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Difference between the dynamic and static behaviour of polymers in dilute solutions: 2. The critical concentration c^*

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The critical concentration, c^*, at which overlapping between macromolecular chains occurs, has been studied using dynamic (viscometry) and static (light scattering) methods. With the same polymer–solvent system this critical concentration has a higher value when viscometry is used, compared to the concentration obtained when using a light scattering technique. This difference is attributed to an incipient decrease of the dimensions of the macromolecular coils above the critical concentration c^{**}, which is observed only under dynamic conditions. Relationship between the critical concentration c^* and both the intrinsic viscosity and the molecular weight of the polymers are proposed.

(Keywords: critical concentration c^*; viscometry; light scattering)

INTRODUCTION

The critical concentration, c^*, introduced by de Gennes, has been the subject of many investigations. Different authors have proposed different equations relating the overlapping chain concentration to the chain dimensions, expressed in terms of the intrinsic viscosity, molecular mass, or the radius of gyration of the coils. Generally, c^* for a given polymer fraction is given as being proportional to M/R^3 (where M is the molecular mass and R is the radius of gyration of this fraction), and by taking into account the fact that the intrinsic viscosity is proportional to R^3/M, c^* is also given as being proportional to the inverse of the intrinsic viscosity.

A problem arises with the proportionality factors in the relationships between c^* and the dimensions of the macromolecular coils[1–3]. More precisely, the proportionality factor in the relationship between c^* and the segment density of the coils, as expressed by the inverse of the intrinsic viscosity, lies between 0.58[1] and 1.08[3].

In this work, the critical concentration c^* is determined with good accuracy when using either dynamic (viscometry) or static (light scattering) methods. The value obtained for c^* (for the same polymer fraction) when using dynamic methods, (c_v^*), is always higher when compared to that obtained using static methods (c_s^*). An explanation is proposed for this difference, based on the observed critical concentration c^{**}[4] that appears only in the case of dynamic measurements. More precisely, a relatively higher compression of the coils above c^{**}, due to the motion of the chains, leads to more compact coils and consequently, in this case, c^* appears at higher concentrations when compared to those obtained using static methods.

EXPERIMENTAL

The polystyrene (PS) and poly(methyl methacrylate) (PMMA) samples used in this work have been prepared by us in the 'Charles Sadron' Institute in Strasbourg (France), by anionic polymerization in tetrahydrofuran at −70°C. The polydispersity, as determined by gel permeation chromatography is always lower than 1.1.

A Schott–Geräte (AVS) automated viscosity measuring system with Ubbelohde-type viscometers, equipped with an automatic injection system (maximum error $\pm 0.03\%$) for *in situ* dilutions, has been used in this study . The temperature was controlled to within ± 0.02°C. The inaccuracies in the flow times were considered negligible, with very good reproducibility being achieved.

The light scattering measurements have been performed using a computer-controlled spectrogoniometer (model SEM RD, Sematech (France)) equipped with a He–Ne laser (633 nm).

RESULTS AND DISCUSSION

In *Figure 1*, we present the variation of η_i/c $(=(t-t_0)/t_0c$, where t is the efflux time of the solution and t_0 is the efflux time of the solvent) as a function of the solution concentration c for various polystyrene (PS) fractions in ethyl acetate solution. A relatively sharp crossover appears, indicating the critical concentration c_v^*, separating dilute from semidilute solutions, which is obtained with these fractions under dynamic conditions.

As was expected, with the low-molecular-weight fractions the crossover point is shifted towards higher concentrations. The values of η_i/c obtained in the region above c^* are higher than the values predicted by extrapolation of the straight line obtained with the points situated below c^*, and this is in accordance with

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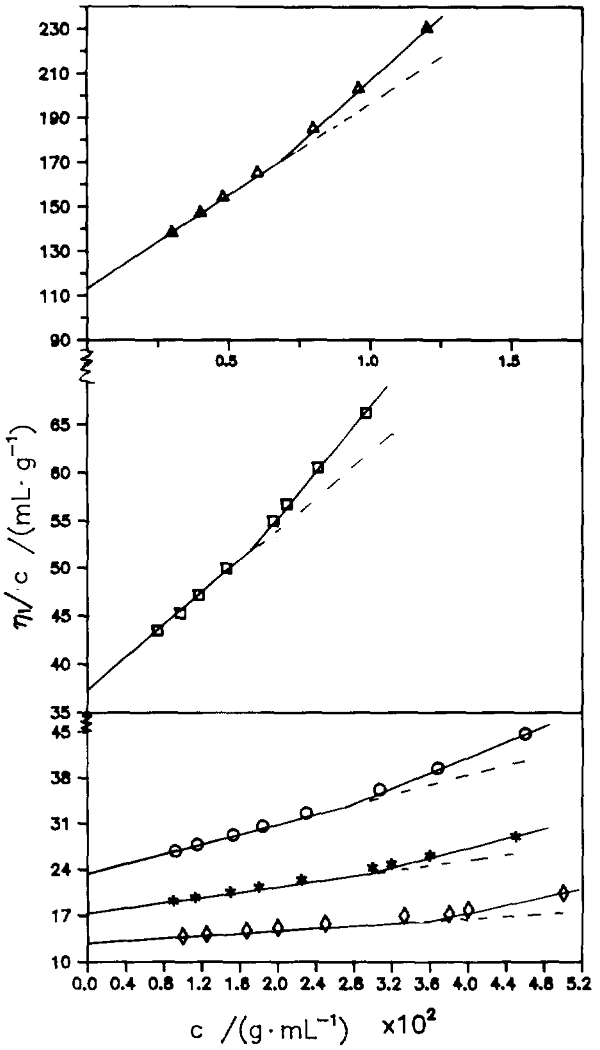

Figure 1 Plots of η_i/c *versus* c for polystyrene fractions with different M_w values in ethyl acetate solutions: (△) 1 000 000; (□) 203 000; (○) 110 200; (*) 56 000; (◇) 32 000

the results already obtained concerning this critical concentration. In contrast to other reports we do not need to present η_i/c *versus* c using a logarithmic scale because our results without such a presentation do allow an accurate determination of the required critical concentration (see *Figure 1*).

Using the PMMA–ethyl acetate and PMMA–benzene systems, the same type of curves were obtained, as can be seen in *Figure 2*.

If we identify the volume occupied by a macromolecular coil, with a molecular weight equal to M, to be $4\pi R^3/3$, the critical concentration c^* must be given by the following relationship:

$$c^* = \frac{1}{N_A}\left(\frac{3M}{4\pi R^3}\right) \tag{1}$$

where N_A is the Avogadro constant and R is the radius of gyration.

Using the Fox–Flory equation we have:

$$[\eta] \propto \frac{R^3}{M} \tag{2}$$

and from equation (1) we obtain the following:

$$c^* \propto [\eta]^{-1} \tag{3}$$

The radius of gyration of a polymer in a good solvent varies as follows:

$$R_G^3 \propto M^{3\nu} \tag{4}$$

where ν is the excluded volume index, and with $3\nu - 1 = a$, where a is the Mark–Houwink–Sakurada (MHS) exponent, we obtain from equation (1) the following:

$$c^* \propto M^{-(3\nu-1)} \propto M^{-a} \tag{5}$$

Plotting the critical concentration determined from viscometry, c_v^*, as a function of the inverse of the intrinsic viscosity, according to equation (3), we obtain the straight line shown in *Figure 3*. This line is described by the following relationship:

$$c_v^* = 0.5[\eta]^{-1} \tag{6}$$

The factor 0.5 is close to the factor proposed by Vidakovic *et al.*[1] who used dynamic methods.

In the following, by presenting $\log c_v^*$ *versus* $\log M$ for the PS–ethyl acetate system, we obtain the straight line shown in *Figure 4* (cf. equation (5)). The equation describing this curve is as follows:

$$c_v^* \propto M^{-0.57} \tag{7}$$

and the absolute value of the exponent is in accordance with the exponent in the MHS equation ($a = 0.58$) for this system[5]. The almost identical absolute values of the exponents in the MHS equation and in equation (7) claim in favour of the validity of equations (1), (2), (4) and (5).

Using the light scattering techniques for three PS fractions dissolved in ethyl acetate and plotting $Kc/\Delta I$ as a function of c (where K is a constant, and ΔI is the difference in the intensities between a solution of

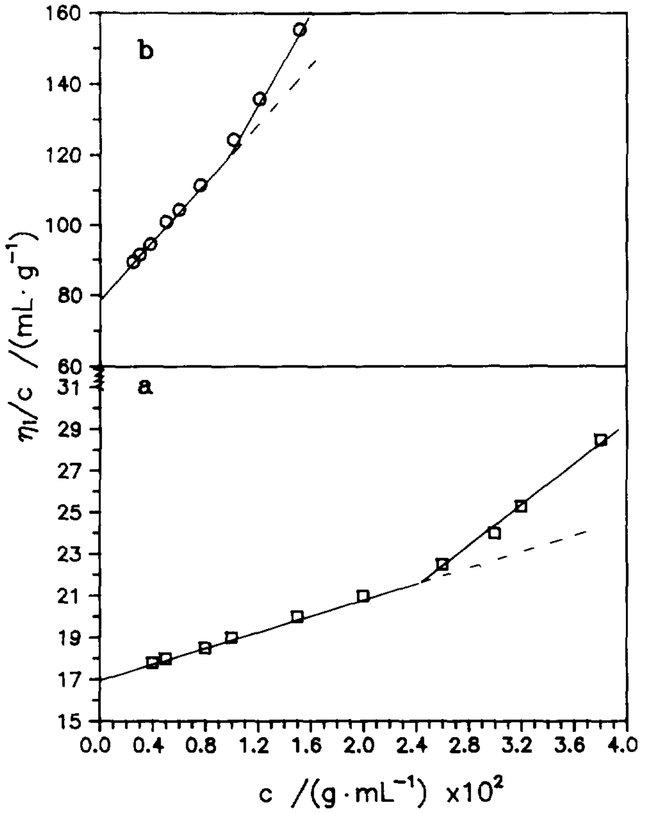

Figure 2 Plots of η_i/c *versus* c for: (a) PMMA ($M_w = 805\,000$) in ethyl acetate; (b) PMMA ($M_w = 34\,000$) in benzene

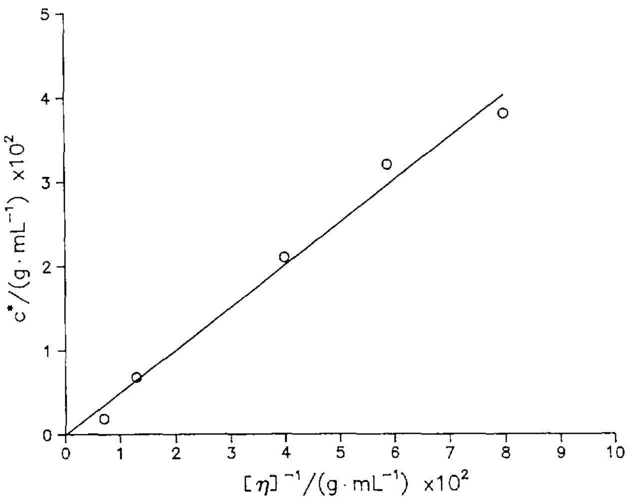

Figure 3 Plot of the critical concentration determined from viscometry, c_v^*, as a function of the inverse of the intrinsic viscosity, for the PS–ethyl acetate system

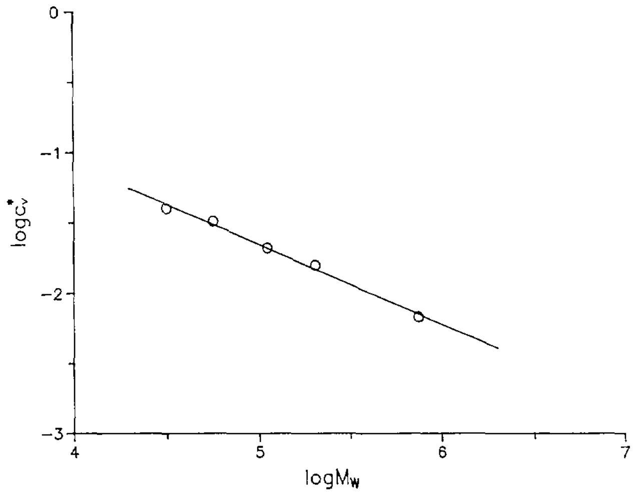

Figure 4 Plot of log c_v^* *versus* log M_w for the PS–ethyl acetate system

concentration c and the pure solvent) we obtain the three curves shown in *Figure 5*. As in the case of the dynamic measurements (see *Figures 1* and *2*) the points lie on two straight lines, the intercept of which gives the critical concentration in the static state, c_s^*. We must state that the curves in *Figure 5* have been drawn automatically by the computer controlling the light scattering apparatus. By comparing the overlapping concentrations obtained either by dynamic or static measurements for the same polymer fractions we observe that in the case of dynamic measurements the critical concentrations are higher than those obtained using static measurements (see *Figures 1* and *5*). Let us also mention that the scaling laws obtained with c_s^* are approximately the same as those obtained with c_v^* (cf. equations (6) and (7)).

As in the previous paper concerning c^{**}[4], the radius of gyration, R_G, of the macromolecular coils, necessary for the calculation of their volume, and subsequently the critical concentration, c_{calc}^*, at which the coils occupy the entire volume of the solution, is obtained from the following equation:

$$[\eta]=6^{3/2}\Phi R_G^3/M \qquad (8)$$

The value of Φ is taken as being equal to 1.7×10^{23}, which is the best value for relating the intrinsic viscosity to the radius of gyration[6]. The values obtained for c_{calc}^* are given in *Table 1*, from which we can see that c_{calc}^* is lower than both c_v^* and c_s^* by about 30% for all of the samples investigated. This result indicates that the assumption made in which the macromolecular coils are regarded as spheres with a radius equal to the radius of gyration (volume of one coil being equal to (4/3) πR^3) must be very close to reality.

In order to explain the difference between the c_v^* and c_s^* values, we must accept that the hydrodynamic volume of the macromolecular chains in the dynamic state is lower than the volume of the chains in the static state.

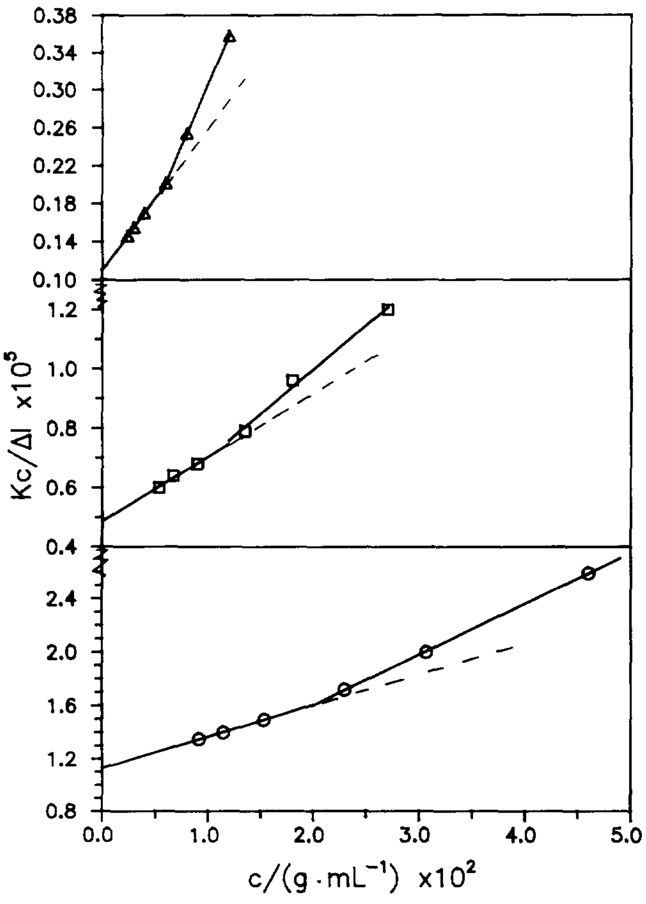

Figure 5 Plots of $Kc/\Delta I$ *versus* c for PS samples in ethyl acetate, with the intensities being measured at 90°: (△) $M_w=1\,000\,000$; (□) $M_w=203\,000$; (○) $M_w=110\,200$

Table 1 Values of the weight-average molecular weight, M_w, the calculated critical concentration, c_{calc}^*, at which the macromolecular coils occupy the entire volume of the solution, the critical concentration, c_s^*, determined by light scattering and the critical concentration, c_v^*, determined by viscometry, obtained for various PS fractions in ethyl acetate

M_w	c_{calc}^* (g per 100 ml)	c_s^* (g per 100 ml)	c_v^* (g per 100 ml)
32 000	2.98	–	3.8
56 000	2.37	–	3.2
110 200	1.47	2.20	2.7
203 000	1.00	1.19	1.5
1 000 000	0.37	0.62	0.7

This explanation is corroborated by the fact that according to our results[4] it is only in the dynamic state that the macromolecular chains present the critical concentration c^{**}, above which these chains show a drastic decrease in their dimensions. In the case of static measurements, c^{**} is not observed and consequently when we reach the critical concentration c_s^* the chains have a higher volume than in the dynamic state, and for this reason, therefore, we find that $c_s^* < c_v^*$.

CONCLUSIONS

In conclusion, we observe two different values for the critical concentration characterizing the crossover between dilute and semidilute solutions. The concentration c_v^*, obtained from dynamic measurements, is higher than the concentration c_s^*, obtained from static measurements (*Table 1*). An explanation is proposed for this difference, based on the fact that the macromolecular chains during their motion show a lower hydrodynamic volume, due to peripheral interchain entanglements and a decrease in their volume because of collisions, particularly in the relatively high concentration region ($c > c^{**}$), when compared to the volume that they present under static conditions. Our calculations show that we can predict the concentration at which the macromolecular chains lose their individuality if we consider these chains to be spheres with a radius equal to the radius of gyration.

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