Hydrogenated polystyrene–poly(methyl methacrylate) diblock copolymer micelles in selective solvent: 1. Single solvent system – effect of temperature

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The association of two block copolymers, hydrogenated polystyrene–poly(methyl methacrylate) (PSH–PMMA) in 1-chloro-n-hexane (a selective solvent for PSH) and deuterated polystyrene–poly(methyl methacrylate) (PSD–PMMA) in dimethyl sulphoxide (a selective solvent for PMMA), has been studied by light and neutron scattering. Unusual large particles are formed in the temperature range corresponding to the theta point of one block of the copolymer whereas small compact micelles are observed at room temperature. At low temperature the results show good agreement with the model of closed association where unassociated molecules are in equilibrium with monodisperse micelles.

(Keywords: diblock copolymer; polystyrene–poly(methyl methacrylate); light scattering; neutron scattering; micelle)

INTRODUCTION

The effect of solvent selectivity on the behaviour of copolymer solutions has been studied for a long time[1–3]. In dilute and semidilute solutions of selective solvents for one component of block or graft copolymers, the authors have shown the presence of micellar aggregates[4,5]. In such solvents the model of 'closed association' describes the equilibrium between monomers P and micelles $(P)_n$ with narrow molar mass and size distributions[6]:

$$nP \rightleftharpoons (P)_n \qquad (1)$$

where the micellar structure consists of a compact core composed mainly of the non-solvated sequences surrounded by a fringe of well solvated blocks. Most of the data available in this field are reviewed by Tuzar and Kratochvíl[7].

Styrene–diene block copolymers have frequently received attention in the study of such polymeric micelles. In this paper and in the following one[8], by studying polystyrene–poly(methyl methacrylate) (PS–PMMA) diblock copolymer, we examine the generalization of the behaviour of copolymers in dilute solutions to a system of different chemical nature.

Light scattering has been used to characterize the variation of the weight average molecular weight M, the radius of gyration R_G and the second virial coefficient A_2 in 1-chloro-n-hexane as a function of the temperature. The temperature at which PMMA homopolymers precipitate in this solvent is around 92°C. On the other hand, small-angle neutron scattering has been used to characterize the compactness of the micellar structure and its evolution with temperature by working in dimethyl sulphoxide (DMSO) solutions (DMSO is a selective solvent of PMMA blocks; cloud point for PS around 133°C).

The present paper is concerned with experimental results obtained in binary solvents formed of a 'good solvent' of both sequences (dioxane) and 1-chloro-n-hexane which is selective for PS. These two solvents present the advantage of having the same refractive index and consequently allow the cancellation of eventual contributions of selective adsorption to light scattering. Thus it is possible to compare the micellization process which occurs either by the decrease of the temperature or by the increase in precipitant fraction.

EXPERIMENTAL

Material

Two block copolymers, PSH47–PMMA22 (hydrogenated polystyrene–poly(methyl methacrylate)) and PSD–PMMA (deuterated polystyrene–poly(methyl methacrylate)), were prepared by sequential anionic polymerization using tetrahydrofuran as solvent and phenyl isopropyl potassium as initiator according to a classical procedure[9].

Molecular characteristics of the purified samples determined by light scattering and ultra-violet (u.v.) spectroscopy are given in *Table 1.* The molecular weights of the hydrogenated and deuterated polystyrene blocks were determined using samples of homopolystyrene which were recovered after the first stage of the polymerization before the addition of the methyl methacrylate monomer.

From molecular weight characterization of the PSH47–PMMA22 sample in benzene and dioxane it can be concluded that the copolymer is homogeneous in composition. U.v. spectroscopy leads to a value of the composition of polystyrene quite close to the value determined by light scattering measurements.

Gel permeation chromatography was used to check the

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Table 1 Molecular characteristics of precursors and diblock copolymers as determined by u.v. and light scattering spectroscopy

Polymer code	Composition (wt% styrene)		Weight average molar mass	
	Light scattering weight average	U.v. number average	$(M_w)_{C_6H_6}$	$(M_w)_{dioxane}$
Precursor PSH47			60000	
PSH47–PMMA22	57	57.6	105000	102000
Precursor PSD			55000	
PSD–PMMA	48		115000	

homogeneity of the samples. No homopolystyrene could be detected in the copolymer samples by this technique.

1-Chloro-n-hexane (Fluka) and dimethyl sulphoxide (Merck) were used for light and neutron scattering, respectively, without further purification. The copolymer solutions were filtered at high temperature (115°C) directly into the scattering cells, which were sealed under vacuum.

Light scattering

The refractive index increments (dn/dc) of the copolymer solutions were measured at 546 nm using a Brice Phoenix differential refractometer. The temperature dependence of dn/dc has been determined between 25 and 70°C, leading to the following relationship in which dn/dc and t are expressed in ml g^{-1} and °C respectively:

$$\mathrm{d}n/\mathrm{d}c = 0.119 + 4\times10^{-4}(t-25) \qquad (2)$$

Light scattering experiments were performed on the photogoniodiffusiometer described by Reiss and Gubler[10] with unpolarized incident light ($\lambda = 546$ nm). Scattering intensities were measured over the angular range 30–150° with benzene as reference.

The light scattered by a dilute polymer solution may be expressed as[11]:

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w P(\theta)} + 2A_2c + \ldots \qquad (3)$$

where c is the polymer concentration, K an optical constant, $R(\theta)$ the difference between the Rayleigh ratio of the solution and that of the pure solvent, M_w the weight average molecular weight, $P(\theta)$ the particle scattering function and A_2 the second virial coefficient.

The application of light scattering theory to A–B diblock copolymer solutions leads to the evaluation of an apparent molecular weight M_w^{ap} and mean-square radius of gyration R_G^{ap}[12]. Taking account of the small difference observed between $(M_w^{ap})_{C_6H_6}$ and $(M_w^{ap})_{dioxane}$ (see *Table 1*), M_w^{ap} and R_G^{ap} values should be close to real values for PSH47–PMMA22 sample.

Neutron scattering

The neutron scattering experiments were performed on the EL3 reactor at Saclay[13]. The domain of scattering vectors q $(=(4\pi/\lambda)\sin(\theta/2))$ investigated ranged from 7×10^{-3} to 5×10^{-2} Å^{-1}.

Coherent scattering has been evaluated after incoherent background subtraction and transmission corrections according to classical data treatment procedures.

Ultracentrifugation

The sedimentation analysis was performed in a Spinco F ultracentrifuge. The overall copolymer concentration was kept constant at 0.7×10^{-2} g cm^{-3}. The rotor and the ultracentrifuge cell were thermostatted at 25°C. The sedimentation velocity measurements were performed at 20410 r.p.m. and 50740 r.p.m. The sedimentation process was recorded using Schlieren optics.

RESULTS AND DISCUSSION

PSH47–PMMA22/1-chloro-n-hexane

For the system investigated in this study the major contribution to the scattering is due to the well solvated PSH sequences ($(\mathrm{d}n/\mathrm{d}c)_{PSH} = 0.168$ cm^3 g^{-1}) compared to the scattering by the PMMA sequences ($(\mathrm{d}n/\mathrm{d}c)_{PMMA} = 0.068$ cm^3 g^{-1}).

The dissymmetry factor Z, i.e. the ratio of the scattering intensities at 45 and 135°, is a parameter that gives an estimate of the scattering profile by polymer solutions. For small particles ($R_G \ll \lambda$) no angular dissymmetry should be observed. In *Figure 1* the variation of Z is plotted as a function of the temperature at three concentrations of PSH47–PMMA22 in 1-chloro-n-hexane solution.

At high temperature, large Z values can be observed. These values depend strongly on the concentration of polymer solutions. When the temperature decreases, between 75 and 55°C, this parameter falls close to unity and becomes quasi-independent of the polymer concentration at room temperature.

Taking account of the thermal variation of the specific volume of the solvent for the correction of polymer concentrations, three kinds of Zimm plots are prominent.

In *Figure 2*, at higher temperature, the shape of the $c/I = f[\sin^2(\theta/2)]$ curves, where I is the scattered intensity at an angle θ, is characteristic of molecular aggregates.

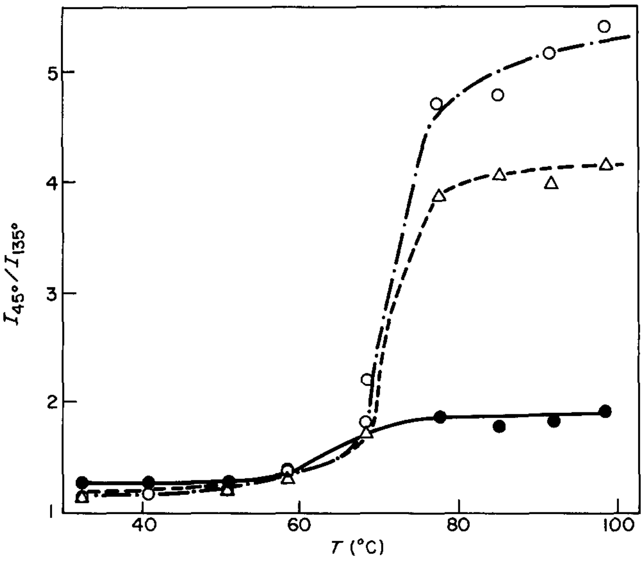

Figure 1 Temperature dependences of the scattering dissymmetry for PSH47–PMMA22 in 1-chloro-n-hexane: ●, $c = 0.103\times10^{-2}$ g cm^{-3}; △, $c = 0.204\times10^{-2}$ g cm^{-3}; ○, $c = 0.398\times10^{-2}$ g cm^{-3}

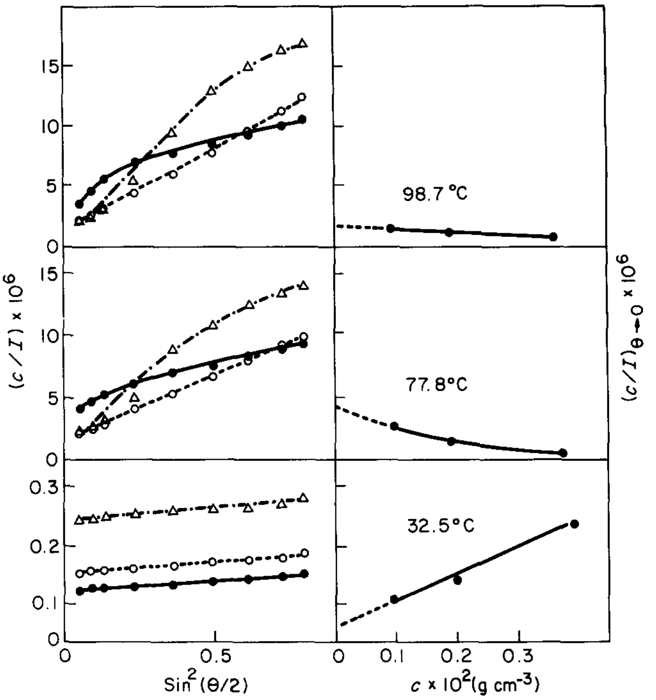

Figure 2 Plot of c/I (arb. units) *versus* $\sin^2(\theta/2)$ (●, $c = 0.103 \times 10^{-2}$ g cm^{-3}; ○, $c = 0.204 \times 10^{-2}$ g cm^{-3}; △, $c = 0.398 \times 10^{-2}$ g cm^{-3}) and $(c/I)_{\theta\to 0}$ *versus* c at different temperatures for PSH47–PMMA22 in 1-chloro-n-hexane

Meanwhile the variation of $(c/I)_{\theta\to 0}$ as a function of the copolymer concentration is linear with a negative slope.

At lower temperature ($T = 32.5$°C) the inverse of the scattered intensity is linear with $\sin^2(\theta/2)$ in the concentration range investigated, but the extrapolation to zero angle is much lower compared to the high-temperature region. Moreover, the variation of $(c/I)_{\theta\to 0}$ as a function of the copolymer concentration has a positive value. Between these two regions the plots are non-linear.

The variations of the molecular weight M, radius of gyration R_G and second virial coefficient A_2 are plotted in *Figure 3* as a function of the temperature. According to these variations two different regions can be defined on this figure.

At high temperature. The molecular weight of the scattering particles is low, almost independent of the temperature and corresponds to the association of 8–10 copolymer molecules.

At equivalent molecular weight ($M \sim 10^6$) the radius of gyration is much higher (150 nm) than the radius of gyration of homopolystyrene. It emerges from the literature that several copolymer/solvent systems show the same anomalous behaviour in the vicinity of the theta point for one component of the copolymer[14–16]. This large value of the radius of gyration in the initial stage of the micellization has been explained on the basis of linear association of monomer giving rise to large anisotropic ellipsoids.

The second virial coefficient is negative and decreases as the temperature decreases. Assuming a segregated model with no contact between PSH and PMMA segments, A_2 is a weighted average between $A_{2,\mathrm{PS}}$ and $A_{2,\mathrm{PMMA}}$. In this range of temperature, the large decrease of $A_{2,\mathrm{PMMA}}$ due to diminution of the quality of the solvent leads to the large decrease of A_2.

At lower temperatures. The molecular weight of the scattering particles increases sharply with decreasing temperature. The degree of association of copolymer molecules is strongly dependent on the temperature, going from $n \sim 10$ at 80°C to $n \sim 300$ at 40°C. The equilibrium between unassociated and associated macromolecules is shifted towards the associated state.

In this low-temperature range the radius of gyration of the particles decreases from 150 to 30 nm as the temperature is lowered. As the solvent quality decreases with regard to PMMA, the insoluble blocks of PMMA collapse and form the compact core of the micellar structure.

The second virial coefficient increases and reaches positive values at room temperature. The solvent is rejected from the core of the micelles giving rise to less unfavourable contacts between the PMMA segments and the solvent molecules. On the other hand the protective shell of well solvated PSH segments prevents long-range PMMA segment–segment interactions.

Several comments can be made on the qualitative behaviour of the variation of M, R_G and A_2 as a function of the temperature. Even at room temperature there still remain unassociated copolymer molecules, although the equilibrium between monomers and oligomers is strongly shifted towards micelles. In fact, from ultracentrifugation experiments (*Figure 4*), it comes out that 29% (weight fraction) of the molecules are not involved in micellar aggregates at 25°C. The first peak on the Schlieren pattern corresponds to micelles and appears at 20410 r.p.m. A second peak appears at high speed (50740 r.p.m.) and is due to the migration of monomer towards the bottom of the cell. A complete description of the system investigated should involve ultracentrifugation measurements at several concentrations and temperatures in order to take account of the respective amount of associated and unassociated molecules in the copolymer solution. As a consequence M, R_G and A_2 values given in *Figure 3* are apparent values, which are underestimated compared to their true ones.

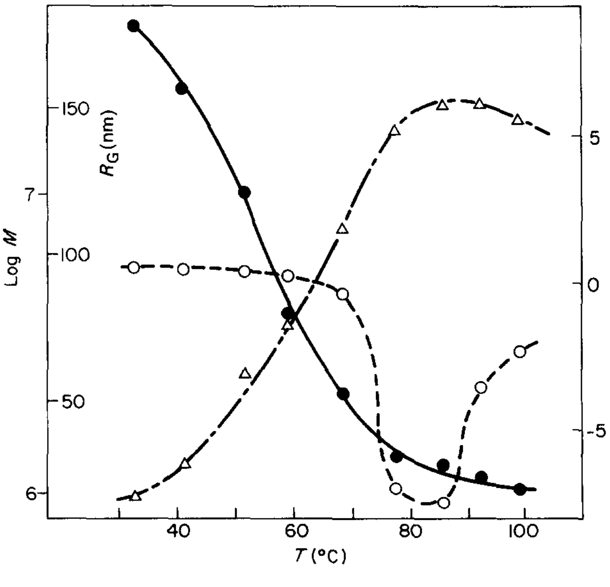

Figure 3 Plot of molecular weight M (●), radius of gyration R_G (△) and second virial coefficient A_2 (○) *versus* temperature T for PSH47–PMMA22 in 1-chloro-n-hexane

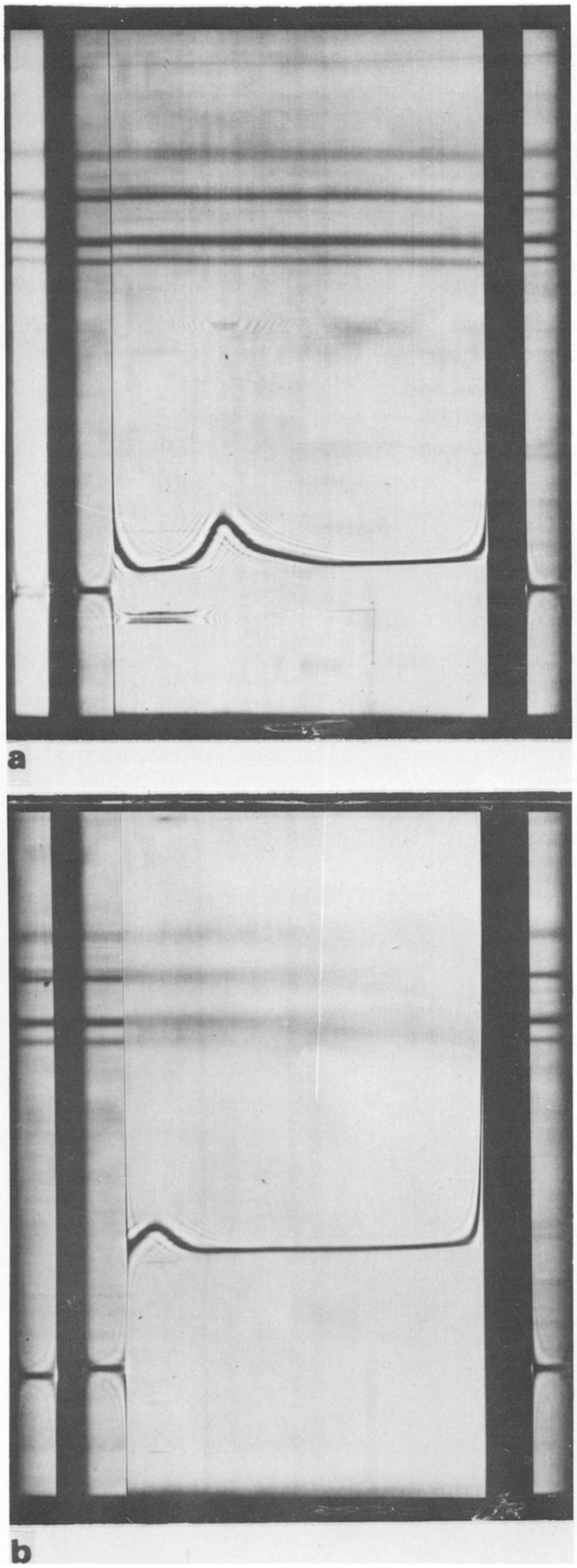

Figure 4 Schlieren patterns of copolymer PSH47–PMMA22 in 1-chloro-n-hexane ($c = 0.7 \times 10^{-2}$ g cm^{-3}; $T = 25$°C): ultracentrifugation at (a) 20410 r.p.m., (b) 50740 r.p.m.

PSD–PMMA/DMSO

Light scattering intensities are averaged intensities scattered by the core, the shell of the micelles or by the monomers. Over the last few years the neutron scattering technique has been a very useful tool to study micellar structures[17]. The contrast between the two parts of the micelle and the solvent can be adjusted in appropriate mixtures of hydrogenated/deuterated solvents for which the thermodynamic quality does not change. Another way to study these multicomponent systems is to label one component selectively by deuteration. This last method has been applied to the study of PSD–PMMA copolymer micelles in DMSO solution at different temperatures. The coherent scattering length per unit volume of DMSO ($-0.004 \times 10^{+10}$ cm cm^{-2}) is slightly different from the PMMA value (1.008×10^{10} cm cm^{-2}) but much lower than the value of the coherent scattering length of PSD (6.5×10^{10} cm cm^{-2}). This value provides a contrast of the PSD core about 40 times higher than the PMMA soluble sequence.

In *Figures 5* and *6* we have plotted, in the Kratky ($q^2 I(q)$) and pseudo-Kratky ($q^4 I(q)$) representations, the variation of the scattering behaviour in the intermediate range of scattering vectors q ($qR_G \gg 1$). At high temperature the shape of the curves $q^2 I(q) = f(q^2)$ (see *Figure 5*) is typical of scattering by dilute linear polymer solutions. As the temperature decreases, a scattering peak appears in the small q range.

At room temperature the shape of $q^4 I(q) = f(q^4)$ (see *Figure 6*) is quite similar to scattering by star solutions where the segment density inside the star is very high. In this representation the compactness of the core of the

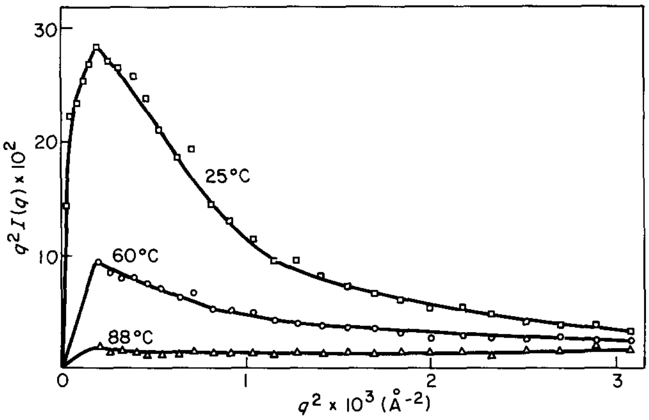

Figure 5 Neutron scattering intensity of dilute solution of diblock PSD–PMMA copolymer in dimethylsulphoxide at different temperatures. Plot of $q^2 I(q)$ as a function of q^2 ($c = 0.6 \times 10^{-2}$ g cm^{-3})

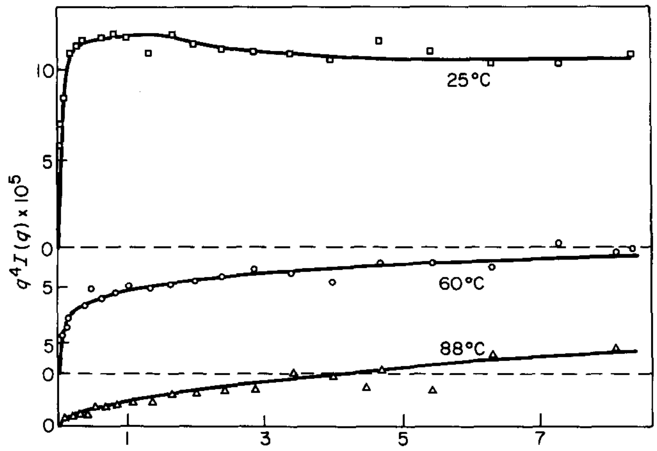

Figure 6 Neutron scattering intensity of dilute solution of diblock PSD–PMMA copolymer in dimethylsulphoxide at different temperatures. Plot of $q^4 I(q)$ as a function of q^4 ($c = 0.6 \times 10^{-2}$ g cm^{-3})

micelle is shown by the occurrence of a plateau region in the intermediate *q* vector range.

As the temperature increases, the equilibrium between isolated macromolecules and micelles is shifted towards isolated macromolecules. Moreover the quality of the solvent for the PSD sequences increases; the segment density inside the micelles decreases and the plateau region on *Figure 6* disappears.

CONCLUSIONS

Dilute PS–PMMA diblock copolymer solution exhibits two types of typical behaviour as a function of the temperature in a selective solvent of one block and a good solvent for the other. In the vicinity of the theta temperature of the PMMA sequences, large structures have been observed, which correspond to linear association of 8–10 molecules[14,15]. Far below this theta temperature, there is an equilibrium between unassociated and associated molecules. The associated state can be described by a micellar arrangement where the core is compacted and formed by the insoluble component of the copolymer surrounded by the solvated shell. In this domain the degree of association is strongly dependent on the temperature.

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