Dilute and semidilute solutions of ABA block copolymer in solvents selective for A or B blocks: 2. Light scattering and sedimentation study*

Z. Tuzar, Č. Koňák, P. Štěpánek, J. Pleštil and P. Kratochvíl

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

and K. Procházka

Charles University, Department of Physical Chemistry, 128 40 Prague 2, Czechoslovakia

Micellar solutions of a triblock copolymer polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, in heptane and in 1,4-dioxane/25 vol% heptane have been studied by light scattering and sedimentation velocity methods. In dilute solutions, micellar molar mass, hydrodynamic radius of micelles, average volume fraction of polymer segments in a micellar core and in the whole micelle, and the unimer/micelles ratio have been determined. While in semidilute mixed solvent solutions only one diffusion mode, corresponding to collective diffusion, has been determined, at least two modes, diffusion and relaxation ones, have been observed in spectra of decay times in semidilute heptane solutions. Micellar models have been proposed for both systems under study, accommodating satisfactorily all experimental results.

INTRODUCTION

In Part 1 of this study[1], micellar solutions of a triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, have been studied by viscometry and small-angle X-ray scattering (SAXS). Two selective solvents have been employed: heptane, a good solvent for hydrogenated polybutadiene and a poor solvent for polystyrene, and the mixture 1,4-dioxane/25 vol% heptane, a good solvent for polystyrene and a poor solvent for hydrogenated polybutadiene. For both systems, the concentration dependence of zero-shear viscosity showed low- and high-slope, or in other words dilute and semidilute, regions, separated by a sort of cross-over concentration, c^+. This concentration is surprisingly small for the heptane solutions ($\sim 1 \times 10^{-2}$ g cm^{-3}) and about 10 times higher for the mixed solvent solutions.

In heptane solutions[1], a side maximum on the SAXS curves pointed to the presence of spherical particles with a concentration-independent radius (6.4 nm) in the whole concentration range under study, i.e. up to $c = 5.2 \times 10^{-2}$ g cm^{-3}. These spherical objects have been identified as polystyrene cores of micelles, shells of which would necessarily be formed by the middle aliphatic blocks. The same value of the micellar molar mass, $M^{(m)} = 2.5 \times 10^6$ g mol^{-1}, has been obtained from intensities on a relative scale (i.e. from the position of the side maximum) and from the absolute intensities of scattered radiation

(i.e. from the height of the side maximum). The existence of multimolecular micelles in heptane solutions contradicts the results, both experimental[2-4] and theoretical[5], suggesting that triblock copolymers of ABA type in selective non-solvents for the outer blocks do not associate intermolecularly. Moreover, the very low c^+ value and the existence of micelles in the semidilute, high-viscosity region[1] contradicts the simple 'pseudo-network' model[6], in which the unsolvated outer blocks would form knots and solvated middle blocks would form bridges.

In the copolymer solutions in the mixed solvent[1], 1,4-dioxane/25 vol% heptane, the SAXS curves showed a similar pattern as those in heptane solutions: a side maximum, the position of which was concentration-independent (up to $c = 0.149$ g cm^{-3}), proved the presence of spherical particles ($R = 20$ nm), identified as aliphatic cores of micelles with polystyrene shells. The large difference between $M^{(m)}$ obtained from the position of the side maximum (24×10^6 g mol^{-1}) and $M^{(m)}$ obtained from the absolute intensities (97×10^6 g mol^{-1}), as well as their extremely large values (higher by one order of magnitude in comparison with those obtained with the same copolymer in similar solvents by light scattering[7,8]), have been explained by a strong swelling of the aliphatic micellar cores.

The single, low-q interference maximum on the SAXS curves in semidilute solutions in both selective solvents[1] gave evidence that micelles are space-correlated, without forming a macrolattice structure described in ref. 9.

The aim of the present study has been to develop in

more detail a model of micelles of a triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, in dilute and semidilute solutions in two selective solvents, heptane and 1,4-dioxane/25 vol% heptane. Three methods have been employed in this paper: static light scattering, dynamic light scattering and sedimentation velocity.

EXPERIMENTAL

Solvents (1,4-dioxane, heptane) and the fraction of triblock copolymer, polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene (Kraton G-1650/F), were the same as in Part 1 of our study[1].

Solutions

Dust-free solutions for both static and dynamic light scattering measurements were prepared as follows. A given amount of maximum 2 mass% solution in cyclopentane (a good solvent for the sample at 25°C) was filtered under nitrogen pressure through a glass G-5 bacterial filter (Jena, GDR) into cylindrical measuring cells; the cyclopentane was then removed by evaporation *in vacuo* at room temperature. For samples of higher concentrations, the procedure was repeated until the desired amount of the copolymer was accumulated in the cell. A filtered selective solvent, heptane or 1,4-dioxane/ 25 vol% heptane, was then added and the cells were sealed. The dissolution of the copolymer fraction of the highest concentrations ($c > 5 \times 10^{-2}$ g cm^{-3} in heptane and $c > 0.1$ g cm^{-3} in 1,4-dioxane/25 vol% heptane) took about three weeks at 80°C.

Static light scattering (SLS)

Time-average intensity measurements were performed with a Sofica instrument equipped with a He–Ne laser (vertically polarized, $\lambda_0 = 633$ nm) in the angular range 30–150°. The mass-average molar mass M_w was evaluated from the equation:

$$Kc/\Delta R(\theta) = M_w^{-1} P^{-1}(\theta) + 2A_2 c \qquad (1)$$

where K is the optical constant, which includes the square of the refractive-index increment, $\Delta R(\theta)$ is the excess Rayleigh ratio, proportional to the intensity of light scattered from measured particles at an angle θ, A_2 is the second virial coefficient and c is the copolymer concentration. The z-average radius of gyration, R_G, was determined from the initial slope of the $P^{-1}(\theta)$ function, i.e. of the angular dependence of $Kc/\Delta R(\theta)$, extrapolated to infinite dilution and normalized as $P^{-1}(0) = 1$:

$$P^{-1}(\theta) = 1 + q^2 R_G^2 \qquad (2)$$

where $q = (4\pi n/\lambda_0) \sin(\theta/2)$ is the length of the scattering vector, n being the refractive index of a given solution, λ_0 is the wavelength of light *in vacuo* and θ is the scattering angle. The refractive-index increment, dn/dc, of G-1650/F in heptane was measured directly with a Brice–Phoenix differential refractometer (0.145 cm^3 g^{-1}), while that in the mixture 1,4-dioxane/25 vol% heptane (0.098 cm^3 g^{-1}) was measured after establishment of osmotic equilibrium between the polymer solution and mixed solvent, using a dialysis cell described in ref. 10.

Dynamic light scattering (DLS)

DLS measurements were performed with a laboratory-

made homodyne photon correlation spectrometer (described in ref. 11) equipped with a He–Ne laser ($\lambda_0 = 633$ nm) in an angular range $\theta = 30$–150°. The intensity signal was analysed by a single-bit digital correlator with 96 channels operating with three simultaneous timescales, covering three-and-a-half decades in delay time. In case of need, two autocorrelation functions obtained in this way were spliced, yielding a composite correlation function extending over seven decades of delay time.

Autocorrelation functions $G(t)$ measured with micellar solutions in 1,4-dioxane/25 vol% heptane in the whole concentration range and with dilute micellar solutions ($c < 1 \times 10^{-2}$ g cm^{-3}) in heptane were fitted by a single-exponential function of the form:

$$G(t) = A \exp(-2t/\tau) + B \qquad (3)$$

where t is the time delay, τ is the decay time, equal to $(Dq^2)^{-1}$, D being the z-average diffusion coefficient and q the length of the scattering vector; A and B are constants. In copolymer solutions of higher copolymer concentrations ($c > 1 \times 10^{-2}$ g cm^{-3}) in heptane, more complicated correlation functions were obtained and were treated by an inverse Laplace transform technique, using a regularized positive exponential sum method (REPES)[12]. Several such autocorrelation functions were analysed by means of the standard program CONTIN[13], which had to be run on a mainframe computer. Both procedures provided nearly identical results; only REPES results are introduced in this paper.

Sedimentation velocity

Sedimentation curves were obtained with a MOM 3170 analytical ultracentrifuge (Hungary) in 10 mm cells, at 40000 r.p.m. The movement of the concentration boundary was followed by the method of crossed slits (angle of the phase plate 23°) and recorded on photographic film. Values of the apparent sedimentation coefficient s^* were evaluated from the plot of ln r vs. time t, using the following expression:

$$s^* = \ln(r/r_m)/\omega^2 t$$

where r is the position of the peak maximum from the angle of rotation, r_m is position of the meniscus and $\omega^2 t$ is the centrifugal potential.

All methods were operated at 25°C.

RESULTS AND DISCUSSION

Copolymer solutions in 1,4-dioxane/25 vol% heptane

DLS measurements provided strictly single-exponential autocorrelation curves for all copolymer concentrations, i.e. up to 0.15 g cm^{-3}. Inverse decay time values were q^2-dependent, indicating that only one diffusion mode characterized the solute dynamics at each concentration. In the dilute solution region, which, in this solvent mixture, can be considered up to almost 0.1 g cm^{-3} (*Figure 1*), the mode can be interpreted as translation-diffusion of micelles, characterized by a diffusion coefficient at a finite copolymer concentration D_c.

The concentration dependences of D_c and $Kc/\Delta R(0)$ in the concentration region below 3×10^{-2} g cm^{-3} (*Figure 2*) are similar to those for another fraction of the same copolymer in 1,4-dioxane/0–30 vol% heptane[8]. Extrapolation of the linear part of $Kc/\Delta R(0)$ and D_c to infinite dilution provides values of micellar molar
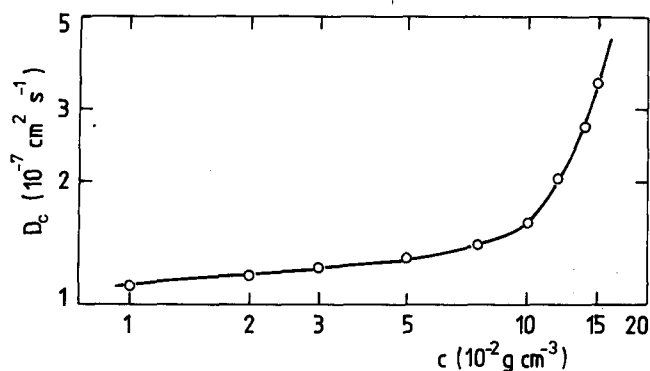
Figure 1 Log–log dependence of the diffusion coefficient at finite concentration, D_c, on the concentration of G-1650/F in 1,4-dioxane/25 vol% heptane
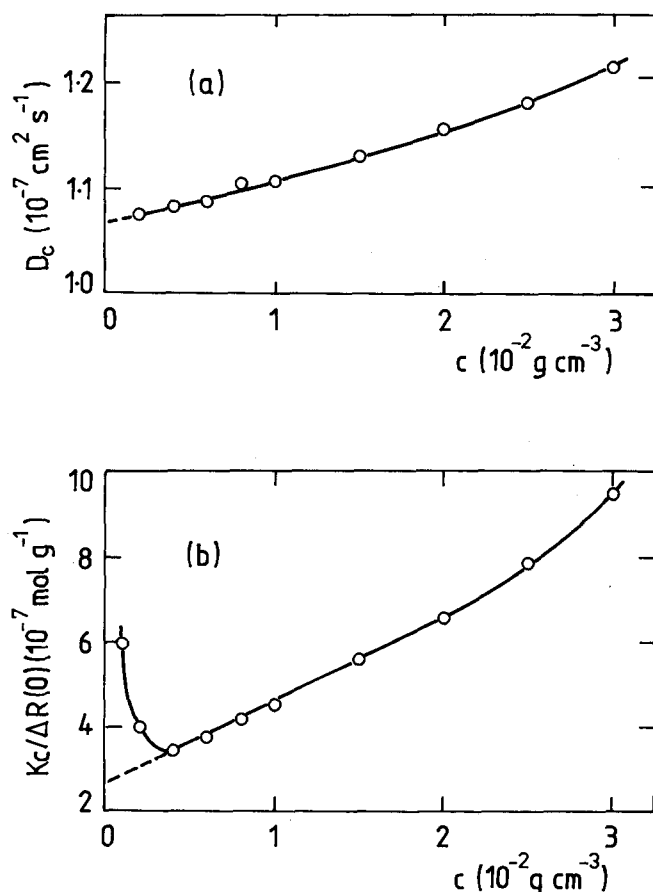

Figure 2 Concentration dependences of (a) D_c and (b) $Kc/\Delta R(0)$ for G-1650/F in 1,4-dioxane/25 vol% heptane

mass ($M_w^{(m)} = 4.35 \times 10^6 \, g \, mol^{-1}$) and diffusion coefficient ($D_0 = 1.06 \times 10^{-7} \, cm^2 \, s^{-1}$). From the latter value, the hydrodynamic radius, $R_H = 24.8$ nm, was calculated using the Stokes–Einstein formula:

$$R_H = kT/6\pi\eta D_0$$

where k is the Boltzmann constant and η is the solvent viscosity. The radius of gyration could not be evaluated owing to practical independence of $Kc/\Delta R(\theta)$ on q.

Using two model-independent values, $M^{(core)}$ from SLS and copolymer composition, and $R^{(core)}$ from SAXS, the average volume fraction of polymer segments in a micellar core, $\alpha^{(core)}$, equal to the reciprocal value of the degree of swelling s, used in Part 1[1], can be calculated:

$$\alpha^{(core)} = \frac{M^{(core)}}{(4\pi/3)(R^{(core)})^3 N_A \rho^{(core)}} \tag{4}$$

For $\rho^{(core)} = 1.07 \, g \, cm^{-3}$ (cf. Part 1[1]), $\alpha^{(core)} = 0.89$ has been obtained. Similarly, $\alpha^{(m)}$ has been estimated under a simplifying assumption that the micellar radius equals R_H and $\rho^{(m)} \simeq 1$. It should be stressed, however, that R_H can be identified with the micellar geometrical radius only if micelles in a given solvent behave like hydrodynamic hard spheres. We have shown[8] that such an assumption is fulfilled for Kraton G-1650 micelles in 1,4-dioxane and its mixtures with up to 30 vol% heptane.

The main difference between micelles in 1,4-dioxane and in the mixture 1,4-dioxane/25 vol% heptane can be seen in the values of $R^{(core)}$ and $\alpha^{(core)}$ (*Table 1*). The unexpectedly large value of $R^{(core)}$ and the small value of $\alpha^{(core)}$ in the mixed solvent can be explained by a strong selective sorption of heptane on the aliphatic blocks, found by SAXS in Part 1. Since our dialysis/refractometry method[10] showed only a small selective sorption effect related to the whole micelle in the mixed solvent, the selective sorption of heptane into the core domain is most probably compensated by the selective sorption of 1,4-dioxane into the shell domain. Two forces would thus be operative in the enlargement of the core volume: (a) the swelling of the core in a thermodynamically better solvent mixture and (b) the stronger pull on the core–shell interface by more swollen polystyrene blocks.

SAXS data showed that above $c \simeq 0.1 \, g \, cm^{-3}$ micelles, without changing their dimensions, begin to become space-correlated, the process being accompanied by a steep increase in zero-shear viscosity (see figures 1 and 4 in Part 1[1]). A similar increase in D_c on this concentration region (*Figure 1*) cannot be interpreted as translation-diffusion any more, but as a collective diffusion of strongly interacting micelles. With the two highest concentrations, 0.14 and 0.15 $g \, cm^{-3}$, another mode on the timescale of 10^2 ms has been detected. This slow mode

Table 1 Structure parameters of G-1650/F micelles in three selective solvents: micellar molar mass, $M^{(m)}$ (SLS); micellar hydrodynamic radius, R_H (DLS); molar mass of the core, $M^{(core)}$ (SAXS, SLS); geometrical radius of the core, $R^{(core)}$ (SAXS); and the average volume fractions of polymer segments in a micelle, $\alpha^{(m)}$, and in a core, $\alpha^{(core)}$

Solvent (selective for)	$M^{(m)}$ ($10^6 \, g \, mol^{-1}$)	$M^{(core)}$ ($10^6 \, g \, mol^{-1}$)	R_H (nm)	$R^{(core)}$ (nm)	$\alpha^{(m)}$	$\alpha^{(core)}$
1,4-Dioxane[a] (PS)	5.10	3.67	19.7	12.5	0.26	0.74
Mixed solvent[b] (PS)	4.35	3.13	24.8	20.0	0.11	0.15
Heptane (hPB)	2.26	0.63	23.8	6.4	0.07	0.89

[a] Data from ref. 7
[b] 1,4-Dioxane/25 vol% heptane

of rather low intensity (5–10%) was poorly reproducible and the corresponding diffusion coefficient is not shown in *Figure 1*.

Copolymer solutions in heptane

DLS measurements in dilute copolymer solutions, up to $c = 1 \times 10^{-2} \, \mathrm{g \, cm^{-3}}$, show a strongly negative concentration dependence of D_c (*Figure 3a*), which has not been encountered with solutions of block copolymer micelles so far. In principle, it can be explained in two ways: either by an increase in the particle size with concentration, or by attractive interparticle interactions. We may exclude the first alternative owing to the constant value of both micellar core radius (cf. SAXS results in Part 1[1]) and micellar molar mass (see SLS results below). If we accept the second hypothesis, we must explain why the attractive interactions do not result in a spontaneous precipitation. We shall return to this problem later when suggesting a model compatible with all experimental data.

Extrapolation of D_c to infinite dilution may be subject to a certain error due to a non-linear D_c vs. c dependence (*Figure 3a*). Nevertheless, $R_H = 24 \, \mathrm{nm}$ calculated from $D_0 \simeq 2.3 \times 10^{-7} \, \mathrm{cm^2 \, s^{-1}}$ is close to the value 22 nm obtained from a similarly non-linear $R_{H,c}$ vs. c dependence (*Figure 3a*), where $R_{H,c}$ are values calculated from the
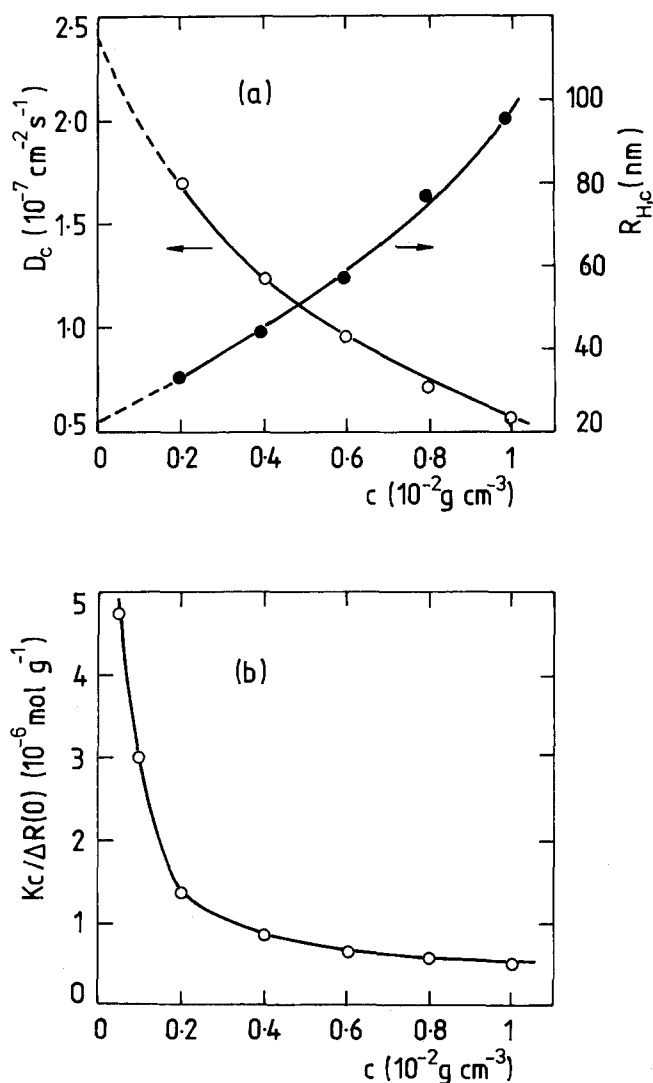

corresponding D_c values, using the Stokes–Einstein formula.

SLS and sedimentation velocity data (*Figures 3b* and *4*) in the dilute concentration region, i.e. below $1 \times 10^{-2} \, \mathrm{g \, cm^{-3}}$, show an almost perfect pattern of closed association. The apparent molar mass, $M_w^* = \Delta R(0)/Kc$, can be expressed as a weighted sum of the molar masses of unimer, $M_w^{(u)}$, and micelles, $M_w^{(m)}$:

$$M_w^* = M_w^{(u)} w^{(u)} + M_w^{(m)} w^{(m)} \qquad (5)$$

where $w^{(u)}$ and $w^{(m)}$ $(= 1 - w^{(u)})$ are the mass fractions of unimer and micelles, respectively. Sedimentation velocity diagrams in *Figure 4* show two well separated peaks: the slow-moving and the faster-moving peak can be ascribed to unimer and micelles, respectively. It has been shown[14] that, for fast reversibly micellizing copolymer systems, the Gilbert theory[15] may be applied for the interpretation of sedimentation velocity diagrams. In the case of a fast association equilibrium with a high value of the association number, the areas under the peaks are proportional to the $w^{(u)}$ and $w^{(m)}$ values. When substituting $Kc/\Delta R(0)$, $w^{(u)}$ and $w^{(m)}$ values for several copolymer concentrations into equation (5), we get $M_w^{(m)}$ values $(2.26 \times 10^6$ $(\pm 7\%) \, \mathrm{g \, mol^{-1}})$ virtually independent of concentration.

Values of $\alpha^{(\text{core})}$ and $\alpha^{(m)}$ (*Table 1*) have been obtained in the same way as in the case of the previous system in the mixed solvent. The relatively large value of $\alpha^{(\text{core})}$, 0.95, and the very small value of $\alpha^{(m)}$, 0.07, suggest micelles with a very dense core and a very highly swollen shell.

A closer investigation of the concentration gradient curves reveals a weak effect that has not been met with block copolymers so far: the 'unimer' peak is getting faster with increasing copolymer concentration. This effect is not yet evident from the sedimentation velocity patterns shown in *Figure 4*, as the 'unimer' peaks are too close to the meniscus. However, sedimentation velocity patterns for longer times (not presented here) give clear evidence for the increase in the apparent sedimentation coefficients of unimer with increasing copolymer concentration, as demonstrated in *Figure 5*. Below, a possibility will be discussed that the effect may be caused by the presence of oligomeric associates in heptane solutions.

The radius of gyration was evaluated from the $Kc/\Delta R(\theta)$ vs. $\sin^2(\theta/2)$ dependence at infinite dilution. It should be stressed, however, that the value $R_G = 24 \, \mathrm{nm}$ thus obtained is only an apparent value[7], lower than the true one due to the core–shell structure of the scattering particles, with the polystyrene core having a larger refractive-index increment in heptane than the aliphatic shell.

Spectra of the decay times in *Figure 6* indicate that the solute dynamics in heptane solutions are far more complex than in 1,4-dioxane/25 vol% heptane solutions. Owing to large differences in the averaged intensities of light scattered by heptane solutions at different copolymer concentrations, the spectra are normalized in such a way that the sum of the amplitudes at peak maxima is kept constant for all concentrations.

There is only one q^2-dependent (i.e. diffusion) mode in dilute heptane solutions with $c < 1 \times 10^{-2} \, \mathrm{g \, cm^{-3}}$, interpreted as translation–diffusion, discussed above and not introduced in *Figure 6*.

In the semidilute region $(1.5 \text{ to } 7) \times 10^{-2} \, \mathrm{g \, cm^{-3}}$, characterized by a steep increase in η^0 with copolymer

Figure 3 Concentration dependences of (a) D_c and $R_{H,c}$ and (b) $Kc/\Delta R(0)$ for G-1650/F in heptane
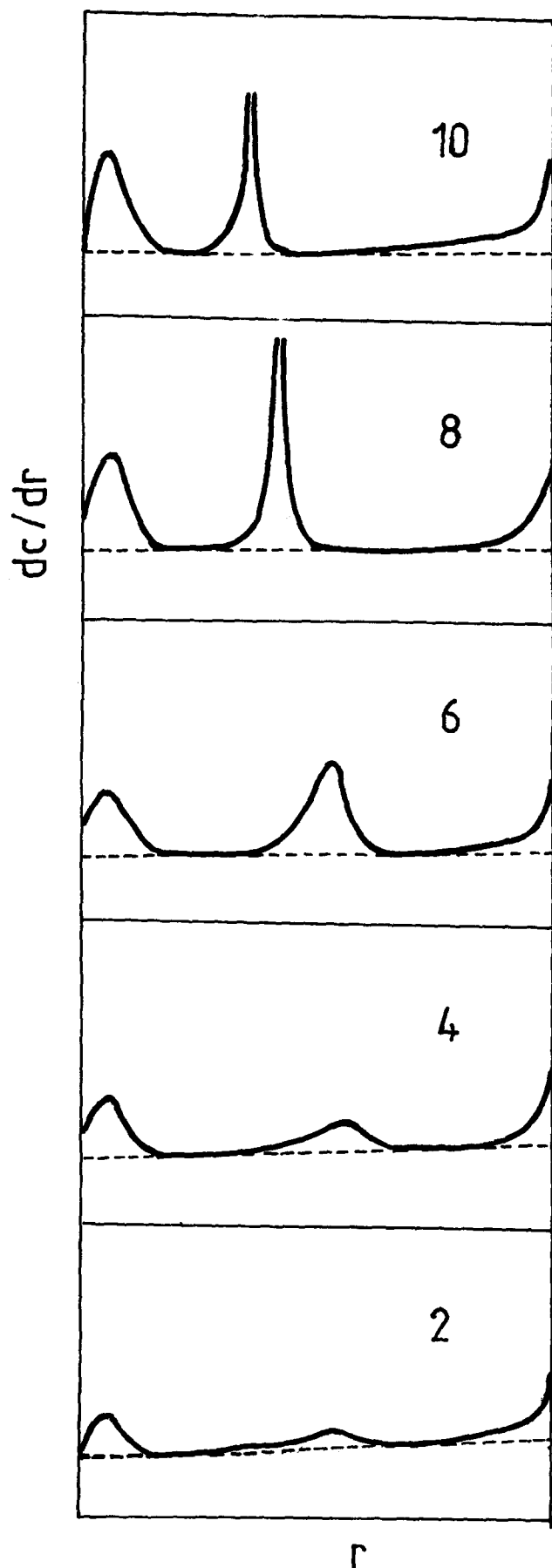
dc/dr

10

8

6

4

2

r

Figure 4 Sedimentation diagrams (concentration gradient, dc/dr, vs. distance in cell, r) of G-1650/F in heptane. The curves are labelled by copolymer concentration ($10^{-3}\,\mathrm{g\,cm^{-3}}$); $t = 32\,\mathrm{min}$
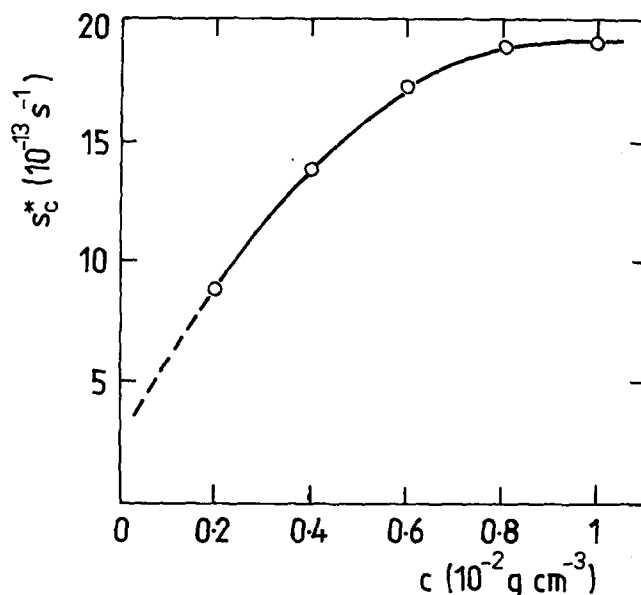

$s_c^* (10^{-13}\,\mathrm{s})$

$c\ (10^{-2}\,\mathrm{g\,cm^{-3}})$

Figure 5 Concentration dependence of the apparent value of the sedimentation coefficient, s_c^*, of the slow-moving peak (unimer) in *Figure 4*

concentration (figure 1 in Part 1[1]) and by a spatial arrangement of micelles (cf. SAXS results in Part 1), at least two well separated modes can be seen in the spectra in *Figure 6*: the inverse decay time of the maximum of the fast mode, $\tau_{f,max}^{-1}$, is q^2-dependent, which indicates its diffusion nature, while that of the slower mode, $\tau_{s,max}^{-1}$, does not depend on q^2, which indicates its relaxation nature. The collective diffusion coefficient, D_c, calculated from $\tau_{f,max}$, scales with the first power of copolymer concentration (*Figure 7*), resembling thus semidilute solutions of linear polymers in Θ solvents[16]. The peak of the relaxation mode broadens with increasing concentration, its $\tau_{s,max}$ slightly increasing. At the two highest concentrations, a very slow diffusion mode appears on the timescale of 10^2 ms. The broad peak at the cross-over concentration ($1.5 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$), roughly dividing the dilute and semidilute regions, scales with $q^{1.2}$. Since such a dependence has no physical meaning, it may be assumed that the peak contains both diffusion (q^2-dependent) and relaxation (q-independent) modes, which both the CONTIN and REPES methods fail to separate.

Based on experimental data, a model of the structure of heptane solutions can be proposed. In dilute solutions, spherical micelles with polystyrene cores and aliphatic shells are characterized by $M^{(m)} = 2.26 \times 10^6\,\mathrm{g\,mol^{-1}}$ (i.e. association number $n = 32$) and $R^{(core)} = 6.4\,\mathrm{nm}$. This means that both polystyrene end-blocks of copolymer molecules are anchored in the micellar core and the middle aliphatic block, located in the micellar shell, forms a loop. The $R^{(core)}$ value, 6.4 nm, corresponds well to the root-mean-square end-to-end distance, $(\overline{r_0^2})^{1/2} = 6.5\,\mathrm{nm}$ (ref. 17), of a polystyrene molecule with $M = 1 \times 10^4\,\mathrm{g\,mol^{-1}}$.

Many of the peculiar features of both dilute and semidilute heptane solutions can be explained under the speculative assumption that some of the 32 copolymer molecules assume an 'open' conformation with one polystyrene block pushed out (*Figure 8*):

(1) The negative slope of the D_c vs. c dependence in *Figure 3a* and the attractive intermicellar forces indicated by SAXS data in Part 1[1] can be explained by the

Figure 7 Concentration dependence of the collective diffusion coefficient, D_c, for G-1650/F in heptane semidilute solutions

Figure 8 Micellar model of G-1650/F in heptane solutions: (——) polystyrene blocks; (— — —) hydrogenated polybutadiene blocks
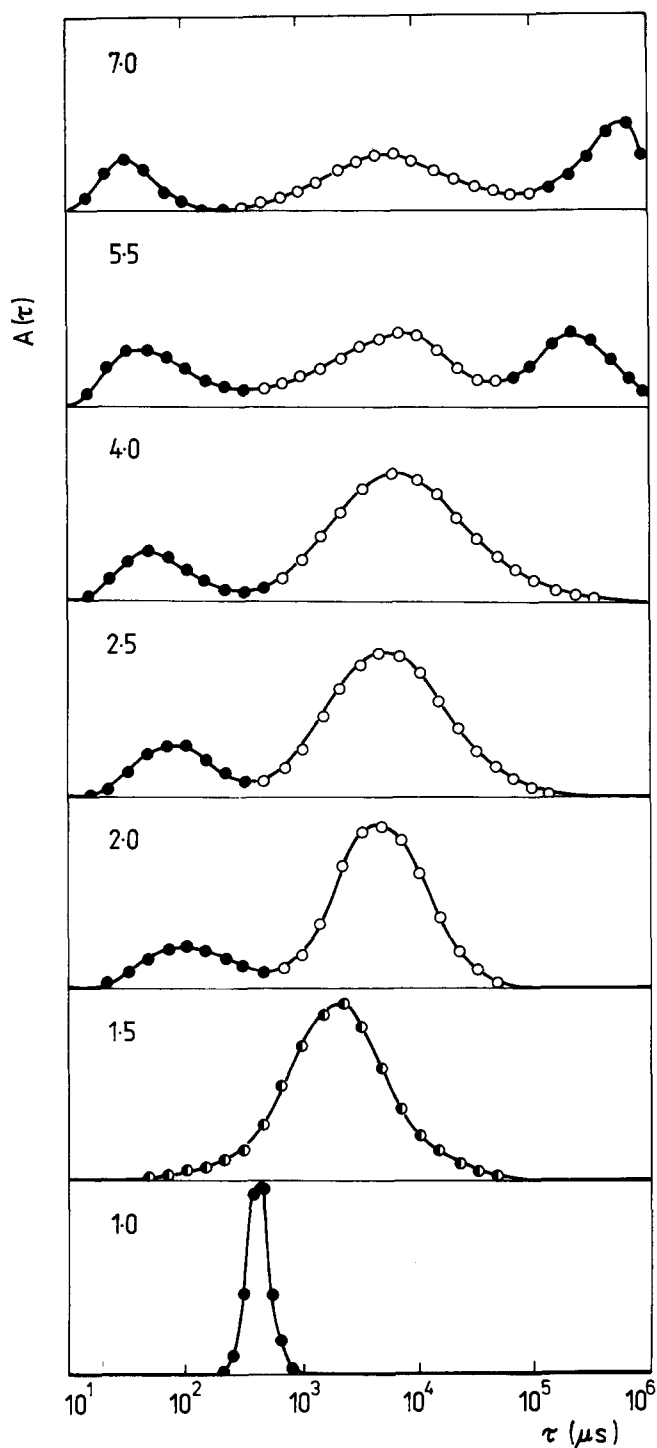
Figure 6 Distribution of the decay times, for solutions of G-1650/F in heptane, obtained using REPES method from the time correlation curves measured at $\theta = 90°$. Full circles, diffusion mode ($\tau^{-1} \sim q^2$); open circles, relaxation mode ($\tau^{-1} \sim q^0$); half-full circles, combined mode ($\tau^{-1} \sim q^{1.2}$). Spectra are marked by concentrations (10^{-2} g cm^{-3})

attractive forces between the outstretched polystyrene blocks. Repulsive forces between micellar shells then prevent micellar aggregation or macroscopic precipitation.

(2) The relatively high value of $\alpha^{(core)}$, 0.89, calculated under the assumption of a simple core–shell model (equation (4)), would decrease if some polystyrene blocks were outside the body of the micelle.

(3) Not only unimers, but also oligomers, the existence of which has been hinted at by the sedimentation velocity experiment (*Figure 4*), can assist on the attractive forces
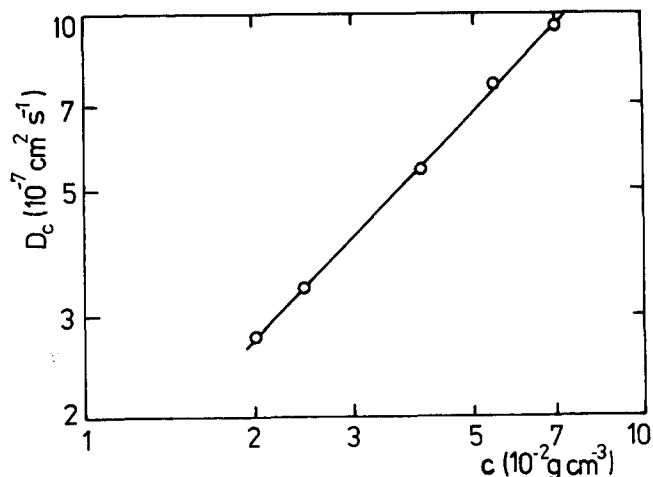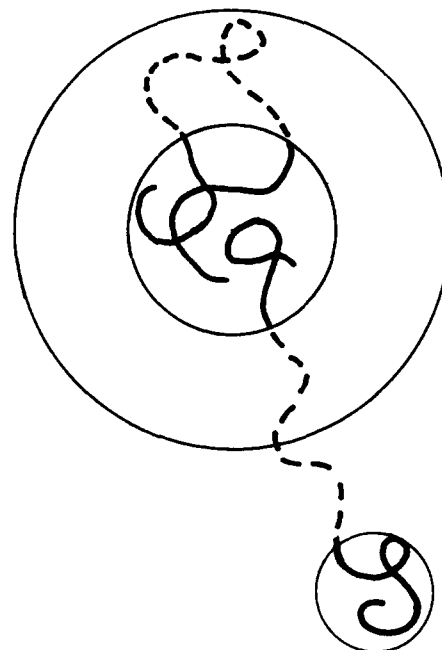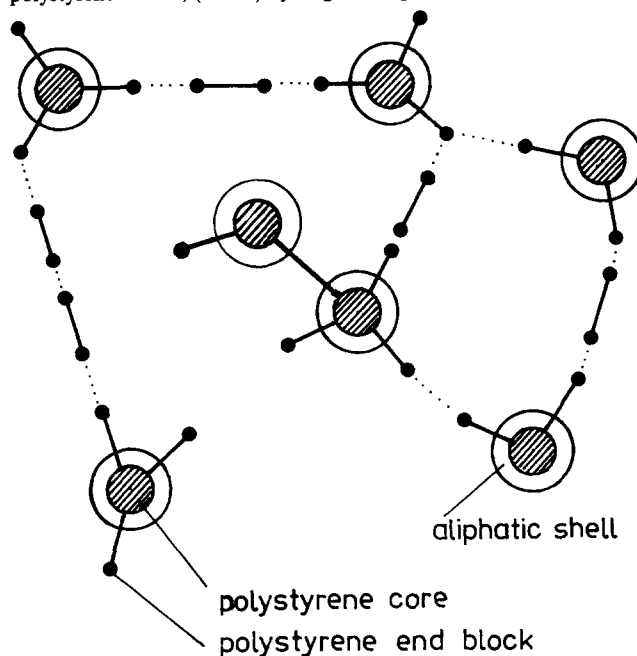

Figure 9 Model of G-1650/F semidilute micellar solution in heptane

operative between polystyrene-ended tentacles (*Figure 9*). Such a model might explain the surprisingly low values of c^+, $\sim 1.5 \times 10^{-2}$ g cm^{-3}. At higher concentrations, micelles can be interconnected also by one unimer molecule as indicated in *Figure 9*.

(4) The fast diffusion mode in semidilute heptane solutions is most probably connected with the collective diffusion of the physically interconnected micelles. The slower relaxation mode may be interpreted as a slow rearrangement of the physical network, not connected with a net micellar mass transport. The very slow diffusion mode at the highest concentrations probably reflects a movement of large clusters or parts of the network.

REFERENCES

1   Pleštil, J., Hlavatá, D., Hrouz, J. and Tuzar, Z. *Polymer* 1990, **31**, 2112
2   Kotaka, T., Tanaka, T. and Inagaki, H. *Polym. J.* 1972, **3**, 327
3   Tanaka, T., Kotaka, T. and Inagaki, H. *Polym. J.* 1972, **3**, 338
4   Tang, W. T., Hadziioannou, G., Cotts, P. M., Smith, B. A. and Frank, C. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1986, **27**(2), 107
5   ten Brinke, G. and Hadziioannou, G. *Macromolecules* 1987, **20**, 486
6   Ceresa, R. J. *J. Polym. Sci., Polym. Symp. (C)* 1969, **26**, 201
7   Tuzar, Z., Pleštil, J., Koňák, Č., Hlavatá, D. and Sikora, A. *Makromol. Chem.* 1983, **184**, 2111
8   Koňák, Č., Tuzar, Z., Štěpánek, P., Sedláček, B. and Kratochvíl, P. *Prog. Colloid Polym. Sci.* 1985, **71**, 15
9   Watanabe, H. and Kotaka, T. *Polym. Eng. Rev.* 1984, **4**, 73
10 Tuzar, Z. and Kratochvíl, P. *Collect. Czech. Chem. Commun.* 1967, **32**, 358
11 Štěpánek, P., Koňák, Č. and Jakeš, J. *Polym. Bull.* 1987, **16**, 67
12 Jakeš, J. to be published
13 Provencher, S. W. *Makromol. Chem.* 1979, **180**, 201
14 Procházka, K., Glockner, G., Hoff, M. and Tuzar, Z. *Makromol. Chem.* 1984, **185**, 1187
15 Gilbert, G. A. *Disc. Faraday Soc.* 1955, **20**, 68
16 Adam, M. and Delsanti, M. *Macromolecules* 1985, **18**, 1760
17 'Polymer Handbook', 2nd Edn. (Eds. J. Brandrup and E. H. Immergut), Wiley-Interscience, New York, 1974, p. IV–40