polymer communications

# The existence of a tetragonal structure in block copolymers

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The morphology of AB and BAB block copolymers consisting of one amorphous block (A) and liquid crystalline blocks (B) has been investigated using TEM, low angle electron diffraction and small angle X-ray diffraction. All samples of poly[styrene-*block*-2-(3-cholsteryl-oxycarbonyloxy)ethyl methacrylate] (PS-PChEMA) with a volume fraction $\Phi_{PS}$ between 0.3 and 0.4 show a morphology consisting of PS rods in a PChEMA matrix. The rods are organized in a tetragonal lattice rather than the expected hexagonal structure.

**(Keywords: morphology; block copolymers; tetragonal structure)**

## *Introduction*

Block copolymers are an interesting and already well studied variation of polymers. In this class of polymers it is possible to combine the properties of two completely different polymers without macroscopic phase separation occurring. Due to the chemical link between the incompatible polymers, the phase separation is limited to a microscopic scale, and is dependent on the volume fraction of the different blocks. Several different morphologies have been predicted and observed. These morphologies are dependent on the volume fraction of one block: spheres in a cubic lattice and rods in a hexagonal lattice, in each case embedded in the matrix of the other component of the block copolymers or lamellae of both[1]. Recently, ordered bicontinuous morphologies were also found[2–4]. These double-diamond structures, space group $P_{n3m}$ (OBDD), were observed for volume fractions in between the lamellar and the rod-like hexagonal phase. So, the scheme for the morphologies of the block copolymers is as described by Bates and Frederickson[1], a sequence of spherical, rod-like hexagonal, double-diamond and lamellar phases.

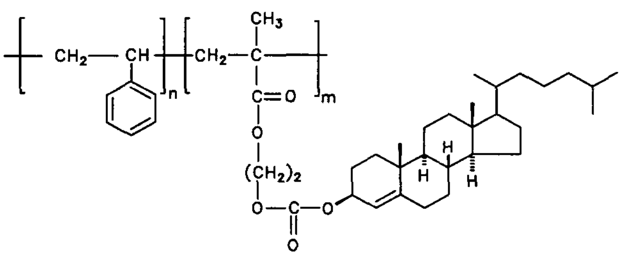
If one of the blocks is a liquid crystalline (LC) side group polymer, two different scales of phase separation might be obtained. It is possible to study the influence of the morphology of the block copolymer on the phase structure of the LC block[5,6]. Initial investigations on the AB type copolymers poly[styrene-*block*-2-(3-cholsteryl-oxycarbonyloxy)ethyl methacrylate] (PS-PChEMA) and poly[butadiene-*block*-2-(3-cholsteryl-oxycarbonyloxy)ethyl methacrylate] (PB-PChEMA) suggested an influence of the amorphous block on the phase structure of the LC block which was dependent on the type of monomer in the A block for a lamellar structure[7]. More systematic investigations are reported here. Di- (AB) and triblock (BAB) copolymers of PS-PChEMA and PChEMA-PS-PChEMA (*Figure 1*) have been studied to determine the influence of the different block lengths and thus the change in the morphology, on the phase behaviour of the LC phase[5].

## *Experimental*

The block copolymers were synthesized as described previously[6,7]. Samples of the polymers were prepared by casting films (~1 mm thick) from dilute solutions of the polymers in toluene, over a period of ~10 days at 25°C and then annealing them at 130°C for 24 h under vacuum. The samples were cut using a diamond knife at room temperature and the thin sections (~10 nm thick) were transferred onto copper grids. In order to obtain sufficient contrast for TEM and low angle electron diffraction studies[8–10], the styrene parts of the samples were stained with $RuO_4$ vapour at 25°C for ~30 min[11]. For the TEM studies and the low angle electron diffraction experiments a Philips EM 301 was used. The diffraction experiments were performed as described elsewhere[9,10]. X-ray studies were carried out using an Eliott GX 21 with a copper target combined with a Rigaku Denki small angle film camera.

## *Results and discussion*

The investigated block copolymers were characterized as described in references 5 and 6 using g.p.c., d.s.c. and polarization microscopy. All the samples reported here show two glass transition temperatures (*Table 1*), indicating that phase separation occurred. The phase separation of the two blocks could be confirmed by small angle X-ray diffraction studies[5]. Also, all samples show a smectic A



PS-block PChEMA-block

**Figure 1** Structure of the block copolymers

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**Table 1** Phase transition temperatures, phase structures and expected morphologies of the samples

| Sample | $\Phi_{PS}$ | Phase behaviour (°C) | Expected morphology |
|---|---|---|---|
| PS | 1.00 | g 102 i | |
| PS-PChEMA | | | |
| 59 | 0.37 | g 103 g 126 $S_A$ 202 i | PS rods |
| PChEMA-PS-PChEMA | | | |
| DB 4 | 0.29 | g 101 g 117 $S_A$ 188 i | PS rods |
| DB 7 | 0.33 | g 102 g 118 $S_A$ 193 i | PS rods |
| DB 5 | 0.35 | g 98 g 118 $S_A$ 180 i | PS rods |
| PChEMA | 0.00 | g 126 $S_A$ 213 i | |

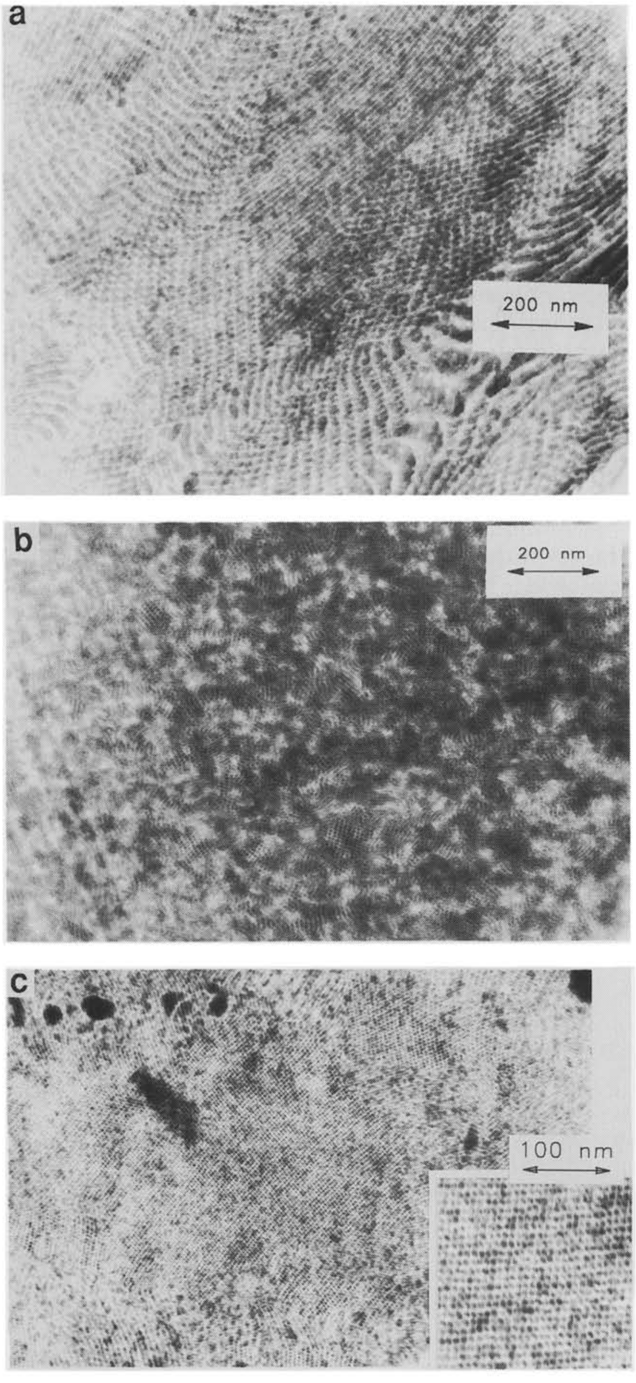

**Figure 2** Transmission electron micrographs of a rod-like morphology of: (a) sample 59; (b) sample DB 4; (c) sample DB 7

phase in the WAXD pattern. The phase transition temperatures, phase structures and expected morphologies are listed in *Table 1*[5]. A direct investigation of the morphology of the phase-separated block copolymers was possible by TEM using sections of the block copolymers. *Figure 2* shows representative transmission electron micrographs of the observed morphology. As expected, PS rods are formed, embedded in a matrix of the LC block. It was not possible to obtain completely uniform areas of orientation, but this was an advantage since views in the rod direction as well as perpendicular to the rods could be recorded simultaneously. Top views of the rods are clearly visible. There is a hexagonal arrangement of the rods only in small areas, possibly because of deformation during the cutting process. Larger areas show a tetragonal arrangement of the rods. This is observed for both the diblock and triblock copolymers.

The tetragonal structure is quite new and unexpected, therefore low angle electron diffraction studies were carried out according to the procedure described by van Mahl and Weitsch[8], Bassett and Keller[9] and Kämpf *et al.*[10]. Compared with X-ray diffraction techniques, the advantages of their method are: the resolution limit is very much smaller (~4000 Å) for low angle electron diffraction[14]; and the exposure time is smaller than in the case of X-ray diffraction. Also, due to the point focus of the electron beam, two-dimensional resolution is immediately obtained without slit desmearing approximation procedures, etc. Finally, the area with a uniform orientation needed for a diffraction experiment can be much smaller (25 $\mu m^2$) compared to that required for small angle X-ray diffraction (~ 1 $mm^2$). Therefore it was possible to select areas with a uniform orientation in the transmission mode prior to switching to the diffraction mode. A disadvantage of low angle electron diffraction is the difficulty in finding a suitable calibration standard. In this case, no suitable standard was available so that the diffraction patterns obtained have only qualitative meaning. *Figure 3* shows the low angle electron diffraction pattern obtained from the sample DB 7. This was the only sample where larger areas of a uniform orientation of the rods were found. The diffraction pattern can be

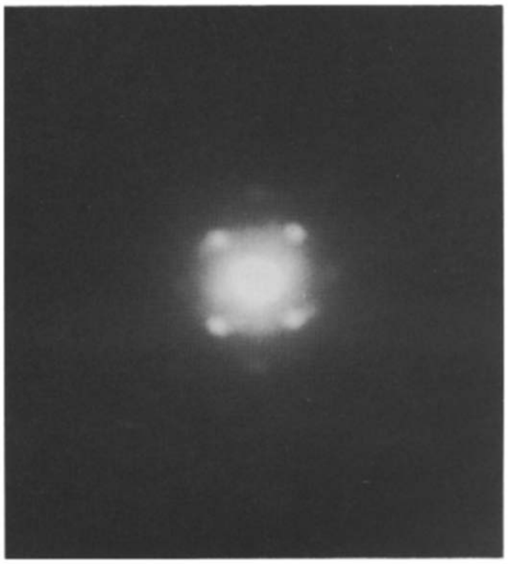

**Figure 3** Low angle electron diffraction pattern of sample DB 7, tetragonal morphology

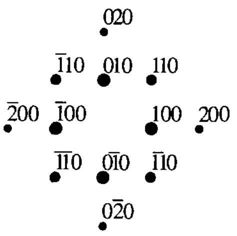

**Figure 4** Schematic diffraction diagram of a tetragonal lattice, [001] plane

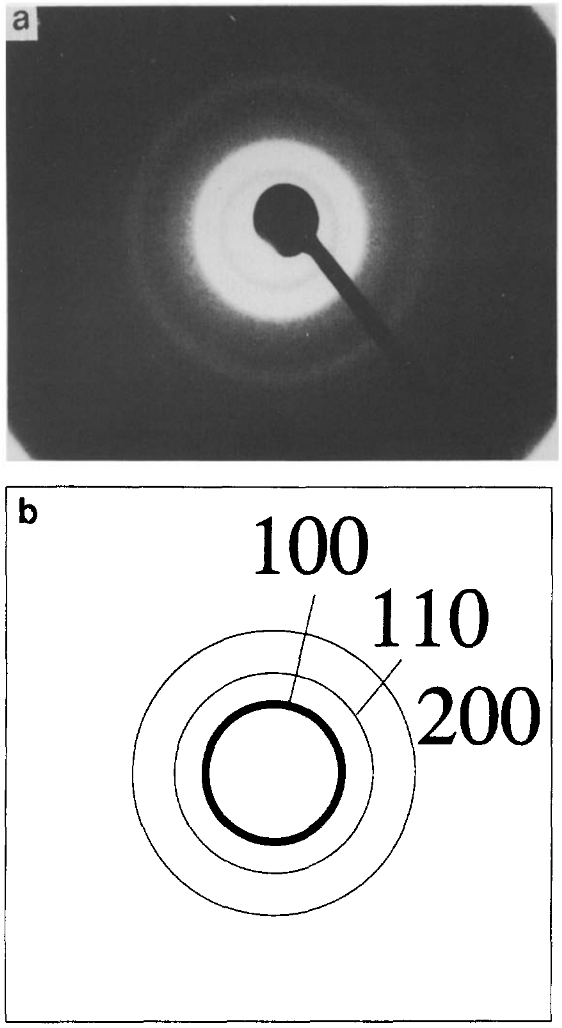

**Figure 5** Small angle X-ray diffraction pattern of sample DB 7: (a) photograph; (b) schematic diagram

indexed as that of a tetragonal lattice looking at the [001] plane, as shown in *Figure 4*. The diameter of the dots in *Figure 4* is proportional to the expected intensity of the diffraction pattern. Due to the uniformity of the area chosen, it was possible to obtain not only the 100 and 110 reflection in *Figure 3* but also very weak 200 reflections are visible. There was now the possibility that a hexagonal lattice had been deformed due to the sectioning process to a tetragonal lattice or that a hexagonal lattice was seen at a certain angle and appeared to be tetragonal. Since the low angle electron diffraction represents the Fourier transform of the observed image, small angle X-ray diffraction studies were carried out on bulk samples to confirm the existence of the tetragonal morphology. *Figure 5* shows the small angle X-ray diffraction pattern of sample DB 7. The reflections are not extremely sharp and strong because the phase boundaries owing to the interfacial region are not very well defined. However, reflections are observed with a *d*-spacing of 212, 152 and 106 Å, and these can be indexed as the 100, 110 and 200 reflections of a tetragonal lattice (*Figure 5b*).

## *Conclusions*

TEM imaging and low angle electron diffraction reveal a tetragonal arrangement of PS rods in the block copolymers investigated in this study rather than the expected hexagonal arrangement. The tetragonal structure is consistent with small angle X-ray diffraction studies. There is only a small energy difference between the hexagonal and the tetragonal lattice, so that it could well be possible that the system described here prefers the tetragonal lattice to the hexagonal lattice. In that case, once the tetragonal morphological structure is formed, annealing experiments to drive the system towards equilibrium will not change the lattice type to the hexagonal lattice.

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