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ORIGINAL CONTRIBUTION

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On the resistance to the interpenetration between macromolecular coils of different segment densities

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Abstract Using viscometry techniques on polymer fractions, we determine the critical concentration c^* (separating the dilute and semi dilute solutions). The same measurements have been conducted with mixtures of these fractions (mixtures 1:1 by weight of fractions differing in molecular mass and chemical nature, or fractions differing only in molecular mass). The determined values of critical concentration c^* of the mixtures are higher than the values calculated based on the critical concentrations of the corresponding fractions. This deviation from the additivity rule is attributed to the resistance in the interpenetration (delay to the attainment of the homogeneous state) between macromolecular coils of different chemical nature or of the same chemical nature but of different molecular mass. Higher values of the reduced viscosities of the mixture of the fractions, compared to the values calculated using the reduced viscosities of the corresponding fractions, are observed above the critical concentration c^*. In this concentration region the interaction parameter between two different polymers is calculated.

Key words Binary polymer mixtures – dilute solutions – semi dilute solutions – overlap concentration c^*

Introduction

The rule of the mean value (or additivity rule) is applied in polymer science in many cases; for example, the refractive index increment of a copolymer and the unperturbed dimensions of block copolymers. This rule has also been applied in the case of the critical overlapping concentration c^*, introduced by de Gennes [1] and calculated for a mixture of two polymers [2, 3]. This proposed mean value means that the interpenetration of the macromolecular coils of two different polymers takes place in the same way as the interpenetration between the coils of one polymer.

The aim of this article is to demonstrate that the additivity rule in the case of the critical concentration c^* cannot be applied. More precisely, our experimental results, obtained by viscometry indicate that the critical concentration c^* of a mixture of two polymers is higher than the calculated mean value of this concentration based on the critical concentrations of each polymer. The same phenomenon is observed even with mixtures of two fractions of the same polymer differing in molecular mass and consequently in segment density. This difference between the calculated value of c^* of the mixtures and its observed value is attributed to the difficulty in the interpenetration of the macromolecular coils differing either in chemical nature or in segment density.

Based on an equation giving the reduced viscosity of a mixture of two polymers, we calculate a value neglecting the interactions between the different fractions. These calculated values are lower than the observed values, and this result indicates that the interactions between the two different polymers, especially above c^*, exist and cause an extra expansion of the *interpenetrating* coils.

Experimental part

We have prepared poly(methyl methacrylate) (PMMA) and polystyrene (PS) samples using anionic polymerization in tetrahydrofuran (THF) at $-70\,^{\circ}\mathrm{C}$. Their ratio of weight to number-average molecular weights $\bar{M}_w/\bar{M}_n$, as was determined by gel permeation chromatography, never exceeds 1.1.

Solutions of pure PS and PMMA and of their mixtures presenting a weight ratio 1 : 1 were prepared in ethyl acetate.

The viscosity measurements were carried out in a Schott Geräte automated viscosity-measuring system with Ubbelohde-type viscometers, equipped with an automatic injection system (maximum error ± 0.03%) for in situ dilutions. In order to eliminate any errors that could have been originated from concentration inaccuracies, some measurements were performed more than once. Reproducibility of the flow times was almost perfect. The temperature was 25 °C and controlled to within ± 0.02 °C.

The viscometric results are analyzed according to the "classic" equation

$$t_c = t_0\{1 + c[\eta] + c^2[\eta]^2k' + \cdots\} \qquad (1)$$

in which t_c is the efflux time of the polymer solution of concentration c, t_0 is the efflux time of the solvent, $[\eta]$ is the limiting viscosity number (intrinsic viscosity) of the polymer and k' is the Huggins constant. Plotting $(t_c - t_0)/t_0\,c$ as a function of c, we obtain a straight line the extrapolation of which to $c = 0$ gives $[\eta]$. The quantity $(t_c - t_0)/t_0$ is called relative viscosity, η_i, and the quantity η_i/c is the reduced viscosity, η_r.

Results and discussion

The critical concentration c^* has been determined with mixtures of fractions of two different polymers and with mixtures of fractions of different molecular masses of the same polymer. It is evident that c^* (crossover point in the variation of η_i/c (reduced viscosity, η_r) versus c, separating the dilute and semi dilute solutions) are also determined for each of the components of the mixtures (Table 1). The values of c^* for PS, determined by viscometry, are well predicted by the relation $c^* = 0.5\,[\eta]^{-1}$ proposed in our previous work [4]. The same relation is proposed by Vidakovic et al. [5]. The values of c^* for PMMA are close to the values of c^* for PS.

The concentration in the onset of the first entanglements between the macromolecular chains is in general ten times lower than the overlap concentration [6]. In this very low concentration region measurements are not presented in this work.

In Figs. 1 and 2, we present the variation of η_i/c as a function of the concentration c for fractions of PS and PMMA and for the corresponding mixtures of these fractions. As we have already described in the experimental part, the mixtures consist of weight ratio 1 : 1 of the corresponding polymers. In these figures the arrows indicate the calculated mean value of the crossover concentrations of

Table 1 Weight-average molecular weight of polystyrene (PS) and of poly(methyl methacrylate) (PMMA) and their critical concentration c^* in ethyl acetate at 25 °C

Sample	$\bar{M}_w$	c^*/(g/100 ml)
PS	52 800	3.4
PS	62 800	3.05
PS	93 000	2.6
PS	203 000	1.51
PS	1 500 000	0.73
PMMA	52 000	2.4
PMMA	82 200	2.2
PMMA	465 000	1.1

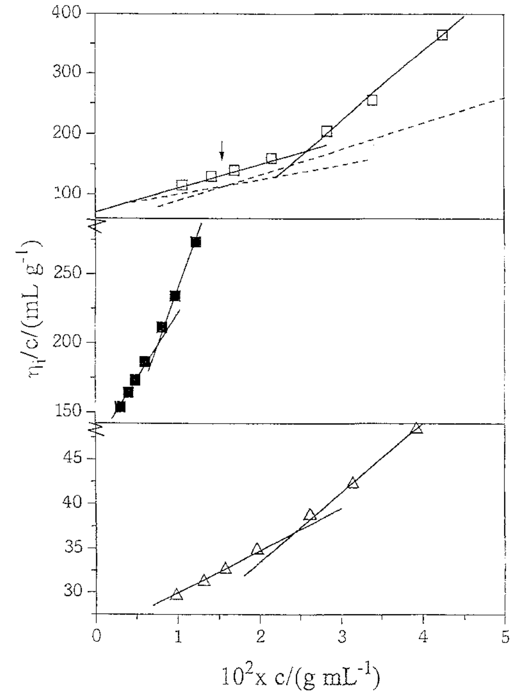

Fig. 1 Plot of η_i/c versus c for: ■, PS ($M_w = 1\,500\,000$); △, PMMA ($M_w = 82\,200$) and □, 1 : 1 by weight mixture of the above polymers. Solvent is ethyl acetate at 25 °C. Dashed curve: see text

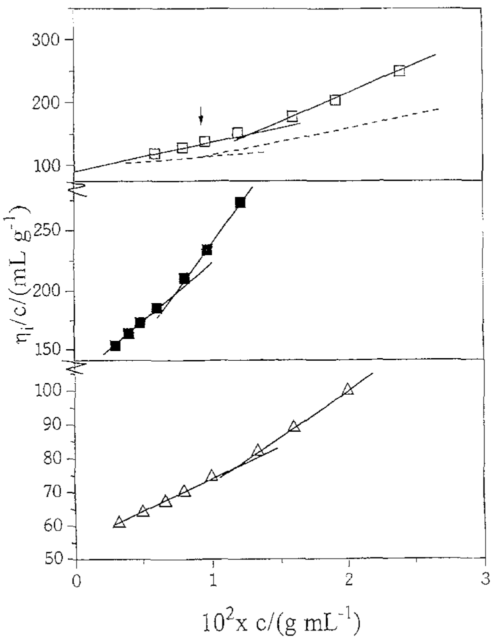

Fig. 2 Plot of η_i/c versus c for: ■, PS (M_w = 1 500 000); △, PMMA (M_w = 465 000) and □, 1 : 1 by weight mixture of the above polymers. Solvent is ethyl acetate at 25 °C. Dashed curve: see text

Table 2 Mixtures of polystyrene (PS) and poly(methyl methacrylate) (PMMA) of weight ratio 1 : 1; the obtained critical concentration c^* of these mixtures in ethyl acetate at 25 °C and the calculated critical concentration of the same mixtures, c^*_{calc}, based on the critical concentrations of each of the components of the mixtures, and applying the additivity rule

Mixture	c^*/(g/100 ml)	c^*_{calc}/(g/100 ml)
PS 1 500 000–PMMA 465 000	1.37	0.91
PS 52 800–PMMA 52 000	3.27	2.90
PS 1 500 000–PMMA 82 200	2.68	1.52
PS 1 500 000–PS 93 000	2.80	1.70
PS 1 500 000–PS 62 800	3.20	1.90
PS 1 500 000–PS 203 000	1.70	1.12

the mixtures from the crossover points of the corresponding polymers (additivity rule). This mean value, c^*_{calc}, for all the PS–PMMA mixtures is lower than the observed critical concentration c^* (Figs. 1, 2 and Table 2).

The calculated mean value of the overlap concentration of the mixture of the two polymers, c^*_{calc}, is obtained from the overlap concentrations of each pure polymer as it is obtained from the variation of η_i/c as a function of c of these polymers (Figs. 1 and 2). More precisely, we have $c^*_{calc} = 0.5\ c^*_{polym1} + 0.5\ c^*_{polym2}$. This relation also expresses the additivity rule or an "ideal" behavior of the mixture of the polymers in the absence of interactions between them.

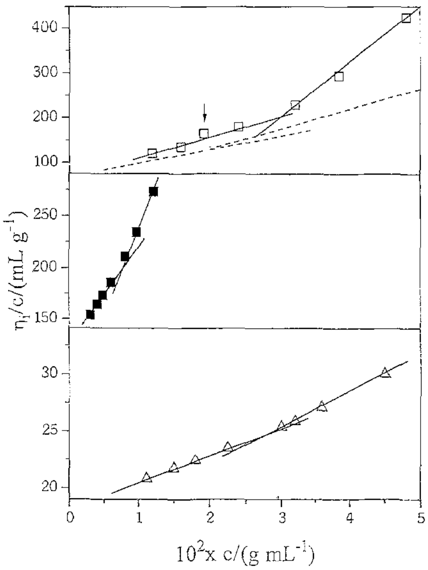

Fig. 3 Plot of η_i/c versus c for: ■, PS (M_w = 1 500 000); △, PS (M_w = 62 800) and □, 1 : 1 by weight mixture of the above polymers. Solvent is ethyl acetate at 25 °C. Dashed curve: see text

In Fig. 3, we present the determination of c^* by viscometry using fractions of the same polymer, PS. The mixtures of the two fractions of the same polymer differing in molecular weight and consequently in segment density, present also a c^* value higher than the concentration calculated from the c^* values of the corresponding fractions. These mean values, c^*_{calc}, are indicated in the figure by an arrow and they are given in Table 2.

The deviation of c^* from the value obtained from the additivity rule, c^*_{calc}, is higher when the difference in the segment density of the corresponding fractions, as it is expressed by the difference of the inverse of their intrinsic viscosities, is also higher. In order to give a more quantitative aspect to the resistance in the interpenetration of two fractions of different segment density, we display in Fig. 4 the difference between c^* and c^*_{calc} as a function of the difference of the segment density $[\eta]_1^{-1} - [\eta]_2^{-1}$. The segment density is expressed here by the inverse of the intrinsic viscosity of each pure polymer of the mixture because we have from the Fox–Flory equation

$$[\eta] = \frac{\Phi(6R^2)^{3/2}}{M} ,$$

where the ratio of the molecular mass of the chain, M, to its volume, expressed by R^3 (R the radius of gyration) is equal to the inverse of the intrinsic viscosity. This ratio gives the segment density of the chain.

In Fig. 4, curve A is obtained with fractions of different chemical nature (PS and PMMA) and curve B is obtained with fractions of the same polymer (PS). It is clear that the

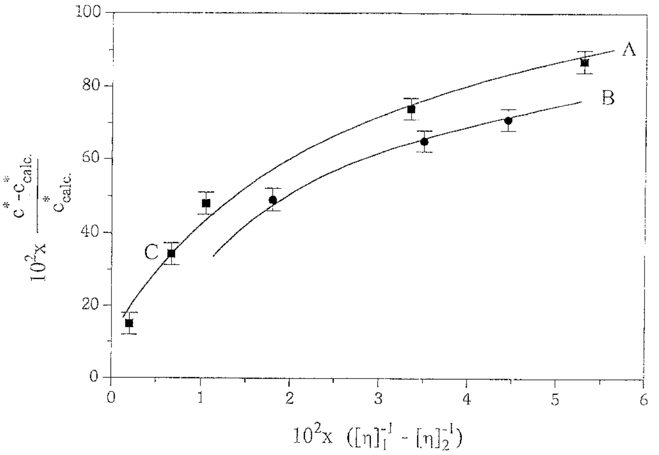

Fig. 4 Plot of $(c^* - c^*_{calc})/c^*_{calc}$ versus $[\eta]_1^{-1} - [\eta]_2^{-1}$ for: ■, PS-PMMA 1:1 by weight mixtures and ●, PS-PS 1:1 by weight mixtures, in ethyl acetate at 25 °C (point C: see text)

deviation from the additivity rule strongly depends on the difference in the segment density or the molecular mass of the two fractions of the mixtures. This result is in accordance with the already observed increase of the incompatibility between two polymers with increasing difference in their molecular masses [7–9]. We also observe that for the same difference in the segment density, the deviation in the case of PS–PMMA mixtures is higher than in the case of PS–PS mixtures. In the same figure we observe that curve A tends to give a certain value for $(c^* - c^*_{calc})/c^*_{calc}$ even for $[\eta]_1^{-1} - [\eta]_2^{-1} = 0$. This deviation between the observed and the calculated value of the critical concentration c^* even in the case of zero difference in the segment density between the two samples, must be attributed to the incompatibility between PS and PMMA due to their different chemical nature. Curve B of Fig. 4 indicates that we have here a "new" incompatibility manifested by the resistance to the interpenetration of two fractions of the same polymer differing in the molecular mass and consequently in the segment density. This incompatibility between fractions of the same polymer but differing in their molecular masses, has been already observed in measurements of the intrinsic viscosity of one of the fractions in the presence of the other [10].

Another way to describe our viscometric results will be based in the following, on polymer solutions viscosity equations. Rewriting Eq. (1) for the efflux time t_{c_A} of the solution of a polymer A that is found at a concentration c_A, we have

$$t_{c_A} = t_0 \{1 + c_A[\eta]_A + c_A^2 b_A + \cdots\} \,, \qquad (2)$$

where b_A is related to the Huggins constant k'_A by the relation $b_A = k'_A[\eta]_A^2$. If now the polymer A presents a concentration $c/2$ (half of the total concentration c of the binary mixture) its reduced viscosity η_{rA} must be given, according to Eq. (2), from the following relation

$$\eta_{rA(c_A=c/2)} = \frac{t_{(c_A=c/2)} - t_0}{t_0(c/2)} = [\eta]_A + \frac{c}{2} b_A + \cdots \,. \qquad (3)$$

An equivalent equation can be written for polymer B.

In the case of the mixture of the two polymers with a weight ratio 1:1 and total concentration c, the efflux time can be written as

$$t_m = t_0 \left\{1 + \frac{c}{2}[\eta]_A + \frac{c}{2}[\eta]_B + \frac{c^2}{4} b_A + \frac{c^2}{4} b_B + \frac{c^2}{4} b_{AB} + \cdots \right\}. \qquad (4)$$

The term $c_A c_B b_{AB}$ or $(c^2/4) b_{AB}$ expresses the interactions between polymer A and polymer B. The reduced viscosity of the mixture, η_{rm}, must be given by the relation

$$\eta_{rm} = \frac{t_{(c_m=c)} - t_0}{t_0 c} = \frac{[\eta]_A}{2} + \frac{c}{4} b_A + \frac{[\eta]_B}{2} + \frac{c}{4} b_B + \frac{c}{4} b_{AB} + \cdots \,, \qquad (5)$$

and from Eq. (3) we obtain

$$\eta_{rm} = \frac{\eta_{rA(c_A=c/2)}}{2} + \frac{\eta_{rB(c_B=c/2)}}{2} + \frac{c}{4} b_{AB} + \cdots \,. \qquad (6)$$

Using Eq. (6) and neglecting the term $(c/4) b_{AB}$, we obtain an "ideal" reduced viscosity of the mixture of the two polymers which is indicated in Figs. 1 to 3 by dashed lines. Comparing these curves with the experimentally obtained curves, we observe that the crossover point coincides with the calculated values by applying the additivity rule on the crossover points of each fraction (these points are indicated, as we have mentioned, in Figs. 1 to 3 by arrows) and this is the principal result of these calculations. We must point out that the reduced viscosity of the mixture, especially above c^*, is higher than the calculated values using the reduced viscosity of each fraction and applying Eq. (6), but ignoring the term $(c/4) b_{AB}$. The non coincidence of the experimentally obtained curves with the so calculated curves, indicates that this term must be significant and provokes an extra expansion of the coils.

The partial interpenetration of the coils starts below the concentration c^* and to this interpenetration must be attributed the higher values of the observed reduced viscosities compared to the calculated ones. In any case the difference between measured and calculated values from Eq. (6) ignoring the term $(c/4) b_{AB}$ is low below the critical concentration c^* (Figs. 1 to 3). This very low difference between observed and calculated values of reduced viscosities indicates a low number of heterocontacts between

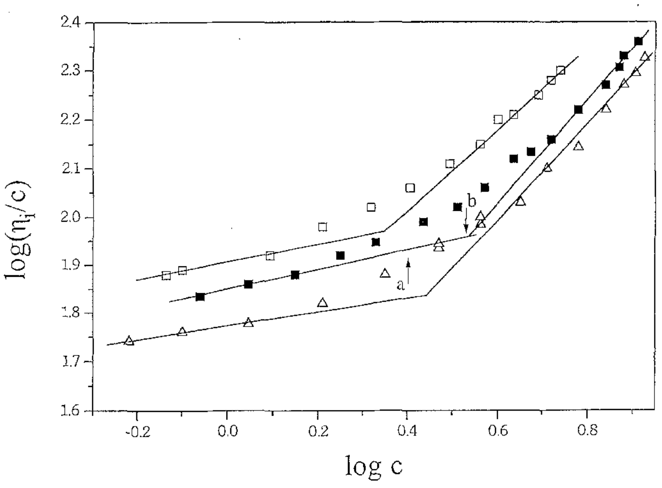

Fig. 5 Plot of log (η_i/c) versus log c for: □, PS ($M_w = 210\,000$); △, PMMA ($M_w = 300\,000$) and ■, 1 : 1 by weight mixture of the above polymers. Solvent is benzene at 30 °C. The arrow a indicates the calculated mean value and the arrow b the observed value of the c^* of polymers mixture. The concentration is given in g/100 mL and η_i/c in mLg^{-1}

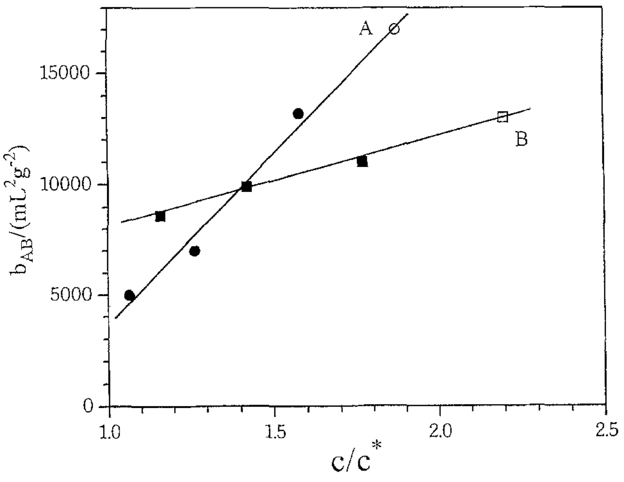

Fig. 6 Variation of the parameter b_{AB} as a function of the reduced concentration c/c^* for the systems: curve A, PS ($M_w = 1\,500\,000$) – PMMA ($M_w = 82\,200$) and curve B, PS ($M_w = 1\,500\,000$) – PMMA ($M_w = 465\,000$). Solvent is ethyl acetate at 25 °C. The unfilled points are obtained by extrapolation of the η_i/c values to the concentration 5×10^{-2} (gr mL^{-1}) for system A (Fig. 1) and $c = 3 \times 10^{-2}$ (gr mL^{-1}) for system B (Fig. 2)

interpenetrating chains of different chemical nature, or simply between chains of different segment density because below c^* we have a low degree of interpenetration. On the contrary, for $c < c^*$ an important number of heterocontacts takes place between *non interpenetrating* chains of different segment density (intermolecular contacts) leading to a delay of the attainment of the homogeneous state of the solution (uniform spatial distribution of monomer units) or the complete interpenetration of the chains. As a consequence of these intermolecular contacts the overlap concentration c^* of the mixtures shifts to higher concentrations compared to the concentrations obtained from an additivity rule. Above c^* the number of heterocontacts of the *interpenetrating* chains becomes increasingly important and the measured η_i/c values become increasingly higher than the calculated ones from Eq. (6) ignoring the term $(c/4)b_{AB}$ (Figs. 1–3).

In Fig. 5, we display the variation of $\log(\eta_i/c)$ as a function of $\log c$ for fractions of PS and PMMA and for the corresponding mixture of these fractions. Although this logarithmic representation does not allow an accurate determination of the crossover point expressing the overlap concentration, the c^* value of the mixture is higher than the mean value obtained from the c^* values of PS and PMMA. This deviation gives the point C in Fig. 4.

It was already shown, studying the viscometric behavior of a polymer in the presence of a second polymer in the extremely dilute solution region, that the parameter b_{AB} expresses a hydrodynamic effect more than a thermodynamic one. For the same system of polymer A–polymer B the values of b_{AB} become more important when the difference between the segment density or the molecular weight of these polymers becomes higher [10]. This parameter was manifested even in the case of a mixture of two polymers of the same chemical nature but presenting a different molecular weight or a different segment density. In this work this "repulsion" between polymers of different segment density is manifested by the resistance to the interpenetration of their molecular coils leading to a delay in the appearance of the overlap concentration. It is evident that the parameter b_{AB} in the semi dilute solution region ($c > c^*$), which we investigate mainly here, must be continuously increasing because the heterocontacts between the two polymers continuously increase as a consequence of the increase of their interpenetration. This is clearly indicated by the deviation between the measured and the calculated "ideal" reduced viscosity, ignoring the parameter b_{AB} in Eq. (6) (Figs. 1–3).

From the difference between the observed reduced viscosity η_{rm} and the "ideal" reduced viscosity of the mixture, $\eta_{rA}/2\,(c_A = c/2) + \eta_{rB}/2\,(c_B = c/2)$, and according to Eq. (6), we have calculated the values of b_{AB} for the two systems PS–PMMA of Figs. 1 and 2. These values are presented, as a function of the reduced concentration c/c^*, in Fig. 6. Using this concentration is reasonable because the number of heterocontacts between the *interpenetrating* chains depends on the "distance" of the concentration c, in which the measurement is contacted, from the overlap concentration c^*.

In Fig. 6, we observe that the values of b_{AB} of the system PS : 1 500 000–PMMA : 82 200 (curve A) are higher than the values obtained with the system PS: 1 500 000–PMMA: 464 000 (curve B) if we are far from the overlap concentration c^*. The two macromolecular chains of the former system present a difference in their segment density which is higher than the difference between the segment density of the chains of the latter system. As in the case of the study of the binary polymer mixtures in dilute solutions [10] the values of b_{AB} are higher in the case of the system consisting of polymers presenting a higher difference in their molecular weight. This result clearly indicates that even here the b_{AB} parameter expresses a hydrodynamic effect.

If we approach the overlap concentration ($c/c^* = 1$), intermolecular contacts between the *non interpenetrating* different chains appear leading to a contraction of these chains. This is to be distinguished from the case where heterocontacts between *interpenetrating* chains lead to an extra-expansion of these chains. The contraction of the *non interpenetrating* chains, due to the intermolecular contacts in the neighborhood and below c^*, must be more pronounced in the case of systems presenting a higher difference in the segment density of the chains [7, 10]. Indeed, for the system PS: 1 500 000–PMMA: 82 200 (curve A, Fig. 6), the values of b_{AB} expressing the extra-expansion of the *interpenetrating* chains presents an important decrease when we approach the overlap concentration. In the neighborhood of c^* the b_{AB} values of this system become even lower than the b_{AB} value of the second system (curve B, Fig. 6), for which we expect a lower degree of contraction due to the intermolecular contacts and, consequently, we observe a slow decrease of the extra-expansion or of the b_{AB}. These polymers present a lower difference of segment density because the difference between their molecular masses ($M_{\mathrm{w\,PS}}/M_{\mathrm{w\,PMMA}} = 3.22$) is lower than in the case of the first system ($M_{\mathrm{w\,PS}}/M_{\mathrm{w\,PMMA}} = 18.2$).

The delay in the appearance of the overlap concentration of a mixture of two polymers comparing to the overlap concentrations of the pure polymers observed in this work, are in accordance with previously obtained results indicating the existence of a resistance in the interpenetration between polymer samples of different chemical nature, or of the same chemical nature, as is manifested by the decrease of the intrinsic viscosity and the second virial coefficient [7, 10–12] or the radius of gyration [13, 14] of the one of the samples by the presence of the other sample. The contraction of the dimensions of one of the polymers (guest polymer) is higher when the difference in the segment density between this polymer and the second polymer (host polymer) is also higher [7, 10, 11]. The resistance to the interpenetration between different polymers which in the dilute solution region has given the decrease in their dimensions (intermolecular contacts) gives now a delay in their interpenetration ($c^* > c^*_{\mathrm{calc}}$). The repulsion between the different *non interpenetrating* chains leading to an extra-shrinking of these chains is also manifested here by the tendency of the experimental curves (η_r versus c) to be situated below the calculated ones when we are far below the overlap concentration c^* (Figs. 1 to 3). Above the overlap concentration we observe an extra-expansion of the chains, in contrast to dilute solutions, because now the contacts are manifested between the *interpenetrating* chains of different segment density.

References

1. de Gennes PG (1979) Scaling Concepts in Polymer Physics. Cornell University Press, Ithaca and London
2. Fukuda T, Nagata M, Inagaki H (1968) Macromolecules 19:1411
3. Ould-Kadour L, Strazielle C (1992) Polymer 33:899
4. Papanagopoulos D, Dondos A (1995) Polymer 36:369
5. Vidacovic P, Allain C, Rondelez F (1982) Macromolecules 15:157
6. Dondos A, Papanagopoulos D (1995) Polymer 36:365
7. Hugelin C, Dondos A (1969) Makromol Chem 126:206
8. Strazielle C (1979) Eur Polym J 15:55
9. Soria V, Figueruelo JE, Campos A (1981) Eur Polym J 17:137
10. Papanagopoulos D, Dondos A (1994) Macromol Chem Phys 195:439
11. Dondos A, Benoît H (1975) Makromol Chem 176:3441
12. Kuhn R, Cantow HJ, Burchard W (1968) Angew Makromol Chem 2:146
13. Kuhn R, Cantow HJ (1969) Makromol Chem 122:65
14. Kent MS, Tirrell M, Lodge TP (1992) Macromolecules 25:5383