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Influence of the shear rate, of the molecular architecture and of the molecular mass on the critical overlapping concentration c^*

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The critical overlapping concentration c^* has been studied in the dynamic state (by viscometry) and in the static state (by light scattering). An increase of the shear rate of the solution provokes an increase of c^* in the case of linear polymers. In the case of a highly branched polymer the shear rate has no influence on its critical concentration. The scaling law between c^* and the molecular mass for a given polymer–solvent system presents two different exponents, depending on the molecular mass region of the polymer. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: overlapping concentration; viscometry; shear rate)

INTRODUCTION

Experimental and theoretical studies concerning the critical overlapping concentration c^* observed by Simha and Zakin[1] and made concrete by de Gennes[2], and separating the dilute from the semi-dilute solutions have been reported in the literature[3–6]. In all these studies the concentration c^* is related to parameters expressing the dimensions of the chains of a polymer; the viscosity and the molecular mass.

In a recent article, the difference between the dynamic and static behaviour of dilute solutions of polymers has been presented[7]. The concentration c^* was found to be higher if determined by viscometry (dynamic state), compared with the value obtained using light scattering (static state), for a given polymer–solvent system.

In this article we study experimentally the dependence of c^* on other parameters that affect the dimensions of a polymer. These parameters are the solution shear rate and the molecular architecture of the polymer. We find that c^* of linear polymers decreases with decreasing shear rate and tends to a limiting value which is obtained in the static state by light scattering. Using a highly branched polymer we do not observe this variation of c^* with shear rate. We have also found that for a polymer–solvent system we have two laws relating c^* to the molecular mass of the polymer if the measurements are conducted in the low and medium molecular mass region or in the high molecular mass region.

EXPERIMENTAL PART

The polystyrene (PS) samples used in this work were prepared using the anionic method and present a very low polydispersity.

The star-shaped PS was also prepared anionically using the "living" PS to initiate the polymerization of the divinylbenzene that forms the core of the star polymer[8] (arm-first method).

The viscometric measurements were conducted using Ubelhode-type viscometers of Schott-Geräte and a Schott-Geräte (AVS) automated viscosity measuring system. With these types of viscometer we have the possibility of changing the capillary diameter, and by having the same geometry we can increase the shear rate by decreasing the efflux time of the solvent using viscometers with larger diameters. The temperature was controlled to within ±0.02°C. The inaccuracies in the flow times were considered negligible, with very good reproducibility being achieved. In order to eliminate any errors that could have originated from concentration inaccuracies, many measurements were performed more than once.

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

RESULTS AND DISCUSSION

Influence of the shear rate

As we have already published[7], the value of the critical overlapping concentration c^* determined by viscometry (dynamic state) is higher than the value obtained for this concentration and for the same fraction of a given polymer–solvent system determined by light scattering (static state). We have now undertaken a systematic study of the variation of c^* as a function of the shear rate of the solution. In *Figure 1* we present the variation of the reduced viscosity as a function of the concentration for the system PS ($M_w = 1.4 \times 10^6$)–ethyl acetate at 25°C. The different curves are obtained using viscometers with different capillary sizes. The efflux time of the solvent, for each experiment, is indicated in this figure. It is evident that the decrease of the efflux time corresponds to an increase of the shear rate of the solution. From the curves of *Figure 1* we can see that the critical overlapping concentration c^* increases with increasing shear rate. Similar results have been obtained with other polymer–solvent systems. The value of the intrinsic viscosity of this PS sample differs according to the capillary size used. This happens because we have not

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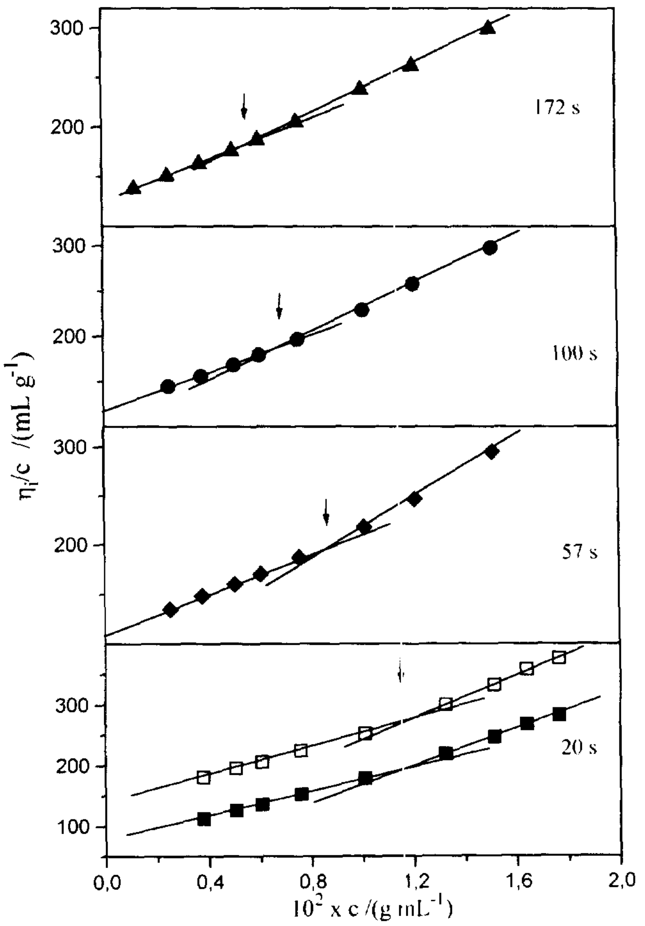

Figure 1 Plot of the reduced viscosity η_i/c *versus* the concentration c for the system PS ($M_w = 1.4 \times 10^6$)–ethyl acetate, at 25°C, with four different capillary size viscometers. The efflux time of the solvent for each viscometer is indicated. For the viscometer with the lower efflux time the curve with open rectangles is derived after kinetic energy corrections

made any kinetic energy corrections except for the viscometer presenting the highest shear rate. Nevertheless, this correction does not alter the value of the concentration c^*. Let us indicate here that the determination of c^* by viscometry can be done using the plot of $\log(\eta_i/c)$ *versus* $\log c$. This plot gives a more accentuated crossover phenomenon, but the precision of our measurements allows an accurate determination of c^* without logarithmic representation (*Figure 1*). Nevertheless, we give an example of this logarithmic representation in *Figure 2* in which the viscometric results are the same as in *Figure 1* with an efflux time equal to 172 s. The value of c^* determined is now equal to 0.55×10^{-2} g ml^{-1}, whereas from *Figure 1* we obtain $c^* = 0.53 \times 10^{-2}$ g ml^{-1}.

In *Figure 3* we present the variation of the overlapping concentration as a function of the efflux time of the solvent, obtained with three different polystyrene samples in solution in ethyl acetate. An important increase of this concentration, viscometrically determined, c_v^*, is observed when the efflux time decreases or the shear rate increases. The variation of c_v^* with the shear rate is more important in the case of high molecular mass fraction of PS. When the efflux time becomes very high, or when we have a very low shear rate, c_v^* tends to a constant value. This asymptotic value, as we can see in *Figure 3*, is about the same for the three fractions of PS as with the value of the overlapping concentration obtained by light scattering, c_s^*. The determination of the overlapping concentration in the static state has been published elsewhere[7].

The increase of c_v^* with the shear rate must be attributed to the deformation of the chains provoked by the flow of the solution[9–11]. An elongation of the chains must provoke a difficulty on their interpenetration expressed by an increase of c_v^*. Onuki[12] predicts the increase of c^* in the dynamic state compared with the value obtained in the static state showing theoretically that in the shear regime the volume of a polymer chain is reduced. A resistance to the interpenetration of the coils, and, consequently, an increase of the critical concentration c^*, has been observed in the case of a

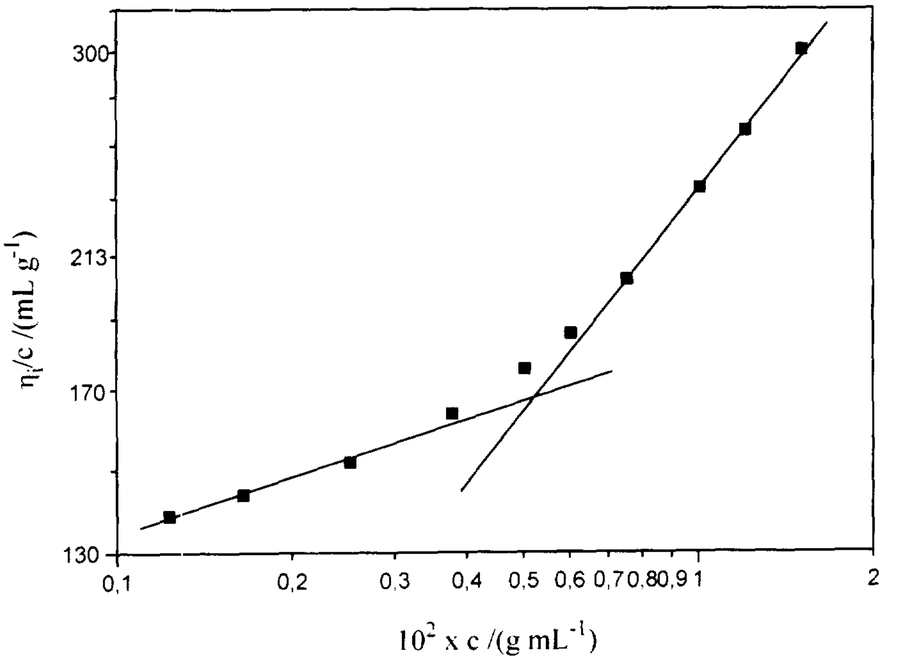

Figure 2 Logarithmic plot of the reduced viscosity η_i/c *versus* the concentration c for the system PS ($M_w = 1.4 \times 10^6$)–ethyl acetate, at 25°C. The efflux time of the solvent is equal to 172 s

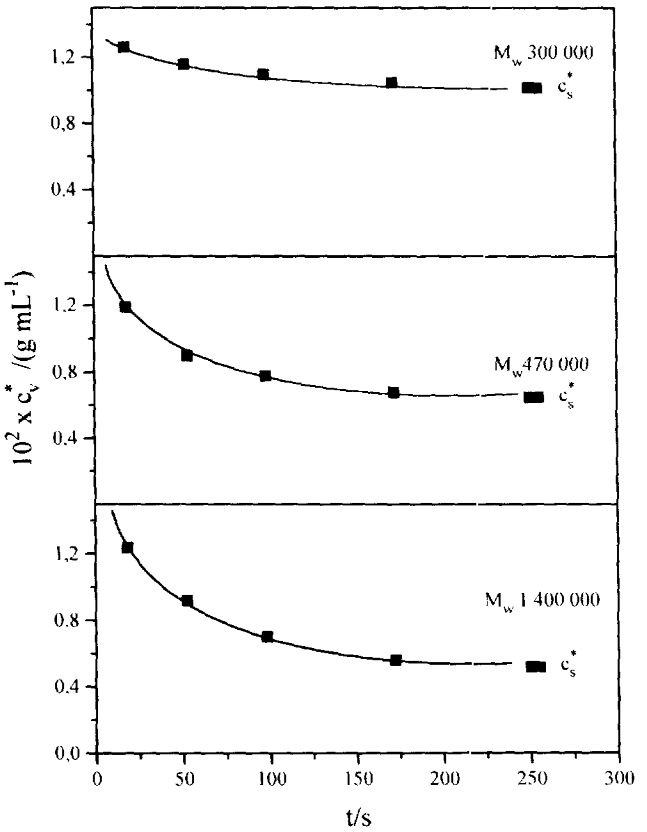

Figure 3 Plot of the dynamically (viscometry) determined critical concentration, c_v^* *versus* the efflux time of the solvent (ethyl acetate, 25°C) for three PS samples. The points marked as c_s^* indicate the statically (light scattering) determined critical concentration for each sample

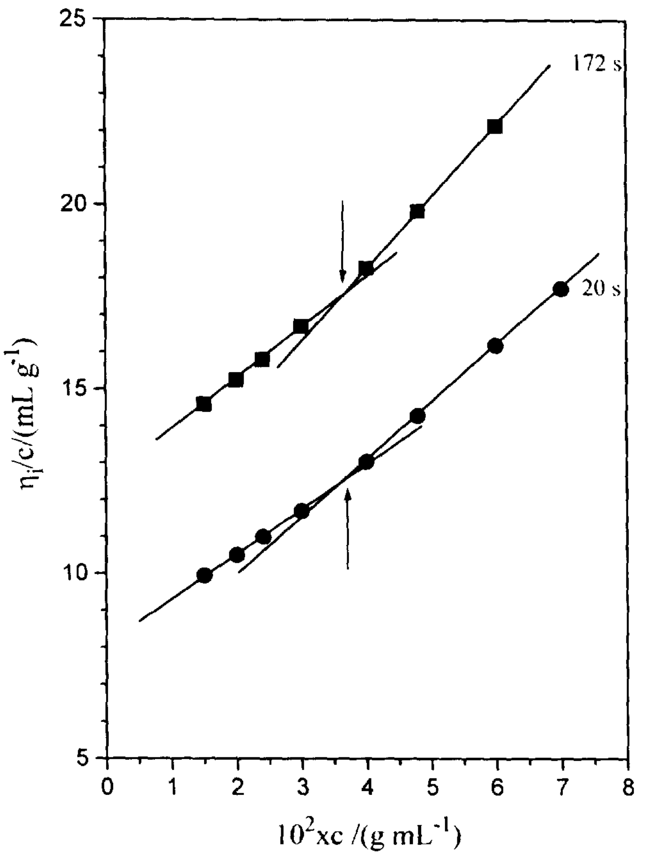

Figure 4 Plot of η_i/c *versus* c for a star-shaped PS (M_w = 270 000, number of branches 17) in ethyl acetate at 25°C. The two curves are obtained with two viscometers. The efflux time of the solvent for each viscometer is indicated

mixture of two different polymers[13]. This resistance to the interpenetration has been attributed to the incompatibility existing between different polymers.

Influence of the molecular architecture

It must be expected that a star-shaped polymer, especially when its segment density is very high, or when it has a large number of branches, will present a resistance to the deformation caused by the solution flow. Consequently, the influence of the shear rate on the critical concentration c_v^* of a branched polymer must be different from the influence of shear rate on the corresponding linear polymer.

We study here a star-shaped PS consisting of 17 branches and presenting a molecular mass equal to 270 000 (molecular mass of the each branch equal to 15 900). In *Figure 4* we present the variation of the reduced viscosity as a function of the concentration obtained with this star-shaped PS in solution in ethyl acetate using two different viscometers. Although the efflux time of the solvent is very different in the two experiments (t = 172 s curve A and t = 20 s curve B) we do not observe any variation of the critical concentration c_v^*. For comparison reasons viscometric measurements have been conducted with a linear PS (M_w = 25 000) sample in solution in ethyl acetate. In *Figure 5* we present the variation of the reduced viscosity as a function of the concentration using the same viscometers as for the branched PS. We can see that the increase of the shear rate provokes an increase of c_v^*, as was the case for the other linear PS samples (*Figures 1, and 3*). We must note here that the hydrodynamic volumes of the linear PS and the star-shaped PS are comparable (about the same values of intrinsic viscosities) although the molecular mass of the star-shaped PS is ten times bigger than the molecular mass of the linear PS. For the same reasons the critical overlapping concentrations of these very different molecular mass PS samples are comparable.

The critical overlapping concentration of the star-shaped PS has also been determined in the static state using light scattering. In *Figure 6* we present the variation of $K_c/\Delta I$ as a function of the concentration of this polymer in ethyl acetate. The crossover point is obtained in the same concentration as the crossover point obtained in the dynamic sate (*Figure 4*). The scattered intensities were measured at 90° because this sample does not present any noticeable angular dissymmetry. The same values obtained for c_v^* and c_s^* with the star-shaped PS clearly indicate that this polymer does not present any deformation under a shear regime.

The resistance to deformation of the star polymers, compared with the corresponding linear polymers, has been shown theoretically by de Gennes[14] when these polymers are sucked into a narrow pore by a solvent flux. Compared with the threshold value of the flux for linear polymers, the threshold value for the star-shaped polymers is multiplied by the factor $(f/2)^2$ where f is the number of branches of these polymers.

Influence of the molecular mass

The dependence of the critical overlapping concentration on the molecular mass of the polymer has been studied extensively[3–7]. We know that by plotting log c^* *versus*

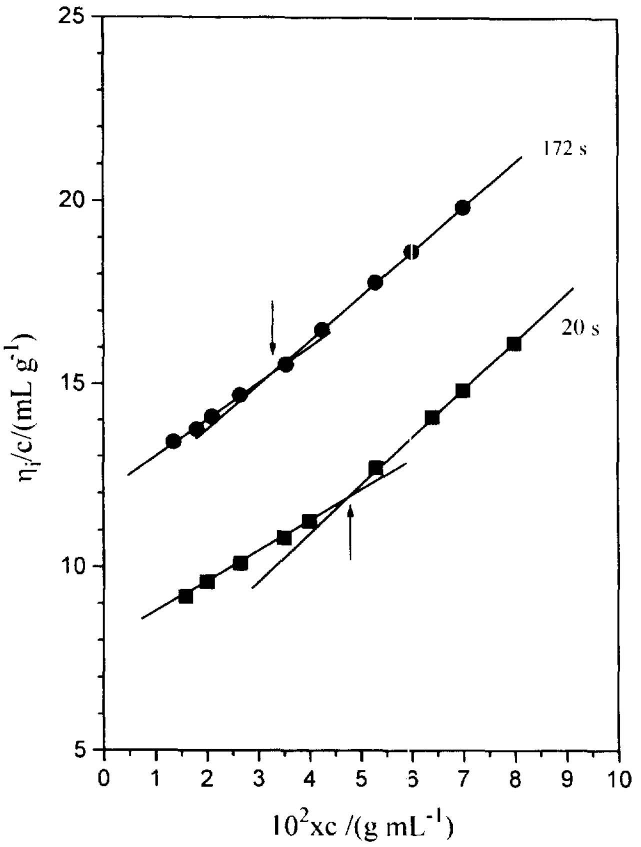

Figure 5 Plot of η_i/c *versus* c for a linear PS ($M_w = 25000$) in ethyl acetate at 25°C. The two curves are obtained with two different viscometers. The efflux time of the solvent for each viscometer is indicated

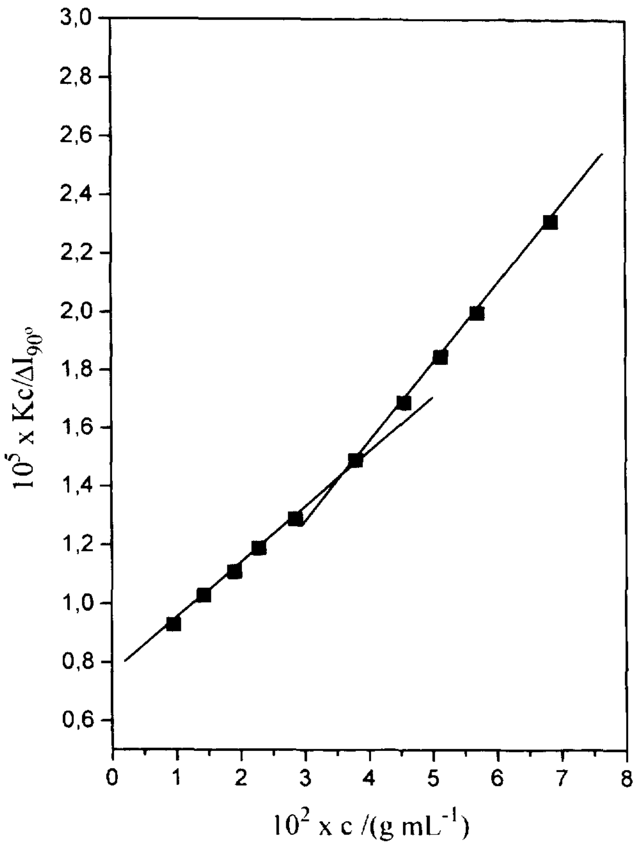

Figure 6 Plot of $Kc/\Delta I$ *versus* c for a star-shaped PS sample with 17 branches and $M_w = 270000$ in ethyl acetate at 25°C. The scattering intensities are measured at 90°

log M, for different fractions of a polymer dissolved in a given solvent, we obtain a straight line the slope of which is equal, but with an opposite sign, to the slope of the straight line obtained with the same polymer–solvent system, plotting log[η] *versus* log M (the Mark–Houwink–Sakurada (MHS) representation).

In *Figure 7* we present the variation of log c_v^* *versus* log M for the system PS–ethyl acetate in a rather broad region of molecular masses; the measurements have been conducted under the same shear rate. We realize that we can draw two straight lines with different slopes. In the region of low and medium molecular masses (region of effective excluded volume indices) we have

$$c* \propto M^{-0.57\pm0.01}$$

while the exponent in the MHS representation is equal to 0.58[15].

For molecular masses higher than 1×10^6, the chains have reached their non-free-draining limit and the excluded volume indices in the asymptotic limit are the same ($\nu_G = \nu_D = \nu = 0.588$)[16]. Since the experimental observations indicate that we have $c* \propto [\eta]^{-1}$ and having[17]

$$[\eta] \propto \frac{R_G^2 R_D}{M} \propto M^{2\nu_G + \nu_D - 1}$$

we could expect

$$c* \propto M^{1-2\nu_G-\nu_D} \propto M^{1-3\nu}$$

or

$$c* \propto M^{-0.764}$$

From *Figure 7* in the high molecular masses region we obtain

$$c* \propto M^{-0.76\pm0.02}$$

The crossover observed here in the variation of c_v^* as a function of the molecular mass shows how this concentration is related tightly to the hydrodynamic volume of the macromolecules. Indeed, a crossover is observed in the same region of molecular mass when we study the variation of other parameters expressing the hydrodynamic volume as a function of the molecular mass. In the MHS representation, for example, the crossover is observed with many polymer–solvent systems in the region of molecular mass that lies near 1×10^6. Moreover, using the viscometric results of Einaga *et al.*[18] for the system PS–benzene, we obtain an exponent in the MHS equation above the crossover point equal to 0.75, while below the crossover point the exponent for this system is equal to 0.725. In the same region of molecular mass a crossover is also obtained, theoretically[17] and experimentally[19], in the variation of the viscometric expansion factor of different polymers as a function of the number of blobs.

In conclusion, the experimental investigations presented in this work show that, besides the molecular mass and the viscosity of a polymer, the critical overlapping concentration also depends on the shear rate of the polymer solution in the case of linear polymers. In the case of a highly branched polymer the shear rate does not affect $c*$,

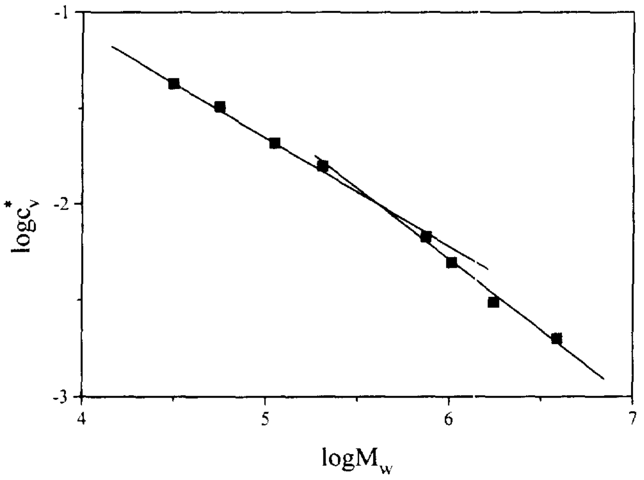

Figure 7 Plot of c^* *versus* the molecular mass for the system PS–ethyl acetate at 25°C

at least for the shear rates used in this work. Moreover, in this work we have shown that the exponent of the scaling law relating c^* to the molecular mass of the polymer varies with the molecular mass region; i.e. the non-free-draining limit region and the effective indices region.

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