

## SCANNING ELECTRON MICROSCOPY OF COPOLYMER MICELLES

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**Abstract**—Particles isolated from a micellar solution of a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-hexane were studied by scanning electron microscopy. Specimens were obtained by evaporating droplets of solution on a mica or carbon substrate and then coated with a film of W/Ta. The use of a scanning instrument with a field-emission source enabled the micellar particles to be clearly resolved and provided useful topographical information.

### INTRODUCTION

Transmission electron microscopy has been extensively used in our laboratory to investigate the shape and size distribution of micelles formed by block copolymers in both organic and aqueous media [1, 2]. The resolution offered by TEM was sufficient to enable distinct images to be formed of the individual micellar particles.

In most cases specimens for study were prepared by allowing the micellar solution to spread and evaporate on a carbon substrate. As the solvent evaporated, the micelles collapsed to form solid particles having a density similar to the bulk density. By selective staining, it was possible to pick out the core and shell components of the micelles. In some cases, there was evidence (from shadowing with a heavy metal) that the particles flattened out somewhat during the drying process. An alternative specimen preparation procedure used in the study of micelles by transmission electron microscopy was freeze-etching [3].

There appear to have been no reported studies of the use of scanning electron microscopy in the study of micellar particles, presumably because until recently the resolution available was insufficient to probe the salient structural features. However, instrumental developments in this field including the use of field-emission sources has significantly improved the range of the technique. The improved resolution, together with the ability of the technique to provide topographical information not available from transmission studies, makes scanning electron microscopy an attractive method for studying micellar particles.

In this paper we report a scanning electron microscopy study of micelles formed by a polystyrene-*block*-poly(ethylene/propylene) copolymer in *n*-hexane which is a selectively bad solvent for polystyrene.

### EXPERIMENTAL PROCEDURES

#### *Instrument and operating conditions*

The instrument used was an Hitachi S400 field emission scanning electron microscope.

In scanning electron microscopy, a fine primary electron beam is rastered over the specimen area and penetrates some way into it. The interaction volume at the point of penetration depends on the accelerating voltage, the beam diameter and the density of the material. Secondary electrons which leave the surface at the point of contact of the primary beam (designated SE 1) carry the true topographical information. However, higher energy back-scattered electrons (designated BSE) emerging from within the interaction volume as well as secondary electrons (designated SE 2) generated by the latter are also collected by the scintillation detector and can easily swamp the SE 1 signal. The BSE and SE 2 signals cannot be separated from the SE 1 signal, but they can be suppressed by:

- (i) choosing a suitable specimen coating material [5]; and
- (ii) reducing the accelerating voltage until the interaction volume is of the order of the primary beam (probe) diameter [6].

There is some question as to whether a coating of W/Ta or Pt has advantages over for example chromium suggested by Hermann *et al.* [8], but it is generally accepted that very fine grain and very thin (*ca* 1–3 nm) homogeneous coatings are necessary.

In a conventional scanning electron microscope using thermionic emission, the probe size (which is approximately the attainable resolution) at low voltage is *ca* 20 nm. In a scanning electron microscope with a field emission source, the probe size at 5 kV is not only much smaller (1.5 nm) but the source is *ca* 1000 times brighter. This results in a greater proportion of SE 1 signal at the detector and a better signal-to-noise ratio. The smaller probe diameter is feasible because the field-emission source is highly monochromatic,  $\Delta V = 0.2$  eV. The highly monochromatic source also serves to reduce chromatic aberrations in the objective lens which can become important at low kV.

#### *Material*

The block copolymer was obtained from Shell Research Ltd. The copolymer had been prepared by first synthesizing a polystyrene-*block*-polyisoprene copolymer by sequential

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anionic polymerization and then hydrogenating the polyisoprene block. It was found by u.v. spectroscopy that the copolymer contained  $38.5 \pm 3.0\%$  by weight polystyrene. The number-average molar mass of the copolymer was found by membrane osmometry to be  $97,000 \text{ g mol}^{-1}$  and the ratio of the weight-average to number-average molar mass ( $\bar{M}_w/\bar{M}_n$ ) was found by gel permeation chromatography to be 1.14; these determinations were carried out in toluene which is a good solvent for both polymer blocks and does not lead to micellization of the system.

#### *Preparation of specimens for TEM*

Droplets of a 0.001% by weight micellar solution of the block copolymer in n-hexane (BDH Analar) were pipetted onto:

- (a) a freshly cleaved mica surface; and
- (b) a carbon substrate supported by a 200 mesh copper grid.

The solvent was allowed to evaporate, the process being aided in its final stages by air-drying. Specimens were then transferred onto the sample stage of a Cressington CFE 50 Freeze-fracture Instrument equipped with an electron-beam evaporator and a thickness monitor facility. A thin layer of tungsten/tantalum alloy [4] was deposited onto the specimen (which was in a vacuum chamber at  $10^{-7} \text{ } \tau$ ) at an angle of  $20^\circ$  to the surface whilst the specimen was rotating at 100 rpm.

#### *Electron microscopy*

The metal-coated specimens were individually attached to 15 mm aluminium stubs using a silver drag and then transferred to the Hitachi S400 field emission scanning electron microscope. Micrographs were then taken at magnifications of 25, 50 and 100 k and accelerating voltages of 5, 10 and 15 kV. The working distance was set at 5 mm, the spot size at 10 and the angle of tilt  $10^\circ$ .

## RESULTS AND DISCUSSION

Micellar particles which had been isolated from solution on a mica surface were generally found in small clusters as shown by the electron micrographs in Figs 1 and 2, which were obtained at accelerating voltages of 15 and 5 kV respectively. The results suggest the micelles were spherical in shape and had a fairly narrow size-distribution. The dark stain emanating from the particle just left of centre in Fig. 1 is the result of beam damage. Reduction of the accelerating voltage from 15 to 5 kV resulted in no significant loss of resolution, but was beneficial in reducing beam damage.

The reduction in beam penetration which accompanied the lower voltage enabled more surface information to be obtained. A particular feature of note is the "wash mark" around the aggregates. This was probably mainly due to the wetting of the mica surface by some of the poly(ethylene/propylene) blocks forming the flexible fringe of the micelles. The region could also contain a very small proportion of unassociated chains.

The spherical shape of the micelles became slightly distorted on drying but their globular nature was basically retained because of the glassy polystyrene core. The diameters of the globular structures were determined from electron micrographs taken at higher magnification as shown in Fig. 3. The number-average diameter of the globular structures in the horizontal plane was 45 nm with the large majority of the particles having a diameter in the range 40–50 nm; a small proportion of particles were to be found in the

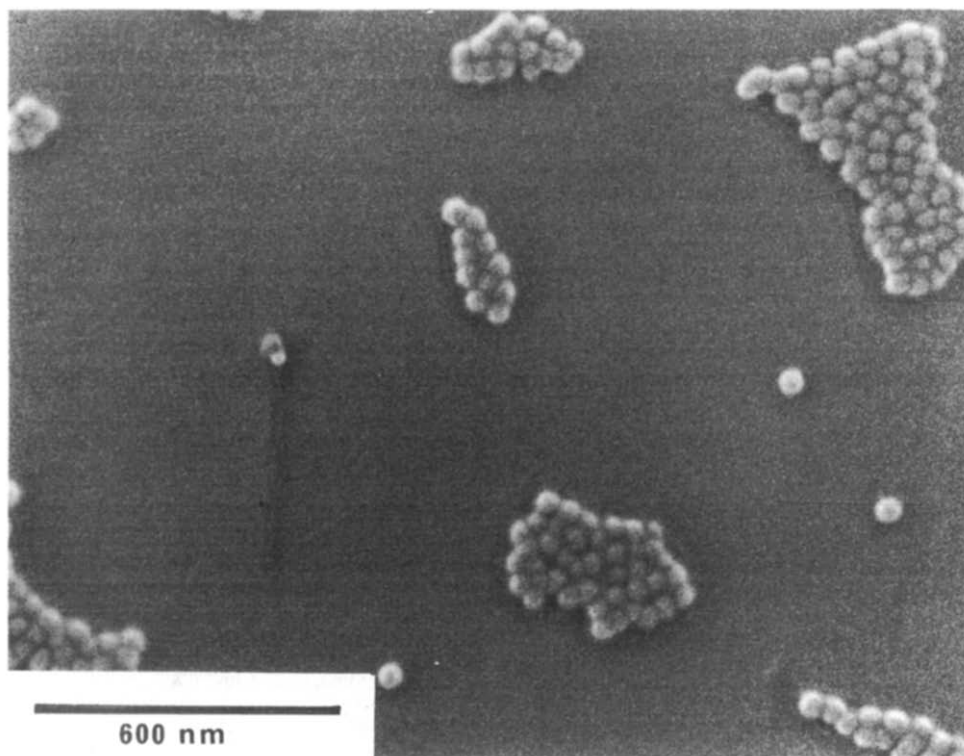


Fig. 1. Electron micrograph of micellar particles of a polystyrene *block*-poly(ethylene/propylene) copolymer on a mica surface (accelerating voltage was 15 kV).

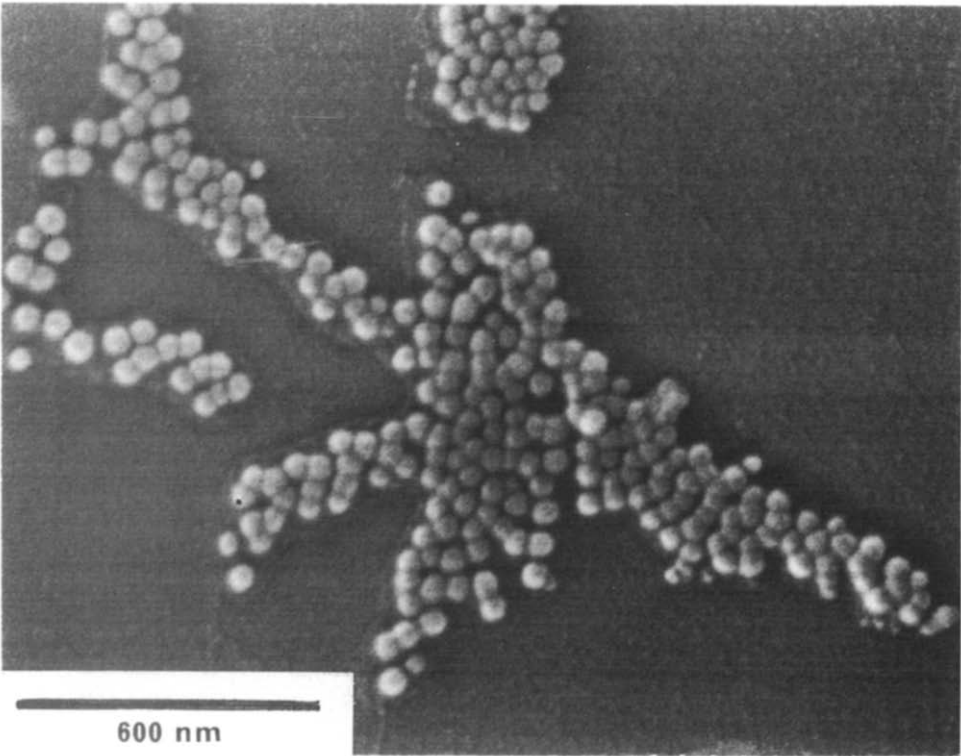


Fig. 2. Electron micrograph of the micellar particles on a mica surface (accelerating voltage was 5 kV).

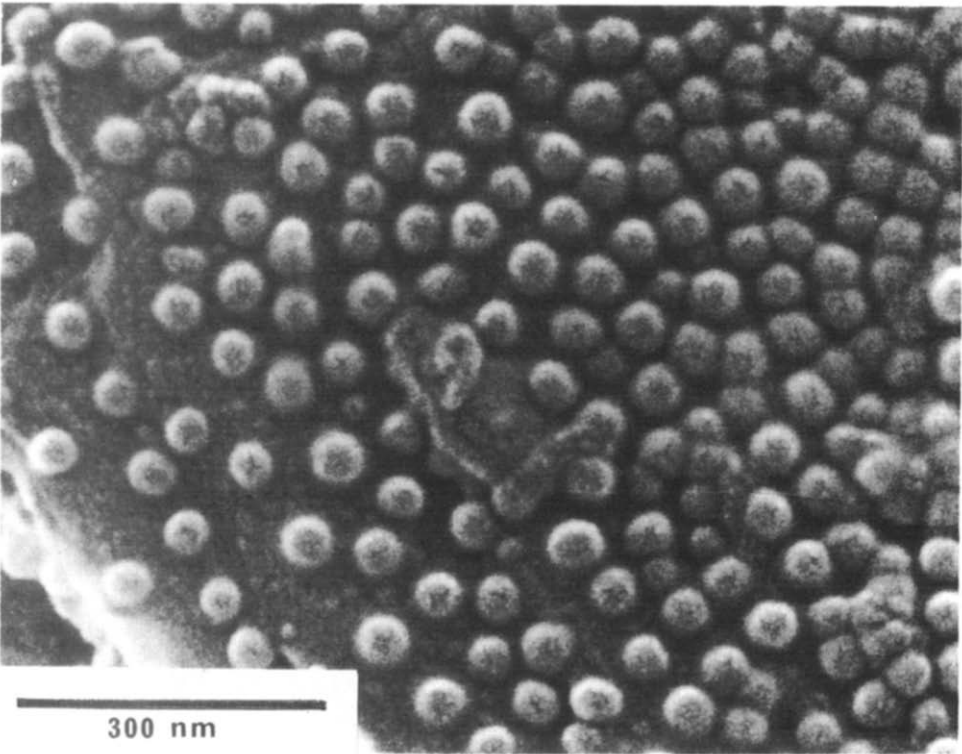


Fig. 3. Electron micrograph of the micellar particles at high magnification (accelerating voltage was 5 kV).

range 10–20 nm. Figure 3 reveals the grain size of the W/Ta coating to be *ca* 1 nm.

When the droplets of solution were evaporated on a carbon substrate, the micellar particles were found to have a similar size distribution to those observed on mica, but there was a much greater tendency for clustering into large arrays.

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