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ORIGINAL CONTRIBUTION

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The influence of shear rate, temperature and chain conformation on the critical concentration c^{**}

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Abstract When viscometry is used, a crossover phenomenon is observed separating the dilute solutions into extremely dilute solutions and dilute solutions. The critical concentration c^{**}, determined from this crossover phenomenon, strongly depends on the shear rate in the solution. At very high values of shear rate the critical concentration c^{**} becomes very low and depends only on the contour length of the elongated chains of different polymers. An increase of the temperature induces an increase of c^{**} because the relaxation time of the chains decreases. If a polymer adopts a rodlike conformation (in a given solvent at a given temperature) the excluded volume of its chains increases and its critical concentration c^{**} decreases.

Key words Extremely dilute solutions – critical concentration c^{**} – chain entanglements – solution shear rate – viscometry

Introduction

In a series of articles [1–6], we have introduced a critical concentration, c^{**}, that separates the dilute solutions into two regimes: the extremely dilute solutions ($c < c^{**}$) and the merely dilute solutions ($c > c^{**}$). The concentration c^{**} has only been detected using dynamic methods (viscometry); in contrast we were not able to detect it through static measurements (light scattering) [7]. Compared to the overlapping concentration c^{*}, introduced by de Gennes [8], for the same polymer fraction dissolved in the same solvent, the concentration c^{**} is in general ten times lower. The appearance of c^{**} has been attributed to entanglements between chains which lead to the formation of polymolecular clusters thus favoring the flow of the solution. Indeed, above the concentration c^{**} the reduced viscosities of the polymer solutions are lower than the predicted ones from the measurements conducted below the concentration c^{**}.

Many other authors have also observed "interactions" between the macromolecular chains in the region of dilute solutions and even in the extremely dilute solution region. In this region the existence of contacts [9, 10] and entanglements [11] between chains has been investigated. The existence of contacts and entanglements between polymer coils has also been found by Brostow et al. [12, 13] using a Brownian dynamics computer simulation technique, even far below the critical overlapping concentration c^{*}. We also would like to point out that during the last years a great interest has been shown in these "interactions" between chains in the dilute solution region because they seem to be related to the so called drag reduction effect [12–14]. This interest in the behavior of polymers in the very dilute solution region motivated us to study the influence of the shear rate, the temperature and the polymer conformation on the crossover phenomena (c^{**}) observed in this concentration region.

Experimental part

The polystyrene (PS), the poly(ethylene oxide) (PEO) and the poly(tertio butyl methacrylate) (PtBuMA) and the poly(2-vinyl pyridine) (P2VP) samples used in this work have been prepared by us in the "Charles Sadron" Institute in Strasbourg by anionic polymerization at low temperature and their polydispersities never exceed 1.15.

Viscosity measurements were carried out in a Schott-Gerate (AVS) automated system with Ubbelohde-type viscometers, equipped with an automatic injection system (maximum error ±0.03%) for in situ dilutions. By changing the capillary size the efflux time is changed, and consequently the shear rate. The temperature was controlled to within ±0.02 °C. The errors that could have originated from concentration inaccuracies were checked by performing independent measurements and can be considered negligible. The capillary diameter of used viscometers are: 0.46, 0.53, 0.63 and 0.84 mm.

Results and discussion

Influence of the shear rate

The variation of the shear rate in the viscometric measurements was achieved in this work by changing the capillary diameter of the viscometer. In Fig. 1 we present the variation of the reduced viscosity as a function of the concentration obtained with a fraction of poly(ethylene oxide) (PEO) of molecular mass equal to 35 000 in water solution. Curve A is obtained with a viscometer which gives an efflux time for the solvent equal to 125 s while curve B is obtained with a viscometer having a capillary of larger diameter giving an efflux time for the solvent equal to 23 s. It is clear that the increase of the shear rate induces a decrease of the critical concentration c^{**} (crossover point in curve B). In Fig. 1 we can also observe that in the case of higher shear rate the crossover phenomenon is also more pronounced.

In Figs. 2–4 we present the variation of c^{**} as a function of the efflux time of the solvent obtained with three polymer-solvent systems (PS-chloroform, Fig. 2; PEO-H_2O, Fig. 3 and poly(tertiobutylmethacrylate-THF Fig. 4). The measurements with each polymer–solvent systems have been conducted at different temperatures as it is indicated in these figures. The results presented in Figs. 2–4 show a very important dependence of the critical concentration c^{**} from the shear rate.

It is well known that if the solution flows we have a modification of the shape of the macromolecular chain and it is accepted that an increase of the shear rate induces important elongation of the polymer coil [15–17]. Elongated chains, during motion, exclude a bigger volume compared to chains presenting coil conformation and this must lead to an increase of the number of contacts per chain. Moreover Brownian simulation studies [12, 13] show that an increase in entanglements with shear rate is due to the dynamic orientation of macromolecules. On the contrary, when the solution is found under a very low shear rate the number of contacts and entanglements should be lower and consequently we need a higher quantity of polymer in order to obtain the critical concentration c^{**}.

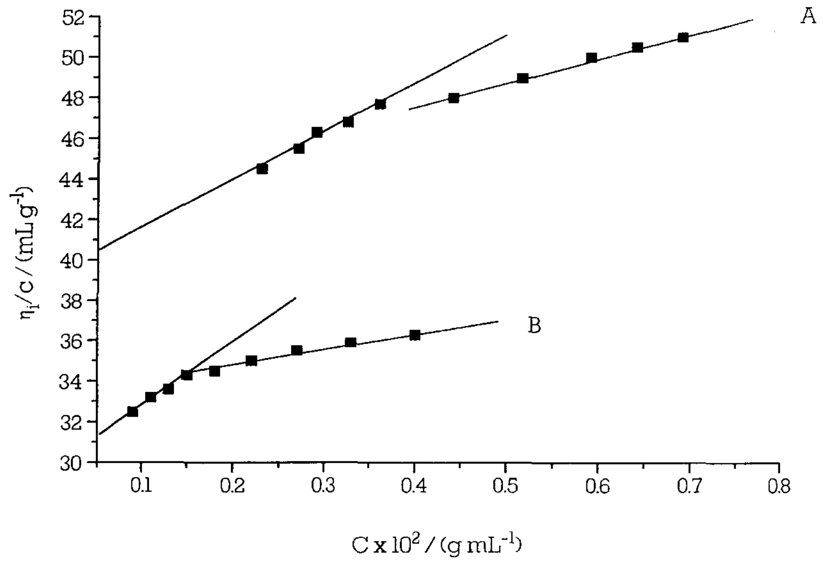


Fig. 1 Plot of η_i/c vs. c for PEO fraction (M_w : 35 000) in water: curve A, low shear rate; curve B, high shear rate

Fig. 2 Plot of c^{**} vs. the efflux time of solvent t, for the system PS (M_w: 52 000)-ethyl acetate, in different temperatures

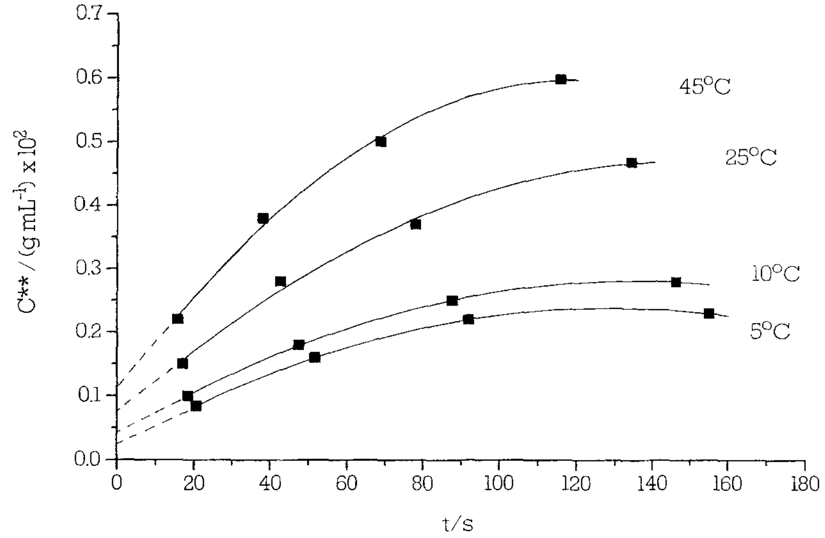
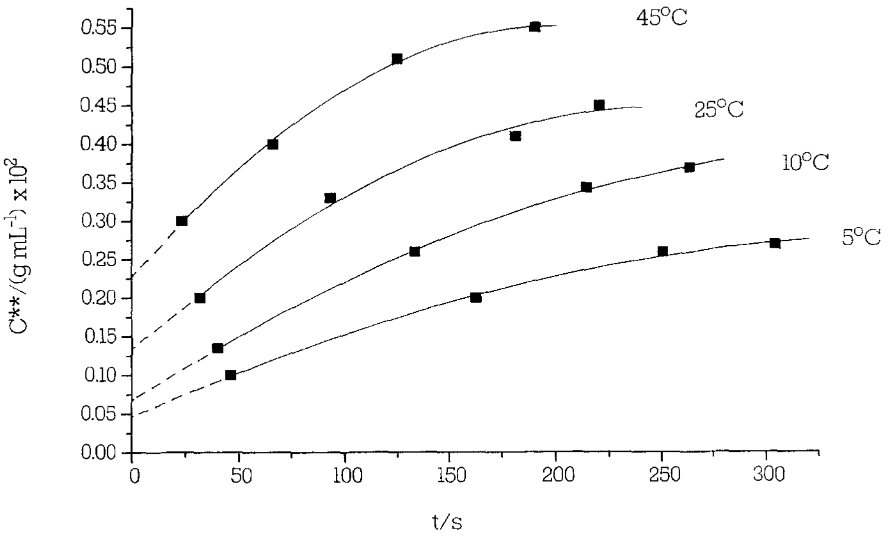


Fig. 3 Plot of c^{**} vs. the efflux time of solvent t, for the system PEO (M_w: 10 000)-water, in different temperatures



Brostow and Drewniak [18] show theoretically that an increase of the shear rate provokes an increase of the number of the entanglements per polymer chain. This is also in accordance with our results which show that an increase of the shear rate provokes a decrease of the critical concentration c^{**}. Nevertheless we must note that Brostow and Drewniak show that although the increase of the shear rate in the relatively low region values enhance interchain entanglements, very high values of shear rates provokes a small decrease of these interactions. Moreover Vrahopoulou and McHugh [19] suggest that above a critical shear rate we have a distraction of molecular entanglements. We believe that with the viscometers we use, we cannot achieve these high values of the shear rate. In the future we plan to study the critical concentration c^{**} applying higher values of shear rates, using a rotating viscometer. In this region of very high shear rates the curves of Figs. 2–4 are presented by dashed lines and the extrapolation to $t = 0$ may be done utilizing the polynomial character of the obtained curves.

As in the case of the overlapping concentration c^{*} [20, 21] we present the variation of c^{**} as a function of the molecular mass, M, of the fractions of a given polymer–solvent system [5, 6] and we have obtained straight lines, the slopes of which are equal to the inverse of the exponent of the Mark–Houwink–Sakurada equation of the system. Presenting now in the variation of log $c^{**}_{t=15}$ (critical concentration obtained with efflux time equal to 15 s) as

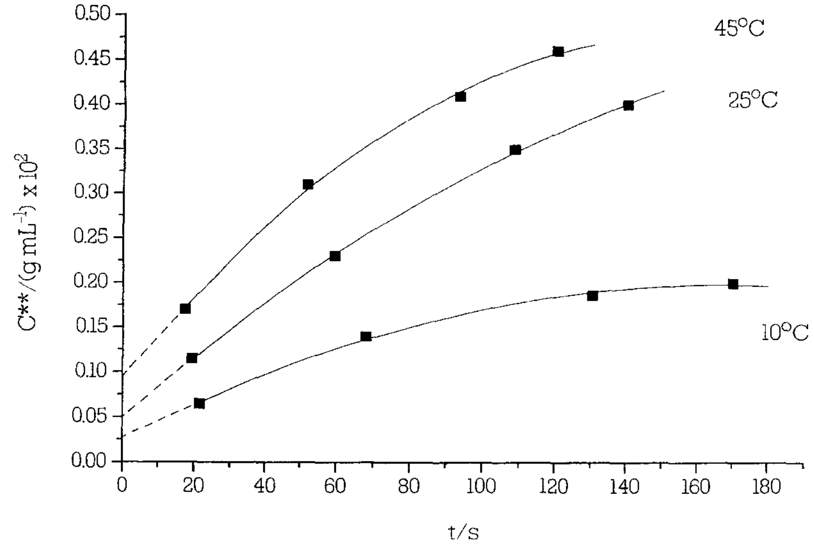


Fig. 4 Plot of c^{**} vs. the efflux time of solvent t, for the system PtBuMA (M_w: 93 000)-THF, in different temperatures

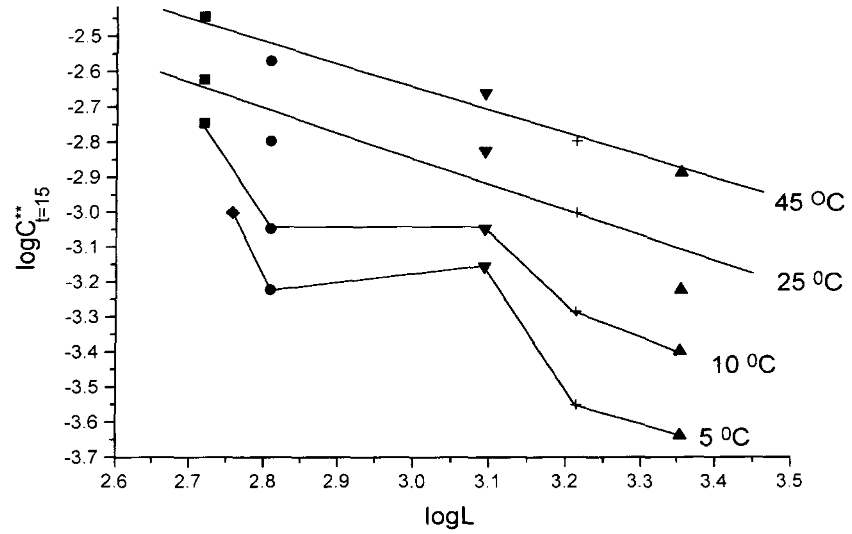


Fig. 5 Plot of $\log c^{**}_{t=15}$ vs. $\log L$ at four different temperatures (L: contour length for the fractions of three different polymers). ■ PS: 22 000; ◆ PS: 24 000; ▼ PS: 52 000; ● PEO: 10 000; ▲ PEO: 35 000; + PtBuMA: 93 000

a function of log M for three different polymers, at different temperatures, we obtain a variation of $c^{**}_{t=15}$ with the molecular mass of these polymers that is not monotonic. This is easily explained because for a same molecular mass the chains of these polymers do not present the same contour length, L, and consequently their hydrodynamic volume is not the same. Knowing the mass per contour length, M_L, of these polymers we have calculated their contour length. The mass per contour length is calculated according to the method proposed by Flory [22] [M_L (daltons A^{-1}): PS = 41.6; PEO = 15.5; PtBuMA = 56.8]. In Fig. 5 we now present the variation of $\log c^{**}_{t=15}$ as a function of $\log L$. As we can see in this figure, the critical concentration presents a monotonic variation with the contour length of the three polymers when the measurements are contacted at 45 °C. A less monotonic variation is obtained at 25 °C while at 10 °C and 5 °C the variation is not monotonic at all. This result can be understood if we accept that the entanglements between the chains depend on their hydrodynamic volume expressed now by their contour length, L. Under a rather high shear rate and a rather high temperature, the chains can unwind from a coil structure to an extended conformation [23] and consequently the contour length of the chains of different polymers, and not their molecular mass, must govern the concentration in which the entanglements appear. In the region of lower temperatures the chains must not be enough unwinded, even in this rather elevated shear rate and we do not observe a monotonic variation of the critical concentration with the contour length of the three polymers.

Influence of the temperature

If we accept that the appearance of the critical concentration c^{**} is due to the existence of entanglements between different chains (nonpermanent topological bonds) we must also accept that these entanglements are of dynamic nature and consequently they must depend on the chain relaxation time. An increase of the temperature decreases the relaxation time and this is unfavorable for the entanglements.

The decrease of the relaxation time with increasing temperature explains the increase of critical concentration c^{**} with increasing temperature as it is presented in Figs. 2–5. This increase of the critical concentration is more important if we take into account that the increase of the temperature provokes a decrease of the efflux time of the solvent and consequently we have an increase of the shear rate which provokes a decrease of c^{**}. Nevertheless the measurements at 40 °C have also been conducted (open circles) with a different viscometer of which the solvent efflux time is about equal with the efflux time of the other viscometer at 10 °C. Now having the same efflux time c^{**} is shifted from $0.1 \times 10^{-2}\,\mathrm{g\,mL^{-1}}$ at 10 °C to $0.18 \times 10^{-2}\,\mathrm{g\,mL^{-1}}$ at 40 °C.

The influence of the temperature on the critical concentration c^{**} is presented in a better way in Fig. 6. The results are coming from Fig. 2 and concerns the system PS (52000-chloroform). Each curve gives for a given shear rate (efflux time of the solvent, *s*) the variation of c^{**} with temperature. The influence of the temperature is more pronounced when the solution is found under low shear (high efflux time).

Influence of the polymer conformation

Having now shown that the elongation of the polymer chain plays an important role in the critical concentration c^{**} we can better understand a result already published [5]. In this article the relation between the critical concentration c^{**} and the intrinsic viscosity for the poly(2-vinyl pyridine) (P2VP) was different if the results were obtained at 25 °C or 45 °C. At 25 °C the concentration c^{**} of the polymer in solution in benzene, is lower than the critical concentration obtained at 45 °C for the same value of the intrinsic viscosity. In Fig. 7a are presented the results already published [5] concerning the variation of c^{**} obtained with the P2VP in benzene solution at 25 °C and 45 °C. Points 1 and 2 are obtained now with another fraction of P2VP. The increase of the temperature cannot explain the observed important difference between c^{**} at 25 °C and 45 °C for the same value of the intrinsic viscosity especially if we take into account that the increase of the temperature provokes a decrease of the shear rate which leads to an increase of the critical concentration c^{**}.

A possible explanation can be based on the different conformation presented by the P2VP at 25 °C and 45 °C. We have shown that this polymer at 25 °C presents a rigid conformation (high value of the persistence length) while at 45 °C the same chain presents a very flexible conformation [24, 25] (conformational transition). Consequently, it

Fig. 6 Plot of c^{**} vs. temperature for the system PS (M_w: 52000)-ethyl acetate in different efflux time of the solvent (the results are obtained from Fig. 2)

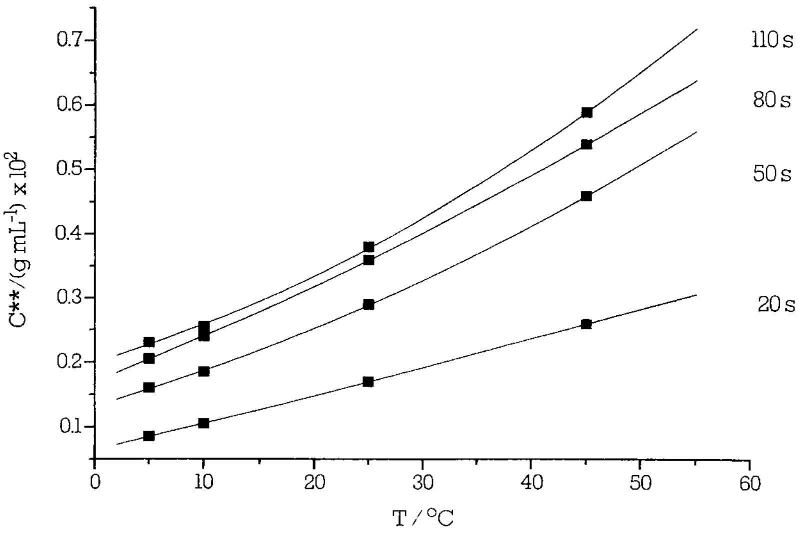
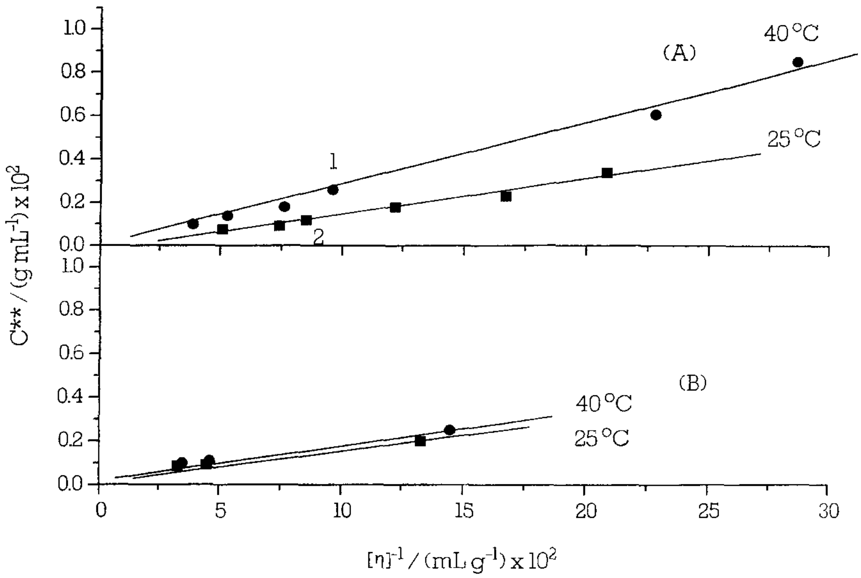


Fig. 7 Plot of c^{**} vs. the inverse of the intrinsic viscosity for P2VP fractions at two different temperatures: (A) in benzene (points 1 and 2 see text), (B) in chloroform



is evident that at 25 °C the chain of P2VP is more elongated than at 45 °C. We can also say that at 25 °C the solution of the P2VP behaves as if it was under a high shear rate leading to an elongation of the chain, while at 45 °C the solution behaves as if it was under a low shear rate and the chain is not elongated. This assumption is verified by the results of Fig. 7a. We have also shown [24] that in chloroform solution the P2VP cannot present a rigid conformation (persistence length corresponding to a flexible vinyl polymer in all the temperature region investigated) and in Fig. 7b we present the relation between c^{**} and $[\eta]^{-1}$ obtained with fractions of this polymer in $CHCl_3$ at 25 °C and 45 °C. On the contrary to what we have obtained in benzene, now we have not a significant difference in the relation between c^{**} and $[\eta]^{-1}$ at the two temperatures.

Conclusion

The observed critical concentration c^{**} in the present and our previous works has been attributed to the appearance of entanglements between chains. These entanglements favor the flow of the solution and it is for this reason that the values of the reduced viscosity above c^{**} are lower than the values predicted by the extrapolation of the straight line obtained with the reduced viscosity values below c^{**} (Fig. 1). The relation between c^{**} and the solution flow could also explain the fact that this concentration is not observed by light scattering [7] (static state).

The results presented in this work corroborate the preceding explanation on the nature of c^{**}. The interchain entanglements should be favored if the chains exclude a greater volume. Our results are in accordance with this assumption because the elongated chains due to the increased shear rate or due to their rodlike conformation present a lower value for the critical concentration c^{**}. On the contrary, an increase of the temperature decreases the relaxation time of the chains and this should shift the critical concentration c^{**} to higher values. Indeed our results are also in accordance with this assumption.

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