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Block copolymer micelles in solutions of a homopolymer: dynamic light scattering and viscosity studies

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Solutions of polystyrene-*b*-poly(ethylene/propylene) block copolymer and homopolystyrene in toluene (a good solvent of both copolymer blocks) were studied by dynamic light scattering and viscometry. The presence of homopolystyrene in the solution induces the formation of micelles with a core which consists of poly(ethylene/propylene) blocks. The dynamic light scattering measurements showed that these micelles have a narrow size distribution. The influence of the polystyrene concentration on the structural parameters of the micelles was analysed. The hydrodynamic radius and molar mass remained constant in the polystyrene concentration range studied. However, the diffusion of the micelles was very influenced by the increment of the solution viscosity caused by the polystyrene chains. Copyright © 1996 Elsevier Science Ltd.

(Keywords: block copolymer; dynamic light scattering; hydrodynamic radius)

INTRODUCTION

Block copolymers have sequences of different homopolymers in the same molecule. Selective solvents can often be found which are good with respect to one of the homopolymer sequences but are poor with respect to the other types of sequences. In dilute solutions of this type of solvent, a block copolymer can intermolecularly associate forming micelles according to the model of a closed association. In general the copolymer micelles are spherical and are formed by a core and an external shell. The core consists of poorly soluble sequences of block copolymer and the shell consists of solvated sequences which prevent macroscopic flocculation of the copolymer[1–4].

A copolymer often used to study micellar systems in organic selective solvents has been the polystyrene-*b*-poly(ethylene/propylene) diblock copolymer[5–11]. In recent investigations[12,13] we have found that a solution of a homopolymer corresponding to one of the copolymer blocks shows a behaviour similar to a selective solvent. Thus, micelles of polystyrene-*b*-poly(ethylene/propylene) (SEP2), have been detected in toluene solutions of homopolystyrene (PS). Toluene is a good solvent for both copolymer blocks. The incompatibility of poly(ethylene/propylene) blocks and polystyrene causes the formation of micelles with a core consisting of poly(ethylene/propylene) blocks. The study of the micellization thermodynamics has shown[13] that the standard Gibbs energy of micellization, ΔG^0, is negative and varies linearly with the polystyrene concentration, becoming more negative as the polystyrene concentration increases. This behaviour suggests that the addition of polystyrene increases the selectivity of the medium, favouring the micelle formation. The standard enthalpy, ΔH^0, and entropy of micellization, ΔS^0, showed negative values and therefore ΔH^0 is solely responsible for the micelle formation. Both magnitudes became more negative as the polystyrene content increased. In conclusion, the investigation showed that the polystyrene content in the micellar system polystyrene-*b*-poly(ethylene/propylene)/polystyrene/toluene strongly influences the thermodynamics of the micellization process.

In this paper, the previously studied block copolymer/homopolymer/good solvent system SEP2/PS/toluene is used. The hydrodynamical behaviour of this system is investigated by dynamic light scattering and viscometry. From the double extrapolation of the linewidth or the first cumulant, $\bar{\Gamma}$, to nil angle and concentration, the concentration coefficient, K_D, and the translational diffusion coefficient of the micelles at infinite dilution, D_0, were determined. By using viscosity data, an attempt to determine the micelle molar mass was made.

EXPERIMENTAL

Materials

The copolymer sample of polystyrene-block-poly(ethylene/propylene), SEP2, was kindly provided by Shell España, S.A. The sample has been characterized previously in detail[14,15]. It is homogeneous in chemical composition and its weight average molar mass, polydispersity and styrene content are 105 000 g mol^{-1}, 1.08 and 35 wt%, respectively. The homopolystyrene sample, PS1, was synthesized via radical polymerization in

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toluene solution at 90°C, using α,α'-azo-bis-isobutyronitrile as initiator. The resulting sample had a weight-average molar mass and polydispersity of 16 000 g mol^{-1} and 2.4, respectively.

Preparation of polymer solutions

Toluene (analytical purity grade) was used without further purification. Sample solutions were prepared by dissolving the polystyrene and copolymer in toluene at 70°C in sealed flasks. In order to clarify the solution for dynamic light scattering measurements, they were filtered at room temperature directly into the scattering cells through a 0.2 μm PTFE Acrodisk CR filter.

Dynamic light scattering

The normalized self-beat photon correlation function $g^{(1)}(\tau)$ of the scattered light from the solutions was measured at 25°C on a PL-LSP-700 instrument (Polymer Laboratories) working in dynamic homodyne mode. The scattering angles measured were seven fixed angles of 30, 45, 60, 90, 120, 135 and 150°. Four PS1 concentrations were studied: 0.12, 0.15, 0.18 and 0.21 g cm^{-3}. Four SEP2 concentrations were used for each PS1 concentration. SEP2 concentrations ranged between 0.3×10^{-3} and 10×10^{-3} g cm^{-3}.

The average linewidth $\bar{\Gamma}$, which is equal to the first cumulant, was estimated by the second order cumulant method[16]

$$\ln[g^{(1)}(\tau)] = -\bar{\Gamma}\tau + \frac{1}{2!}\mu_2\tau^2 \tag{1}$$

where $g^{(1)}(\tau)$ is the electric field autocorrelation function and τ is the delay time. The variance of the size distribution function $\mu_2/\bar{\Gamma}^2$ was also determined.

Viscometry

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. Measurements were carried out at 25°C within the SEP2 concentration range $2 \times 10^{-3} \le c \le 11 \times 10^{-3}$ g cm^{-3}. The data were evaluated according to the Huggins and Kraemer equations[17] considering a PS1 solution of the same concentration as the polystyrene one in the ternary system SEP2/PS1/toluene as the solvent.

RESULTS AND DISCUSSION

To study the hydrodynamic behaviour of the micelle system SEP2/PS1/toluene, dynamic light scattering (DLS) measurements on sixteen solutions were carried out. Four PS1 concentrations were considered: 0.12, 0.15, 0.18 and 0.21 g cm^{-3}. The SEP2 copolymer in these solutions at 25°C showed a critical micellar concentration (CMC) of 1.15×10^{-3}, 2.12×10^{-4}, 1.58×10^{-5} and 1×21.10^{-6} g cm^{-3}, respectively[13]. Four SEP2 concentrations were also used for each PS1 concentration. These SEP2 concentrations were chosen to be sufficiently higher than the *CMC*s so that the micelle formation was overwhelmingly favoured. SEP2 concentrations ranged from 0.3×10^{-3} to 10×10^{-3} g cm^{-3} depending on the PS1 concentration. The linewidths, $\bar{\Gamma}$, were estimated as functions of the scattering vector, K, and SEP2 concentration, their normalized second moment, i.e. the variance, resulting in 0.008 – 0.03. The small values of the variance confirmed that we observed a dynamic process of particles composed of near monodisperse size. Since the micelle/free chain equilibrium was overwhelmingly displaced in the direction of the micelle concentration and the PS1 chains were enough small to be detected by our DLS device. Thus the dependence of $\ln[g^{(1)}(\tau) - 1]$ as a function of the delay time were almost linear (*Figure 1*). This behaviour is analogous to that found for this same copolymer sample in selective solvents (ketones)[18,19].

The translational diffusion coefficients at finite polymer concentration, $D(c)$, were estimated from the linewidth extrapolated to nil angle, $\Gamma(c) = D(c)K^2$. *Figure 2* shows the extrapolations of $\Gamma(K, c)$ to $K = 0$ where $\Gamma(K, c)/\sin^2(\theta/2)$ values at four SEP2 concentrations are plotted against $\sin^2(\theta/2)$ for a PS1 concentration of $0.12\,\mathrm{g} \times \mathrm{cm}^{-3}$. The data at each SEP2

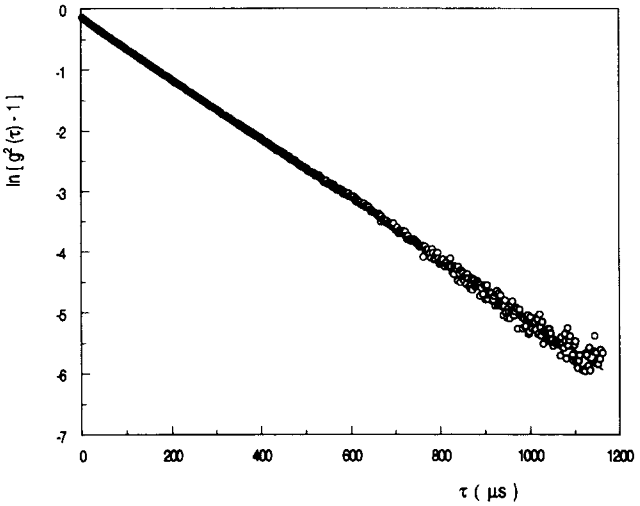

Figure 1 Plot of $\ln[g^{(1)}(\tau) - 1]$ *versus* delay time, τ, for a SEP2/PS1/toluene solution at 25°C. $c(\mathrm{SEP2}) = 6.27 \times 10^{-3}$ g cm^{-3}, $c(\mathrm{PS1}) = 0.21$ g cm^{-3} and observation angle = 90°

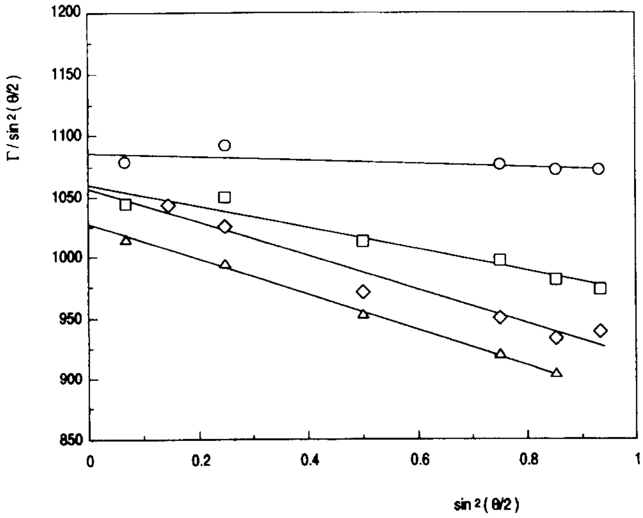

Figure 2 Scattering angle, θ, dependence of the first cumulant, Γ, measured for a polystyrene-*b*-poly(ethylene/propylene) copolymer SEP2 in a toluene solution of a polystyrene PS1 ($c_{\mathrm{PS}} = 0.15$ g cm^{-3}) for four SEP2 concentrations: ○, 3.65×10^{-3}; □, 5.78×10^{-3}; △, 8.00×10^{-3}; ◇, 10.2×10^{-3} g cm^{-3}

concentration fit straight lines well. The slopes are negative and the absolute magnitudes of the slopes decrease on decreasing the SEP2 concentration, becoming nearly zero for the lowest concentration ($c = 3.65 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$). At this concentration, $\Gamma(K, c)/\sin^2(\theta/2)$ is hardly dependent on the scattering angle. The constant behaviour of $\Gamma(K, c)$ is characteristic of translation diffusions and is related to the translational diffusion motion of near monodisperse micellar particles as a whole. The negative slopes in $\Gamma(K, c)/\sin^2(\theta/2)$ *versus* $\sin^2(\theta/2)$ and the variation of their values with the copolymer concentration have been already described by Tsunashima[20] for a polystyrene–polybutadiene diblock copolymer in *n*-decane. He suggests that this behaviour might be related to internal motions in the micellar particles.

The same behaviour were found for the PS1 concentrations of 0.15 and $0.18\,\mathrm{g\,cm^{-3}}$. However, for the PS1 concentration of $0.21\,\mathrm{g\,cm^{-3}}$ the dependencies of $\Gamma(K, c)/\sin^2(\theta/2)$ on $\sin^2(\theta/2)$ are also linear but the slopes are positive (*Figure 3*).

The $D(c)$ values for all four PS1 concentrations are plotted as functions of SEP2 concentrations in *Figure 3*. All the data are well represented by the linear relation

$$D(c) = D_0(1 + K_D c) \tag{2}$$

where D_0 is the translational diffusion coefficient at infinite dilution and k_D the diffusion second virial coefficient. K_D and D_0 were estimated from the slopes and intercepts in *Figure 4*.

Figure 5 shows the K_D values as a function of the PS1 concentration. For all the PS1 concentrations K_D shows small positive or negative values suggesting an enhancement of solute–solute interactions. At higher PS concentration K_D becomes more negative. *Figure 6* shows the D_0 values as a function of the PS1 concentration. The variation of D_0 with the PS1 concentration was linear and negative. As the PS concentration increases the micelle interacts more with the polystyrene coils decreasing the mobility of micelles. This D_0 decrease concurs with an increment in the viscosity of the toluene

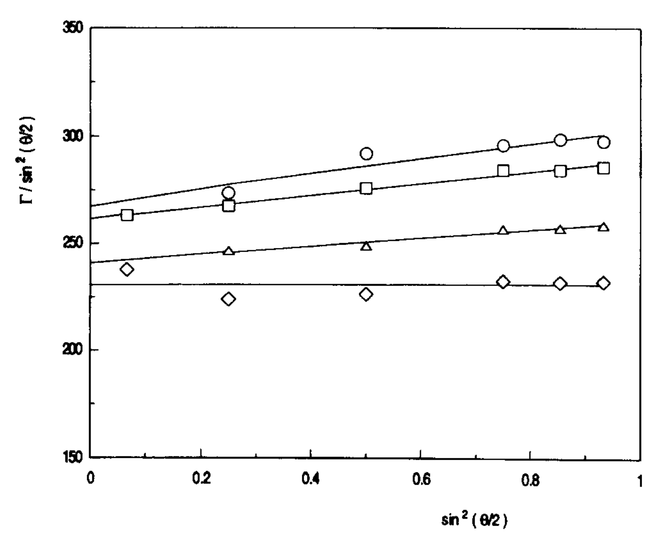

Figure 3 Scattering angle, θ, dependence of the first cumulant, Γ, measured for a polystyrene-*b*-poly(ethylene/propylene) copolymer SEP2 in a toluene solution of a polystyrene PS1 ($c_{PS} = 0.21\,\mathrm{g\,cm^{-3}}$) for four SEP2 concentrations: ○, 0.295×10^{-3}; □, 0.492×10^{-3}; △, 2.19×10^{-3}; ◇, $6.27 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$

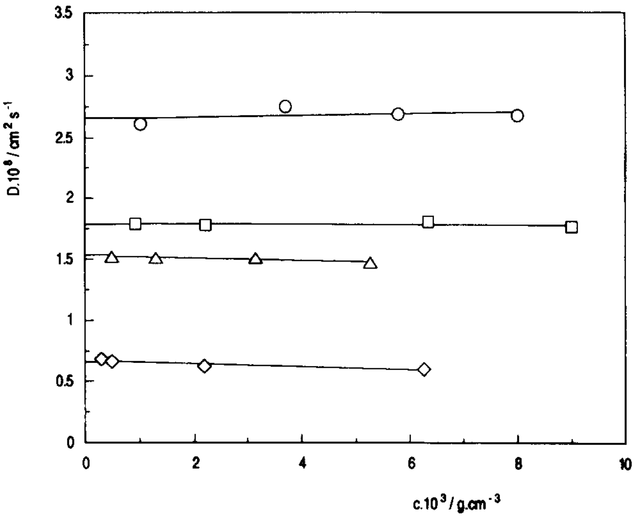

Figure 4 Diffusion coefficients $D(c)$ plotted against the SEP2 concentration c for SEP2/PS1/toluene solutions at four PS1 concentrations: ○, 0.12; □, 0.15; △, 0.18; ◇, $0.21\,\mathrm{g\,cm^{-3}}$ at 25°C

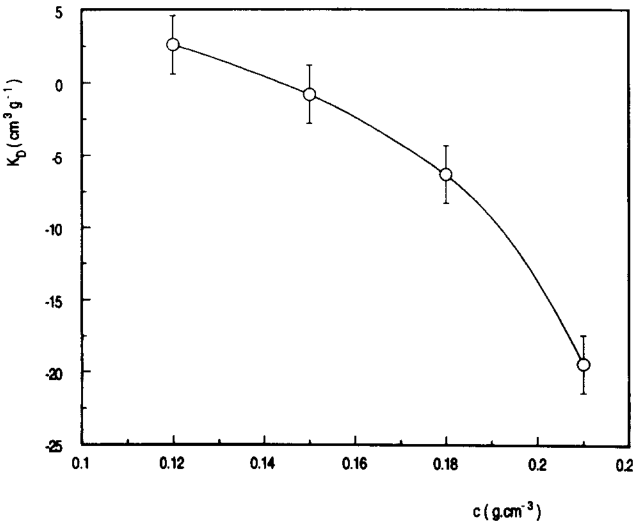

Figure 5 Diffusion second virial coefficient, K_D, of the system SEP2/PS1/toluene as a function of the PS1 concentration at 25°C

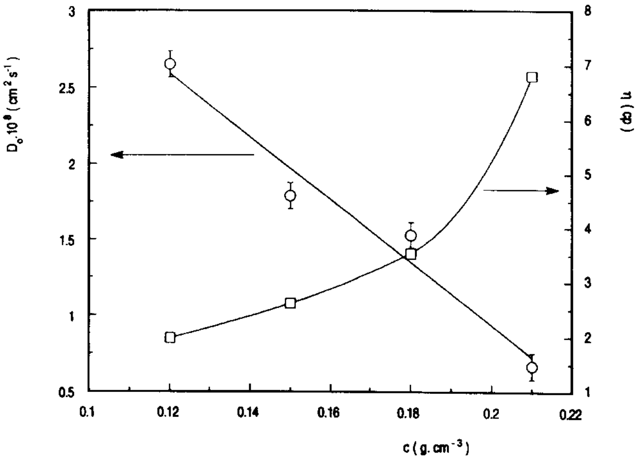

Figure 6 Diffusion coefficients at infinite dilution, D_0, of the system SEP2/PS1/toluene and viscosity, η, of PS1 solutions plotted against the PS1 concentration at 25°C

solutions of PS1 (*Figure 6*), i.e. the diffusion of SEP2 micelles is governed by the macroscopic viscosity of the medium. A similar behaviour has been found by Konák *et al.*[21] for the micellar system polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene/polystyrene/1,4-dioxane at high PS concentrations. 1,4-Dioxane is a selective solvent of the PS block.

From the D_0 values, the hydrodynamic radii R_H of the scattering particles were calculated using the well-known Stokes–Einstein relation for diffusion

$$R_H = \frac{k_B T}{6\pi\eta_0 D_0} \qquad (3)$$

where k_B is the Boltzmann constant, T the absolute temperature and η_0 the viscosity of the solvent (for the system SEP2/PS1/toluene, η_0 is the viscosity of the PS1 solutions in toluene).

The R_H values obtained for the four PS1 concentrations are listed in *Table 1*. No dependence of the PS1 concentration on the hydrodynamic radius of the SEP2 micelles is found. The constant behaviour of R_H has been already observed in different SEP micelle systems with a variable selectivity (binary solvent mixtures)[18,19,22].

The intrinsic viscosities, $[\eta]$, of the SEP2 micelles were estimated by extrapolating the reduced viscosity, η_{sp}/c, and the inherent viscosity, $\ln \eta_r/c$, to infinite dilution according to the Huggins and Kraemer equations respectively

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

$$\frac{\ln \eta_r}{c} = [\eta] - k_K[\eta]^2 c \qquad (4)$$

The PS1 solutions were considered as solvents. C was the SEP2 concentration and $\eta_r = \eta/\eta_{PS}$, where η is the viscosity of the system SEP2/PS1 toluene and η_{PS} the viscosity of the PS1 solution in toluene at the concentration of the ternary system. The plots of the reduced and inherent viscosities against the SEP2 concentration for the PS1 concentration of 0.12 g cm^{-3} are plotted in *Figure 7*. Similar plots were found for the other PS1 concentrations. The $[\eta]$ obtained are tabulated in *Table 1*.

Assuming that the micelles have a sphere shape, the molar mass, M, can be estimated from the intrinsic viscosity and hydrodynamic radius data using the expression

$$M = \frac{10\pi R_H^3 N_A}{3[\eta]} \qquad (5)$$

Taking into account that in the experimental conditions used the micellization process is overwhelmingly favoured and the micelles have a narrow size distribution such as the DLS measurements suggest, we have considered a good approximation to use the hydrodynamic radius values obtained by DLS though they are z-averaged quantities. The micelle molar mass values obtained for the different PS1 concentrations are listed in *Table 1*. These values have a considerable experimental error. However, a non-dependence of the PS content on the micelle molar mass seems to be in the concentration range studied. This behaviour contrasts with the influence that the PS content has in the thermodynamics of micellization of this micellar system[13].

Table 1 Hydrodynamic radius, R_H, intrinsic viscosity, $[\eta]$, and molar mass, M, for solutions of copolymer SEP2 in four solutions of PS1/toluene at 25°C

c_{PS}(g cm^{-3})	R_H(nm)	$[\eta]$(cm^3 g^{-1})	M(g mol^{-1})
0.12	42	60.7	7.10^6
0.15	47	61.7	10.10^6
0.18	41	60.1	7.10^6
0.21	48	60.1	10.10^6

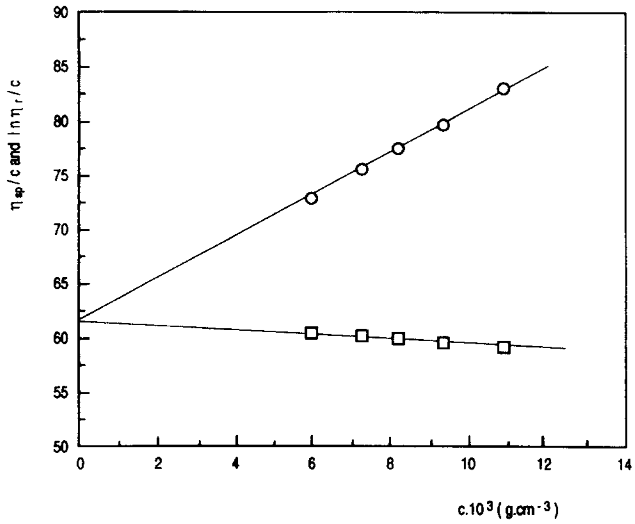

Figure 7 Plots of reduced and inherent viscosities *versus* SEP2 concentration for the system SEP2/PS1/toluene at the PS1 concentration of 0.12 g cm^{-3} at 25°C

The micelles existing in the system SEP/PS/toluene will have a core formed by the PEP blocks and a shell composed of the PS ones, i.e. they will have the same structure as those formed in selective solvents of the PS blocks. However, the molar mass that they have is quite different. Whereas the SEP2 micelles formed in solutions PS/toluene have molar mass close to 10 × 10^6 g mol^{-1}, the micelles formed in ketones[14] have in general a molar mass near 40 × 10^6 g mol^{-1}.

The low molar mass found might be related to the core solvation by toluene. This solvent is thermodynamically good for both copolymer blocks. We have found that the molar mass of the micelles formed in the system SEP2/4-methyl-2-pentanone/2-chlorobutane[19] and in the system SEP2/1,4-dioxane/n-dodecane[22] decreases as the content of 2-chlorobutane or n-dodecane increases. Both solvents are good for the poly(ethylene/propylene) block and therefore will solvate the micelle core.

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