Study of micelle formation by the diblock copolymer polystyrene–b-(ethylene-co-propylene) in dodecane by small-angle neutron scattering

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The diblock copolymer polystyrene–b-[ethylene-co-propylene] forms micelles with polystyrene cores in dodecane at concentrations between 1.4 and 10% solids. Neutron scattering experiments allow determination of the dimensions of the polystyrene cores and show a very highly ordered simple cubic arrangement of the micelles. A preferred orientation of the cubic lattice is found.

(Keywords: diblock copolymers; micelles; order; preferred orientation; small-angle neutron scattering; particle size)

INTRODUCTION

Diblock copolymers dissolved in solvents which are selectively poor for one component and good for the other are well known to form micellar aggregates[1,2].

When the copolymers are highly monodisperse, as can be the case for example for polystyrene–polybutadiene systems, the resulting micelles are also monodisperse and show a tendency to order into 'crystalline' structures in certain ranges of temperature and concentration[1]. Such ordered systems have been extensively studied by small-angle X-ray scattering[1] and by rheological techniques[2]. We report here a small-angle neutron scattering study of such a diblock copolymeric system, polystyrene–b-poly(ethylene-co-propylene) in solution in n-dodecane. This system had already been shown to form micelles with a very narrow size distribution[3,4] and might be expected to show similar ordering to other block copolymer systems. It will be seen that the advantage of neutrons over X-rays for the scattering studies lies more in the longer wavelengths of the former and in the use of area detectors in the spectrometers than in the possibility of contrast enhancement via use of deuterated samples as is more usually the case[5].

EXPERIMENTAL

Diblock copolymers

Samples of the diblock copolymer polystyrene–b-(ethylene-co-propylene), which were kindly provided by Dr B. Wright, Shell Research Centre, Thornton, Chester, Dr A. Bull, Shell Research BV, Amsterdam, and Ms. K. F. Churchley, Shell Centre, London, had a styrene content of 38.5% by weight. These samples, which will be designated diblock copolymer containing a PS(H) block, had been prepared by hydrogenating the polyisoprene block in a polystyrene–b-polyisoprene diblock copolymer synthesized by anionic polymerization. Diblock copolymer containing a deuterated polystyrene block PS(D) was prepared by aromatic deuteration involving hydrogen–deuterium exchange. The procedure consisted of dissolving PS(H) diblock copolymer in benzene-d_6 followed by the addition of a solution of ethylaluminium dichloride as catalyst. A trace of water as co-catalyst was then added. Full details of the deuteration experiments will be published separately[6]. Up to 3.5 protons per ring (as determined by ^{1}H n.m.r.) were exchanged with only minor degradation of the block copolymer molecular weights, as shown in *Table 1*. These values of the number-average and weight-average molecular weights $\bar{M}_n$ and $\bar{M}_w$ were determined by gel permeation chromatography (calibration with polystyrene standards), and for the as-received PS(H) diblock copolymer our results were somewhat higher than the values $\bar{M}_n = 104\,000$ and $\bar{M}_w = 118\,000$ provided by Dr B. Wright.

Micellized solutions for neutron scattering experiments were prepared as follows. A known weight of diblock copolymer was dissolved in methylene chloride. The required volume of n-dodecane was added, and the methylene chloride removed by evaporation at elevated temperature. Solutions having 2 and 10% by weight copolymer were prepared. Further samples at 1.4 wt% for PS(H) copolymer and at 2% for PS(D) copolymer were obtained by dilution from 10% samples. Samples were syringed into flatsided quartz cells of cross section 15 × 20 mm and path length 2 mm and sealed under vacuum.

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Neutron scattering theory and experiment

Experiments were carried out using the small-angle scattering spectrometers D11 and D17[7] at the Institut Laue-Langevin, Grenoble[8]. The experimental conditions are summarized in *Table 2*.

The sample scattering was corrected for background (including that for solvent and sample container) and normalized for flux and geometric effects using the incoherent scattering from water in order to obtain the scattering law $S(Q)$. Q, the wave vector change on scattering at scattering angle θ for wavelength λ is given by

$$Q=\frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{2}$$

For a system of interacting particles it is usual to separate $S(Q)$ into two terms: $S_f(Q)$ the interparticle structure factor and $P(Q)$ the single particle form factor.

For a system of homogeneous, spherical particles

$$S(Q)=KNM^2P(Q)S_f(Q) \tag{2}$$

where K is the contrast factor[9] between particles and solvent, N the number density of particles of mass M. In these experiments the contrast factors between the solvent and polymer are respectively for PEP, 0.39, for PS, 12.61 and for PSd 52.5. The dominant signal is thus between the polystyrene cores and the solvent.

$$S_f(Q)=1+4\pi N\int[g(r)-1]\frac{\sin Qr}{Qr}r^2\mathrm{d}r \tag{3}$$

where $g(r)$ is the radial distribution function of particles a distance r apart. At $Q=0$,

$$S_f(Q)\rightarrow kT(d\rho/d\pi) \tag{4}$$

where π is the osmotic pressure. $S_f(Q)$ is thus a measure of the osmotic compressibility of the system and hence of the interparticle forces. For even a random 'gaseous' array the suppression of $S_f(Q)$ as $Q\rightarrow 0$ tends to give rise to an apparent peak in $S(Q)$ such that $Q_{\max}d\simeq 2\pi$ where d is the average interparticle distance. Pusey[10] has shown experimentally for a liquid-like organization that $Q_{\max}\times d/2\pi=1.18$ while theoretical calculation[11] for close-packing gives a value of 1.22. As Q increases $S_f(Q)\rightarrow 1$ (and as the particle density decreases this is also true). Thus at higher values of Q and in dilute systems the single particle form factor $P(Q)$ will dominate $S(Q)$. For solid spheres

$$P(Q)=\frac{\pi}{2}\left(\frac{3(\sin QR-QR\cos QR)^2}{(QR)^3}\right) \tag{5}$$

The first minimum in $P(Q)$ occurs at $QR=4.5$ while the smallest possible value of the interparticle spacing, $d=2R$. Thus the peak in S_f (at $Q\simeq 2\pi/d$, i.e. $QR\sim\pi$) and the structure in $P(Q)$ (at $QR\sim 4$) occur in different regions of Q space and are normally separable. The higher Q data are dominated by the particle structure, while the lower Q data contain information about $g(r)$.

Table 1 Diblock copolymer molecular weight distribution

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PS(H) copolymer	121 700	128 700	1.06
PS(D) copolymer	115 400	125 400	1.09

Table 2 SANS experimental conditions

	λ (Å)	Sample detector distance (m)	$Q_{\min}$ (Å^{-1})	$Q_{\max}$ (Å^{-1})
D11	8	10.6	5.2×10^{-3}	2.6×10^{-2}
D17	15	1.4	2.1×10^{-2}	1.05×10^{-1}

RESULTS

High Q—the particle dimensions

Figure 1 shows the corrected scattering, $S(Q)$, plotted logarithmically against Q for 10%, 2% and 1.4% micellized solutions of PS(H) and PS(D) copolymers. The curves for the two 2% samples of PS(D) coincide exactly. The structure typical of equation (5) is clearly seen. For the 10% samples in *Figure 1a* at least two minima are visible while for the 2% and 1.4% samples the minima after the first are lost because of lack of signal intensity. The value of the particle radius can be obtained by fitting the first minimum[12] ($QR=4.49$) or the distance between two minima $\Delta QR=\pi$. Results are summarized in *Table 3*. *Figure 1a* shows clearly the increased polydispersity of the PS(D) micelles (in the lack of sharp minima) and *Table 3* shows they are somewhat smaller. Consequently the calculated number of molecules/micelle is somewhat smaller. The solid lines in *Figure 1a* are the best fits of equation (5) in which a Gaussian distribution of particle radii has been included. For the PS(H) micelles the best fit was obtained for $R=127$ Å with a standard deviation of 16 Å, while for the PS(D) micelles $R=112$ Å, with a somewhat larger standard deviation of 20 Å. As mentioned in the previous section the dominant contrast is for the polystyrene cores, so that the increased polydispersity and reduced size may be due to increased polydispersity of the polystyrene segments introduced during the deuterium exchange (see *Table 1*). The data at high Q (particularly for the PS(H) system) are essentially background noise and do not indicate a deviation from the model calculation. Richards *et al.*[13] have recently calculated the scattering from solid microphase block copolymers. They show that there is a considerable distortion at the lower Q values of the particle scattering function $P(Q)$ by the interference function $S(Q)$. *Figure 1a* shows apparently little deviation of the data from the model fit at low Q. Inspection of *Figure 3*, which shows the experimental $S(Q)$, confirms that $S(Q)$ and $P(Q)$ are rather well separated because of the high dilution of the particles in the current work. For the PS(H) micelles the values of R are in excellent agreement with values obtained from transmission electron micrographs of samples prepared in n-heptane by the same procedure. The microscopy involved deposition of the solution on a carbon grid followed by evaporation.

The ratio of the scaling factors used to fit the model to the two sets of data in *Figure 1a*, taking account of the larger number of particles per unit volume for smaller particle radii, is 5.1. This should correspond to the different contrast factors for PS(H) and PS(D) cores. The

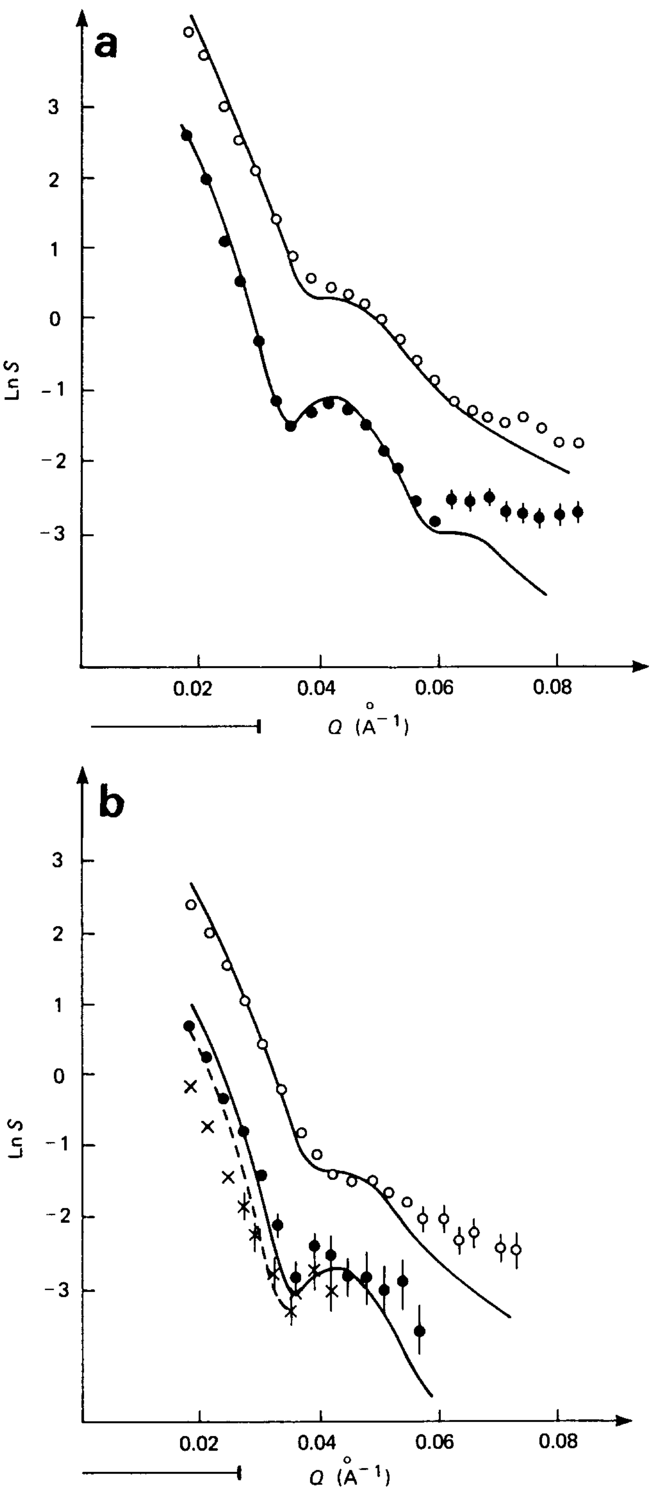

Figure 1 Scattered intensity $S(Q)$ plotted logarithmically against Q for (●) PS(H) and (○) PS(D) micelles: (a) 10% solids; (b) 2% solids (●) direct dissolution (○) dilution from (×) 1.4% solids PS(H) micelles. The bar shows the limit of the Q range in *Figure 4*. Except where shown statistical errors are smaller than the points as drawn. The curves in *Figure 1a* are the fit of equation (5). Those in *Figure 1b* are the same fits reduced by a factor 5 (———) and (– – –) 7.1, respectively

Table 3 Particle radii from observation of minima in $P(Q)$

Sample	Q_{min} (Å^{-1})	R (Å)	ΔQ (Å^{-1})	R (Å)	Molecules/ micelle
PS(H) micelle 2% direct dissolution	0.0358	125	–	–	–
PS(H) micelle 1.4% by dilution	0.0358	125	–	–	–
PS(H) micelle 10%	0.0358	125	0.0241	130	114 (128)
PS(D) micelle 2% direct dissolution	0.0419	107	–	–	–
PS(D) micelle 2% by dilution	0.0419	107	–	–	–
PS(D) micelle 10%	0.0389	116	0.027	116	91

calculated contrast ratio for pure polystyrene cores is 4.14; however, we have made no attempt to account for the polydispersity in calculating the number of particles per cm^3 since the Gaussian distributions used are clearly unrealistic.

The same best fit curves in *Figure 1a* have been rescaled by a factor 5 to scale to both the 2% samples in *Figure 2b*, and by a factor 7.1 to scale to the 1.4% sample of PS(H) obtained by dilution from 10%. While the statistics are very poor for the 1.4% sample there does seem to be evidence that there may have been a change in the shape of the scattering curves for this sample. This may indicate a genuine change in particle shape, though it is notable that the first minimum in $P(Q)$ is apparently not shifted, or that the concentration is low enough for there to be a significant change in the micelle–free chain equilibrium[4]. On the other hand, from the data for the samples at 10 and 2% there is strong evidence both for the integrity of the particles (same particle radii at different dilutions) and for the purity of the polystyrene cores.

Expanding this latter point: in order to account for the discrepancy of the observed PS(D)/PS(H) intensity ratio from the calculated contrast ratio it is tempting to propose a dilution of the PS cores (by CH_2Cl_2, dodecane or ethylene-co-propylene blocks) or of the solvent (CH_2Cl_2 or free chain). However calculation shows that none of the possibilities mentioned, if present in the cores at reasonable concentration, could change the ratio as desired, while any contamination of the solvent would be expected to show up in the dilution experiments. It thus seems more likely that the observed discrepancy is due to ignoring the different polydispersities in the calculation of the particle number densities for the two types of micelles. It is worth considering at this point whether some of the observed effects would be accounted for by non-spherical micelle shapes. It is well known[14] that, depending on the relative lengths of the two blocks in the diblock, solid morphologies corresponding to cylinders or even lamellae may be obtained. The clear minima seen in the scattering functions for all concentrations rule out, however, any major departure from spherity—the polydispersity used to fit the data in *Figure 1* indicates that the aspects ratios should not be greater than about 1:1.2—a barely 'egg-shaped' micelle.

Low Q—the interparticle structure factor

Figures 2 and *3* show contour maps of the full scattering pattern on the area detector for the 10% PS(H) and PS(D) micelles. These contour maps effectively outline areas of high or low intensity. These plots are characterized both by a high degree of order, evidenced by the narrow diffraction rings and by (two different) preferred orientations inferred from the angular modulation of intensity in these rings. In this Q range $P(Q) \rightarrow 1$. The radially averaged $S_f(Q)$ taken from these Figures and shown in *Figure 4* indicate that the underlying structures are the same for the two samples. Three maxima are clearly visible in each case, and we proceed to analyse

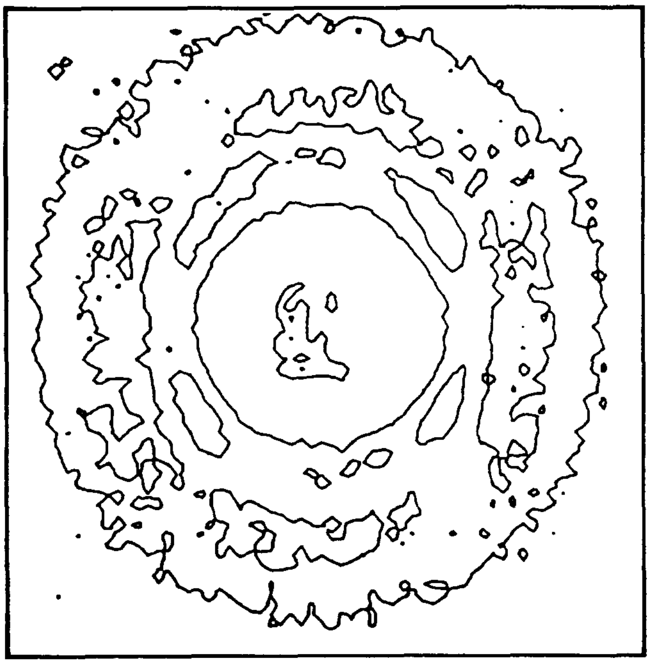

Figure 2 Contour map of the full pattern on the detector for 10% deuterated micelles

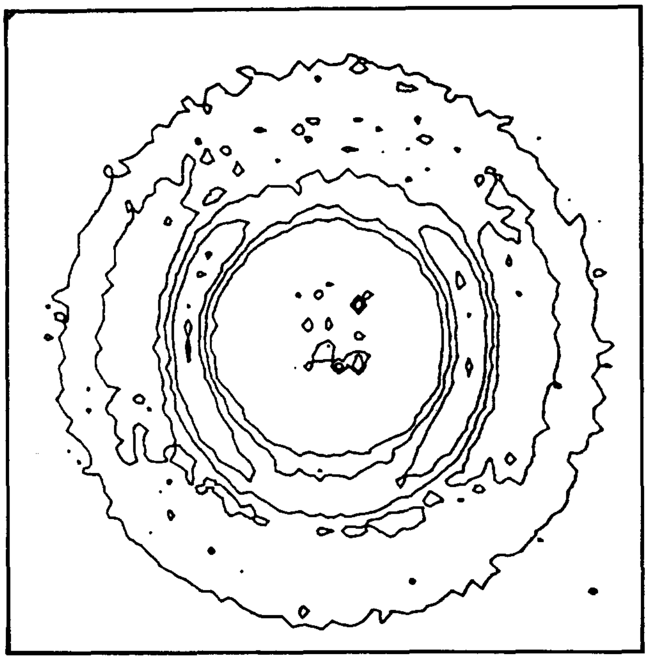

Figure 3 As for *Figure 2*—hydrogenous micelles

their positions in terms of possible crystal structures. We concentrate on cubic structures because of the evident cubic symmetry of the diffraction patterns. (Similar cubic symmetries have been described for polystyrene–polybutadiene micelles^1.)

Table 4 shows the positions of the maxima and the corresponding d-spacings taken from *Figure 4*. For cubic symmetry the interplane spacings are given by

$$d_{hkl}=a_0(h^2+k^2+l^2)^{-\frac{1}{2}} \qquad (6)$$

where h, k, l are the Miller indices and a_0 is the dimension of a unit cell. *Table 5* shows the possible values of $[a_0/d_{hkl}]^2$ for the planes in the three cubic symmetries. Comparison with *Table 4* shows that the positions of the three observed diffraction maxima with their ratio 1:2:3 could not correspond to a face centred cubic structure (3:4:8 = 1:1.33:2.66) but could correspond to either simple cubic or body centred cubic structures (1:2:3 and 2:4:6). The distinction between these two structures cannot be made on the basis of the diffraction maxima alone unless the seventh ring can be observed ($h^2+k^2+l^2=7$ is missing for simple cubic structure but $h^2+k^2+l^2=14$ occurs for the (321) planes in the body centred cubic structure).

However, distinction can be made by comparison with the known concentrations of polymer in the samples. The unit cell dimension a_0 is calculated from equation (6) for the three observed diffraction maxima assuming either simple or body centred cubic structures. From this we can calculate N, the number of lattice points per cm^3. For simple cubic N is just a_0^{-3} but for body centred cubic it is $2a_0^{-3}$ since there are two lattice points per unit cell. If each lattice point is occupied by a sphere radius R as

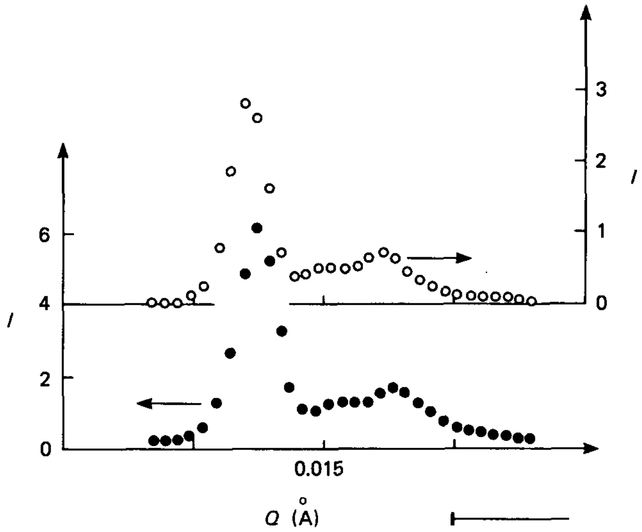

Figure 4 Radially averaged version of *Figure 2* (●) and *Figure 3* (○). The bar shows the limits of the Q range in *Figure 1*. Statistical errors are smaller than the points as drawn

Table 4 Diffraction maxima

Sample	Q_{max} (Å^{-1})	$d(=2\pi/Q_{max})$ (Å)	ratio d_1^2/dn^2
PS(H) micelles	0.0106	592	1
	0.0150	419	2
	0.0184	342	3
PS(D) micelles	0.011	571	1
	0.016	393	2.1
	0.019	329	3

Table 5 Possible values of $(h^2+k^2+l^2)$ for three cubic structures

$(h^2+k^2+l^2)$	Simple cubic	Face centred cubic	Body centred cubic
1	100	–	–
2	110	–	110
3	111	111	–
4	200	200	200
5	210	–	–
6	211	–	211
7	–	–	–
8	220	220	220

determined in *Table 3* and if we assume the density of polystyrene in the cores, ρ, is about 1.0 then the mass of PS cm^{-3} is given by

$$m/\mathrm{cm}^{-3} = \frac{4}{3}\pi R^3 N\rho$$

The mass density from *Table 1* is 0.381×0.1 for a 10% sample. The simple cubic structure gives a very good agreement with this value for both micelles. It is worth noting that the calculated mass cm^{-3} is directly proportional to ρ, the assumed density of the PS cores. Since this is more likely to reduce rather than increase above unity the figures in the last column of *Table 6* are likely to be over- rather than under-estimates.

Figure 5 shows the radially averaged $S(Q)$ for a sample at 2% concentration. The corresponding contour map is isotropic. The preferred orientation has been lost and the order is much less well defined. The average intersphere spacing d can be calculated from the position of the first maximum in $S(Q)$, $Q_{\max}$ using

$$\frac{Q_{\max} d}{2\pi} = 1.18$$

For the PS(D) micelles in *Figure 5* this value of d is 1059 Å. In order to calculate the mass fraction for this less ordered system we 'expand' a close packed (fcc) lattice. In the close packed structure $d = 2R$ and the volume fraction is 0.74.

Thus the volume fraction for the PS(D) micelles would be

$$c = 0.74\left(\frac{2R}{1059}\right)^3 = 0.0078$$

If we assume again that the cores have density of about unity, this value compares very well with the known volume fraction for this sample ($0.02 \times 0.385 = 0.0077$).

Analyses of the preferred orientation in 10% samples

The differences in the contour map in *Figures 2* and *3* are unlikely to arise from effects of deuteration since a previous pair of samples at this concentration (but in n-heptane) both showed the same pattern as in *Figure 3*. A brief investigation indicated no effects of heating the samples to 100°C but dilution to 5% reduced the viscosity dramatically and removed the order. A detailed investigation of the effects of shear, temperature and dilution on the order and orientation are left to the future.

Nevertheless, by comparing *Figures 2* and *3* with analysis used for fibres[15] (one preferred axis) some information on the orientation in fibres can be obtained. For Bragg angle 2θ and angle α between the normal to the diffraction planes and the vertical, the angles, σ, at which maxima in the diffraction ring occur can be calculated. σ is measured in the plane of the diffraction pattern with respect to the vertical. In general there are four spots with

$$\cos\sigma \simeq \cos\alpha/\cos\theta$$

Since in the present results $\theta \ll 1$, $\cos\sigma \simeq \cos\alpha$, i.e. the azimuthal angle of the intense scattering arcs is equal to the angle between the normal to the planes and the sample axis. Two special cases occur.

(a) $\alpha = 90°$—only two spots on the equator XX'.

(b) $\alpha = 0$—only two spots at the poles YY'.

Table 6 Unit cell dimensions and calculated number density of micelles

Sample	Structure	Unit cell (Å)	N (spheres cm^{-3})	Mass (g cm^{-3})
PS(H) micelles	Simple cubic	592	4.8×10^{21}	0.0392
($R = 125$ Å)	b.c.c.	835	3.4×10^{21}	0.0281
PS(D) micelles	Simple cubic	571	5.4×10^{21}	0.0351
($R = 116$ Å)	b.c.c.	805	3.8×10^{21}	0.0250

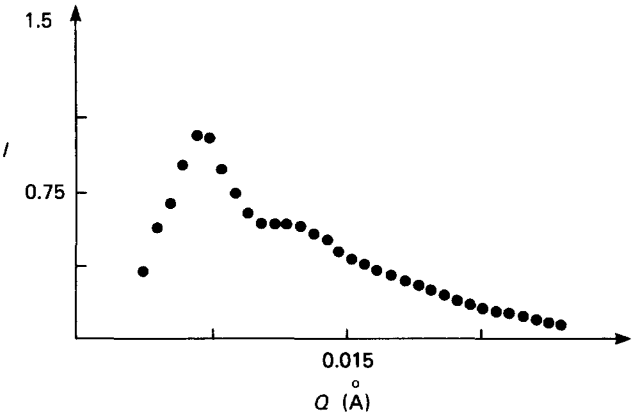

Figure 5 Radially averaged signal for 2% deuterated micelles

The diffraction rings in the maps have been identified as the (100), (110) and (111) planes of a simple cubic lattice. For the PS(H) micelles in *Figure 3* the first ring has only two intense areas on the equator, suggesting that the (100) planes (cube faces) are parallel to vertical. If however the (100) planes are in position to scatter on the equator the (010) planes of a cubic structure should scatter at the poles. One possible explanation is that there are sheets with cubic symmetry 'slipping' with respect to each other in the vertical direction. The 010 order would be lost. The PS(D) micelles in *Figure 2* show four spots in this ring with $\sigma \simeq 45°$, i.e. the cube faces are twisted with respect to the vertical. The structure in the other rings is not yet clear enough for further analysis. Clearly this analysis is by no means complete and is included here only to give an idea of the possibilities for the future—when a systematic investigation of the causes of the preferred orientation is undertaken.

CONCLUSIONS

Diblock copolymers having a polystyrene block with a block of ethylene–propylene copolymer form highly monodisperse micelles in dodecane. The methods used to exchange aromatic hydrogen for deuterium in the polystyrene blocks increase the polydispersity and slightly reduce the dimensions of the polystyrene cores. The micelles retain their integrity and maintain the same dimensions over a concentration range from 1.4 to 10% solids. The 10% samples show both 'crystalline' (simple cubic) packing and a preferred orientation which is apparently dependent on the introduction of the viscous samples into the quartz experimental cells, but does not relax in the time scale of our experiments and is unaffected by heating to 100°C.

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