

Communications to the Editor

Environment-Controlled Spin Coating To Rapidly Orient Microdomains in Thin Block Copolymer Films

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Nanoscale patterns formed from block copolymer (BCP) thin films with controlled orientation of microdomains have been used in patterning substrates to build electronic devices such as capacitors and memories.^{1,2} More recently, a single field effect transistor (FET) device was fabricated as a prototype using BCP cylindrical microdomains oriented parallel to the surface.³ Usually, creating thin films containing such nanoscale aligned patterns from unaligned microdomains requires long thermal annealing times, which limits their throughput for applications requiring high throughput manufacturing.⁴ Several papers have demonstrated that it is possible to trap block copolymer morphology in a nonequilibrium orientation by solvent casting.^{5–14} According to these reports, the cylindrical microdomains of an asymmetric block copolymer of polystyrene and poly(ethylene oxide) (PS-*b*-PEO) can be oriented normal to the surface of a thin film within seconds. Further, the orientation and ordering of the morphology could be improved by relatively long-term (>48 h) solvent annealing in benzene. We performed a more systematic investigation of solvent vapor induced orientation in PS-*b*-PEO thin films during the spin-coating process. Here, we report on a strategy for faster processing in order to control orientation of microdomains. The typical spin-coating process was modified to study effects of environmental atmosphere. We also discuss the effect of surface energy on the solvent-induced microdomain orientation using a surface energy gradient substrate.

Asymmetric diblock copolymer of polystyrene and poly(ethylene oxide) (PS-*b*-PEO) with a molecular weight of 25.4 kg/mol was purchased from Polymer Source, Inc., and used as received. The PS-*b*-PEO has a PEO mass fraction of 0.25 and forms PEO cylinders in a PS matrix in bulk samples. PS-*b*-PEO was dissolved in toluene at the concentration of 1% (by mass). Though toluene is a selective solvent for PS, dynamic light scattering results confirmed that micelles were not formed in solution. After depositing a 1% (by mass) PS-*b*-PEO (filtered through 0.2 μ m poly(tetrafluoroethylene) (PTFE) filter) solution

in toluene onto a silicon substrate, spin-coating was performed in a spin-coater which was encased to control the atmosphere. Prior to spin-coating, the enclosed chamber (volume = 2.84×10^{-3} m³) was partially saturated for >30 s using an excess of a given liquid solvent. Vapor atmospheres used in this study included toluene and distilled water. After a 40 s waiting period, the solutions were spin-coated at 3000 rpm, and the film-coated wafers were immediately removed from the chamber. Films were also prepared on substrates with a surface energy gradient created using a self-assembled monolayer (SAM) of adsorbed octyldimethylchlorosilane (ODS) exposed to varying doses of ultraviolet light as described elsewhere.^{15,16} The surface energy gradient was evaluated from the spatially resolved contact-angle measurement using water and diiodomethane with the Good and Girifalco geometric mean approximation.^{15,17–19} The water contact angle spans from 96° (hydrophobic ODS SAM) to ~5° (equivalent to Si substrate with a native oxide layer) continuously, which corresponds to the surface energy varying from 15.4 to 53.2 mJ/m². Thin film surface morphology and topology were characterized using a Dimension 3100 scanning force microscope (SFM, Digital Instruments, Inc.) in tapping mode. The thicknesses were determined using UV–vis interferometry (model F20, Filmetrics, Inc.) operated in reflectance mode with a spot size of 0.5 mm.

Thin films spin-coated without any environment control exhibit a mixed orientation of PEO cylinders, i.e., parallel and perpendicular orientation with respect to the substrate, without any significant long-range ordering (Figure 1a). The film thickness at 3000 rpm was 28 nm as measured by interferometry and confirmed by SFM measurement on scratched samples. A previous study reported the cylinder diameter and center-to-center distance of the cylindrical domains to be 24 and 33.7 nm, respectively, for the same molecular weight of PS-*b*-PEO.⁶ Because the PEO block has a favorable interaction with Si substrate and PS block has a lower surface energy than PEO, the equilibrium morphology tends to have cylinders preferentially oriented parallel to the surface. The observed *mixed* morphology suggests it should be feasible to control the orientation because both orientations of PEO cylinders compete with each other during the short time scale of the spin-coating process. In an attempt to control the orientation, various vapor atmospheres for spin-coating were explored, and here we report only on the ones of interest for producing vertically oriented cylinders. First, a PS-*b*-PEO toluene solution was spin-coated under a toluene vapor atmosphere. We note that toluene vapor, however, does not fully eliminate water vapor in the chamber (relevant to our further discussion in this paper). Figure 1b shows that a large fraction of PEO cylinders are oriented parallel to the surface, and the overall phase contrast in SFM phase image is relatively large. We believe this results from the fact that toluene is a good solvent for PS (the matrix material). In comparison, spin-coating with a toluene and water vapor atmosphere (as water is a relatively good solvent for PEO) gives a morphology of vertically oriented cylinders as shown in

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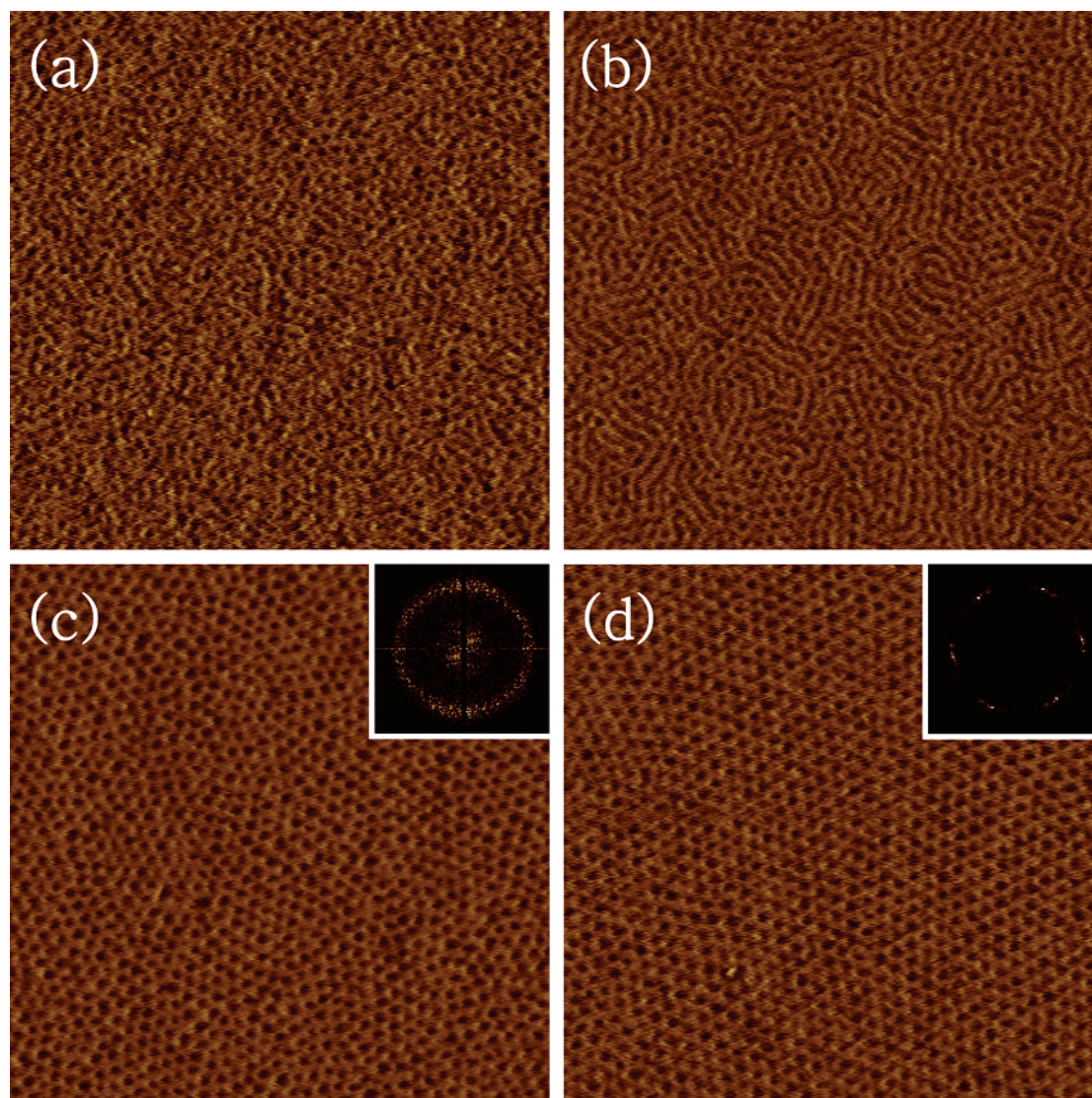


Figure 1. Tapping mode SFM phase images obtained from PS-*b*-PEO thin films spin-coated (a) in an open environment, (b) under toluene vapor, (c) under toluene and water vapor, and (d) water vapor. The insets in (c) and (d) are the Fourier transforms of the AFM images. The scan areas are $1\ \mu\text{m} \times 1\ \mu\text{m}$.

Figure 1c. Vertical orientation appears to be favored when evaporation of the spun film occurs in the presence of two competing solvent vapors which selectively prefer each block. In the phase contrast SFM image in Figure 1c, the minor component of PEO block forms the darker cylindrical domains distributed in the lighter matrix of the PS major component. The inset in Figure 1c is a fast Fourier transform (FFT) of the SFM image. The FFT exhibits a ring which is characteristic of a microphase-separated structure which lacks long-range and orientational order. The normal orientation of the PEO block shown in Figure 1c suggests that adding water to the toluene atmosphere modified the atmosphere during spinning to be more favorable for the PEO. As shown in Figure 1d, a normal orientation of PEO microdomains was also obtained when only water vapor was used in the spin-coating atmosphere. The inset Fourier transform of AFM image in Figure 1d shows a hexagonal packed cylinder structure indicating significantly improved lateral order.

For solvent-cast poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer thin films, it was reported that relatively fast evaporation of solvent (~ 3 h) apparently generated large gradients in solvent concentration through the film thickness and allowed an orientation of PS cylinders perpendicular to the plane of the

film.⁵ Solvent evaporation in PS-*b*-PEO thin films apparently also causes a strong and unidirectional field that induces self-assembly at the air surface and propagates ordering through the entire film.^{6,7} The SFM results shown in Figure 1 indicate that the morphologies produced by spin-coating are strongly dependent on the details of the spin-coating atmosphere. Because the vapor pressure at room temperature and boiling point of toluene ($P_{\text{vp}} = 0.0342$ bar) are relatively similar to those of water ($P_{\text{vp}} = 0.0313$ bar),²⁰ the preferential affinity of the atmosphere which includes toluene vapor (evaporated from the spinning solution) was modified by adding (additional) toluene or water to the chamber. As a result, the interfacial energy at the air/film interface was varied to be from PS-favorable to both PS and PEO-favorable. Also, the evaporation of toluene in the latter stages of spin-coating can cool the film surface, which may possibly increase local concentration of water vapor above the film surface that favors the development of vertically oriented PEO cylinders. As reported using benzene, a good solvent for both PS and PEO,^{6,7} vertical cylinders were also produced under mixed vapor atmosphere of toluene and water, where any preferential affinity was suppressed. Figure 2 shows humidity changes in the encased spin-coater from distilled water. When the relative atmospheric humidity at room temperature

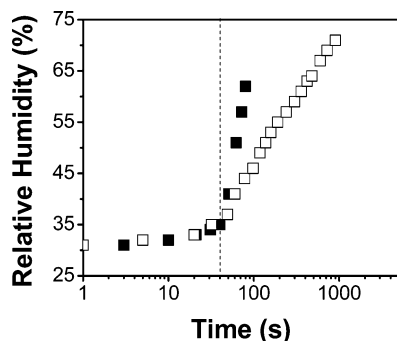


Figure 2. Relative humidity change in an environmentally encased spin-coater including 8 mL of water in a $2.84 \times 10^{-3} \text{ m}^3$ enclosure: without spinning (open square) and with spinning after 40 s (filled square). The dashed line indicates an interval of 40 s before the spinning starts. Importantly, after spin-coating, the film is not processed any further in these studies.

($\approx 22^\circ\text{C}$) was 31%, in the chamber it slowly increased and reached around 63% over a period of 400 s. When the solution was spin-coated after an initial waiting time of 40 s, the relative humidity increased sharply up to 62% over the 80 s at the end of the spin-coating cycle. The color change of the film during spinning was completed in 20 s after the spinning starts. It

suggests that the effective humidity window to control the orientation of PEO domains is between 35% and 51%.

The normal orientation of cylinders was reported to occur when the interfacial energies of two immiscible blocks became nearly equivalent at both air/film and film/substrate interfaces.^{8,21} To confirm the hypothesis that films cast in the presence of solvent vapor order only from the air surface down, the orientation of PS-*b*-PEO cylinders in films spin-cast from toluene solution was systematically investigated on a gradient substrate with a spatially varying surface energy. The vapor atmosphere was mixed toluene and water as in previous measurements. Figure 3 shows typical phase images of PS-*b*-PEO film cast on the substrates having various contact angles, i.e., different surface energy. The PEO cylinders are oriented perpendicular to the film plane with almost the same degree of lateral order over the entire surface energy range from 15.4 to 53.2 mJ/m². We conclude that for this film thickness ($\sim 28 \text{ nm}$) cylinder orientation is predominantly controlled by the liquid/vapor interface by solvent evaporation and the surrounding vapor environment and shows no dependence on the surface energy of the substrate. This result is consistent with an ordering front that propagates through the film from the top vapor/film interface.⁷ Suppression of any orientation occurring at the

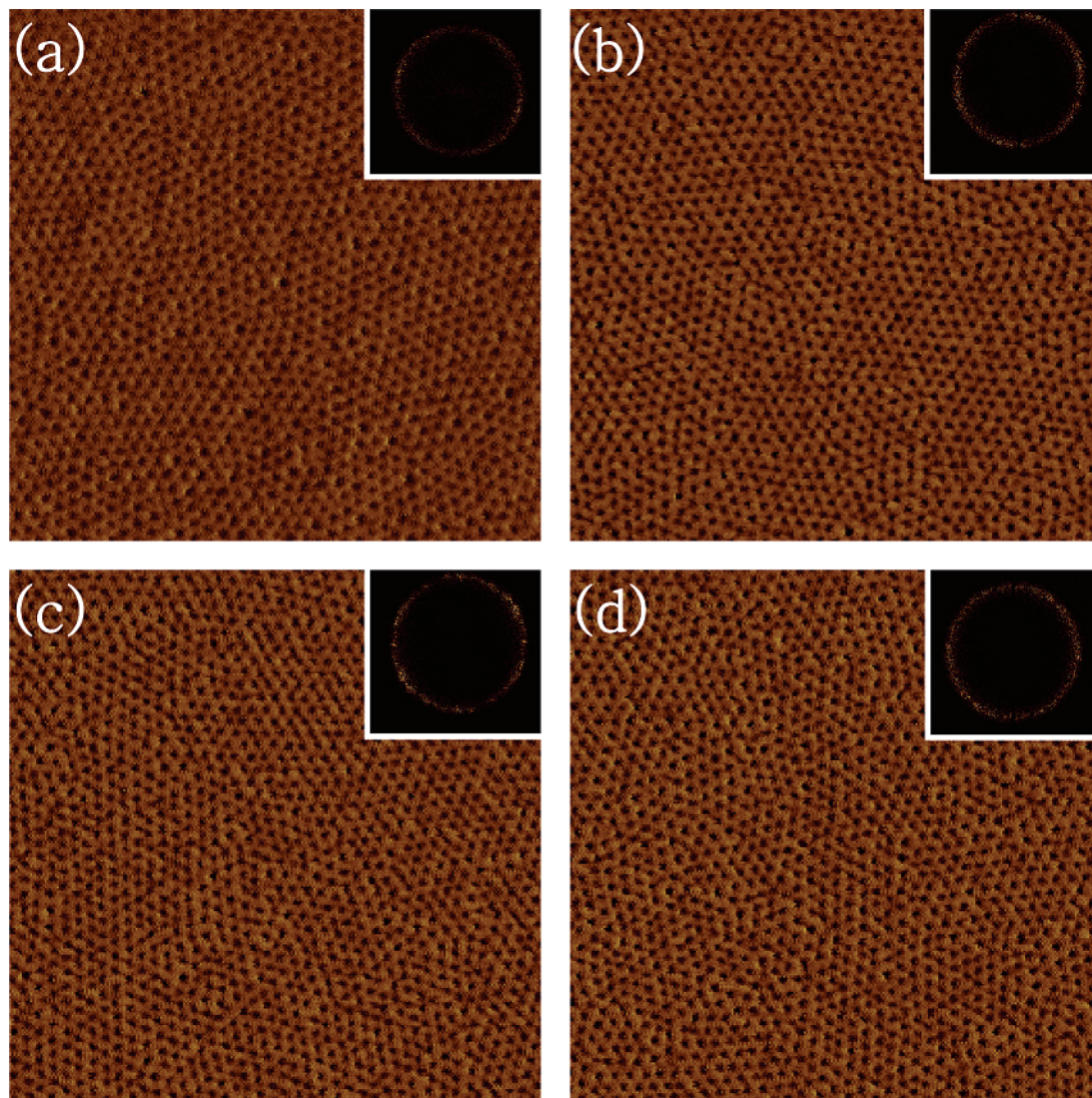


Figure 3. Tapping mode SFM phase images obtained by spin-coating PS-*b*-PEO solution under toluene and water vapor on surface energy gradient substrate with water contact angles of (a) 96° , (b) 63° , (c) 47° , and (d) $\sim 5^\circ$. The insets are the Fourier transforms of the AFM images. The scan areas are $1 \mu\text{m} \times 1 \mu\text{m}$.

substrate interface may be assisted by the presence of trapped residual solvent at the film/substrate interface. Any residual good solvent at the substrate interface can mitigate preferential block interaction with the substrate. This effect scales with the solvent volume fraction as $\sim \phi_s(t) \chi_{\text{block/substrate}}$, where $\phi_s(t)$ is residual (local) solvent fraction that ultimately evaporates.

In summary, we demonstrate a simple and fast (<2 min) methodology to control the orientation of cylindrical microdomains in thin (≈ 30 nm) block copolymer films using an environmentally “benign” atmosphere controlled spin-coating process. During spinning, the preferential affinity of water vapor allows the PS-*b*-PEO cylinder orientation to be controlled from parallel to perpendicular with respect to the film surface and with a relatively high degree of lateral order for perpendicular orientations. A combinatorial gradient technique was used to prove that the interfacial energy at the vapor/film interface is more important than the substrate interfacial energy (varied from 15.4 to 53.2 mJ/m²) for controlling PS-*b*-PEO block copolymer orientation in kinetically trapped morphologies produced by environment-controlled spin-coating.

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