

Study on polymer solutions in solvent mixtures in the vicinity of the critical point of the solvents: 4*. Saturation phenomena

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(Received 5 October 1983)

Turbidimetric results have been obtained with the ternary system *N,N*-dimethylformamide/cyclohexane/polystyrene. The displacement of the heterogeneous region depends on the molecular weight of the polystyrene sample and for each polystyrene sample the displacement changes with the concentration of the polymer. Above a certain molecular weight of the polymer, with a given concentration, the displacement reaches a plateau region. A plateau is also obtained when we change the concentration of the polymer of a given molecular weight. The crossover region, which is determined by the appearance of the plateau region, obeys the scaling laws and is probably the region where the distance between the macromolecular coils is comparable to their diameters.

(Keywords: polystyrene; ternary system; non-miscible solvents; coexistence curves; saturation phenomena; polymer critical concentration)

INTRODUCTION

It has been demonstrated¹⁻⁴ that a very small quantity of a polymer gives a high displacement of the heterogeneous region of two non-miscible liquids, especially in the neighbourhood of the critical point of the two non-miscible liquids. This 'co-nonsolvency' is more pronounced when we go from the critical composition of the solvent mixture to compositions richer in poor solvent of the polymer.

In this article we present new turbidimetric results obtained with the ternary system *N,N*-dimethylformamide/cyclohexane/polystyrene, which show that, apart from displacement of the coexistence curves, saturation phenomena occur as well. This saturation phenomenon is related with a critical concentration at which the macromolecular coils approach each other to a distance comparable to their diameters. It is evident that this concentration is lower in the case of high molecular weight chains, since in this case the chains are more expanded.

EXPERIMENTAL

The samples of polystyrene (PS) used in this work are anionically prepared at the Centre des Recherches sur les Macromolécules in Strasbourg (France) and their polydispersity is very low ($M_w/M_n < 1.2$). The star shaped PS samples have also been prepared in the same laboratory by anionic methods using divinylbenzene as coupling agent. Their polydispersity is practically equal to 1.

The *N,N*-dimethylformamide (DMF) was lab grade (Merck) and the cyclohexane (CH) used was of p.a. grade (Merck). If the DMF was in contact for a relatively long time with the air, it was distilled.

The turbidimetric measurements were conducted with

hermerically closed tubes. The temperature at which homogeneity appeared, was obtained by very slow heating of the mixtures. The rate of heating was lower than 0.1°C per minute. The critical solution temperature (T_c) was visually determined within a precision of $\pm 0.2^\circ\text{C}$.

The composition of the binary solvent mixtures is expressed in this article in volume per cent (vol-%). The polymer concentration is expressed in weight per volume (g cm^{-3}).

The intrinsic viscosity measurements were made by means of a Cannon-Ubbelohde viscometer and the accuracy and reproducibility were within 1%.

RESULTS AND DISCUSSION

Influence of the molecular weight and the structure of the polymer on the critical solution temperature

In this work a systematic turbidimetric study of the ternary system DMF/CH/PS has been carried out. Initially we determined the influence of the molecular weight of linear PS samples, of a given concentration, on the critical solution temperature (T_c) of the solvent mixture DMF/CH in a given composition of this mixture. In *Figure 1* we give the results in three different compositions of the solvent mixture (75%, 85% and 90% CH). We point out here that the critical composition of the two liquids is approximately determined at a solvent composition 32 vol-% DMF, 68 vol-% CH. The constant concentration of the polymer is equal to $5 \times 10^{-3} \text{ g cm}^{-3}$.

As seen in *Figure 1*, the demixing point of the ternary system is drastically elevated when the molecular weight of the polymer is increased and this happens for the relatively low molecular weight polystyrene samples. A plateau appears in the region of the high molecular weight samples. For the very high molecular weight PS samples the demixing point is not practically changed with molecular weight.

* Parts 1, 2 and 3: cf^{1,2,3}

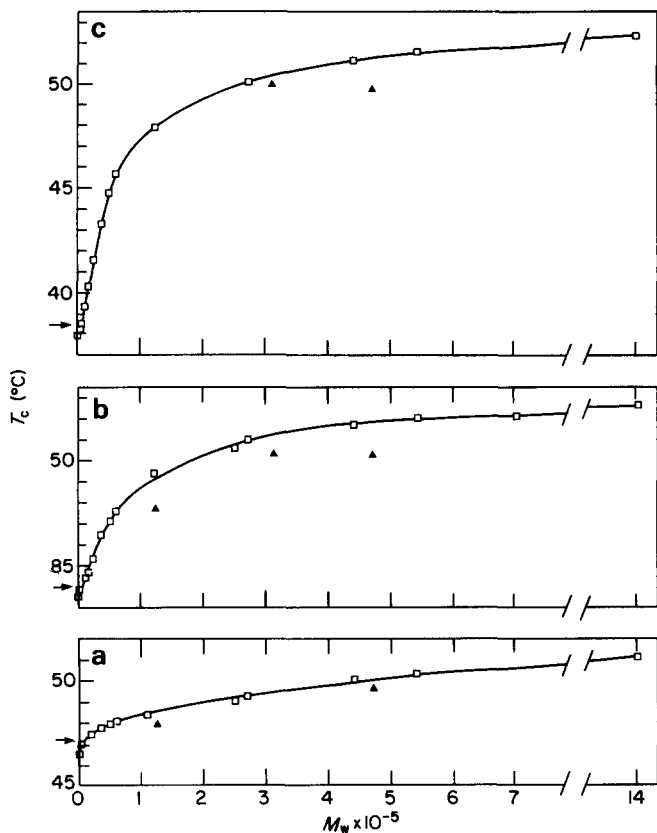


Figure 1 Variation of the critical solution temperature (T_c) of the system *N,N*-dimethylformamide(DMF)/cyclohexane(CH)/polystyrene(PS) as a function of the molecular weight (M_w) of PS, in three different solvent compositions: (a) 75 vol-%CH, (b) 85 vol-%CH, (c) 90 vol-%CH. The concentration of PS in the solvent mixture is always the same ($c=5 \times 10^{-3} \text{ g cm}^{-3}$). (\square) Linear PS samples; (\blacktriangle) star shaped PS samples; (\circ) T_c obtained with the monomer styrene. The arrows indicate the T_c of the pure solvent mixtures

The observed phenomenon of the increasing of the critical solution temperature of the two liquids is 'polymeric'. The monomer styrene and the very low molecular weight samples of PS give, on the other hand, a lowering of the critical solution temperature (see arrows in *Figure 1*).

In *Figure 1* the results with three star shaped PS samples are given; the obtained points do not fit in the curves with the linear PS samples. The discrepancy in the displacement of the T_c by the linear and the star shaped PS samples, prompted us to give a new representation of the obtained results. In *Figure 2* the T_c of the system DMF/CH/PS is given as a function of $[\eta]M$ of each sample. The product $[\eta]M$ represents the hydrodynamic volume of the samples. As seen in *Figure 2* all the points obtained with the linear and the star shaped PS samples fit in the same curve for each solvent composition. The results indicate that the main factor for the displacement of the critical solution temperature of the non-miscible liquids is the hydrodynamic volume of the polymer.

Above a certain hydrodynamic volume (*Figure 2*) or above a certain value of M (*Figure 1*) no increase of T_c was observed from which we infer that a saturation phenomenon takes place. Indeed the high molecular weight macromolecular chains present a higher expansion and for the same concentration occupies a higher hydrodynamic volume in the solution compared to the low molecular weight samples. We deduce that the PS con-

centration with which we have obtained the turbidimetric results of *Figures 1* and *2* is high enough for the high molecular weight samples to allow the chains to give some contact; consequently a saturation phenomenon occurs.

In *Figure 3* the variation of T_c with M is shown for the mixture 15 vol-% DMF/85 vol-% CH obtained with a much lower concentration in PS ($5 \times 10^{-5} \text{ g cm}^{-3}$). A saturation phenomenon does not appear, as it did in the case in *Figure 1b*.

Influence of the polymer concentration on the critical solution temperature

The turbidimetric results given in *Figure 4* are obtained in a given solvent mixture (85 vol-% CH) with five PS samples of different molecular weight changing the concentration of each PS sample. As we can see in this *Figure*, an initial increase of the polymer concentration leads to an increase of T_c especially in the case of high molecular weight samples. Beyond a certain concen-

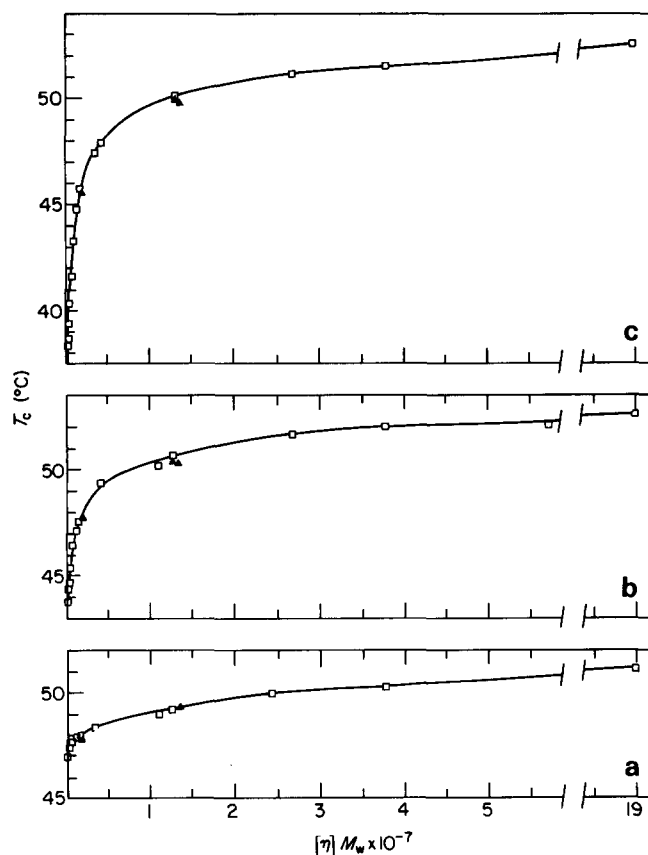


Figure 2 T_c as a function of $[\eta]M_w$ for the same PS samples and in the same solvent compositions as in *Figure 1*

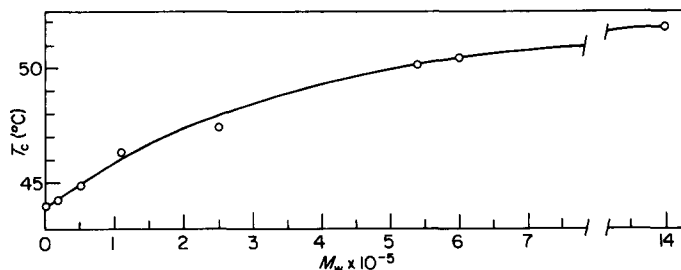


Figure 3 Variation of T_c as a function of M_w of the system DMF/CH/PS. The solvent composition is equal to 85 Vol-%CH, as in *Figure 1b* and the polymer concentration is $5 \times 10^{-5} \text{ g cm}^{-3}$

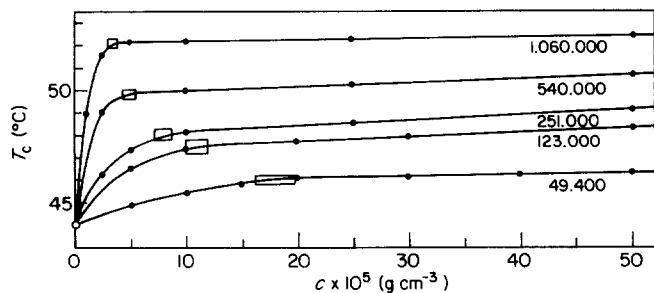


Figure 4 Variation of T_c as a function of the concentration c for five PS samples of different molecular weight in a given solvent composition (85 Vol-%CH). The crossover concentration regions (c^{**}) are indicated by the rectangles

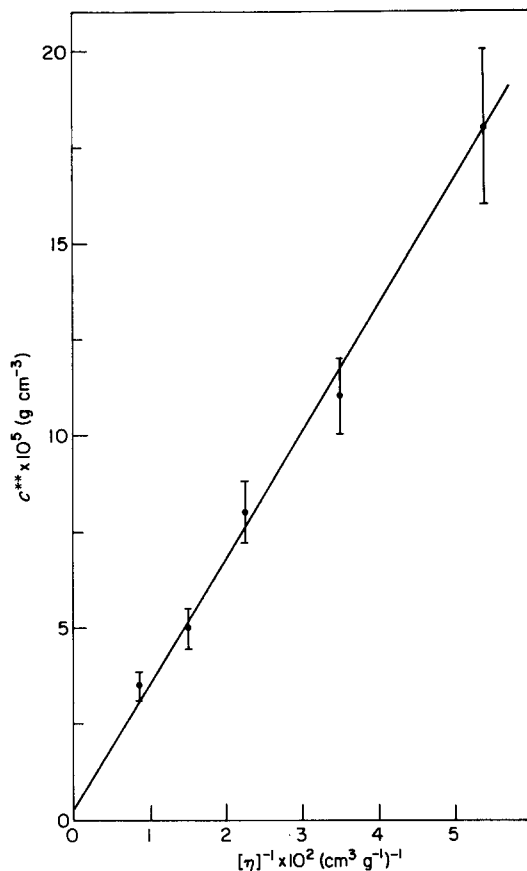


Figure 5 Variation of the critical concentration (c^{**}) as a function of the inverse of the intrinsic viscosity $[\eta]^{-1}$ for the five PS samples indicated in *Figure 4*

tration T_c levels off as c increases. This concentration may be considered as a crossover point or as a critical concentration according to the scaling laws⁵. As was expected this concentration becomes lower as the molecular weight of PS becomes higher.

These results lead to an explanation based on the critical concentration introduced by P. G. de Gennes⁵. When the concentration reaches the point at which the distance between the molecules is of the order of the diameters a saturation phenomenon appears and an increase of the polymer concentration does not lead to any appreciable increase in T_c . The critical concentration must be more precisely identified with c^{**6-7} . In the following we will try to establish a relation between this critical concentration and the hydrodynamic dimensions of the macromolecular coils. We will express the hydrodynamic dimensions by the intrinsic viscosity of the

samples as it was used by Simha and coworkers^{8,9} in the case of the overlap of the macromolecular coils ($c^* \sim [\eta]^{-1}$). The intrinsic viscosity $[\eta]$ of each PS sample, in our case, was determined one degree above the T_c and in the same solvent composition (85 vol% CH).

If we now consider that c^{**} is proportional to c^* ,

$$c^{**} \sim [\eta]^{-1} \quad (1)$$

In *Figure 5* we see a very good verification of the above relation which permits us to consider that we have a critical concentration, above which T_c does not increase (*Figure 4*) and we consider this concentration as a crossover point. The very low values of the critical concentration indicate that there is no overlap of the macromolecular coils but the distance between their centres becomes comparable to their diameters.

Using now the same values of $[\eta]$ in a Mark-Houwink-Sakurada plot ($[\eta] \sim M^a \sim N^a$) we obtain an a value equal to 0.58 (*Figure 6*). We have¹⁰ $a = 3\nu - 1$ (because $[\eta] \sim N^{3\nu-1}$) and knowing that¹¹

$$c^{**} \sim \frac{N}{R_G^3}$$

and that $R_G^3 \sim N^{3\nu}$ we get

$$c^{**} \sim N^{-(3\nu-1)} \sim N^{-a} \quad (2)$$

(In the above relations N is the degree of polymerization and R_G the radius of giration of the macromolecular coil).

If now we plot $\log c^{**}$ vs. $\log N$ or $\log M$ (*Figure 7*) we obtain the value of the exponent $3\nu - 1$ equal to 0.55 and this is very close to the value obtained for the a ($a = 0.58$) from the M-H-S plot. This result, corroborating equation (2), offers one more indication that, in our turbidimetric study, we have a saturation phenomenon that obeys the scaling laws.

The c^{**} values determined in this work are very low compared to other determinations^{6,7}. Nevertheless the difference could be explained by the fact that in our case we have a solvent mixture and that DMF is a better solvent for PS compared to CH and that the mixture contains only 15% DMF. If we accept that in the critical temperature we have the 'isorange lines'¹² the polymer

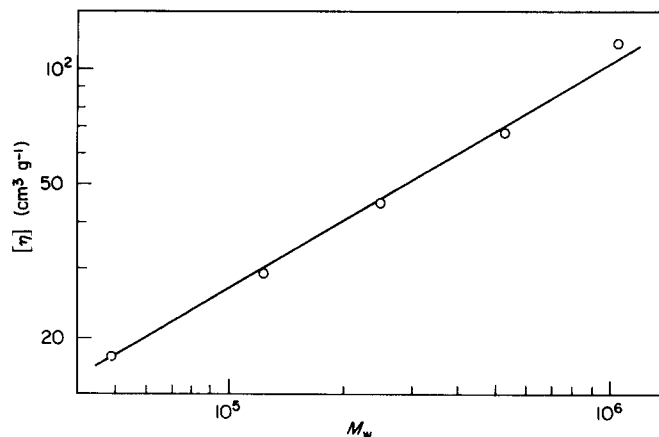


Figure 6 M-H-S plot for the PS sample indicated in *Figure 4* in the solvent mixture 85 Vol%CH and in a temperature one degree above T_c for each PS sample

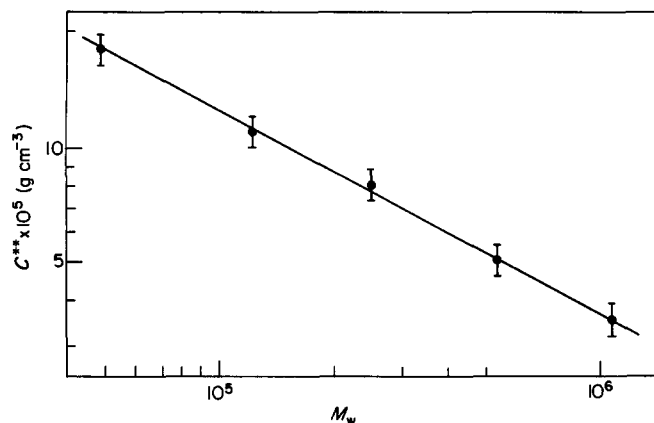


Figure 7 Variation of $\log c^{**}$ as a function of $\log M_w$ for the same PS samples as in Figures 4 and 6

must be located in the regions richer in DMF and its concentration c^{**} must be higher than the analytical concentrations given in Figure 4.

CONCLUSION

Our results show that the displacement of the critical solution temperature of the two non-miscible solvents in the presence of the macromolecular coils is due only to a polymeric phenomenon. As we can see in Figure 1, the

monomer and the very low PS samples give a lowering of the critical solution temperature.

The T_c displacement is directly related to the hydrodynamic volume of the polymer and not to its molecular weight (Figures 1 and 2).

The main result obtained in this work is that the displacement of T_c arrives to a saturation point (c^{**}) and that this saturation obeys the scaling laws introduced by de Gennes.

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