A study of micelle formation by a polystyrene–poly(ethylene/propylene) block copolymer in a base lubricating oil

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Over the years numerous studies have been made of micelle formation by amphiphiles in aqueous media[1]. More recent studies have shown that when a block copolymer is dissolved in a hydrocarbon solvent that is selectively bad for one of the polymer components, the copolymer molecules can also associate reversibly to form large stable aggregates[2–5]. Since the process appears to be cooperative in nature, leading in some cases to particles with a very narrow size distribution[4], the concept of micellization may be usefully extended to include such block copolymer systems.

Here we report an investigation of micelles formed from a polystyrene–poly(ethylene/propylene) two-block copolymer in a lubricating oil (base oil stock HVI60) derived from a light Iranian crude oil. The oil is a selectively bad solvent for polystyrene, and so polystyrene blocks form the cores of the micelles. In order to study the size distribution of the micelles, we have developed a technique for isolating micellar particles from the oil so that they may be examined by electron microscopy; the technique is a modification of an earlier procedure of ours used with more volatile solvents[4]. We also report an investigation of the hydrodynamic size of the micelles in solution by laser light scattering photon correlation spectroscopy (p.c.s.).

Experimental and Results

Material The block copolymer was provided by Shell Research Ltd. It had been prepared by hydrogenating the polyisoprene block of a polystyrene–polyisoprene block copolymer. The copolymer contained 40% by weight polystyrene. Its weight-average molecular weight $\bar{M}_w = 1.06 \times 10^5$ g mol^{-1} and the ratio of its weight-average to number-average molecular weight $\bar{M}_w/\bar{M}_n = 1.1$.

Electron Microscopy. Specimens were prepared in two slightly different ways using a spreading-drop technique[4].

(i) A drop of the solution was allowed to spread and form a thin film on a clean surface of water. Sections of film were picked up on a carbon substrate supported by a copper grid. The specimen was then put into a bell jar and the system evacuated. After approximately 30 min the specimen was shadowed with C/Pt.

(ii) The solution was very thinly painted onto a freshly cleaved mica surface. The specimen was put into a bell jar and the system evacuated. After approximately 30 min the specimen was thinly coated with C/Pt (or C). The mica was then dipped carefully into water so that the micellar particles mounted on C/Pt became detached. Finally the specimen was picked up from the water surface on a carbon substrate supported by a copper grid and shadowed with C/Pt.

The two methods outlined above gave similar results, but (ii) was preferred because the thinning process was found to be more easily controlled on mica. The micelles were able to remain intact during the process because their cores were only slightly swollen by the oil.

A typical electron micrograph obtained using an AEI 6G electron microscope operating at 80 kV is shown in *Figure 1.* During specimen preparation the micelles collapsed to form particles with a density similar to that of bulk polymer. From the shadowing, it was deduced that, on isolation, the micelles became approximately disc-shaped because they tended to flow and wet the substrate surface. From the micrographs we calculated that for the micelles $\bar{M}_n = 1.2 \times 10^7$ g mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.05$. Measurements from 500 particles were used in this calculation.

P. c. s. experiments. These were carried out as described previously[5]. Measurements were made at four temperatures in the range 50°–120°C and at various concentrations between 0.5×10^{-3} g cm^{-3} and 6.0×10^{-3} g cm^{-3}. The z-average translational diffusion coefficients obtained by extrapolating the results for each temperature to infinite dilution are given in *Table 1.* Assuming the micelles were spherical in shape, the z-average reciprocal hydrodynamic radii $(\overline{R_D^{-1}})_z$, also listed, were calculated from the $\bar{D}_z$ values via the Stokes–Einstein relation:

$$D = kT/6\pi\eta R_D$$

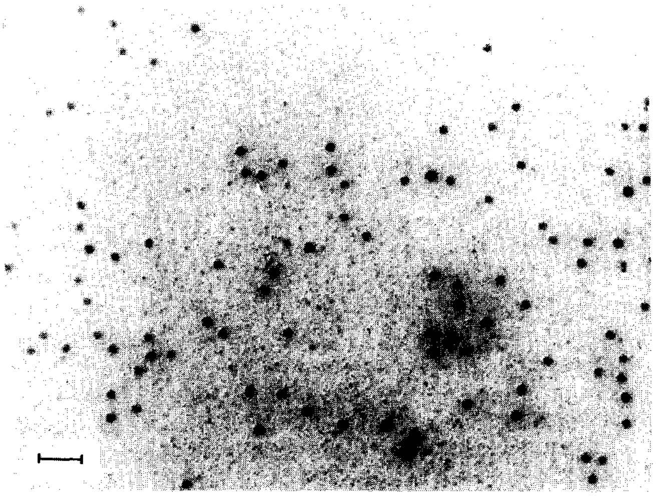

Figure 1 Electron micrograph of collapsed micelles isolated from a micellar solution of the polystyrene–poly(ethylene/propylene) block copolymer in a base lubricating oil. The scale mark is 200 nm

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Table 1 Effect of temperature on the translational diffusion coefficient and hydrodynamic radius of the micelles

T/°C	$(\bar{D}_0)_z/10^{-8}$ cm^2 s^{-1}	$(\bar{R}^{-1})_z^{-1}$/nm
50	0.17	74
75	0.38	79
100	0.68	89
120	1.00	96

where η is the viscosity of the oil and k the Boltzmann constant. The results suggest that as the temperature is raised, the micelles swell somewhat due to an increase in the solvent power of the oil.

Other Studies. Conventional light scattering measurements made over the temperature range 20°–80°C confirmed the presence of compact globular micelles. They also indicated that, up to 80°C, the micelle/free-chain equilibrium was overwhelmingly in favour of the micelles. Light-ultramicroscopy studies enabled the movement of the micelles to be observed directly and supported the electron microscopy result that the size distribution of the micelles was narrow.

A full account of the work recorded in this communication together with a study of the effect of micelles on solution viscosity will be presented later.

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Network changes in natural rubber vulcanizate subjected to different physical tests

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Introduction

During service, rubber products are exposed to tension, compression, cyclic deformation and a variety of other factors leading to, in many cases, a rise in temperature inside the product. It is very likely, therefore, that the rubber vulcanizate may undergo structural changes due to mechanical and thermal effects during use. Cunneen and Russell[1] reported changes in chemical structure of natural rubber tyre tread vulcanizates during service. The changes include a marked reduction in the concentration of polysulphidic crosslinks and an increase in the amount of monosulphidic crosslinks and main-chain modifications. Howard and Wilder[2] observed that tyre treads undergo structural changes, i.e. increase of crosslink density during service. The extent of increase of crosslinking depends on the curative system and nature of the base polymer. Podkolzina, Petrova and Fedorova[7] studied the structural changes in *cis*-1,4-polyisoprene vulcanizate during heat ageing and fatigue at elevated temperatures. They showed that the structural changes in the vulcanizate network in heat ageing and fatigue are similar. With fatigue, however, there was a marked increase in the degree of modification of the polymer chains by cyclically-bound sulphur and by residues of combined sulphur. This is stated to be one of the causes of the reduced vulcanizate life under dynamic load conditions.

In the present work, we have studied changes in the network structure of both gum and filled natural rubber vulcanizate subjected to tensile, compression, Goodrich heat build-up, de Mattia flexing, and other tests, in the hope that these tests singly or in combination, will simulate at least a few service conditions. Knowledge of such structural changes will help in predicting the behaviour of rubber during prolonged use. We have chosen a conventional vulcanization system.

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Experimental

Formulation of the mixes is shown in *Table 1*. Samples for tensile and de Mattia tests were cured at optimum cure times, while thicker samples (for Goodrich flexometer, compression set and abrasion tests) were overcured in order to prevent undercure in the core of the sample. Different curing times are summarized in *Table 2*. The physical tests were carried out according to ASTM methods[3].

Original vulcanizate samples from before and after completion of the physical tests were used for chemical analyses. For tensile (2.0–2.5 mm thickness), abrasion and flexing tests (1.0 mm thickness), samples for analyses were collected from the fracture surfaces, while for heat build-up and compression set tests, middle sections (1.0 mm thickness) were used. Methods of estimation of chemical crosslink density, $[2M_{c,chem}]^{-1}$, of gum and filled natural rubber vulcanizate have been described earlier[4,5]. The method of determination of network combined sulphur (S_c) is as recently described[6].

Table 1 Composition of the mixes

Ingredients	Conventional system Gum	Conventional system Filled
Natural rubber[a]	100	100
Zinc oxide	5	5
Stearic acid	2	2
MOR[b]	0.5	0.5
Sulphur	2.5	2.5
HAF-black	0	40
Process oil	0	5

[a] Crumb grade, obtained from the Rubber Research Institute of India, Kerala, India
[b] Benzothiazyl-2-sulphene morpholide