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SHORT COMMUNICATION

I. W. Hamley
V. Castelletto
J. Fundin
Z. Yang
M. Crothers
D. Attwood
Y. Talmon

Cryo-TEM imaging of block copolymer micelles containing solubilized liquid crystal

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I.W. Hamley (✉) · V. Castelletto
J. Fundin · Z. Yang
Dept of Chemistry, University of Leeds,
Leeds, LS2 9JT, UK
E-mail: I.W.Hamley@chem.leeds.ac.uk

M. Crothers · D. Attwood
School of Pharmacy,
University of Manchester,
Manchester, M13 9PL, UK

Y. Talmon
Department of Chemical Engineering,
Technion-Israel Institute of Technology,
32000 Haifa, Israel

The ability to pattern liquid crystal nanodroplets at the nanoscale is not required for conventional display applications (which do not require a resolution beyond that of visible light) but may find applications in phased array optics. Phased array optics is a method for reconstructing a three-dimensional image on a two-dimensional surface [1]. Optics allows this to be done if the phase and amplitude of the light waves from the virtual image are controlled. An array of switchable light sources 200 nm apart is sufficient to reconstruct any desired light wave pattern [1]. It has been proposed that liquid crystals can be used as switchable birefringent phase shifters. However, as yet the means to arrange the liquid crystal in nanometre-scale arrays has been lacking. Patterning of liquid crystals in micelles or microemulsions is a promising way to achieve this.

Here, we show that close-packed arrays can be fabricated using block copolymer micelles containing solubilized liquid crystal. Films were prepared by quench cooling and the structure was imaged by cryo-transmission electron microscopy (TEM). The solubilization of liquid crystals in block copolymer micelles has been quantified in previous work by our group [2, 3, 4]. In the present work, we use diblock $S_{17}E_{65}$ where S denotes oxyphenylethylene (styrene oxide), E denotes oxyethylene (ethylene oxide) and the subscripts denote the number of repeats. Details of its synthesis and characterization as well as micellar and gel properties can be found elsewhere [5]. The liquid crystal used was a commercial mixture, Licrilite BL002, from Merck, UK. This contains 40–60% 4-*n*-pentyl-4'-cyanobiphenyl, the remainder being other alkyl and oxyalkyl substituents. The mixture is designed to have a wide nematic range $-20\ ^\circ\mathrm{C} < T < 80\ ^\circ\mathrm{C}$.

Measurements of the amount of solubilized liquid crystal were performed via UV/vis spectroscopy. Copolymer solution (0.25 or 0.5 g in 25 cm^3) and BL002 (0.2 g) were stirred together at a fixed temperature (22 or 40 °C). After several hours, three small samples of the solution were removed and filtered to remove excess

BL002. A Perkin Elmer Lambda 2 UV/vis spectrometer was used for the analysis. It was calibrated by recording the absorbances of methanol solutions of BL002 against a solvent blank. The absorbance at 288 nm gave a satisfactory Beer's law plot. The dilutions used in the experiments resulted in solutions containing no more than 0.2 wt% water, and the calibration for methanol solutions was used without correction. Dilution with water was not an option, since that led to dissociation of the micelles and precipitation of the solute. Results from the solubilization analysis are presented in Table 1. It is clear that selective solubilization occurs, this being enhanced at high temperature. The swelling of micelles in the presence of liquid crystal also supports this interpretation. Dynamic light scattering measurements were performed in dilute solution, and the hydrodynamic radius, R_h, obtained via the Stokes-Einstein equation. The result at 50 °C was $R_h = 10$ nm for a 1 wt% solution of the diblock at 50 °C, in good agreement with a prior report [5]. However, in the presence of liquid crystal (54 mg per g of copolymer) this increased to $R_h = 12.1$ nm, remaining as a narrow distribution, consistent with the retention of a spherical micellar shape. This increase in radius represents a 77% increase in volume upon solubilization, although the measurement of R_h is not an accurate way to determine the extent of solubilization, since it is determined largely by the width of the E-block corona.

Having established that the micelles selectively solubilize liquid crystal, the patterning of micelles in thin films was investigated by transmission electron microscopy (TEM), which is a powerful tool for investigation of the nanostructures formed by soft materials [6, 7, 8]. It has been exploited to image micelles formed by conventional surfactants as well as block copolymers. A number of methods have been employed. Freeze etching has been used to investigate polystyrene–polyisoprene in an aliphatic oil [9].In this method, a drop of solution is rapidly frozen by shock-cooling with liquid nitrogen. Solvent is then allowed to evaporate off from a freshly microtomed surface and a replica made of any collapsed micelles on the frozen surface. Booth et al. [10] obtained good images of a polystyrene-polyisoprene diblock in *N*,*N*-dimethylacetamide by allowing a drop of micellar solution to spread and evaporate directly on a carbon TEM substrate. The micelles were stained with osmium tetroxide to enhance contrast for TEM. Eisenberg and co-workers deposited block copolymers from aqueous solution onto carbon-coated TEM grids and then shadowed with a metal alloy [11, 12]. However, cryo-TEM permits examination of vitrified specimens without the need for microtoming, staining or the preparation of replicas, all possible sources of microstructural artefacts. The technique has been used to image micelles formed by several types of block copolymer[13, 14, 15] and is employed here.

Table 1 Solubilization of liquid crystal BL002 in aqueous solutions of copolymer $S_{17}E_{65}$[a]

Copolymer g dm^{-3}	T °C	BL002 solubilized mg (g of copolymer)$^{-1}$	BL002 solubilized mg (g of hydrophobe)$^{-1}$
10	22	52	126
10	40	54	132
20	22	62	151
20	40	62	151

[a]Estimated uncertainty in mass BL002, ±10%

Vitrified specimens for cryo-TEM were prepared in a controlled environment vitrification system (CEVS), where temperature and relative humidity are controlled. A drop of about 3 μL is placed on a copper grid covered with a perforated carbon film; the grid is held by tweezers attached to a spring-loaded plunging device. Most of the liquid is blotted away, leaving behind thin (ideally 100–200 nm thick) liquid films supported on the edges of the 3–10 μm holes. Upon activation of the plunging mechanism, the grid is propelled through an opening trap door into a reservoir of liquid ethane at its freezing point, and thus the liquid is vitrified. The specimens were stored under liquid nitrogen, and examined in a Philips CM120 cryo-transmission electron microscope at about −180 °C, held in an Oxford CT-3500 cooling holder. The specimens were imaged at minimal electron dose condition to minimize beam damage. Images were recorded digitally by a Gatan MultiScan 791 cooled-CCD camera system. More details about cryo-TEM and digital imaging cryo-TEM can be found elsewhere [16, 17].

Small-angle x-ray scattering was performed to confirm the bulk structure of concentrated solutions of the diblock, termed "gels" [18]. Above a critical concentration/temperature, which can be determined by mobility experiments or rheometry, the copolymer forms a cubic-packed phase of spherical micelles. Only a single-order Bragg peak was detected from the gels examined. Therefore, it proved necessary to shear the gel to confirm the structure from the azimuthal location of the Bragg reflections in the oriented crystal. Experiments were carried out on beamline 2.1 of the synchrotron radiation source (SRS) at the Daresbury Laboratory, Warrington, UK. The beamline is configured for SAXS experiments using monochromatic radiation of wavelength $\lambda = 1.5$ Å. Scattered photons were collected on a multiwire gas-filled area detector. A scattering pattern from a specimen of wet collagen (rat-tail tendon) was used for calibration of the q scale ($q = |\mathbf{q}| = 4\pi\sin\theta/\lambda$, where the scattering angle is 2θ). The SAXS data were corrected to allow for sample transmission and detector response. Gels were subjected to steady shear in a polycarbonate Couette cell at different shear rates. Diffraction patterns were recorded in the radial direction (i.e. through the centre of the Couette cell), which gives diffraction patterns in the (**v**,**e**) plane where **v** is the shear direction and **e** the

neutral direction. The temperature ($T = 25$ °C) was controlled via a water bath.

Cryo-TEM images of micelles without and with liquid crystal are shown in Fig. 1 and Fig. 2, respectively. A close-packed structure of micelles is apparent in both cases. The ordering extends over several hundred nanometres within quite well-defined grains. Larger dark particles are frost (hexagonal ice) occasionally deposited on the specimen during preparation or transfer. On the left-hand side of Fig. 2 we see a single layer of micelles. Several other grains to the right comprise two or three layers of micelles. A more ordered sample is seen in the composite image of Fig. 3, showing another micrograph of the LC-containing micelles prepared from the solution with an initial concentration of 3 wt% copolymer (similar to Fig. 2). In the upper left, the panel shows well-ordered micelles. The next panel to the right is the Fourier transform (FFT) of that area, showing clearly several orders of "diffraction" spots, the six-fold symmetry and noise. The next panel (lower left) is the filtered FFT and the last one is the inverse FFT, that is the filtered image of the first panel. In this image of well-ordered domains the darker circular objects each correspond to superposition of two micelles in layers 1 and 3. The lighter circular objects are probably the micelles in the second layer. In the case of the TEM specimens the initial bulk concentration was 3 wt% . In the areas shown the local concentration is, of course, much higher, a result of "crowding" during specimen preparation. We have seen similar effects in surfactant micelles [19] and more recently in diblock copolymer micelles [20]. For ultimate applications in photonics or phased array optics, the long-range ordering would need to be improved. Techniques such as thermal annealing or flow alignment by controlled dip coating (rather than spin coating) might be applicable.

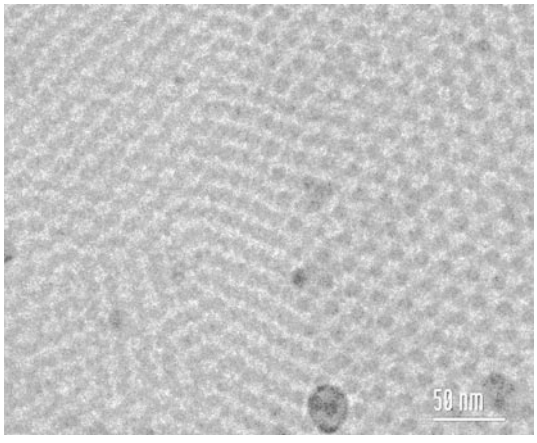

Fig. 1 TEM image of a vitrified film of a 3% aqueous solution of $S_{17}E_{65}$

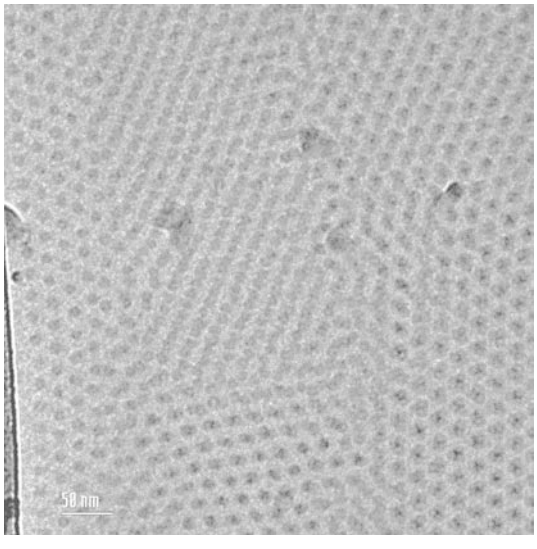

Fig. 2 Cryo-TEM image obtained from an initially 3% aqueous solution of $S_{17}E_{65}$ containing solubilized nematic liquid crystal mixture

The TEM images indicate a close-packed structure, i.e. the concentration of copolymers in the films is high. Small-angle x-ray scattering was used to identify the structure of micellar structures in concentrated bulk solutions. Samples were subjected to shear to facilitate phase identification [21], from oriented diffraction patterns. A representative SAXS pattern from a 30 wt% gel

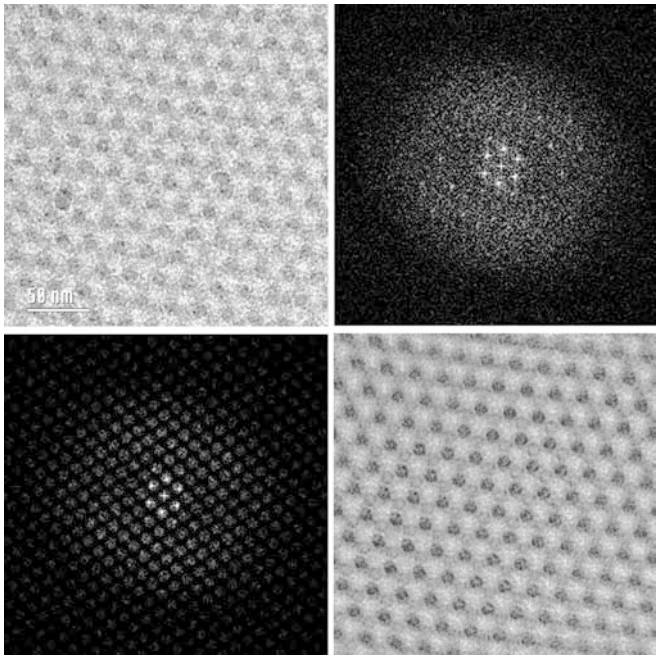

Fig. 3 Vitrified LC-containing micellar film prepared from a 3 wt% solution (*upper left*) and the Fourier transform (FFT) of that area (*upper right*); the filtered FFT (*lower left*), and (*lower right*) the inverse FFT, i.e. the filtered image of the first panel

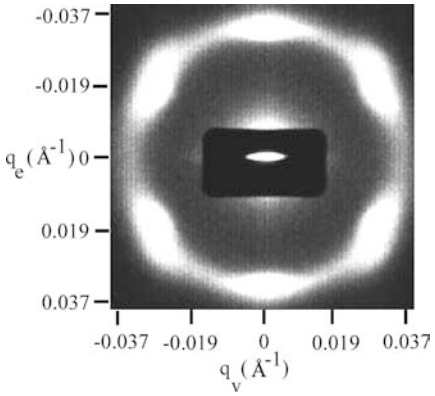

Fig. 4 SAXS pattern obtained for a 30 wt% gel of $S_{17}E_{65}$ under shear at a shear rate $\dot{\gamma} = 200\ s^{-1}$. The shear direction is horizontal

is shown in Fig. 4. This consists of a hexagon of six 111 reflections. This type of diffraction pattern has been discussed in detail elsewhere [22]. It corresponds to a face-centred cubic (fcc) gel under shear in which the predominant flow mechanism is that of hexagonal close-packed planes in the shear plane. From the position of the reflections, the lattice parameter was determined to be $a = (30.2 \pm 0.4)$ nm, from which a micellar radius $r_m = (10.7 \pm 1.3)$ nm can be calculated. This is in good agreement with the value obtained from the TEM images and the thermodynamic radius obtained from previous light scattering experiments ($r_h = 10.4$ nm at $T = 25$ °C). The confirmation of a close-packed structure of micelles in the bulk in concentrated solution suggests that the close-packed two-dimensional structure may be in equilibrium (being trapped by vitrification).

Finally, we note that for applications in photonics, it would also be necessary to switch the orientation of the solubilized liquid crystal. Attempts have been made to investigate the orientational order of liquid crystal solubilized in the micellar core. A selectively deuterated sample of 4-*n*-(d_{11})pentyl-4'-cyanobiphenyl was prepared (at Manchester) for the purpose of undertaking deuterium NMR experiments, in particular measurements of quadrupolar spittings. However, the concentration of the solubilized LC within the block copolymer micelles was found to be below the limit of detection for studies of orientation to be performed.

In summary, we have shown that nanoscale close-packed arrays of liquid crystal-containing entities can be prepared by solubilization in block copolymer micelles. Cryo-TEM provides a high resolution technique for imaging the micelles.

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