Keywords: cloud point curves; critical solution temperatures; polystyrene; cycloalkanes; free volume; contact interaction)

INTRODUCTION

Polymers dissolved in poor, or moderately poor, solvents will normally exhibit a phase diagram having two regions of limited miscibility[1]. At elevated temperatures phase separation, associated with the lower critical solution temperatures (*LCST*), is brought about as a result of the large differences in free volume between the solute, and the relatively highly expanded solvent[2]. Demixing at the upper critical solution temperature (*UCST*) often occurs at or near room temperatures, and is a result of increasingly unfavourable solute–solvent contact interactions. At both the *LCST* and the *UCST* the polymer coil attains its unperturbed or θ dimensions, and between these limits coil expansion and related hydrodynamic properties pass through a maximum[3,4].

Recent theories of polymer solution thermodynamics[2,5] account for both critical solution temperatures by considering not only the energetics of polymer–solvent interactions but also the temperature dependence of the free volume. For any given polymer, demixing behaviour is governed by the nature of the solvent chosen, and the separation of the *LCST* and *UCST* (i.e. the temperature miscibility range), may be taken as a useful measure of the quality of the solvent. In sufficiently poor solvents the critical solution temperatures may coalesce for polymers of finite molecular weight, and the resulting phase diagrams are of a characteristic hour-glass form[6].

Several groups of workers have established the phase behaviour of polystyrene in a wide range of solvents, and in particular demixing studies have been carried out in both linear[7] and cycloalkanes[8,9]. The former will dissolve only very low molecular weight polystyrene, whereas the latter are much better solvents, exhibiting both upper and lower critical points for infinite molecular weight polymer but with a substantial miscibility range in between. Since the energies of the polymer–solvent contacts should be the same, or very nearly so, for the two groups of solvents, the differences in behaviour are surprisingly large and this will be the subject of a future communication. The paper presented here reports and analyses the phase behaviour of polystyrene in two methyl substituted cycloalkanes, methyl cyclopentane (MCP) and 1,4-dimethyl cyclohexane (DMCH), and compares the behaviour with other polystyrene–cycloalkane systems.

EXPERIMENTAL

Cloud point curves for polystyrene in each of the solvents were established, as reported previously[6]. Precipitation points were taken at the onset of visible turbidity on heating (for *LCST*) and on cooling (for *UCST*) solutions, which were vacuum sealed in thick-walled Pyrex tubes. Precipitation temperatures are believed to be accurate to ± 0.5 K, ignoring pressure effects.

The polystyrene fractions used were supplied by the Pressure Chemical Co. and have $\bar{M}_w/\bar{M}_n$ values of less than 1.1. The solvents were dried and distilled prior to use.

The density of the 1,4-dimethyl cyclohexane, a mixture (1:1) of *cis* and *trans* isomers, was measured at two temperatures using a picnometer. While use of either pure *cis* or pure *trans* might have produced differences in *UCST*, it was decided to use the mixture for these initial studies.

RESULTS AND DISCUSSION

Cloud point curves for polystyrene in MCP and DMCH are shown in *Figure 1*, and it can be seen that both upper and lower critical solution temperatures can be located. The two systems are different in that the miscibility range

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of any particular fraction is considerably larger in MCP and the phase boundaries occur at generally low temperatures. Although the maxima and minima of such curves are properly termed upper and lower precipitation thresholds, little error is introduced if they are identified as the corresponding critical points $(T_c)^{10}$. The dependence of T_c on molecular weight in each system is compared in *Figure 2* which shows Schultz-Flory plots[11] of T_c against $r^{-1/2}+(1/2r)$, where r is the degree of polymerization. As has previously been found, this dependence is much greater when the critical temperatures are close together than when far apart, and, in the case of DMCH, the data cannot be extrapolated to give the Flory or θ-temperatures.

The data for polystyrene in MCP is also noticeably curved. However, application of a least squares linear treatment yields upper and lower θ-temperatures (θ_u and θ_L) for the system. The slopes of the Schultz–Flory plots can then be identified with the corresponding entropy terms ψ_{1u} and ψ_{1L} (the latter is negative as expected for an entropically controlled *LCST* demixing process). The values of the θ and ψ parameters are recorded in *Table 2*.

A much higher correlation of the polystyrene–MCP data is obtained if non-linear extrapolations are chosen, giving $\theta_u=358$ K and $\theta_L=411$ K respectively. Nonlinearity in critical data is accounted for by the form of the Patterson–Prigogine expression[2,10] which relates T_c to $r^{-1/2}$ via

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

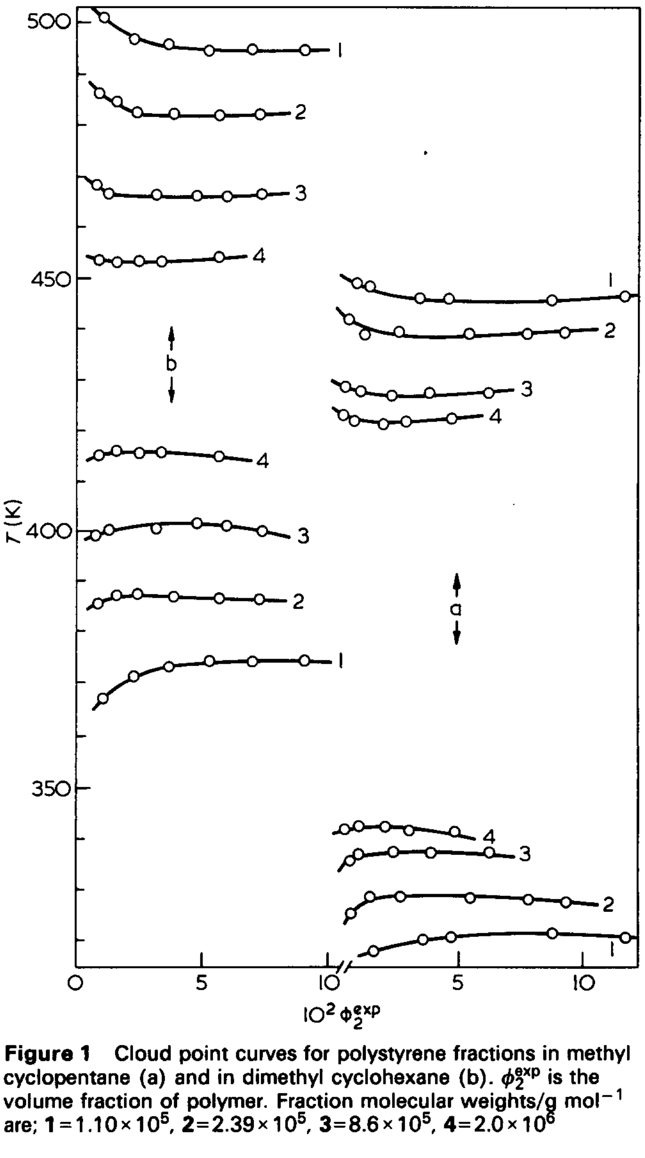

Figure 1 Cloud point curves for polystyrene fractions in methyl cyclopentane (a) and in dimethyl cyclohexane (b). ϕ_2^{exp} is the volume fraction of polymer. Fraction molecular weights/g mol^{-1} are; **1**=1.10×10^5, **2**=2.39×10^5, **3**=8.6×10^5, **4**=2.0×10^6

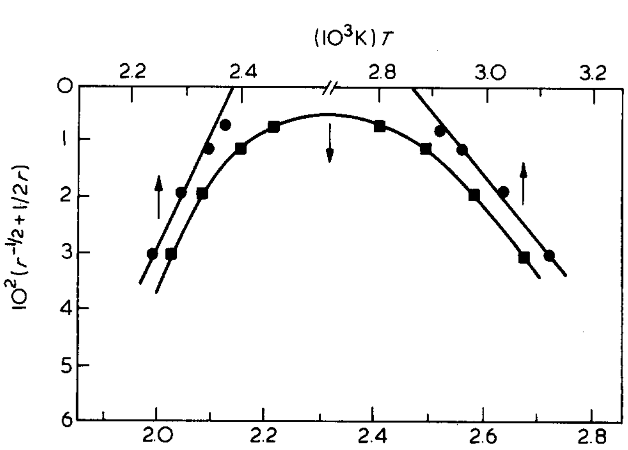

Figure 2 Schultz–Flory plots of the *UCST* and the *LCST* for polystyrene in methyl cyclopentane (●) and in dimethyl cyclohexane (■). r is the degree of polymerization

The reduced volume of the solvent is calculated from its thermal expansion coefficient α_1 through

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

and the temperature reduction parameter T_1^* follows in turn from the reduced temperature $\tilde{T}_1$ given by

$$\tilde{T}_1=T/T_1^*=\tilde{V}_1(1-\tilde{V}_1^{-1/3}) \qquad (4)$$

where T is the temperature measured on the Kelvin scale. The 'hard core' volume V_1^* and pressure reduction parameter p_1^* are obtained from

$$\tilde{V}_1=V_1/V_1^* \qquad (5)$$

and

$$p_1^*=\gamma T\tilde{V}_1^2 \qquad (6)$$

respectively. V_1 is the molar volume of the solvent and γ its thermal pressure coefficient. Note that a tilde such as ˜ denotes a reduced quantity and an asterisk such as * represents a reduction parameter.

The remaining terms in equation (1), $C_1\nu^2$ and $C_1\tau^2$, characterize the differences in contact energies between the pure components and those in the mixture, and the difference in free volume between polymer and solvent respectively. C_1 and τ^2 are defined via the expressions

$$C_1=p_1^*V_1^*/RT_1^* \qquad (7)$$

and

$$\tau^2=(1-T_1^*/T_2^*)^2 \qquad (8)$$

where R is the gas constant and T_2^* the polymer temperature reduction parameter. The energy term ν^2 remains undefined and is treated as an adjustable parameter whose value is fixed by experiment.

The experimental T_c values, plotted as a function of $r^{-1/2}$ (where r is defined as the ratio of the hard core volumes of polymer to solvent), are shown for the two systems in *Figures 3* and *4* along with the theoretical dependence of the two quantities calculated from equation (1). The equation of state parameters required for this calculation are listed in *Table 1* (along with the source references). The values of ν^2 which give the best fit to the data are shown in *Table 2*.

The correlation obtained between the experimental results and theory is poorer than has been obtained in other systems[8,9,12,13]; with a considerable overestimation of the separation of *UCST* and *LCST* at finite molecular weights. This appears to be a characteristic of the theory in its present form when applied to systems such as these here which have relatively closely spaced upper and lower critical regions[6,7]. A second defect is the inability to predict the absolute values of the critical points, and a temperature shift is necessary to match theoretical and experimental dependencies. This shift is noted on the Figures.

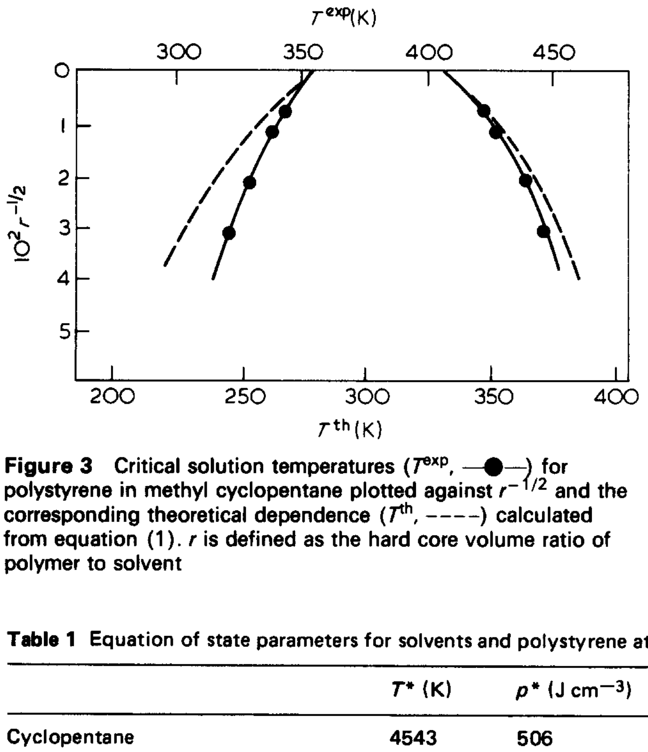

Figure 3 Critical solution temperatures (T^{exp}, —●—) for polystyrene in methyl cyclopentane plotted against $r^{-1/2}$ and the corresponding theoretical dependence (T^{th}, ----) calculated from equation (1). r is defined as the hard core volume ratio of polymer to solvent

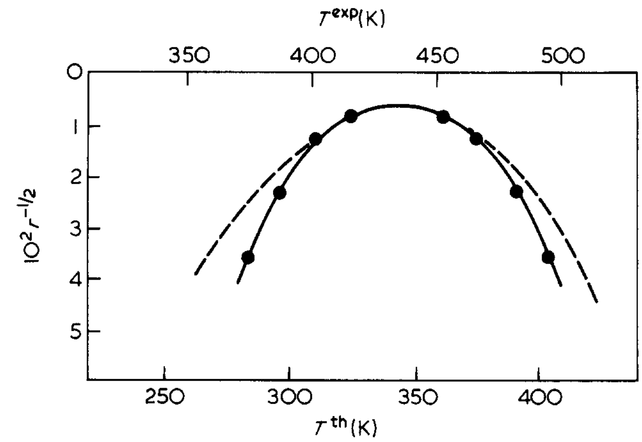

Figure 4 Critical solution temperatures (T^{exp}, —●—) for polystyrene in dimethyl cyclohexane as a function of $r^{-1/2}$ and the corresponding theoretical dependence (T^{th}, ----) calculated from equation (1). r is the hard core volume ratio of polymer to solvent

It is possible to overcome the drawback of the arbitrary temperature shift, by chosing a temperature other than 298 K at which to calculate T_1^* which, contrary to the corresponding states principle, is not temperature independent. The temperature shifts shown in *Figures 3* and *4* become zero with T_1^* (methyl cyclopentane) = 5000 K, and T_1^* (dimethyl cyclohexane) = 5390 K, these values are in excellent agreement with the semi-empirical method of estimating T_1^* previously described[14]. Nevertheless, the fits shown in *Figures 3* and *4* allow an interesting comparison to be drawn between the binary systems, polystyrene + DMCH, and polystyrene + MCP, reported here and the related cycloalkane solvents for polystyrene, cyclopentane (CP), cyclohexane (CH), and methyl cyclohexane (MCH), for which demixing data are already available in the literature[8,9]. This can be conveniently done through the Schultz–Flory θ parameters and through the ν^2 and τ^2 values for the five systems, and all the relevant data have been collated in *Table 2*.

In the absence of other factors, θ_L (for polystyrene in the various cycloalkanes) should related to temperatures at which the free volume differences between the polymer and each solvent are comparable. This being the case, θ_L

Table 1 Equation of state parameters for solvents and polystyrene at 298 K

	T^* (K)	p^* (J cm^{-3})	V^* (cm^3 mol^{-1})	c_1	S_1/S_2	Refs.
Cyclopentane	4543	506	72.36	0.97	2.06	19, 20
Methyl cyclopentane	4600	424	86.91	0.96	1.94	21, 22
Cyclohexane	4717	530	84.26	1.14	1.96	15
Methyl cyclohexane	4892	490	100.71	1.21	1.85	21, 23
Dimethyl cyclohexane	5002	458	115.43	1.27	1.77	this work†, 24
Polystyrene	7420	–	97.23	–	–	25

† Calculated from experimental specific volume at 293 K of 1.2942 cm^3 g^{-1} and corresponding expansion coefficient of 1.07 x 10^{-3} K^{-1}

Table 2 Schultz–Flory parameters and Patterson parameters for polystyrene/cycloalkane binary systems

	θ_u (K)	θ_l (K)	ψ_{lu}	ψ_{lL}	$10^3\,\nu^2$	τ^2	Refs.
Cyclohexane	307	486	0.79	–1.19	9.49‡	0.133‡	8
Methylcyclohexane	344	484	0.56	–0.94	11.54‡	0.116‡	8
Cyclopentane	293	427	0.55	–0.86	13.30‡	0.151‡	9
Methyl cyclopentane	348	417	0.39	–0.53	15.90	0.144	–
Dimethyl cyclohexane	–	–	–	–	13.61	0.106	–

‡ These values have been recalculated from the original critical data using the value of T_2^* = 7420 K (for consistancy with the present work) and the solvent parameters shown in *Table 1*

would be expected to increase in the order CP < MCP < CH < MCH in line with the decrease in the free volume parameter τ^2. (θ_L for polystyrene in DMCH, of course, cannot be defined.) This is only the case if the solvents are regarded as pairs, i.e. cycloalkanes and methyl cycloalkanes, but otherwise methyl substitution has the effect of reducing θ_L slightly with respect to the unsubstituted solvent. The opposite is true at θ_u with the result that each methyl cycloalkane is considerably poorer as a solvent for polystyrene when measured by the value of $\Delta\theta = \theta_L - \theta_u$. The effect of a second methyl group on the cyclohexane ring is to decrease further the solvent quality such that $\Delta\theta$ is zero in DMCH.

A more effective way to examine the relative importance of free volume and exchange energy in this series of solvents is to recast equation (1) in the form

$$\chi_1 = \chi_1^H + \chi_1^s \qquad (9)$$

such that the v^2 and τ^2 terms can then be identified with the enthalpic (H) and entropic (S) components of the interaction parameter χ_1. Using the data in *Tables 1* and *2*, the temperature dependence of χ_1^H and χ_1^s for each polystyrene–solvent systems may be calculated and the results of this exercise are shown in *Figure 5*. The χ_1^s curves indicate, in terms of free volume difference, that improved solvation for polystyrene is obtained in the solvent order CP, MCP, CH, MCH, DMCH, and that the effect is greatest at higher temperatures. Compatibility in free volume terms simply reflects the relative rates of expansion (α) of solvent and solute.

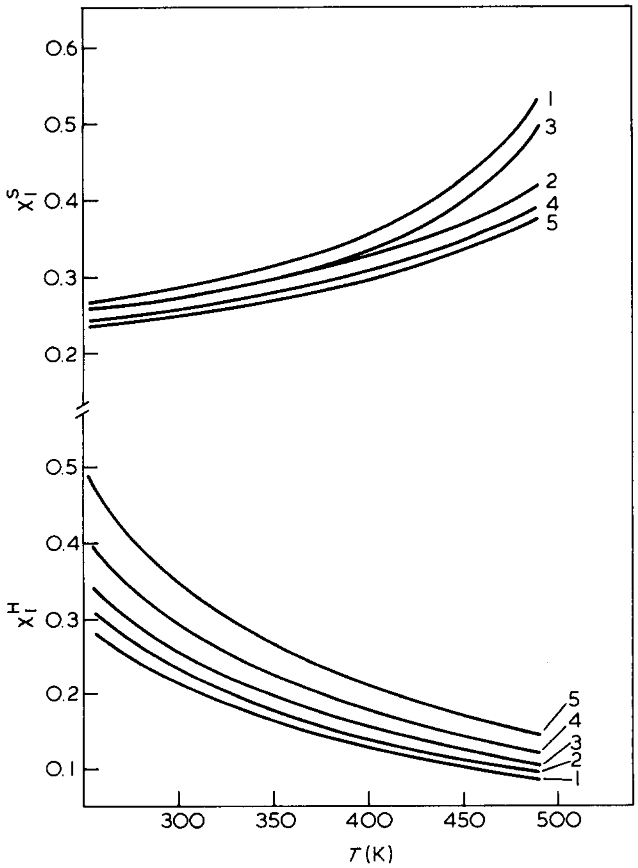

Figure 5 Calculated dependence of χ_1^H and χ_1^s on temperature for polystyrene in cycloalkanes; **1** = cyclopentane, **2** = cyclohexane, **3** = methyl cyclopentane, **4** = methyl cyclohexane, **5** = dimethyl cyclohexane

The χ_1^H behaviour shown in *Figure 5* indicates a different solvent order in contact energy terms. The preference of polystyrene for the cycloalkanes is in the order CP, CH, MCP, MCH, DMCH and this suggests that two effects may be instrumental in reducing solvent quality, (a) increases in the ring size and (b) increases in the methyl substitution. Accepting that the formation of 1–2 contacts in polystyrene(1)–cycloalkane (2) solutions involves the same, or nearly the same, energy, no matter what solvent is used, then the origin of these effects must lie elsewhere.

In his treatment of liquid mixtures Flory introduces the quantity S_1/S_2 [5,15], which is the ratio of the surface to volume ratios of the solvent (1) molecule and polymer (2) segment. Both S_1 and S_2 are taken to provide a measure of the number of sites available on the molecular surface per unit of core volume. The treatment used here is due to Patterson who does not invoke such effects, so that the v^2 parameter (and hence χ_1^H) will not only reflect exchange energies but also other geometric considerations associated with 1–2 contact formation, as originally predicted[16]. Thus it would seem in order to consider (a) and (b) above as geometric effects related to contact site availability in the series of cycloalkanes and, to this end, the ratios of S_1 to S_2 are recorded in *Table 1*. These have been calculated such that each solvent molecule is a sphere† of volume V_1^*, and that the polystyrene segment is a right cylinder of length 2.5×10^{-8} cm [15] and of hard core volume $V_2^* = 97.23$ cm^3 mol^{-1}.

From the values of S_1/S_2 it is apparent that the relative number of surface sites per solvent molecule decreases in the same order as the values of χ_1^H increases, suggesting that these changes in solvent quality result from parallel changes in surface site availability. The correlation may be quite fortuitous and the analysis takes no account of the separate influences of molecular size and shape which is known to affect solution behaviour in other systems[17,18]. However, this does provide an interesting interpretation of solubility in these systems, and work is presently in progress to provide further information in this area.

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† By treating the solvent molecules alternatively as ellipsoids with dimensions obtained from molecular models the same conclusions are reached.

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