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Difference between the dynamic and static behaviour of polymers in dilute solutions: 1. The critical concentration c^{**}

Anastasios Dondos* and Dimitrios Papanagopoulos
Department of Chemical Engineering, University of Patras, 26500 Patras, Greece
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Using dynamic (viscometry) and static (light scattering) measurements we study solutions of polystyrene and poly(methyl methacrylate) fractions ranging from extremely dilute solutions up to the critical concentration c^*. When viscometry is used, a crossover phenomenon is observed, separating the dilute solutions into extremely dilute and dilute solutions. The critical concentration c^{**}, determined from this crossover phenomenon, depends on the hydrodynamic volume of the macromolecular coils and is lower when the molecular weight of the coils becomes higher, as has been observed for the critical concentration c^*. By changing the shear rate, c^{**} also changes and tends to disappear at a practically zero shear rate. The variation of c^{**} with the shear rate implies that this crossover phenomenon is a dynamic phenomenon and for this reason it is not observed when using static measurements.

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

INTRODUCTION

On the basis of dynamic measurements (viscometry) and using a mixture of two polymers dissolved in a common solvent, or by using a polymer dissolved in a solvent containing another polymer, a critical concentration c^{**} that separates the dilute solutions in extremely dilute solutions ($c<c^{**}$) and dilute solutions ($c>c^{**}$) was established[1–6]. This critical concentration has also been established by using only one polymer dissolved in a pure solvent[7–9]. For one polymer, or for a mixture of two polymers, c^{**} increases with the decrease of the hydrodynamic volume of the macromolecular chains or with the increase of their segment density. Expressing the segment density of the chains by the inverse of their intrinsic viscosity, linear relationships between this quantity and c^{**} were obtained[7]. Linear relationships are also obtained between the inverse of the intrinsic viscosity and the critical concentration c^*[10,11] introduced by de Gennes, and which separates the dilute solutions from the semidilute solutions.

It was proposed[5,7,8] that at the critical concentration c^{**} the macromolecular chains present an incipient overlapping that provokes a decrease of their hydrodynamic volume. Nevertheless, the macromolecular chains conserve their individuality even above c^{**}, and lose their individuality only at the critical concentration c^*. An individual chain occupies a certain domain in the solution, inside of which the segment density decreases from the central to the peripheral region.

In this article we will present recently obtained results that indicate that for the same polymer–solvent system the crossover point (c^{**}) observed in the plot of the variation of the reduced viscosity as a function of the concentration, depends on the capillary diameter of the viscometer. More precisely, c^{**} moves to higher concentrations if the efflux time increases (decrease of the shear rate). This result leads us to investigate whether the appearance of c^{**} is only a dynamic phenomenon. Indeed, c^{**} appears only when the macromolecular chains flow, and on the contrary, when using static methods (light scattering) the critical concentration c^{**} does not appear.

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 $-70°C$, and their polydispersities never exceed 1.15.

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. By changing the capillary size the efflux time is changed, and consequently the shear rate. The temperature was controlled to within $\pm 0.02°C$. The same viscosity measurements have been performed more than once in order to eliminate any errors that could have originated from concentration inaccuracies. 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).

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* To whom correspondence should be addressed

RESULTS AND DISCUSSION

In this work, for the viscometry measurements, we use only one polymer dissolved in a pure solvent. With the system PS ($M_w = 32000$)–ethyl acetate, by plotting η_i/c ($= (t - t_0)/t_0c$, where t is the efflux time of the solution, t_0 is the efflux time of the solvent and c is the polymer concentration) as a function of c we obtain the three curves shown in *Figure 1* when using three viscometers with different capillary sizes. Curves A and C are obtained with the lowest and the highest shear rate viscometers, respectively, while curve B is obtained with a viscometer of an intermediate shear rate. As we can see in this figure the crossover point, which indicates the critical concentration c^{**}, moves to higher concentrations with decreasing capillary size, i.e. a decreasing shear rate. The same variation of c^{**} with shear rate is also obtained with the systems PMMA ($M_w = 45000$)–ethyl acetate (*Figure 2*) and PS ($M_w = 24800$)–cyclohexane (*Figure 3*). In both *Figures 2* and *3*, the shear rate increases from curve A to curve B.

In all of the measurements presented in *Figures 1–3* the values of η_i/c above the concentration c^{**} are lower than the values predicted by extrapolation of the straight lines obtained with the points situated below c^{**}. (This is clearly indicated in *Figures 1–3*.) The lowering of η_i/c must be attributed to a compression of the chains due to repulsive interactions between them, as has been previously proposed[12,13].

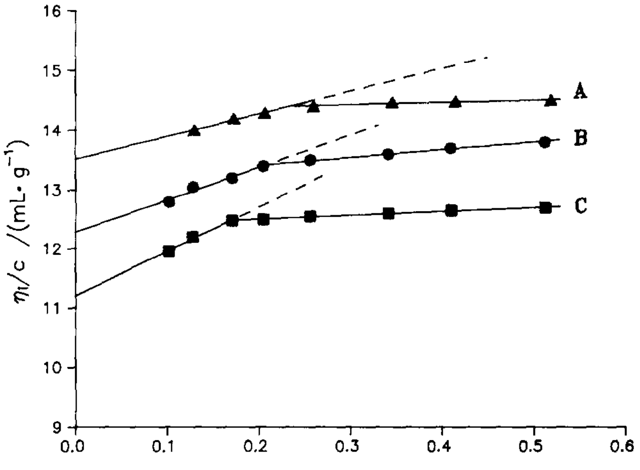

Figure 1 Plot of η_i/c *versus* c for a PS sample ($M_w = 32000$) in ethyl acetate using three different capillary viscometers: curve A, viscometer with the lowest shear rate; curve C, viscometer with the highest shear rate

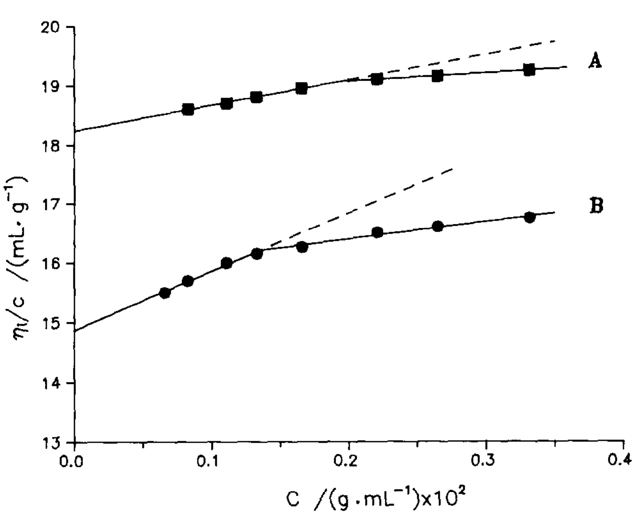

Figure 2 Plot of η_i/c *versus* c for a PMMA sample ($M_w = 45000$) in ethyl acetate: curve A, low shear rate; curve B, high shear rate

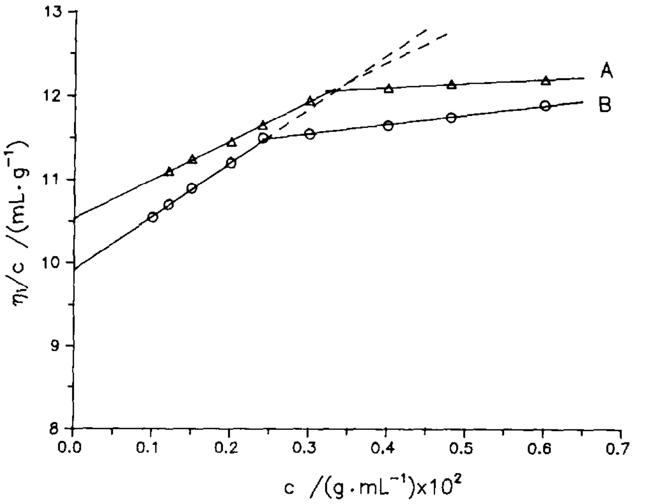

Figure 3 Plot of η_i/c *versus* c for a PS sample ($M_w = 24800$) in cyclohexane at 55°C: curve A, low shear rate; curve B, high shear rate

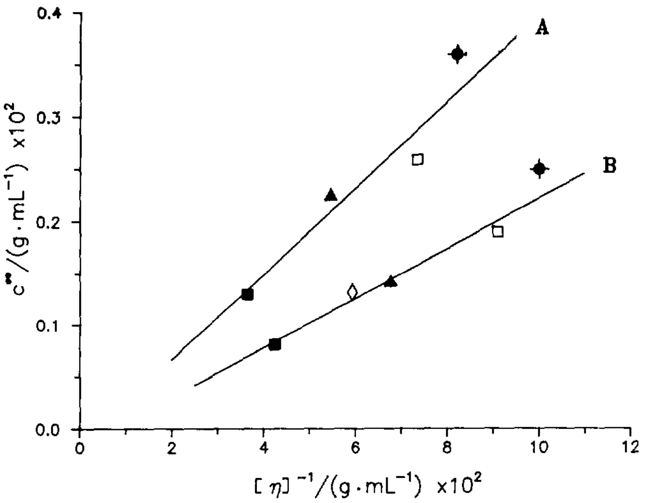

Figure 4 Plot of c^{**} *versus* $[\eta]^{-1}$ for various polymer samples in ethyl acetate: curve A, low shear rate; curve B, high shear rate; ✦, PS ($M_w = 24800$); □, PS ($M_w = 32000$); ▲, PMMA ($M_w = 45000$); ◇, PS ($M_w = 52800$); ■, PS ($M_w = 110200$)

As we have already mentioned, the critical concentration c^{**} shows a linear variation with the segment density of the samples. This density, given by the inverse of the intrinsic viscosity, represents the expansion of the macromolecular coils. The relationship between c^{**} and $[\eta]^{-1}$ is presented in *Figure 4*. The points obtained using fractions of the two polymers investigated here (PS and PMMA) lie on the same straight line if the viscosity measurements have been carried out with the same capillary viscometer. By changing the viscometer a second straight line is obtained with these two polymers. The scaling laws obtained between $[\eta]$ and c^{**} are as follows:

$$c^{**} = 0.041[\eta]^{-1} \qquad (1)$$

in the case of a low shear rate and

$$c^{**} = 0.025[\eta]^{-1} \qquad (2)$$

in the case of a high shear rate.

These two equations express the above observation that for the same segment density of a polymer fraction its critical concentration is higher when the shear rate is lower.

With the lowering of the shear rate we have not only a shift of the crossover point towards higher concentrations, but in addition this crossover becomes smoother (*Figures 1–3*). These two observations lead us to study the same polymer–solvent systems using static methods, such as the light scattering technique.

In *Figure 5* we present the results obtained by light scattering measurements on different fractions of PS dissolved in ethyl acetate. More precisely, in this figure we display the variation of $Kc/\Delta I$ as a function of c, where K is a constant, and ΔI (or I–I_0) is the difference between the intensities of a solution of concentration c and the pure solvent. The scattered intensities were measured at a fixed angle (90°) and were not extrapolated to zero angle, which does not introduce any appreciable difference in the second virial coefficient A_2, due to the relatively low molecular weights of the samples investigated. The concentration regions are approximately the same as those investigated for the dynamic measurements. The crossover points obtained by viscometry are indicated in *Figure 5* by arrows. The arrow on curve A of *Figure 5* corresponds to the c^{**} of the same system shown in *Figure 1* (curve A), as obtained by viscometry. Some results obtained by light scattering measurements on the PS–benzene system are presented in *Figure 6*. As in the case of the systems in *Figure 5* we have chosen to use the concentration regions in which these fractions present crossover points in the dynamic measurements. As can be seen from *Figures 5* and *6* no crossover points are obtained when using static measurements.

In the following, we will try to see if at the critical concentration c^{**} the macromolecular coils occupy the entire volume of the solution. For this, by using the well known equation

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

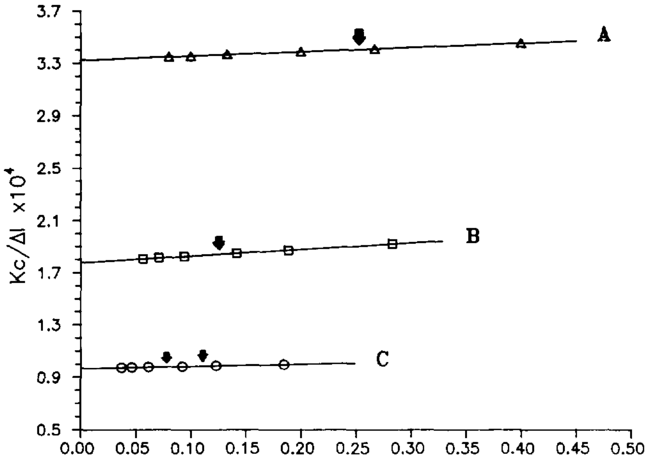

Figure 5 Plot of $Kc/\Delta I$ *versus* c for PS samples in ethyl acetate, with the intensities being measured at 90°: A, $M_w = 32\,000$; B, $M_w = 52\,800$; C, $M_w = 110\,200$

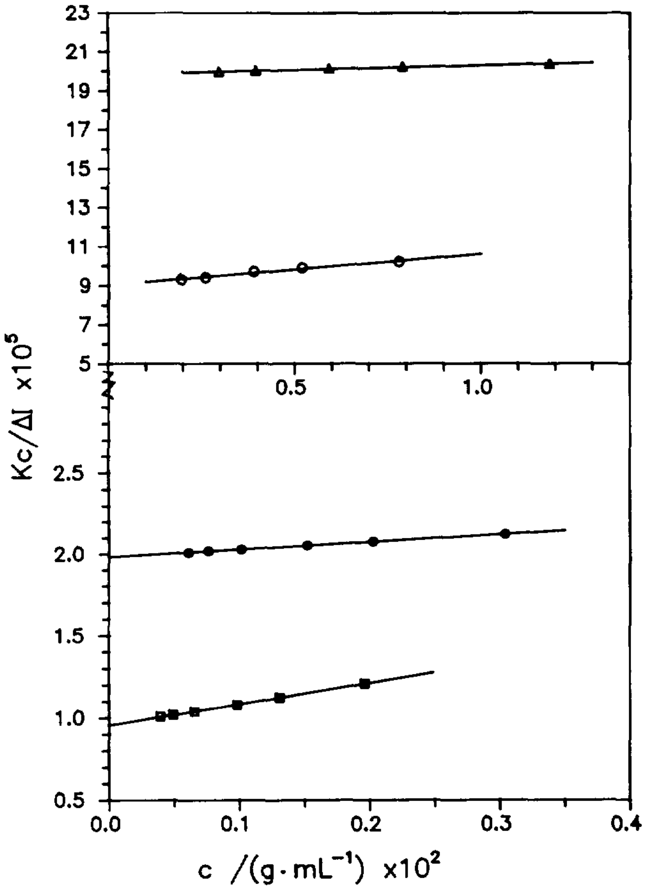

Figure 6 Plot of $Kc/\Delta I$ *versus* c for PS samples in benzene, with the intensities being measured at 90°: ●, $M_w = 52\,800$; ■, $M_w = 110\,200$; ▲, $M_w = 3700$; ○, $M_w = 9600$

in which Φ is the Flory constant and M is the molecular weight of the fraction, we obtain the radius of gyration R_G of the coil, and therefore the volume occupied by the chains, assumed as being represented by spheres of radius equal to R_G, must then be equal to $4\pi/3\ R_G n$, where n is the number of macromolecular coils. The value of Φ in equation (3) is taken as being equal to 1.7×10^{23}, i.e. the value relating the intrinsic viscosity to the radius of gyration of the coils[14]. The values of 2.5×10^{23} or 2.6×10^{23} are not used here because these values are obtained using the following equation derived from the scaling concept[15]:

$$[\eta] = 6^{3/2}\Phi R_G^2 R_H/M \qquad (4)$$

in which the intrinsic viscosity is related not only to the radius of gyration (static parameter) but also to the hydrodynamic radius R_H (dynamic parameter). Thus, consequently, we can calculate the polymer concentration (expressed in g per 100 ml) which is needed to achieve complete occupation of the solution volume by the macromolecular coils.

These results for some PS and PMMA fractions are given in *Table 1*. In the same table the experimentally determined values of c^{**} for the same fractions are also given. The results presented in *Table 1* clearly indicate that the macromolecular chains at the critical concentration c^{**} do not occupy the entire volume of the solution. The decrease in the η_i/c values above c^{**}, when compared to the values that extrapolation of the straight line obtained with the values of η_i/c below c^{**}

Table 1 Values of the weight-average molecular weight, M_w, the calculated concentration, c^*_{calc}, at which the macromolecular coils occupy the entire volume of the solution, and the experimentally determined critical concentration, c^{**}, obtained for various polymer fractions in ethyl acetate

Polymer	M_w	c^*_{calc} (g per 100 ml)	c^{**} (g per 100 ml)
PS	24 800	3.31	0.36
PS	32 000	2.98	0.25
PS	52 800	2.00	0.16
PS	110 200	1.47	0.12
PMMA	7500	8.09	1.07
PMMA	45 000	2.21	0.19
PMMA	95 000	1.93	0.14
PMMA	465 000	0.88	0.045

gives, cannot be attributed to an incipient overlapping at the coils due to lack of free space in the solution. This decrease must be attributed to interactions between the chains that appear only during the flow of the latter.

The drag reduction phenomenon observed in flowing polymer solutions has already been attributed to interactions between macromolecular chains, even in extremely dilute solutions, and these interactions are related to flow improvement[16]. Using a Brownian dynamics computer simulation technique it has been demonstrated that these interactions become more significant when the flow is increased[17]. This result is in accordance with our observations, i.e. an increase in the value of the crossover point in the plot of η_i/c *versus* c (see *Figures 1–3*) with increasing shear rate.

CONCLUSIONS

In conclusion, the observed critical concentration c^{**} is a concentration that depends on the hydrodynamic volume of the chains as the critical concentration c^*, but appears before entire occupation of the solution volume by the macromolecular chains, and only when this solution flows. In contrast, with the static measurements we do not observe this phenomenon. As we have already pointed out, the appearance of c^{**} under dynamic conditions must be attributed to the collisions between the chains, or to a peripheral entanglement that leads to the formation of polymolecular clusters. As a result of these collisions, a decrease in the hydrodynamic volume of the coils must be expected due to the difficult interpenetration between the coils. This difficulty in interpenetration is more accentuated in the case of a mixture of two different polymers, where the crossover phenomenon at c^{**} is more pronounced[1–3]. This 'incompatibility' between macromolecular chains, even of the same chemical nature, is also observed when we measure the intrinsic viscosity of a polymer (guest polymer) in a solvent in which the same polymer exists at a constant concentration (host polymer), and the total concentration is below the critical concentration c^{**}[8].

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