Equilibrium and non-equilibrium copolymer micelles: polystyrene-*block*-poly(ethylene-*co*-propylene) in decane and in diisopropylether

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When selective solvents are used for the dissolution of block copolymers, their solid-state structure may be partly preserved in solution. At room temperature, polystyrene-*block*-poly(ethylene-*co*-propylene) dissolves in decane, a selective solvent for the aliphatic block, to form a solution of metastable micellar structures with polystyrene core. These convert to stable micelles at elevated temperature; the molar mass of the micelles is reduced several times after the heat treatment. The change of the structure is explained by the existence of a frozen state of the micellar core at room temperature. A possible connection with the glass transition of the core is discussed. Static and dynamic light scattering, small-angle X-ray scattering, differential scanning calorimetry and viscometry have been used to characterize equilibrium and non-equilibrium micelles. A pronounced mutual interaction of micelles has been observed by light scattering even at a concentration as low as 5×10^{-4} g cm^{-3}. The concept of sticky chains is introduced to explain the association of the micellar shells. The behaviour of micelles in another selective solvent, diisopropylether, is simpler, both effects observed in decane being absent.

(Keywords: diblock copolymer; block copolymer micelles; static light scattering; dynamic light scattering; small-angle X-ray scattering)

INTRODUCTION

In previous studies[1,2] our interest has been concentrated on the light scattering characterization of poly(methyl methacrylate) dispersions stabilized in decane by a diblock copolymer. A copolymer comprising a block of polystyrene units and a block of the hydrogenated polyisoprene, polystyrene-*block*-poly(ethylene-*co*-propylene) (PS-PEP), has been used. Decane is a selective solvent for the PEP block, i.e. the PS block is insoluble in this solvent. The formation of micelles with PS core and PEP shell is thus anticipated[3] and observed[2]. In order to link the properties of the dispersion particles to those of block copolymer micelles present at the onset of polymerization, we investigated the solution behaviour of micelles (e.g. molar mass, size, etc.) in decane. Even though we thought this was going to be a simple task, some phenomena were observed which made interpretation of the results rather difficult:

(1) The change of structure induced by heating. The dissolution of the block copolymer at ambient temperature yielded stable opalescent solutions, which could be readily characterized by static and dynamic light scattering (SLS and DLS), small-angle X-ray scattering (SAXS) and viscometry. When the solutions were heated to 100°C and then cooled down, the intensity of scattered light dropped down to about one-tenth of the initial value. The change was clearly visible by the naked eye. On the other hand, the viscosity of the solutions increased. The solutions thus treated were again stable and their properties did not change with time. After evaporation of decane, drying and repeated dissolution in decane, the whole cycle could be repeated.

(2) Interaction and/or ordering of micelles. SLS revealed dissymmetries of scattered light lower than unity for both unheated and heat-treated solutions in the concentration range below 1 wt%. This implied the existence of interparticle interaction, the nature of which could neither be visualized nor understood. The viscosities of the diblock copolymer solutions in decane were surprisingly high compared to those expected for ordinary micellar solutions or for true solutions of a diblock copolymer. The reduced viscosity steeply grows with increasing concentration of the copolymer.

These rather puzzling effects have been to some extent described in the literature dealing with copolymers composed of PS blocks and aliphatic blocks (polybutadiene, polyisoprene and their hydrogenated derivatives). However, an unambiguous explanation has not been given.

For instance, Stacy and Kraus[4] examined the polystyrene-*block*-polybutadiene (PS-PB) micelles in hexane, heptane and decane. In many cases, they found a substantial decrease of the association number after heating and cooling of solutions in comparison with solutions prepared at room temperature. The change of

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the turbidity from opaque milk white to clear light-opalescent upon heating to ~50°C and cooling is mentioned by Tsunashima *et al.*[5] for diblocks of the same type in decane. Price *et al.*[6] describe a similar effect for polystyrene-*block*-polyisoprene (PS-PIP) in *N*,*N*-dimethylacetamide produced by heating solutions to 70°C. The original structures in solution were recovered after evaporation of the solvent and redissolution of the copolymer. Higgins *et al.*[7] found by small-angle neutron scattering (SANS) that the radius of PS-PEP micelles in dodecane was reduced at elevated temperatures and retained the smaller value after cooling. Schouten *et al.*[8] made a similar observation with micelles of the same type in octane and dodecane.

Schouten *et al.*[8] and Mandema *et al.*[9] described a transition at elevated temperature accompanied by a decrease of viscosity. This is contrary to expectation, because dissociation of micelles to individual macromolecules is usually manifested by an increase in viscosity. To interpret these phenomena, Mandema *et al.*[9] speculate that the individual polymer molecules associate at higher temperatures to form entirely different structures—cylinders or lamellae—in contrast to spherical micelles observed at low temperature. On the other hand, Price *et al.*[6] conclude that worm-like micelles dissociate at high temperature to form spherical micelles. Once the spherical micelles are formed, they show no tendency to revert to worm-like micelles. Virtually all authors agree that these phenomena are connected with some change of the supermolecular structure. Recently, Yeung and Frank[10] reported the existence of a local maximum for the concentration dependences of reduced viscosity for PS-PEP diblock in heptane. The phenomenon has been interpreted in terms of a change in the free chain–micelle equilibrium. The micellar behaviour has also been investigated in this sytem by fluorescence[11] of an intrinsic excimer.

Concerning the second point, mutual interaction of micelles, interparticle interference of PS-PEP micelles in octane and dodecane has been observed by SANS by Schouten *et al.* at a concentration as low as 0.5 wt%. Higgins *et al.*[7] reported for the same system that, above 3–4 wt% concentration, the micelles formed ordered arrays or layered structures. In SLS experiments with PS-PIP in decane, Mandema *et al.*[9] found dissymmetries of scattered light lower than unity. This is a typical manifestation of strong intermolecular interactions. Price and co-workers made the same finding at copolymer concentration $>8 \times 10^{-4}\ \mathrm{g\ cm^{-3}}$ for PS-PEP in hexane[12] and in decane[13].

Concept of partial preservation of solid-state structure in solution

It is well established that in the solid state microphase separation of diblock copolymers results in the formation of regular arrays of spheres, cylinders or lamellae[14,15] or even more complex structures[16], depending on the volume fraction of the individual blocks and on the casting solvent[17]. In the presence of homopolymers or in mixtures of block copolymers onion-like[18] and vesicular structures[18,19] were also reported.

In our opinion, the solid-state structure of any kind can be preserved to some extent even in solution if selective solvents in the specified range of temperatures are used for dissolution. For the sake of illustration, let us assume that an AB diblock copolymer has a microphase-separated structure with lamellar or spherical microdomains in the solid state (*Figure 1*). By applying a solvent which is selective for blocks B, the lamellae will open by a zip mechanism, or, similarly, the matrix of blocks B will dissolve. Blocks A, which are insoluble in the solvent, may maintain their contacts and the structures they form will survive to some extent. Such dissolution would result in a dispersion or solution of sheet-like or micellar structures, the size and shape of which would depend on the original morphology. By this mechanism layered or even vesicular structures could be maintained in solution. Similarly, a cylindrical solid-state structure could be a precursor for worm-like micelles in solution as described by Price *et al.*[6,13].

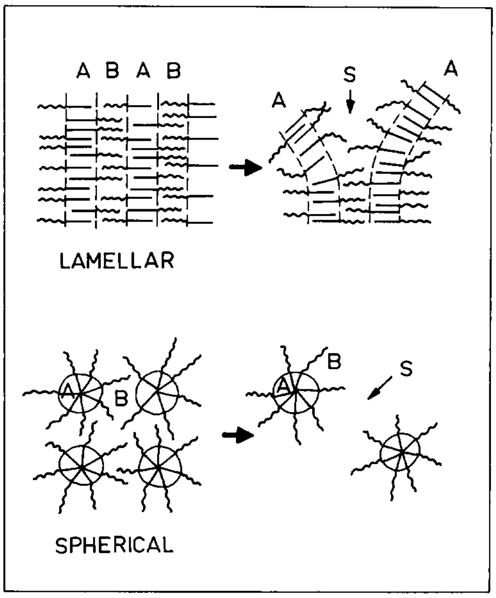

Figure 1 Schematic representation of the solid-state structure of an AB diblock copolymer and its selective dissolution by the penetration of solvent S which is a selective solvent for blocks B

Systems of this type need not be in true thermodynamic equilibrium. In fact, they are metastable and can transform into stable spherical micelles under favourable conditions. This may happen when the contacts between the insoluble blocks A (here PS) are loosened, e.g. by an increase of temperature above their glass transition temperature (T_g) or by a decrease of the T_g caused by addition of a good solvent for blocks A. The simultaneous presence of two types of micelles, small and large, has also been reported[20,21].

It was our primary objective to confirm the above hypothesis with experimental evidence. Moreover, a majority of the observed anomalies are connected with the use of hydrocarbon solvents. In diisopropylether (DIPE), PS-PEP also forms micelles with a PS core, PS being insoluble in DIPE, and a PEP shell. Introductory experiments showed that the micellar behaviour in DIPE was much more straightforward. Our next goal was to find out why PS-PEP micelles behave in different manners in various solvents.

EXPERIMENTAL

Materials

Decane (Fluka, Switzerland, purum) and DIPE (BDH, UK, purum) (*Table 1*) were used as received. Tetrahydrofuran (THF; VEB Laborchemie Apolda,

Table 1 The refractive index, n, viscosity, η, and boiling point, T_b, of the solvents used and the refractive index increment, ν, of PS-PEP diblock copolymer in these solvents at 25°C

Solvent	n^a (546 nm)	η (cP)	T_b (°C)	ν(cm^3 g^{-1}) (546 nm)	(633 nm)
Decane^b	1.412	0.854^c	174	0.120	0.117
DIPE	1.369	0.320	68	0.180	0.177
THF	1.407	0.460^c	67	0.112	0.110

[a] At wavelength $\lambda_0 = 546$ nm, taken from ref. 48
[b] Copolymer in micellar form
[c] Taken from ref. 5

Germany, purum) was dried over sodium hydroxide, by calcium hydride, and distilled on a laboratory column. Solvent purity (>99 wt%) was checked by gas chromatography (g.c.).

The PS-PEP diblock copolymer (manufactured by Shell Chemical Company under the trademark Kraton G1701) had a mass-average molar mass $M_w = (1.05 \pm 0.05) \times 10^5$ g mol^{-1} (by light scattering in THF) and the ratio of mass- to number-average molar mass $M_w/M_n = 1.28$ (by g.p.c. in THF) or 1.24 (by DLS in THF). According to the manufacturer[22] the styrene/rubber mass ratio is 37/63. U.v. spectroscopy in chloroform yielded the styrene unit content as 34 wt% (from the PS absorbance at 262 nm). An identical result, 34 wt% PS, was provided by ^{1}H n.m.r. No butylene units were identified. The ethylene/propylene mole ratio was 0.93. The copolymer was used for solution preparation without further treatment.

Preparation of solutions

Weighed amounts of copolymer and solvent were sealed into 20 ml glass ampoules. The samples were shaken for 12 h at room temperature (20–25°C). The solutions were filtered (Selas silver-metal membranes, Selas Corporation of America, USA; porosity 5.0 μm) into new dust-free glass ampoules. These were sealed and used directly both in SLS and DLS experiments. In several cases, centrifugation was used for optical clarification[23] (Beckman L-55 ultracentrifuge, swinging-bucket rotor SW 28, 15000 rev min^{-1} for 1 h). Selected solutions were heated for 10 min to 100°C (decane) or 70°C (DIPE) and allowed to cool down to room temperature. Each solution was prepared separately; only in SAXS experiments was dilution used.

Alternatively[24], Kraton G1701 was dissolved in THF (to form a molecular solution) or in DIPE (to form a micellar solution) and an aliquot of decane was added. THF or DIPE were selectively evaporated at reduced pressure and 25°C. Due to the large difference in the boiling points of the solvents and decane (*Table 1*), the separation proceeded easily. No residual traces of THF or DIPE could be detected in solutions by g.c. The concentration of the diblock copolymer in decane was determined by u.v. spectroscopy.

Critical micelle concentration

Light scattering experiments were performed over a concentration range down to 8×10^{-7} g cm^{-3}, where the intensities of scattered light could still be registered reliably. No decomposition of micelles was observed in this concentration range and, therefore, the critical micelle concentration (CMC), if non-zero, must be still lower. For a PS-PEP copolymer of comparable molar mass and composition Price[13] reports a CMC of 2.4×10^{-8} g cm^{-3} in decane at 30°C. Consequently, the presence of the unimer can be neglected in the interpretation of data and the concentration of micelles can be taken as equal to the overall copolymer concentration.

Static light scattering

Light scattering was measured with a Fica 50 apparatus (France) using a non-polarized primary beam of wavelength $\lambda_0 = 546$ nm. The intensity of scattered light was attenuated by insertion of a neutral filter (10 × or 30 ×) placed in front of the photomultiplier when needed. Some independent measurements were done with a modified Sofica 42.000 apparatus (France) using a He–Ne laser light source ($\lambda_0 = 633$ nm). The refractive index increments (*Table 1*) were determined with a Brice-Phoenix BP-2000-V differential refractometer. All measurements were performed at 25°C.

Dynamic light scattering

A laboratory made homodyne photon correlation spectrometer[25] equipped with a He–Ne laser ($\lambda_0 = 633$ nm) was used in the DLS measurements. The intensity signal was analysed with a 96-channel digital correlator covering three-and-a-half decades in delay time. In analysing[26] the autocorrelation function, the decay-time distribution was assumed to be of Pearson type. The hydrodynamic radius has been calculated from the Stokes–Einstein equation: $R_h = kT/(6\pi\eta D_c)$, where k is the Boltzmann constant and D_c the diffusion coefficient. The above analysis[26] also allowed the non-uniformity of micelles to be estimated. A simple scaling law between the diffusion coefficient and molar mass valid for homogeneous spherical particles was assumed, $D_c \sim M^{-1/3}$.

Small-angle X-ray scattering

The scattering curves were registered on a Kratky camera and converted to absolute scale by means of a Lupolen standard. The differential scattering cross-section, $d\Sigma(q)/d\Omega$, where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector, was obtained from measured intensities by means of Glatter's ITP desmearing programme[27,28]. The details of the experimental method and evaluation of the data have been described elsewhere[29]. The scattering curves were recorded for four copolymer concentrations from 0.005 to 0.02 g cm^{-3} but no concentration dependence was found in the investigated range of scattering vectors. Molecular parameters were evaluated from the measurement at the highest copolymer concentration.

The M_w of micelles was determined according to the formula[30]:

$$M_w = \frac{N_A}{c(\Delta b)^2} \frac{d\Sigma(0)}{d\Omega} \qquad (1)$$

where N_A is the Avogadro constant, c is the polymer concentration and Δb is the excess scattering amplitude. For the solutions of the PS-PEP copolymer we may write:

$$\Delta b = w_{PS}(b_{PS} - \bar{v}_{PS}\rho_0) + w_{PEP}(b_{PEP} - \bar{v}_{PEP}\rho_0) \qquad (2)$$

where w_i is the mass fraction of substance i, b_i is the scattering amplitude per gram of substance i, $\bar{v}_i$

is its partial specific volume and ρ_0 is the solvent scattering density. The subscripts PS and PEP refer to the individual blocks, respectively. The Δb values have been calculated using[31] $b_{PS} = 9.137 \times 10^{10}\,\mathrm{cm\,g^{-1}}$, $b_{PEP} = 9.696 \times 10^{10}\,\mathrm{cm\,g^{-1}}$, $\bar{v}_{PS} = 0.929\,\mathrm{cm^3\,g^{-1}}$, $\bar{v}_{PEP} = 1.17\,\mathrm{cm^3\,g^{-1}}$ and $\rho_0 = 6.94 \times 10^{10}\,\mathrm{cm^{-2}}$ for decane and $\rho_0 = 7.055 \times 10^{10}\,\mathrm{cm^{-2}}$ for DIPE. The scattering amplitude of a single electron[32], $b_e = 0.281 \times 10^{-12}\,\mathrm{cm}$, was used for evaluating the scattering amplitudes and densities.

The geometric radius of the micellar core, R_c, can be calculated from the position of a side maximum localized at the scattering vector q_m using the relation[32]:

$$R_c = 5.76/q_m \qquad (3)$$

which follows from a simple analysis of the particle scattering function for uniform spheres. The molar mass of micelles can be then calculated from the relation:

$$M = \frac{4\pi N_A R_c^3}{3 w_{PS} \bar{v}_{PS} \Phi_c} \qquad (4)$$

where $\Phi_c = V_c^*/V_c$ is the ratio of the swollen to dry volume of the core. The degree of swelling, Φ_c, was calculated from the mean-square fluctuation of the scattering density[29] $\langle(\Delta\rho)^2\rangle$, which can be derived directly from the measured scattering curve.

For the evaluation of the micellar mass, the intensity of the side maximum, $\mathrm{d}\Sigma(q_m)/\mathrm{d}\Omega$ can also be used[32] (*Table 2*). However, these values are not very reliable because the system is not strictly monodisperse and the magnitude of $\mathrm{d}\Sigma(q_m)/\mathrm{d}\Omega$ is subject to a large experimental error at these q values. For the unheated samples, the maximum is less clearly developed.

Differential scanning calorimetry

The T_gs of PS and of PS blocks in the PS-PEP copolymer swollen with decane or DIPE were evaluated from the temperature dependences of the heat capacity measured with Perkin-Elmer DSC-2 calorimeter. Concentrated solutions were prepared directly in the aluminium pans by weighing polymer and solvent, and hermetically sealing. The measurements were performed in the temperature range 230–410 K at a heating rate of $10\,\mathrm{K\,min^{-1}}$. The T_gs were evaluated from the second heating runs. The baseline was determined with empty aluminium pans. The temperature and power calibrations were performed with indium and aluminium oxide.

Viscometry

The viscosities were determined at 25.0°C with a modified Ubbelohde viscometer using capillaries with 0.47 and 0.60 mm diameters.

RESULTS AND DISCUSSION

The experimental results are presented and discussed in two separate sections. In the first one, we report phenomena observed on dissolution of block copolymers in selective solvents, on the metastable structures surviving in decane solutions from the solid state, and on their conversion to stable micelles at elevated temperature. In the second section, we deal with the problem of interactions and/or ordering of micelles.

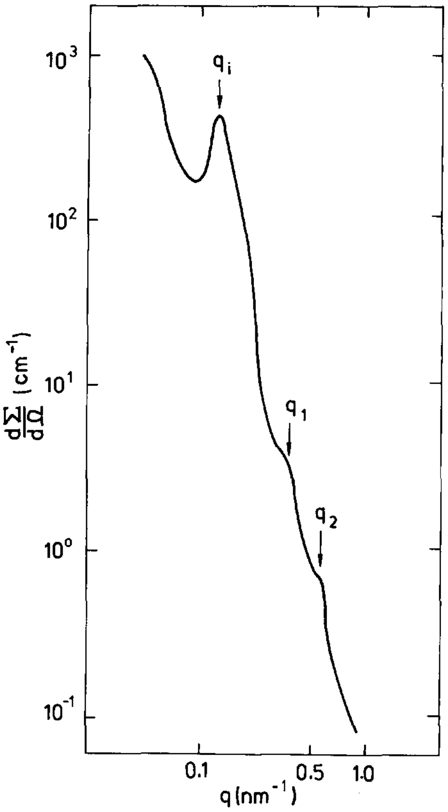

Figure 2 SAXS curve of the solid PS-PEP diblock copolymer

Dissolution of a diblock copolymer in selective solvents

SAXS characterization of the solid-state structure. The scattering curve of the PS-PEP copolymer in the solid state shows a pronounced interparticle interference peak at a scattering vector of $q_i = 0.131\,\mathrm{nm^{-1}}$ (*Figure 2*), which corresponds to the correlation length $d_c = 2\pi/q_i = 48\,\mathrm{nm}$. Two additional, poorly developed peaks at $q_1 = 0.357$ and $0.571\,\mathrm{nm^{-1}}$ were identified as the first and second side maximum of the single particle form factor of PS spheres. The corresponding radii of these spheres are[32] $R_1 = 16.1\,\mathrm{nm}$ [equation (3)] or $R_2 = 9.1/q_2 = 15.9\,\mathrm{nm}$, respectively. We use the average value $R_c = 16.0\,\mathrm{nm}$ hereafter.

Dissolution of the diblock copolymer in decane. The behaviour of PS-PEP solutions in decane depends distinctly on the thermal history. At laboratory temperature (between 20°C and 25°C), the PS-PEP copolymer dissolves easily to micellar solution. The properties of the solution do not change even after months; the measurement of the intensities of scattered light is reproducible. Below ~20°C, the dissolution is difficult; when kept at 4°C, the diblock copolymer remains completely undissolved. Once the copolymer is dissolved, the micelles do not precipitate even at −29°C when decane freezes. The character of the solutions changes substantially on heating. The turbidity diminishes by an order of magnitude when the temperature is increased above ~60°C. After returning to room temperature, the opalescence of the solutions remains low.

Micelles in unheated solutions. Let us suppose that the micelles dissolved in a selective solvent (*Figure 1*) at room temperature possess a PS core of the same mass as the

Table 2 Light scattering and SAXS characterization of PS-PEP micelles

	$10^{-6}M_w$ ($g\ mol^{-1}$)				R_h (nm)	R_c (nm)	Φ_c
Solvent/history	SLS	SAXS[a]	SAXS[b]	SAXS[c]	DLS	SAXS	SAXS
Decane							
Unheated	65.7	30.6	33.2	20	71	18.2	1.45
Heat-treated	8.7	9.0	14.4	10	42	13.8	1.45
DIPE	10.1	13.6	14.9	11	34	14.1	1.50

[a] From $d\Sigma(0)/d\Omega$ according to equation (1)

[b] From the position of the maxima on SAXS curves according to equation (4)

[c] From the intensity of the side maximum, $d\Sigma(q_m)/d\Omega$, cf. ref. 32

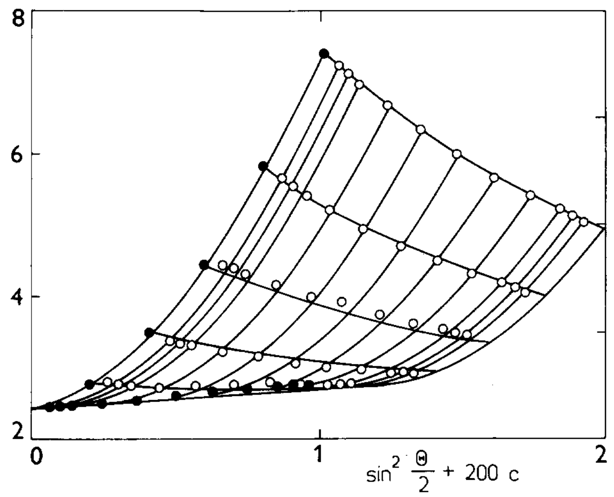

Figure 3 Zimm plot for the diblock copolymer in decane (K is the optical constant and R_θ is the Rayleigh ratio at scattering angle θ). The solutions were heat-treated and centrifuged

PS spheres found in the solid copolymer. If it were the case, then dry micelles, which have a core radius $R_c = 16.0$ nm, would have a diameter of 43.8 nm, as ensues from the diblock composition and densities of components. McMahon and Price[33] have recently investigated a practically identical copolymer and its micelles cast from hexane solutions by scanning electron microscopy. The micelles had diameters between 40 nm and 50 nm, in good agreement with expectation.

The micelles were characterized in the native, i.e. unheated, decane solutions by SLS, DLS and SAXS (*Table 2*). In SLS, the M_w of micelles can be evaluated by the routine Zimm method with good accuracy on the condition that a sufficiently low copolymer concentration is used ($c < 1 \times 10^{-3}\ g\ cm^{-3}$). At higher copolymer concentration the Zimm plots are distorted due to an intermicellar interaction, as discussed below (*Figure 3*), and the extrapolation of the data to zero angle and concentration is not reliable.

Figure 4a shows the SAXS curves for the native and heat-treated solutions of the diblock copolymer in decane. The scattering curves exhibit a side maximum in the range of $q_m = 0.32–0.42\ nm^{-1}$, which can be ascribed to the scattering of spheres with a relatively narrow size distribution. In micellar solutions, such a maximum can be attributed to the scattering from the dense PS core[31] and its radius can be calculated according to equation (3). Micellar molar masses derived from the core radius and taking into account the degree of swelling [equation (4)] and those calculated from $d\Sigma(q_m)/d\Omega$ are also summarized in *Table 2*.

The molar mass of micelles obtained by SAXS is in good agreement with the molar mass of the hypothetical micelles having a core of the same mass as that found for PS microdomains in the solid state, $M = 32.7 \times 10^6\ g\ mol^{-1}$, calculated from equation (4) for a dry core ($\Phi_c = 1$). SLS yields a molar mass more than twice this value (or even greater, depending on the procedure used for the clarification of solutions). This difference cannot be attributed to the experimental error of measurement.

Similarly, the radius of the micellar core $R_c = 18.2$ nm (*Table 2*) is in good agreement with the value based on the solid-state measurement corrected for swelling, $R_c = 16.0 \times (1.45)^{1/3} = 18.1$ nm. The difference between the hydrodynamic radius obtained from DLS ($R_h = 71$ nm) and the radius of the swollen core from SAXS, R_c, is too large to be attributed to the thickness of the shell. The latter parameter can be approximated by the end-to-end distance of moderately expanded PEP with an estimated value[1] of 28 nm.

We conclude that, in the unheated decane solution, the micelles formed from the solid-state PS microdomains survive to a large extent, their size being increased by swelling. We suspect that they form dimicellar or trimicellar aggregates, which are observable by light scattering but their contribution to the X-ray scattering intensity is not detectable in the q-range covered by our SAXS experiments.

Change of micellar structure induced by heating. The changes of micellar structure in decane solutions induced by heat treatment can be readily monitored by measurement of the concentration (*Figure 5a*) and angular dependences (*Figure 5b*) of scattered-light intensity. After heating the solutions for 10 min to 100°C and cooling down to ambient temperature, the molar mass of the micelles decreased by about one order of magnitude (*Table 2*). It is evident from the position of the side maximum on the SAXS curves of PS-PEP in decane solution that larger particles are present in solutions prepared at room temperature, than in heat-treated solutions (*Figure 4a*). Comparison of the $d\Sigma(0)/d\Omega$ values leads to the same conclusion.

A good agreement between the molar masses of micelles obtained by SLS and SAXS has been found in this case (*Table 2*). Micellar masses are comparable to those quoted for similar systems in the literature. For instance, Price *et al.*[13,34] investigated several PS-PEP copolymers with molar masses and compositions close to ours. Molar masses of micelles in decane in the range

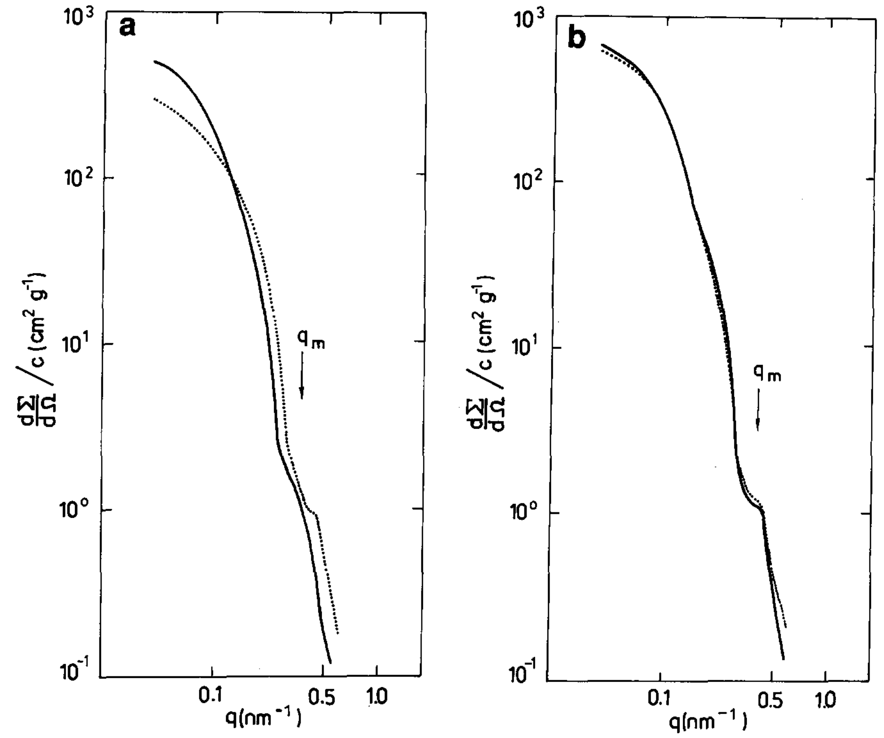

Figure 4 SAXS curves for the PS-PEP micelles in (a) decane and (b) DIPE measured after dissolution at room temperature (——) and after heating (······). Copolymer concentration $c = 0.02\ g\ cm^{-3}$

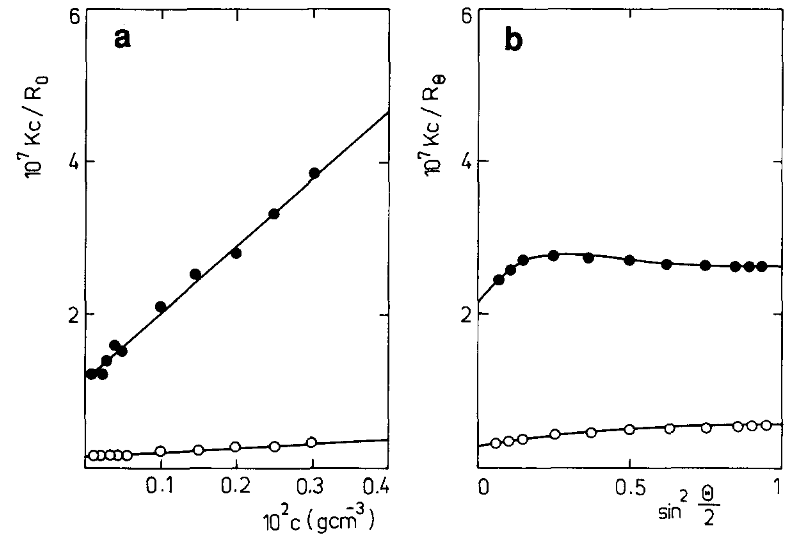

Figure 5 (a) Concentration dependences at zero angle and (b) angular dependences for copolymer concentration $c = 2.05 \times 10^{-3}\ g\ cm^{-3}$ of light scattered by solutions of the PS-PEP copolymer in decane. Solutions were prepared at room temperature (○), then exposed to 100°C for 10 min and cooled down (●)

$M_w = 6.5\text{–}9.0 \times 10^6\ g\ mol^{-1}$ have been reported. Tsunashima[35] explored a PS-PB diblock copolymer ($M_w = 9.3 \times 10^4$, 29.3 wt% PS) also in decane, finding for micelles $M_w = 9.7 \times 10^6$ and $R_h = 43.5$ nm.

A change of the micellar structure induced by heating is reflected also in the viscosity of solutions (*Figure 6*). After heat treatment of solutions and repeated measurement at 25°C, the viscosity substantially increases. We cannot offer any straightforward interpretation of this phenomenon in terms of changes in micellar structure.

Micelles in DIPE. Only PS-PEP diblock copolymer micelles in aliphatic hydrocarbons have been described in the literature. These micelles have a PS core. We were looking for a solvent of different chemical nature, where micelles with a PS core would also form. DIPE is such a solvent. It does not dissolve PS alone, but the PS-PEP diblock copolymer dissolves easily at room temperature yielding a typical micellar solution. Unlike in decane, the behaviour of the micelles in DIPE is simple. The molar mass of micelles is close to 10×10^6 (*Table 2*), indicating that the solid-state structure has not been preserved. After

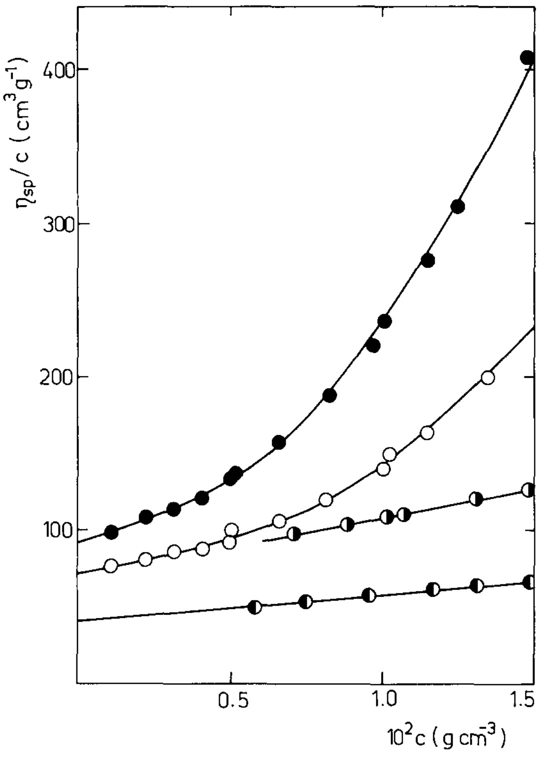

Figure 6 Concentration dependence of the reduced viscosity η_{sp}/c for PS-PEP diblock micelles in decane before (○) and after (●) heating, in DIPE (◐), and in the non-selective solvent toluene (◑) at 25°C

heating the solutions in sealed ampoules to 70°C (i.e. a few degrees above the boiling point of DIPE, cf. *Table 1*) and cooling to room temperature, no change in the light scattering behaviour has been observed. Similarly, DLS shows that R_h is practically the same as that of the micelles in decane after heat treatment (*Table 2*).

SAXS measurements did not detect any effect of heat treatment either (*Figure 4b*), in accord with the SLS data. The molar mass of micelles calculated according to equation (1) (*Table 2*) agrees well with that obtained by SLS. The properties of micelles in DIPE and in decane after heat treatment seem to be virtually the same.

The viscosity behaviour is in accord with intuitive expectation. Due to the compact structure of micelles, the viscosity of their solutions should be lower than that of the corresponding diblock copolymer coils. This is indeed true for DIPE solutions (*Figure 6*). Their viscosity is lower than that of solutions in toluene, which is a good solvent for both copolymer blocks. The concentration dependence in the Huggins plot (*Figure 6*) is also linear over the entire range investigated.

Indirect preparation of decane solutions. In the next step, we tried to prepare micellar solutions in decane by various routes, namely, via true solutions, where the solid-state structure is completely destroyed. The PS-PEP copolymer is molecularly dissolved in the THF; this solvent has also been used for its molecular characterization. An approximately equal volume of decane was added to the THF solution and THF was selectively evaporated (cf. Experimental). Thus we obtained a decane solution of micelles with no remnants of the solid-state structure. The molar mass and dimensions of micelles prepared in this way are comparable to those found in decane after the heat treatment (*Table 3*). Heating up to 100°C and cooling down to room temperature has also some additional effect (*Figures 5b* and *7b*), but the molar mass remains unaffected (*Table 3*).

In DIPE, the PS-PEP copolymer forms micelles. If decane again is added to such a solution and DIPE is removed by selective evaporation, the properties of the micelles remain unchanged. The structure originally formed in DIPE persists in decane (*Table 3*). After heating, however, the micelles convert to equilibrium ones with a lower molar mass (*Table 3*).

Obviously, the change of molar mass and size of micelles induced by heating in decane must be connected with the redistribution of the diblock copolymer macromolecules in micelles. To explain this effect in decane and its absence in DIPE, we investigated in more detail the properties of the micellar core.

Swelling and T_g *of the micellar core.* The T_g of PS or the PS core of micelles is substantially affected by the degree of swelling. The dependences of T_g on overall polymer concentration in polymer–solvent mixtures are shown in *Figure 8*. Due to the sensitivity limit of d.s.c., only the T_g of concentrated solutions could be determined. In decane, T_g decreases from 373 K for unswollen PS to 305 K for PS swollen in decane to equilibrium at 100°C (equilibrium mass fraction of decane $w_d = 0.14$). In mixtures containing more decane than the equilibrium amount, part of the solvent is free and does not cause any additional swelling (*Figure 8*). From the magnitude of the endotherm of melting for free decane one can estimate the fraction of the swelling agent in PS, $w_d = 0.125$–0.148, in good agreement with the value for the equilibrium swelling at 100°C, $w_d = 0.14$. In a similar experiment, the equilibrium content of DIPE at 50°C has been found to be $w_{DIPE} = 0.23$; accordingly, decane is a stronger non-solvent for PS than DIPE.

From the degree of swelling of the PS in the micellar core, Φ_c, in dilute solutions as observed by SAXS (*Table 2*) we obtain $w_d = 0.22$ and $w_{DIPE} = 0.25$. By extrapolation of T_g for homopolymer PS in decane (*Figure 8*) to PS concentration $w_p = 0.22$, the T_g of the micellar core in the diluted solution can be estimated to be between 250 K and 280 K.

By comparing the equilibrium swelling of PS homopolymer in decane and in DIPE, one can conclude that, in decane, the micellar core is more swollen than the homopolymer PS, while in DIPE, the degree of swelling is practically the same. This is a consequence of the pull exerted by chains in the shell on the core. It

Table 3 Light scattering characterization of PS-PEP micelles in decane and dependence on solution history

Solution history	$10^{-6}M_w$ (g mol^{-1}) SLS	R_h (nm) DLS
Transfer from THF		
Unheated	5.2	41
Heat-treated[a]	5.2	44
Transfer from DIPE		
Unheated	8.1	45
Heat-treated[a]	5.2	45

[a] Solutions were heated to 100°C for 10 min and then cooled down to room temperature

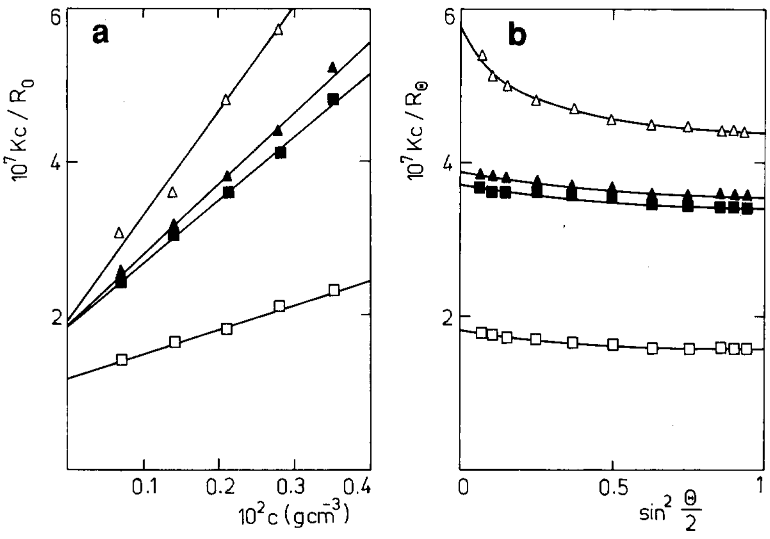

Figure 7 (a) Concentration dependences at zero angle and (b) angular dependences for copolymer concentration $c = 2.05 \times 10^{-3}$ g cm^{-3} of light scattered by PS-PEP copolymer in decane. Solutions were prepared via THF (△) and heat-treated (▲) or via DIPE (□) and heat-treated (■)

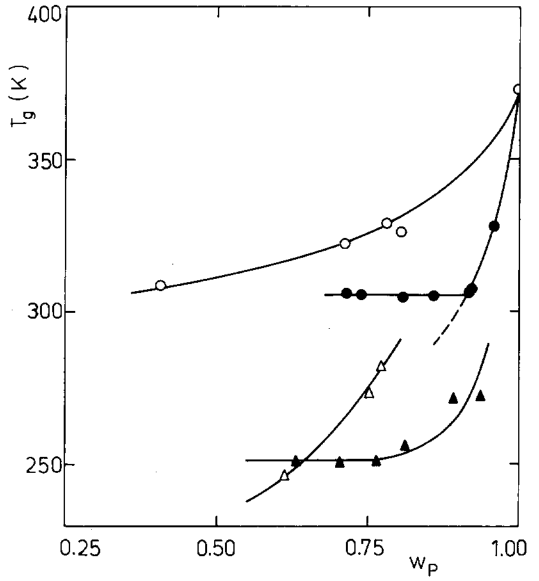

Figure 8 T_g of PS (solid symbols) and of PS block in PS-PEP copolymer (open symbols) swollen by decane (circles) or DIPE (triangles) dependence on the mass fraction of the polymer (including PEP block in copolymer), w_P, in a polymer–solvent mixture

results in larger swelling and in extended chain dimensions within the core, compared to random-coil size[36]. The different extent of swelling of micellar core is a consequence of different interaction of the shell with the solvent (decane is a good solvent for the shell, while DIPE is a poor one).

During the first heating run, a broad but unpronounced endotherm is visible for the temperature dependence of the specific heat at ~350 K (*Figure 9*). After heating it disappears, but after a long time (2–3 months at room temperature) the endotherm reappears. This endotherm may be caused by the presence of ordered domains in polyolefinic blocks of the copolymer.

The solid-state structure of PS cores can be preserved even after the copolymer is dissolved in decane at room temperature because of two effects: (1) the pull of the chains in the shell on the core is reduced, e.g. due to the suspected existence of organized polyolefin domains or because of the molecular orientation of decane molecules, which has been experimentally observed by Costas and Patterson[37]; and/or (2) the attractive interactions within the core are large and do not allow the release of individual chains. This may be reflected, e.g. by the fact that the T_g of the PS core in decane is relatively close to room temperature and much higher compared to DIPE. In other words, decane is a stronger precipitant for PS than DIPE and mutual contacts between the styrene units within the core are expected to be preferred. Consequently, the PS blocks can be regarded as being absorbed (or trapped) in the micellar core and their release, needed for the equilibration of the system, is difficult or unfeasible on a realistic time-scale. The core is virtually frozen, no unimers are detected in solution outside the micelles, and the apparent CMC is zero. When exposed to an elevated temperature well above the glass transition, the micelles persisting from the solid-state structure reorganize themselves and classical equilibrium micelles[3] are formed. The latter state gets frozen again when the system is cooled down to ambient temperature.

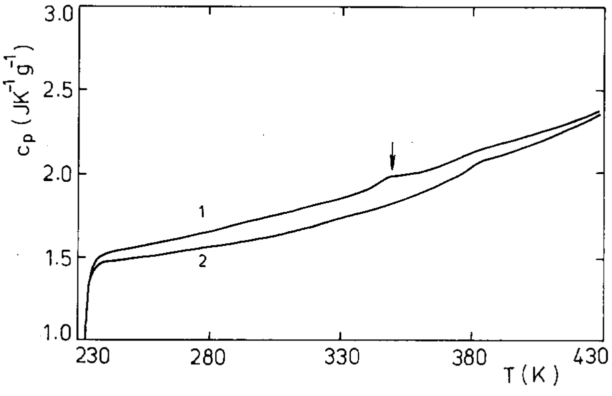

Figure 9 Temperature dependence of the specific heat, c_p, for a solid PS-PEP diblock copolymer in the first (1) and second (2) heating run

Intermicellar interactions

Light scattering from micellar solutions. In the dilute

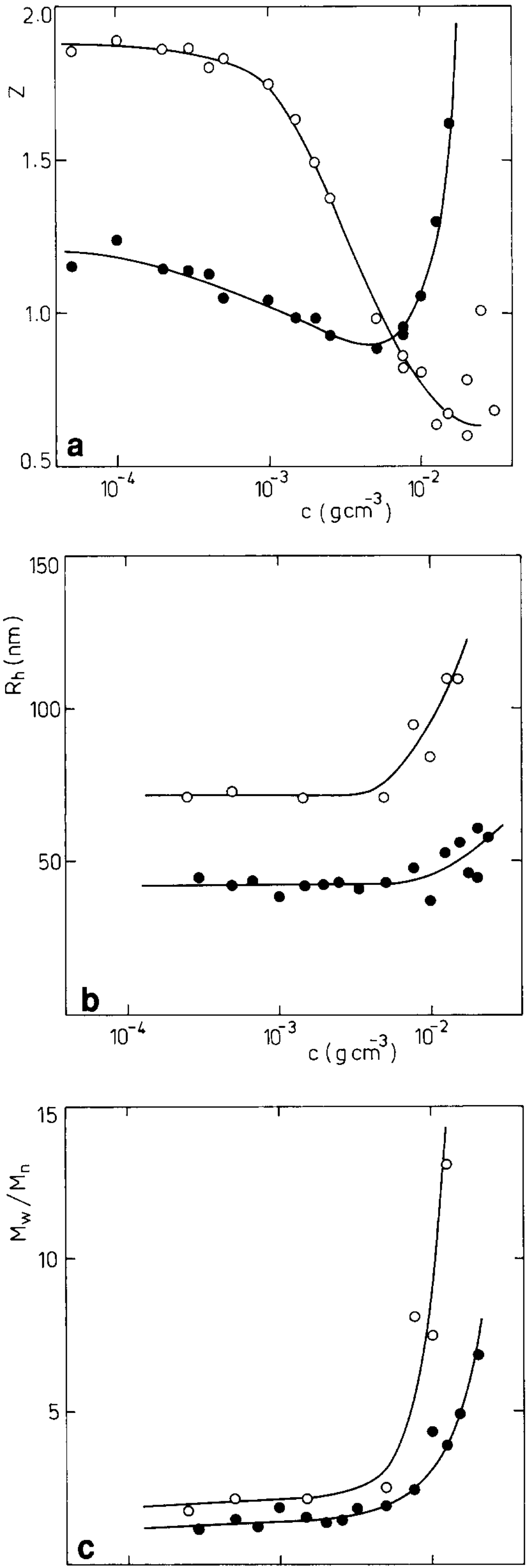

Figure 10 Dependence of (a) the dissymmetry of scattered light, Z, (b) the hydrodynamic radius, R_h, and (c) the apparent M_w/M_n ratio on copolymer concentration, c, in decane for the native (○) and heat-treated (●) solutions

concentration region ($c < 10^{-3}$ g cm^{-3}), the SLS measurements can be evaluated by the routine Zimm method, both for native and heat-treated solutions. In the medium concentration range, the dissymmetries of scattered light are often lower than unity (*Figure 10a*). The dissymmetry Z is defined as the ratio of the intensities of light scattered at 45° and 135°. In practice, this means that the angular dependences in the corresponding Zimm plots have a negative slope (*Figure 3*). Plots of this type have been observed for systems of strongly interacting polymer chains, e.g. in salt-free polyelectrolyte solutions[38] (repulsive interactions) or in ensembles of molecules which are prone to association or gelation[39] (attractive forces).

The concentration dependence of dissymmetry has a pronounced minimum for the heat-treated samples (*Figure 10a*). For the native unheated samples, the existence of such an extreme can only be suspected due to the large scatter of the experimental values in the high concentration region. In this respect, an analogy with the behaviour of polyelectrolytes also pertains[38]. The decrease of the dissymmetry with increasing copolymer concentration (*Figure 10a*) seems to be one of the most sensitive indications of interactions between micelles. These manifest themselves clearly at a concentration as low as 5×10^{-4} g cm^{-3}. The hydrodynamic radii are practically constant in dilute solutions (*Figure 10b*) and start to grow at concentrations which roughly correspond to the minimum dissymmetry. Needless to say, in DIPE the dissymmetry of scattered light attains its usual values, namely from 1.00 to 1.08 in the concentration range 5×10^{-4}–5×10^{-3} g cm^{-3}.

Another hint on interaction between micelles can be seen in the relatively high apparent non-uniformity of micelles, as indicated by DLS. The M_w/M_n ratio differs substantially from unity even at low concentrations (*Figure 10c*), although the block copolymer micelles are usually almost uniform[3] (e.g. in DIPE, $M_w/M_n = 1.06$ at $c = 2.06 \times 10^{-3}$ g cm^{-3}). The observed high apparent non-uniformity of micelles is a consequence of the fact that the autocorrelation function in DLS cannot be fitted by a single exponential. The broad distribution of decay times need not, in our opinion, reflect the true non-uniformity of particles, but may result from interactions between micelles. If there were a broad distribution of micellar sizes, the side maximum on SAXS curves, corresponding to the particle scattering of uniform spheres, could not be detected. In fact, the shape of the scattering curve in the side-maximum region for decane solutions is very similar to that for DIPE solutions (*Figure 4*). The true non-uniformity of micelles in decane thus has to be as low as in DIPE. An increase in the apparent non-uniformity of particles with concentration has been also described by Tsunashima[35] for PS-PB diblock in decane. At higher concentrations, the non-uniformity of the system becomes very high (*Figure 10c*).

Viscosity of micellar solutions. The high viscosity of micellar solutions in decane and the strong non-linear concentration dependence of the reduced viscosity (*Figure 6*) also support the hypothesis of intense interactions between micelles. Although the viscosity of solutions increases after heat treatment, the character of the dependence remains unaffected. The reduced viscosity remains higher than that of true solutions in toluene and its concentration dependence is non-linear. In the literature, the viscosity of PS-PEP solutions has been investigated only rarely[10,40–42]. The general trends reported in this study are the same as those described by Yeung and Frank[10] for PS-PEP diblock copolymer in heptane. However, unlike them, we have not observed any local maxima on the concentration dependences of reduced viscosity.

The concept of sticky contacts. Atypical values of dissymmetry in SLS, the high apparent non-uniformity from DLS and high viscosity indicate that, with increasing concentration, the point of gelation may be approached. The experimental data outlined above could be explained by assuming attractive interaction among the individual micelles. Before analysing this hypothesis any further, the spatial situation in solution should be considered. Obviously, when the micelles fill the available volume completely, physical contact between their shells is unavoidable and a macrolattice forms.

The concentration $c^{\#}$ at which the micelles start to fill the volume by formation of a microlattice without overlap of shells can be estimated as:

$$c^{\#} = 0.74 \frac{3M}{4\pi N_{\mathrm{A}} R_{\mathrm{h}}^{3}} \qquad (5)$$

This formula assumes that uniform spheres of mass M and radius R_{h} are closely packed, i.e. that their volume fraction is[43] 0.74.

For the block copolymer structures under discussion (*Table 2*), the critical concentrations $c^{\#}$ are 0.054 and 0.034 g cm^{-3} for the unheated and heat-treated decane solution, respectively, and 0.075 g cm^{-3} for solutions in DIPE. This is in accord with the finding of Higgins *et al.*[7] who used SANS to localize the onset of formation of ordered PS-PEP micellar structures in dodecane to 3–4 wt% concentration. The interaction among the individual micelles, as reflected, e.g. in the dissymmetries of scattered light lower than unity, occurs without doubt at much lower concentrations[8,9,12,13]. Therefore, we suppose that the nature of the interaction among the micelles consists in a limited and temporary association of chains, which form the shells of the micelles.

To explain the steep concentration dependence of the reduced viscosity and increasing of the apparent non-uniformity of micelles formed by PS-*block*-poly-(ethylene-*co*-butylene)-*block*-PS triblock copolymer in heptane, Tuzar *et al.*[44] suggested the existence of tentacled micelles. It was assumed that, while one PS block is incorporated in the core of the micelle, the other may be relatively free and act as an association site (tentacle) for contact with other tentacles or collapsed PS blocks in unimers. Such a model, however, applies only to triblock copolymers and cannot account for the phenomenologically similar behaviour of the diblocks in our case.

Data interesting in this context, based on light scattering experiments, have been published by Poddubnyi *et al.*[45]. These authors describe the association of PB chains even in thermodynamically good solvents. Polydisperse aggregates were found in octane, decane and dichloroethane, while in cyclohexane and chloroform the PB chains were molecularly dissolved. Another case of association, this time of ethylene–propylene–diene (EPDM) terpolymer in good solvents like toluene, has been observed in viscometric measurements by Horský and Bohdanecký[46]. Thermoreversible gelation due to microcrystallization of polyethylene sequences occurs both in benzene and toluene below room temperature. The association of EPDM chains in solution has been observed even at higher temperatures. Organization of ethylene–propylene copolymer in paraffinic oil has been also reported by Rubin[47].

In our opinion, the interaction of micelles is not directly connected with the micellar nature of the system, but rather with the simple fact that the polyolefinic chains forming the shell (PEP, PB, PIP, etc.) are able to associate in hydrocarbons, even though these are thermodynamically good solvents for them. We are well aware of the somewhat contradicting character of this statement. Stereoregular sequences of the constitutional units may enhance temporary contacts of precrystalline nature between individual chains. These interactions, called here sticky contacts, would lead to association in the system. They would become operative when the chains get close to each other, and their frequency is likely to decrease on dilution of the system. There should also be a temperature limit to such sticky contacts, above which they would no longer form.

Although the hypothesis of sticky contacts is speculative, it explains the majority of the observed experimental facts: interaction of micelles in dilute solutions as revealed by the scattering methods, the apparent non-uniformity of micelles (by DLS) and the high viscosity of solutions. It is also consistent with the observation that the behaviour of diblocks in non-hydrocarbon solvents, such as DIPE, is less complex, even though the micelles have practically the same structure, mass and size.

CONCLUSIONS

1. The supermolecular structure formed by block copolymers in the solid state can be, under favourable conditions, to some extent preserved in solution, if specific selective solvents are used for dissolution. Decane is an example of such a solvent for the PS-PEP diblock copolymer. The surviving structures are metastable. They are likely to exist if the chains are firmly bound in the core and unimers cannot be exchanged between micelles. This may be expected, e.g. if the core is in the glassy state, if it is too compact (unswollen), if there are bonding interactions within the core, or when these effects are combined. These frozen structures transform into the equilibrium spherical micelles, when the chains in the core are loosened. This may happen if the temperature is sufficiently increased, or after the core has been swollen by a convenient solvent and the T_{g} of the swollen micellar core is thus decreased.
2. Some polyolefins are known to form aggregates or even gels in thermodynamically good solvents (e.g. PB or EPDM terpolymer). This effect may be caused by the presence of constitutional units which are able to crystallize or associate; in solution, they create temporary physical crosslinks, here called sticky contacts. The attractive forces among the chains in the micellar shell are responsible for the interaction of micelles even at low concentrations and enhance the formation of organized structure in dilute and moderately concentrated solutions.
3. In DIPE, the behaviour of PS-PEP micelles is simpler. Neither any relation to their solid-state structure nor an interaction of micelles have been observed.
4. When studying the properties of micellar solutions, one should deliberate whether the solid-state structure

can partly survive in solution and thus affect the solution properties.

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