

Block copolymer micelle solutions: 1. Concentration dependence of polystyrene- poly(ethylene propylene) in heptane

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The concentration dependence of micelle formation by a diblock copolymer of polystyrene-poly(ethylene propylene) (PSPEP) in n-heptane is examined by turbidity, viscosity and photon correlation spectroscopy (p.c.s.). The critical micelle concentration (c.m.c.) as determined by p.c.s. is estimated to be 0.002 wt%. At $c=0.003\%$, an unusually large hydrodynamic radius is found, in agreement with the anomalous increase in hydrodynamic size near the c.m.c. previously reported by Tuzar *et al.* in 1985. The average micellar weight obtained from turbidity measurements and the hydrodynamic radius for non-interacting micelles as measured by p.c.s. were relatively constant for $c=0.01-0.5\%$. A comparison of the second virial coefficients from the turbidity and viscosity measurements suggests that the relatively large Huggins constant of $k_H=2.4$, obtained from viscosity measurements, may be explained in terms of an excluded-shell model. At a critical concentration above 0.5%, an increasing amount of freely dispersed polymers is present in the solution. The driving force for this change in the free chain-micelle equilibrium is believed to arise from the concentration gradient of PEP segments between the micelle corona and the dispersed phase. The amount of free chains relative to micelles is found to increase from 0.7% up to 2% based on p.c.s. results. It is not clear, however, if the equilibrium is further shifted in favour of the free chains from 3 to 5%, since the weight fractions of free chains and micelles cannot be deduced from p.c.s. data at such high concentrations. However, turbidity and viscosity data seem to suggest that the relative amount of free chains at 3% is lower than that at 2%. At even higher concentrations (4-5%), the viscosity of the micelle solutions increases drastically, presumably because of the formation of a macrolattice.

(Keywords: block copolymer solutions; dynamic light scattering; concentration dependence; semidilute)

INTRODUCTION

The dispersal of diblock copolymers in a selective solvent favourable to one constituent block and unfavourable to the other often results in the formation of micelles. At concentrations above the so-called critical micelle concentration (c.m.c.), essentially all polymers added to the solution presumably aggregate to form block copolymer micelles¹, each of which consists of a core composed primarily of chain segments of the insoluble block surrounded by a corona of chain segments of the soluble block. The factors that influence the formation of multimolecular micelles also include polymer composition and architecture, compatibility of the copolymer blocks with the solvent, molecular weight, temperature and preparation methods. The study of micelle formation is of both practical and fundamental interest, since the rheological behaviour of such polymer solutions is a strong function of the structure and stability of such micelles. For instance, at sufficiently high polymer concentrations, a non-linear, plastic flow behaviour has been observed in block copolymer micelle solutions^{2,3}. In these cases, changes in the size and organization of micelles may cause a rather substantial change in the rheological behaviour. Moreover, the morphology of polymer films cast from micelle solutions would ultimately depend on the structure of these multimolecular micelles prior to solvent evaporation⁴.

One of the central questions of interest has been the effect of concentration on micelle structure and morphology. Indeed, the effect of concentration has been studied before, both in the dilute region^{5,6}, where intermicellar interactions are negligible, and in the more concentrated region, where formation of a long-range superstructure occurs^{2,3,7-9}. Some time ago, Horii *et al.*¹⁰ suggested that the micellar weight in dilute solutions is rather insensitive to concentration. They concluded that the size of micelles for a given copolymer is independent both of its initial concentration and of the selective solvent, at least within the concentration range studied. However, in a recent study, Tuzar *et al.*¹¹ have reported an increase of the hydrodynamic radius and micellar weight in the concentration region near the c.m.c. On the other hand, the formation of a macrolattice at high copolymer concentrations has been well documented using small-angle X-ray scattering (SAXS)^{2,3,6}, small-angle neutron scattering (SANS)^{8,9}, nuclear magnetic resonance (n.m.r.)¹² and rheological measurements^{2,3}. These recent studies have provided data relevant to, and indeed provided some motivation for, this study.

The present work centres on the investigation of any possible changes in structure and dimensions of micelles formed by a diblock copolymer of polystyrene-*b*-poly(ethylene propylene) (PSPEP), in n-heptane as a function of concentration. Since heptane is a good solvent for the PEP block and a poor solvent for the PS block, the micelles are composed of a PS core surrounded by

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a PEP corona. Here we utilize a combination of turbidity, viscosity and photon correlation spectroscopy (p.c.s.) to examine the micelle size from the dilute region to the semidilute region, where the formation of a macrolattice is expected. We will present evidence that the free chain-micelle equilibrium is significantly altered in the semidilute region, just prior to the formation of the macrolattice.

THEORETICAL BACKGROUND

Turbidity and p.c.s. have proven useful for the characterization of size distribution in solutions, particularly in determining the size and shape of particles^{13,14}. Since this study relies on the application of such an analysis, we present a brief review of the appropriate theory, which will facilitate subsequent discussion of the experimental results.

Turbidity and Rayleigh's theory

The turbidity of a solution is defined as:

$$\tau = \frac{1}{l} \ln \left(\frac{I_0}{I} \right) \quad (1)$$

where I_0 and I are the intensities of the incident and transmitted light, and l is the optical path length. The turbidity of a solution can also be expressed as the intensity attenuation of transmitted light due to scattering over all possible directions. Hence:

$$\tau = \int_0^{2\pi} d\phi \int_0^\pi r^2 (i_\theta / I_0) \sin \theta d\theta \quad (2)$$

In equation (2) the angular dependence of scattered intensity is given by:

$$\frac{i_\theta}{I_0} = \frac{R_\theta (1 + \cos^2 \theta)}{r^2} \quad (3)$$

where i_θ is the scattered intensity per unit volume, R_θ is the Rayleigh factor and r is the distance between the scattering volume and detector.

The Rayleigh factor contains information about the mass and dimensions of the particles. For spherical particles:

$$\frac{Kc}{R_\theta} = \frac{1}{P(qR)} \left(\frac{1}{M_m} + 2A_2c + 3A_3c^2 + \dots \right) \quad (4)$$

where K is a constant, c is the concentration, M_m is the micellar weight, q is the scattering vector, R is the particle radius, A_i is the i th virial coefficient and $P(qR)$ is the form factor. The scattering vector is given by:

$$q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (5)$$

where λ is the wavelength and n is the refractive index of the solution. The form factor for spherical particles with radius R is¹⁵:

$$P(qR) = \left(\frac{3[\sin(qR) - qR \cos(qR)]}{(qR)^3} \right)^2 \quad (6)$$

and the constant K is given by:

$$K = \frac{2\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (7)$$

where dn/dc is the specific refractive index increment of

the solute in the solvent and N_A is Avogadro's number.

For light scattered over all angles, the turbidity in the limit of infinite dilution can be rewritten as:

$$\left(\frac{Kc}{\tau} \right)_{c=0} = \frac{1}{\Omega(R)M_m} \quad (8)$$

where

$$\Omega(R) = 2\pi \int_0^\pi P(qR)(1 + \cos^2 \theta) \sin \theta d\theta \quad (9)$$

The dependence of $\Omega(R)$ on particle radius R can be computed numerically. Hence, a plot of Kc/τ vs. c , giving $1/\Omega(R)M_m$ in the limit of $c=0$, can be used to estimate the micellar weight, analogous to the use of a plot of Kc/R_θ vs. c to obtain $1/M_m$ in the case of integral light scattering.

Photon correlation spectroscopy

In photon correlation spectroscopy, the intensity of scattered light can be related to the self-diffusion of micelles in solutions. The fluctuation of the scattered light intensity can be expressed in terms of the normalized second-order autocorrelation function¹⁵:

$$g^{(2)}(\tau_c) = \frac{\langle I(\tau_c)I(0) \rangle}{\langle I(0) \rangle^2} \quad (10)$$

where $\langle I(\tau_c) \rangle$ is the time-averaged intensity of the scattered light at time τ_c . This correlation function can be written as:

$$g^{(2)}(\tau_c) = 1 + C[g^{(1)}(\tau_c)]^2 \quad (11)$$

where $g^{(1)}(\tau_c)$ is the normalized first-order autocorrelation function and C is an empirical constant.

For a monodisperse system, the normalized first-order autocorrelation function is simply:

$$g^{(1)}(\tau_c) = \exp(-\Gamma \tau_c) \quad (12)$$

where Γ is the decay rate, which can be written in terms of the translational diffusion coefficient D as:

$$\Gamma = q^2 D \quad (13)$$

For a polydisperse system the normalized first-order autocorrelation function is then:

$$g^{(1)}(\tau_c) = \int_0^\infty G(\Gamma) \exp(-\Gamma \tau_c) d\Gamma \quad (14)$$

with

$$\int_0^\infty G(\Gamma) d\Gamma = 1 \quad (15)$$

where $G(\Gamma)$ is the distribution function of decay rates Γ .

According to the Stokes-Einstein relation, for non-interacting particles, the hydrodynamic radius R is given by:

$$R = \frac{kT}{6\pi\eta D} \quad (16)$$

where η is the viscosity of the solvent, k is Boltzmann's constant and T is the temperature.

The particle size distribution in terms of light scattered can be represented by¹⁶:

$$F(R) = B\alpha^2(R)f_n(R)P(qR) \quad (17)$$

where $\alpha(R)$ is the polarizability of particles with radius R , $f_n(R)$ is the number-averaged distribution, $P(qR)$ is the form factor and B is a constant. Here, the polarizability is simply given by¹⁶:

$$\alpha(R) = \frac{4}{3}\pi R^3 \alpha_v \quad (18)$$

where α_v is defined as the polarizability per unit volume.

Assuming that the density of the underlying particles is independent of R , the weight-averaged distribution function $f_w(R)$ can be expressed as:

$$f_w(R) = B' R^3 f_n(R) \quad (19)$$

where B' is the normalization constant.

A typical way of quantifying the relative width of the distribution function is with the relative variance¹⁷:

$$POLY = (\overline{R^2} - \bar{R}^2) / \bar{R}^2 \quad (20)$$

such that a size distribution with $POLY \leq 0.02$ is generally regarded to be monodisperse.

For rigid spheres, the combination of photon correlation spectroscopy and viscosity measurements on the micelle solutions can be used to estimate the micellar weight via the Einstein relation¹⁸:

$$[\eta] = \frac{10\pi R^3 N_A}{3M_m} \quad (21)$$

where $[\eta]$ is the intrinsic viscosity of the micelles.

EXPERIMENTAL

Materials and sample preparation

The PSPEP copolymer was kindly provided by Shell Development Co. and was prepared from hydrogenation of the isoprene block of a poly(styrene-co-isoprene) diblock copolymer. The polymer has a molecular weight of 1.35×10^5 and polydispersity of 1.15, as determined from gel permeation chromatography, and styrene content of 37% by weight. Repeated precipitation from tetrahydrofuran (THF) into methanol was undertaken to remove any trace amount of homopolymer of polystyrene, which may be found in commercial block copolymers of this kind.

The solvents, heptane (Burdick & Jackson), methylene chloride and THF (Aldrich), were of spectrophotometric grade and checked for optical integrity before use. Solvent filtration was carried out with a 25 mm filter assembly with $0.2 \mu\text{m}$ pore size. Similarly, dust particles were removed by filtration of the dilute polymer solutions in THF. Cylindrical quartz tubes were thoroughly cleaned with Allied Chemical RT-2 sulphuric-chromic acid mixture in an ultrasonic bath for 1 h, followed by rinsing with soap and distilled water. The rinsed cells were then dried upside down to prevent dust from re-entering the cell.

Sample degassing was achieved by four freeze-pump-thaw cycles with vacuum sealing of the sample cells at a pressure lower than 5×10^{-5} Torr. Thus, we were able to dissolve the polymer at a temperature above the normal boiling point of heptane without loss of solvent. Samples with concentrations of 0.001–5% by weight were prepared by maintaining the sample tubes at a temperature of 423 K for 6 h before allowing them to cool to

room temperature slowly. The total cooling time was approximately 12 h.

Methods

Turbidity measurements were obtained with a Cary model 210 spectrophotometer using matched 1 cm quartz cells. Incident light for the turbidity measurements was at 633 nm, where no appreciable absorption by phenyl groups was detected. All measurements were made with a bandwidth of 0.5 nm dispersion in reference to blank solvent (heptane) and corrected for instrument drift.

The refractive index increment was measured at 298 K with a Chromatix KMX-16 Laser Differential Refractometer, which was calibrated with a series of sodium chloride solutions of known concentration. All refractive index increments were in reference to pure heptane at 298 K at 633 nm.

Flow times were measured in a Ubbelohde-type viscometer immersed in a water bath at 298 K. Repeated measurements were made to obtain flow times of 240 s or longer and were typically reproducible within 1%. Plots of η_{sp}/c versus c were extrapolated to zero concentration to obtain the intrinsic viscosity $[\eta]$.

A Lexel model 95-2 2 W argon-ion laser was used as the light source for photon correlation measurements. The incident wavelength was 514.5 nm. A Brookhaven Instruments Corp. multiangle light scattering goniometer was used to measure the intensity fluctuations. The apparatus was of modular design and was equipped with a specimen cell assembly with separate temperature control and index-matching liquid systems. Temperature stability of within 0.1 K was effected by circulating a mixture of water and ethylene glycol through copper coils surrounding and below the cell holder. Filtration and circulation of the index-matching fluid are provided by a peristaltic pump and membrane filters. The main detector optical assembly uses a 200 mm focal length lens as part of an optical transfer system. A photon counting system mounted on the optical rail afforded the light scattering measurements. The signal was typically integrated for $(1.5-2) \times 10^7$ photon counts. The autocorrelation function of the photocurrent was determined using a Brookhaven Instruments Corp. BI-2030AT 136-channel, four-bit digital correlator, and the measured baseline was determined from the long-time asymptote of the measured correlations using eight delay channels. The autocorrelation functions are considered acceptable only if the measured baselines lie within 0.02% of the calculated baselines, obtained from the square of the average photon flux. Data acquisition is facilitated by interfacing the real-time correlator to a microcomputer for initial analysis.

For the determination of the size distribution, $F(R)$ or $G(\Gamma)$, one must invert equation (14) numerically. The inversion of $g^{(1)}(\tau_c)$ is known to be ill-conditioned for the standard least-squares method. Here we utilized the program CONTIN^{19,20}, kindly provided by Dr S. W. Provencher, to perform the inversion of the correlation data obtained from p.c.s. This program has been shown to be effective in yielding smooth distribution functions of the decay rates in photon correlation spectroscopy without *a priori* knowledge of the size distribution¹³. The simplest best-fit solution was found by minimizing the sum of the least-squares error between experimental and fitted values of the autocorrelation function and the

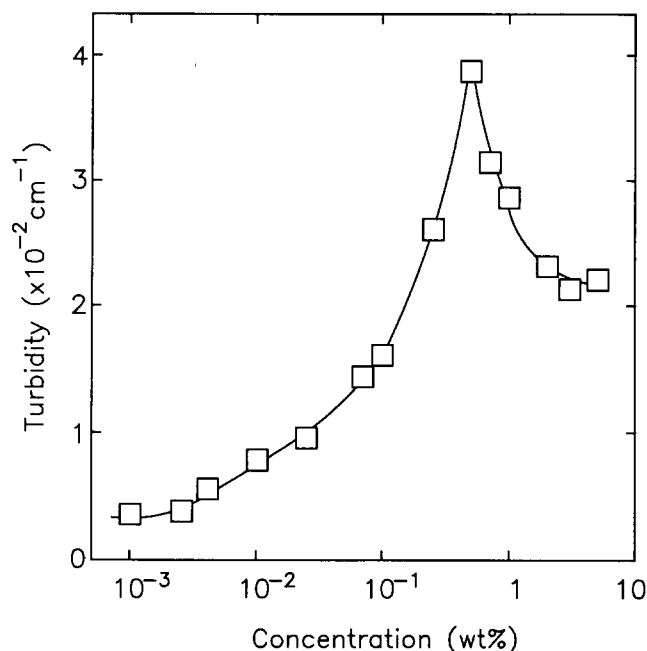


Figure 1 Concentration dependence of turbidity for PSPEP in n-heptane

penalty function consisting of a regulator and the third derivative of the decay rate distribution function¹⁹.

RESULTS

The turbidity τ of the block copolymer solutions was measured to characterize the micelle weight. At very low concentrations (0.001–0.003%), the turbidity for the block copolymer solution shows a weak dependence on concentration, as shown in Figure 1. Above 0.003%, a progressive increase in τ is clearly observable, although no obvious indication of a c.m.c. can be found. Further increase in concentration causes a continued rise in τ , whereas a bluish tint, normally associated with micelle formation, is observed for concentrations higher than 0.1%. The turbidity increases markedly to a concentration of 0.5%, above which an equally dramatic decline in turbidity is observed up to a concentration of 4%, the highest concentration at which the turbidity was measured. Here we define the critical concentration, c_1 , occurring between 0.5 and 0.7%, to be the point where the anomalous drop in turbidity commences and considerable intermicellar interactions become observable. The significance of c_1 will be discussed further later. It is noteworthy that the bluish opalescence remains evident at all concentrations above 0.1% despite the reduction of turbidity at c_1 .

Figure 2 shows the concentration dependence of the refractive index of the PSPEP solutions. At concentrations below 0.1%, the refractive index remains relatively insensitive to concentration, indicating that the polymer concentration is not yet high enough to affect the overall polarizability of the solution. Above 0.1%, we observed a marked increase in refractive index up to 3%, in contrast to the decline of turbidity at 0.5%, shown in Figure 1. As with the turbidity data, however, there is a transition in the specific refractive index increment $\Delta n/dc$ in the form of a break when Δn , the difference in refractive index between the solution and the pure solvent, is plotted

against the concentration c . The specific refractive index increment is about $0.3 \text{ cm}^3 \text{ g}^{-1}$ below 0.7% and is reduced to $0.1 \text{ cm}^3 \text{ g}^{-1}$ over the range from 0.7 to 3%. It will become clear that such a decrease of contrast in the refractive index upon traversing c_1 is a consequence of the presence of free chains in the solution.

Figure 3 displays a plot of Kc/τ against concentration c , where an extrapolation of Kc/τ to zero concentration was made to estimate the micellar weight. Scattered values of Kc/τ were obtained for concentrations below 0.01%, illustrating the limitation of the method in measuring the c.m.c. The noise of the data at low

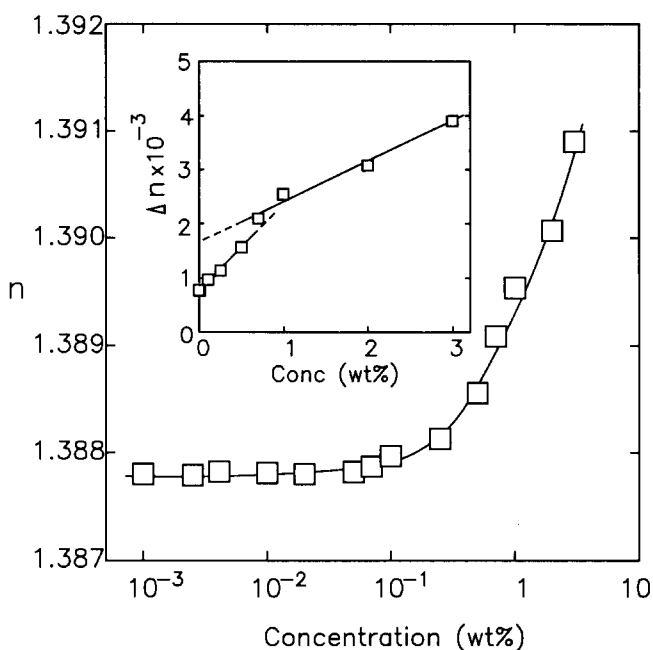


Figure 2 Concentration dependence of the refractive index for PSPEP in n-heptane

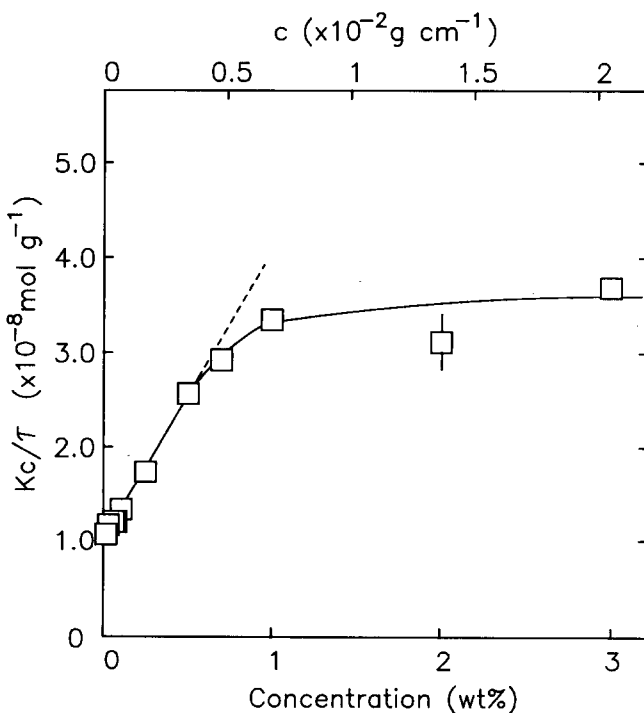


Figure 3 A plot of Kc/τ versus c for PSPEP in n-heptane

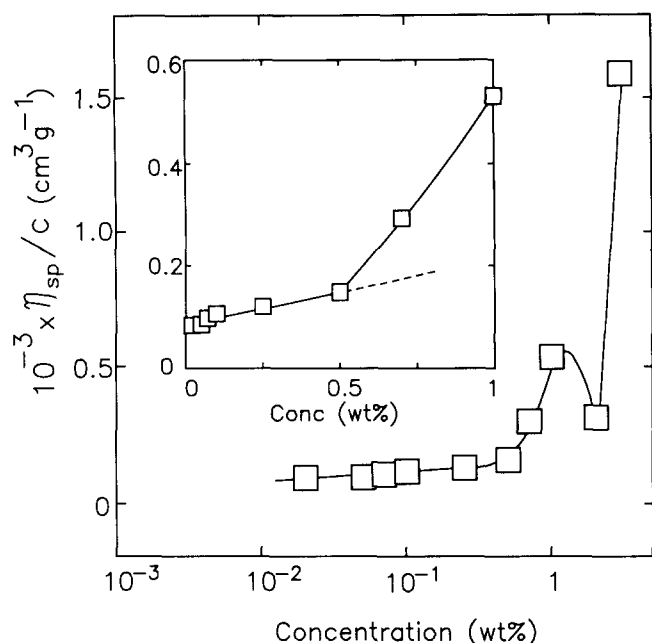


Figure 4 Concentration dependence of the reduced specific viscosity η_{sp}/c for PSPEP in n-heptane

concentrations is due in part to the error in measuring optical density where scattered light collected by the detector is rather significant¹³. For concentrations between 0.01 and 0.5%, we obtain a constant value of $1/\Omega M_m$, which in turn gives a micellar weight of $M_m = (6.8 \pm 0.4) \times 10^6$ and a second virial coefficient of $A_2 = (3.6 \pm 0.6) \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$. The micellar weight obtained is somewhat higher than the value of $M_m = 5 \times 10^6$ reported by Candau¹² for a similar PSPEP micelle solution in n-decane. On the other hand, Mandema *et al.*²¹ gave $M_m = 4 \times 10^6$ and $A_2 = 2.4 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$ for a PSPEP polymer with molecular weight of 48 000 (48 K) PSPEP in decane.

Interestingly, Kc/τ appears to level off above 0.7% and even reduces somewhat at 2%, although the magnitude of such depression is only slightly greater than the experimental error. Values of Kc/τ for 4 and 5% are not reported here since the viscosity of these solutions is rather high (see Figure 4) and the Rayleigh-Debye treatment of light scattering in dilute solutions is clearly inappropriate. In any case, an extrapolation of Kc/τ to zero concentration yields an estimate of the 'apparent' molecular weight of the particles, $M_p = (2.4 \pm 0.3) \times 10^6$ for $c = 1-3\%$. Results from p.c.s. (to be discussed later) and excimer fluorescence²² seem to suggest that this plateau of Kc/τ at 1-3% is caused by the presence of a significant amount of freely dispersed polymers in the solution. At this point, however, we are unable to determine from the turbidity data whether the reduction in M_m is due to the formation of smaller micelles or to the existence of both free chains and micelles.

The specific viscosity η_{sp} was measured for each of the micelle solutions at 298 K. The results, expressed in terms of the reduced viscosity η_{sp}/c , are plotted against c in Figure 4. It is interesting to note that the 4 and 5% samples are highly viscous and hardly flow even when turned upside down. For concentrations between 0.01 and 0.5%, a linear relationship of η_{sp}/c and c is found, suggesting that the hydrodynamic size of the micelle is relatively constant. The intrinsic viscosity $[\eta]$, determined by extrapolating η_{sp}/c to zero for concentrations below

0.5%, as given by:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c + \dots \quad (22)$$

is found to be $84 \text{ cm}^3 \text{ g}^{-1}$. Using the values of $[\eta] = 53 \text{ cm}^3 \text{ g}^{-1}$ and $M_m = 4 \times 10^6$ for micelles formed by a 48 k PSPEP polymer in decane²¹, the compactness of the PSPEP micelles can be examined using the Mark-Houwink equation:

$$[\eta] = kM_m^a \quad (23)$$

The Mark-Houwink coefficient a is estimated to be 0.8-0.9, indicative of the large hydrodynamic volume of micelles. The Huggins constant k_H is found to be 2.4 ± 0.3 , considerably higher than the value of 0.96 reported for the 80 k PSPEP in decane. Above 0.5%, η_{sp}/c increases quite markedly, and the intrinsic viscosity can no longer be obtained by extrapolating to zero concentration. This concentration dependence of specific viscosity is reminiscent of the anomalous turbidity behaviour at c_1 .

The normalized first-order autocorrelation functions for the micelle solutions were measured, and representative decay curves are displayed in Figures 5 and 6. At 0.001%, we were unable to detect any scattering due to either micelles, or isolated polymers, perhaps because of the exceedingly low concentration of polymers at this point. A relatively weak signal with a considerable amount of noise was observed at 0.003%. The fact that no detectable signals of micelles were obtained at 0.001% may indicate that all molecules exist in the dispersed form below 0.002-0.003% and that the concentration of 0.002% may be taken to be the c.m.c. as determined by p.c.s. Over the range of $c = 0.003-0.5\%$, the autocorrelation function can truly be represented by a single-exponential decay function, indicative of monodisperse distributions of micelle sizes. At 0.7% and above, however, the decay functions can no longer be satisfactorily represented by single-exponential decays, as shown in Figure 6.

Figure 7 illustrates a series of distribution curves, $F(R)$

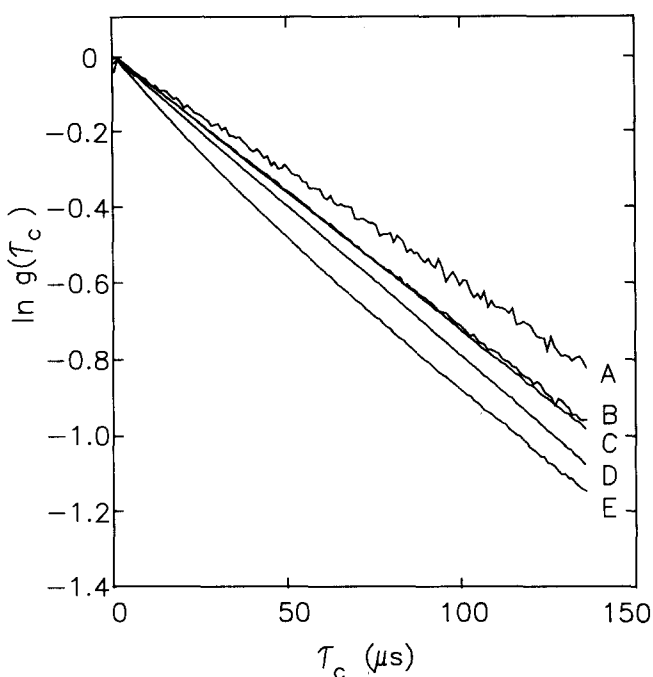


Figure 5 A comparison of the normalized first-order autocorrelation functions for (A) 0.003%, (B) 0.05%, (C) 0.1%, (D) 0.5% and (E) 2% PSPEP solutions

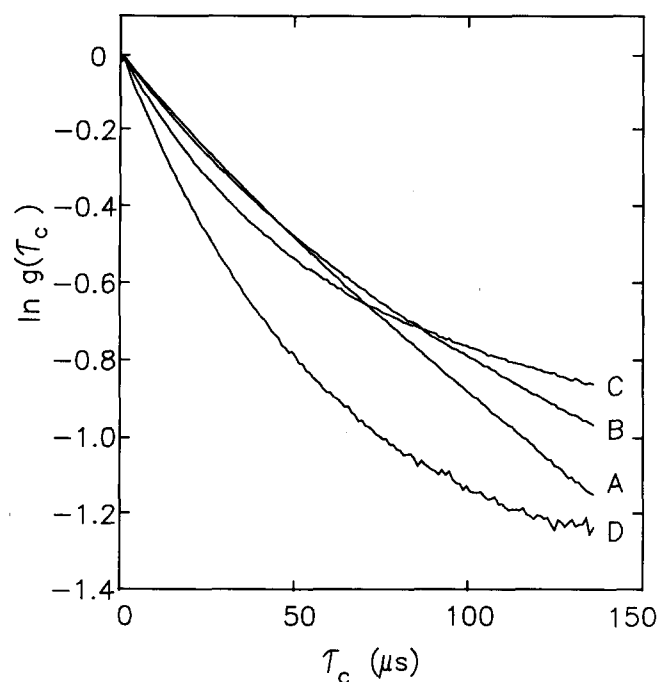


Figure 6 A comparison of the normalized first-order autocorrelation functions for (A) 2%, (B) 3%, (C) 4% and (D) 5% PSPEP solutions

(or $G(\Gamma)$), for the hydrodynamic radius, R (or Γ), measured over a wide range of concentrations, as determined by the CONTIN program. Also included is the distribution function for a 0.5% solution of PSPEP in methylene chloride. The apparent hydrodynamic radius, micelle polydispersity factor and the integrated intensity ratio of the fast and slow decay rates, A_f/A_s , are listed in Table 1. While the apparent hydrodynamic radius is found to be essentially constant ($\bar{R}=46.3 \pm 0.8$ nm) between 0.01 and 0.07%, a somewhat larger hydrodynamic radius ($R=59.2$ nm) is initially observed at 0.003%. As the concentration is increased, there is a gradual reduction of the apparent hydrodynamic size from a value of $R=44.9$ nm at 0.1% to a value of $R=41.4$ nm at 0.5%. As will be discussed later, such a reduction in R is due to the collective diffusion of micelles as intermicellar interactions become increasingly significant with increasing concentration. Although this reduction of R continues for $c=0.7-1\%$, a small additional peak with an average hydrodynamic radius of about 6–7 nm is observed at these concentrations. The hydrodynamic radius represented by this peak can be compared with the value of $R=12.5$ nm for the 0.5% PSPEP solution in methylene chloride, which is a good solvent for both PS and PEP.

In utilizing the CONTIN program for inverting equation (14), the emergence of a second peak in $F(R)$ is rather significant, since CONTIN tends to penalize statistically the representation of $F(R)$ with more than a single peak, and the smoothing parameter, *PROB1*, remains in an acceptable range of 0.4–0.6¹⁹. Recall that the first-order autocorrelation functions for concentrations from 0.7 to 5% cannot be characterized as single-exponential decays. The autocorrelation function between 0.7 and 2% can only be fitted with a bimodal distribution according to CONTIN. While the decay rate of the slow component (larger R) resembles the translational diffusion behaviour of micelles found in more dilute solutions, the faster component (smaller R) initially

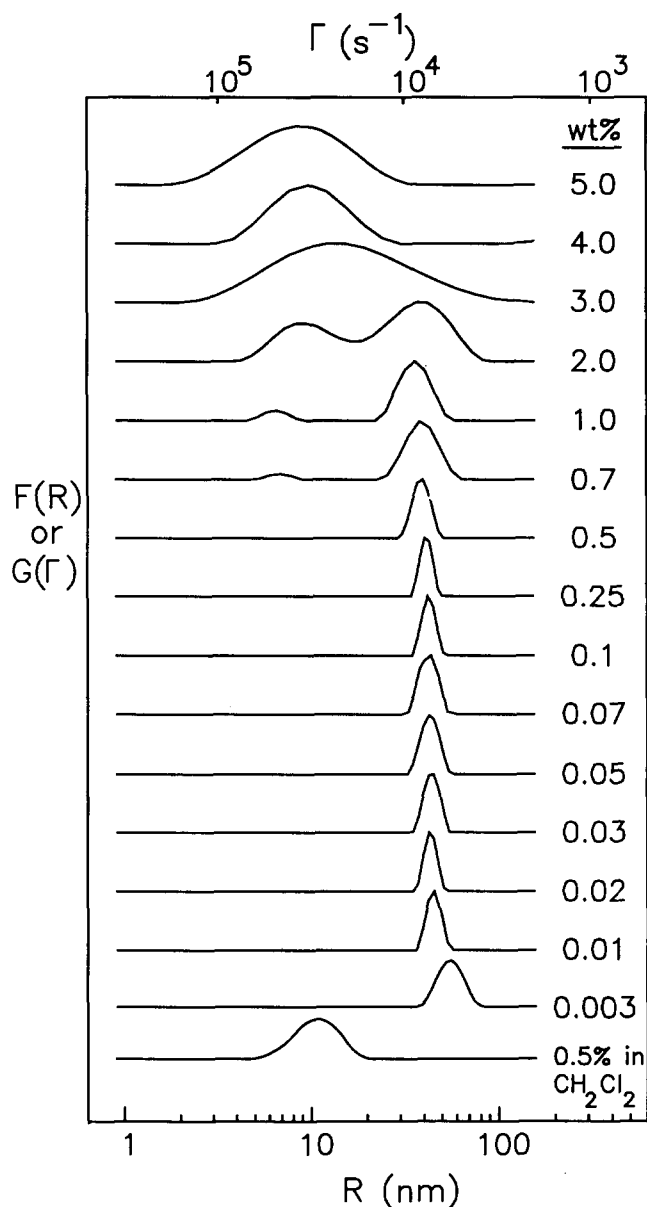


Figure 7 The intensity-averaged distribution curves, $F(R)$, for 0.5% PSPEP in methylene chloride and PSPEP micelle solutions in *n*-heptane as functions of concentration

Table 1 P.c.s. characterization results for PSPEP micelles as determined by CONTIN

| Conc. (wt%) | R (nm) | <i>POLY</i> | A_f/A_s |
|-------------|------------|--------------|-----------|
| 0.003 | 59.2 | 0.032 | — |
| 0.01 | 47.2 | 0.012 | — |
| 0.02 | 45.7 | 0.014 | — |
| 0.03 | 46.2 | 0.012 | — |
| 0.05 | 45.5 | 0.014 | — |
| 0.07 | 47.1 | 0.012 | — |
| 0.10 | 44.9 | 0.014 | — |
| 0.25 | 43.6 | 0.012 | — |
| 0.50 | 41.4 | 0.023 | — |
| 0.70 | 5.6, 42.8 | 0.014, 0.044 | 0.0073 |
| 1.0 | 6.1, 38.8 | 0.032, 0.044 | 0.020 |
| 2.0 | 10.8, 45.0 | 0.084, 0.123 | 0.143 |
| 3.0 | 37.5 | 0.608 | — |
| 4.0 | 12.7 | 0.152 | — |
| 5.0 | 13.2 | 0.240 | — |

Table 2 P.c.s. characterization results for PSPEP micelles as determined by statistical fits as biexponential decays

| Conc. (wt%) | R (nm) | A_f/A_s |
|-------------|------------|-----------|
| 0.7 | 6.3, 42.2 | 0.020 |
| 1.0 | 7.4, 38.5 | 0.035 |
| 2.0 | 10.5, 44.7 | 0.197 |
| 3.0 | 11.9, 77.1 | 0.529 |
| 4.0 | 9.7, 149 | 0.791 |
| 5.0 | 9.3, 134 | 1.57 |

emerges as a small peak and becomes broader and more predominant with increasing concentration, until it merges with the slow component at 3%. We found no dependence of the emergence of the second peak on the decay rate window used in CONTIN, and such a peak cannot be attributed to artifacts resulting from the inversion method used.

Instead, this second peak is believed to be related to the diffusion of freely dispersed polymer chains, which are now at a concentration detectable by p.c.s. In a poor solvent for PS, such as heptane, the free chain will presumably be collapsed due to the association of PS segments shielded by the PEP segments from the solvent, causing a smaller hydrodynamic size. Hence, a hydrodynamic radius of 6–7 nm for the free chains in heptane at 0.7–1% is consistent with the value of 12.5 nm for a more expanded coil in methylene chloride. At even higher concentrations (3–5%), the bimodal distributions can no longer be satisfactorily resolved, owing to various complications. The apparent hydrodynamic radii of about 13 nm at 4 and 5% may reflect a combination of various effects, including strong intermicellar interactions, multiple scattering, as well as the diffusion of free chains in the interstitial spaces between the micelles.

While the size distributions derived from CONTIN were informative, it remains instructive to compare the results determined by CONTIN with those obtained by fitting the autocorrelation functions with sums of exponential terms using a non-linear least-squares method. As shown in Figure 6, the first-order autocorrelation function $g^{(1)}(\tau_c)$ for $c=0.7$ –5% cannot be satisfactorily fitted with a monoexponential decay. On the other hand, excellent fits were obtained for all concentrations from 0.7 to 5% using a biexponential form of:

$$g^{(1)}(\tau_c) = A_f \exp(-\Gamma_f \tau_c) + A_s \exp(-\Gamma_s \tau_c) \quad (24)$$

where from equations (13) and (16):

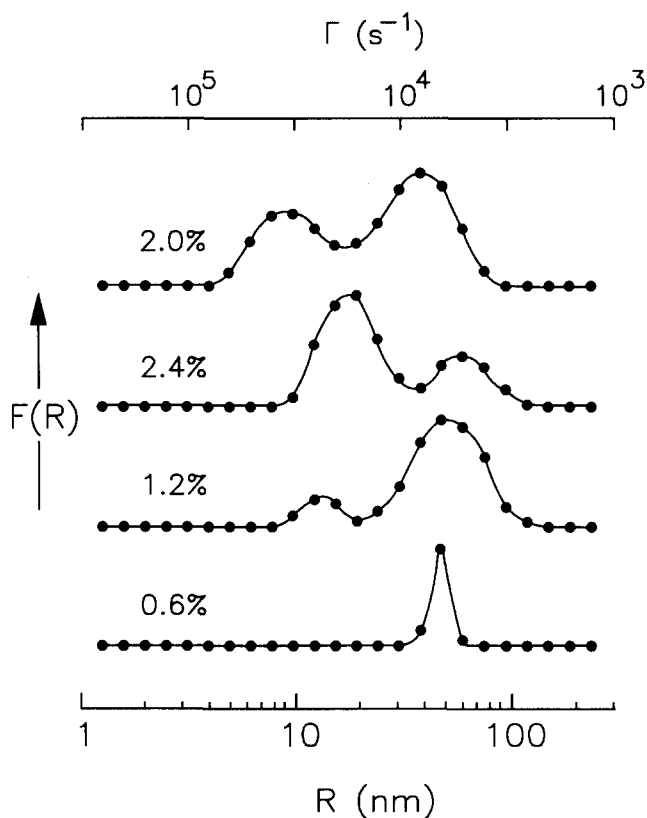
$$\Gamma_i = q^2 \frac{kT}{6\pi\eta R_i} \quad (25)$$

The results of these biexponential fits are summarized in Table 2. For $c=0.7$ –2% the hydrodynamic radii from the biexponential fits are in excellent agreement with the CONTIN results. The ratios A_f/A_s obtained by biexponential fits are, however, greater than those suggested by CONTIN. This is not surprising since the CONTIN inversion program tends to give somewhat broader peaks and has a bias towards the more populated peak. While the agreement of hydrodynamic radii is very good for concentrations between 0.7 and 2%, considerable differences are observed for $c=3$ –5%. For 3% the biexponential fit gives values of 11.9 and 77.1 nm for the hydrodynamic radii, whereas inverting $g^{(1)}(\tau_c)$ with CONTIN gives a broad, unimodal distribution. Because the viscosity of

the micelle solution is very high, it is obvious that intermicellar interactions are rather substantial. As a result, the values of 11.9 and 77.1 nm obtained from the biexponential fit should be regarded as the apparent hydrodynamic radii, which may embody a number of complicating effects. As discussed previously, at high concentrations the analysis of hydrodynamic sizes is invariably complicated by the mutual diffusion of free chains and micelles.

To explore further the origin of the broad distribution of decay constants at high concentrations, we have allowed the solvent to escape from a 2% solution by controlled evaporation at room temperature to obtain a slightly more concentrated solution. The resulting solution, estimated to have a concentration of 2.4%, appears to be composed of two types of particles with 'apparent' hydrodynamic radii of 18 and 61 nm according to CONTIN. The solution was then diluted to 1.2% and the correlation function was remeasured immediately. We observed a shift in the intensity of scattered light from the small component to the large one, as illustrated in Figure 8. Further dilution to 0.6% yields a sharp peak at $\Gamma = 70\,000 \text{ s}^{-1}$, indicating a monodisperse system of micelles with a hydrodynamic radius of 47 nm, a value more in line with those found between 0.01 and 0.07%. This suggests that either the true micelle size at 2.4% is represented by the value determined from the 0.6% solution, or that the kinetics of micelle formation by free chains upon dilution is much faster than the time elapsed in the dilution process.

It is well known that the correlation time of the single-scattered polarized component of light scattered from a system of Brownian particles decreases with increasing concentration²³, and that multiple scattering

**Figure 8** A comparison of the intensity-averaged distribution curves, $F(R)$, for 2, 2.4, 1.2 and 0.6% PSPEP solutions in n-heptane

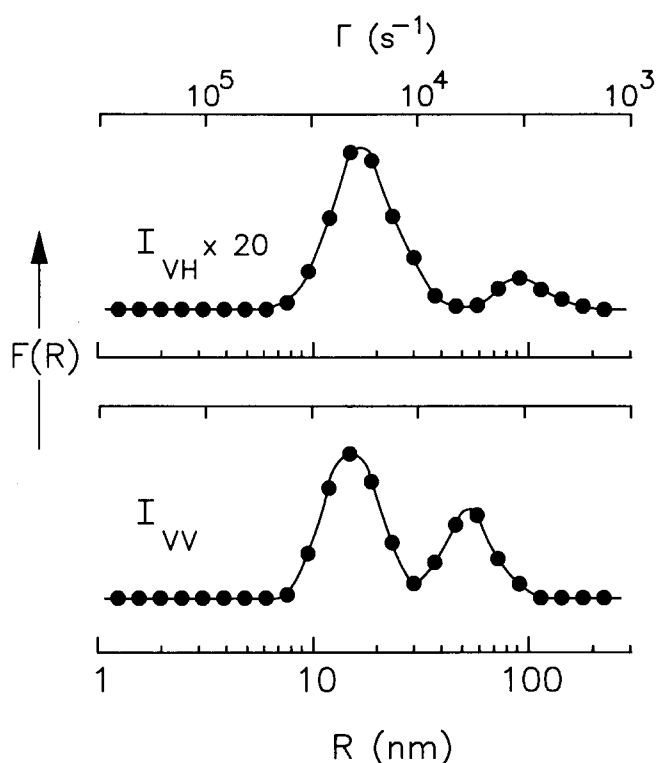


Figure 9 A comparison of the intensity-averaged distribution curves, $F(R)$, determined from polarized (I_{VV}) and depolarized (I_{VH}) scattering for a 2.4% PSPEP solution in n-heptane

can contribute to the observation of multiple peaks in the decay rate distribution²⁴. Thus, it is conceivable that multiple scattering could perturb the decay rate distribution and, therefore, the hydrodynamic radius that we have determined. To determine whether this is indeed an important consideration, we investigated the effect of multiple scattering on the existence of a bimodal distribution and its apparent size distribution at 1, 2 and 2.4%. The apparent size distributions of polarized (I_{VV}) and depolarized (I_{VH}) scattering for a 2.4% solution are contrasted in *Figure 9*. Since the autocorrelation function for I_{VH} is expected to exhibit faster decays than I_{VV} if multiple scattering is significant, the manifestation of somewhat similar distribution functions in I_{VV} and I_{VH} suggests that the existence of a bimodal distribution of $F(R)$ may not be due to multiple scattering effects. A more quantitative measure of multiple scattering effects can be provided by the depolarization ratio, $R^n = I_{HH}/I_{HV}$. For $c = 1, 2$ and 2.4% , we found $R^n = 0.07, 0.11$ and 0.19 , respectively. Based on a method developed by Grüner and Lehmann²⁴, the average number of scattering events \bar{n} as measured in p.c.s. is quite close to unity for $c = 1\%$, and increases to $\bar{n} \sim 1.8$ at $c = 2\%$ and to $\bar{n} \sim 2.6$ at $c = 2.4\%$. Hence, we conclude that the emergence of a second peak in $F(R)$ (for $c = 0.7\%$) is not due to multiple scattering effects of micelles.

As a further attempt to prove the origin of various changes observed above c_1 , we examined the effect of the scattering angle on the apparent decay constant distribution. At concentrations below c_1 (0.003–0.5%), the decay constant distribution function does not depend on the scattering vector q , confirming that the micelles are indeed spherical. At higher concentrations, however, the decay times show a systematic dependence on the scattering vector, which may be accounted for in terms of the influence of the form factor. *Figure 10* displays a

comparison of $F(R)/P(qR)$ for the 2.4% solution as a function of scattering angle. Obviously, the existence of two decay peaks is independent of scattering vectors. While there appears to be a slight shift to a larger apparent size with increasing scattering angle, no simple trend in A_f/A_s is observed with varying q , as measurements at $\theta = 65^\circ$ and 90° indicate a greater proportion of the smaller particles, whereas measurements at other angles suggest otherwise. Since PSPEP micelles in n-dodecane have been found to be spherical at a concentration as high as 10% ^{8,9}, the existence of bimodal distributions in $G(\Gamma)$ is unlikely to be caused by the formation of cylindrical or other non-spherical micelles. Such shifts in component decay constants and the changes in 'apparent' population of the fast and slow components may be attributed to the limitations of the current method, since an error of 30% has been reported in the measurements of average hydrodynamic size with different scattering angles¹³. In any case, the angular independence of the bimodal distributions seems to rule out the existence of species with different shapes.

DISCUSSION

Near the c.m.c.

Turbidity and viscosity measurements were not sensitive enough to determine the c.m.c. From Price²⁶, a c.m.c. of 0.04% was reported for a similar PSPEP micelle in n-decane at 359 K. Therefore, the c.m.c. is expected to be significantly lower at room temperature. The unusually broad distribution observed for 0.003% is due to the excessive noise in the autocorrelation function obtained. Such an effect has been well documented²⁷. From *Figure 5*, however, it is apparent that the increase in micellar

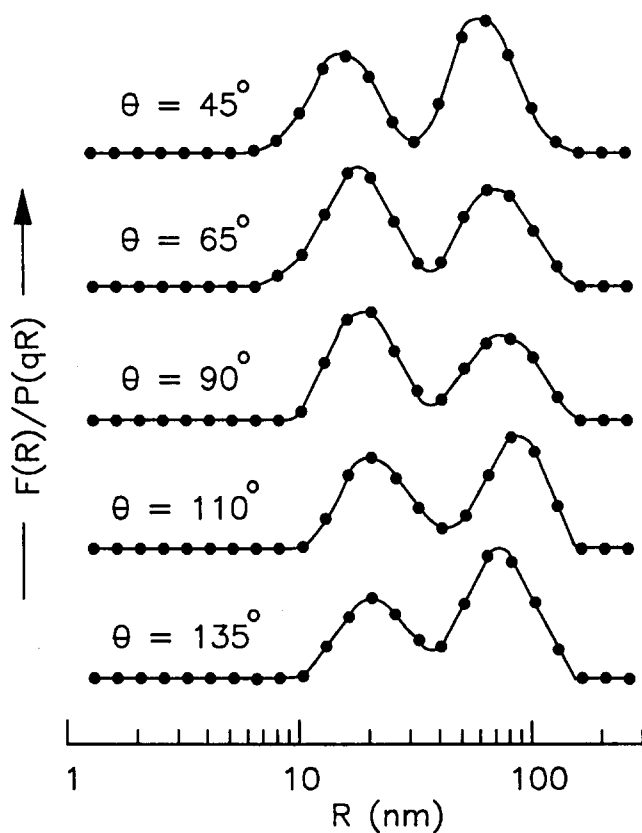


Figure 10 A comparison of $F(R)/P(qR)$ for a 2.4% PSPEP solution in n-heptane as a function of scattering angle

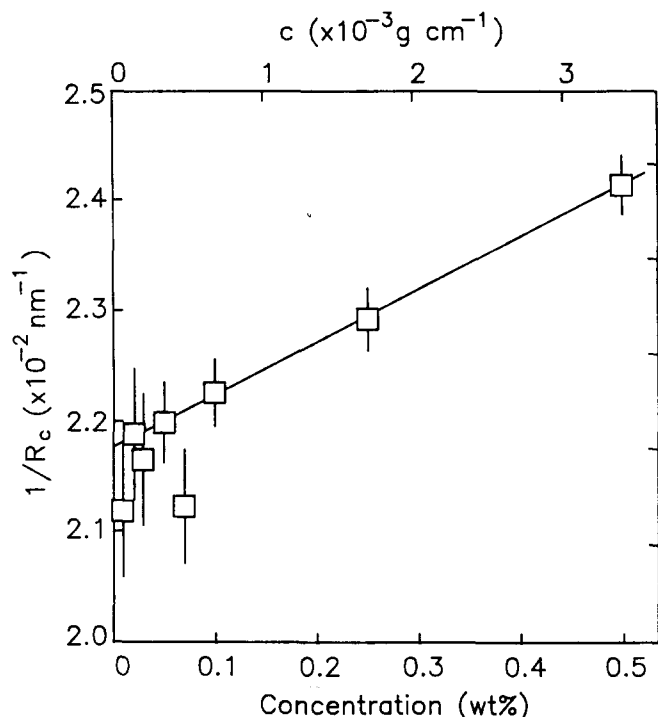


Figure 11 A plot of $1/R_c$ versus concentrations for PSPEP solutions in heptane

size cannot be ascribed to an artifact of the inversion method. Instead, such an observation is in agreement with Tuzar *et al.*¹¹, who reported the presence of larger micelles near the c.m.c. with sizes up to twice the size at higher concentrations. While the observation of increasing micellar weight with increasing temperature^{1,28} was previously attributed to the existence of PS homopolymers in solution, no appreciable amount of PS homopolymers should be found here with the proper sample purification stated above. Therefore, it is likely that the increase in micellar size observed near the c.m.c. here is not related to the aggregation of PS homopolymers. A possible explanation is that the micelles formed in the concentration region slightly above the c.m.c. are highly swollen with solvent molecules, especially within the core. More on the PS segment density within the micellar core will be discussed in the following paper²².

Between c.m.c. and c_1

Although turbidity and viscosity measurements suggest that the average micellar weight and intrinsic viscosity do not change over the range of 0.01–0.5%, p.c.s. indicates a gradual reduction of the apparent hydrodynamic radius over the narrow range of concentration below c_1 (0.1–0.5%). Tuzar and coworkers²⁹ investigated the interactions between micelles at various concentrations and found that the reduction of apparent hydrodynamic radius of micelles with increasing concentration can be explained in terms of mutual or collective diffusion of micelles.

It is well known that the diffusion coefficients of particles in solutions depend on the particle concentration. For pair interactions of hard spheres, the collective diffusion coefficient D_c may be given by¹⁵:

$$D_c = D_0(1 + k_D\phi) \quad (26)$$

where D_0 is the diffusion coefficient at infinite dilution, k_D is the interaction parameter and ϕ is the volume fraction of micelles.

According to the Stokes–Einstein relation, the apparent hydrodynamic radius R_c can be expressed as:

$$\frac{1}{R_c} = \frac{1}{R_0} (1 + k_D\phi) \quad (27)$$

where R_0 is the hydrodynamic radius of the particles at infinite dilution. In this study, the volume fraction of micelles can be calculated from:

$$\phi = \frac{4\pi R_0^3 c N_A}{3M_m} \quad (28)$$

and the second virial coefficient for hydrodynamic interactions between hard spheres can be written as²⁹:

$$A_2^{\text{HS}} = \frac{16\pi N_A R_0^3}{3M_m^2} \quad (29)$$

Figure 11 shows a plot of $1/R_c$ versus c , where values of $R_0 = 46 \text{ nm}$, $k_D = 0.94 \pm 0.25$ and $A_2^{\text{HS}} = 2.1 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$ are obtained. The value of $k_D = 0.94$ is comparable with the values of $k_D = 1.0$ – 1.2 reported for a hydrogenated polystyrene–polybutadiene (PS–PB) micelle solution²⁹. In addition, the fact that A_2^{HS} is lower than the second virial coefficient $A_2 = 3.6 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$ obtained from turbidity measurements is analogous to that reported by Tuzar *et al.*²⁹. To characterize the deviations of hydrodynamic interactions from hard-sphere behaviour, Russel has derived the relationships of k_H and A_2/A_2^{HS} in terms of different model interaction potentials³⁰. For a ratio of $A_2/A_2^{\text{HS}} = 1.7$, the interactions between PSPEP micelles may be represented by an excluded-shell model. As will be further discussed later, a similar model of hard-core and soft-shell potentials has been proposed for the interactions of PSPEP micelles in a macrolattice⁹. In light of the relatively large corona radius (estimated from the difference of $R_0 = 46 \text{ nm}$ and $R_{\text{core}} = 10$ – 15 nm), it is possible that an excluded-shell model may be appropriate.

Above c_1

As illustrated in Figure 7, the changes of turbidity and reduced viscosity at a concentration above c_1 may be attributed to the presence of free chains. It is noteworthy that Price⁵ gave a crossover of dissymmetry ratio of 1 at 0.7% for a similar PSPEP in hexane, indicating a change in particle dimension. Here, the abrupt decrease in turbidity above 0.5% is confirmed by both photon correlation spectroscopy and viscosity measurements. The presence of free chains in solution is consistent with the reduction of Kc/τ at 2%. Based on the p.c.s. data on the diluted solutions, we conclude that the anomalous change of turbidity at concentrations above c_1 is not due to a decrease in the molecular weight of micelles, but primarily to the increasing amount of free chains in solution.

While the abrupt increase in reduced viscosity at c_1 signifies that interactions between the micelles develop quite rapidly with concentration, the pronounced reduction in reduced viscosity at 2% depicts a change in the average hydrodynamic volume of the particles in solution. Previously, Mandema *et al.*²¹ reported that in a poor solvent the effective hydrodynamic volumes of isolated PSPEP chains are less compact and have a lower intrinsic viscosity than the micelles. Thus, the increase in η_{sp}/c with concentration above c_1 may be somewhat offset by the increasing amount of free chains with lower $[\eta]$. A qualitative check on this proposal can be made

by estimating the intrinsic viscosity of the free chain from equation (20). For a hydrodynamic radius of 5.6 nm for a single chain, we obtain $[\eta] = 8.2 \text{ cm}^3 \text{ g}^{-1}$. Hence, an increase in free chain concentration would necessarily lower the reduced viscosity η_{sp}/c and the average intrinsic viscosity. Apparently, this effect manifests itself most strongly at 2%, when compared to the 1 and 3% solutions.

It is possible to estimate the weight fractions of free chains and micelles from the apparent molecular weight of these particles for $c = 1\text{--}3\%$, which has been found to be $M_p = (2.4 \pm 0.3) \times 10^6$ by turbidity measurements. To calculate the weight fractions, we employ:

$$M_p = X_R M_m + (1 - X_R) M \quad (30)$$

where X_R is the weight fraction of micelles, and M is the molecular weight of the polymer. For $M = 1.35 \times 10^5$ and $M_m = 6.8 \times 10^6$, $X_R = 0.33$. Alternatively, it would be desirable to estimate the weight fractions of free chains and micelles from the p.c.s. results. However, an unequivocal determination of such weight fractions is fraught with difficulty. According to Tuzar *et al.*³¹, the concentration dependence of diffusion of micelles in solutions of freely dispersed polymers is rather complicated. Furthermore, problems can arise in the determination of X_R since it is unclear whether the specific polarizabilities α_v of the free chains and micelles can be assumed to be identical. Recognizing the lack of some required data, we have chosen to give a rough estimate of X_R based on the apparent hydrodynamic radii of the micelles and freely dispersed chains, as illustrated in Table 1. Assuming identical α_v for the micelles and free chains, X_R can be calculated from A_f/A_s using equations (17)–(19). For $c = 0.7, 1$ and 2% , the corresponding values of X_R are found to be 0.23, 0.16 and 0.1, respectively. Such values of free chain volume fractions are rather low when compared to the values reported by Plestil and Baldrian³². They studied the micelle formation of a 0.85 wt% micelle solution of PS–PB copolymer ($M = 65\,000$) in heptane, and found $X_R = 0.52\text{--}0.54$ using SAXS and sedimentation velocity measurements. Thus, it is possible that the current estimates of X_R may be somewhat low. We shall compare our values of X_R with results obtained from SANS and n.m.r. in more detail later.

Macrolattice formation

Although the formation of a macrolattice of micelles cannot be confirmed by turbidity or p.c.s. data, the concept of the crossover concentration c^* , introduced by Simha³³, may be used to estimate the critical concentration above which a macrolattice is formed². The crossover concentration for spherical particles in a cubic structure is given by³⁴:

$$c^* = 2.5f/[\eta] \quad (31)$$

where f is the packing fraction of the cubic lattice. Since simple cubic (s.c.) and body-centred cubic (b.c.c.) structures have been proposed as possible lattice structures for a macrolattice formed by a similar PSPEP polymer in dodecane^{8,9}, it would be interesting to compare the crossover concentration for these two packings. For the micelles the intrinsic viscosity $[\eta]$ is found to be $84 \text{ cm}^3 \text{ g}^{-1}$, which would give, for a simple cubic structure, a crossover concentration of $c^* = 2.3\%$, whereas for a

body-centred cubic structure, a value of $c^* = 3.0\%$ is obtained.

Alternately, the crossover concentration can also be calculated from the average micellar weight and the hydrodynamic radius such that:

$$c^* = f \frac{3M_m}{4\pi R^3 N_A} \quad (32)$$

For $R = 38.5 \text{ nm}$ and $M_m = 6.8 \times 10^6$, crossover concentrations of 3.7 and 4.8% are obtained for simple cubic and body-centred cubic structures, respectively. Unfortunately, no experimental data are available on the concentration at which a macrolattice of PSPEP micelles is formed in heptane. However, it is known that the formation of macrolattices of PSPEP micelles in dodecane is found to occur at concentrations above 3%⁹. Since c_1 is higher for PSPEP in heptane when compared to dodecane solutions²², we expect the crossover concentration c^* for heptane solutions to be higher than the value of $c^* = 3\%$ for dodecane.

At concentrations of 3–5%, the high viscosity of the micelle solutions indicates that intermicellar interactions are rather strong such that p.c.s. can no longer be used to probe self-diffusion. Furthermore, the effect of multiple scattering has been shown to be rather serious for $c > 2\%$. Thus, the decay rates obtained from the p.c.s. measurements no longer correlate with the motion of micelles. At 4–5%, it is plausible that these decay rates are more relevant to the diffusion of free chains within the interstitial space between the lattice points (the micelles). Thus, a distribution of diffusion coefficients may be possible since the frictional drag on these free chains should depend on how close they are to the nearest lattice points. At the present time, we do not wish to give much significance to the absolute distribution of diffusion coefficients in this region as determined from CONTIN or biexponential fits. However, it would be desirable to be able to quantify such motions, perhaps with respect to the interparticle separations, free chain and micelle volume fractions. We will defer the determination of the true hydrodynamic radius at such high concentrations until complications, such as the presence of free chains and intermicellar interactions, can be resolved.

Comparison with previous results

Here we compare our results with those reported by Higgins^{8,9} and Candau¹². While these workers have utilized a number of novel techniques such as SANS, n.m.r. and rheology measurements to study the structure and formation of macrolattices of PSPEP micelles, these experiments do not provide a direct measurement or detection of free chains. However, observations and discussions on the structure of macrolattices from these studies have proven valuable for our interpretations.

At concentrations above c_1 , for instance, our data show a concomitant reduction in the average hydrodynamic radius along with an apparent increase in polydispersity of size distributions as measured by p.c.s. To the best of our knowledge, there has been no report suggesting that a wide range of smaller micelles exists at high concentrations. Based on the position of the form factor peak and on the intermicelle separation from the position of the lower-angle interference peaks, Higgins and coworkers⁸ have determined the core radius of the micelles. They studied a macrolattice of PSPEP in dodecane and gave

a core radius of 12.7 nm for a 10% solution. Assuming a Gaussian distribution of core radius with a standard deviation of 1.6 nm, they were able to obtain an excellent fit of the spherical form factor in their SANS data. This is equivalent to a *POLY* value of 0.016, in excellent agreement with the *POLY* values of 0.012–0.023 for 0.01 to 0.5%. Although such an agreement does not necessarily confirm that the size distribution of micelles is indeed Gaussian, it nevertheless establishes that the distribution of micellar sizes in a macrolattice is indeed monodisperse, and further confirms that the distributions of hydrodynamic radii for micelles above c_1 , as given by p.c.s. in Figure 7, have been artificially broadened.

In a more recent study, Higgins *et al.*⁹ proposed a model incorporating a hard core and a soft shell to represent the interaction potentials of the micellar core and corona with neighbouring micelles. They consistently found that the best fits of the scattering law were obtained only by assuming a fraction of the PS blocks to lie outside of the micelle cores⁹. For instance, optimization of statistical fits was achieved for 8 and 4% solutions only if $X_R = 0.77$ and 0.73, respectively.

In an n.m.r. study of a 2.7% PSPEP solution in octane, Candau *et al.*¹² reported that a significant portion of the n.m.r. signal can be related to the mobility of PS segments. They attributed such an observation to the penetration of solvent or PEP chains into the core, and estimated that 40% of the PS chains in the core are mobile. However, it is also possible that part of that signal is due to the presence of free chains in the dispersed phase, since the micellar core is generally very dense at high concentrations. A more detailed study on the chain dynamics of PS within the core may clarify this point.

Driving force for the existence of free chains in the dispersed phase

Watanabe and coworkers^{2,3} previously proposed that the formation of a macrolattice in block copolymer solutions is intimately related to the change of segment density of the soluble blocks in the corona. Although the presence of free chains in the matrix phase was not considered in their discussion, their analysis may be used to account for the change in free chain–micelle equilibrium above c_1 .

They proposed that the physical properties of micelles in dilute solutions are governed by the intrinsic properties of the individual micelles, and the equilibrium between micelles and free chains is shifted towards the formation of micelles. As the concentration is increased above c_1 , intermicellar interactions will gradually develop. At this point, however, the concentration of micelles is not high enough to sustain a macrolattice. Although the segment density in the dispersed phase is kept uniform almost exclusively by the solvent molecules, the density deficiency and excess of PEP segments brought about by the fluctuations of the intermicellar distance (through Brownian motions) will be more substantial with increasing concentration. This local osmotic pressure gradient will tend to increase the free energy of the system.

To compensate for such an osmotic pressure gradient, the PEP chains of a micelle may stretch to fill the space in the dispersed phase. Notwithstanding the increase of R from 38.8 nm at 1% to 45 nm at 2%, as illustrated in Table 1, a reduction of the apparent hydrodynamic radius with increasing concentration has been observed for

concentrations above 0.1%. Therefore, the PEP chains are apparently not stretched to compensate for this concentration gradient. An alternative way to lower the free energy is to allow for the presence of free chains in the dispersed phase, thereby lowering the concentration gradient of PEP segments between the corona and the dispersed phase. Watanabe *et al.*^{2,3} have shown that, if homopolymers of the soluble block are added to the solution, the tendency to form a macrolattice is substantially reduced. They concluded that the lattice disordering is stabilized via the elimination of concentration gradient in the matrix phase by the presence of homopolymers. Since no PS segments are added to the dispersed phase in this case, destabilizing effects of the interactions between the insoluble block and the solvent can be avoided.

In the present study, the driving force for the dissolution of free chains in the matrix phase is apparently strong enough to overcome the incompatibility of PS with the solvent. A further increase in concentration will lower the intermicellar separation and will also perturb the micellar size. At the crossover concentration c^* , the micelles are in contact with each other, and the concentration gradient of PEP segments between the corona phase and the matrix is no longer significant. The fact that this effect is of very short range in nature may explain the abrupt changes of free chain–micelle equilibrium with concentration, especially at 2% where X_R is believed to be a minimum. Therefore, the driving force for the presence of freely dispersed chains becomes weakened as the requirement of more free chains in the now-diminished dispersed phase is unimportant.

SUMMARY

We have examined the concentration dependence of PSPEP micelles in heptane, and found that the average micellar weight and hydrodynamic size of micelles are constant for $c = 0.01$ –0.5%. Owing to the collective diffusional motions of the micelles, a reduction in the apparent hydrodynamic radius was observed for $c = 0.1$ –0.5%, preceding a shift of the free chain–micelle equilibrium in favour of an increased presence of free chains at $c > 0.5\%$. Estimates of the weight fraction of micelles have been obtained from turbidity and p.c.s. results. The values of $X_R = 0.33$ from turbidity and $X_R = 0.1$ –0.23 from p.c.s. appear to be rather low when compared to literature values. A more direct means of measuring X_R would be desirable.

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