Dilute and semidilute solutions of ABA block copolymer in solvents selective for A or B blocks: 1. Small-angle X-ray scattering study*

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Solutions of a triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, in a selective solvent either for the aliphatic middle block (heptane) or for the polystyrene outer blocks (1,4-dioxane/25 vol% heptane) were studied by viscometry and small-angle X-ray scattering. In both systems, micelles were detected with uniform spherical cores formed by insoluble copolymer blocks. In semidilute solutions, in concentration regions above 0.01 g cm^{-3} in heptane and ~0.1 g cm^{-3} in the mixed solvent, micelles were found to be space-correlated, the effect being accompanied by a steep increase in zero-shear viscosity. Aliphatic micellar cores in the mixed solvent are highly swollen due to the effect of selective sorption.

(Keywords: block copolymer micelles; zero-shear viscosity; small-angle X-ray scattering; space correlation in semidilute solutions)

INTRODUCTION

Triblock ABA copolymers show different association behaviour in solvents selective for the outer blocks A or for the middle block B. It has been recognized that, in the former case, triblock copolymers form uniform spherical micelles, which are in equilibrium with molecularly dissolved copolymer (unimer)[1,2]. Micelles have a concentric-sphere core–shell structure, the core being formed by insoluble middle blocks and the shell by solvated outer blocks. The association number (i.e. the number of unimer molecules in a micelle), typically several tens, sometimes even a few hundreds, does not depend on copolymer concentration in a given solvent and at a constant temperature. No basic differences in the equilibrium behaviour of micelles in dilute solutions of triblock copolymers in solvents selective for the outer blocks and in dilute solutions of diblock copolymer micelles have been reported[1,2]. Although micelles of triblock copolymers have not been studied yet in more concentrated solutions, it can be expected that they would behave similarly to diblock copolymer micelles. The latter were found to form a three-dimensional organized structure, the so-called macrolattice[3].

Relatively little is known about the association of triblock copolymers in solvents selective for the middle block. In dilute solutions of a few such systems several authors[4–6] failed to detect any multimolecular association. It has been suggested for one particular case of poly(methyl methacrylate)-*block*-polystyrene-*block*-poly(methyl methacrylate) in a solvent mixture toluene/*p*-cymene, mildly selective for polystyrene, that the outer blocks associate intramolecularly and the polystyrene middle block envelopes the 'core' thus formed[4,5]. Only in solvent mixtures with a high *p*-cymene content, which are more strongly selective precipitants for the outer blocks, have multimolecular associates been found. Static light scattering data on the particles did not fit the pattern of the spherical core–shell model. The authors[7] speculated that the particles possessed a network-like or a highly branched structure. Ten Brinke and Hadziioannou[8] questioned the idea of an intramolecular association given in refs 4 and 5. They argued that, if association of the outer blocks were thermodynamically favourable, the formation of a real multimolecular micelle would be even more favourable. Nevertheless, they advocated the idea that a triblock copolymer in a solvent selective for the middle block does not micellize at all due to the entropy loss accompanying a back-folding of the middle block. For another copolymer with poly(2-hydroxyethyl methacrylate) outer blocks and a poly(ethylene oxide) middle block, rather puzzling data have been reported[9]. Micellar radius (95.4 nm) and micellar molar mass (45×10^6 g mol^{-1}) lead to a lower value of the average volume fraction of polymer segments in a micelle (0.02) than for a polymer coil. Also, the association number (~4000) was unusually high, at least in comparison with common polymolecular micelles. With increasing concentration of triblock copolymer in a selective solvent for the middle block, a steep increase in viscosity and the formation of viscoelastic gels have been reported[10,11]. This behaviour was attributed to the formation of an infinite network in which the unsolvated blocks form 'knots' or pseudo-crosslinks[10].

In this paper we present experimental small-angle X-ray scattering and viscosity data on dilute and semidilute solutions of a triblock copolymer, polystyrene-

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* This paper is dedicated to Dr Karel Dušek on the occasion of his 60th birthday

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block-poly(hydrogenated butadiene)-*block*-polystyrene, in a solvent mixture selectively good for polystyrene, 1,4-dioxane/25 vol% heptane, and in a solvent selectively good for poly(hydrogenated butadiene), heptane.

EXPERIMENTAL

Copolymer

A triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene (the Shell product, Kraton G-1650), has been fractionated[12] and the middle fraction, 15 mass% of the raw sample, free from homopolystyrene, was used in our study. Molecular characteristics of the fraction, G-1650/F, and of the unfractionated sample are given in *Table 1*.

Solvents

Heptane and 1,4-dioxane (analytical grade, Lachema, Czechoslovakia) were distilled on a laboratory column before use.

Solutions

Solutions for viscosity and small-angle X-ray measurements were prepared in sealed ampoules by direct dissolution in respective solvents at 80°C.

Viscometry

Zero-shear viscosity of copolymer solutions, η^0 (Pa s), was measured on a Rheometrics Four (liquid mode, ultrasensitive transducer, cone-and-plate geometry, cone angle 0.02 rad, nominal gap 0.05 mm) at 25°C. Measurements were performed in a steady regime, the rate depending on solution viscosity. For $\eta^0 < 10^{-2}$ Pa s, the rate was 10–100 s^{-1}; for higher viscosities, 0.01–1 s^{-1}. Values of $\eta^0 < 10^{-3}$ Pa s were checked by capillary viscometry. Since heptane tended to evaporate during measurements, the process leading to crust formation at the solution/air phase boundary, longer-time experiments, e.g. determination of the frequency characteristics, could not be performed.

Small-angle X-ray scattering (SAXS)

Scattering curves were registered on a Kratky camera and converted to absolute scale by means of a Lupolen standard using the formula[14]:

$$\frac{\mathrm{d}\tilde{\Sigma}(q)}{d\Omega} = \frac{a}{\tilde{I}_{\mathrm{L}} K_{\mathrm{L}} T t} \tilde{I}(q) \tag{1}$$

where $\tilde{I}(q)$ is the measured scattered intensity, $q = (4\pi/\lambda)\sin(\theta/2)$ is the length of the scattering vector, λ is the wavelength of the radiation, θ is the scattering angle, a is the sample–detector distance, T is the sample transmission, t is the sample thickness, K_{L} is a calibration constant and $\tilde{I}_{\mathrm{L}}$ is the intensity of radiation scattered by the standard at $q = (2\pi/15\,\text{nm})$. The differential scattering cross-section $\mathrm{d}\Sigma(q)/\mathrm{d}\Omega$ (cm^{-1}) was then obtained from $\mathrm{d}\tilde{\Sigma}(q)/\mathrm{d}\Omega$ by means of Glatter's desmearing program[15].

Table 1 Characteristics of the Kraton G-1650 and its fraction. M_{w} was determined by static light scattering and $M_{\mathrm{w}}/M_{\mathrm{n}}$ by dynamic light scattering[13], both values in cyclohexane. The mass fraction of styrene units, $w^{(\mathrm{S})}$, and the ratio of ethene and butene units, E/B, in the aliphatic middle block, were determined by ^{1}H n.m.r.

Sample	M_{w} (g mol^{-1})	$M_{\mathrm{w}}/M_{\mathrm{n}}$	$w^{(\mathrm{S})}$	E/B
G-1650	74 000	1.30	0.28	0.55
G-1650/F	70 000	1.05	0.28	0.53

The mean-square fluctuation of scattering density is related to the scattering cross-section by the expressions:

$$\overline{(\Delta\rho)^2} = (1/2\pi^2)\int_0^\infty q^2[\mathrm{d}\Sigma(q)/\mathrm{d}\Omega]\,\mathrm{d}q \tag{2a}$$

$$\overline{(\Delta\rho)^2} = (K/4\pi^2)\int_0^\infty q[\mathrm{d}\tilde{\Sigma}(q)/\mathrm{d}\Omega]\,\mathrm{d}q \tag{2b}$$

where $K = 2\pi/a\lambda$.

For a solution of N-component particles $\overline{(\Delta\rho)^2}$ can be calculated as[16,17]:

$$\overline{(\Delta\rho)^2} = \frac{\sum_{i=1}^{N} (c_i/s_i\bar{v}_i)(\Delta b_i)^2}{\sum_{i=1}^{N} c_i} - c^2\left(\frac{\sum_{i=1}^{N} c_i(\Delta b_i)}{\sum_{i=1}^{N} c_i}\right)^2 \tag{3}$$

where $\Delta b_i = b_i - \bar{v}_i\rho_0$ represents the excess scattering amplitude of the ith component, b_i is the scattering amplitude relating to 1 g of the ith component, $\bar{v}_i$ and s_i are the partial specific volume and the swelling factor of the ith component, respectively, ρ_0 is the scattering density of the solvent and $c = \sum_{i=1}^{N} c_i$ is the overall solute concentration.

The last expression is a modification of the well known relation for an N-phase system characterized by volume fractions ϕ_i and scattering densities ρ_i:

$$\overline{(\Delta\rho)^2} = \sum_{i<j}^{N} \phi_i\phi_j(\rho_i - \rho_j)^2 \tag{4}$$

The following relationships have been used for the determination of the structure parameters[18,19].

(i) Weight-average molar mass, M_{w}:

$$M_{\mathrm{w}} = \frac{N_{\mathrm{A}}}{c(\Delta b)^2}\frac{\mathrm{d}\Sigma(0)}{\mathrm{d}\Omega} \tag{5}$$

where N_{A} is the Avogadro number.

(ii) Radius of a homogeneous sphere, R:

$$R = 5.76/q_1 \tag{6}$$

where q_1 is the position of the first side maximum of the scattering curve.

Scattering intensity at $q = 0$ is related to that at $q = q_1$ by the relation:

$$\frac{\mathrm{d}\Sigma(0)}{\mathrm{d}\Omega} = \frac{\mathrm{d}\Sigma(q_1)}{\mathrm{d}\Omega}\Big/ 0.00745 \tag{7}$$

Space-correlated, liquid-like organization of particles gives rise to a scattering maximum at[20]:

$$q = 1.22 \times 2\pi/d \tag{8}$$

where d is the average interparticle distance.

RESULTS AND DISCUSSION

Choice of selective solvents

It has been found in our earlier studies on micellar solutions of the Kraton G-1650 copolymer that 1,4-dioxane is a selective solvent for the polystyrene blocks while heptane is a selective solvent for the hydrogenated polybutadiene block[21,22]. Micelles with aliphatic cores and polystyrene shells are present in dilute solutions in 1,4-dioxane with up to 30 vol% heptane, behaving like hydrodynamically hard spheres[23]. Solutions with a higher amount of heptane, up to ~85 vol%, contain only molecularly dissolved copolymer. Only low-viscosity micellar solutions in the concentration range $c < 0.1\,\mathrm{g\,cm^{-3}}$ can be prepared in mixtures with up to 20 vol% heptane. Thus a mixture 1,4-dioxane/25 vol% heptane was chosen, in which our copolymer sample could be dissolved directly up to $c = 0.15\,\mathrm{g\,cm^{-3}}$. In heptane, solutions up to $c = 7 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$ could be prepared.

Viscosity

The concentration dependence of the zero-shear viscosity of G-1650/F sample in both solvents shows low- and high-viscosity, or dilute and semidilute, regions (*Figure 1*). The cross-over concentration c^+ dividing these low- and high-slope concentration dependences differs markedly for the two solvents. For heptane, c^+ is around $1 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, while for 1,4-dioxane/25 vol% heptane this concentration is almost 10 times higher. In semidilute regions in *Figure 1*, η^0 scales with $c^{6.3}$ for heptane solutions and with c^{50} for solutions in 1,4-dioxane/25 vol% heptane. For the sake of comparison, for a linear polymer in the semidilute regime, $\eta^0 \sim c^{3.4}$ (ref. 24); and for semidilute solutions of a radial block copolymer with four branches consisting of inner polybutadiene and outer polystyrene blocks in a selective solvent for the polybutadiene blocks, a relation $\eta^0 \sim c^{12}$ has been found[25].

SAXS from heptane solutions

The shape of SAXS curves obtained from heptane solutions at copolymer concentrations below c^+ (*Figure 2*) does not seem to be influenced by interparticle interference. Above c^+, at $c = 2.9 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, a pronounced scattering maximum appears at $q = 0.15\,\mathrm{nm^{-1}}$, indicating a space-correlated arrangement of the scattering objects. At a still higher concentration, $c = 5.2 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, the maximum shifts to a higher q value ($0.18\,\mathrm{nm^{-1}}$). Interpretation of this interference maximum will be discussed below.

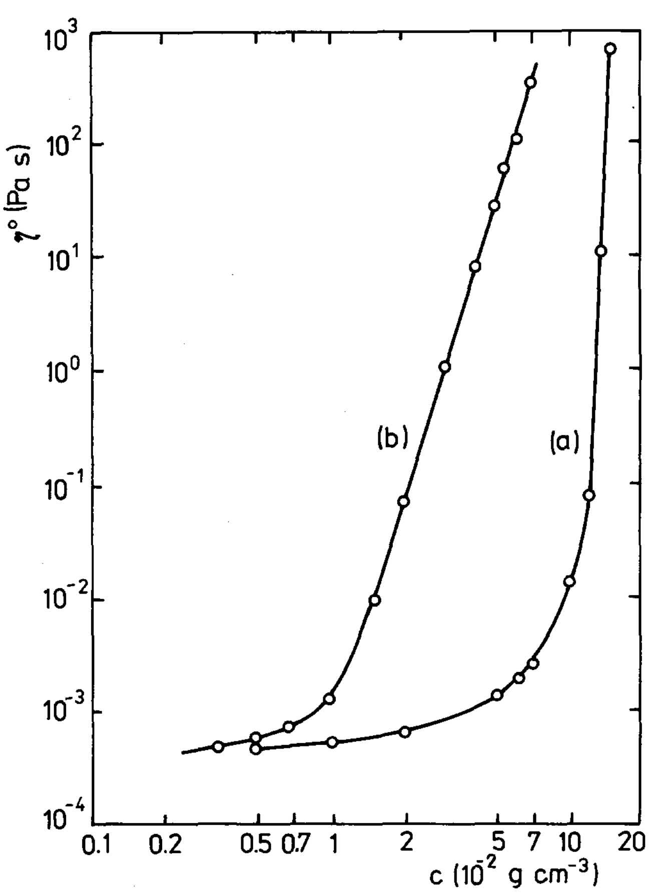

Figure 1 Concentration dependence of zero-shear viscosity η^0 for G-1650/F solutions in (a) 1,4-dioxane/25 vol% heptane and (b) heptane

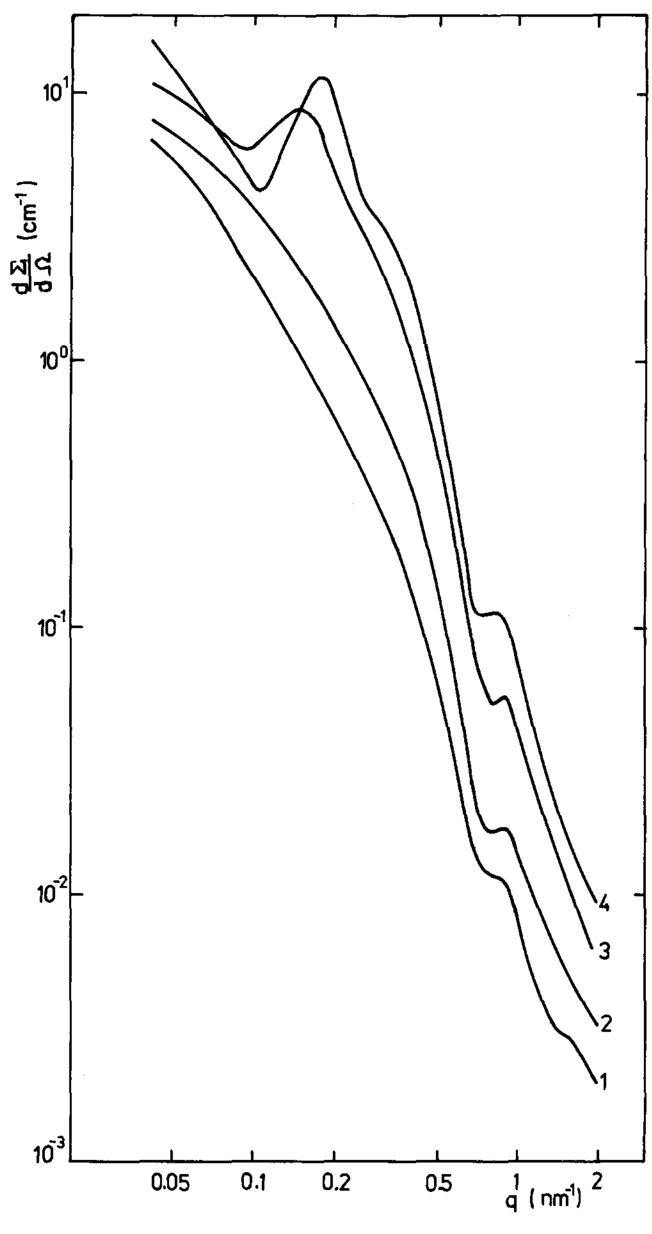

Figure 2 SAXS curves of G-1650/F in heptane at various copolymer concentrations ($10^{-2}\,\mathrm{g\,cm^{-3}}$): 0.51 (curve 1), 0.97 (curve 2), 2.93 (curve 3) and 5.20 (curve 4)

A dominant feature of SAXS curves in *Figure 2* is a side scattering maximum, the position of which is independent of the copolymer concentration. This pattern indicates that the copolymer solutions under study contain particles having a relatively narrow size distribution and a concentration-independent geometry. Owing to the fact that the highly swollen micellar shells have a larger radius of gyration and a lower scattering contrast, in comparison with the less swollen micellar cores, it can be assumed that the side maximum corresponds practically to the scattering from polystyrene micellar cores. For the position of the side maximum, $q = 0.90\,\mathrm{nm^{-1}}$, and under the assumption of the homogeneous-sphere model, we get for the core radius, using equation (6):

$$R^{(\mathrm{core})} = 6.4\,\mathrm{nm}$$

If the core contained only solvent-free polystyrene blocks with density $1.07\,\mathrm{g\,cm^{-3}}$, the mass of the core would be $M^{(\mathrm{core})} = 0.71 \times 10^6\,\mathrm{g\,mol^{-1}}$. Taking into account the mass fraction of polystyrene in the copolymer sample, the micellar molar mass would then be $M^{(\mathrm{m})} = 2.5 \times 10^6\,\mathrm{g\,mol^{-1}}$.

For an estimation of the $M^{(\mathrm{m})}$ value from the absolute scattering intensities, the unimer/micelles ratio must be known. Sedimentation velocity data in Part 2[26] show that, in the concentration region below c^+, the unimer concentration is about $2 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$, independent of the copolymer concentration. The scattering intensity value at $q = 0$ pertaining to micellar cores and normalized for micellar concentration, $c^{(\mathrm{m})} \simeq c - 2 \times 10^{-3}\,(\mathrm{g\,cm^{-3}})$, has been obtained using equation (7):

$$\frac{1}{c^{(\mathrm{m})}}\left(\frac{\mathrm{d}\Sigma(0)}{\mathrm{d}\Omega}\right)^{(\mathrm{core})} = 300 \pm (10\%)\,\mathrm{cm^2\,g^{-1}}$$

The value obtained with the lowest concentration ($482\,\mathrm{cm^2\,g^{-1}}$) has been disregarded since it may be subject to a large statistical error and also it may be affected by scattering from unimer. Excess scattering amplitude $\Delta b = b - \bar{v}\rho_0$ has been calculated using the partial specific volume of polystyrene in heptane, $\bar{v}^{(\mathrm{PS})} = 0.929\,\mathrm{cm^3\,g^{-1}}$ (ref. 27), the scattering density of heptane, $\rho_0 = 6.72 \times 10^{10}\,\mathrm{cm^{-2}}$, and the scattering amplitude of one electron, $b_e = 0.282 \times 10^{-12}\,\mathrm{cm}$. The excess scattering amplitude then is $\Delta b^{(\mathrm{PS})} = 2.89 \times 10^{10}\,\mathrm{cm\,g^{-1}}$. Employing the mass fraction of polystyrene, $w^{(\mathrm{PS})} = 0.28$, equation (5) leads to $M^{(\mathrm{core})}$ and $M^{(\mathrm{m})}$ values of 0.77×10^6 and $2.8 \times 10^6\,\mathrm{g\,mol^{-1}}$, respectively.

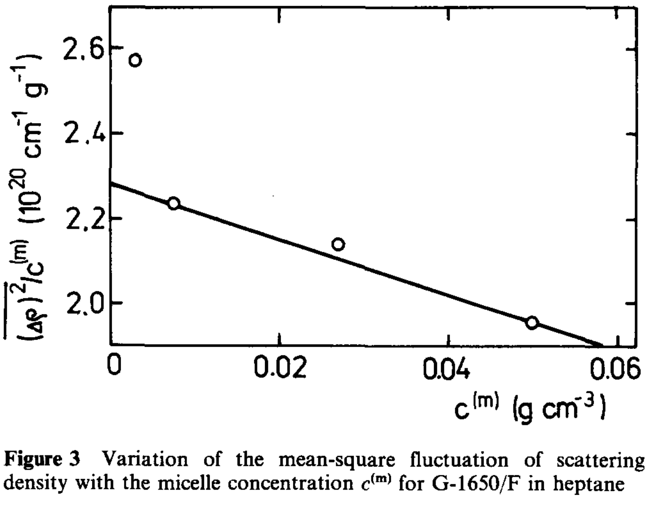

Figure 3 Variation of the mean-square fluctuation of scattering density with the micelle concentration $c^{(\mathrm{m})}$ for G-1650/F in heptane

Table 2 Excess scattering amplitudes Δb ($10^{10}\,\mathrm{cm\,g^{-1}}$) of G-1650/F and its constituents in two solvents)

	Heptane	1,4-Dioxane/ 25 vol% heptane
Hydrogenated polybutadiene	1.87	−0.62
Polystyrene	2.89	0.91
Copolymer	2.16	−0.19

The concentration dependence of the mean-square fluctuation of the scattering density (*Figure 3*) has been determined from the smeared SAXS curves using equation (2b). Disregarding the value at the lowest concentration, the reason being the same as in the case of the intensity at $q = 0$, $(\mathrm{d}\Sigma(0)/d\Omega)^{(\mathrm{core})}$, a linear decrease of $\overline{(\Delta\rho^2)}/c^{(\mathrm{m})}$ with $c^{(\mathrm{m})}$ can be observed. The slope of the dependence gives the excess scattering amplitude of micelles, $\Delta b^{(\mathrm{m})} = 2.5 \times 10^{10}\,\mathrm{cm\,g^{-1}}$ (cf. equation (3) and refs 16 and 17), which is about 20% higher than the value calculated from the copolymer composition (*Table 2*). The value of $\overline{(\Delta\rho^2)}/c^{(\mathrm{m})}$ extrapolated to infinite dilution ($2.3 \times 10^{10}\,\mathrm{cm\,g^{-1}}$) can provide information on the swelling of a micellar core. Employing equation (3), a relation has been derived for our system:

$$\left(\frac{\overline{(\Delta\rho)^2}}{c}\right)_{c\to 0} = \frac{w^{(\mathrm{PS})}[(\Delta b)^2]^{(\mathrm{PS})}}{s^{(\mathrm{PS})}\bar{v}^{(\mathrm{PS})}} + \frac{w^{(\mathrm{hB})}[(\Delta b)^2]^{(\mathrm{hB})}}{s^{(\mathrm{hB})}\bar{v}^{(\mathrm{hB})}} \tag{9}$$

where superscripts PS and hB stand for polystyrene and hydrogenated polybutadiene, respectively; w is the mass fraction and s is the degree of swelling. Substituting the known values in equation (9), we get, under the assumption of strong swelling of the soluble component ($s^{(\mathrm{hB})} \simeq 10$; cf. ref. 27), the degree of swelling of the polystyrene micellar core, $s^{(\mathrm{PS})} \simeq 1.2$. This value is not too sensitive to the assumed $s^{(\mathrm{hB})}$ value and corresponds well with the results obtained with similar systems[27]. It should be stressed, however, that when estimating the $M^{(\mathrm{m})}$ value from the position of the side maximum on the SAXS curves, a solvent-free core was assumed ($s^{(\mathrm{PS})} = 1$); the true value of the micellar molar mass should be 20% lower than our value. The direct method of static light scattering (cf. Part 2[26]) provided $M^{(\mathrm{m})} = 2.26 \times 10^6\,\mathrm{g\,mol^{-1}}$, which is lower—as it should be—than the two values obtained from the position and the height of the side maximum, 2.5×10^6 and $2.8 \times 10^6\,\mathrm{g\,mol^{-1}}$, respectively. Considering the rather simplified model used for interpretation of the SAXS data, agreement between the $M^{(\mathrm{m})}$ values obtained is strikingly good. The very pronounced, low-q maximum on the SAXS curves for the two highest concentrations in *Figure 2* results from interparticle interference. The existence of only one interference maximum implies that micellar cores are not arranged in a regular macrolattice. Using equation (8) for liquid-like structures, the average mutual core distance d has been estimated as 51 and 43 nm for solutions of concentrations 2.93×10^{-2} and $5.2 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, respectively. For these concentrations, the corresponding values of the volume fractions of polystyrene cores[28]:

$$\phi^{(\mathrm{core})} = 0.74(2R^{(\mathrm{core})}/d)^3$$

are 1.2×10^{-2} and 2.0×10^{-2}, respectively, both values being ~30% higher in comparison with those calculated from the copolymer concentration and the degree of swelling. The discrepancy can be explained, for example, by attractive interparticle forces. This explanation is also supported by the scattering patterns (*Figure 2*). The inner part of the scattering curves tends to a maximum rather than a minimum. As follows from the discussion of scattering functions of interacting colloidal particles published by Chen and Lin[29], such behaviour implies an aggregation of micelles[30]. Independent evidence of the attractive forces has been obtained by dynamic light scattering in Part 2[26]. A possible source of attractive forces may be sharing of one copolymer molecule by two micellar cores. With the molar mass of the middle block of the copolymer used ($50 \times 10^3\,\mathrm{g\,mol^{-1}}$), this might

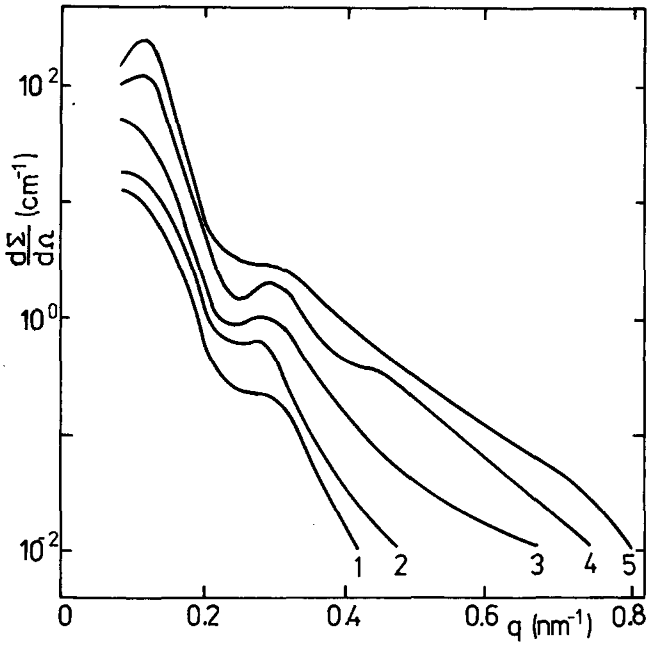

Figure 4 SAXS curves of G-1650/F in 1,4-dioxane/25 vol% heptane at various copolymer concentrations ($10^{-2}\,\mathrm{g\,cm^{-3}}$): 1.030 (curve 1), 1.97 (curve 2), 3.62 (curve 3), 8.59 (curve 4) and 14.9 (curve 5)

occur even at low copolymer concentrations. A model of the micellar structure and intermicellar interactions in dilute and semidilute heptane solutions will also be discussed in more detail in Part 2.

SAXS from 1,4-dioxane/25 vol% heptane solutions

Like for heptane solutions, the SAXS curves in *Figure 4* show a side maximum, the position of which is concentration-independent, and a low-q interference maximum at the highest concentrations.

The side maximum implies the presence of particles, which in this system can be identified with micellar cores formed by insoluble hydrogenated polybutadiene blocks. The core radius, estimated from the position of the side maximum, is:

$$R^{(\mathrm{core})} = 20\,\mathrm{nm}$$

Assuming a solvent-free core, we get, in the same way as for heptane solutions, the micellar molar mass values: $24 \times 10^6\,\mathrm{g\,mol^{-1}}$ from the position of the side maximum, and $97 \times 10^6\,\mathrm{g\,mol^{-1}}$ from the height of the side maximum. In contrast to the heptane solutions, there is a substantial difference between these two results. We used a simple model that does not include the polydispersity and contingent diffuseness of the core–shell boundary. These factors would lead to an underestimation of the mass obtained from the height of the side maximum as compared with that from the position. However, the observed trend is just the opposite. Hence, we believe that the main reason for the discrepancy is the false assumption of a solvent-free core. A reliable, model-independent value of $M^{(\mathrm{m})}$, obtained by static light scattering in Part 2[26], is much lower: $4.35 \times 10^6\,\mathrm{g\,mol^{-1}}$. Comparing this value with that calculated from the position of the side maximum (i.e. based on the core volume), we get the degree of core swelling:

$$s^{(\mathrm{hB})} = 24/4.3 = 5.6$$

This value is surprisingly large in comparison with the core swelling of the same copolymer in one-component solvents, 1,4-dioxane[21] and heptane.

The high degree of swelling of the core in 1,4-dioxane/25 vol% heptane mixture can be explained by the different affinity of 1,4-dioxane and heptane for the hydrogenated polybutadiene core and polystyrene shell. Owing to the selective sorption of heptane on hydrogenated polybutadiene and of 1,4-dioxane on polystyrene, the mixed solvent will be richer in heptane in the core area and richer in 1,4-dioxane in the shell area, with respect to the composition of the bulk solvent.

The selective sorption argument is corroborated by values of the mean-square fluctuation of the scattering density. A theoretical value has been calculated using equation (9) with the help of Δb values from *Table 2*, and under the assumption of non-swollen micelles ($s^{(\mathrm{hB})} = s^{(\mathrm{PS})} = 1$):

$$\left(\frac{\overline{(\Delta\rho)^2}}{c}\right)_{\mathrm{dry}} = 0.49 \times 10^{20}\,\mathrm{cm^{-1}\,g^{-1}}$$

This theoretical value is about 50% lower than the experimental one (*Figure 5*). It is a known fact that the swelling of a particle by a solvent or, in the case of a mixed solvent, by a mixture of the same composition as that outside the particle must lead to a decrease of $\overline{(\Delta\rho)^2}$. Since our experimental values of $\overline{(\Delta\rho)^2}$ for swollen particles are higher, selective sorption can be considered as a likely explanation for the effect. We have estimated, using experimental values of $\overline{(\Delta\rho)^2}/c$, that the volume fraction of heptane in a mixed solvent in the micellar core changes from 0.30 for $c = 14.9 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$ to 0.40 for $c = 1.03 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$. It means that for these two concentrations the volume fraction of heptane in the micellar cores increases by 0.05 and 0.15, respectively.

Contrary to the previous system (heptane solutions), values of $\overline{(\Delta\rho)^2}/c$ are concentration-independent in the mixed solvent solutions (*Figure 5*). This behaviour can be explained by a low value of the excess scattering amplitude of the copolymer in the given mixed solvent (*Table 2*). The concentration-dependent contribution to $\overline{(\Delta\rho)^2}/c$ (equation (3)) is, for the highest concentration, $0.149 \times (-0.19 \times 10^{10})^2 = 0.005 \times 10^{20}$, which is only 0.5% of the experimental $\overline{(\Delta\rho)^2}/c$ value.

At the highest copolymer concentrations, the micellar cores occupy a substantial part of the solution volume. The volume fraction of cores:

$$\phi^{(\mathrm{core})} = (cN_{\mathrm{A}}/M^{(\mathrm{m})})(4\pi/3)(R^{(\mathrm{core})})^3$$

is 0.70 for $c = 14.9 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, which is close to the maximum volume fraction of uniform spheres ($\phi_{\mathrm{max}}^{(\mathrm{sphere})} = 0.74$). It suggests an almost close packing of micellar

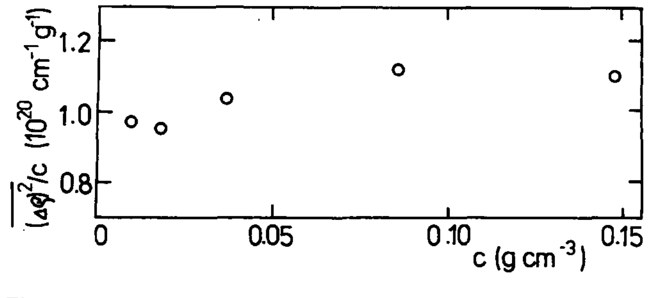

Figure 5 Mean-square fluctuation of scattering density for G-1650/F in 1,4-dioxane/25 vol% heptane

cores at this concentration. In this case, the side maximum is rather damped (*Figure 4*). This could indicate micellar distortions[30] or a broadening of the micelle size distribution. The SAXS curves in *Figure 4* do not indicate any regular macrolattice structure similar to that in ref. 3. Contrary to the heptane solutions, no indication of attractive interaction of micelles is observed. The correlation peak in the scattering patterns for two highest copolymer concentrations is typical of systems with repulsive interactions[30].

CONCLUSIONS

Solutions of a triblock copolymer with polystyrene outer blocks and hydrogenated polybutadiene middle block in two selective solvents, heptane and 1,4-dioxane/25 vol% heptane, show a behaviour peculiar in some respects.

In heptane solutions, micelles are present with cores formed by outer polystyrene blocks and shells formed by aliphatic middle blocks. Above a surprisingly low cross-over concentration ($\sim 1\times 10^{-2}\,\mathrm{g\,cm^{-3}}$), SAXS data point to rather strong intermicellar interactions, the effect being accompanied by a steep increase in zero-shear viscosity with concentration.

In the mixed solvent, micelles are formed with aliphatic cores and polystyrene shells, as expected[21–23]. Unlike solutions in the one-component solvent, micellar cores were found to be strongly swollen, most probably due to the effect of selective sorption. Above a cross-over concentration ($\sim 0.1\,\mathrm{g\,cm^{-3}}$), a very steep increase in zero-shear viscosity with concentration has been observed.

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