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Monolayer films of diblock copolymer microdomains for nanolithographic applications

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Several techniques have been investigated for creating large-area thin films of diblock copolymers, with well-ordered two-dimensional periodic microstructure on the scale of a few tens of nanometres. Such structures might potentially be used as templates for lithography, at a length scale not easily accessed by electron-beam methods. Using a copolymer with a spherical microdomain structure, we find that it is quite easy to obtain large-area films consisting of a monolayer of spherical domains, arranged on a hexagonal lattice with a lattice constant of 33 nm. Copolymers with cylindrical microstructure typically orient parallel to the substrate and free surface, it has been found that the perpendicular orientation is metastable: if a well- or poorly-ordered film is initially prepared with the cylinders perpendicular to the surface, annealing results in a well-ordered film with the same orientation, with a lattice constant of 27 nm for the polymer used in this study. For both cylinders and spheres, grains measuring typically 30 × 30 lattice constants are readily obtained.

Introduction

A/B diblock copolymers are large amphiphiles which can self-assemble into a variety of structures, dependent primarily on the ratio of the degree of polymerization of the A block to the B block, N_A/N_B. When the fraction of A components, $N_A/(N_A + N_B)$ is small, spheres of A pack on a body centred cubic lattice, surrounded by a matrix of B. At higher fractions of A, cylinders of A pack into a two-dimensional hexagonal lattice, followed by a double diamond network of A and finally alternating lamellae of A and B layers [1]. The length scale of the periodic structures is typically on the 10 nm scale, scaling with $(N_A + N_B)^{2/3}$.

Microdomain ordering has been extensively studied in bulk, with a smaller amount of work on the structures occurring in thin films and near interfaces [2–6]. In this paper, two techniques are described for creating thin diblock films with a two-dimensionally periodic arrangement of the microdomains. This study was motivated by the potential usefulness of such films as templates for lithography on the scale of a few tens of nanometres. There is an extensive body of theoretical work on the properties of electrons moving in a two-dimensional periodic potential, in the presence of a perpendicular magnetic field, and a fascinating fractal energy band structure has been predicted to occur [7, 8]. Experimental work on this and related subjects has been limited in part due to the limitations of electron-beam lithography: it has proved difficult to achieve a periodicity much below the 100 nm scale (e.g. [9, 10]). Deckman and Dunsmuir have developed a technique for creating well-ordered monolayers of hexagonally close-packed polystyrene spheres, by spin casting from aqueous colloidal solution [11]. Several approaches to transferring the pattern to the substrate have been developed for various applications [12, 13]. However, good ordering has not been obtained for spheres of less than about 100 nm diameter [14]. The length scale and self-assembling nature of block copolymer films make them an attractive alternative to conventional lithography for this type of application.

2. Experimental procedure

Two polystyrene/polybutadiene (PS/PB) diblocks with spherical microstructure were investigated. These are designated SB 65/10 and 10/65, where A/B represents the block molecular weight (kg mol^{-1}). e.g. SB 65/10 is a 65 000 polystyrene–10 000 polybutadiene diblock. A third block copolymer, SB 23/10, which forms cylindrical domains of polybutadiene was also examined. The copolymers were dissolved in toluene to

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form solutions of 2 wt vol% concentration. Carbon-coated 1 inch (2.54 cm) square glass sheets were mounted on a spin coater and flooded with the solution at room temperature. Spinning speeds of several thousand revolutions per minute were used to produce films of uniform thickness. By observing the interference colours of the films, the spinning speed was adjusted to attain a light brown colour, indicative of a film approximately 50 nm thick. Samples were substantially dry after about 5 s. The carbon film substrate and diblock overlayer were then divided into ~ 1 mm^2 pieces by scoring the film with a sharp metal tip, and lifted off the glass carrier via surface tension, by immersion of the scored glass in distilled room-temperature water. Pieces of the sample were picked up from the water surface on to 400 mesh copper grids and annealed at 110 °C for 1–12 h to improve domain ordering. Mass thickness contrast for bright-field transmission electron micrographs was provided by selective staining of the polybutadiene regions with OsO_4 vapours. A Philips 400 TEM operated at 100 kV was employed and images recorded on Kodak SO 163 image plates.

3. Results and discussion

3.1. Spherical microstructure

It proved surprisingly easy to produce uniform monolayers of well ordered arrays of PB spheres of the SB 65/10 diblock. Fig. 1a shows a bright-field transmission electron micrograph of a 0.4 μm × 0.3 μm region of one such film. This monolayer structure was found on all grids examined; therefore, it most likely covers the entire glass substrate. Fig. 1b is a higher magnification image of a region containing several grains. Each grain consists of well-ordered butadiene spherical domains. The two-dimensional hexagonal lattice parameter is 33 nm and the sphere radius is about 16 nm. Previous work on the SB 65/10 sample investigated the structure of small (approximately 1 μm diameter) droplets of polymer solution after evaporation on to a carbon support film [2]. Upon evaporation of solvent, the polymer formed terraced structures with the discrete thickness changes corresponding to additional layers of unit domain thickness. For spin-cast films with an excess of polymer, terraced structure is also found, with excess material forming approximately circular islands of a second layer of spheres. This has also been observed in spin-cast films of lamellar diblocks after annealing [3].

While the SB 65/10 material exhibited well-ordered structure, the SB10/65 material did not. Fig. 2a shows a monolayer film of the SB 10/65, prepared in an identical manner to the SB 65/10 material. The film is quite uniform in thickness, but the packing of the polystyrene spheres is more liquid-like than crystalline. This may seem surprising at first because the SB 10/65 material has the majority component with the lower T_g, whereas in SB 65/10 the matrix component has the higher T_g. But this argument pertains to bulk microdomain structure, whereas we are observing monolayers of domains in a thin film. Here the strong preference of the lower surface tension block,

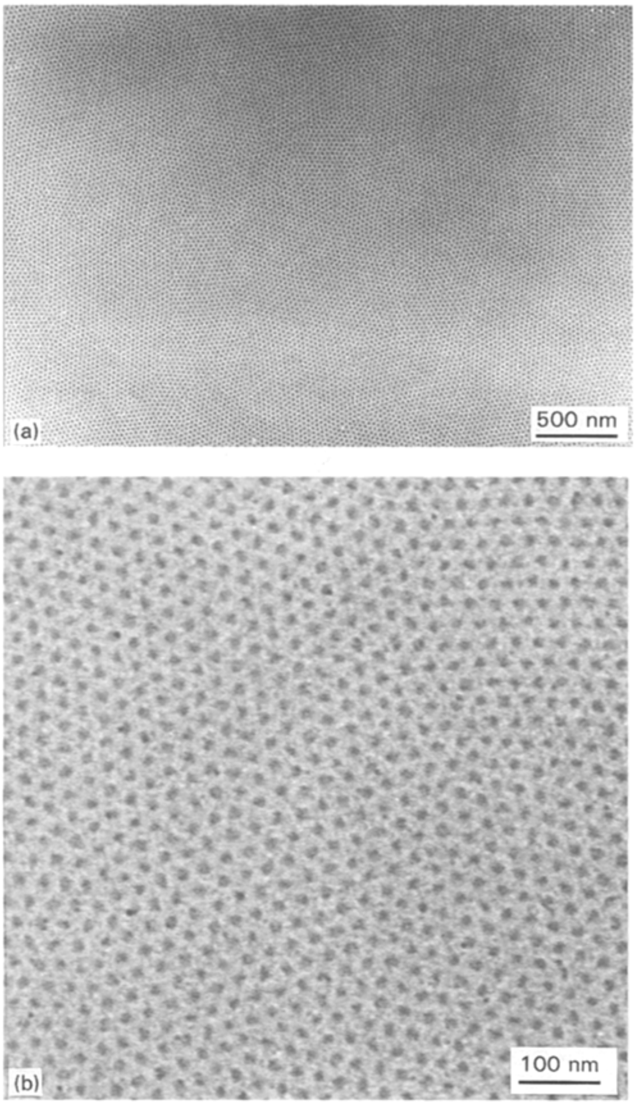

Figure 1 (a) Bright-field transmission electron micrograph of a monolayer film of SB 65/10. Dark regions are OsO_4-stained PB micelles. (b) Higher magnification of SB 65/10 film showing several grains.

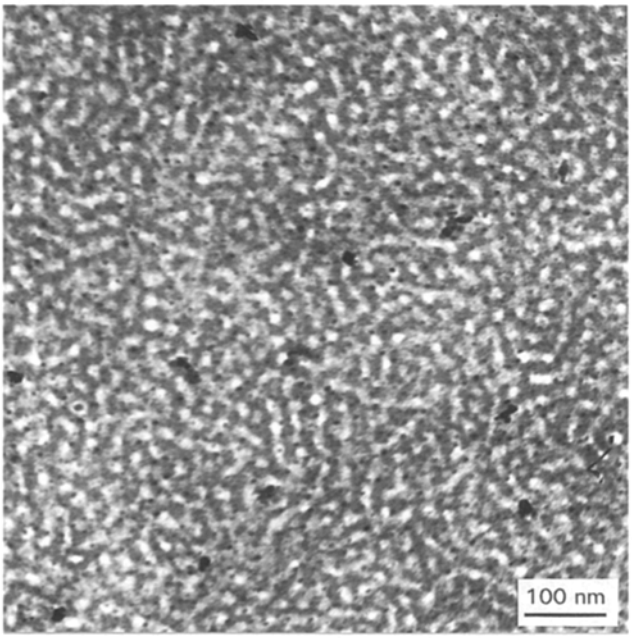

Figure 2 Bright-field transmission electron micrograph of a monolayer film of SB 10/65. This film displays liquid-like ordering of the PS micelles.

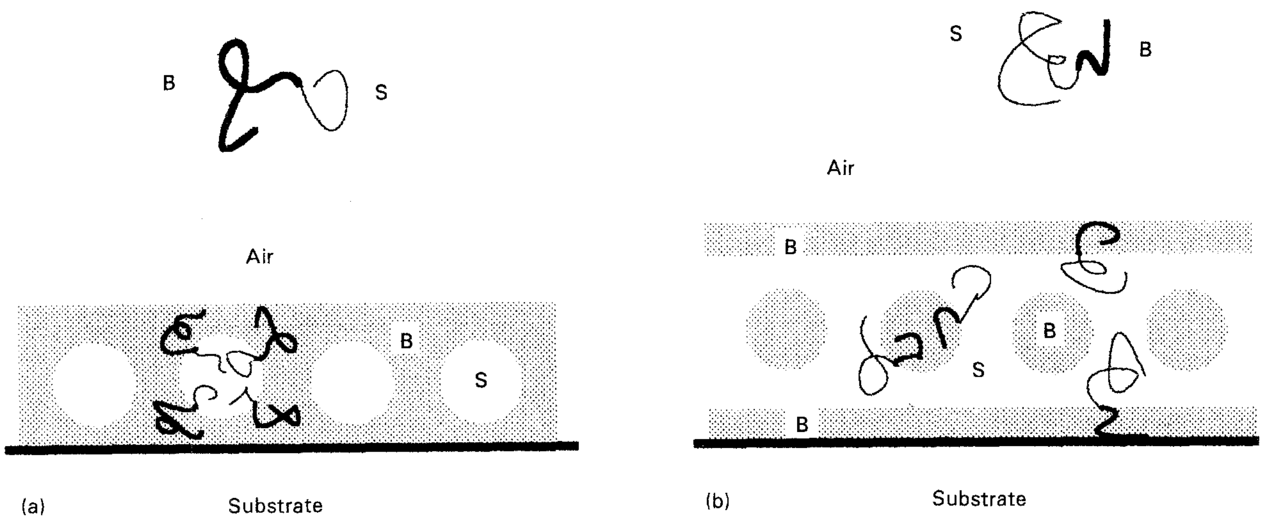

Figure 3 Proposed cross-sectional schematic drawings of the microdomain arrangement of (a) SB 10/65 and (b) 65/10. Note the preference of PB at upper and lower surfaces of the thin film in (b).

polybutadiene, for both the substrate and air interfaces [2] can introduce both equilibrium and kinetic barriers to ordering. Fig. 3a and b depict the proposed chain and domain arrangements in a monolayer film for the different diblock systems. The SB 65/10 film is composed of polybutadiene micelle cores surrounded by a polystyrene block corona region, which in turn are sandwiched between upper and lower layers of PS/PB chains with the PB chains at both the outer air and carbon substrate surfaces. The polybutadiene spheres that form within the majority PS phase are free to move without interaction with the surface or substrate. On the other hand, the polystyrene micelles in the SB 10/65 material are directly attached to the PB block which form the continuous matrix. With this arrangement, some of the corona PB chains are highly deformed and domain rearrangements during annealing are more restricted because of the constraints imparted to the PS micelle core by the surrounding PB blocks which are anchored to the carbon film.

3.2. Cylindrical microstructure

In both types of monolayer with spherical microstructure, the domains are isolated from the surface by a PB layer. This is a potential drawback for lithographic applications in which one would like to remove selectively the minority block in order to expose the surface, creating a film of the majority block with a periodic array of holes. To circumvent this problem, SB 23/10, a diblock with cylindrical PB domains, was investigated. Spin casting of this material, however, resulted in butadiene cylinders oriented parallel to the film surface, presumably sandwiched between upper and lower half bi-layers as shown in Fig. 3b for SB 65/10. Previously, Henkee *et al.* [2] had noted both in-plane and *perpendicular* orientations of the PB cylinders in solution-cast droplet films, with the perpendicular orientation occurring only in the thickest regions (the centres) of some of the larger droplets. Therefore, quiescent casting was tried by flooding the substrate and allowing evaporation to take place, but this also yielded the in-plane orientation, regardless of the film thickness. The dynamics of evaporation and microdomain assembly in small droplets may differ considerably from those involved in forming a uniform film.

Perpendicular orientation of cylinders was achieved by depositing a drop of the polymer solution on the surface of a bath of deionized water. Because the toluene solution does not wet the water surface, the casting process was highly chaotic and resulted in a variety of fragments of different thicknesses and textures, rather than a uniform film. Pieces of film, were chosen, typically a few square millimetres in area, which were fairly uniform in thickness and approximately 100–150 nm thick, as judged by the uniform gold/purple interference colours observed while the films sat on the water surface. These were picked up directly on to carbon-coated copper mesh TEM grids and examined both before and after 6 h anneal at 110 °C.

Fig. 4a shows the structure of the film as-cast (before annealing). It is clear that the formation of cylindrical domains is already well advanced, despite the rapidity of the casting process (a few seconds for the solvent to evaporate), and that the cylinders are oriented perpendicular to the plane of the film. The lateral ordering of the cylinders, however, is liquid-like with no long range order. Annealing preserves the perpendicular cylinder orientation while improving the lateral order (Fig. 4b), which is remarkably good within the individual grains. Because previous work [2] indicates that the parallel orientation is the equilibrium one, it is suggested that the perpendicular orientation is metastable: if a film is somehow initially prepared in this orientation, the large energy barrier involved in globally reorienting the cylinders prevents this from occurring.

This hypothesis was supported by the success of another film preparation method. Bulk samples of SB 23/10 were oriented by shearing a molten sample between parallel plates, a technique first developed by Hadziioannou and Skoulios [15]. This yielded a

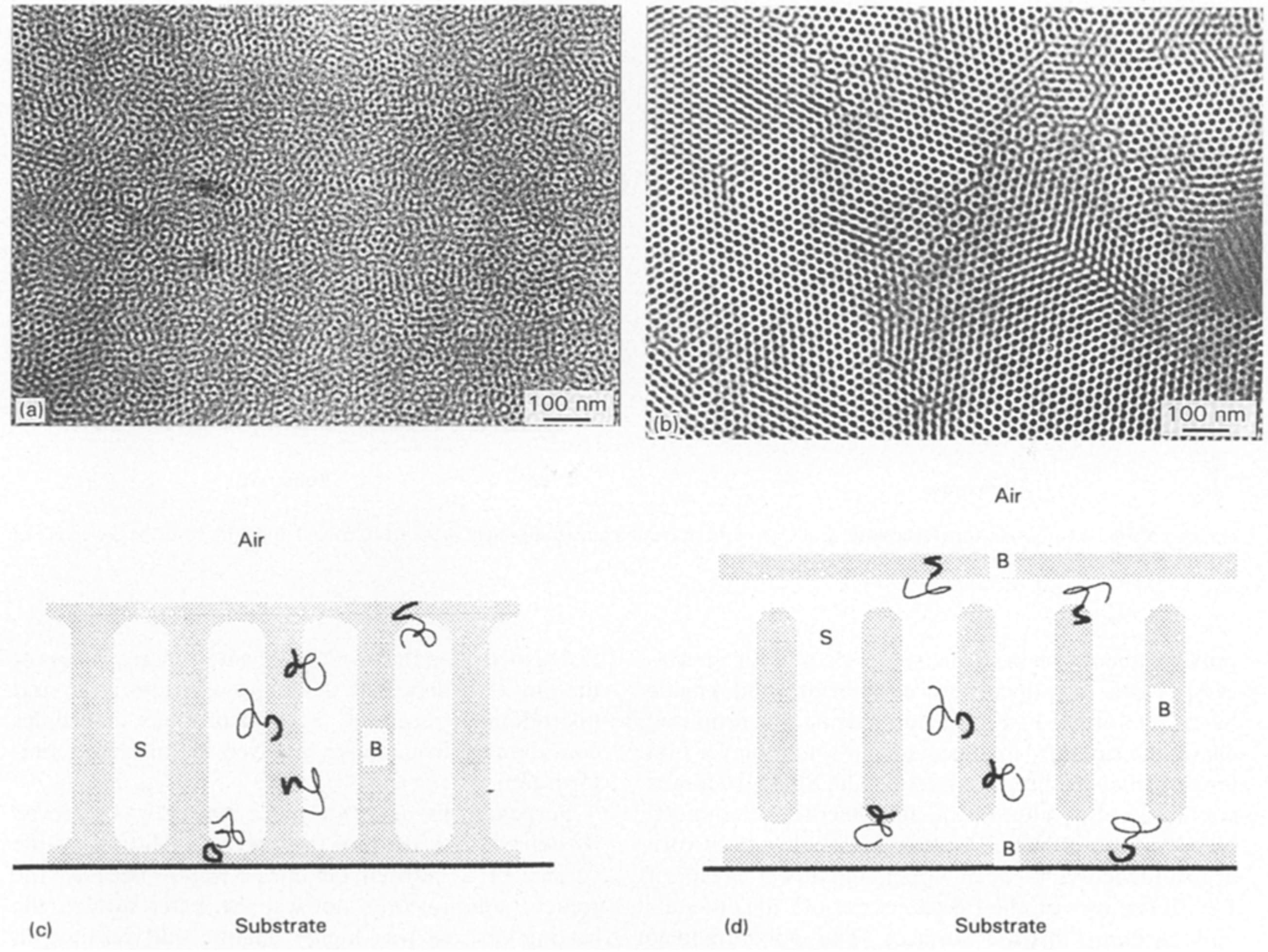

Figure 4 (a) Bright-field transmission electron micrograph of an as-cast film of SB 23/10. Dark regions are OsO_4-stained cylinders viewed end-on. (b) A similar sample of SB 23/10 after annealing at 110° for 6 h. The lateral order has improved. Note the interesting patterns at the grain boundaries. (c, d) Cross-sectional schematic drawings of possible microdomain arrangements in SB 23/10.

common orientation of the cylinder axes everywhere in the sample, as evinced both by TEM and by observing the sample between crossed polarizers. The sample was then microtomed to obtain thin sections (approximately 80 nm thick) with the cylinder axis normal to the plane of the film. Distortion induced by the microtoming process was partially relieved by floating the sections on hot water, and they were then picked up on carbon-coated copper mesh TEM grids, annealed for 6 h at 110 °C, and fixed with OsO_4. The perpendicular orientation of the cylinders in the microtomed thin sections was preserved and the quality of the ordering was very good, though not as good as for the films cast on water.

Perpendicularly oriented lamellar films have previously been observed by Schwark *et al.* [16]. For this case of lamellar microdomains, the thermodynamic equilibrium structure is that of parallel stacks of lamellae, with the PB block forming at the top and bottom layers. The appearance of a 90 ° change in the orientation of the lamellae is due to solvent evaporation – the faster growth rate of the microphase-separated domains for this orientation is due to the direct access of the high transport pathways of the solvent to the surface through PB, rather than serial transport of the solvent through alternating PS and PB layers. This mechanism may also be partly responsible for the creation of perpendicular cylinders by the water-casting technique, but is not a sufficient explanation, because quiescent casting directly on a substrate yields the parallel orientation. A key contributing factor may be the pre-orientation of the chains parallel to the plane of the film due to equi-biaxial flow elongation of the solvent–polymer drops on the water surface during film preparation prior to microphase separation. Such an orientation would bias the self-assembly such that for chain axes oriented in the plane of the film, cylindrical axes would form preferentially normal to the plane of the film.

Fig. 4c depicts the suggested microstructure of the film, viewed in cross-section. Cylindrical PB domains are shown connecting the PB layers at the top and bottom surfaces of the film. The interfacial curvature at the joints of the cylinders to the upper PB layer is of opposite sign to the preferred value. An alternative but somewhat more complicated structure is shown in Fig. 4d. Here the PB cylinders are capped off with the correct mean interfacial curvature corresponding to the copolymer composition, and are sandwiched between single PB/PS monolayers at the top and bottom surface. This alternative arrangement introduced two extra PB/PS interfaces.

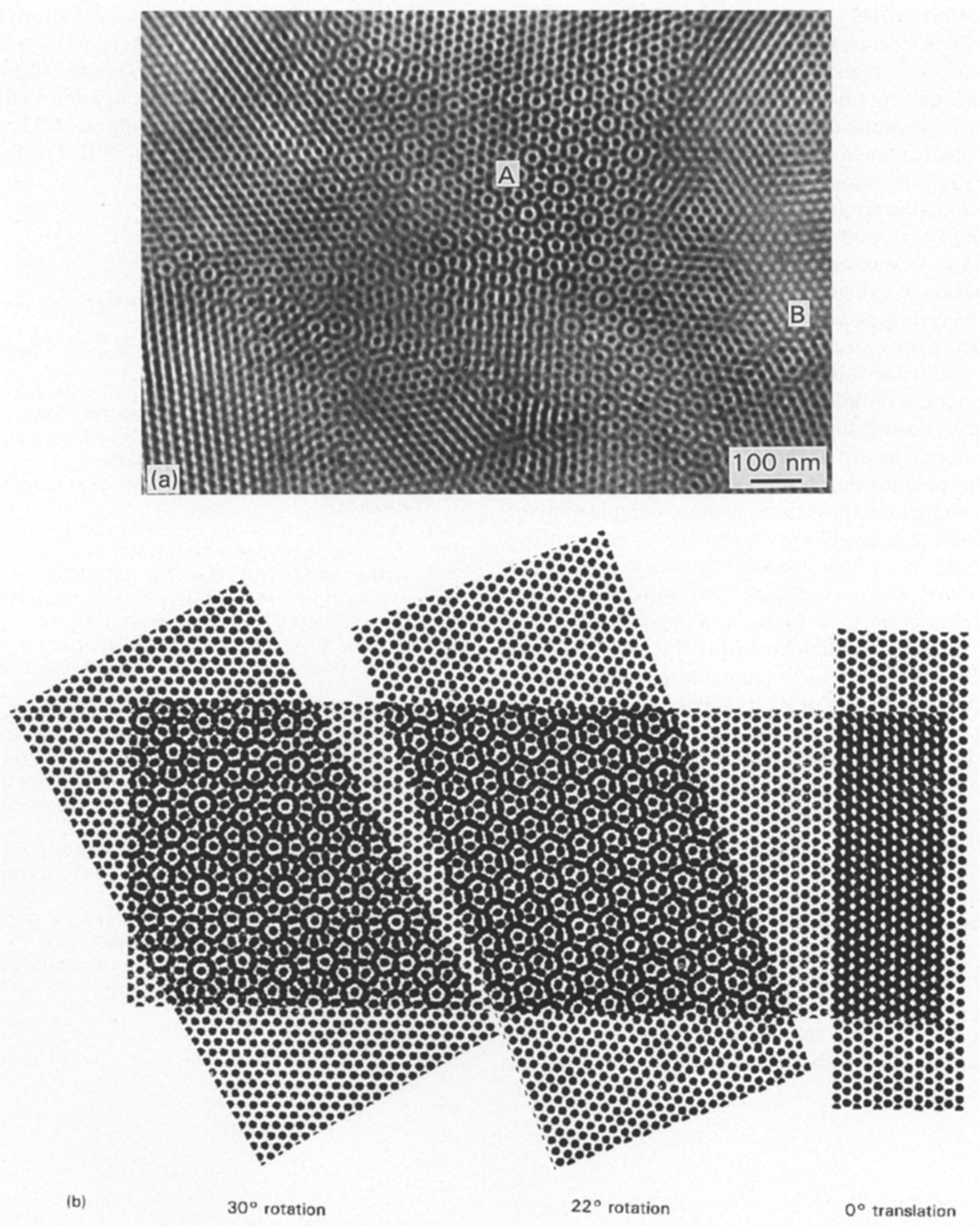

Figure 5 (a) Novel patterns observed in an annealed film of SB 23/10, at the intersection of several grains with different orientations. (b) Simulations of the novel pattern in the cylindrical structure by the superposition of two hexagonal lattices.

An interesting feature of the cylindrical domain films is the appearance of novel patterns. Fig. 5a shows several different patterns which probably arise as adjacent growing regions of two-dimensional hexagonal order layered upon each other, which have both relative translational and rotational lattice mismatch. All of the novel patterns occurring can be reproduced by simple superposition of two hexagonal lattices with a relative translation and rotation between them. Moiré patterns are evident in regions "A" (the two lattices are related by pure rotation) and "B" (the two lattices are related by pure translation). The superposition of the two layers accounts well for regions of contrast reversal, where a white lattice of cylinders results from the two sets of dark cylinders. Simulations of three of the commonly observed patterns are shown in Fig. 5b. The correspondence with regions in Fig. 5a is striking. This suggests two possibilities – either (a) the structures consist of two overlapping films, with the cylinders of each terminated at the mutual interface and not connected to each other, or (b) the cylinders of the two overlapping regions of different orientations are connected, with kinks occurring at some regions of the layer interface. The latter possibility would involve a complicated set of connections between the two layers. This subject seems to warrant further study.

4. Conclusions

It has been demonstrated that it is possible to create large-area thin films of block copolymers with a two-dimensionally periodic nanoscale microstructure. The simplest technique employs spin casting of a diblock with spherical microdomain morphology. The quality of the ordering obtained is greatly enhanced when the microdomains are free to move between separate interfacial layers, and are not in direct contact with the substrate. It was also found that the perpendicular orientation of cylindrical microdomains is stable, and that the cylinders can be prepared in this orientation by casting on water. This morphology is likely to be more useful for lithographic applications, However, the dynamics of flow, evaporation, and microdomain assembly during film formation are not at present understood and are likely to be complex. It should be possible to tailor the films to lithographic applications by choosing an appropriate chemical composition for the blocks, e.g. one block which behaves as a positive resist and one which is a negative resist [11]. Some preliminary success was achieved with lithographic pattern transfer to a GaAs/AlGaAs heterojunction using a SB 185/28 diblock with PB spheres, and the effect of this on the low-temperature magnetoresistance and Hall effect of the two-dimensional electron gas at the GaAs/AlGaAs interface has been observed [17]. Recent experiments with SB 10/65 have shown somewhat improved order over that depicted in Fig. 2. Nevertheless, the order does not approach that found for SB 65/10.

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