Viscometric study of aggregation phenomena in polymer dilute solutions and determination of the critical concentration c^{**}†

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(Received 17 October 1988; accepted 20 December 1988)

A crossover is observed in the variation of the reduced viscosity, η_{sp}/c, as a function of the concentration, c, for the systems poly(methyl methyacrylate)/nitromethane and poly(vinyl-2 pyridine)/benzene. This crossover is correlated with the critical concentration of the polymer c^{**} in which the macromolecular coils start their contacts. The critical concentration c^{**} is related with the molecular weight and the intrinsic viscosity of the polymer through the scaling laws: $c^{**} \propto M^{-\alpha}$ and $c^{**} \propto [\eta]^{-1}$.

(Keywords: critical concentration; incipient overlap; aggregation; scaling laws)

INTRODUCTION

In recent years experimental and theoretical works have established the existence of three concentration regimes of macromolecular solutions[1–3] namely dilute, semidilute and concentrated. The transition, in general, from one region to another does not occur abruptly. Instead it occurs rather gradually and it is not always possible to establish a well defined transition concentration separating the different concentration regimes.

In dilute solutions the macromolecules behave as individual units and a characteristic length scale is the radius of gyration of the molecule. At a certain concentration, c^*, the domains of the polymer molecule begin to overlap and the molecules lose their individuality (formation of infinitely large networks of overlapping molecules).

We have suggested[4] the existence of a new critical concentration, c^{**}, which separates the dilute solution in extremely dilute solutions and dilute solutions. At the concentration c^{**} ($c^{**} < c^*$) the macromolecular chains start contacts and occupy the entire volume of the solution. In other words, c^{**} corresponds to the incipient overlap of the macromolecular coils. However, in the region between c^{**} and c^*, the macromolecular chains conserve their individuality.

The critical concentration c^{**} has been studied using ternary systems polymer A/polymer B/solvent[4–6]. When a macromolecular chain of polymer A contacts a macromolecular chain of polymer B, in the concentration c^{**}, a decrease of their hydrodynamic volumes occurs because incompatibility acts strongly against overlapping. This decrease of the hydrodynamic volume of the macromolecules yields a change in the slope of the curve relating the variation of the reduced viscosity, η_{sp}/c, with the concentration, c, of the polymers. This critical concentration was related to the molecular weight and the intrinsic viscosity of the two polymers[4–6].

In this work we determine by viscometry the critical concentration c^{**} using binary polymer/solvent systems, in which the polymer forms aggregates. The viscometric study of the binary systems was used until now only for the determination of the critical concentration c^* (refs. 5, 7). Also in this work we correlate the critical concentration c^{**} with the molecular weight and the intrinsic viscosity of the polymer for a given polymer/solvent system.

EXPERIMENTAL

The poly(methyl methacrylate) (PMMA) and poly(vinyl-2 pyridine) (PV2P) samples were prepared by anionic polymerization. The ratio of the weight-average molecular weight to the number-average molecular weight, M_w/M_n, of the samples never exceeds the value of 1.2. The samples of PMMA and PV2P are not isotactic because of their preparation by anionic polymerization. A very highly branched PV2P sample ($M_w = 575000$) is also used in this work. Its preparation has been described elsewhere[8].

The viscosity measurements were conducted with an automatic viscometer (AVS, Schott-Gerate). The reproducibility was of the order of ±1%.

RESULTS

It is well known that the atactic poly(methyl methacrylate) (PMMA) presents the phenomenon of aggregation via intermolecular interactions and that this phenomenon is influenced by the molecular weight of the polymer sample[9–11]. In this work we use the nitromethane as a solvent for PMMA because such a marginal solvent of the polymer favours the interactions between polar groups of the polymer which will lead to the formation of polymolecular micelles.

In *Figure 1* we display the variation of reduced viscosity, η_{sp}/c, as a function of concentration, c, of two samples of PMMA in nitromethane solution at two

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† Dedicated to Dr P. Rempp on his 60th birthday

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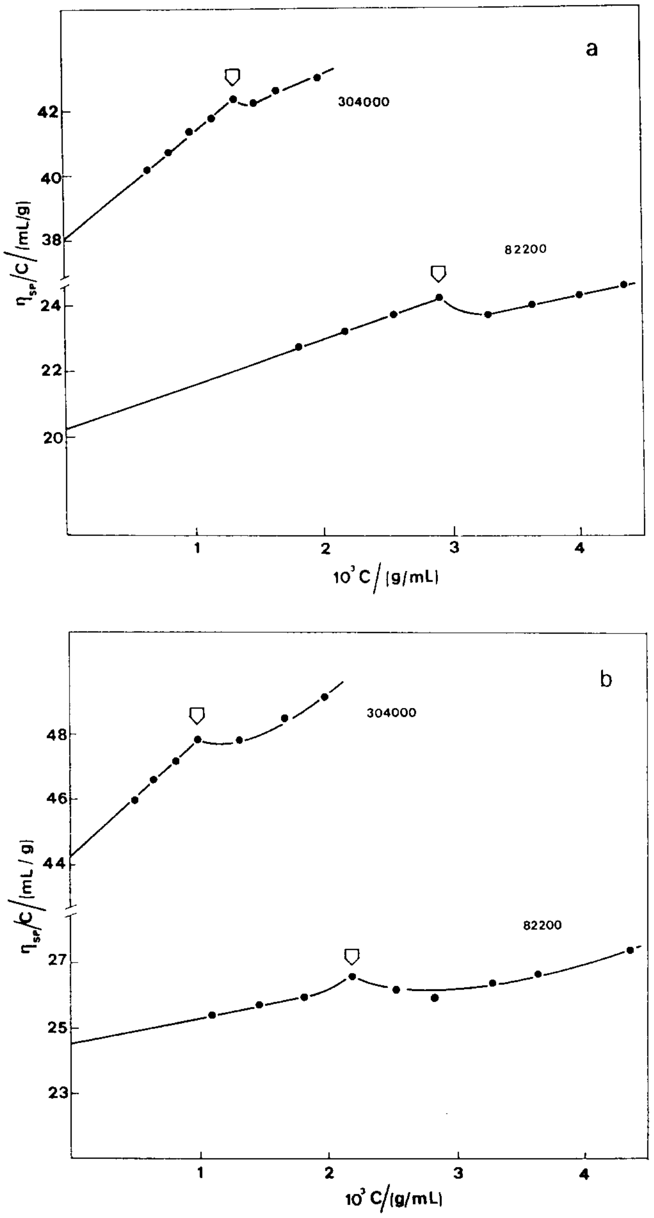

Figure 1 (a) Variations of reduced viscosity η_{sp}/c as a function of concentration c of the two PMMA samples in nitromethane solution at 10°C. (b) As in (a) but at 19°C

different temperatures. We observe a sharp crossover which permits the determination of a critical concentration, c^{**}, with a good accuracy. It is evident that this crossover appears in a lower concentration in the case of the polymer sample of high molecular weight because in a given concentration this sample presents a higher hydrodynamic volume than the low molecular weight sample. It is also evident that the same sample of PMMA presents a lower value of c^{**} in the higher temperature because at this temperature the solvent becomes a better solvent for the polymer and the macromolecular chains present a higher hydrodynamic volume.

The second polymer/solvent system studied in this work is the system poly(vinyl-2 pyridine) (PV2P)/ benzene. The PV2P also exhibits the phenomenon of aggregation[12]. At room temperature benzene is a poor solvent of the polymer and this favours the formation of micelles. In a very good solvent of the polymer, as for example in chloroform, the PV2P does not exhibit the phenomenon of aggregation[12].

In *Figure 2* we present the variation of η_{sp}/c as a function of c for two fractions of PV2P in benzene solutions at two different temperatures. As in the case of PMMA, the high molecular weight PV2P exhibits a lower critical concentration c^{**} than the low molecular weight sample.

Calculation of the Huggins coefficient, k', for the different systems below c^{**} (*Figures 1* and *2*) gives very high values, of the order of 1.5. In some cases k' reaches the value of 20. This result is observed in systems which form aggregates.

The critical concentrations c^{**} determined for the two polymers are of the order of the critical concentrations already determined using a mixture of two polymers in one solvent[4–6]. These concentrations are much lower than the concentration c^{*} (refs. 5, 7).

For the same sample of PV2P, the increase of the temperature provokes an increase in the value of c^{**} in contrast to that which we observed in the case of PMMA. This result can be explained if we take into account the

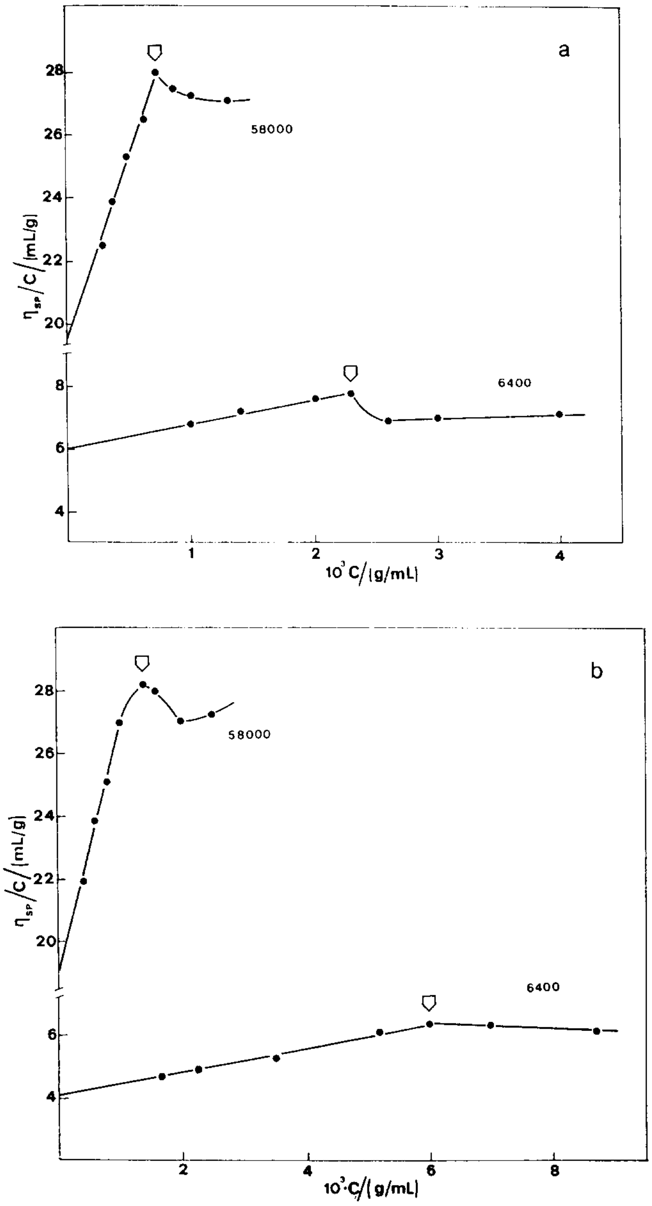

Figure 2 (a) Variation of reduced viscosity η_{sp}/c as a function of concentration c of the two PV2P samples in benzene solution at 25°C. (b) As in (a) but at 40°C

transition exhibited by the PV2P in solution in benzene at 25°C[12,13]. Indeed, at this temperature the PV2P presents an abrupt decrease of its unperturbed dimensions which is expressed by a decrease of its intrinsic viscosity especially for the low molecular weight samples.

Using the values of intrinsic viscosity, $[\eta]$, obtained with the samples of PMMA in nitromethane (10°C and 19°C) and with the samples of PV2P in benzene (25°C and 40°C) we display the variation of log $[\eta]$ *versus* log M in *Figures 3* and *4*. From this representation we derive the following Mark–Houwink–Sakurada (MHS) equations:

$$[\eta]=4.2\times 10^{-2}M^{0.54} \tag{1}$$

for the PMMA/nitromethane system at 10°C

$$[\eta]=4.5\times 10^{-2}M^{0.56} \tag{2}$$

for the PMMA/nitromethane system at 19°C

$$[\eta]=6.2\times 10^{-2}M^{0.53} \tag{3}$$

for the PV2P/benzene system at 25°C and

$$[\eta]=2.1\times 10^{-2}M^{0.62} \tag{4}$$

for the PV2P/benzene system at 40°C.

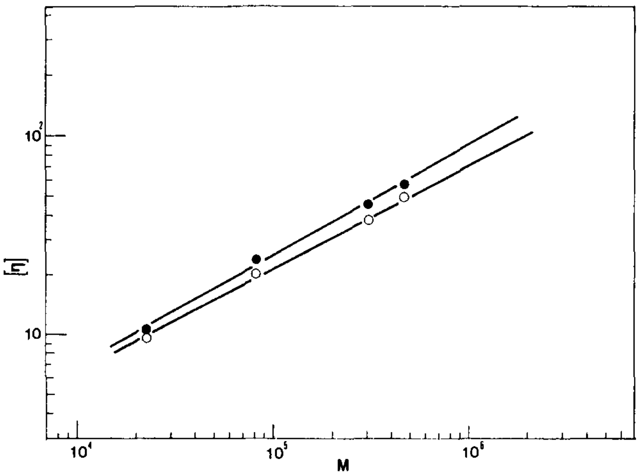

Figure 3 Log $[\eta]$ *versus* log M of the system PMMA/nitromethane (○, 10°C; ●, 19°C)

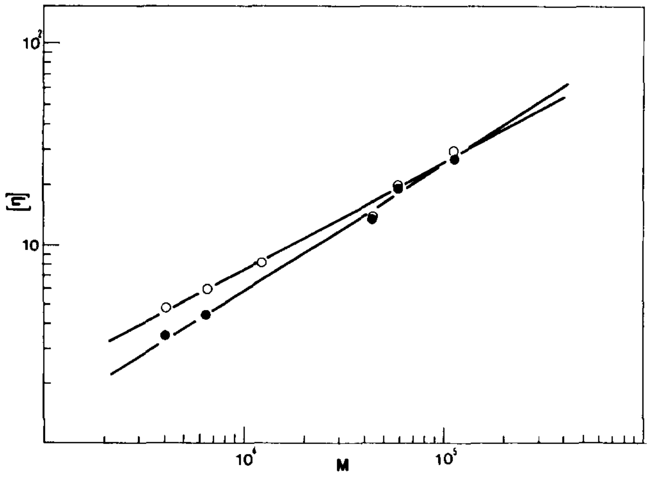

Figure 4 Log $[\eta]$ *versus* log M of the system PV2P/benzene (○, 25°C; ●, 40°C)

DISCUSSION

As shown in *Figures 1* and *2* the critical concentration c^{**} is determined with good accuracy. This concentration is much lower than the critical concentration c^* (refs. 5, 7, 14) and it is comparable to the critical concentration c^{**} determined in the case of ternary systems[4–6]. Above the critical concentration c^{**}, the curve of η_{sp}/c *versus* c exhibits a decrease in slope. In some cases this slope even becomes negative. This decrease of the reduced viscosity above c^{**} must be attributed to the formation of polymolecular micelles or aggregates. In these aggregates the increase of the hydrodynamic volume is smaller than the increase of their molecular mass. According to the relation $\eta_{red}\propto V/M$, we have the observed decrease in reduced viscosity.

Let us first note that the relations which have been proposed[3,15–18] in order to correlate c^* with the molecular weight and the intrinsic viscosity of the polymer are:

$$c^*\propto M^{-\alpha} \tag{5}$$

and

$$c^*\propto[\eta]^{-1} \tag{6}$$

where α is the exponent of the M–H–S equation. Equations (5) and (6) have been experimentally verified[19,20].

We will now try to correlate c^{**} with M and $[\eta]$ of the polymer in the case of the binary systems which we studied in this work. We suppose that the critical concentration c^{**} is the concentration at which the volume of the macromolecular coils, which start their contacts, plus the volume between these coils, v^0, is equal to the entire volume, v^{**}, of the solution

$$v^{**}=n^{**}(4/3)\pi R^3+v^0 \tag{7}$$

where n^{**} is the number and R the radius of gyration of the coils.

If the molecular weight of the polymer is equal to M, the critical concentration will be given by the relation

$$c^{**}=(1/N_A)(n^{**}M/v^{**}) \tag{8}$$

From equation (7) we have $v^{**}\propto n^{**}R^3$ because we have,

$$v^{**}=n^{**}(4/3)\pi R^3+\text{constant} \tag{9}$$

and equation (8) becomes,

$$c^{**}\propto M/R^3 \tag{10}$$

Let us note here that the volume v_0 in equation (7) is considered to be independent of the size of the coils but must depend on their shape. In the case of spherical coils v_0 must represent its minimum value. Consequently, the constant in equation (9) is not the same for all the polymer–solvent systems.

In the asymptotic non-free draining limit, the intrinsic viscosity scales as

$$[\eta]\propto R^3/M$$

and from equation (10) we obtain:

$$c^{**}\propto[\eta]^{-1} \tag{11}$$

Assuming now that for a series of linear fractions of a polymer we have,

$$R^3\propto M^{3\nu} \tag{12}$$

where ν is the excluded volume index, we obtain from equation (10)

$$c^{**} \propto M^{-(3\nu-1)} \qquad (13)$$

and having,

$$[\eta] \propto M^{3\nu-1} \propto M^{\alpha} \qquad (14)$$

which is the M–H–S equation, we finally obtain:

$$c^{**} \propto M^{-\alpha} \qquad (15)$$

Equations (11) and (15) are the same relations as the relations obtained for the critical concentration c^* (equations 5 and 6).

In *Figure 5* we display the variation of log c^{**} as a function of log M for the system PMMA/nitromethane in two different temperatures (10°C and 19°C). We obtain two straight lines described by the relations:

$$c^{**} \propto M^{-0.58} \qquad 10°\mathrm{C}$$

and

$$c^{**} \propto M^{-0.60} \qquad 19°\mathrm{C}$$

This result verifies equation (15) because the absolute values of the exponent are about the same as in equations (1) and (2).

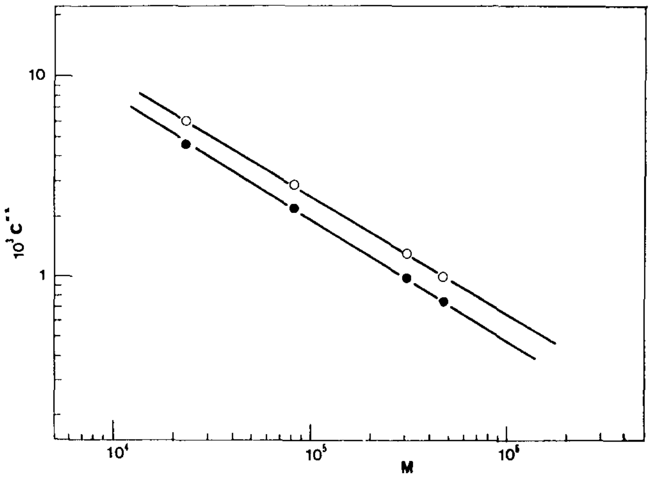

Figure 5 Variation of log c^{**} as a function of log M for the system PMMA/nitromethane (○, 10°C; ●, 19°C)

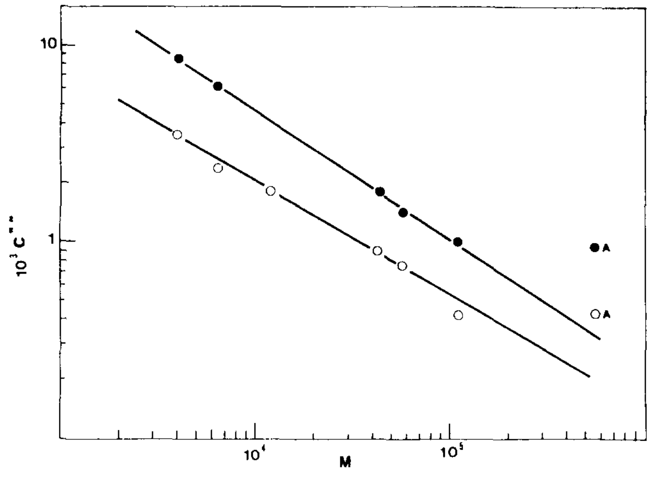

Figure 6 Variation of log c^{**} as a function of log M for the system PV2P/benzene (○, 25°C; ●, 40°C). Points labelled A correspond to the branched PV2P sample

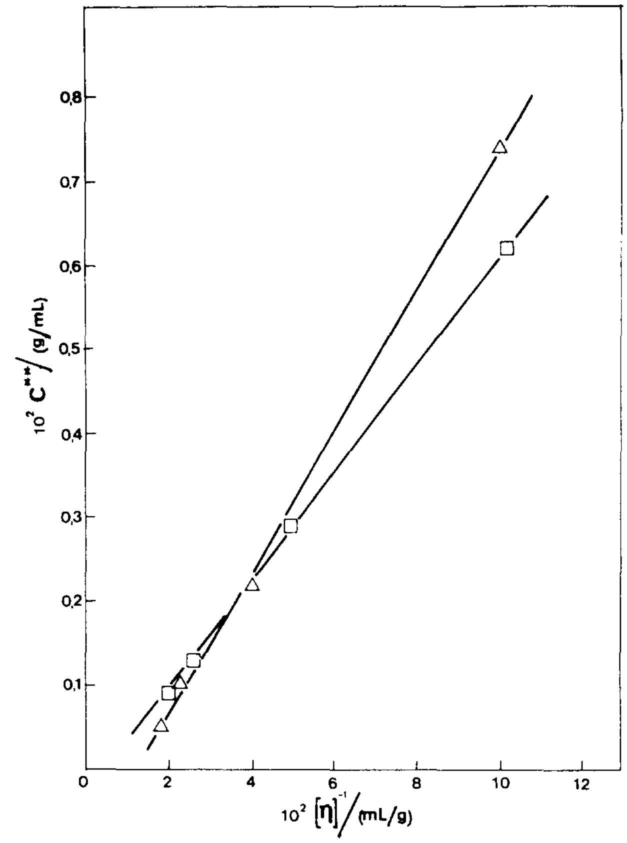

Figure 7 Variation of c^{**} as a function of $[\eta]^{-1}$ for the system PMMA/nitromethane (□, 10°C; △, 19°C)

The same procedure has been applied with the system PV2P/benzene. In *Figure 6* we display the variation of log c^{**} as a function of log M for this system in two different temperatures. We also obtain two straight lines which are described by the relations:

$$c^{**} \propto M^{-0.56} \qquad 25°\mathrm{C}$$

and

$$c^{**} \propto M^{-0.65} \qquad 40°\mathrm{C}$$

The exponents obtained have about the same absolute values as the values of the exponents of equations (3) and (4) and this is a verification of equation (15) also by this system.

The points labelled A in *Figure 6*, obtained with the branched sample of PV2P, lie away from the straight lines obtained with the linear fractions of PV2P. This is due to the fact that equation (12), from which equation (15) is derived, is valid only for a linear series of fractions.

Finally, we present in *Figures 7* and *8* the variation of c^{**} as a function of $[\eta]^{-1}$ for the two systems studied in this work at two different temperatures. We always obtain straight lines and these results verify equation (11).

The points labelled A in *Figure 8*, obtained with the branched PV2P sample lie now on the straight lines obtained with the linear PV2P samples. This is due to the fact that the quantity $[\eta]^{-1}$ expresses the segment density of the polymer sample, no matter what the architecture of the polymer sample.

If now we calculate the quantity $[\eta]c^{**}$ from *Figures 7* and *8* we obtain different values for the systems PMMA/nitromethane and PV2P/benzene. This result implies that c^{**} is not a unique function of the intrinsic viscosity, as expected from equation (11). Nevertheless

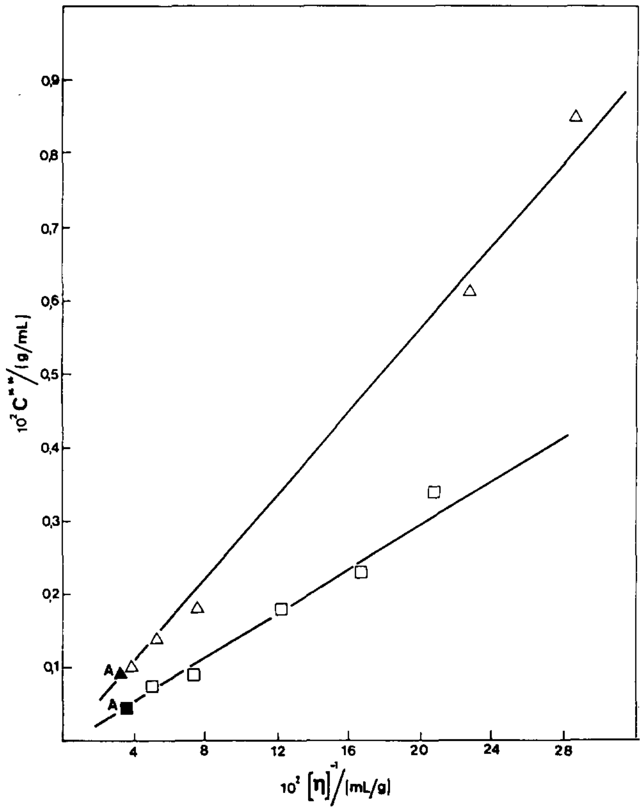

Figure 8 Variation of c^{**} as a function of $[\eta]^{-1}$ for the system PV2P/benzene (□, 25°C; △, 40°C). Points labelled A correspond to the branched PV2P sample

this differentiation of the product $[\eta]c^{**}$ from one polymer to another polymer must be attributed to the different flexibility of the polymers which leads to different shapes of the macromolecular coils giving different values of the constant in equation (9).

CONCLUSIONS

Using binary polymer/solvent systems we determined the critical concentration c^{**} of the polymers. This concentration separates the dilute solution region into very dilute and dilute regions.

We have proposed relations which correlate c^{**} with the molecular weight and the intrinsic viscosity of the samples of a polymer (relations 11 and 15). The experimental verification of these relations indicates that the scaling laws obtained here for c^{**} are the same as the scaling laws already obtained for c^*.

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