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Difference between the dynamic and static behaviour of polymers in dilute solutions.
3. Influence of the host polymer on the dimensions of the guest polymer

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Light scattering and viscosity measurements have been conducted on polystyrene samples (guest polymer) in pure toluene and in the isorefractive mixture toluene–poly(methyl methacrylate). The second polymer (host polymer) is present at constant concentration in the solution. In the dilute solution region in which the measurements are conducted, only when the solution flows does the host polymer provoke a decrease in the dimensions of the guest polymer, while in the static state the dimensions of the guest polymer are not affected by the presence of the host polymer.

(Keywords: guest polymer; host polymer; light scattering; viscometry; polymer dimensions)

Introduction

Several solution studies have been performed on the ternary systems polymer 1–polymer 2–solvent focused either on the determination of the Flory–Huggins interaction parameter between the two polymers[1–5] or on the modification of the dimensions of one of the polymers by the presence of the second polymer[6,7].

In a recent article[8] we studied the viscometric behaviour of a polymer, named guest polymer, in solution in a solvent in which a second polymer, named host polymer, is found at a constant concentration. The concentration of the host polymer was very low and it is not only lower than the critical overlapping concentration c^* but it is also lower than the critical concentration c^{**} in which the entanglements between macromolecular coils appear[9–11]. It was found that the intrinsic viscosity of the guest polymer is lower in the solvent containing the host polymer compared to its intrinsic viscosity obtained in the pure solvent. This decrease is more and more important as the difference in the segment densities or the molecular masses of the two polymers is more and more important[8]. A decrease of the intrinsic viscosity of the guest polymer was observed even when the host polymer is of the same chemical nature but differs in the molecular mass or the segment density of the former polymer[8].

In this article we compare results obtained for a guest–host polymer system using light scattering with results obtained for the same system using viscometry. The results obtained using static or viscometric techniques are different and more precisely, in the static state (light scattering) the presence of the host polymer in the solution, but in a very low concentration, does not provoke any decrease in the dimensions of the guest polymer, while a decrease is observed when the viscometry technique is used on the same system. The observed difference in the results obtained by light scattering and viscosity indicates that in the dilute solution region the interactions between macromolecular coils appear only when the solution flows. Important differences in the behaviour of polymers in the static and dynamic state have been also observed in the determination of critical concentrations c^{**}[11] and c^*[12].

Experimental

The polystyrene (PS) and poly(methyl methacrylate) (PMMA) samples used in this work were prepared anionically in THF at −70°C by the authors at the "Charles Sadron" Institute in Strasbourg; their polydispersity never exceeded 1.15.

A Schott–Gerate (AVS) automated viscometry measuring system with Ubbelohde-type viscometers, equipped with an automatic injection system (maximum error ±0.03%) for *in situ* dilutions, was used in this study.

The light scattering measurements were performed using a computer controlled spectrogoniometer model SEM RD of Sematech (France) equipped with a He–Ne laser (633 nm). The Zimm plots were given directly from the software controlling the apparatus.

Results and discussion

PS was used as the guest polymer in this work, and PMMA as the host polymer. PMMA forms an isorefractive mixture with toluene, which is used as solvent. In this isorefractive mixture we determined the radius of gyration and the second virial coefficient of a PS sample and compared the values obtained with the corresponding values obtained with the same PS sample when it was found in solution in pure toluene.

In *Figure 1a* we present the Zimm plots obtained with a PS sample ($M_w = 1\,400\,000$) dissolved in pure toluene and in *Figure 1b* the Zimm plots obtained with the same PS sample dissolved in toluene containing PMMA ($M_w = 10\,000$) at constant concentration (0.1×10^{-2} g ml^{-1}). The values obtained for the radius of gyration (R_G) of the PS sample are almost identical in both measurements ($R_G = 72$ nm in pure toluene and $R_G = 71$ nm in the solvent toluene + PMMA). The corresponding values of the second virial coefficient, A_2, are 3.79×10^{-4} and 3.71×10^{-4} cm^3 mol g^{-2} in both

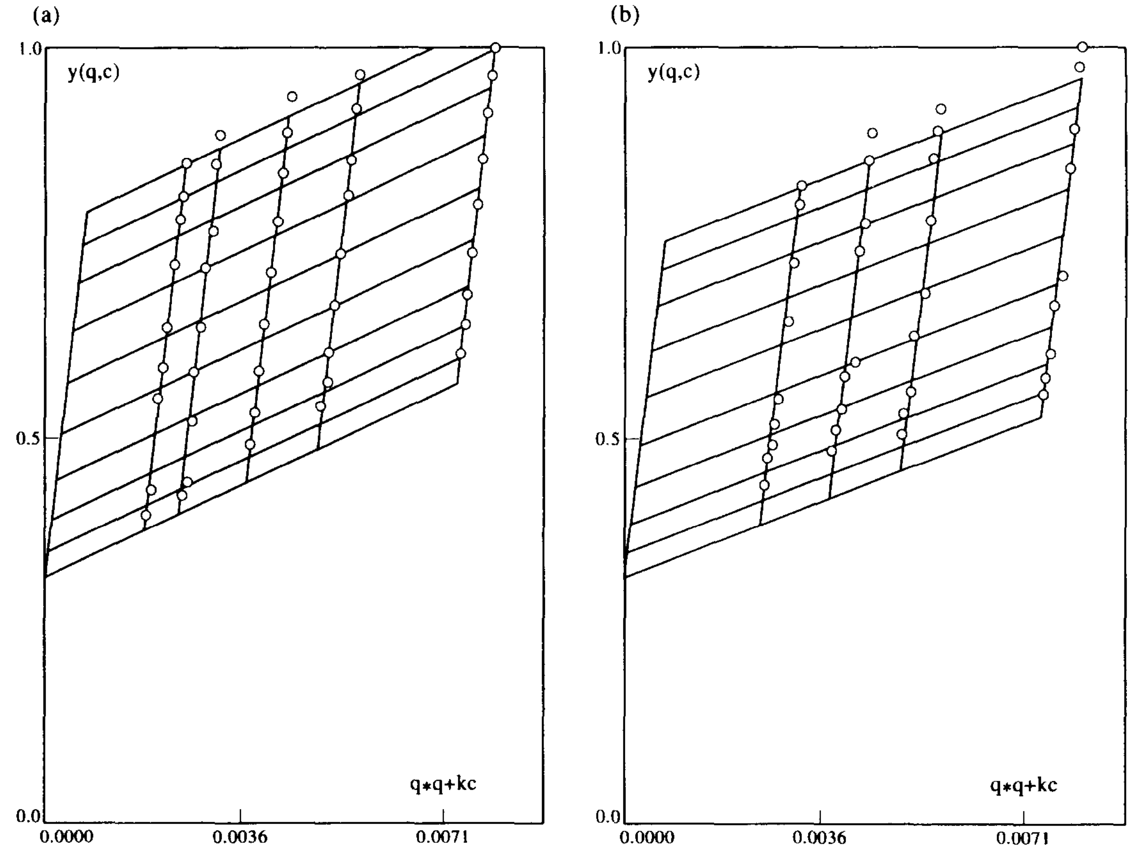

Figure 1 Zimm plots of PS ($M_w = 1.4 \times 10^6$) in pure toluene (a) and in toluene containing PMMA ($M_w = 10000$) at a constant concentration of 0.1×10^{-2} g ml^{-1} (b). The highest concentration of PS is 0.75×10^{-3} g ml^{-1} for (a) and 0.736×10^{-3} for (b). The axes are normalized

cases. The values of R_G and A_2 are given by the software controlling the apparatus.

The same measurements were conducted with a second PS sample ($M_w = 1050000$) as guest polymer and a PMMA sample ($M_w = 4000$) as host polymer. In *Figure 2a* we present the Zimm plots obtained with this PS sample in pure toluene and in *Figure 2b* the Zimm plots obtained with the same PS sample dissolved in toluene containing PMMA at constant concentration (0.1×10^{-2} g ml^{-1}). A radius of gyration equal to 57 nm for this PS sample is obtained in pure toluene and the same value is obtained when the host polymer is present in the isorefractive mixture. The second virial coefficient is also identical in both cases.

The results obtained by static measurement are completely different from the results obtained by viscometry. We have already established that the intrinsic viscosity of a guest polymer is decreased by the presence of a host polymer in the solution even in the extremely dilute concentration region[8,13].

In order to clearly demonstrate this difference between the static and viscometric results we present in *Figure 3a* the variation of the reduced viscosity as a function of the concentration for the PS sample ($M_w = 1400000$) in pure toluene and in toluene + PMMA ($M_w = 10000$, host polymer). The solutions are the same as those used for the light scattering measurements. An important decrease in the intrinsic viscosity of the guest polymer is observed by the presence of the host polymer. In *Figure 3b* the viscometric results obtained with PS ($M_w = 1050000$) in pure toluene and in toluene containing PMMA ($M_w = 4000$) at constant concentration are presented and here a decrease in the dimensions of the PS were also observed. Let us repeat that the light scattering measurements showed that the radius of gyration of these PS samples are not at all affected by the presence of the host polymers (*Figures 1b* and *2b*).

Having directly determined the radius of gyration of the guest polymer and having the possibility to obtain the radius of gyration of the host polymer (from the intrinsic viscosity and using the Fox–Flory equation) and considering the macromolecular coils as spheres, we have calculated the volume occupied by these two polymers in the concentration region in which the light scattering and viscosity measurements were conducted (these concentrations are given in the captions of *Figures 1* and *2*). This volume is much lower than the total volume of the solution and consequently we are in the concentration region below the critical concentration c^*. More precisely, the critical overlapping concentration of PS ($M_w = 1400000$) is ten times higher than the highest concentration in which we operate ($c^* = 0.73 \times 10^{-2}$ g ml^{-1}). The concentration of the host polymer is even lower than the critical concentration c^{**}, in which the first entanglements between chains start[9-11]. Kent *et al.*[7] (in the concentration region below c^* for the host polymer) also do not observe any significant decrease in the radius of gyration of the guest polymer as is the case for the results presented in this work. A decrease in the dimensions of the guest polymer in the static state have been observed only when the host polymer is found at a concentration higher than the critical concentration c^*[7].

In conclusion, the results obtained in this work, by comparing the static and viscometric measurements

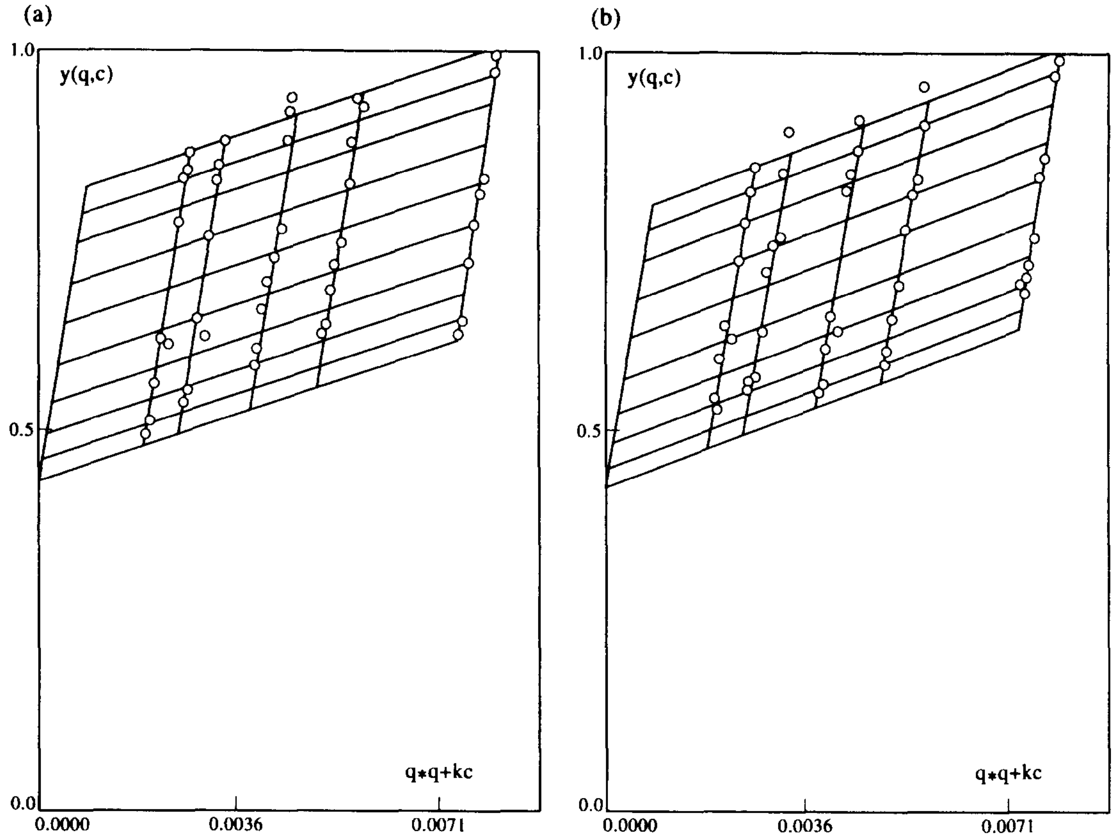

Figure 2 Zimm plots of PS ($M_w = 1.05 \times 10^6$) in pure toluene (a) and in toluene containing PMMA ($M_w = 4000$) at a constant concentration of 0.1×10^{-2} g ml^{-1} (b). The highest concentration of PS is 0.73×10^{-3} g ml^{-1} for (a) and 0.72×10^{-3} for (b)

obtained for the same guest–host polymer system in the dilute solution region ($c < c^*$), indicate that only when the solution flows does the presence of the host polymer induce a decrease in the dimensions of the guest polymer. An explanation of our results can be proposed, accepting that during its translation the high-molecular-weight coils of the guest polymer are perturbed by the presence of the chains of the dense coils of the low-molecular-weight host polymer. In favour of this explanation are the results obtained if we reverse the roles of the two polymers; the dimensions of the low-molecular-weight guest polymer are not perturbed by the presence of the high-molecular-weight host polymer[8]. In this case the coils of the guest polymer translate even through the host polymer which presents a very low segment density[14]. In the case of static measurements, we accept that the existence of available volume permits the coils of different polymers to avoid interacting with each other (incompatibility) and consequently the presence of the host polymer in the solution does not perturb the dimensions of the guest polymer.

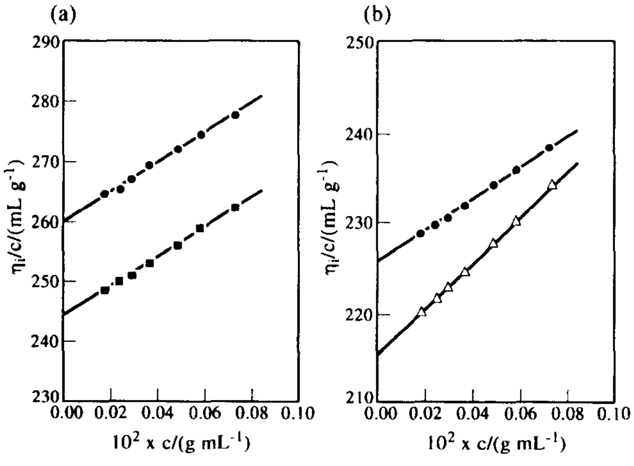

Figure 3 Variation of the reduced viscosity η_i/c as a function of the concentration c: (a) of polystyrene ($M_w = 1.4 \times 10^6$) in pure toluene (●) and in toluene + PMMA ($M_w = 10000$) at a constant concentration of 0.1×10^{-2} g ml^{-1} (■); (b) of polystyrene ($M_w = 1.05 \times 10^6$) in pure toluene (●) and in toluene + PMMA ($M_w = 4000$) at a constant concentration of 0.1×10^{-2} g ml^{-1} (△)

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