Figure 2 Cracks induced around a cobaltous chloride inclusion present in a rigid epoxy by water absorption

The original inclusion was cubical in shape. The fine lines which radiate from the particle constitute a system of hundreds of small cracks. The main crack is located on the upper right hand side of the photograph. *Figure 2* shows a crack produced by a cobaltous chloride inclusion. The other features represent air bubbles and smaller crystals of the inclusion that have not yet led to cracks. The potassium acetate system is interesting in that numerous smaller radially disposed cracks also form. Normally, only one crack forms and grows and this is typified by *Figure 2*.

The gradual formation, growth and sometimes cracking of these cavities has been followed microscopically and measured as a function of time. In addition, by using solutes which form coloured solutions, such as cobaltous chloride, it is possible to measure the optical density and thereby calculate the osmotic pressure. This technique seems to be a convenient tool for determining the strength of a transparent material under pure hydrostatic triaxial tension.

pressure or triaxial load on the surface of the cavity of about 19 000 psi — a considerable loading. It is now apparent that sufficient pressures are developed to cause cracks to be initiated and to grow.

An example of such a process is shown in *Figure 1*. The inclusion is potassium acetate and the cracks were observed after about 1 800 days' immersion time in distilled water.

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A corresponding states interpretation of the temperature dependence of the intrinsic viscosity of polystyrene in isopropyl acetate

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INTRODUCTION

Dilute solution properties of polymers are generally described via the excluded volume parameter[1]. In its turn, the excluded volume parameter has, in the main, been expressed by the original equation given by Flory[2], since this contains the temperature dependence directly as $(1 - \theta/T)$ where θ is the theta temperature of the polymer–solvent system. The limitations of such an expression to the neighbourhood of the theta temperature have been recognized for some years[3].

Additionally, the original Flory theory cannot predict the presence of a lower critical solution temperature, a general phenomena of all polymer solutions. In recent years, the thermodynamics of polymer solutions have been re-described by equation of state[4a, b, c] and corresponding states theories[5a, b], either of which predict the presence of a lower critical solution temperature. Thus far, to our knowledge, no attempt has been made to incorporate such theories into the excluded volume parameter expression and compare the predictions with experiment. This paper presents such an
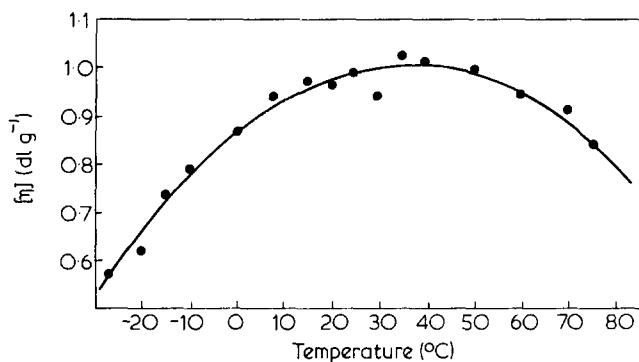
Figure 1 Intrinsic viscosity of polystyrene in isopropyl acetate as a function of temperature. The full line is an empirical best fit to the data

RESULTS

Phase separation temperatures at the upper and lower critical solution temperatures showed no dependence on PS weight fraction. The lower critical solution temperature was determined as 107° whilst the upper critical solution temperature was −25°. These values are in good agreement with the much more detailed work of Kuwahara et al.[6] who have reported values of 107° and −27° respectively.

Intrinsic viscosities, $[\eta]$, were obtained from double extrapolations of η_{sp}/c and $(\ln \eta_{rel})/c$ as a function of c, the concentration. Figure 1 shows the variation of $[\eta]$ with temperature. Values of α^3 have been calculated from equation (1) below, using $[\eta]$ at −27° as $[\eta]_\theta$ since Kuwahara et al.[6] have shown this temperature to be a θ temperature.

attempt for the system polystyrene in isopropyl acetate. Reasons for choosing this system were:

(1) phase separation studies by other workers had obtained the upper and lower critical solution temperatures[6];
(2) parameters in the corresponding states expression for the polymer-solvent interaction parameter were known[6];
(3) the highest temperature at which measurements could be made without adopting specialized procedures was reasonably close to the lower critical solution temperature.

EXPERIMENTAL

Materials

The polystyrene (PS) used for this work was a narrow distribution sample kindly donated by Dr. R. A. Pethrick of the University of Strathclyde. From gel permeation chromatography, $\bar{M}_w = 1.1 \times 10^6$ and $\bar{M}_w/\bar{M}_n = 1.07$. Subsequent light scattering on this sample gave $\bar{M}_w = 1.045 \times 10^6$ and this value was used in all calculations.

Isopropyl acetate (IPA) was dried over magnesium sulphate and distilled at atmospheric pressure (b.p. 90°).

Viscometry

An Ubbelohde suspended level viscometer was used to measure the intrinsic viscosity of PS in IPA over the temperature range −27° (theta temperature − upper critical solution temperature) to 75°. Kinetic energy corrections were negligible and shear effects were absent. Flow times were reproducible at ±0.1 s and the temperatures used were constant to ±0.05°.

Phase Separation

For this work, a PS of $\bar{M}_w = 4.5 \times 10^6$ was used and four solutions in IPA with PS weight fractions of 0.01, 0.02, 0.04 and 0.06 were sealed under vacuum into 2 mm internal diameter capillary tubing. For determination of the LCST these solutions were heated slowly ($\sim 2°$ min^{-1}) in an oil bath and the phase separation (clear to turbid) observed by eye. Upper critical solution temperatures were determined by immersing the tubes in methanol at −30° contained in a dewar flask. At this temperature complete precipitation occurred. The temperature was slowly increased by addition of methanol at room temperature; phase separation (turbid to clear) was again observed by eye.

ANALYSIS

Dilute solution properties of polymers are frequently described by a two parameter theory[1]. The two parameters are the unperturbed dimensions and the expansion factor α. It is this latter quantity which is of importance here since:

$$\alpha^\gamma = [\eta]/[\eta]_\theta \tag{1}$$

where $[\eta]_\theta$ is the intrinsic viscosity at the theta temperature and γ has been assigned values of 2.33, 2.5 and 3.0[7-9]. Furthermore the expansion factor has been related to the excluded volume parameter, Z, by a number of closed expressions. Four such expressions are considered here:

$$\alpha^5 - \alpha^3 = 1.276Z \quad \text{modified Flory}[10](F_m)$$

$$(\alpha^3 - \alpha)(3\alpha^3 + 1)^{3/2} = 6.159Z \quad \begin{array}{l}\text{Kurata, Stockmayer}[11]\\ \text{Roig (KSR)}\end{array}$$

$$\alpha^2 = 0.541 + 0.459(1 + 6.04 Z)^{0.46} \quad \begin{array}{l}\text{Yamakawa–Tanaka}[12]\\ \text{(YT)}\end{array}$$

$$\alpha^3 = 1 + 1.914 Z \quad \text{Fixman}[13](F)$$

where

$$Z = \frac{4}{3^{3/2}} \frac{27}{2^{5/2}\pi^{3/2}} \frac{\bar{v}_2^2}{N_A V_1} \left[\frac{<r^2>_0}{M}\right]^{-3/2} \psi_1(1 - \frac{\theta}{T})M^{1/2} \tag{2}$$

with

$\bar{v}_2$ = polymer specific volume;

V_1 = solvent molar volume;

ψ_1 = Flory entropy parameter;

θ = theta temperature.

Newer theories of polymer solution thermodynamics have recently appeared. Their aim has been to account for the lower critical solution temperature which is now recognized as a general property possessed by all polymer solutions. Two approaches have been particularly successful, the corresponding states theory of Patterson[5a, b] and the equation of state approach of Flory[4a, b, c]. In particular, from corresponding
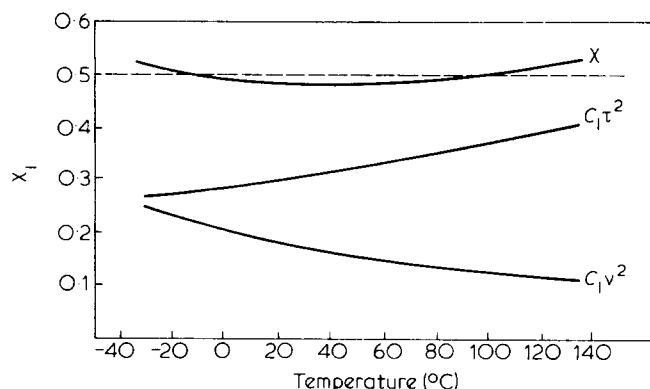
Figure 2 Polymer—solvent interaction parameter, χ_1, as a function of temperature for polystyrene in isopropyl acetate calculated from equation (3)

states theory, the temperature dependence of the polymer—solvent interaction parameter, χ_1, at the critical miscibility point and zero pressure may be expressed as:

$$\chi_{1(crit)} = \frac{C_1 \nu^2}{1 - \tilde{V}_1^{-1/3}} + \frac{C_1 \tau^2}{2[(4/3)\tilde{V}_1^{-1/3} - 1]} \qquad (3)$$

where $3 C_1$ is the number of external degrees of freedom of the solvent;

ν^2 is related to cohesive energy and size difference between solvent and polymer molecules;

τ^2 reflects free volume changes on mixing polymer and solvent;

$$\tilde{V}_1 = V_1/V_1^*$$

with $V_1^* =$ characteristic volume reduction parameter of the solvent.

For PS in IPA, $C_1\nu^2$, $C_1\tau^2$ and V_1^* have been obtained from phase separation studies of Kuwahara et al.[6] Consequently, the temperature dependence of χ_1 can be calculated from equation (3) and this is shown in *Figure 2* together with the contributions of the $C_1\nu^2$ and $C_1\tau^2$ terms. Since[14]:

$$\psi_1(1 - \theta/T) = (\tfrac{1}{2} - \chi_1)$$

then:

$$Z = \frac{4}{3^{3/2}} \frac{27}{2^{5/2}\pi^{3/2}} \frac{\bar{\nu}_2^2}{N_A V_1} \left[\frac{<r^2>_0}{M}\right]^{-3/2} (\tfrac{1}{2} - \chi_1) M^{1/2} \quad (4)$$

Values of α^3 have been calculated as a function of temperature using equation (4) for Z and the F_m, KSR, YT and F relations between Z and α. For this purpose, the value of ($<r^2>_0/M$) has been calculated from experimental and theoretical values of the characteristic ratio reported for atactic polystyrene[15]. Due notice has been taken of the temperature dependence of $\bar{\nu}_2$ in equation (4). The formula obtained by Hocker et al.[16] describing the density of polystyrene as a function of temperature *above* the glass transition temperature has been used to calculate $\bar{\nu}_2$.

Experimental values of α^3 have been calculated from equation (1) with $\gamma = 3$. These values, together with the values from theoretical expressions are presented in *Figure 3*.

DISCUSSION

The curve of [η] as a function of temperature (*Figure 1*) is similar to that observed for other polymer solvent systems. Such curves have been analysed by a different approach from that adopted here, the intention being to obtain such parameters as the temperature coefficient of the unperturbed dimensions and the theta temperature[17].

Corresponding states theory has been used to describe, in general terms, the observed temperature dependence of [η] [18,19]; however, no detailed comparison was made with excluded volume theories.

The results of the detailed comparison made here are summarized in *Figure 3*. Qualitatively, all the theoretical expressions (F_m, KSR, YT, F) in conjunction with corresponding states theory of χ_1 reproduce the shape of the curve. The sideways displacement of the theoretical curves of α^3 with respect to the experimental values is due to the values of χ_1. A common feature of comparison of the temperature dependence of χ_1 with observed upper and lower critical solution values is that, to obtain $\chi_1 = 0.5$ at these temperatures, the curve for χ_1 has to be displaced sideways[6]. Generally, the disagreement is worse near the lower citical solution temperature, a fact which is accounted for by the lack of knowledge of the volume expansion of liquids at such high temperatures. For PS in IPA the reverse situation holds, i.e. the theoretical prediction of $\chi_1 = 0.5$ at 102° is in excellent agreement with the *LCST* of 107°. This may be due to the greater contribution of the free volume term ($C_1\tau^2$) to the value of χ_1 (*Figure 2*).

More perturbing is the diagreement between experimental and theoretical magnitudes of α^3 ($\sim 10\%$ at the maxima of the curves). Examination of the theoretical expressions used to calculate α^3 reveal two factors which may be the source of this disagreement. An additional source is the value of γ used in equation (1) to calculate α^3 from intrinsic viscosity data. Firstly, the numerical factors in the F_m, KSR, YT and F equations influence the value of α^3. However, as shown by Yamakawa[1], apart from the F equation which consistently
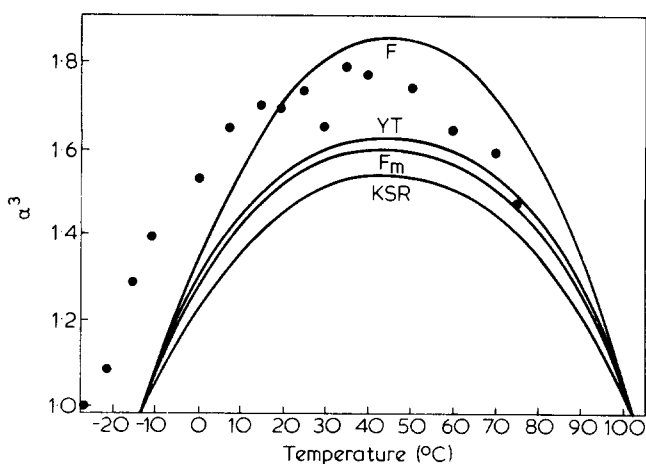

Figure 3 Expansion factor α^3 as a function of temperature compared with theoretical predictions (full lines). F = Fixman; F_m = modified Flory; YT = Yamakawa—Tanaka; KSR = Kurata, Stockmayer and Roig

overestimates the dependence of α^3 on Z, all the equations are in quite good agreement with experimental data up to $\alpha^3 \simeq 2$ and therefore the numerical factors are not thought to be the cause of the disagreement. Similarly, the value of γ used in equation (1) is not thought to be the source of error. Using $\gamma = 2.33$ or 2.5, instead of 3, produces experimental values of α^3 greater than those predicted by the Fixman expression. As noted above, this expression consistently overestimates α^3 and this militates against using $\gamma = 2.33$ or 2.5. On the other hand, there is no evidence for using γ values greater than 3, which would reduce the experimental values of α^3 to the values predicted by the F_m, KSR or YT equations.

Finally, there remain the values of χ_1 used to calculate Z from equation (4). Throughout no account has been taken of the concentration dependence of χ_1. Generally χ_1 has a positive concentration dependence[5b,20-22] and thus for infinitely dilute solutions the values of χ_1 should be less than those shown in *Figure 2*. Consequently, this reduction in χ_1 would increase the values of α calculated from the theoretical expressions; however, since the exact dependence of χ_1 on concentration in PS–IPA solutions is not known the magnitude of this change cannot be calculated.

CONCLUSION

It has been shown that a combination of corresponding states theory of polymer solutions with closed expressions for the expansion coefficient are able to explain qualitatively the temperature dependence of the intrinsic viscosity. Disagreements between theory and experiment appear to be due to the lack of knowledge of the complete behaviour of the χ_1 parameter. A suitable system for a fuller study would be PS in cyclohexane[23], however practical diffisulties in making measurements at circa $200°C$ ($LCST = 213°$) may circumvent such a study.

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