Micellization of a Polystyrene-*b*-poly(ethylene/propylene) Block Copolymer in *n*-Dodecane/1,4-Dioxane Mixtures. 2. Structure and Dimensions of Micelles

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ABSTRACT: The concentration and temperature dependencies of micelle formation by a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane, 1,4-dioxane, and mixtures of both solvents are examined by light scattering and viscometry. At concentrations just above the critical micelle concentration an unusually large scattering intensity is found. The experimental dependencies of light scattering and viscosity data on concentration were always linear within the concentration range 1×10^{-3}–5×10^{-3} g·cm^{-3} for the extremes and middle of the composition range of the solvent mixture. The molar mass and dimensions of the micelles formed in *n*-dodecane and 1,4-dioxane are different due to the nature of the blocks that form the core and the shell of both types of micelles. Aggregation number seems to be related to the standard entropy of micellization. a comparison is made between the effect of the addition of the selective solvent for one block and the temperature increase. As the percentage of the minority solvent increases, or at constant composition as the temperature increases, dissociation of the copolymer chains occurs. We have found that temperature and selective solvent addition markedly influence the free chain–micelle equilibrium. However, this influence is relatively small on the molar mass and size of the micelles. Heller equations have been employed to determine the limiting viscosity number of the micelles, since the Huggins and Kraemer equations do not lead to the same value.

Introduction

Block copolymers in solution form micelles in selective solvents which are thermodynamically good solvents for one block and precipitants for the other block.[1-3] The micelles formed are constituted by a relatively compact core of insoluble blocks and a highly swollen shell of soluble blocks. In most cases, block copolymer micelles have a spherical shape in a dilute solution and a narrow distribution of both mass and size. Similar to conventional low molecular mass surfactants, micellization of block copolymers obeys the model of closed association.[4]

The factors that influence the micellization process and the structural parameters of the micelles include composition,[5] structure[6] and molar mass[7] of the copolymer, interactions between the copolymer blocks and the solvent,[8,9] copolymer concentration,[9] temperature,[9] and preparation methods.[10]

The present work centers on the investigation of any possible changes in the structure and dimensions of micelles formed by a polystyrene-*b*-poly(ethylene/propylene) block copolymer in *n*-dodecane/1,4-dioxane mixtures as a function of concentration and temperature. *n*-Dodecane is a good solvent for the poly(ethylene/propylene) block and a poor solvent for the polystyrene block, whereas 1,4-dioxane is a good solvent for the polystyrene block and a poor solvent for the poly(ethylene/propylene) block. Mixtures of both solvents with different compositions have been used instead of single solvents in order to vary in a continuous way the thermodynamic quality of the solvent and to analyze the influence of copolymer block/solvent interactions on the structure and dimensions of micelles. Thus, if the solvent mixture has an excess of *n*-dodecane, the micelles are composed of a polystyrene core surrounded by a poly(ethylene/propylene) shell, whereas if the solvent mixture has an excess of 1,4-dioxane, the micelles are constituted by a poly(ethylene/propylene) core surrounded by a polystyrene shell.

The size and molar mass of micelles have been measured using light scattering in combination with viscometry. Both solvents are miscible and can be practically considered isorefractive. Thus *n*-dodecane/1,4-dioxane seems to be a very suitable binary system for light scattering measurements. The interpretation of the results is simplified because the effect of preferential solvation can be neglected.[11]

The influence of selective solvent on the thermodynamics of micellization of the same copolymer in dilute solutions of *n*-dodecane/1,4-dioxane mixtures has been investigated in a previous paper.[12] The temperature dependence of the critical micelle concentration was determined from measurements of light scattering intensity as a function of temperature carried out at different concentrations. Plots of ln (c) against (cmt)$^{-1}$ were linear over the dilute solution range studied. These plots were used to calculate the standard Gibbs energies ($\Delta G°$), the standard enthalpies ($\Delta H°$), and the standard entropies ($\Delta S°$) of micellization. $\Delta G°$, $\Delta H°$, and $\Delta S°$ were negative and markedly dependent on the composition of the solvent mixture. The standard entropy is unfavorable to micelle formation, and the standard enthalpy is solely responsible for micelle formation. No micelles were detected in *n*-dodecane/1,4-dioxane mixtures with similar percentages of both solvents.

The aim of the present paper is to extend the investigations of the previous paper to micelle structural parameters.

Experimental Section

The polystyrene-*block*-poly(ethylene/propylene) copolymer sample, designated SEP1, was synthesized by Shell Research plc. It was prepared by hydrogenating the polyisoprene block of an anionically synthesized polystyrene-*block*-polyisoprene copolymer. UV spectroscopy of the copolymer in tetrahydrofuran showed that SEP1 contains 34 ± 3% by weight polystyrene. The weight-average molar mass, M_w, of the copolymer determined by light scattering in tetrahydrofuran and chloroform at 25 °C was 1.05×10^5 g·mol^{-1}. The application of light scattering theory to

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diblock copolymer solutions leads to the determination of an apparent weight-average molar mass and mean square radius of gyration,[13] R_G. In view of the small difference observed between the weight-average molar mass of the copolymer in tetrahydrofuran and chloroform, solvents with different refractive indexes, this copolymer can be considered homogeneous in chemical composition, and the apparent M_w and R_G values should be close to the real values for the block copolymer used. The ratio of the weight-average molar mass to number-average molar mass of the copolymer determined by gel permeation chromatography at 25 °C using chloroform as solvent was 1.08.

1,4-Dioxane and *n*-dodecane (analytical purity grade) were used without further purification. Solvent mixtures were made up by volume. Solutions were prepared by dissolving the copolymer in the solvent mixtures. To clarify copolymer solutions, they were filtered at room temperature directly into the scattering cells, which were sealed. Solution concentrations were recalculated at each temperature. As used polymer solutions are diluted, we have assumed that these solutions have the same thermal expansion coefficient as that of pure solvent.

Light scattering measurements were made at ten angles between 37.5° and 150° for each solution at 25, 40, 55, 70, and 85 °C. Experiments were performed on a modified FICA 42000 light scattering photometer. Both the light source and optical block of the incident beam were replaced by a Spectra-Physics He–Ne laser, Model 105, which emits vertically polarized light at 632.8 nm with a power of 5 mW. The photogoniodiffusometer was calibrated with pure benzene, taking the Rayleigh ratio at 25 °C as 12.55×10^{-6} cm^{-1}.[14]

The light scattered by a dilute polymer solution may be expressed as[15]

$$\frac{Kc}{\Delta R(\theta)} = \frac{1}{M_w}\left(1 + \frac{16\pi^2 n_0^2 R_G^2}{3\lambda_0^2}\sin^2(\theta/2) + \ldots\right) + 2A_2c + \ldots \quad (1)$$

where c is the polymer concentration, K an optical constant, $\Delta R(\theta)$ the difference between the Rayleigh ratio of the solution and that of the pure solvent, M_w the weight-average molar mass, R_G^2 the mean square radius of gyration, n_0 the solvent refractive index, λ_0 the wavelength in vacuo, and A_2 the second virial coefficient.

To estimate M_w and R_G, it is necessary to know the refractive index increments (dn/dc) and the solvent refractive index (n_0). The refractive index increments of the copolymer solutions were measured at 632.8 nm using a Brice-Phoenix differential refractometer, previously calibrated with solutions of highly purified NaCl, using a He–Ne laser (Spectra-Physics, Model 156) with a power of 1 mW as the light source. The temperature dependence of the refractive index increments was determined between 25 and 85 °C, leading to the following relationship, in which dn/dc and temperature are expressed in cm^3·g^{-1} and °C, respectively:

$$\mathrm{d}n/\mathrm{dc} = 0.1 + 2.0 \times 10^{-4}(T - 25) \quad (2)$$

The same relationship was found for the different solvent mixtures, as expected since both solvents are almost isorefractive throughout the whole temperature range studied (1,4-dioxane: $n_{25\,°\mathrm{C}} = 1.4185$, $n_{85\,°\mathrm{C}} = 1.389$; *n*-dodecane: $n_{25\,°\mathrm{C}} = 1.418$, $n_{85\,°\mathrm{C}} = 1.392$; measured at 633 nm).

The viscosity measurements were made in a Lauda automatic Ubbelohde viscometer, Model Viscoboy 2, which was placed in a thermostatically controlled bath with a precision of ±0.01 °C. The viscometer was calibrated using several standard solvents. Kinetic energy corrections were carried out by means of the equation

$$\eta = A\rho t - \frac{B\rho}{t} \quad (3)$$

where ρ is the density of the liquid, t is the efflux time, and A ($=1.01 \times 10^{-4}$) and B ($=5.6 \times 10^{-4}$) are the calibration constants. The viscosity measurements were carried out within the polymer concentration range $1 \times 10^{-3} \le c \le 5 \times 10^{-3}$. The basic solution was diluted directly in the viscometer. The data were evaluated according to the Heller equations[16]

$$\frac{c}{\eta_{\mathrm{sp}}} = \frac{1}{[\eta]} - k_1c \quad (4)$$

$$\frac{c}{\ln \eta_{\mathrm{r}}} = \frac{1}{[\eta]} + k_1'c \quad (5)$$

where c is the polymer concentration, η_{sp} the specific viscosity, η_{r} the viscosity ratio, and $[\eta]$ the limiting viscosity number.

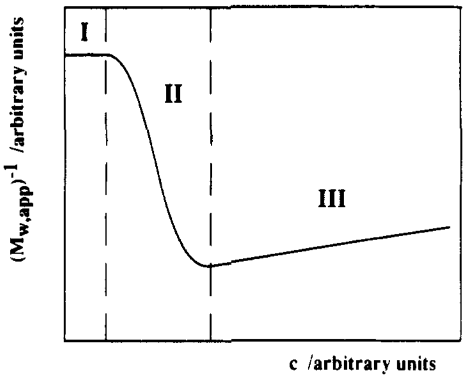

Figure 1. Concentration dependence of $(M_{w,app})^{-1}$ of associating solutes according to the model of closed association. (In region I only free chains exist, in region III micelles are predominant, and in region II both species coexist.)

Results and Discussion

The variations of $Kc/\Delta R$ extrapolated to angle zero, i.e., the inverse of the apparent molecular weight, $(M_{w,app})^{-1}$, and the scattering angle dependence of $Kc/\Delta R$ with concentration and temperature have been evaluated from the light scattering data for *n*-dodecane/1,4-dioxane binary mixtures with different compositions.

The concentration dependencies of $(M_{w,app})^{-1}$ vary with the thermodynamic quality of the solvent, i.e., with the composition of the binary solvent mixture. Although we have not found the ideal concentration dependence corresponding to the model of closed association[4] which is schematically plotted in Figure 1, every concentration dependence of $(M_{w,app})^{-1}$ for the different compositions of the binary mixture can be considered as a part of the curve plotted in Figure 1.

First, we analyze the binary solvent mixtures with a larger capacity for micelle formation. These correspond to the solvent mixtures with a high percentage of *n*-dodecane or 1,4-dioxane. As we have reported in the previous paper,[12] the more negative standard Gibbs energies of micellization have been found at the extremes of the solvent composition range. As an example, the concentration dependence of $(M_{w,app})^{-1}$ for *n*-dodecane is plotted in Figure 2a. As can be seen, the concentration dependence is linear, the same as for the curve of Figure 1 for high concentrations (region III). This behavior is according to the results shown in the thermodynamic study,[12] where a low value of the critical micelle concentration (cmc) is found for these solvents at 25 °C (Table I). The concentration range studied is far above that of the critical micelle concentration, and the free chain–micelle equilibrium overwhelmingly favors micelle formation. Under such experimental conditions the weight-average molar mass determined from the extrapolation of this straight line at nil concentration can be considered as the true molar mass of the micelles, since the copolymer sample is homogeneous in chemical composition and the concentration of free copolymer chains is negligible compared to the micelle concentration.

On the other hand, a sharp decrease of $(M_{w,app})^{-1}$ is also observed at lower copolymer concentration in the same Figure 2a. Anomalous behavior has also been reported in other copolymer/solvent systems and always at concentrations just larger than the critical micelle concentration. In some cases,[17-21] an abrupt increase of the dissymmetry

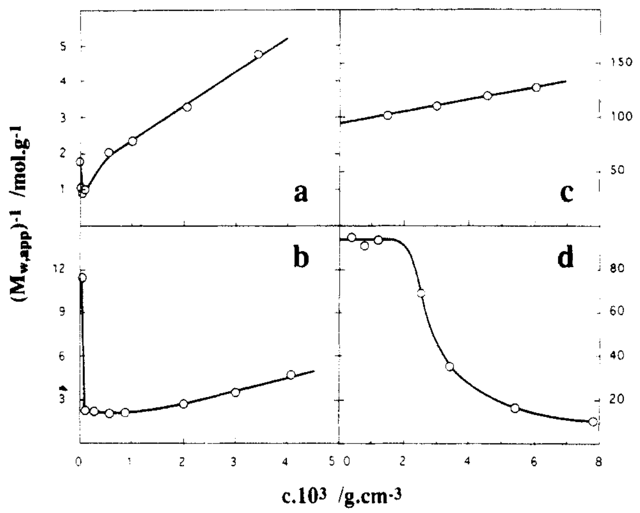

Figure 2. Plots of $(M_{w,app})^{-1}$ versus concentration for SEP1 in *n*-dodecane (a), *n*-dodecane/1,4-dioxane (80:20) (b), *n*-dodecane/1,4-dioxane (60:40) (c), and *n*-dodecane/1,4-dioxane (40:60) (d) at 25 °C.

Table I
Values of cmc's (g·cm^{-3}) Calculated for SEP1 in *n*-Dodecane, 1,4-Dioxane, and Mixtures of Both Solvents at 25 and 85 °C

% *n*-dodecane	cmc(25 °C)	cmc(85 °C)
0		<4 × 10^{-7}
10	3.5 × 10^{-16}	5.8 × 10^{-4}
20	1.0 × 10^{-9}	1.4 × 10^{-1}
40	1.7 × 10^{-3}	2.6
50	>4 × 10^{-3}	
60	>4 × 10^{-3}	
70	1.7 × 10^{-3}	3.6 × 10^{-1}
80	5.7 × 10^{-5}	4.1 × 10^{-2}
100	6.4 × 10^{-10}	3.3 × 10^{-5}

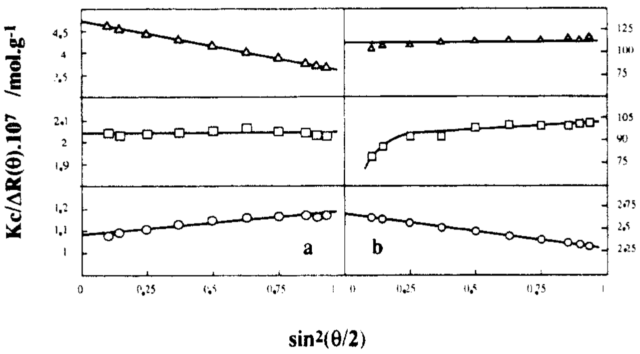

Figure 3. Plots of $Kc/\Delta R$ versus $\sin^2(\theta/2)$ (a) for several solution concentrations of SEP1 in *n*-dodecane at 25 °C [1.0 × 10^{-4} (○), 5.6 × 10^{-4} (□), and 3.4 × 10^{-3} (△)/g·cm^{-3}] and (b) for a solution of SEP1 in *n*-dodecane/1,4-dioxane (80:20) of concentration 2.01 × 10^{-3}/g·cm^{-3} at several temperatures [25 (○), 55 (□), and 85 °C (△)].

ratio, Z, i.e., the ratio of the intensities scattered at angles of 45° and 135°, or an increase of the intensity scattered at low angles appears as the temperature of micelle solutions is varied and just before the micelles disappear or just after they appear. In other cases,[9,22] a decrease of $(M_{w,app})^{-1}$ is observed as the concentration decreases just before the $(M_{w,app})^{-1}$ increase according to the model of closed association. We think that the two phenomena can be different. In fact, we have not found an increment of the dissymmetry ratio for concentrations at which $(M_{w,app})^{-1}$ presents this decrease, as can be seen in Figure 3a. To explain this anomalous behavior, Mandema,[20] Chu,[21] and Tuzar[22] have suggested the formation of macrostructures which would increase the weight-average molar mass of the system. It has also been suggested that an increase of the scattered intensity can be attributed to concentration fluctuations related to the micelle–free chain equilibrium.[19]

The scattering angle dependence of $Kc/\Delta R$ varies with the concentration in a similar way both for pure solvents and for binary mixtures with a high percentage of either solvent. As an example, scattering angle dependencies of $Kc/\Delta R$ for various solutions of SEP1 in *n*-dodecane with different copolymer concentrations are plotted in Figure 3a. $Kc/\Delta R$ varies linearly with observation angle for all concentrations. However, the slope of each line decreases as the concentration increases, reaching negative values at the higher copolymer concentrations. The concentration at which the scattering angle dependence becomes negative varies from 1 × 10^{-3} g·cm^{-3} to higher concentration values, depending on the binary solvent mixture and temperature. This has also been reported by Price[23,24] and Mandema[20] for SEP copolymers in *n*-decane and by Quintana et al.[9] for an SEP copolymer in various *n*-alkanes, where they found that the dissymmetry ratio depended on concentration. According to these authors, the most probable interpretation is that there exists some kind of weak intermicellar interaction causing a macroscopic ordering in the solutions and affecting the scattering pattern through interference.

As the percentages of both solvents in the binary mixture become more similar, the concentration dependence of $(M_{w,app})^{-1}$ shows a shape similar to that of region II of the curve plotted in Figure 1. The concentration dependence of $(M_{w,app})^{-1}$ for SEP1 in the binary solvent mixture *n*-dodecane/1,4-dioxane (80:20) is plotted in Figure 2b. The sharp increase of $(M_{w,app})^{-1}$ observed at lower copolymer concentrations is due to an increase of the number of free copolymer chains. As Quintana et al.[12] have reported for this system, the critical micelle concentration is higher than for the solvent systems mentioned above (Table I).

The concentration dependence of $(M_{w,app})^{-1}$ for SEP1 in *n*-dodecane/1,4-dioxane (40:60) is plotted in Figure 2d. In this case, the experimental curve has a shape similar to that of regions I and II of the curve plotted in Figure 1. This means that the lower experimental concentrations are lower than the critical micelle concentration.

The concentration dependence of $(M_{w,app})^{-1}$ for SEP1 in *n*-dodecane/1,4-dioxane (60:40) is plotted in Figure 2c. The variation of $(M_{w,app})^{-1}$ is linear and corresponds to region I of Figure 1, where no micelles exist in the copolymer solutions. For this solvent system the experimental concentrations are lower than the critical micelle concentration, as reported in the previous paper[12] (Table I). The extrapolation of $(M_{w,app})^{-1}$ to nil concentration is equal to the inverse of the copolymer molar mass.

The variation of the concentration dependence of $(M_{w,app})^{-1}$ with the temperature shows a behavior similar to that obtained with the composition of the binary solvent system.

The scattering angle dependencies of $Kc/\Delta R$ for several temperatures of an SEP1 solution in *n*-dodecane/1,4-dioxane (80:20) with a concentration of 2.01 × 10^{-3} g·cm^{-3} are plotted in Figure 3b. As the temperature increases, the concentration of micelles decreases until no micelles exist in the copolymer solution. For this system, a negative apparent radius of gyration is shown, suggesting macroscopic ordering in solution at 25 °C. Few micelles remain at 55 °C, and the line $Kc/\Delta R = f[\sin^2(\theta/2)]$ shows curvature at the lowest observation angles. Observation angle dependence of $Kc/\Delta R$ with an important curvature at low angles appears generally in polymer solutions that contain some kind of aggregates.[25,26] Finally, the micelles disappear at 85 °C, and the observation angle dependence of

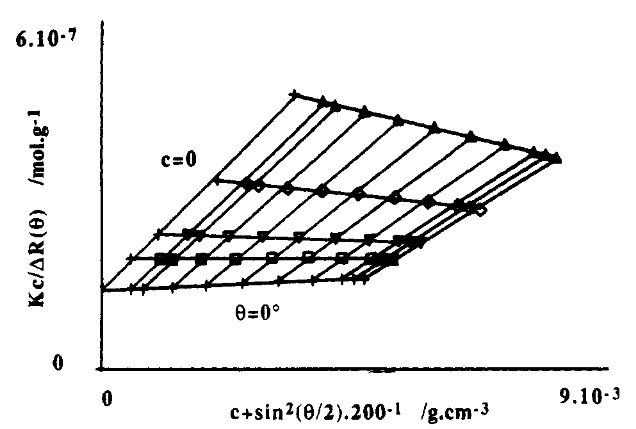

Figure 4. Zimm plot for micellar solutions of SEP1 in *n*-dodecane at 25 °C.

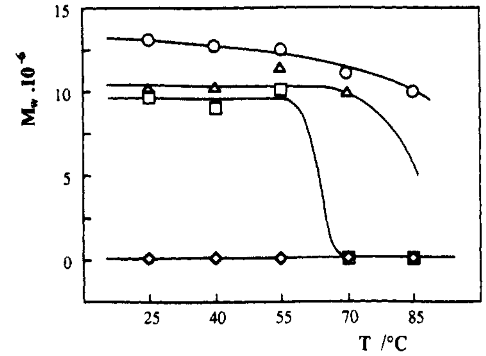

Figure 5. Temperature dependence of weight-average molar mass, M_w, for SEP1 in 1,4-dioxane and *n*-dodecane/1,4-dioxane with a low percentage of *n*-dodecane: 0% (○), 10% (△), 20% (□), and 50% (◇).

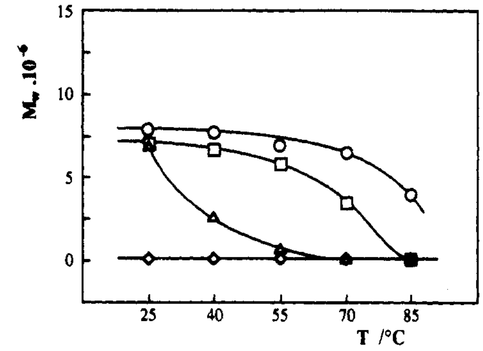

Figure 6. Temperature dependence of the weight-average molar mass, M_w, for SEP1 in *n*-dodecane and *n*-dodecane/1,4-dioxane with a high percentage of *n*-dodecane: 100% (○), 90% (□), 80% (△), and 60% (◇).

$Kc/\Delta R$ corresponds to that of unassociated copolymer SEP1.

In those systems where the concentration dependence of $(M_{w,app})^{-1}$ was linear for higher concentrations, the weight-average molar mass, M_w, was determined by extrapolating to nil concentration using the Zimm plot method (Figure 4). The dependencies of M_w of SEP1 on temperature for 1,4-dioxane, *n*-dodecane, and its binary mixtures are shown in Figures 5 and 6. As can be observed, M_w remains constant at low temperatures, which suggests that micelle molar mass does not depend on temperature. However, M_w decreases abruptly at high temperatures. This behavior can be explained by taking into account that as the temperature increases, the free chain–micelle equilibrium is displaced in the direction of the free chain concentration until reaching a temperature at which only free chains exist in solution. Figure 5 corresponds to solutions of SEP1 in 1,4-dioxane and solvent mixtures with a high content of 1,4-dioxane. In these solutions the micelles are constituted by a core of PEP and a shell of PS. On the other hand, Figure 6 corresponds to solutions of SEP1 in *n*-dodecane and solvent mixtures with a high content of *n*-dodecane. In this system the micelles are constituted by a core of PS surrounded by a shell of PEP. On comparing both figures, some differences are observed. In Figure 5, M_w remains constant for a greater temperature range as temperature increases and shows a sharper decrease at high temperatures. The different temperature dependencies of M_w can be explained by thermodynamic data. SEP1 has lower cmc's in solutions with an excess of 1,4-dioxane (Table I). Therefore, only at higher temperatures is the number of free chains high enough to decrease M_w. On the other hand, SEP1 shows a more negative standard enthalpy of micellization in solutions with a high content of 1,4-dioxane than in solutions with a high content of *n*-dodecane;[12] i.e., the temperature dependence of cmc is larger in the former than in the latter. Therefore the decrease of M_w is more abrupt in Figure 5 than in Figure 6.

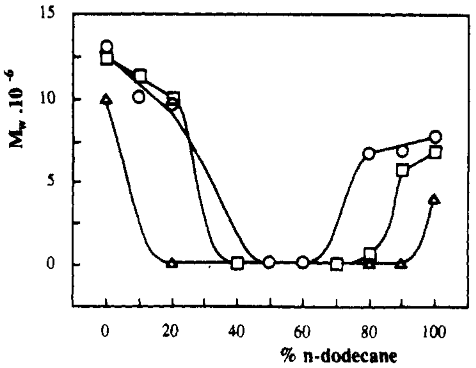

Figure 7. Dependence of the weight-average molar mass, M_w, on the *n*-dodecane percentage for SEP1 in *n*-dodecane/1,4-dioxane mixtures at various temperatures: 25 (○), 55 (□), and 85 °C (△).

Weight-average molar mass is plotted in Figure 7 as a function of solvent mixture composition at several temperatures (25, 55, and 85 °C). Three regions are clearly distinguished in this figure, and they correspond to solutions which contain different particles. In solvent mixtures with a low percentage of *n*-dodecane, SEP1 forms micelles with a core of PEP and a shell of PS, whereas it forms micelles with the inverse structure in solvent mixtures with a high percentage of *n*-dodecane. In the case of solvent mixtures with intermediate compositions, SEP1 remains in solution as free chains. As the temperature increases, the selective capacity of the solvent mixture decreases, decreasing the micelle stability and therefore increasing the free chain concentration. This fact leads to an enlargement of the median region until no micelle are detected in almost all the solvent mixtures studied at 85 °C.

As can be seen in Figure 7, the micelles with a core of PEP show a larger molar mass than the other ones. This behavior could be explained by taking into account that PS blocks are about 3 times shorter than PEP blocks and a larger aggregation number is necessary to stabilize the micelles. A similar behavior has been reported by Bahadur et al.[27] These authors found that for several polystyrene-*b*-polyisoprene block copolymers containing a polyisoprene sequence of the same molar mass and a polystyrene sequence of a different molar mass, the aggregation number of the micelles formed in *n*-heptane solutions increases as the molar mass of the PS block increases.

The differences found in the molar masses of both types of micelles agree with the differences in the standard entropy of micellization that we have reported[12] for this copolymer in solutions of *n*-dodecane/1,4-dioxane mixtures with a high content of 1,4-dioxane and in solutions of

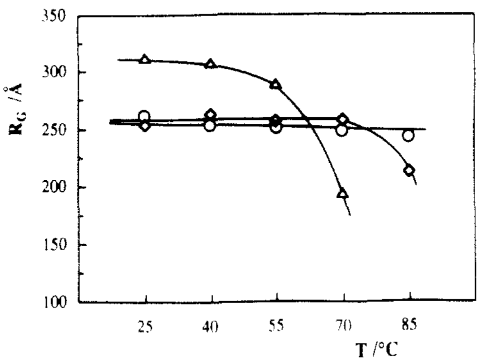

Figure 8. Temperature dependencies of radius of gyration, R_G, for SEP1 in n-dodecane/1,4-dioxane mixtures with different n-dodecane percentages: 0% (○), 90% (△), and 100% (◇).

n-dodecane/1,4-dioxane mixtures with a high content of n-dodecane. As the aggregation number of the micelles increases, the standard entropy of micellization becomes more negative.

On the other hand, the micelle molar mass decreases as a selective solvent of the micelle core is added to a selective solvent of the micelle shell. This fact agrees with the standard entropy of micellization becoming less negative.

For some compositions of the binary solvent system and temperatures it has been possible to determine the radius of gyration of the micelles, R_G, from the observation angle dependence of $Kc/\Delta R$ extrapolated to nil 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/propylene) blocks. Thus, when the PS blocks form the micelle shell, the R_G value obtained is higher than the true one, and when the PS blocks form the core of the micelle, the R_G experimental value is lower.

All R_G values determined are markedly lower than those expected for the weight-average molar masses obtained. This fact suggests that micelles have a compact and spherical structure, as has been verified by TEM for other micelle systems.[28,29] In Figure 8 the radius of gyration is plotted against temperature for some compositions of the n-dodecane/1,4-dioxane mixtures. Paying attention to R_G for SEP1 in n-dodecane, where the micelle–free chain equilibrium overwhelmingly favors micelle formation, we can see how the R_G values remain constant with temperature, which suggests that the radius of gyration of the micelles hardly varies with temperature. Radius of gyration decreases at high temperatures because it is an average and at these temperatures the concentration of free chains is important and its dimensions are small.

On the other hand, it is observed in Figure 8 that as 1,4-dioxane is added to n-dodecane, the radius of gyration increases; however, as seen in Figure 7, the weight-average molar mass decreases. This behavior may be due to the fact that the 1,4-dioxane molecules are preferentially adsorbed by the PS blocks solvating the core in a larger extension and therefore micelle dimensions increase.

To get complementary information about the micelle dimensions, viscometry measurements were carried out. Extrapolations to zero concentration according to the Huggins and Kraemer equations lead to different values of the limiting viscosity number, $[\eta]$, as expected for systems where the Huggins coefficient is greater than 00.5.[5] We have used the Heller equations[16] as an alternative extrapolation. These equations are recommended when the Huggins coefficient is greater than 0.5.[30] The concentration dependencies of c/η_{sp} and $c/\ln(\eta_r)$ for the SEP1 in n-dodecane/1,4-dioxane (10:90) at 25 °C are plotted in Figure 9. As can be seen, both equations extrapolate to a single value of limiting viscosity number. For all solvent systems and temperatures studied, the experimental dependencies of c/η_{sp} and $c/\ln(\eta_r)$ on the concentration were always linear within the concentration range used. Identical values of limiting viscosity number are obtained employing eqs 4 and 5.

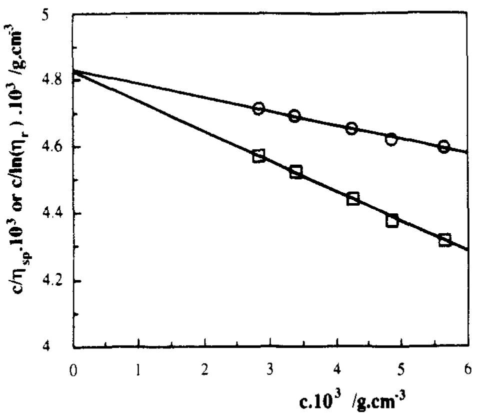

Figure 9. Concentration dependencies of c/η_{sp} (□) and $c/\ln(\eta_r)$ (○) for SEP1 in n-dodecane/1,4-dioxane (10:90) at 25 °C.

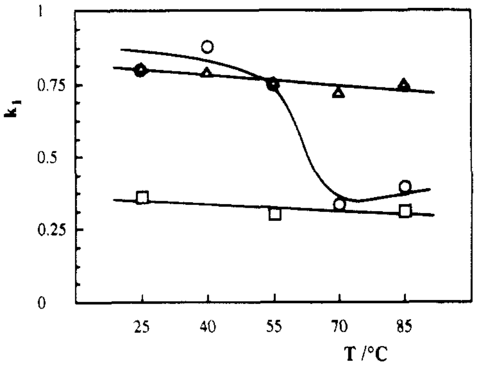

Figure 10. Temperature dependence of Huggins coefficients, k_1, for SEP1 in n-dodecane/1,4-dioxane mixtures with different n-dodecane percentages: 20% (○), 50% (□), and 100% (△).

The linear relationships of viscosity data and concentration found for all the systems suggest that the hydrodynamic dimensions of the micelles are relatively constant with the concentration. The linear relationships allowed us to determine the Huggins coefficients, k_1. The obtained k_1 values were greater than 0.5 for all systems where micelles exist, decreasing below this value when micelles disappear either by temperature increase or by change in solvent mixture composition.

The temperature dependencies of the Huggins coefficients for different compositions of the solvent system are plotted in Figure 10. This figure shows how whereas the micelle–free chain equilibrium overwhelmingly favors micelle formation (n-dodecane) or free chain presence (n-dodecane/1,4-dioxane (50:50)), the Huggins coefficient hardly depends on temperature. On the contrary, for the solvent system n-dodecane/1,4-dioxane (20:80), where a temperature increment into the experimental range studied leads to a displacement of the micelle–free chain equilibrium to free chain concentration, an abrupt decrease of k_1 is observed to reach proper values of a homopolymer in a good solvent.

Figure 11 shows the variation of the Huggins coefficient with the solvent composition at 25 °C. Only those solvent compositions which do not allow micelle formation show k_1 values less than 0.5. On comparing both ends of the composition range, k_1 values are higher for solvent mixtures with higher content of 1,4-dioxane, as expected for solutions in which the micelles have a higher aggregation number.

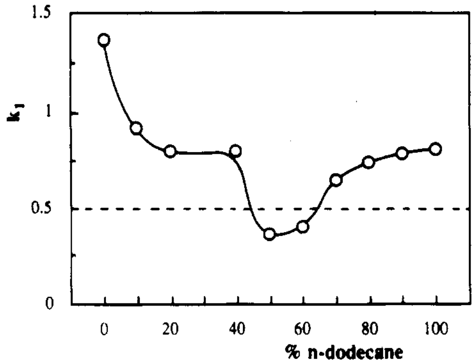

Figure 11. Variation of Huggins coefficient, k_1, as a function of *n*-dodecane percentage for SEP1 in *n*-dodecane/1,4-dioxane mixtures at 25 °C.

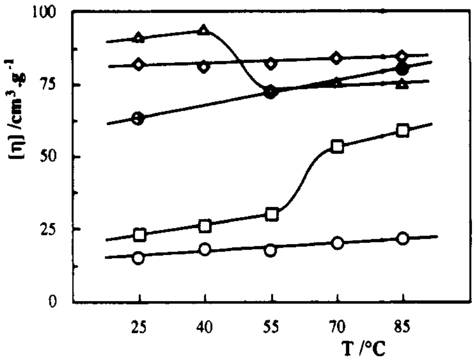

Figure 12. Temperature dependence of limiting viscosity number, [η], for SEP1 in *n*-dodecane/1,4-dioxane mixtures with different *n*-dodecane percentages: 0% (○), 20% (□), 50% (⊕), 80% (△), and 100% (◇).

In Figure 12 the variations of the limiting viscosity number as a function of the temperature for several compositions of the binary solvent system are plotted. As can be seen in this figure, the limiting viscosity number corresponding to the unassociated copolymer (50% of *n*-dodecane) shows a value between those corresponding to both types of micelles (*n*-dodecane and 1,4-dioxane). Thus, when the micelles with a core of PEP are broken by a temperature increase, the limiting viscosity number increases. On the contrary, when the micelles with a core of PS are broken, the limiting viscosity number decreases.

If the hydrodynamically equivalent sphere model is applied to the spherical micelles, the limiting viscosity number can be expressed by

$$[\eta] = \frac{10\pi N_A}{3}\frac{R_\eta^3}{M} \tag{6}$$

where N_A is Avogadro's number and M and R_η are the molar mass and the hydrodynamic radius of the micelles. According to eq 6, the limiting viscosity number is inversely proportional to the density compactness of the micelles. This explains why SEP1 shows a lower value of [η] in 1,4-dioxane than in *n*-dodecane. Since the poly(ethylene/propylene) block is longer than the polystyrene block, the width of the micelle solvated shell in *n*-dodecane is greater than in 1,4-dioxane. Therefore, the micelles are less compact in *n*-dodecane solutions than in 1,4-dioxane solutions.

The hydrodynamic radius of the micelles has been calculated by means of eq 6, and its values are shown in Table II. As can be seen, the hydrodynamic radius of the micelles hardly depends on the temperature. On the other hand, the micelles formed in solutions with an excess of 1,4-dioxane have a lower hydrodynamic radius than those formed in solutions with an excess of *n*-dodecane. Taking into account that the micelle shell is highly solvated whereas the micelle core hardly contains solvent molecules, the hydrodynamic radius becomes larger when the largest copolymer block forms the micelle shell. In our systems this is the case for the mixtures with a high content of *n*-dodecane.

Table II
Values of the Hydrodynamic Radius (nm) Calculated for the Micelles at Several Temperatures and Solvent Compositions

	% *n*-dodecane					
T, °C	0	10	20	80	90	100
25	31.4	32.2	33.0	46.2	46.8	46.7
40	33.1		33.6			46.2
55	32.4	34.8	36.5		44.6	44.9
70	32.8					44.1
85	32.4					37.6

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