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Ordered structures and phase transitions in thin films of polystyrene/polyisoprene block copolymer and blends with the corresponding homopolymers

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It is well established that the addition of a homopolymer to a block copolymer may cause changes in the microdomain structure of the block copolymer [1]. In such blends there is an interplay between macrophase separation of the homopolymers and microphase separation of the block copolymer. Which effect predominates depends on the relative lengths of the polymers, and on the composition of the blend. A key parameter controlling the microdomain morphology of such a system is the ratio, r (= the degree of polymerization of homopolymer/the degree of polymerization of corresponding block chain) [2]. Three extremes of the possible states after phase separation are possible: (i) wet brush regime when $r \ll 1$, (ii) dry brush regime when $r \approx 1$ and (iii) macrophase separation when $r \gg 1$. Numerous studies have appeared on the phase behavior and phase transitions of block copolymer—homopolymer mixtures in all regimes. Most thin film and bulk studies have focused on symmetric diblock copolymers having lamellar microdomains [3–6]. The distribution of homopolymer and changes in lattice spacing have been quantitatively described. An investigation of thin films of an asymmetric diblock copolymer [7] concentrated on the changes in the domain spacing rather than phase transitions. In contrast to diblock copolymer/homopolymer blends, addition of a homopolymer to an ordered triblock copolymer is expected to have a far more significant effect on the properties and phase behavior of the resulting blend. Most studies on triblock copolymers have been concerned with the bulk behavior of almost symmetric triblock copolymers having a lamellar morphology, blended with midblock associating homopolymer [8–10]. Lamellar swelling induced by homopolymer has been characterized. Temperature dependent bulk phase transitions have been investigated in binary blends consisting of a highly asymmetric triblock copolymer (Vector 4111) and the endblock associating polystyrene homopolymer [11].

In this study, ordered structures and phase transitions in thin films of asymmetric block copolymers possessing cylindrical microdomains oriented parallel to the substrate are investigated upon addition of homopolymers (midblock associating as well as endblock associating and both together) in the wet brush regime.

A commercially available polystyrene-polyisoprene-polystyrene (PS-PI-PS) block copolymer Vector 4111 (Dexco Polymers Co.) was used. Vector 4111 contains >99% triblock and has a weight-average molecular weight (M_w) of 128,000 gmol^{-1} and a polydispersity (M_w/M_n) of 1.11. The PS content in the copolymer is 18 wt% (15.6 vol%). Low molecular weight polystyrene (PS) (Alfa Aesar) with $M_w = 1300$ and $M_w/M_n = 1.06$, and low molecular weight polyisoprene (PI)(Polymer Source) with $M_w = 1280$ and $M_w/M_n = 1.11$ were also used. Samples were prepared by first dissolving a predetermined amount of PS-PI-PS and PS and/or PI in toluene (2 wt% in solution) in the presence of 0.1 wt% of antioxidant (2,6-di-tert-butyl-p-cresol; Fluka) and then spin coating the solution onto silicon wafers at 2000 rpm. Typical film thicknesses ranged from 128 nm to 91 nm. Film thicknesses were measured by an ellipsometer (Beaglehole Instruments). Samples were annealed in a vacuum oven for 3 h at 130 °C. AFM characterization was performed immediately after annealing.

The AFM images were obtained using a Digital Instrument Multimode AFM with a Nanoscope IIIa controller. Topographic and phase images were recorded simultaneously using tapping mode with Si tips. The topographic and phase image revealed the same features but only the phase images are presented as they had more contrast.

A representative AFM image of neat Vector 4111 shows a "fingerprint" structure formed by parallel cylinders (Fig. 1). The bright and dark areas in the image correspond to PS cylinders and PI matrix, respectively. The bulk structure of this polymer has previously been confirmed as hexagonal-packed cylinders [11, 12].

Vector 4111 + homopolystyrene. The effect of adding homopolystyrene to Vector 4111 was investigated over the range 7–51 wt% added PS (corresponding total PS volume fraction 0.21–0.56). Small concentrations of minority-component homo-PS (7 or 14 wt%) lead to a significant increase in the curvature of the PS

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Figure 1 AFM image (phase contrast) of the neat Vector 4111 sample (2 μm scale).

cylinders lying parallel to the surface (e.g., Fig. 2a), while AFM revealed an irregular, apparently disordered structure for higher concentrations of homo-PS ($\geq$27%) (e.g., Fig. 2b). The increased curvature on addition of PS may be due to re-orientation of cylinders into a partly perpendicular configuration, or may reflect a decreased end-cap energy on swelling the PS domains, favoring shorter more worm-like structures. In the light of results on further increasing the amount of homo-PS (Fig. 2b) the latter interpretation is favored–addition of PS eventually leading to a complete loss of stripe ordering.

The lack of a regular, ordered structure for mixtures with large PS concentrations may be due to two possibilities:

1. All samples with PS concentration $\geq$ 27 wt% have total PS volume fraction between 0.36 and 0.56. For neat diblocks, a lamellar phase is generally observed and theoretically expected in this composition range [1]. In thin films, an alternating structure of PS and PI parallel to the surface is expected, with PI at the silicon substrate and polymer-air interface. For such a structure the AFM image would correspond to the top polymer layer and the inner lamellae structure would not be probed.
2. The region of stability of different phases for diblock PS-PI/homo-PS blends have been mapped out [13] as a function of homopolymer molecular weight, copolymer composition and homopolymer concentration. Blends of PS-PI diblocks (average M_n = 54 000 gmol^{-1}) with homo-PS (M_n = 5900 gmol^{-1}) exhibit transitions from a cylindrical to two-phase macrophase-separated structures when the PS content in a blend exceeds 40 wt% [13]. We can expect that for our Vector 4111/homo-PS mixture the transition point will be comparable which could lead to the disordered structure observed in the AFM image (Fig. 2b).

Unfortunately, AFM on its own cannot distinguish between the two possibilities. A depth profiling technique is required.

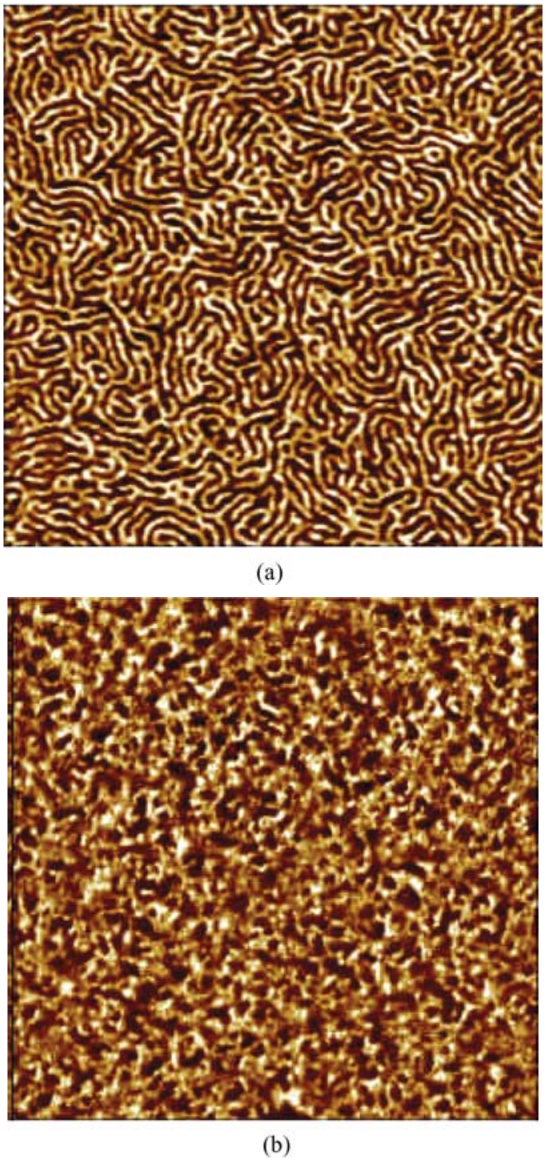


Figure 2 AFM image (phase contrast) of the Vector 4111/homo-PS mixture: (a) 14 wt% homo-PS added and (b) 27 wt% homo-PS added (2 μm scale).

Vector 4111 + homopolyisoprene. The effect of adding homo-PI to Vector 4111 was investigated over the range 7–51 wt% added PI (total PI volume fraction 0.86–0.93). The mixtures Vector 4111/homo-PI with r = 0.05 are in the wet brush regime [2]. They undergo a morphological transition from cylinders (Fig. 1) to spheres (Fig. 3d) on increasing the volume fraction of PI from 0.84 to $\geq$0.89. Such a transition is expected on the basis of increased interfacial curvature as for samples with added homo-PS [2, 13].

A biphasic intermediate state with coexisting cylindrical and spherical domains was observed (Fig. 3a and b) for blends with an intermediate amount of homo-PI (volume fraction 0.86). The main features of this structure are: (i) the appearance of a "patch work quilt" effect (Fig. 3a) consisting of grains containing cylinders aligned (mostly) in parallel stripes but with sharp grain boundaries that can have large tilt angles, (ii) the apparent nucleation of spheres at grain boundaries, in an epitaxial relationship to cylinders [14]. Based on the AFM image in Fig. 3c, the film with a PI volume

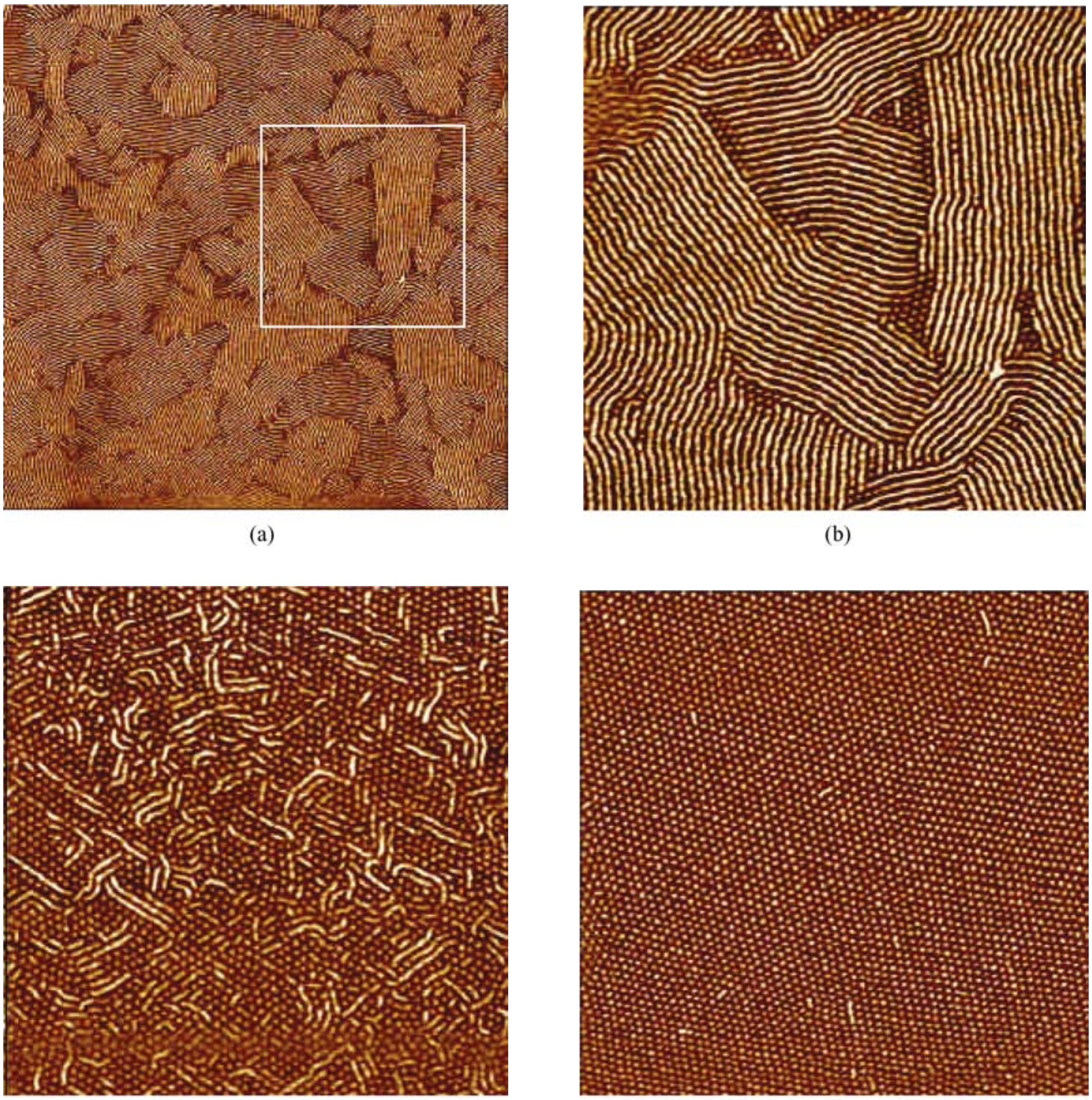

(a)
(b)
(c)
(d)

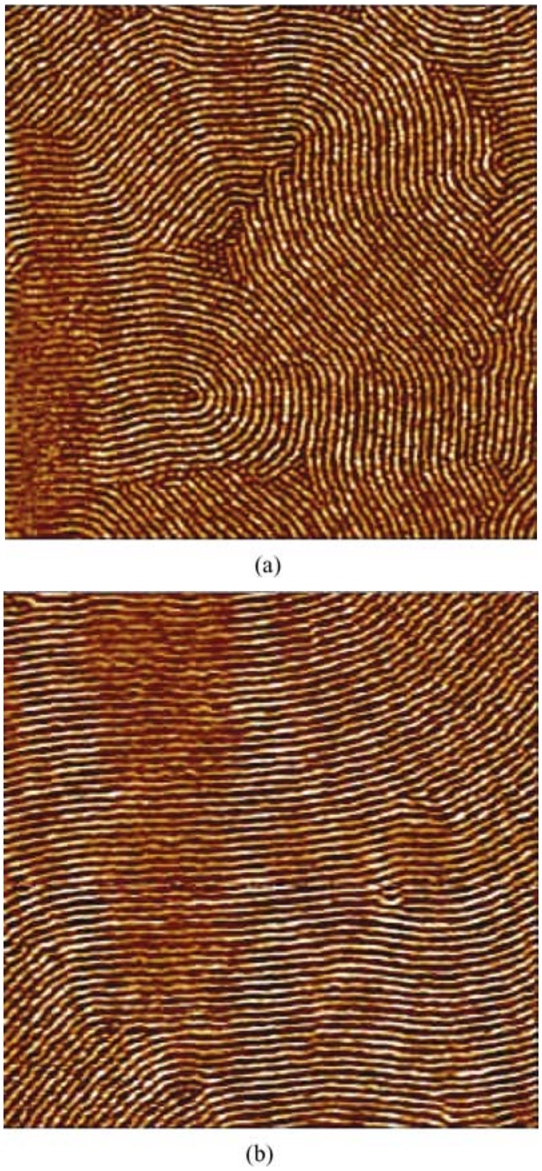
Figure 3 AFM image (phase contrast) of the Vector 4111/homo-PI mixture: (a) 7 wt% homo-PI added (5 μm scale), (b) (enlarged portion of Fig. 3a) 7 wt% homo-PI added (1.84 μm scale), (c) 14 wt% homo-PI added (2 μm scale) and (d) 27 wt% homo-PI added (2 μm scale).

fraction of 0.87 appears to be at a boundary point between the biphasic intermediate state and the sphere morphology. This structure was reproduced in repeated experiments.

Vector 4111 + homopolyisoprene (50%) + homopolystyrene (50%). Addition of equal amounts of both homopolymers together (3.5–25.5 wt% of each, making a total PI volume fraction of 0.82–0.70) results in an aligned cylindrical microdomain structure (Fig. 4a and b). We can expect that, as long as we do not exceed the critical PS concentration for the cylinder—lamellar phase transition, the cylindrical morphology will be conserved. The observed increase in alignment of the cylinders may be due to either of two possibilities: (i) a reduction in pinning of defects in the stripe pattern [15] on the substrate due to preferential segregation of PI to the substrate, (ii) "plasticization" by low molecular weight polymer "diluent" leading to a reduced viscosity and easier local alignment upon annealing.

In summary, the addition of a homopolymer to a block copolymer is shown to be an easy means of changing and controlling the microdomain structures in thin films.

- The addition of majority-component homo-PI to Vector 4111 caused a transition from a cylindrical to a spherical microdomain structure.
- The intermediate state with biphasic coexistence between the cylindrical and the spherical phase showed that (i) formation of spheres starts from the boundary regions between clusters of cylinders and (ii) these two phases have a structural relationship and that spheres form epitaxially, following the direction of former cylinders.
- The addition of a small concentration of minority-component homo-PS in a mixture leads to a significant increase of the cylindrical microdomain curvature.
- Addition of a 50:50 homo-PI and homo-PS mixture leads to enhanced alignment of cylinders parallel



(a)

(b)

Figure 4 AFM image (phase contrast) of the Vector 4111/homo-PI/homo-PS mixture: (a) 14 wt% homo-PS/homo-PI (50/50) added (2 μm scale) and (b) 27 wt% homo-PS/homo-PI (50/50) added (1.68 μm scale).

to the surface (i.e., a longer persistence length of the cylinders).

Further investigations of block copolymers, with different compositions and molecular weights, and including additional techniques, are in progress to shed further light on the control of block copolymer surface structure through blending with homopolymers.

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