Associative Behavior of a Triblock Copolymer in Mixed Selective Solvents

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ABSTRACT: The associative behavior of a triblock copolymer polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene dissolved in solvent mixtures of *n*-octane and 4-methyl-2-pentanone has been studied. When the solvent composition was varied, the solvent mixture shifted from a selective solvent of the end copolymer blocks (polystyrene) to a selective solvent of the middle block (poly(ethylene/butylene)). For solvent mixtures with a high 4-methyl-2-pentanone content (selective solvent of polystyrene), only one kind of particles has been detected in solution. These particles have a high molar mass and compactness and a small size ($R_h \approx 32$ nm). However, for solvent mixtures with a high *n*-octane content (selective solvent of poly(ethylene/butylene)), two types of particles of different size were detected. The smaller ones ($R_h \approx 22$ nm) were considered as free copolymer chains and they were the more numerous in the solution. The larger ones ($R_h \approx 210$ nm) were assigned to aggregates with a loose structure different to ordinary micelles. The *n*-octane/4-methyl-2-pentanone mixture with a 50% of ketone behaved as a nonselective solvent, and no aggregates were detected at 25 °C and at concentrations so high as 10×10^{-3} g·mL^{-1}.

Introduction

A large number of studies have been reported on the formation and the structural characteristics of micelles formed by diblock and triblock copolymers in selective solvents, i.e., a good solvent for one block and a bad or nonsolvent for another block. The micellization behavior of AB diblock and ABA triblock copolymers in dilute solutions of selective solvents of the A blocks has been well characterized, both theoretically[1−5] and experimentally.[6−12] The copolymer chains tend to associate, forming uniform spherical micelles with the insoluble block forming a relatively compact core and the soluble blocks constituting a swollen protective corona. The micellization process obeys the closed association mechanism. On the other hand, much less understanding has been achieved about the association phenomenon of triblock copolymers disolved in selective solvents for the middle block. In dilute solutions of a few such systems, several authors[13,14] failed to detect any multimolecular association while others[15−19] have found well-defined micelles. In addition, some authors[20,21] have recently reported the existence of loose and polydisperse aggregates rather than spherical micelles. Several authors[22−25] have found thermoreversible gels in solutions of triblock copolymers in selective solvents of the middle block at surprisingly low concentrations.

Considering the small number of investigations carried out and the relatively little information known about the aggregation process of ABA copolymers in selective solvents of block B, we have undertaken a series of investigations both in diluted solutions[19,27] and in semidiluted ones (gels).[25,28−30] This paper aims at studying the self-association of polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene copolymer chains (SEBS) in *n*-octane/4-methyl-2-pentanone mixtures of different compositions. *n*-Octane is a selective solvent for poly(ethylene/butylene) whereas 4-methyl-2-pentanone is a selective solvent of polystyrene. The SEBS copolymer will form ordinary micelles with a PEB core in solvent mixtures with high ketone percentage. However the PS blocks will self-associate in solvent mixtures with a high *n*-octane content. So by varying the solvent mixture composition, we will be able to control the kind of SEBS aggregates and to compare them. Viscosity and light scattering measurements have been carried out as a function of solvent mixture composition. Both solvents can be practically considered isorefractive. Thus *n*-octane/4-methyl-2-pentanone seems to be a very suitable binary system for light scattering measurements. The interpolation of the results is simplified because the effect of preferential solvation can be neglected.

Experimental Section

Materials and Solution Preparation. Polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene copolymer sample, SEBS3, is a commercial product kindly provided by Shell España, S.A. The sample has been previously characterized in detail.[31] Its mass average molar mass, polydispersity index, and polystyrene weight percentage are 260 000 g·mol^{-1}, 1.18, and 30 wt %, respectively. Solvents (analytical purity grade) were used without further purification. The solvents used for light scattering measurements were filtered four times using a 0.02 μm aluminum oxide membrane filter. Solvent mixtures were made up by volume. Solutions were prepared by dissolving the copolymer in the solvent mixtures at temperatures close to 70 °C and in sealed flasks. To clarify copolymer solutions for light scattering measurements, they were filtered at 60 °C directly into the scattering cells using 0.2 μm PTFE Acrodisc CR filters. Copolymer solutions were filtered with number 3 glass filters for the viscosity measurements.

Viscometry. The viscosity measurements were made in a Landa automatic Ubbelhode viscometer model Viscoboy 2, which was placed in a thermostatically controlled bath with a precision of ±0.01 °C. The data were evaluated either accord-

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ing to Huggins and Kraemer equations[32]

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c$$

$$\frac{\ln \eta_r}{c} = [\eta] - k'_1[\eta]^2 c$$

or according to Heller equations[32]

$$\frac{c}{\eta_{sp}} = \frac{1}{[\eta]} - k_1 c$$

$$\frac{c}{\ln \eta_r} = \frac{1}{[\eta]} + k'_1 c$$

where η_{sp} is the specific viscosity, η_r is the viscosity ratio, $[\eta]$ is the intrinsic viscosity, k_1 and k'_1 are the Huggins and Kraemer coefficients, respectively, and c is the copolymer concentration.

Static Light Scattering. Measurements were performed on a modified FICA 42000 light scattering photogoniodiffusometer. Both light source and optical block of the incident beam were replaced by a He−Ne laser which emits vertically polarized light at 632.8 nm. The instrument was calibrated with pure benzene taking the Rayleigh ratio at 25 °C as 12.55×10^{-6} cm^{-1}.

To determine the mass average molar mass, M_w, and the radius of gyration, R_G, light scattering measurements were made at 11 angles between 30 and 150° for the solvent and each copolymer solution at 25 °C. The light scattered by a dilute polymer solution may be expressed as[33]

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{16\pi^2 n^2}{3\lambda_0^{\,2}} R_G^{\,2} \sin^2\frac{\theta}{2}\right) + 2A_2 c$$

where K is an optical constant, c the polymer concentration, ΔR_θ the difference between the Rayleigh ratio of the solution and that of the pure solvent, n the solution refractive index, λ_o the wavelength in a vacuum, A_2 the second virial coefficient, and θ the scattering angle.

The extrapolation of $Kc/\Delta R(\theta)$ at $\theta = 0$ by means of a mean square linear fit allows the calculation of the apparent radius of gyration, R_{app}, from the slope and the apparent mass, M_{app}, from the ordinate.

Dynamic Light Scattering. A light scattering spectrometer Antec was used at an angle of 90°. Intensity correlation function measurements were carried out in the self-beating mode by using a Brookhaven BI-9000AT 522-chanel digital correlator. A He−Ne laser operating at 632.8 nm was employed as light source. We accepted only those photoelectron count time correlation functions where the measured baseline, i.e., the average value of the correlation function at very long delay times, agreed with the computed baseline within ∼ 0.1%. A nonnegative constrained least-squares method[34] was used for the data analysis of the dynamic light scattering results.

Refractive Index Increment. The refractive index increment of the copolymer solutions was measured using a Brice-Phoenix differential refractometer equipped with a He−Ne laser which emits vertically polarized light at 632.8 nm. The dn/dc values of SEBS3 in the different binary solvent mixtures at 25 °C were equal to 0.117. The refractive indexes of n-octane and 4-methyl-2-pentanone at 25 °C were 1.3873 and 1.3853, respectively.

Results and Discussion

In a previous paper[27] it was reported that whereas some copolymers SEBS, with a lower molar mass than SEBS3, form stable solutions in n-octane, SEBS3 does not dissolve or form clusters which can be seen with the naked eye at concentrations so low as 8×10^{-5} g·mL^{-1}. We failed to found SEBS3 micelles in solutions of n-octane. On the other hand SEBS3 form ordinary micelles in solutions of 4-methyl-2-pentanone.[31] Both solvents are inverse relative solvents. Therefore, we have considered that the study of the SEBS3 aggregation in mixtures of both solvents will help us to get a better comprehension of the aggregation process of triblock copolymers in selective solvents. By varying the composition of the binary solvent mixture, we can go gradually from a conventional micelle system to the aggregation phenomenon found in pure n-octane. The election of these two solvents has the advantage that they are practically isorefractive. Thus, the use of light scattering becomes very simple because the effect of preferential solvation can be neglected.[35]

We have found that SEBS3 does not form homogeneous solutions in n-octane and in the solvent mixture with a 10% of 4-methyl-2-pentanone. In these solvents the existence of microgels or clusters could be appreciated with the naked eye at concentrations of 8×10^{-5} g·mL^{-1} (n-octane) and 3×10^{-4} g·mL^{-1} (n-octane/4-methyl-2-pentanone, 90/10). Thermoreversible gels were formed at concentrations as low as 2×10^{-2} g·mL^{-1} in these solvent systems.

For the other compositions of the binary solvent mixture, homogeneous solutions of SEBS3 were found in the whole concentration range studied. We have focused our investigations on these compositions.

Static Light Scattering. Static light scattering measurements were performed on solutions of SEBS3 which concentrations ranged between 1×10^{-3} and 10×10^{-3} g·mL^{-1} in solvent mixtures with a 4-methyl-2-pentanone percentage ranging between 20 and 100%. Plots of the reciprocal apparent mass, $1/M_{app} = Kc/\Delta R_o$, as a function of concentration are shown in Figure 1.

$Kc/\Delta R_o$ is plotted as a function of concentration for the end compositions of the binary solvent mixture in Figure 1a. The mixtures corresponding to high contents of n-octane or 4-methyl-2-pentanone show linear variations of $Kc/\Delta R_o$ with the SEBS3 concentration, suggesting that, under these experimental conditions, micelle or aggregate formation is overwhelmingly favored. Thus the weight average molar mass, M_w, determined from the double extrapolation to zero angle and concentration could be considered as the micelle molar mass. The M_w values obtained are plotted as a function of 4-methyl-2-pentanone percentage in Figure 2. The great difference in the molar mass found for both kinds of relative solvents is remarkable. Whereas for the solvent mixtures with a ketone percentage of 80 and 100% M_w ranges between 18×10^6 and 24×10^6 g·mol^{-1}, for the solvent mixtures with a ketone percentage of 20 and 30% the molar mass of the aggregates ranges between 2×10^6 and 5×10^6 g·mol^{-1}.

If we consider the existence of micelles in the solvent mixtures with a ketone percentage of 20 and 30%, the low association number of the copolymer can be attributed to the difficulty of the SEBS3 chains to form a micelle with a core constituted by the outer blocks. The micelle must have loops formed by the middle block, and even some outer blocks will be out of the micelle shell. The lower order that this kind of micelle will have will not allow a larger number of chains to become a part of the micelle.

However, the experimental results could be also explained considering the existence of a few large and loose aggregates. We have to take into account that the molar mass obtained by static light scattering is an

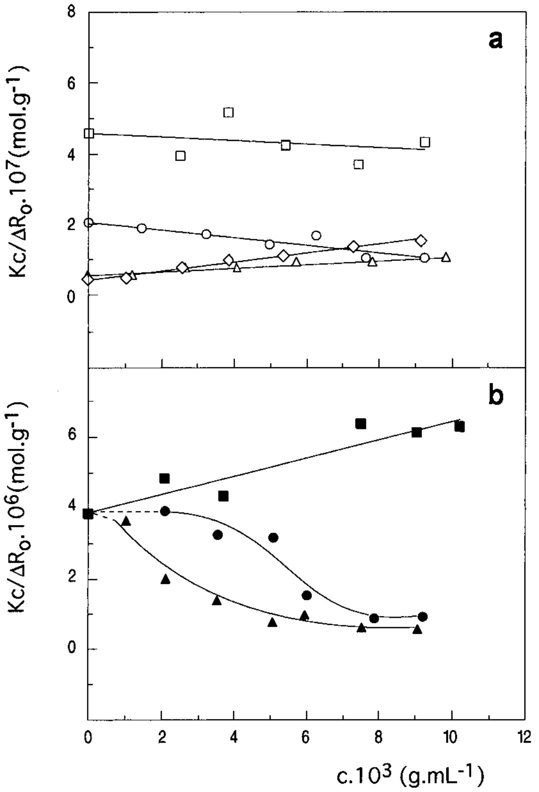

Figure 1. Concentration dependence of the reciprocal apparent mass, $Kc/\Delta R_o$, for the copolymer SEBS3 in *n*-octane/4-methyl-2-pentanone mixtures at 25 °C. Key: (a) 80/20 (○), 70/30 (□), 20/80(◇), and 0/100(△); (b) 60/40 (●), 50/50 (■), and 40/60 (▲).

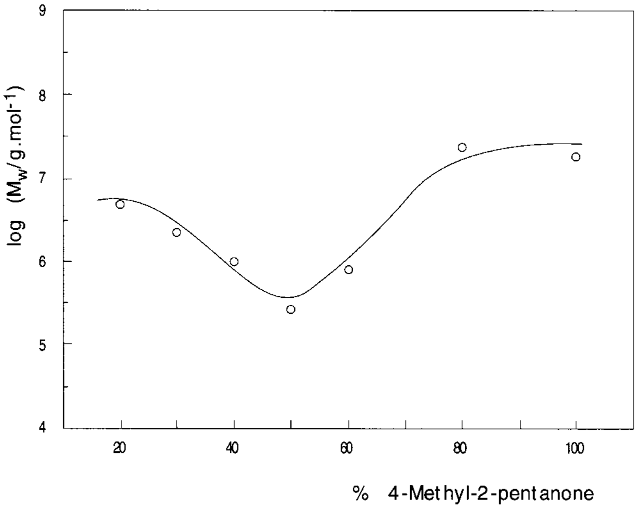

Figure 2. Dependence of weight average molar mass, M_w, on the 4-methyl-2-pentanone percentage for SEBS3 in *n*-octane/4-methyl-2-pentanone mixtures at 25 °C.

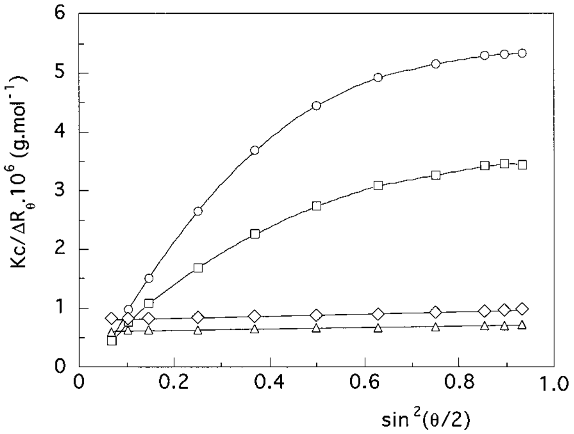

Figure 3. Plots of $Kc/\Delta R_\theta$ versus $\sin^2(\theta/2)$ for several solution concentrations of copolymer SEBS3 in the mixture *n*-octane/4-methyl-2-pentanone (40/60) at 25 °C. Copolymer concentrations: 1.03×10^{-3}(○), 2.14×10^{-3}(□), 5.10×10^{-3}(◇), and 7.53×10^{-3} g·mL^{-1}(△).

average mass; therefore, the existence of few large aggregates could lead to the same results as a large number of low molar mass micelles.

In Figure 1b the reciprocal apparent mass, $Kc/\Delta R_o$, is plotted as a function of SEBS3 concentration for the solvent mixtures with ketone percentages of 40, 50, and 60%. The $1/M_{app}$ dependence on concentration is not linear for the ketone percentages of 40 and 60%. The existence of a curvature suggests that the equilibrium is not shifted totally toward the formation of aggregates or micelles, with unimers and aggregates coexisting in solution. The $Kc/\Delta R_o$ increase observed at low concentration is caused by the increment in the free chain content which leads to a decrease of the apparent molar mass. For the highest concentrations, the $Kc/\Delta R_o$ dependence on concentration becomes linear, suggesting that the formation of aggregates is favored. The molar mass obtained by the double extrapolation at zero angle and concentration for the highest concentrations can be considered approximately as the mass average molar mass of the particles existing in the copolymer solutions.

The variation of $Kc/\Delta R_o$ with the concentration for the binary mixture with a ketone percentage of 50% is linear in the whole experimental concentration range. The mass average molar mass found for the system is equal to the mass average molar mass of the free SEBS3 chains, indicating a lack of aggregates in solution at the experimental concentrations used.

The angle dependence of $Kc/\Delta R_\theta$ was linear for all studied SEBS3 solutions except for the binary mixture with a 60% ketone content. In Figure 3, the variation of $Kc/\Delta R_\theta$ is plotted as a function of the observation angle for different solutions corresponding to 60% of 4-methyl-2-pentanone. The angle dependence of $Kc/\Delta R_\theta$ shows a curvature at low angles for the lowest concentrations. This phenomenon suggests that the high particle polydispersity is a consequence of a small number of aggregates and pure copolymer chains coexisting in solution. As the concentration increases and the equilibrium shifts toward the aggregate formation, the curvature disappears and the angle dependence of $Kc/\Delta R_\theta$ becomes linear. This behavior can sometimes be seen in systems that show some kind of association.[36] For the solutions in which $Kc/\Delta R_\theta$ show curvature, the extrapolation to zero angle has been done only using angles at which the angle dependence of $Kc/\Delta R_\theta$ was practically linear.

The variation of the logarithm of the mass average molar mass as a function of the solvent mixture composition is shown in Figure 2. For the ketone percentage of 50%, the copolymer SEBS3 does not form any kind of aggregate at 25 °C and at concentrations lower than 10×10^{-3} g·mL^{-1}. This solvent composition is a boundary which divides the composition range into two parts with two different types of associations. For mixtures with higher ketone contents, the binary mixture works as a selective solvent of end polystyrene blocks leading to ordinary micelles.

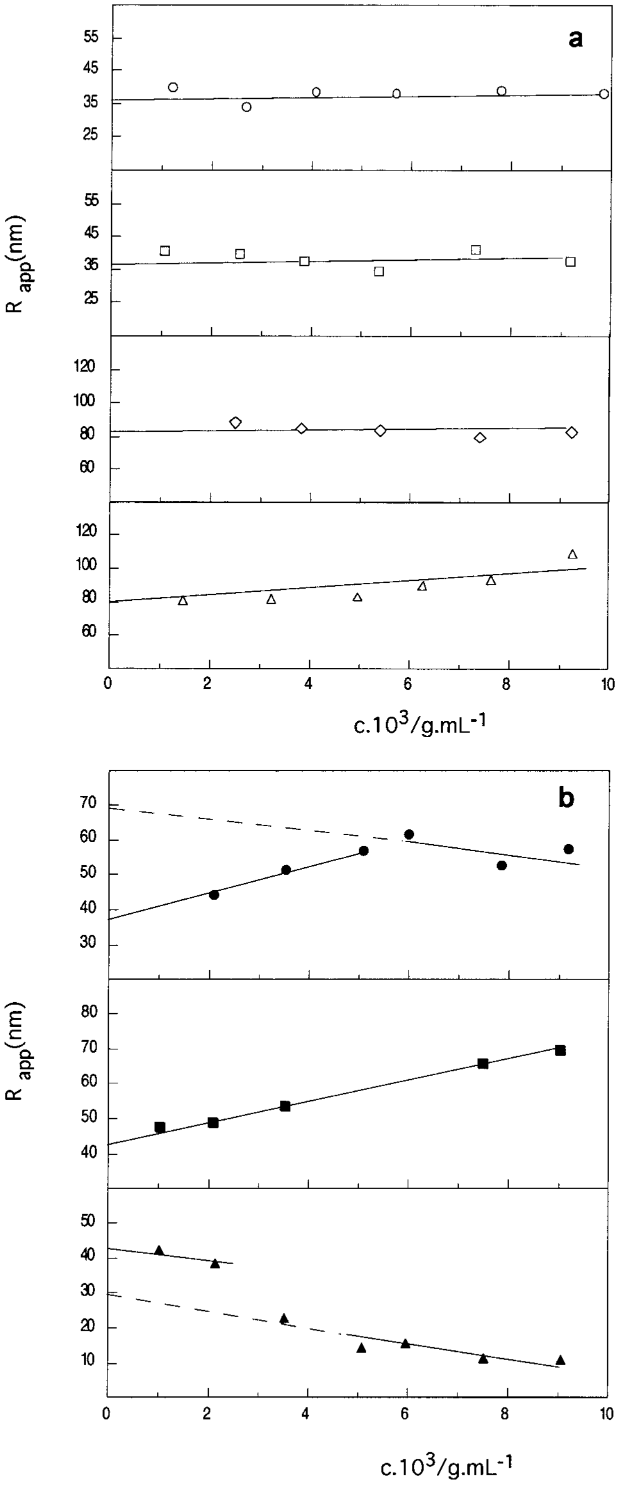

Figure 4. Concentration dependence of the apparent radius of gyration, R_{app}, for the copolymer SEBS3 in binary solvent *n*-octane/4-methyl-2-pentanone mixtures at 25 °C. Key: (a) 80/20 (△), 70/30 (◇), 20/80 (□), and 0/100 (○); (b) 60/40 (●), 50/50 (■), and 40/60 (▲).

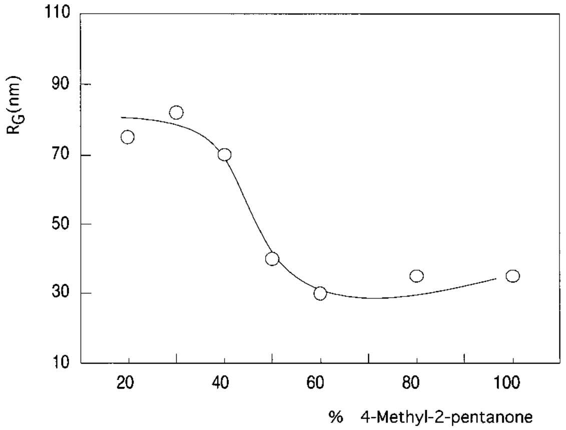

Figure 5. Dependence of radius of gyration, R_G, on the 4-methyl-2-pentanone percentage for SEBS3 in *n*-octane/4-methyl-2-pentanone mixtures at 25 °C.

For some compositions of the binary solvent system it has been possible to determine the radius of gyration of the micelles, R_G, from the observation angle dependence of $Kc/\Delta R_\theta$ extrapolated to zero concentration. It should be pointed out that the R_G values thus obtained are only apparent ones. The polystyrene blocks have a larger refractive index increment in the solvent mixture used than the poly(ethylene/butylene) blocks. Thus, when the polystyrene blocks form the micelle shell, the R_G values obtained are higher than the true one, and if the polystyrene blocks form the core of the micelle, the R_G experimental value will be lower.

In Figure 4a, the apparent radius of gyration, R_{app}, is plotted as a function of the copolymer concentration for the solvent mixtures with ketone percentages of 20, 30, 80, and 100%. In every case the copolymer association is strongly favored and the copolymer dependences of R_{app} are linear. The R_G values obtained from the extrapolation at zero concentration for the binary mixtures with a high *n*-octane content are much larger than those obtained for binary mixtures with high 4-methyl-2-pentanone contents. Although the R_G values are really apparent, these values suggest that both types of micelle or aggregate have quite different structures.

In Figure 4b, the apparent radius of gyration, R_{app}, is plotted as a function of the SEBS3 concentration for the solvent mixtures with ketone percentages of 40, 50 and 60%. For the solvent mixture with a 50% ketone percentage no associates were detected and therefore a linear plot of R_{app} vs C was observed. The extrapolation to zero concentration leads to the radius of gyration of the free copolymer chains. For the solvent mixtures where the association is not totally favored, a discontinuance is observed in the R_{app} dependence on SEBS3 concentration. Two values of R_G were obtained depending on the concentration range used to extrapolate to zero concentration. Thus, on extrapolation to zero concentration from the lowest concentrations, the R_G value obtained corresponds to the free copolymer chains, whereas if we use the highest concentrations, the R_G values obtained are similar to those obtained for aggregates. For the binary mixture with a 40% ketone content the R_G value obtained from the highest concentrations was similar to those found for the solvent mixtures with 20% and 30% ketone contents, whereas for the solvent mixture with a 60% ketone content the R_G value found was very similar to that obtained for the solvent mixture with the highest ketone content (80%) and with pure 4-methyl-2-pentanone.

The values of the mean square radius of gyration, R_G, obtained from the highest concentrations, are shown as a function of the solvent mixture composition in Figure 5. A great difference in the R_G values can be observed. Thus, the R_G values obtained for solvent mixture with a high *n*-octane content were close to 80 nm whereas the solvent mixtures with a high 4-methyl-2-pentanone content showed values which ranged between 30 and

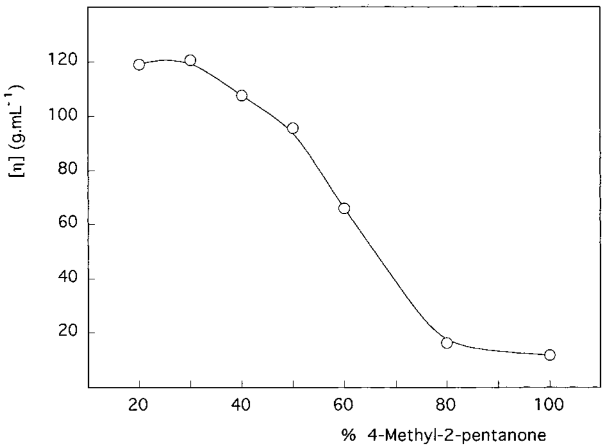

Figure 6. Dependence of intrinsic viscosity, [η], on the 4-methyl-2-pentanone percentage for SEBS3 in *n*-octane/4-methyl-2-pentanone mixtures at 25 °C.

35 nm. Taking into account the high M_w values obtained (20×10^6 g·mol^{-1}) for these systems, we can observe that the aggregates have a large association number and are very small and compact, corresponding to the micelles found for diblock copolymers in organic selective solvents. The results suggest that the aggregates found in these solvent mixtures are ordinary copolymer micelles. However the aggregates found for the solvent mixtures with a high *n*-octane content show lower molar mass, higher size, and lower compactness than the standard copolymer micelles. The solvent mixture with a ketone percentage of 50% shows a R_G value of 40 nm that corresponds to the free copolymer chains.

To get a complementary information and to confirm the results obtained by means of static light scattering, viscometry and dynamic light scattering measurements were carried out.

Viscometry. Viscometry measurements were carried out to get the intrinsic viscosity,[34] [η], from the extrapolation to zero concentration. The experimental dependences of the reduced viscosity, η_{sp}/c, (Huggins equation) and of the logarithm viscosity number, $\ln(\eta_r/c)$, (Kraemer equation) on the concentration were linear within the concentration range employed for all the systems studied. However, for the solvent mixtures with a high *n*-octane content, the extrapolation to zero concentration according to Huggins and Kraemer equations leads to different values of the intrinsic viscosity. Therefore, we used the Heller equations as an alternative extrapolation method. These equations are recommended when the Huggings coefficient is higher than 0.5 and the intrinsic viscosity is high.[37] Huggings, Kraemer, and Heller equations extrapolated to the same intrinsic viscosity values for the solvent mixtures with a high 4-methyl-2-pentanone content.

The variation of the intrinsic viscosity as a function of the solvent mixture composition is plotted in Figure 6. The binary solvent mixture *n*-octane/4-methyl-2-pentanone (20:80) and 4-methyl-2-pentanone show very much lower [η] values than the free copolymer chains (50% of 4-methyl-2-pentanone). These values suggest the existence of particles with a high compactness according to the static light scattering results, and this high compactness is found in standard micelle systems. However, the associates formed in solvent mixtures with high *n*-octane content have higher [η] values than the free copolymer chains, suggesting loose structures.

Dynamic Light Scattering. Dynamic light scattering measurements were made in order to obtain data for the size distribution functions. The nonnegative constrained least-squares method was employed. For the mixture with a ketone percentage of 80% and 4-methyl-2-pentanone only one peak could be observed at a hydrodynamic radius that ranges between 31 and 34 nm. This peak has been assigned to ordinary micelles formed in a selective solvent of the outer blocks. Similarly, for the solvent mixture with a ketone percentage of 50% only one peak was observed at a hydrodynamic radius of 15 nm. This peak would correspond to the free copolymer chains. However, for the solvent mixtures with percentages of 30 and 40% of 4-methyl-2-pentanone, two peaks could be observed. The larger peak appeared at a hydrodynamic radius of 21−23 nm whereas the smaller peak appeared at a hydrodynamic radius which varied between 200 and 225 nm. We have assigned the first peak to free copolymer chains whereas the second peak has been assigned to different loose aggregates to ordinary micelles. A similar peak at $R_h = 200$ nm was reported by Zhou et al.[18] for a copolymer poly(*tert*-butylstyrene)-*b*-polystyrene-*b*-poly(*tert*-butylstyrene) in *N*,*N*-dimethylacetamide, a selective solvent for the middle block. The authors attributed this peak to the so-called anomalous micellization, and it is ascribed to the copolymer composition heterogeneity. At lower temperatures the author found another peak at lower R_h that was assigned to flowerlike micelles.

Conclusions

The SEBS3 chains associate in two very different ways when they are dissolved in binary solvent mixtures of *n*-octane and 4-methyl-2-pentanone. The solvent mixtures with a high content of 4-methyl-2-pentanone behave as selective solvents of the end copolymer blocks (polystyrene). In these solvent mixtures only one kind of particle has been detected by DLS. Taking into account the high mass average molar mass and the low values of the mean square radius of gyration, hydrodynamic radius, and intrinsic viscosity, we can conclude that these associates have a high association number, a high compactness, and a low size. They can be considered as ordinary micelles. On the other hand the solvent mixtures with a high *n*-octane content behave as selective solvents of the middle copolymer block (poly(ethylene/butylene)). The size distribution functions obtained by DLS for these solvent mixtures show two kinds of particles of very different sizes. The smaller particles exist in larger concentrations, and we consider them as free copolymer chains. The larger particles exist in a smaller proportion and their sizes ($R_h - 200-225$ nm) are very much larger than those of ordinary micelles. We think that these aggregates have a loose structure according to that found by Raspaud et al.[20,21] Taking into account the particle polydispersity found for these solvent mixtures and the lower aggregate concentration, the molar mass and radius of gyration of these large aggregates will be very much higher than the mass average molar mass and mean square radius of gyration determined by static light scattering.

For the solvent mixture with 50% 4-methyl-2-pentanone, no aggregates were found at 25 °C and at concentrations as high as 10×10^{-3} g·mL^{-1}. The mixture of two inverse selective solvents can behave as a nonselective solvent. This result has been also found for the copolymer polystyrene-*b*-poly(ethylene/propylene) in n-dodecane/1,4-dioxane mixtures.[12]

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