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

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ABSTRACT: The thermodynamics of micelle formation by a polystyrene-*block*-poly(ethylene/propylene) copolymer (PS-*b*-PEP) in *n*-dodecane/1,4-dioxane mixtures was investigated. *n*-Dodecane is a good solvent for the PEP block and a poor solvent for the PS block, whereas 1,4-dioxane is a good solvent for the PS block and a poor solvent for the PEP block. The temperature dependence of the critical micelle concentration was determined at different copolymer concentrations from light scattering intensity measurements as a function of temperature. Light scattering results 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 found to be negative and markedly dependent on the composition of the solvent mixture. The standard entropies were unfavorable to micelle formation, and the standard enthalpies are solely responsible for micelle formation. No micelle structures were detected in the *n*-dodecane/1,4-dioxane mixtures with similar percentages of both solvents.

Introduction

Spherical micelles are usually formed in dilute solutions of block copolymers in selective solvents that thermodynamically favor one block but, at the same time, are unfavorable to others. Each of these consists of a compact core composed primarily of chain segments of the soluble block surrounded by a shell of chain segments of the soluble block.[1,2] At concentrations above the so-called critical micelle concentration (cmc), all copolymer chains added to the solution aggregate to form block copolymer micelles. Thus, the critical micelle concentration is defined as the concentration at which the experimental method in use can just detect the presence of micelles in the system as the concentration is increased at constant temperature.

A thermodynamic study of micelle formation can be carried out from the temperature dependence of the critical micelle concentration. It is assumed in the analysis that micellization is a single-stage equilibrium between unassociated copolymer molecules and micelles with an association number m[3]

$$mA_1 \rightleftarrows A_m \tag{1}$$

It is also assumed that m is independent of temperature and that the copolymer solution can be considered as ideally dilute except for intramicelle interactions between copolymer molecules.

For micelles having a narrow size distribution, the standard Gibbs energy of micellization per mole of copolymer chain is given by

$$\Delta G° \simeq RT \ln (\mathrm{cmc}) - RTm^{-1} \ln ([A_m]) \tag{2}$$

For copolymer systems with a high enough association number and a low micelle concentration, the second term of the above equation is very small and so

$$\Delta G° \simeq RT \ln (\mathrm{cmc}) \tag{3}$$

If the association number is independent of temperature, the above equation and the Gibbs–Helmholtz equation yield

$$\Delta H° \simeq R \frac{\mathrm{d} \ln (\mathrm{cmc})}{\mathrm{d}T^{-1}} \tag{4}$$

This equation allows one to estimate the contribution of the enthalpy term to the standard Gibbs energy of micellization, and from both magnitudes it is possible to determine the standard entropy of micellization, $\Delta S°$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{5}$$

The standard enthalpy of micellization, $\Delta H°$, can also be determined from direct calorimetric measurements.[4–6] Though this last method is the most satisfactory from a thermodynamic standpoint, both approaches lead to similar values for block copolymers as Price et al.[7] have reported. The agreement of results of both methods supports the assumptions that block copolymers undergo closed association in dilute solutions to form micelles and that the association number of micelles is independent of temperature. The use of the closed association model in treating the thermodynamic data is also supported by the narrow size distribution that the spherical copolymer micelles have as electron micrographs of micellar particles isolated from dilute copolymer solutions show.[8–10]

Although block copolymer micelles have certain features in common with surfactant micelles formed in aqueous media, the thermodynamic factors responsible for association in both cases are quite different. For surfactant molecules in aqueous media, a positive standard entropy of micellization is the thermodynamic factor mainly responsible for micelle formation. Thus, the standard enthalpy of micellization is generally small and positive or negative depending on the system.[4,5] For block copolymers in organic solvents, the standard enthalpy of micellization is solely responsible for micelle formation.[11–13] The entropy is negative and therefore unfavorable to micelle formation as would be expected from simple statistical arguments. In thermodynamic investigations of copolymer micellization there can exist difficulties due to rate effects, in contrast to the micellization of oligomers, which, in general, is very rapid. On the other hand, the presence of solvent in the cores of the block copolymer

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micelles increases the rate at which the free chain–micelle equilibrium is achieved. Therefore, the existence of solvent in the micelle cores and its concentration can be important factors in reaching thermodynamic equilibrium.[14,15]

In the present study, the thermodynamics of micelle formation of a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane mixtures of different compositions was investigated. 1,4-Dioxane is a selectively poor solvent for poly(ethylene/propylene), whereas *n*-dodecane is a selectively poor solvent for polystyrene. Both solvents can be practically considered isorefractive over the whole temperature range studied. Light scattering measurements have been carried out to determine the dependence of the critical micelle concentration on temperature. Light scattering is an appropriate technique to determine the critical micelle concentration due to the fact that light scattering intensity rises markedly in the presence of large particles.[16]

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. The weight-average molar mass of SEP1 determined by light scattering in tetrahydrofuran and chloroform at 25 °C was 1.05×10^5 g·mol^{-1}. The difference of molar mass in both solvents was smaller than the experimental error. As both solvents have different refractive indexes, this copolymer can be considered homogeneous in chemical composition. The ratio of the weight-average molar mass to number-average molar mass of SEP1 determined by gel permeation chromatography (SEC) at 25 °C using chloroform as solvent and a standard polystyrene calibration was 1.08. UV spectroscopy of SEP1 in tetrahydrofuran showed that SEP1 contains $34 \pm 3\%$ by weight polystyrene.

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. The copolymer solutions were filtered at room temperature directly into the scattering cells, which were then sealed.

Light scattering measurements were made using a modified FICA 42000 equipped with a He–Ne laser (Spectra-Physics, Model 105) which emits vertically polarized light at 632.8 nm with a power of 5 mW.

Investigations of the thermodynamics of micellization of block copolymers in organic solvents[10,13] have shown that it is far better experimentally to carry out measurements in which the concentration is kept constant and the scattered light intensity is monitored over a range of temperatures in order to find the critical micelle temperature (cmt) than keeping the temperature constant and varying the concentration so as to find the critical micelle concentration. The critical micelle temperature of a solution at a given concentration is the temperature at which the formation of micelles can just be detected experimentally. Therefore, for block copolymers in organic solvents it has been shown[13] that within the experimental error

$$\frac{d \ln (\mathrm{cmc})}{dT^{-1}} = \frac{d \ln (c)}{d(\mathrm{cmt})^{-1}} \qquad (6)$$

Thus, eq 4 becomes

$$\Delta H^\circ \simeq R \frac{d \ln (c)}{(\mathrm{cmt})^{-1}} \qquad (7)$$

To establish critical micelle temperatures in the solvent mixtures, measurements of light scattered intensity were made at a series of temperatures within the range 25–90 °C at three scattering angles (45°, 90°, and 135°).

Solution concentrations were recalculated at the critical micelle temperatures. As used polymer solutions were diluted, we have assumed that the solutions have the same thermal expansion coefficient as that of pure solvent.

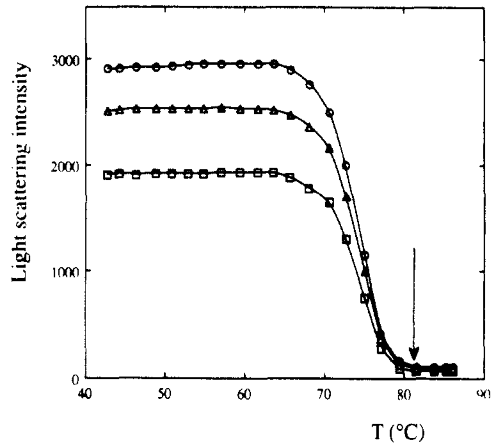

Figure 1. Plot of light scattering intensity against temperature for a solution of the polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane (10/90). The concentration of the solution was 1.22×10^{-4} g·cm^{-3}, and the scattering angles were 45° (○), 90° (□), and 135° (△).

Results and Discussion

The thermodynamic equations described in the Introduction correspond to a single system block copolymer/solvent. When copolymer is dissolved in a solvent mixture, the thermodynamic treatment becomes very complex. The expressions of the chemical potentials include more terms due to the preferential adsorption of a solvent by micelles. However, we shall use the above equations as a simplified treatment without considering the extra terms. This simplification is validated by the experimental results described in the second paper.[17]

The relationship of concentration and cmt for SEP1 in *n*-dodecane and *n*-dodecane/1,4-dioxane mixtures of different compositions (10/90, 20/80, 40/60, 70/30, and 80/20) was determined. It was not possible to find this relationship for pure 1,4-dioxane because cmt's are higher than the maximum temperature that our experimental device allows us to reach. To find lower cmt's we must employ solutions of so low concentration that the light scattering technique does not allow us to study them. Considering that the cmt corresponding to a solution of concentration 4.0×10^{-7} is higher than 85 °C, we can say that the cmc at 85 °C is lower than this concentration. So, the standard Gibbs energy of the micellization of SEP1 in 1,4-dioxane at 85 °C is lower than −57.7 kJ·mol^{-1}.

On the other hand, for the solvent mixtures of compositions 50/50 and 60/40 (v/v) no micelle formation was detected in solutions of concentration around 5×10^{-3} g·cm^{-3} at 25 °C. Therefore, it is possible to say that for these solvent mixtures the standard Gibbs energy of micellization at 25 °C is higher than −24 kJ·mol^{-1}. Solutions of higher concentrations were not studied because we would have gone into the range of semidilute and concentrated solutions. In this region it seems that the copolymer does not form multimolecular micelles but a periodic regular structure.[18]

A plot of light scattering intensity at 45°, 90°, and 135° versus temperature for SEP1 at a concentration of 1.22×10^{-4} g·cm^{-3} in *n*-dodecane/1,4-dioxane (10/90) is shown in Figure 1. The shape of the plot is due to the influence of temperature on the equilibrium between micelles and free chains. At low temperatures the equilibrium is overwhelmingly in favor of micelle formation, whereas at the upper end of the temperature range studied only free chains exist in the solution. Lowering the temperature, a sharp increase in scattering intensity is observed due to the appearance of micelles. Increasing and decreasing the

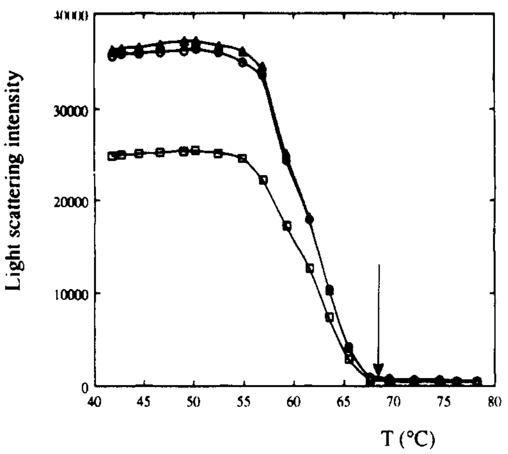

Figure 2. Plot of light scattering intensity versus temperature for a solution of the polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane (20/80). The concentration of the solution was 6.06×10^{-3} g·cm^{-3}, and the scattering angles were 45° (○), 90° (□), and 135° (△).

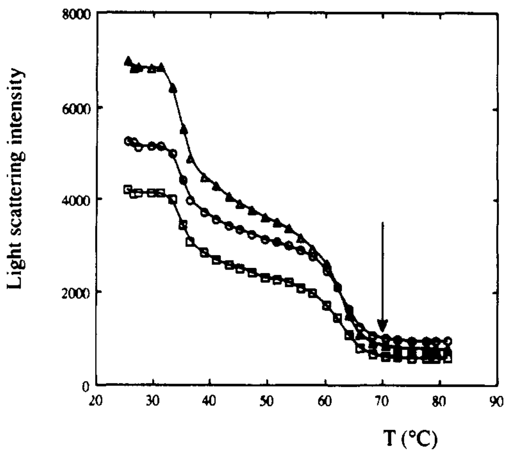

Figure 3. Plot of light scattering intensity against temperature for a solution of the polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane (80/20). The concentration of the solution was 1.08×10^{-2} g·cm^{-3}, and the scattering angles were 45° (○), 90° (□), and 135° (△).

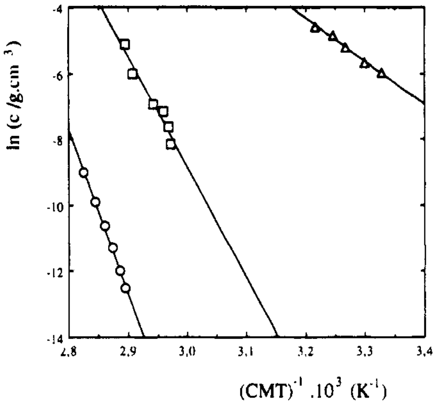

Figure 4. Plots of the logarithm of the solution concentration as a function of the reciprocal of the critical micelle temperature for the polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane mixtures with 1,4-dioxane excess: 10/90 (○), 20/80 (□), and 40/60 (△).

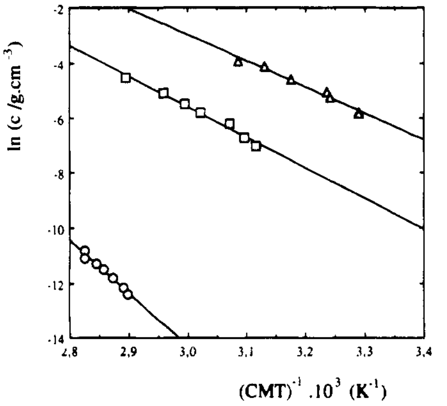

Figure 5. Plots of the logarithm of the solution concentration as a function of the reciprocal of the critical micelle temperature for the polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-dodecane (○) and in *n*-dodecane/1,4-dioxane mixtures with *n*-dodecane excess: 80/20 (□) and 70/30 (△).

temperature, we obtain curves $I = f(T)$ that are coincident in all the cases. The temperature at which the presence of micelles in the solution can just be detected is considered as the critical micelle temperature. Plots similar in shape to the one shown in Figure 1 were also obtained for most of the solutions studied.

We have found some different shapes for solutions with a relatively high concentration. A plot of scattered intensity against temperature for SEP1 at a concentration of 6.06×10^{-3} g·cm^{-3} in the *n*-dodecane/1,4-dioxane mixture of composition 20/80 is shown in Figure 2. As can be seen in this figure, at the lower end of the temperature range the intensity scattered at 45° is lower than that scattered at 135°. So, at low temperatures, the dissymmetry factor, Z, i.e., the ratio of the scattering intensities at 45° and 135°, shows values less than unity. This behavior could be predicted by assuming that the micelles pack together like hard spheres.[19] As the temperature increases, the micelle–free chain equilibrium is displaced in the direction of the free chain concentration. Decreasing the micelle concentration, the micelle package disappears and the system behaves as at low concentrations.

For the *n*-dodecane/1,4-dioxane (80/20) mixture the curves of light scattering intensity versus temperature show a singular shape. A plot of scattered intensities at 45°, 90°, and 135° against temperature for SEP1 at a concentration of 1.08×10^{-2} g·cm^{-3} is shown in Figure 3. As can be seen in this figure, two sharp increases of the intensity appear as temperature decreases. The first abrupt increase is caused by the appearance of the first micelles. As temperature decreases, the intensity scattered at 135° becomes higher than that scattered at 45° because of increasing the micelle concentration, these pack together, as in other solvent mixtures with high copolymer concentrations. Lowering the temperature more, a second rapid increase in scattering intensity appears at 38 °C over a fairly narrow range. This second increase in scattering intensity occurs also at lower concentrations, though it is less appreciable.

Plots of ln (c) as a function of (cmt)$^{-1}$ for solutions of SEP1 in *n*-dodecane/1,4-dioxane mixtures with a high content of 1,4-dioxane are shown in Figure 4. All of these plots were linear within the experimental error over the dilute solution range studied. It can be seen in this figure how as the *n*-dodecane content increases, the slope of the straight line decreases. Plots of ln (c) as a function of (cmt)$^{-1}$ for solutions of SEP1 in *n*-dodecane/1,4-dioxane mixtures with a high content of *n*-dodecane are shown in Figure 5. As in Figure 4, all plots were linear over the dilute solution range studied. However, the slopes have a lower dependence on the solvent composition.

The values of the standard Gibbs energy ($\Delta G°$), the standard enthalpy ($\Delta H°$), and the standard entropy of micellization ($\Delta S°$) have been calculated from the experimental data by means of eqs 3–5. The standard Gibbs energy of micellization shows negative values for the polystyrene-*block*-poly(ethylene/propylene) copolymer in all solvent mixtures studied in which micelles were

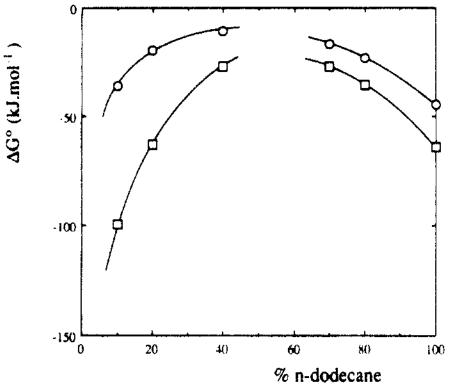

Figure 6. Variation of the standard Gibbs energy of micellization as a function of the composition of the *n*-dodecane/1,4-dioxane mixture. T = 25 °C (□) and T = 85 °C (○).

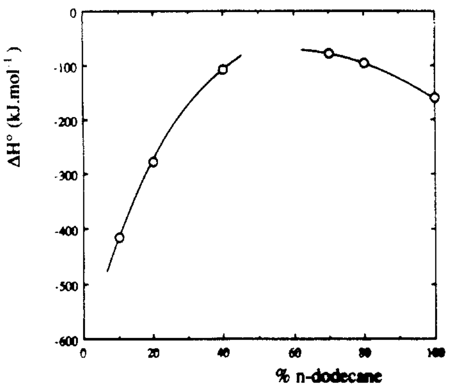

Figure 7. Variation of the standard enthalpy of micellization as a function of the composition of the *n*-dodecane/1,4-dioxane mixture.

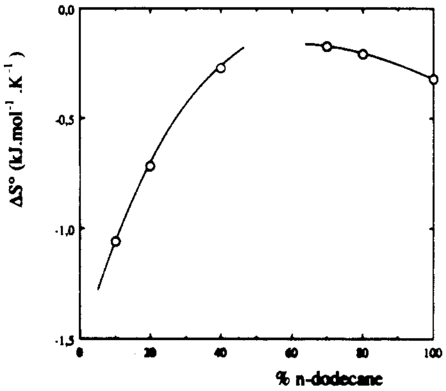

Figure 8. Variation of the standard entropy of micellization as a function of the composition of the *n*-dodecane/1,4-dioxane mixture.

detected, as expected. The standard entropy of micellization is also negative for all of the systems studied and, thus, unfavorable to the micellization process. The negative values of the standard entropy of micellization can be explained by simple statistical arguments. The fact that the copolymer chains are less swollen in the micelles than are free chains leads to a loss in combinatorial entropy. The standard enthalpy of micellization also shows negative values for all of the systems studied. These negative values result from the exothermic interchange energy accompanying the replacement of polystyrene segment/*n*-dodecane interactions by polystyrene segment/polystyrene segment and *n*-dodecane/*n*-dodecane interactions for one case (mixtures with a high content of *n*-dodecane) or poly(ethylene/propylene) segment/1,4-dioxane interactions by poly(ethylene/propylene) segment/poly(ethylene/propylene) segment and 1,4-dioxane/1,4-dioxane interactions for the other case (mixtures with a high content of 1,4-dioxane) in the formation of the micelle cores. The experimental results show that for the polystyrene-*b*-poly(ethylene/propylene) copolymer in *n*-dodecane/1,4-dioxane mixtures the enthalpy is solely responsible for the micelle formation, in agreement with different copolymer/organic solvent systems reported.[10,13,20-22]

The variation of the standard Gibbs energy of micellization, $\Delta G°$, for 25 and 85 °C as a function of the *n*-dodecane percentage in the solvent mixture is plotted in Figure 6. As can be seen in this figure, the standard Gibbs energy of micellization is less negative as the proportion of both solvents becomes similar; i.e., the mixing of two selective solvents causes a decrease in the copolymer capacity to form micelles in the solvent mixture. Also it can be observed in Figure 6 how the variation of $\Delta G°$ as a function of the solvent mixture composition for both extremes of the composition range has a different behavior. The variation of $\Delta G°$ with temperature also depends on the composition of the solvent mixture composition. For a better understanding of the behavior of the Gibbs energy of micellization, it is necessary to decompose it into the enthalpy and entropy contributions.

The variation of the standard enthalpy of micellization, $\Delta H°$, as a function of the *n*-dodecane percentage in the solvent mixture is plotted in Figure 7. As can be observed in this figure, $\Delta H°$ is more negative for solvent mixtures with low content of *n*-dodecane than for those with high content. To explain this fact it is necessary to take into account the different structures of the micelles in both ranges of the solvent mixture composition and the sizes of both blocks of the copolymer. The micelles existing in the solvent mixtures with a low percentage of *n*-dodecane consist of a swollen core of poly(ethylene/propylene) surrounded by a flexible fringe of polystyrene, whereas in solvent mixtures with a high percentage of *n*-dodecane the core is formed by polystyrene block and the fringe by poly(ethylene/propylene) blocks. Taking into account that the poly(ethylene/propylene) block has a molar mass 1.94 times larger than the polystyrene block, the exothermic interchange energy per mole of copolymer accompanying the replacement of copolymer block/solvent interactions by copolymer block/copolymer block and solvent/solvent interactions when the micelle core is formed is higher for a micelle core of poly(ethylene/propylene) than for a micelle core of polystyrene. Therefore, the standard enthalpy of micellization has more negative values when the *n*-dodecane/1,4-dioxane mixture has a low content of *n*-dodecane.

The variation of the standard entropy of micellization, $\Delta S°$, as a function of the solvent mixture composition is plotted in Figure 8. The same $\Delta S°$ values were found at all temperatures studied as expected from eqs 3–5. As can be seen in this figure, $\Delta S°$ is also more negative in solvent mixtures with a low content of *n*-dodecane than in mixtures with a high content of *n*-dodecane. The explanation of this behavior is supported by the same arguments as above. The proportion of copolymer making up the micelle core is higher in solvent mixtures with a lower *n*-dodecane content. Therefore, the loss in combinatorial entropy becomes larger as the number of monomeric units forming the micelle core increases. The more negative values of $\Delta S°$ for *n*-dodecane/1,4-dioxane mixtures with a low content of *n*-dodecane explained the fact that the temperature dependence of the standard Gibbs energy of micellization is greater for these solvent mixtures than for those with a higher content of *n*-dodecane.

On the other hand, it can be observed in Figures 7 and 8 that both ΔH° and ΔS° become less negative as the content of the minor solvent in the mixture increases. This phenomenon is caused by the copolymer segment/solvent interactions. Considering the solvent mixtures with a low content of *n*-dodecane, the negative values of ΔH° arise from the replacement of poly(ethylene/propylene) segment/1,4-dioxane by poly(ethylene/propylene) segment/poly(ethylene/propylene) segment and 1,4-dioxane/1,4-dioxane interactions in formation of the micelle cores. Then, on adding *n*-dodecane to copolymer solution in 1,4-dioxane, a part of the poly(ethylene/propylene) segment/1,4-dioxane interactions is replaced by poly(ethylene/propylene) segment/*n*-dodecane interactions since *n*-dodecane is a good solvent for poly(ethylene/propylene) and a poor solvent for polystyrene. This way, the number of poly(ethylene/propylene)/1,4-dioxane interactions which are replaced by poly(ethylene/propylene) segment/poly(ethylene/propylene) segment and 1,4-dioxane/1,4-dioxane in formation of the micelle cores is smaller and therefore ΔH° becomes less negative. The loss in combinatorial entropy, which occurs when the micelle core of poly(ethylene/propylene) is formed, decreases as the content of *n*-dodecane increases in the solvent mixture since *n*-dodecane, being a good solvent for poly(ethylene/propylene) and a poor solvent for polystyrene, will be preferentially adsorbed by the micelle core, increasing the combinatorial entropy. Similar arguments explain that ΔH° and ΔS° also become less negative when 1,4-dioxane is added to copolymer solutions in *n*-dodecane.

It seems likely from the evidence presented that the thermodynamics of micellization of polystyrene-*block*-poly(ethylene/propylene) in *n*-dodecane/1,4-dioxane mixtures depends mainly on the interactions between the copolymer segments forming the micelle core and the solvent molecules. Finally, the experimental results point out that the mixture of two selective solvents corresponding to both copolymer blocks may hinder the formation of copolymer micelles.

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