

Upper and Lower Critical Solution Temperatures for Star Branched Polystyrene in Cyclohexane

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SUMMARY

Upper and lower critical solution temperatures have been measured for star polystyrene samples, with varying degrees of branching, dissolved in cyclohexane. The effect of branching on the phase separation of these solutions is small in the lower critical region but becomes significant in the upper critical region. In all cases branching tends to extend the solubility range for polystyrene in cyclohexane. This is accentuated when the degree of branching is high and also when the molecular weight is low.

INTRODUCTION

The dilute solution behaviour of star and comb-shaped polystyrene samples has been studied by a number of workers, most of whom agree that branching tends to lower the θ -temperature in comparison with linear polymers dissolved in the same solvent (CANDAUI et al. 1972). One exception was the report (BERRY 1971) that the θ -temperature for star polystyrenes in cyclohexane was 2K higher than that for the linear form. This was not confirmed by later work (ROOVERS and BYWATER 1974) on carefully synthesised four and six-branched star polystyrenes, where depressions of the θ -temperature of up to 9K were observed, depending on the molecular weight and the degree of branching in the sample. The observation that both increased branching and decreasing molecular weight result in greater depressions of the θ -temperature, appears to be quite general.

To date the phase behaviour of branched polymers has not been examined in much detail and we present here a preliminary report of measurements of the cloudpoint curves and critical temperatures for star branched polystyrene solutions in cyclohexane in both the upper (ucst) and lower (lcst) regions, compared with linear polystyrene dissolved in the same solvent.

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EXPERIMENTAL

Two series of branched polystyrene fractions were examined. Five samples of Y-branched polystyrene were kindly donated by Dr. W.A.J. Bryce, University of Aberdeen, and four samples of star polystyrenes were generously provided by Drs. Hild and Rempp, Centre de Recherches sur les Macromolecules, Strasbourg. One sample, with nine branches was obtained from Polysciences.

Cloudpoint curves (cpc) were established, in both the upper and lower critical region, for each sample dissolved in cyclohexane, using the method which has been described previously (COWIE et al. 1971). As the c.p.c. were relatively flat, critical temperatures T_c were normally taken as the maxima or minima of the respective c.p.c. Critical temperatures were also estimated in the upper critical region, using the phase volume method (KONINGSVELD and KLEINTJENS 1973), and values were usually within 0.5K of T_c measured from c.p. maxima. The c.p.c. in the upper critical region were measured before and after those in the lower critical region. Data were normally in agreement to better than 0.5K indicating that thermal degradation was negligible in the temperature range studied.

Molecular weights of the Y-branch series were checked by measuring the limiting viscosity number in toluene and cyclohexane and using the Mark-Houwink relations reported (BRYCE 1971). Quoted data were taken for the remaining fractions.

RESULTS AND DISCUSSION

All the c.p.c.'s for branched polystyrene solutions in the l.c.s.t. region were similar to those obtained for linear polymers. Values of T_c are summarised in Table 1 together with the corresponding values measured for the u.c.s.t. Molecular weights are expressed also in terms of r , the ratio of molar volumes of polymer and solvent.

Sigmoidal shaped c.p.c. have been observed for comb branched polystyrene (DERHAM 1975) but most of the curves here behaved normally in the concentration range studied, with the exception of two Y-branch fractions. Estimation of the critical temperature indicated that it was normally located on the right hand side (high concentration) of the c.p.c. In samples 11Y_{2.2} and 9Y_{2.3}, it was found that the T_c was located on the left side of the c.p.c. as shown in Fig.1 although in both cases the curves seemed to rise with concentration rather than decrease as

TABLE 1

Molecular weights and critical temperatures for star-branched polystyrenes dissolved in cyclohexane

Polystyrene	$10^{-5}M_w$	$10^{-3}r$	Average number of arms	T(ucst)/K	T(lcst)/K
16Y ₂	0.93	0.78	3	292.2	503.0
15Y ₃	1.31	1.10	3	294.0	499.7
9Y _{2.3}	2.30	1.94	3	297.1	496.8
12Y ₃	2.65	2.24	3	297.4	495.7
11Y _{2.2}	4.10	3.46	3	300.9	493.6
S27	1.25	1.05	8	288.1	504.8
S26	2.06	1.75	6.5	294.1	498.9
S29	6.05	5.11	7	299.3	493.8
S31	7.90	6.67	7.5	299.9	492.2
PS.9	9.60	8.10	9	300.4	491.9

expected. Other samples did not exhibit this anomalous behaviour. No irregularities could be detected in fractions 11Y_{2.2} or 9Y_{2.3}; both appear essentially monodisperse according to gel permeation chromatography and contaminating material was absent. No explanation can be offered at this time for this anomaly.

A comparison of the phase behaviour of linear and branched polystyrenes may be made by plotting T_c^{-1} against $(r^{-\frac{1}{2}} + \frac{1}{2}r^{-1})$ and the differences can readily be seen in Fig.2. Published data for linear polystyrene in cyclohexane (SAEKI et al. 1973) are included and spot measurements in this laboratory on linear polystyrene confirm the accuracy of these results. Thus the measurements are internally consistent.

In the l.c.s.t. region the data for linear and Y-branch polystyrene can be described by one line extrapolating to $\theta_L = 486K$ for $r = \infty$. Star fractions with six to nine arms can be represented by a second line located at higher temperatures over the complete range studied. The differences in T_c are small, but increase steadily as the molecular weight decreases. Phase separation is delayed at the l.c.s.t. by the presence of branching in low molecular weight fractions but the line extrapolates to a common value of θ_L indicating that this level of branching becomes less important as $r \rightarrow \infty$. Small differences of this magnitude may be due simply to minor differences in the expansivity of the linear and branched polystyrene.

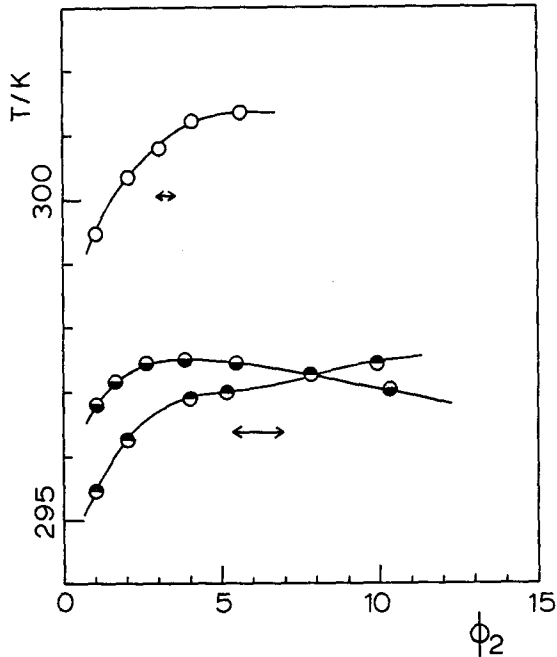


Figure 1. Cloudpoint curves for samples 11Y_{2.2} (-O-), 9Y_{2.3} (-●-), and 12Y₃(-●-) in cyclohexane. The region in which the critical temperature was estimated to lie, from phase volume measurements, is indicated by the arrows.

Branching effects are much more pronounced in the upper critical region. Linear polystyrene data lie on a line extrapolating to $\theta_u = 307\text{K}$ for $r = \infty$, but now the Y-branch fractions are located on a distinctly separate parallel line. The difference ΔT_c is small, averaging about 2K over most of the samples. Much larger differences are detected when the star-polystyrene are examined. Again a common

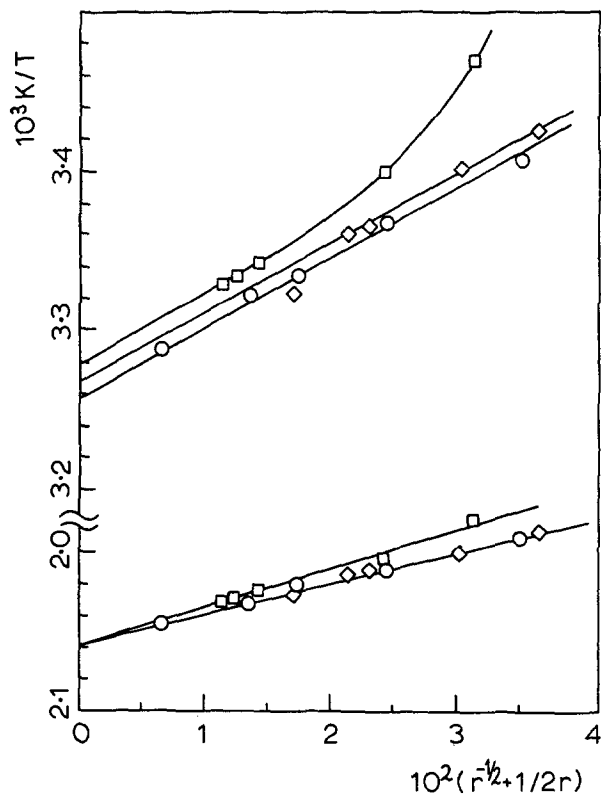


Figure 2. Comparison of critical temperatures for linear (-O-), Y-branch (-◇-) and star-branch (-□-) polystyrene in cyclohexane. Top: upper critical region. Bottom: lower critical region.

curve can be constructed for the samples with a higher branching density, which is no longer linear and shows pronounced deviations as a function of the molecular weight. In common with most other workers it is found that branching reduces the u.c.s.t. and enhances the solubility of the polymer. Depression of T_c is greatest in the low molecular weight, more highly branched, samples with ΔT_c being as great as 7K at $M_w = 1.25 \times 10^5$.

Extrapolation of the data for star branched fractions to $r = \infty$, leads to a lower value of θ_u than the linear polymers, but in this case one must question the meaning of this value. It has been suggested that so-called θ conditions no longer characterize a given polymer system when branched samples are used (CANDAU et al. 1972). The results obtained here tend to support that view for branched polymers in the u.c.s.t. region. This means that each sample should be considered individually.

Depression of the θ temperatures in the u.c.s.t. region has been attributed to deviations from the expected segment density of a linear polymer coil, brought about by branching. An alternative proposition (ROOVERS and BYWATER 1976) is that the structure and chemical anomalies introduced by the incorporation of foreign groups used to effect coupling reactions in the polymers, alters the enthalpy factor but has little influence on the entropy parameter. Thus T_c in the u.c.s.t. region would be influenced to a greater extent than T_c in the l.c.s.t. region. Whatever the explanation, it is confirmed by our results that structural differences, such as branching in polymers are much less likely to influence the phase behaviour in the l.c.s.t. region than in the u.c.s.t. region.

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