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Micellization of a Polystyrene-*block*-poly(ethylene/propylene) Copolymer in *n*-Alkanes. 2. Structural Study

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ABSTRACT: The concentration and temperature dependences of micelle formation by a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-hexadecane are examined by light scattering and viscometry. At concentrations above the cmc an unusually large scattering intensity is found. The experimental dependences of light scattering and viscosity data on the concentration were always linear within the concentration range of 1×10^{-3} to 5×10^{-3} g·cm^{-3} for all the *n*-alkanes and temperatures studied. Molar mass and dimension of the micelles have been found to be independent of temperature. The variation of weight-average molar mass and hydrodynamic radius with the carbon number of the *n*-alkane shows a minimum for *n*-octane at higher temperatures (70 °C), whereas at low temperatures (25 °C) these magnitudes increase as the carbon number of the *n*-alkane increases. This behavior agrees with the values of the standard Gibbs energy of micellization that we have found for the different *n*-alkanes. Small and positive values of the second virial coefficient have been found, and they can be explained by taking into account that the formation of micelles leads to less unfavorable contacts between the polystyrene segments and the *n*-alkane molecules. The apparent radius of gyration of the micelles hardly depends on the *n*-alkane except for *n*-heptane. A larger value of the apparent radius of gyration has been found in this solvent. 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. The hydrodynamic radius varies with temperature and carbon number of the *n*-alkane in a very similar way to the weight-average molar mass. We have found that temperature and solvent markedly influence the free chain–micelle equilibrium. However, this influence is relatively small on the molar mass and size of the micelles.

Introduction

The influence of selective solvent on the thermodynamics of micellization of a polystyrene-*block*-poly(ethylene/propylene) copolymer in dilute solutions of *n*-alkanes has been investigated in a previous paper.[1] In that paper, the thermodynamic quality of the solvent was modified by using *n*-alkanes of different carbon numbers. Plots of ln (*c*) against (cmt)$^{-1}$ were linear over the dilute solution range studied. The values of the standard Gibbs energy, $\Delta G°$, the standard enthalpy, $\Delta H°$, and the standard entropy, $\Delta S°$, of micellization have been calculated for the different *n*-alkanes. The results showed that the enthalpy contribution to the Gibbs energy is solely responsible for the micelle formation of polystyrene-*block*-poly(ethylene/propylene) in all the studied *n*-alkanes. The entropy contribution is unfavorable to the micelle formation, contrary to what happens with micromolecular surfactants in aqueous media. The large exothermic interchange of energy accompanying replacement of many polystyrene segment/*n*-alkane interactions by polystyrene segment/polystyrene segment and *n*-alkane/*n*-alkane interactions on formation of the micellar cores is the cause of the observed negative enthalpy change.

The standard Gibbs energy of micellization becomes more negative as the carbon number of the *n*-alkane increases except for *n*-heptane and *n*-hexane at high temperature. On the other hand, the standard enthalpy of micellization decreases with the carbon number of the *n*-alkane, showing a sharp diminution up to *n*-octane, keeping almost constant for higher *n*-alkanes. The values of the standard entropy of micellization are similar for *n*-octane, *n*-decane, and *n*-dodecane, but they are much smaller for *n*-heptane and *n*-hexane.

In this paper, light scattering has been used to characterize the variation of the weight-average molar mass, M_w, the radius of gyration, R_G, and the second virial coefficient, A_2, as a function of the carbon number of the *n*-alkane and of the temperature. Viscometry has been used as a complementary technique. The hydrodynamic radius of the micelles has been calculated from the values of the limiting viscosity number and the weight-average molar mass.

Experimental Section

The molecular characteristics of the polystyrene-*block*-poly(ethylene/propylene), SEP1, and the purity of the *n*-alkanes are reported in the previous paper.[1]

Solutions were prepared by dissolving the copolymer in the *n*-alkanes at 90–100 °C. For *n*-hexadecane, frequent agitation of the solutions was required for periods up to 24 h to ensure that all the copolymer was dissolved. 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.

The viscosity measurements were made in a Lauda Model Viscoboy 2 automatic Ubbelohde viscometer, 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 carry out by means of the equation

$$\eta = A\rho t - B\rho/t \qquad (1)$$

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 $1 \times 10^{-3} \leq c$ (g·cm^{-3}) $\leq 5 \times 10^{-3}$; the basic solution was diluted directly in the viscometer. The intrinsic viscosities are calculated by extrapolation methods.

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 light source and optical block of the incident beam were replaced by a He–Ne laser (Spectra Physics Model 105) which emits vertically polarized light at 632.8 nm with a power of 5 mW. The photogoniodiffusometer was

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Table I
Values of d*n*/d*c* (*A*) and Solvent Refractive Index (*C*) at 25 °C and Their Temperature Dependences (*B* and *D*) for Copolymer SEP1 and *n*-Alkanes Used

solvent	A	$B \times 10^4$	C	$D \times 10^4$
n-hexane	0.170	3.3	1.371	5.9
n-heptane	0.142	5.7	1.383	5.1
n-octane	0.130	4.7	1.395	4.6
n-decane	0.109	2.5	1.408	4.4
n-dodecane	0.100	2.0	1.418	4.3
n-hexadecane	0.083	1.6	1.431	3.7

calibrated with pure benzene, taking the Rayleigh ratio at 25 °C as 12.55×10^{-6} cm^{-1}.[2]

The light scattered by a dilute polymer solution may be expressed as[3]

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

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 vacuum, and A_2 the second virial coefficient.

The application of light scattering theory to diblock copolymer solutions leads to the determination of an apparent weight-average molar mass and mean square radius of gyration.[4] In view of the small difference observed between the weight-average molar mass of the copolymer in tetrahydrofuran and 1-chlorobutane, the apparent M_w and R_G values should be close to the real values for the block copolymer used.

To estimate M_w and R_G, it is necessary to know the refractive index increments, d*n*/d*c*, 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 a solution of highly purified NaCl, using a He–Ne laser (Spectra Physics Model 156) which emits with a power of 1 mW as a light source.

Results and Discussion

Differential Refractometry. Temperature dependences of refractive index increment, d*n*/d*c*, have been determined between 25 and 70 °C, leading to the following relationship, in which d*n*/d*c* and *T* are expressed in mL·g^{-1} and °C, respectively:

$$\mathrm{d}n/\mathrm{d}c = A + B(T - 25) \quad (3)$$

A and *B* are numerical constants, and their values for each *n*-alkane are given in Table I.

Temperature dependences of solvent refractive index, n_0, have been determined between 25 and 70 °C, leading to the following relationship:

$$n_0 = C - D(T - 25) \quad (4)$$

C and *D* are numerical constants, and their values for each *n*-alkane are given in Table I.

In Figure 1, refractive index increments are plotted as a function of the solvent refractive index at 25 °C. As can be seen, the experimental results for the different *n*-alkanes agree with the equation

$$\mathrm{d}n/\mathrm{d}c = \bar{v}_2(n_2 - n_0) \quad (5)$$

This equation has been obtained assuming the additivity of volumes in the equation

$$\mathrm{d}n/\mathrm{d}c = v_2(n_2 - 1) - \bar{v}_2(n_0 - 1) \quad (6)$$

where n_2 and n_0 are the copolymer and solvent refractive index, and v_2 and $\bar{v}_2$ are the specific and partial specific volumes of the copolymer.

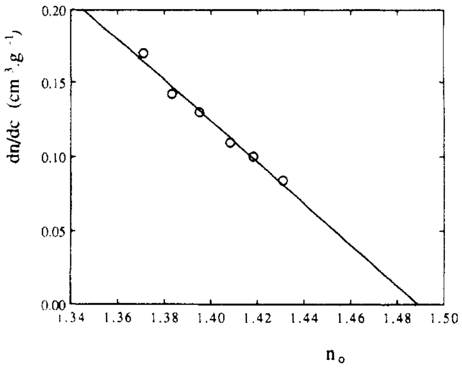

Figure 1. Plot of refractive index increment, d*n*/d*c*, against solvent refractive index, n_0, for copolymer SEP1 at 25 °C.

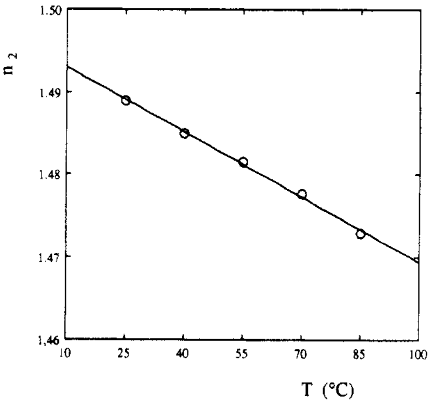

Figure 2. Temperature dependence of refractive index of copolymer SEP1.

From the experimental results plotted in Figure 1 and according to eq 6, we have found the values of 1.3919 cm^3·g^{-1} and 1.489 for the partial specific volume and the refractive index of the copolymer, respectively.

The same behavior has been found at higher temperatures. In Figure 2, values of the copolymer refractive index at several temperatures are plotted. As can be seen, its variation with temperature is linear.

Laser Light Scattering. Zimm plots have been obtained for the different *n*-alkanes at 25, 40, 55, 70, and 85 °C. The patterns of all Zimm plots are very similar for the different *n*-alkanes studied. Zimm plots for SEP1/*n*-octane at 25, 55, and 85 °C are shown in Figure 3. $Kc/\Delta R$ varies linearly with scattering angle, θ, for all concentrations and temperatures. However, the slope of each line decreases as the concentration increases, reaching negative values at the higher SEP concentrations. This phenomenon has been also reported by Price[5] for an SEP in *n*-decane, where they found that the dissymmetry ratio depended on concentration. According to Price, this behavior can be explained by considering that, on increasing the concentration, the micelles pack together like hard spheres.

In the same Figure 3, it can be seen how at high concentrations (>0.001 g/cm^3), the dependence of $Kc/\Delta R$ on concentration is linear as expected for concentrations very much higher than the critical micelle concentration.[1] The weight-average molar mass determined from the extrapolation of this straight line at null concentration can be considered at the true molar mass of the micelles since the copolymer sample had a low degree of chemical heterogeneity and under these experimental conditions the micelle formation is overwhelmingly favored. At lower copolymer concentrations, a sharp increase of $Kc/\Delta R$ is observed due to an increase of the number of free copolymer chains. This behavior is more marked as the

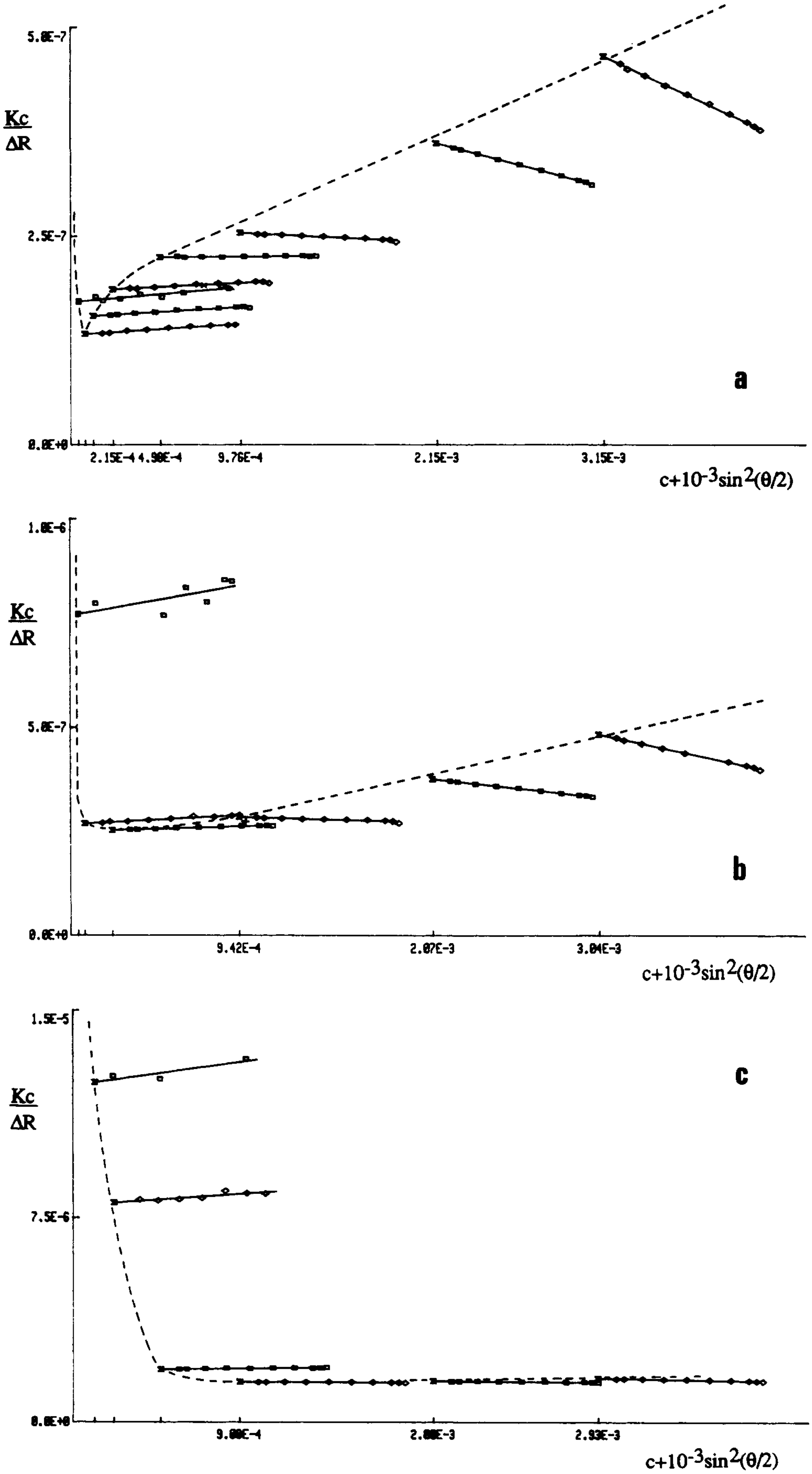

Figure 3. Plots of $Kc/\Delta R$ versus $c + 10^{-3}\sin^2(\theta/2)$ for SEP1 in *n*-octane at 25 (a), 55 (b), and 85 °C (c).

temperature increases due to the fact that the critical micelle concentration, cmc, of the system increases with temperature.[1]

On the other hand, as can be observed in Figure 3a, for concentrations near the cmc (see Table II), $Kc/\Delta R$ shows an anomalous behavior. This behavior has been reported in other copolymer/solvent systems and always at concentrations near the cmc.[6,7] Some authors[8] suggest the formation of a macrostructure, which would increase the weight-average molar mass. It has also been suggested

Table II
Values of cmc's (g·cm^{-3}) for Copolymer SEP1 in *n*-Alkanes at 25 and 85 °C

solvent	cmc (25 °C)	cmc (85 °C)
n-hexane	3.0×10^{-7}	1.0×10^{-5}
n-heptane	1.1×10^{-7}	6.6×10^{-5}
n-octane	6.3×10^{-9}	2.5×10^{-4}
n-decane	2.4×10^{-9}	1.1×10^{-4}
n-dodecane	6.4×10^{-10}	3.3×10^{-5}
n-hexadecane		$>2.7 \times 10^{-6}$

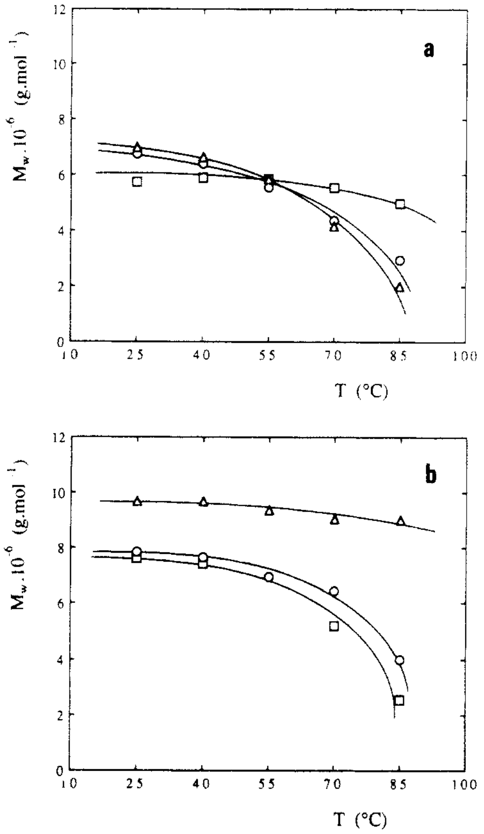

Figure 4. Temperature dependence of weight-average molar mass, M_w, for copolymer SEP1 in different *n*-alkanes: (a) *n*-hexane (□), *n*-heptane (○), and *n*-octane (△); (b) *n*-decane (□), *n*-dodecane (○), and *n*-hexadecane (△).

that this increase in the scattered intensity can be attributed to concentration fluctuations related to the micelle–free chain equilibrium.[9]

The temperature dependence of the weight-average molar mass of copolymer SEP1 for several *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-hexadecane) is shown in Figure 4. As can be observed, at high temperature the weight-average molar mass decreases abruptly except for *n*-hexane and *n*-hexadecane. 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. However, when the system is far above the cmc, the weight-average molar mass remains constant, which suggests that micelle molar mass does not depend on temperature. As can be seen in Table II, *n*-hexane and *n*-hexadecane have the lowest cmc values at 85 °C.

In Figure 5, the weight-average molar mass is plotted as a function of carbon number of *n*-alkane at several temperatures (25–85 °C). As can be seen, the pattern of these curves depends on the temperature; i.e., at 25 and 40 °C the weight-average molar mass increases as carbon number of *n*-alkane increases, while at 55, 70, and 85 °C the curves show a minimum for *n*-octane. The behavior observed at low temperature is probably due to the fact that, as carbon number increases, the solvent power of the *n*-alkane decreases, and this favors the micelle formation. Likewise, the observed behavior at high temperatures indicates that for *n*-octane the free-chain concentration is the higher. This fact agrees with the results reported in the previous paper,[1] where it is shown how, at 25 °C, the variation of the standard Gibbs energy of micellization becomes more negative as the carbon number increases. However, at 85 °C the $\Delta G°$ presents a maximum for *n*-octane.

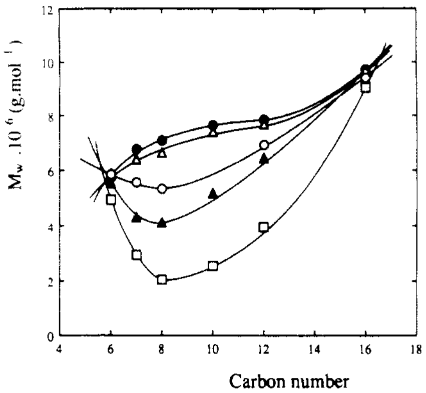

Figure 5. Dependence of weight-average molar mass, M_w, on carbon number of *n*-alkane for copolymer SEP1 in *n*-alkanes at different temperatures: 25 (●), 40 (△), 55 (○), 70 (▲), and 85 °C (□).

The radius of gyration of the micelles, R_G, has been determined as a function of *n*-alkane and temperature from laser light scattering measurements. It should be pointed out that the R_G values thus obtained are only apparent values, lower than the true ones due to the core–shell structure of the micelles. The polystyrene core has a larger refractive index increment in the *n*-alkanes than the poly(ethylene/propylene) shell. In Figure 6, R_G is plotted against temperature for all *n*-alkanes studied. In this figure we can see that the R_G values remain constant up to 70 °C with temperature. On the other hand, the obtained values are remarkably lower than expected for the weight-average molar masses. This is due to the fact that micelles have a compact and spherical structure and has been verified by TEM[10,11] and neutron diffraction.[12]

The curves corresponding to *n*-heptane, *n*-octane, *n*-decane, and *n*-dodecane show a sharp decrease for temperatures higher than 70 °C. This decrease in R_G is explained by a rise in the free-chain concentration and by the small dimensions of the copolymer chain. For *n*-hexane and *n*-hexadecane we have not found any variation of R_G on temperature. The constancy of R_G with T correlates the constancy previously observed of M_w with T for the same solvents.

Figure 7 shows the variation of the apparent radius of gyration as a function of the carbon number of the *n*-alkane. As can be seen, the values of R_G are similar for all *n*-alkanes except for *n*-heptane. This peculiar behavior appears for all temperatures. This increase in the micelle dimensions may suggest that the micelles are more solvated in *n*-heptane than in the rest of the *n*-alkanes studied. This fact seems logical if *n*-heptane is compared to the higher *n*-alkanes that have larger molecules and therefore more steric hindrance. However, for the same reason, the micelles in *n*-hexane would be more solvated than in *n*-heptane. We feed unable to offer any plausible explanation of this anomalous behavior at present.

The values of the second virial coefficient, A_2, have been determined from the concentration dependence of $Kc/\Delta R$ for concentrations between 0.001 and 0.005 g·cm^{-3}.

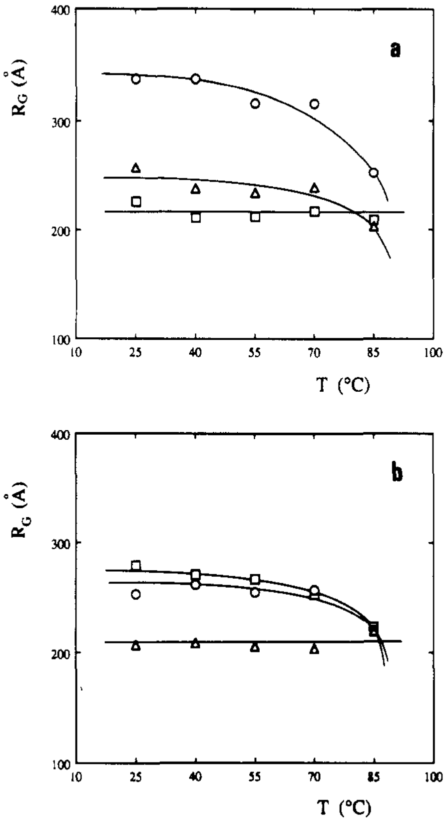

Figure 6. Temperature dependence of radius of gyration, R_G, for copolymer SEP1 in different *n*-alkanes: (a) *n*-hexane (□), *n*-heptane (○), and *n*-octane (△); (b) *n*-decane (□), *n*-dodecane (○), and *n*-hexadecane (△).

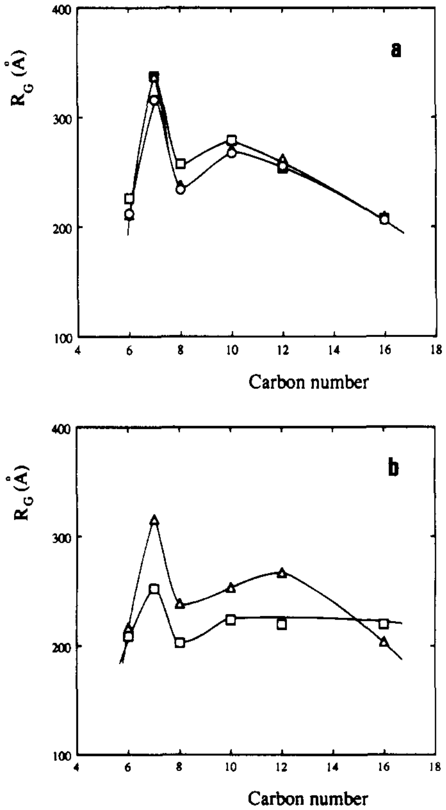

Figure 7. Dependence of radius of gyration, R_G, on carbon number of *n*-alkane for copolymer SEP1 in *n*-alkanes at different temperatures: (a) 25 (□), 40 (△), and 55 °C (○), (b) 70 (△) and 85 °C (□).

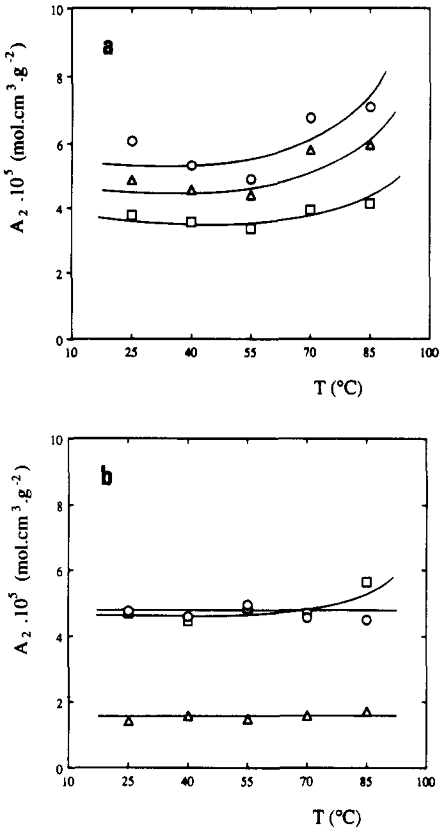

Figure 8. Temperature dependence of second virial coefficient, A_2, for copolymer SEP1 in different *n*-alkanes: (a) *n*-hexane (□), *n*-heptane (○), and *n*-octane (△); (b) *n*-decane (□), *n*-dodecane (○), and *n*-hexadecane (△).

Assuming a segregated model with no contact between polystyrene and poly(ethylene/propylene) segments, A_2 is a weighted average between $A_{2,PS}$ and $A_{2,PEP}$. The second virial coefficient is plotted against temperature for the different *n*-alkanes in Figure 8. In all cases the second virial coefficient shows positive values, which can be explained by taking into account that the solvent is rejected from the core of the micelles, giving rise to less unfavorable contacts between the PS segments and the *n*-alkane molecules. On the other hand, the protective shell of solvated PEP segments hinders long-range PS segment/PS segment interactions. The second virial coefficients remain almost constant for all temperatures; only a slight increase with temperature, due to augmentation of the quality of the solvent, is observed for some *n*-alkanes.

The variation of the second virial coefficient as a function of carbon number of the *n*-alkane molecule for different temperatures is plotted in Figure 9. As can be observed, the pattern of the curves is similar to the ones corresponding to the apparent radius of gyration. This fact seems logical since the dimensions of the micelles will depend on the solvation degree of the polymer segments and this will depend likewise on the polymer/solvent interactions.

Some of the weight-average molar mass and second virial coefficient values obtained are similar to the ones reported in the bibliography. So for our SEP1 copolymer in *n*-heptane at 25 °C we have found a micellar molar mass of $M_w = 6.8 \times 10^6$ and a second virial coefficient of $A_2 = 6.1 \times 10^{-5}$ cm^3·mol·g^{-2}. Yeung et al.[13] gave $M_w = 6.8 \times 10^6$ and $A_2 = 3.6 \times 10^{-5}$ cm^3·mol·g^{-2} for an SEP copolymer with a molar mass of 1.15×10^5 and a styrene content of 37% by weight in the same experimental conditions. On the other hand, for the system SEP1/*n*-decane at 25 °C, we have found a micelle molar mass of $M_w = 7.6 \times 10^6$ and a second virial coefficient of $A_2 = 4.7 \times 10^5$ cm^3·mol·g^{-2}. In the same experimental conditions, Price et al.[14] reported $M_w = 6.5 \times 10^6$ for an SEP copolymer with a molar mass of 1.06×10^5 and a styrene content of 38% by weight, and

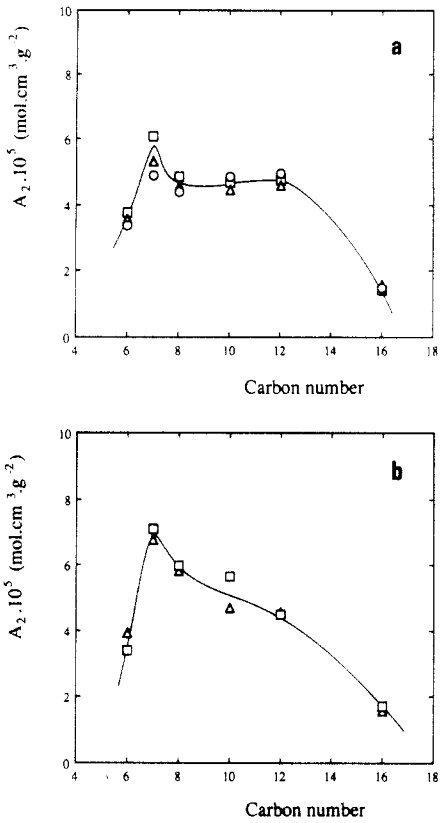

Figure 9. Dependence of second virial coefficient, A_2, on carbon number of n-alkane for copolymer SEP1 in n-alkanes at different temperatures: (a) 25 (□), 40 (△), and 55 °C (○); (b) 70 (△) and 85 °C (□).

Mandema et al.[8] gave $M_w = 4 \times 10^6$ and $A_2 = 2.4 \times 10^{-5}$ cm^3·mol·g^{-2} for an SEP copolymer with a molar mass of 4.8×10^4 and a styrene content of 38% by weight.

Viscometry. The experimental dependences of the reduced viscosity, η_{sp}/c, and of the logarithmic viscosity number, $\ln(\eta_r)/c$, on the concentration were always linear within the concentration range employed for all n-alkanes and temperatures studied. However, the extrapolation to zero concentration according to the Huggins and Kraemer equations leads to different values of the limiting viscosity number, $[\eta]$. This behavior can be explained if we take into account that model calculations[15] based on the Baker equation[16] indicate that if the Huggins coefficient, k_1, is higher than 0.5, the concentration dependences of η_{sp}/c and $\ln(\eta_r)/c$ are curved and the linear extrapolation according to the Huggins equation will give lower limiting viscosity number and higher Huggins coefficient values. This is the case of micelle solutions, where values of Huggins coefficients higher than 0.5 have been reported.[8,13] In our systems, we had found linear concentration dependences, but in a small concentration range, which does not allow us to know if there exists a curvature at concentrations lower than 2×10^{-3} g·cm^{-3}. This concentration range has been chosen to achieve experimental conditions that overwhelmingly favor the micelle formation, since at lower concentrations the free chain–micelle equilibrium will influence the concentration dependence.

As an alternative extrapolation we have used the Heller equations[17]

$$\frac{c}{\eta_{sp}} = \frac{1}{[\eta]} - k_1 c \qquad (7)$$

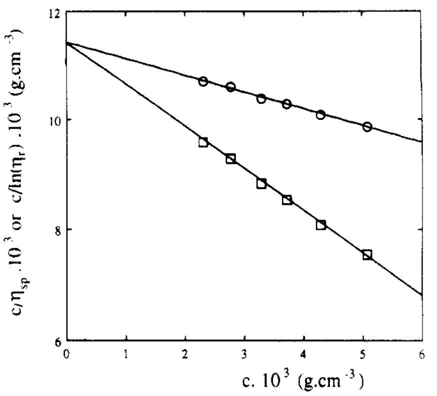

Figure 10. Concentration dependences of c/η_{sp} (□) and $c/\ln(\eta_r)$ (○) for copolymer SEP1 in n-octane at 25 °C.

$$\frac{c}{\ln(\eta_r)} = \frac{1}{[\eta]} + k_1'c \qquad (8)$$

which are readily obtained from the Huggins and Kraemer equations. Equations 7 and 8 are recommended when the Huggins coefficient is higher than 0.5.[15] The concentration dependences of c/η_{sp} and $c/\ln(\eta_r)$ for copolymer SEP1 in n-octane at 25 °C are plotted in Figure 10. As can be seen, both equations extrapolate to the same value of limiting viscosity number. For all the studied copolymer/n-alkane/temperature systems, the experimental dependences of c/η_{sp} and $c/\ln(\eta_r)$ on the concentration were always linear within the concentration range employed, and the same value of limiting viscosity number is obtained from both eqs 7 and 8.

The linear relationship of viscosity data with concentration found for all the systems suggests that the hydrodynamic size of the micelles is relatively constant with the concentration. The found values of k_1 range between 0.6 and 0.9. These values are higher than those corresponding to homopolymers (<0.5). However, they are lower than other ones reported for micellar systems. Yeung and Frank[13] found a value of 2.4 for an SEP in heptane at 25 °C, and Mandema et al.[8] reported a value of 0.96 for an SEP in decane. In both cases the authors employed the Huggins equation. The high Huggins coefficient values obtained show the high compactness of the micelles according to the values of the weight-average molar mass and radius of gyration.

The variation of the limiting viscosity number with the temperature for the different n-alkanes is plotted in Figure 11. Contrary to what happens with the weight-average molar mass and radius of gyration, the viscosity hardly changes when the micelles start to break. Thus, no marked change is found on increasing the temperature from 70 to 85 °C. On the other hand, there exists a great dependence of the limiting viscosity number with the carbon number of the n-alkane molecule (Figure 12).

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

$$[\eta] = \frac{10\pi N_A}{3} \frac{R_\eta^{\,3}}{M} \qquad (9)$$

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 9, the limiting viscosity number is inversely proportional to the density of the compactness of the micelle. Although the limiting viscosity number measured is an average in which the free chains have a larger contribution than in the weight-average molar mass, for low temperatures the system is far enough from the critical

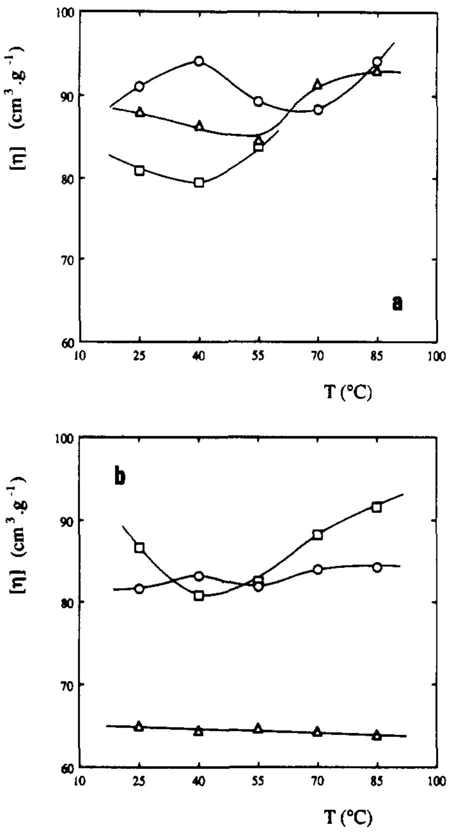

Figure 11. Temperature dependence of limiting viscosity number, [η], for copolymer SEP1 in different n-alkanes: (a) n-hexane (□), n-heptane (○), and n-octane (△); (b) n-decane (□), n-dodecane (○), and n-hexadecane (△).

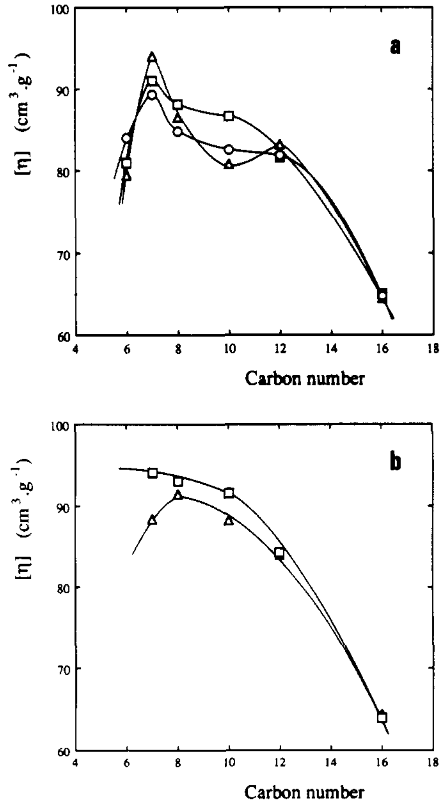

Figure 12. Dependence of limiting viscosity number, [η], on carbon number of n-alkane for copolymer SEP1 in n-alkanes at different temperatures: (a) 25 (□), 40 (△), and 55 °C (○); (b) 70 (△) and 85 °C (□).

micellar concentration to consider the experimental limiting viscosity number as that corresponding to the micelles.

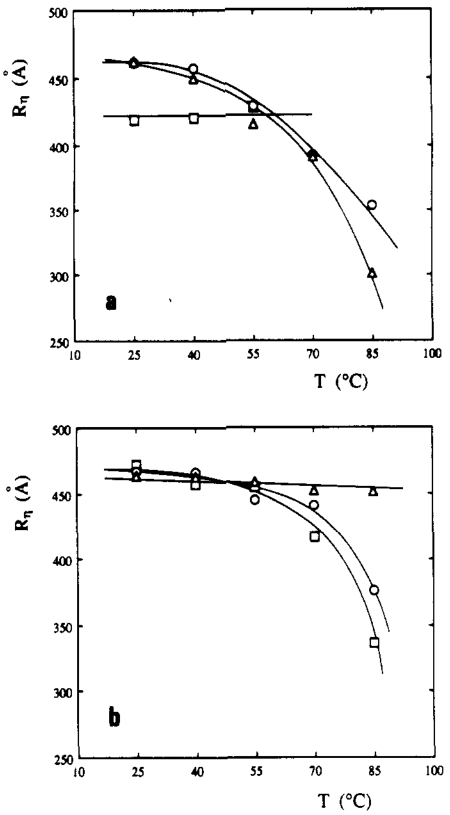

Figure 13. Temperature dependence of hydrodynamic radius, R_η, for copolymer SEP1 in different n-alkanes: (a) n-hexane (□), n-heptane (○), and n-octane (△); (b) n-decane (□), n-dodecane (○), and n-hexadecane (△).

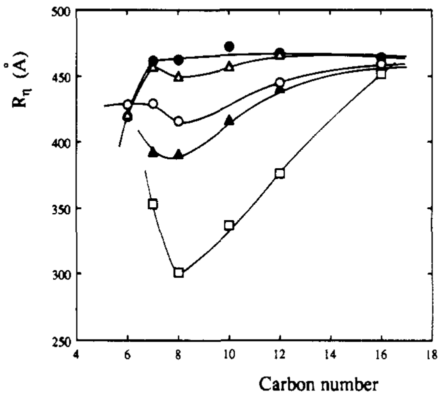

Figure 14. Dependence of hydrodynamic radius, R_η, on carbon number of n-alkane for copolymer SEP1 in n-alkane at different temperatures: 25 (●), 40 (△), 55 (○), 70 (▲), and 85 °C (□).

As can be seen in Figure 12, the limiting viscosity number for the copolymer in n-hexadecane is much lower than for the other n-alkanes, evidencing a larger compactness of the micelles in n-hexadecane. A maximum in the limiting viscosity number or minimum in the compactness of the micelles is also observed for the n-heptane.

The temperature dependences of the hydrodynamic radius deduced from eq 9 for the different n-alkanes are plotted in Figure 13. This figure shows how the hydrodynamic radius decreases sharply at high temperature, except for n-hexane (T_b = 68 °C) and n-hexadecane. This diminution in the hydrodynamic radius is due to an increase in the free-chain concentration. However, this behavior is not observed for n-hexadecane because the higher experimental temperature is much lower than the critical micelle temperature corresponding to the experimental concentrations employed.[1] Therefore it is possible to say that the hydrodynamic radius of the micelles does not depend on the temperature.

The variation of the hydrodynamic radius with the carbon number of the *n*-alkane molecule is shown in Figure 14. As can be seen, the hydrodynamic radius of the micelles hardly depends on the *n*-alkane. For high temperatures, the variation of the hydrodynamic radius of the copolymer solutions with the *n*-alkane carbon number shows a minimum for *n*-octane. This behavior is similar to that found for the weight-average molar mass, and it is explained by taking into account that, at high temperatures, the standard Gibbs energy of micellization is higher for *n*-octane. Therefore, the free-chain concentration is higher in *n*-octane than in the other *n*-alkanes.

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