Observation of Perpendicular Orientation in Symmetric Diblock Copolymer Thin Films on Rough Substrates

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In the past decade, there has been a significant amount of research related to the orientation of lamellar block copolymer thin films supported on a solid substrate. Following the first reports of *parallel* lamellar orientation in supported thin films,[1] further studies revealed terrace-like formation of lamellar domains and the intrinsic relationship between thin film thickness and the resulting so-called "island or hole" polymer surface morphology.[2] While excellent reviews are given elsewhere,[3] the most relevant discovery was that the block copolymer interactions at the substrate and air surfaces were crucial. When there was a preferential enthalpic attraction for one of the block copolymer components at these surfaces, a surface-directed parallel orientation of block copolymer lamellae was observed. Equalizing the enthalpic interactions between the block copolymer components and the bounding surfaces alters this orientation. A block copolymer thin film symmetrically bounded by two neutral surfaces led to the observation of *perpendicular* orientation in poly(styrene)-*block*-poly(methyl methacrylate) (PS−PMMA) thin films.[4] A mixed orientation (parallel and perpendicular) is seen under asymmetric boundary conditions, e.g., when the upper surface of the PS-*b*-PMMA thin film is exposed to a nonneutral atmosphere (e.g., air).[5]

More recently, some research has looked at the effects of substrate topography or roughness in determining the behavior of lamellar block copolymer thin films. Following predictions by Turner and Joanny,[6] Li et al.[7] looked for the appearance of anticonformal oscillations of a parallel lamellar orientation on a substrate containing a periodic grating-like substrate topography. Fasolka et al.[8] observed "lateral domains" in ultrathin (less than the lamellar domain size) block copolymer films on grooved silicon substrates.

To our knowledge, there are no reports in the literature to suggest that the roughness of a substrate can be used to inhibit the growth of substrate-directed parallel lamellae formation. In this brief communication we present situations where this phenomenon was inferred to have occurred and resulted (in conjunction with a neutral air/polymer interface) in the formation of perpendicularly oriented lamellae.

The grating-like substrates used in refs 7 and 8 are considered ideal in the sense that they have a vertical amplitude (R) and lateral characteristic wavelength (λ) that are well-controlled and anisotropic. qR (where $q \equiv 2\pi/\lambda$) is a convenient parameter to characterize the roughness of the substrate. We have found that certain indium tin oxide (ITO) coatings on glass substrates (Furuuchi Chemical Co., Tokyo, Japan) can have similarly well-controlled substrate roughness, though not exhibiting the anisotropic topographical characteristics. Though this communication does not try to understand the nature of structure formation in ITO, this feature is related to crystallization of the condensed ITO alloy during deposition.

The ITO glass was cut to 1 cm^2 pieces and ultrasonically cleaned in chloroform prior to use. The roughness characteristics of the ITO substrates were analyzed by atomic force microscopy (AFM; Nanoscope III Multimode, from Digital Instruments, Santa Barbara, CA). A 2D-averaged power spectral analysis (available in the AFM software) of 8 μm × 8 μm AFM images of ITO revealed an approximately Gaussian distribution of lateral roughness length scales, λ, centered around ~150 nm (with a variance of ±50 nm at fwhm). These structures gave rise to (root-mean-square) values of R of ~15 nm as determined from height profiles of the AFM images. On nearby random locations on these substrates, qR (~0.6) did not differ by more than 2−3%. Because the ITO coatings are mass-produced on large (50 cm × 50 cm) glass sheets, there is a variation of about 10% in R within one batch of ITO glass. λ did not vary as significantly over the range of ITO substrates used. It is also possible to prepare polyimide (PIM) substrates whose surfaces replicate the topographical features of the ITO surface. A polyamic precursor solution was spun-cast onto the ITO substrates. Curing at 300 °C for 2 h in air produced a 100 nm thick polyimide film (that is composed of biphenyltetracarboxylic dianhydride and oxydianiline) with an approximate glass transition temperature of 260−270 °C. This supported film was submerged in a hydrochloric acid bath that etched away the underlying ITO substrate and released the PIM layer. The PIM film floating on the surface of the HCl bath was then picked up onto an ITO support substrate in such a way so as to have the replicated rough surface topmost. The ITO support substrate is used in this case because it can be conveniently etched at a later stage to assist the preparation of microtomed cross sections. The PIM replica produced similarly rough substrates with R and λ values of 14−15 nm and 150 nm, respectively. A comparison of power spectral analyses from AFM images of the PIM and ITO substrates showed the relevant roughness features of ITO to have been reasonably replicated.

The behavior of an anionically synthesized 38K−36.8K poly(styrene)-*block*-poly(methyl methacrylate) (where $N_{\mathrm{PS}} = 380$ and $N_{\mathrm{PMMA}} = 368$, and N_k is the weight-averaged polymerization index of the block copolymer component k) is reported here. This particular molecular weight block copolymer (purchased from Polymer Source Inc., Canada) has an order−disorder transition temperature well in excess of accessible annealing temperatures. Thin films (300−400 nm; about 7.5−10 times thicker than the bulk lamellar spacing) of the block copolymer were spun-cast from toluene solution onto our substrates and dried overnight (at 60 °C) before annealing in a nitrogen-purged oven at 230 °C for 5−6 h. The samples were then cooled to room

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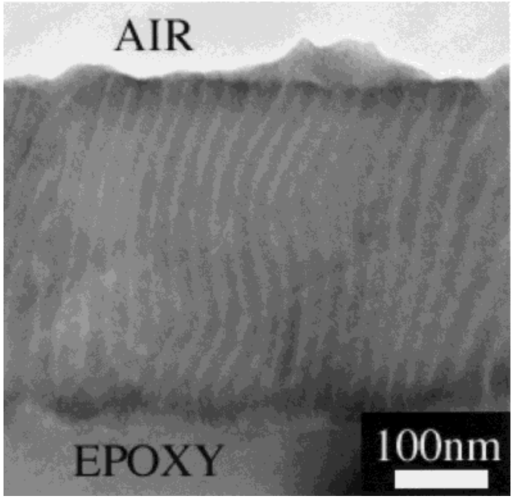

Figure 1. XTEM micrograph of PS-*b*-PMMA (38K−36.8K) after annealing on ITO.

temperature by placing onto a cool metal surface. Observation by optical microscopy concluded that no dewetting of the film had occurred during annealing. The block copolymer microdomain structure was subsequently monitored with cross-sectional transmission electron microscopy (XTEM; JEM2000FXZ, JEOL, Tokyo, Japan operated at 120 kV) and AFM. For XTEM imaging, block copolymer films (or block copolymer films on PIM) are removed from their ITO supports by immersion in HCl, supported onto epoxy substrates, microtomed in cross section, and stained using RuO_4 (that stains PS and enhances contrast). A detailed experimental description will be provided in a future publication.[9]

Figure 1 shows a typical XTEM image observed for our PS-*b*-PMMA thin films that had been annealed on ITO substrates. Figure 2 shows XTEM images of similar PS-*b*-PMMA thin films that had been annealed on the replica PIM substrates. The observed perpendicular lamellae in these figures are confirmed to persist at the sample surface via AFM micrographs (see Figure 3a). The observation of perpendicular lamellar orientation on rough PIM and ITO needs to be understood with respect to the effects of the air and substrate surfaces. It is known that the differences in air surface tensions of PS and PMMA become near zero at high enough temperatures (>200 °C).[10] Therefore, we assume the air surface in our experiments is neutral with respect to the block copolymer components. However at lower temperatures, the air surface is preferentially wet by only one of the block copolymer components. This was verified by observing air surface directed parallel lamellae in similarly thick PS-*b*-PMMA films annealed on rough ITO substrates at low temperatures (<200 °C).[9] Previous research suggests that (in the absence of a chemically patterned substrate[11]) the combination of a neutral upper and lower bounding surfaces to the block copolymer results in a perpendicularly oriented lamellae. Since we propose that substrate roughness can affect lamellar orientation, we then need to resolve whether the substrate is neutral. One way to do so is to measure δ_{ITO} ($\equiv |\gamma_{\mathrm{PS,ITO}} - \gamma_{\mathrm{PMMA,ITO}}|$) and δ_{PIM}, the difference in the wetting energies of PS and PMMA on the substrates, where γ denotes an interfacial tension. A more elegant way to distinguish whether surface roughness or surface neutrality is culpable is employed here.

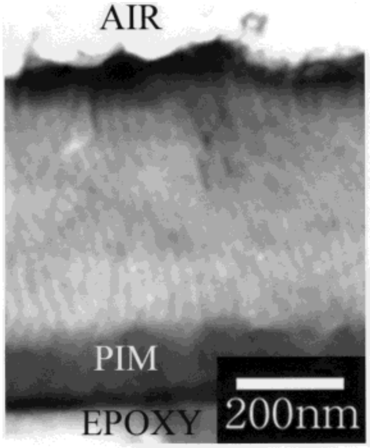

Figure 2. XTEM micrograph of PS-*b*-PMMA (38K−36.8K) after annealing on a rough PIM substrate.

The advantage of using a rough polyimide substrate is that it may be annealed above its glass transition temperature to produce a smooth surface that maintains its inherent surface wetting properties. This was done (by annealing the rough PIM substrates at 290 °C for 2 h) to produce surfaces that had an R value of 4 ± 1 nm ($qR \sim 0.17$). Neither λ nor the shape of the substrate surface power spectra changed appreciably during annealing. When PS-*b*-PMMA films were spun-cast and annealed on this smooth PIM substrate, "island or hole" block copolymer surface topographies, indicative of a parallel lamellar orientation, were observed via AFM (see Figure 3b). At the neutral air surface both orientations, perpendicular or parallel, are possible. A fully parallel orientation may have been produced to avoid defect formation that arises from mixed orientations (parallel from substrate, perpendicular elsewhere). This result then implies that the smooth PIM surface is enthalpically nonneutral.

The structures observed may be construed to be in equilibrium after (quite protracted) annealing at an elevated temperature since two types of orientation were observed that depended only on the substrate roughness conditions. The contrasting behavior of the block copolymer on the rough and smooth PIM substrates can be qualitatively explained; thus, a substrate-directed parallel block copolymer orientation may *not* be observed if one has a sufficiently rough substrates where (a) there is a significant deformation of the lamellar domains involved with the formation of a parallel orientation that attempts to follow the peaks and valleys of a rough substrate and (b) there is a small enough difference in the interfacial tensions of each of the block copolymer components and the substrate.[12] Thus, by making the substrate rough enough, the attractive potential for one component of the block copolymer to the PIM substrate is diminished. In our case, in conjunction with a neutral air/polymer surface, perpendicular orientations are observed.

In this brief communication and in the interests of space we have only shown data from a restricted parameter space. It will be shown in a future paper that in fact this phenomenon was observed for a range of molecular weights, film thicknesses in the submicron range, for annealing temperatures above 200 °C, and for a variety of cooling conditions.

Our results must be placed within the context of existing methods to perpendicularly align domains in

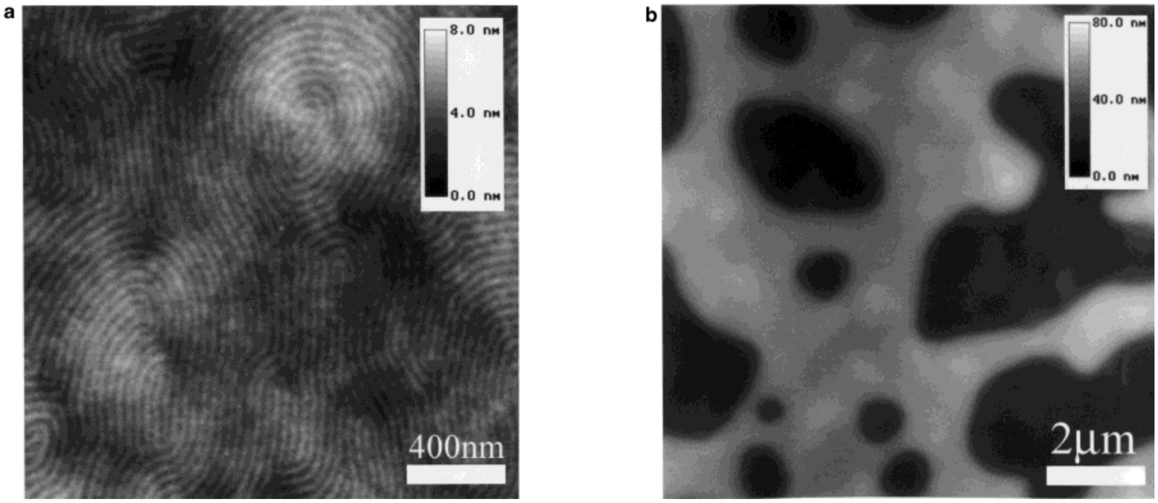

Figure 3. Height mode AFM image of PS-*b*-PMMA (38K−36.8K) after annealing on (a) rough PIM; phase mode image; (b) smooth PIM.

thin block copolymer films. We can observe perpendicular lamellae throughout the thin film because (a) the substrate is sufficiently rough, (b) $\delta_{\text{substrate}}$ for our block copolymer/substrate couple is sufficiently low (but not zero), and (c) and the air surface is sufficiently enthalpically neutral. Previous observations of block copolymers on rough substrates, e.g., refs 7 and 8, may not have satisfied these conditions. However, the novelty of this work is in the realization that a rough nonneutral substrate can mimic a smooth neutral substrate in its ability to prevent substrate surface-directed parallel orientation. Previous methods have employed systems where both bounding surfaces of the block copolymer thin film are neutral. Future experiments may result in the discovery that a pair of rough bounding surfaces have the equivalent effect.

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