Mechanism and dynamics of block copolymer directed assembly with density multiplication on chemically patterned surfaces

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(Received 13 July 2010; accepted 27 October 2010; published 29 November 2010)

In this work, we used scanning electron microscopy (SEM), *in situ* coherent small angle x-ray scattering (SAXS), and Monte Carlo molecular simulation to gain insights into the dynamics of block copolymer directed assembly with density multiplication on chemically patterned surfaces. During directed assembly, it was observed with SEM that poly(styrene-*block*-methyl methacrylate) initially formed discrete polystyrene domains that lacked long-range order at the free surface. After further annealing, the polystyrene domains gradually coalesced into linear domains that were not registered fully with the underlying chemical pattern. The linear domains could be trapped in metastable morphologies. Finally, the linear polystyrene domains formed perpendicular lamellae in full registration with the underlying chemical pattern. It was revealed with SAXS that scattering peaks characteristic of the period of the chemical pattern appeared and disappeared at the early stages of assembly. Finally, the morphological evolution of directed assembly of block copolymer on chemically patterned surfaces was modeled by molecular simulations. © 2010 American Vacuum Society. [DOI: 10.1116/1.3518918]

I. INTRODUCTION

Directed assembly of block copolymers and block copolymer/homopolymer blends has been demonstrated to be an attractive means to fabricate patterned templates with dimensions of 5–50 nm for applications such as microelectronics and magnetic data storage media.^{1–3} As the required feature resolution approaches 20 nm, traditional photolithographic techniques, broadly used in the microelectronic industry today, have met tremendous challenges, such as control of critical dimensions (CD), line edge roughness (LER), and linewidth roughness. Because of the propensity of block copolymers to microphase separate, they have the ability to assemble into features with a variety of shapes and a high degree of size uniformity. Previous work has demonstrated many advantages of inserting block copolymer directed assembly into the traditional photolithographic process, such as the ability to fabricate a variety of morphologies that are in registration with the underlying substrate and have a high degree of perfection, as well as LER and CD control.^{3–8} In addition, complex geometries for integrated circuits, including bends, jogs, terminations, and junctions, can be assembled by these materials.^{2,9–11} Recent developments in the directed assembly of block copolymers with density multiplication on chemical patterns have shown that the resolution of a patterned template can be significantly enhanced.^{7,12–14} The density multiplication of regular features such as hexagonal spots,^{13–15} periodic lines,^{7,16} and nonregular device-

oriented features^{17,18} could be achieved via the directed assembly of block copolymer and block copolymer-homopolymer blends on chemically patterned surfaces following specific pattern design rules. Most of these examples focused on the formation of features at equilibrium, but the mechanism and dynamics of directed assembly with density multiplication are still underdeveloped. A knowledge of the dynamics of a block copolymer directed assembly is desirable to improve and optimize the density multiplication process.

The dynamics of block copolymer assembly have been studied in solutions, melts, electrical fields, and confined geometries using a variety of analytical techniques, such as scanning force microscopy, scanning probe microscopy, atomic force microscopy, polarized optical microscopy, and molecular simulation.^{19–29} Previously, Edwards *et al.*³⁰ investigated the directed assembly of lamellae-forming poly(styrene-*block*-methyl methacrylate) [P(S-*b*-MMA)] block copolymer on chemically patterned surfaces without density multiplication. They used experiments and single chain in mean field simulations to gain insight into the time-dependent, three-dimensional behavior of block copolymer directed assembly on a chemical pattern. Formation of hexagonally close-packed polystyrene (PS) domains, coalescence of the PS domains to linear PS domains that were not fully registered with the underlying chemical pattern, and registration of the linear PS domains with the chemical pattern, were the distinct stages of block copolymer directed assembly that they identified. In addition, Stuen *et al.*³¹ used *in situ* coherent small angle x-ray scattering (SAXS) to ex-

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perimentally probe the three-dimensional dynamics of directed assembly of block copolymer-homopolymer ternary blends. In the work we present here, we used *in situ* SAXS, top-down scanning electron microscopy (SEM), and Monte Carlo molecular simulation to monitor and characterize the dynamics of the directed assembly of block copolymers with density multiplication on chemical patterns.

II. EXPERIMENT AND SIMULATION

A. Materials

Hydroxyl-terminated polystyrene (PS-OH, number average molecular weight, $M_n=3.7 \text{ kg mol}^{-1}$, polydispersity index, $\text{PDI}=1.08$), and P(S-*b*-MMA) ($M_n=52\text{-}b\text{-}52 \text{ kg mol}^{-1}$, $\text{PDI}=1.09$) were purchased from Polymer Source, Inc., and used as received. The P(S-*b*-MMA) had a styrene fraction of 49%, and it formed lamellae with a bulk natural period (L_o) of 47.7 nm, as previously characterized by small angle x-ray scattering.²⁵ Poly(methyl methacrylate) (PMMA, $M_n=950 \text{ kg mol}^{-1}$) photoresist was purchased from MicroChem, Corp. Polished, test grade (100) silicon wafers were purchased from Montco Silicon Technologies, Inc. Toluene, chlorobenzene, methyl isobutyl ketone, and isopropanol were purchased from Sigma-Aldrich, Milwaukee, WI.

B. Sample preparation

Figure 1 schematically illustrates the directed assembly of block copolymers with density multiplication on chemically patterned surfaces. The silicon wafer was cleaned in an oxygen plasma chamber for 5 min to remove any organic residue and to ensure the presence of a layer of silicon oxide. A solution of PS-OH in toluene (1.5 wt %) was spin-coated onto the silicon substrate, resulting in an initial $\sim 40\text{-nm}$ -thick film of PS-OH. The film was annealed at 160°C for 1 day under vacuum to graft the PS-OH brush onto the substrate. The elevated temperature and long annealing time were sufficient to ensure that the brush layer reached the density limit of grafted PS.³² After annealing, the substrates were quenched to room temperature and rinsed with toluene to remove any excess, unreacted PS, yielding a $\sim 3\text{-nm}$ -thick PS brush layer.³³ Afterward, the PS-OH grafted substrates were covered with a $\sim 40\text{-nm}$ -thick layer of PMMA photoresist and subsequently patterned with x-ray interference lithography (XIL) at the Swiss Light Source of the Paul Scherrer Institut, Switzerland. After the lithographic exposure, the PMMA photoresist was developed with a mixture of methyl isobutyl ketone and isopropanol (1:3 v/v) and dried in a nitrogen stream. The resulting pattern had a period, L_s , of 100 nm ($\sim 2L_o$), an exposed linewidth, W , of $\sim 25 \text{ nm}$ ($\sim L_o/2$), and spanned an area of $1.0 \times 0.5 \text{ mm}^2$. The patterned photoresist was exposed to oxygen plasma for 10 s to ensure that the exposed regions were preferentially wet by the PMMA domain of the block copolymer. The remaining PMMA photoresist was removed by rinsing in chlorobenzene, resulting in chemical patterns of alternating PS brush

FIG. 1. (Color online) Schematic of the block copolymer directed assembly with $2\times$ density multiplication ($L_s/L_o=2$) on a chemical pattern.

[preferentially wet by the PS block of the P(S-*b*-MMA)] and oxidized regions [preferentially wet by the PMMA block of the P(S-*b*-MMA)]. The final substrates were then spin-coated with a dilute solution of P(S-*b*-MMA) in toluene to yield a $\sim 50\text{-nm}$ -thick film of P(S-*b*-MMA). For *in situ* SAXS analysis, the sample was mounted onto a copper heating stage, which had a hole in the center to allow scattered x rays to pass through. The heating stage in air was ramped from 40 to 240°C for 6 min and held at 240°C for ~ 60 min. The scattering was performed in transmission mode with the incoming coherent x-rays from the synchrotron source oriented perpendicular to the substrate. The scattered x-rays traveled through a 7 m flight tube and were collected by a PILATUS detector. It was observed by eye that the samples annealed at 240°C in air for longer than 2 h were degrading. To obtain information about directed assembly of the block copolymers over longer annealing times, the substrates were ramped from 40 to 240°C for 6 min on a heating stage in air and then transferred immediately to a

vacuum chamber at 240 °C for annealing times ranging from 10 min to 64 h. The sample transfer time was so short that the temperature change was negligible. The resulting block copolymer films were imaged with a field emission scanning electron microscope (LEO 1550 VP) using a 1 kV accelerating voltage. In the SEM images, PS domains appear bright and PMMA domains appear dark.

C. Molecular simulation

Monte Carlo molecular simulations, based on the coarse-grained bead-spring model, were used to gain insight into the morphological evolution inside the film, as described previously.^{14,16} The block copolymers were represented as n Gaussian chains and each chain was composed of N beads and $N-1$ springs. The beads of types $K=A$ and $K=B$ represented PMMA and PS, respectively. The position of the bead j in chain i was denoted as $r_{i,j}$. The length of the springs, or bond length, $b_{i,j}=|r_{i,j}-r_{i,j+1}|$. For a block copolymer melt at temperature T and in volume V , the Hamiltonian H was given by

$$\frac{H}{k_B T} = \frac{3}{2} \sum_{i=1}^n \sum_{j=1}^{N-1} \frac{N-1}{R_e^2} b_{i,j}^2 + \sqrt{N} \int_V \frac{d^3 r}{R_e^3} \left[\chi N \phi_A \phi_B + \frac{\kappa N}{2} (1 - \phi_A - \phi_B)^2 \right], \quad (1)$$

where k_B is the Boltzmann constant, R_e^2 is the mean squared end-to-end distance of an ideal chain, ρ_o is the bead density, and $\sqrt{N} = \rho_o R_e^3 / N$. The local densities ϕ_K are the bead compositions in a grid. χN and κN are the Flory–Huggins interaction and the incompressible interaction, respectively. To model the block copolymers in thin films, the chains are confined between two hard walls. The top wall is neutral, while the bottom wall has chemically patterned stripes, $S=s$ for PMMA wetting stripes or b for PS wetting stripes, with a potential, U_S^K , to bead $K=A$ or B defined as

$$\frac{U_S^K}{k_B T} = - \frac{\Lambda_S^K}{d_S / R_e} \exp \left[- \frac{z^2}{2 d_S^2} \right], \quad (2)$$

in which z is the distance of the bead from the chemically patterned surface, and Λ_S^K and d_S are the strength and range of interaction between substrate S and bead K , respectively. To model the system used in our experiments, we chose $\chi N = 36.7$, $\kappa N = 50$, $\sqrt{N} = 128$, and a simulation box size of $4L_o \times 2L_o \times L_o$.

III. RESULTS AND DISCUSSION

To capture the dynamics of block copolymer density multiplication on chemically patterned surfaces, a series of samples was annealed at 240 °C for various times ranging from 10 min to 64 h after ramping from 40 to 240 °C for 6 min. Figure 2 presents the top-down SEM images that show the morphological behavior of P(S-*b*-MMA) on the free surface during directed assembly with density multiplication. The corresponding fast Fourier transform (FFT) patterns are

FIG. 2. Top-down SEM images of thin films of P(S-*b*-MMA) annealed at 240 °C for various times [(a)–(g) show images of block copolymer annealed for 10 min, 30 min, 1 h, 2 h, 4 h, 16 h, and 64 h, respectively] on chemical patterns designed for density multiplication and (h) for 10 min on chemical patterns without density multiplication. The chemically patterned lines on the PS brush run from top to bottom in the images. The natural period of block copolymer, L_o , was 47.7 nm, and the pattern period, L_s , was 100 nm ($\approx 2L_o$). PS appears light and PMMA appears dark. Each image represents an area of $2 \times 2 \mu\text{m}^2$.

shown in the insets of the SEM images. After 10 min, the P(S-*b*-MMA) formed discrete dotlike PS domains in a matrix of PMMA on the free surface. The PS domains on the free surface were more or less aligned along the chemical patterned stripes. After 30 min, the dotlike PS domains gradually coalesced into linear domains (highlighted in solid circle) that were not in full registration with the underlying chemical pattern. In some areas, the block copolymer formed 100 nm periodic stripes along the direction of the chemical pattern stripes (highlighted in dashed circle). As we increased the annealing time to 1 h, part of the block copolymer film formed periodic linear domains that were in full registration with the underlying chemical pattern and multiply the feature density on the chemical pattern, yet most areas of the film remained dotlike domains or linear domains. Upon further annealing to 2 h, the area of periodic linear domains that were in registration with the chemical pattern expanded and the rest of the film formed short-range-ordered PS domains perpendicular to the direction of chemical patterns. These short-range-ordered PS domains were morphologies trapped in a metastable state, similar to the PS-dot structure observed previously.¹⁶ Longer annealing times eliminated the regions that had the metastable structures, and the block copolymer formed long-range, ordered, periodic lamellae along the direction of chemical patterns with the domains oriented perpendicular to the substrate. A comparison of these top-down SEM images with the compositional averages obtained from previously reported molecular simulations showed a remarkable agreement between the experiments and simulations.¹⁶

In contrast to previous analyses of directed assembly on a one-to-one chemical pattern, in which perfect assembly at 230 °C was achieved in a matter of minutes,³⁵ the block copolymer films annealed for 16 h in this work still had defective areas and reached perfect assembly after 64 h. For a direct comparison, chemical patterns with periods of 50 and 100 nm were fabricated on the same sample that was annealed at 240 °C for 10 min. After the annealing, the

FIG. 3. (Color online) SAXS patterns of the *in situ* annealing of P(S-*b*-MMA) on chemically patterned surfaces designed for density multiplication. The temperature was ramped from 40 to 240 °C for 6 min and held at 240 °C afterward. The scattering peak characteristic of 100 nm spacing appeared in the pattern of $t=30$ min and was about to disappear in the pattern of $t=60$ min. The dark rectangle in the $t=60$ min pattern is an empty area between two adjacent detector modules. The bright lines across the patterns are scattering noise from the scratches on the sample that were used to locate the pattern areas.

block copolymer on a 50 nm chemical pattern achieved perfect assembly in 10 min, while that on a 100 nm chemical pattern had only dotlike PS domains, indicating that directed assembly on a one-to-one chemical pattern had much faster dynamics than that with density multiplication.

FFT of the SEM images were only representative of the morphologies on the free surface as a result of the limited probe depth of top-down SEM. More importantly, the block copolymer morphologies in the interior of the films were different from that at the free surface during the dynamic evolution process, and thus the SAXS and FFT results were not directly comparable in the determination of a dynamic behavior. SAXS in transmission mode, which probed the entire block copolymer film, could give volume-averaged reciprocal space information to determine the dynamics. The progression of P(S-*b*-MMA) morphology during the directed assembly with density multiplication on a chemical pattern was analyzed by SAXS. Due to practical and technical issues, the SAXS was performed on a heating stage in air atmosphere, and *in situ* data with annealing time from 10 min to 1 h were collected. The same heating ramp profile from 40 to 240 °C for 6 min was applied before the annealing. The SAXS patterns obtained from the P(S-*b*-MMA) films during the annealing process are shown in Fig. 2, and

FIG. 4. SAXS spectra of P(S-*b*-MMA) directed assembly with density multiplication on chemically patterned surfaces for various annealing times, as shown in the graph. The temperature was ramped from 40 to 240 °C for 6 min and held at 240 °C for ~60 min. The first-order scattering peak of 100 nm spacing appeared at $t=20$ min and disappeared at $t=24$ h. The spectra are offset, and only the first characteristic peaks are plotted for clarity. The spectra for times less than 1 h were acquired *in situ*, and those for 1 and 24 h spectra are *ex situ*. The first-order characteristic scattering peak at 100 nm appeared at $t=20$ min and disappeared at $t=24$ h. The unit of the intensity is arbitrary.

the corresponding SAXS spectra along the scattering peak direction are plotted in Fig. 3. The SAXS spectra could be plotted azimuthally, which have similar profiles to the spectra along the scattering peak direction, but the characteristic intensity at the scattering peaks are much less pronounced as a result of averaging over pixels without much scattering intensities. For clarity, the spectra were collected along the scattering peak direction, and the positions of the first characteristic peaks of the 50 and 100 nm spacings were highlighted by arrows on the patterns (Fig. 3) and the spectra (Fig. 4). Initially, no scattering peak was observed, indicating that the block copolymer was disordered. The scattered stripes on the pattern were attributed to the noise from the scratches that were used to find the areas of interest. After annealing for 10 min, the SAXS spectra showed a first-order scattering peak at $q=0.01255 \text{ Å}^{-1}$, characteristic of lamellae with a periodic spacing of 50 nm. The appearance of the distinct scattering peaks was due to the directed assembly on the predefined chemical patterns. On unpatterned areas, the block copolymer domains had no preference in any direction, and ring patterns were observed. It should be noted that even though no fingerprintlike structure was observed on the free surface, block copolymer microphase separation occurred inside the film, resulting in a ringlike scattering pattern. On the chemically prepatterned surface, the block copolymer domains preferred to form lamellae along the patterned stripes, and distinct scattering peaks, instead of a ring pattern, were observed. The characteristic peak at 50 nm was present, albeit with different magnitudes, throughout the annealing process. After 20 min, the block copolymer exhibited a scattering peak at $q=0.00620 \text{ Å}^{-1}$ in the pattern, corresponding to a periodic spacing of 100 nm. The intensity of this scattering peak increased until $t=30$ min, then decreased as t further increased, and became indistinguishable after 24 h of annealing. The appearance and disappearance of the scattering peak of 100 nm indicated that the dynamics of directed assembly

FIG. 5. (Color online) Cross-sectional average compositions obtained from steps of a Monte Carlo simulation of directed assembly of P(S-*b*-MMA) with density multiplication. The chemical pattern and the scale bar are illustrated at the bottom. The period of the chemical pattern is 100 nm, and the width of PMMA wetting stripe is 25 nm.

of block copolymer with density multiplication was complex, compared with that on a one-to-one chemical pattern ($L_s = L_o$).³¹ The *in situ* ($t < 1$ h) scattering intensity of the first-order characteristic peak of 50 nm decreased continuously. We attributed this to the degradation of P(S-*b*-MMA) by the x rays.³⁴

In addition to the top-down SEM, which revealed the block copolymer morphologies on the free surface, and SAXS, which provided volume-average information through the film, we also used molecular simulation to further gain insights into the three-dimensional structure of the block copolymers in thin films. We used Monte Carlo molecular simulations to investigate the morphology evolution inside the film of the block copolymer during density multiplication on a chemical pattern with $L_s = 2L_o$. Figure 5 shows the average composition of a $2L_o$ -thick cross-section slice of the film as a function of the number of steps in the Monte Carlo simulation, with blue and red (black and grey in hard copy) representing PS and PMMA, respectively. The corresponding chemical pattern is illustrated at the bottom, with light blue and light red (black and grey in hard copy) representing PS and PMMA wetting surfaces, respectively.

The progression of the Monte Carlo simulation (Fig. 5) shows the evolution of the three-dimensional structures that could give rise to the SAXS spectra and the metastable morphology in the top-down SEM images we observed. At the beginning of the simulation (zero steps), the block copolymer was in a disordered state. PS and PMMA were randomly distributed throughout the film and there was no significant phase separation. After 100 Monte Carlo steps, evidence of microphase separation began to appear, with the block copolymer forming a weakly ordered, periodic structure. PMMA domains wet the PMMA wetting stripes of the chemical pattern (bottom left and center). The diffuse domains that were evident in the simulation had a spacing of roughly $50 \text{ nm} = L_s/2 \approx L_o$, matching the observation from SAXS, which had a first-order characteristic scattering peak corresponding to a 50 nm spacing. At 250 and 500 Monte Carlo steps, the block copolymer morphology evolved into more distinct domains, albeit with a complicated structure with a mixture of domain spacings. The domains had a spacing of 50 nm at the interface with the chemical pattern, indicating an interpolated structure given $L_s = 100 \text{ nm}$. However, the interpolated structure at the chemical pattern interface did not propagate perpendicularly through the entire film. Some of the block copolymer domains had a spacing of 100 nm along the direction perpendicular to the patterned stripes, as highlighted by the arrow in Fig. 5. As a result, the SAXS spectrum along the scattering peak direction, which probed the spacing parallel to the substrate and perpendicular to the patterned stripes, would detect both the 100 and 50 nm spacings, in agreement with the two SAXS peaks shown for $20 \text{ min} < t < 1 \text{ h}$ in Fig. 4. In the 500 step simulation, the interpolated domains at the substrate have progressed further toward the center of the film than in the 250 step simulation. As a result, SAXS would detect more horizontal spacing at 50 nm, and less spacing at 100 nm, in agreement with the SAXS results that showed a decrease in the 100 nm peak. The morphology on the right is reminiscent of the metastable PS-dot morphology on a weakly preferential background from previous simulations,¹⁶ in agreement with the observation from the top-down SEM images that the block copolymers could be trapped in a metastable morphology before reaching equilibrium. After 2500 steps, the interpolated domains at the substrate propagated toward the free surface of the film such that the 100 nm spacing that existed in the interior of the film in shorter simulations disappeared, and only the 50 nm spacing remained in the film. This simulation result corresponded to the disappearance of the scattering peak at $q = 0.00620 \text{ \AA}^{-1}$, characteristic of 100 nm spacing, in the SAXS results. Eventually, the block copolymer formed lamellae perpendicular to the substrate and reached the equilibrium morphology, in agreement with previous work¹⁶ and similar to previous simulations of one-to-one directed assembly.³⁰

The dynamics of directed assembly of block copolymers on chemical patterns with $L_s/L_o = 2$ had some similarities, and some differences, from the dynamics of directed assembly on chemical patterns with $L_s/L_o = 1$. First, the appearance

and disappearance of the scattering peak at 100 nm (L_s) was a unique behavior of directed assembly of block copolymer with density multiplication, and it was not observed in directed assembly on one-to-one chemical patterns.³¹ Second, for both one-to-one directed assembly and for directed assembly with density multiplication ($L_s/L_o=1$ and $=2$, respectively), dotlike PS domains were observed at the free surface during the early stage of annealing, then coalesced to form linear domains, and eventually, with longer annealing times, these linear domains were ordered and registered with the chemical pattern. Without density multiplication, the dynamics of directed assembly consisted mainly of the coalescence of the domains into linear domains and the registration of the linear domains with the underlying chemical pattern.³⁰ With density multiplication, however, the block copolymers could be trapped in a metastable state, likely caused by a localized energy minima.¹⁶ The dynamics not only consisted of the coalescence of domains into linear domains and the registration of the linear domains with chemical pattern, but also included the removal of the dynamically trapped metastable morphology. Finally, it should be noted that due to the higher annealing temperature, the directed assembly of block copolymer with density multiplication in this report reached equilibrium faster than that without density multiplication as reported previously,³⁰ yet a direct comparison on the same sample and at same annealing temperature demonstrated that directed assembly with density multiplication had much slower dynamics than that without density multiplication. In addition, the dynamics of block copolymer density multiplication would be faster if a lower molecular weight block copolymer⁷ or higher annealing temperature³⁵ was used.

IV. CONCLUSION

This work is the first investigation of the dynamics of the directed assembly of block copolymers with density multiplication. We used SEM to obtain the top-down views of the morphologies at the free surfaces, SAXS to extract the volume-averaged reciprocal space information, and molecular simulation to provide three-dimensional insights into the morphology evolution inside the block copolymer films during density multiplication. It was observed with SEM that the block copolymer formed morphologies from discrete polystyrene domains to linear domains not fully in registration with the underlying chemical pattern, to linear domains with metastable morphologies, and to perpendicular lamellae in registration with the underlying chemical pattern. The dynamics of block copolymer density multiplication was a combination of the alignment of linear domains to the underlying chemical pattern and the removal of metastable morphologies. In contrast to the directed assembly of block copolymer on a one-to-one chemical pattern without density multiplication, at the early stages of density multiplication, SAXS revealed unique scattering peaks that corresponded to the period of the chemical pattern, and the peaks disappeared at a longer annealing time. Molecular simulations were also used to understand the three-dimensional morphological evolution of the block copolymers during the directed assembly.

This dynamic investigation of block copolymer density multiplication can offer a better understanding of the block copolymer behavior on chemically patterned surfaces and can give insight for the applications of the block copolymer directed assembly.

ACKNOWLEDGMENTS

The XIL patterning and SAXS measurements were performed at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland. This work was supported by the Semiconductor Research Corporation (SRC) and NSF through the UW-Nanoscale Science and Engineering Center (NSEC) (Grant No. DMR0425880).

- ¹J. Y. Cheng, C. A. Ross, H. I. Smith, and E. L. Thomas, *Adv. Mater.* **18**, 2505 (2006).
- ²M. P. Stoykovich, H. Kang, K. C. Daoulas, G. Liu, C. C. Liu, J. J. de Pablo, M. Mueller, and P. F. Nealey, *ACS Nano* **1**, 168 (2007).
- ³M. P. Stoykovich and P. F. Nealey, *Mater. Today* **9**, 20 (2006).
- ⁴E. W. Edwards, M. F. Montague, H. H. Solak, C. J. Hawker, and P. F. Nealey, *Adv. Mater.* **16**, 1315 (2004).
- ⁵S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, and P. F. Nealey, *Nature (London)* **424**, 411 (2003).
- ⁶E. W. Edwards, M. Muller, M. P. Stoykovich, H. H. Solak, J. J. de Pablo, and P. F. Nealey, *Macromolecules* **40**, 90 (2007).
- ⁷J. Y. Cheng, C. T. Rettner, D. P. Sanders, H. C. Kim, and W. D. Hinsberg, *Adv. Mater.* **20**, 3155 (2008).
- ⁸K. C. Daoulas, M. Muller, M. P. Stoykovich, H. Kang, J. J. de Pablo, and P. F. Nealey, *Langmuir* **24**, 1284 (2008).
- ⁹S. M. Park, Y. H. La, P. Ravindran, G. S. W. Craig, N. J. Ferrier, and P. F. Nealey, *Langmuir* **23**, 9037 (2007).
- ¹⁰M. P. Stoykovich, M. Muller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, and P. F. Nealey, *Science* **308**, 1442 (2005).
- ¹¹G. M. Wilmes, D. A. Durkee, N. P. Balsara, and J. A. Liddle, *Macromolecules* **39**, 2435 (2006).
- ¹²S. Xiao, X. Yang, S. Park, D. Weller, and T. P. Russell, *Adv. Mater.* **21**, 2516 (2009).
- ¹³I. Bita, J. K. W. Yang, Y. S. Jung, C. A. Ross, E. L. Thomas, and K. K. Berggren, *Science* **321**, 939 (2008).
- ¹⁴R. Ruiz, H. M. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. de Pablo, and P. F. Nealey, *Science* **321**, 936 (2008).
- ¹⁵Y. Tada, S. Akasaka, M. Takenaka, H. Yoshida, R. Ruiz, E. Dobisz, and H. Hasegawa, *Polymer* **50**, 4250 (2009).
- ¹⁶F. A. Detcheverry, G. L. Liu, P. F. Nealey, and J. J. de Pablo, *Macromolecules* **43**, 3446 (2010).
- ¹⁷G. L. Liu, C. S. Thomas, G. S. W. Craig, and P. F. Nealey, *Adv. Funct. Mater.* **20**, 1251 (2010).
- ¹⁸G. Liu, M. P. Stoykovich, S. Ji, K. O. Stuen, G. S. W. Craig, and P. F. Nealey, *Macromolecules* **42**, 3063 (2009).
- ¹⁹C. Harrison, D. H. Adamson, Z. D. Cheng, J. M. Sebastian, S. Sethuraman, D. A. Huse, R. A. Register, and P. M. Chaikin, *Science* **290**, 1558 (2000).
- ²⁰L. Tsarkova, A. Knoll, and R. Magerle, *Nano Lett.* **6**, 1574 (2006).
- ²¹L. Tsarkova, A. Horvat, G. Krausch, A. V. Zvelindovsky, G. J. A. Sevink, and R. Magerle, *Langmuir* **22**, 8089 (2006).
- ²²V. Olszowska, M. Hund, V. Kuntermann, S. Scherdel, L. Tsarkova, and A. Boker, *ACS Nano* **3**, 1091 (2009).
- ²³A. Horvat, G. J. A. Sevink, A. V. Zvelindovsky, A. Krekhov, and L. Tsarkova, *ACS Nano* **2**, 1143 (2008).
- ²⁴S. Rehse, K. Mecke, and R. Magerle, *Phys. Rev. E* **77**, 051805 (2008).
- ²⁵R. A. Farrell, T. G. Fitzgerald, D. Borah, J. D. Holmes, and M. A. Morris, *Int. J. Mol. Sci.* **10**, 3671 (2009).
- ²⁶W. H. Li, F. Qiu, Y. L. Yang, and A. C. Shi, *Macromolecules* **43**, 1644 (2010).
- ²⁷J. Hahn and S. J. Sibener, *J. Chem. Phys.* **114**, 4730 (2001).
- ²⁸J. Hahn, W. A. Lopes, H. M. Jaeger, and S. J. Sibener, *J. Chem. Phys.* **109**, 10111 (1998).
- ²⁹M. R. Hammond, E. Cochran, G. H. Fredrickson, and E. J. Kramer,

- Macromolecules **38**, 6575 (2005).
- ³⁰E. W. Edwards, M. P. Stoykovich, M. Müller, H. H. Solak, J. J. De Pablo, and P. F. Nealey, J. Polym. Sci., Part B: Polym. Phys. **43**, 3444 (2005).
- ³¹K. O. Stuen *et al.*, J. Vac. Sci. Technol. B **26**, 2504 (2008).
- ³²S. X. Ji, G. L. Liu, F. Zheng, G. S. W. Craig, F. J. Himpsel, and P. F. Nealey, Adv. Mater. **20**, 3054 (2008).
- ³³G. L. Liu, S. X. Ji, K. O. Stuen, G. S. W. Craig, P. F. Nealey, and F. J. Himpsel, J. Vac. Sci. Technol. B **27**, 3038 (2009).
- ³⁴E. Kim, H. Ahn, D. Y. Ryu, J. Kim, and J. Cho, Macromolecules **42**, 8385 (2009).
- ³⁵A. M. Welander, H. M. Kang, K. O. Stuen, H. H. Solak, M. Muller, J. J. de Pablo, and P. F. Nealey, Macromolecules **41**, 2759 (2008).