

Bending Soft Block Copolymer Nanostructures by Lithographically Directed Assembly

Gregg M. Wilmes,^{†,‡} David A. Durkee,[†]
Nitash P. Balsara,^{*,†,‡,§} and J. Alexander Liddle^{*,‡}

Department of Chemical Engineering, University of California, Berkeley, California 94720, and Materials Sciences and Energy and Environmental Technologies Divisions, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received December 11, 2005

Revised Manuscript Received February 14, 2006

Many strategies for synthesizing nanostructures such as dots, wires, rods, belts, and capsules have been developed in recent years.^{1–15} Arrangement of these on surfaces and within thin films may enable the development of applications ranging from fuel cells to optoelectronic devices. Many of these applications require that the nanostructures be organized into specific patterns. Unfortunately, strategies for controlling their organization are significantly less developed than those for their synthesis. In pioneering work, Nealey and co-workers studied the assembly of block copolymer nanostructures on lithographically patterned substrates.^{5,16,17} They showed that matching the period of a striped lithographic pattern with the domain spacing of the polymer leads to near-perfect alignment of the lamellae to the stripes. In this case, the equilibrium morphology of the block copolymer matches the striped pattern. This opens up the possibility of creating complex patterns in polymer thin films with precisely placed nanostructures by the relatively simple process of spin-casting block copolymers on patterned substrates. Many applications will, however, require the presence of different kinds of patterns within the same film, and a thorough understanding of the energetics of polymer assembly in the films will be necessary for the design of complex patterns. If each pattern requires the use of a different copolymer system with a particular equilibrium morphology, then the patterns that can be created by lithographically directed block copolymer self-assembly will be extremely limited. The purpose of this paper is to examine the extent to which patterns with different curvatures can be created within the same block copolymer thin film. In particular, we show that the block copolymer lamellae conform to patterns with radii of curvature equal to the equilibrium domain spacing.

Following Nealey et al.,¹⁷ hydroxyl-terminated polystyrene (PS-OH) with number-averaged molecular weight $M_n = 5.1$ kg/mol was synthesized using standard anionic polymerization techniques, capped with 1 equiv of ethylene oxide, and terminated with methanol. A 40 nm film of PS-OH was applied to the oxide coating of a piranha-cleaned silicon wafer by spin-coating from a toluene solution. After annealing under N_2 for 2 days at 140 °C to form a polystyrene brush, unreacted polymer was removed by rinsing in hot toluene with sonication. The brush was patterned with electron-beam lithography using a 30 nm film of poly(methyl methacrylate) (PMMA) ($M_n = 950$ kg/mol) as a photoresist. Several identical patterns were written

into the brush by electron-beam lithography, with doses varying from 673 to 1200 $\mu\text{C}/\text{cm}^2$. The PMMA was developed in a 1:3 mixture of methylisobutylketone and isopropanol at 21 °C. The exposed regions of the brush were chemically modified by reactive ion etching with an O_2/Ar plasma, after which the remaining PMMA resist was removed by rinsing in CH_2Cl_2 .

We focus on a 2 μm diameter pattern with a 12 nm radius circle of unmodified polystyrene at the center and a series of 24 nm wide concentric rings of plasma-etched and unmodified polystyrene emanating from the center. We also present results obtained from 20 $\mu\text{m} \times 20 \mu\text{m}$ arrays of 24 nm wide parallel lines.

A symmetric poly(styrene-*block*-methyl methacrylate) (PS–PMMA) copolymer with number-averaged molecular weight $M_n = 104$ kg/mol was purchased from Polymer Source, Inc. The volume fraction of the poly(methyl methacrylate) block was 0.49, and the equilibrium morphology of the polymer in the bulk, as measured by small-angle neutron scattering, is a lamellar phase with a period of 49 nm. The unperturbed radius of gyration of the copolymer, R_g , is estimated to be 15 nm.¹⁸ A 49 nm film of the PS–PMMA copolymer was coated on the patterned substrates described above and annealed under N_2 for 3 days at 195 °C.

Three observations lead us to suspect that the energetic cost of lamellar curvature is relatively small. First, the well-known fingerprint patterns exhibited by these types of diblocks on neutral surfaces contain many regions of high curvature.^{5,19} Second, small radius structures have been observed in cylindrically confined geometries.^{11,12} Third, we see extremely abrupt transitions in the orientation of lamellae between patterned and unpatterned regions: Figure 1 is a scanning electron microscopy (SEM) micrograph taken with a LEO FE-SEM operating at 2 keV, showing the result of annealing a diblock film on a brush patterned with parallel lines. As is the case in previous publications,^{5,16,17} the thin dark lines in the micrographs (Figures 1 and 3) represent the PMMA block. In the unpatterned regions, the block copolymer lamellae are parallel to the substrate. This is due to the presence of the PS block at both polymer/air and polymer/substrate interfaces (symmetric wetting). The film outside the patterned regions is smooth because the thickness of the film matches the domain spacing of the block copolymer.²⁰ In the patterned region the block copolymer lamellae are oriented perpendicular to the substrate. The image in Figure 1 indicates that the transition from perpendicular to parallel lamellae occurs over a distance comparable to, if not less than, the domain spacing.

The free energy penalty for bending a lamellar block copolymer along a circle of radius R_c in the small curvature limit may be estimated as²¹

$$\Delta f_c = \frac{1}{2} K_1 \left(\frac{1}{R_c} \right)^2 \quad (1)$$

where Δf_c is the free energy penalty per chain and K_1 is the splay elastic coefficient of the lamellar phase. In the strong segregation limit, K_1 is given by^{22,23}

$$K_1 = \frac{\pi^2}{1024} \frac{L^4 k_B T}{N a^2} \quad (2)$$

where L is the lamellar domain spacing, k_B is the Boltzmann constant, T is temperature, N is the polymerization index, and

[†] University of California, Berkeley.

[‡] Materials Sciences Division, Lawrence Berkeley National Laboratory.

[§] Energy and Environmental Technologies Division, Lawrence Berkeley National Laboratory.

* Corresponding authors. E-mail: nbalsara@berkeley.edu, jaliddle@lbl.gov.

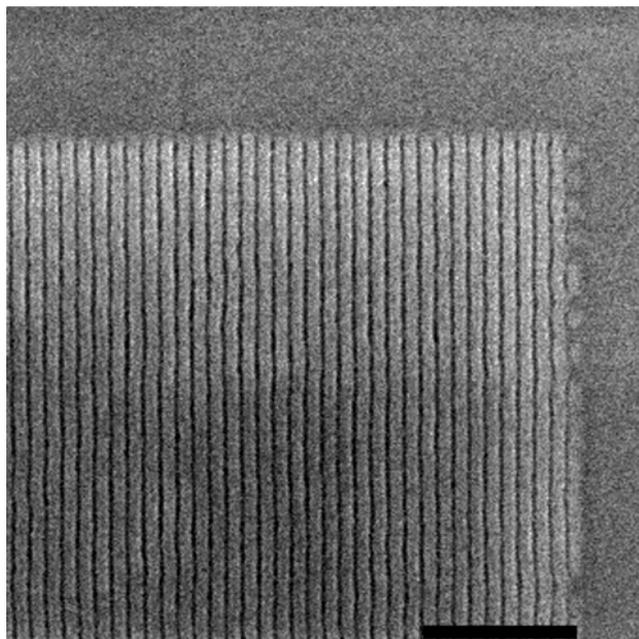


Figure 1. SEM micrograph of poly(styrene-*block*-methyl methacrylate) diblock copolymer on a silicon wafer with 48 nm period patterned into the polystyrene brush. Note the abrupt transition from perpendicular to parallel lamellae at the pattern edge. Scale bar is 500 nm.

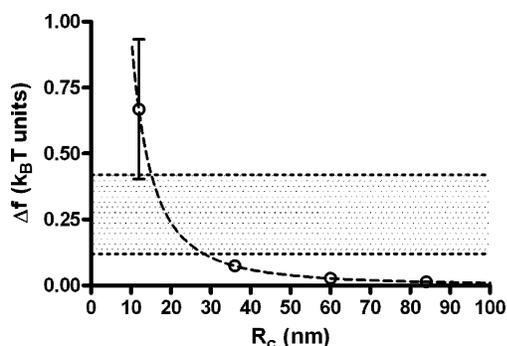


Figure 2. Free energy penalty per chain in units of $k_B T$ of bending a block copolymer lamellar phase to conform to a circle of radius R_c . The shaded region shows the range of the calculated interfacial energy gain between the patterned brush and the diblock copolymer (eq 4).

a is the statistical segment length. For our system, L is 49 ± 1 nm, a is 0.52 ± 0.05 nm,^{24,25} and N is 1068 ± 50 (both N and a are based on a reference volume, v , of 100 \AA^3). Thus

$$\frac{\Delta f_c}{k_B T} = 96 \text{ nm}^2 \left(\frac{1}{R_c} \right)^2 \quad (3)$$

The validity of the approximations used to obtain eq 3 increases with increasing R_c . The bending free energy of our PS-PMMA chains in units of $k_B T$ is plotted vs R_c in Figure 2.²⁶ It is clear that these types of block copolymer nanostructures are inherently soft due to the entropic elasticity of the blocks.

Figure 3 shows a SEM micrograph of the PS-PMMA block copolymer film on the patterned concentric circles. The pattern, wherein the radius of curvature changes from 12 to 1000 nm in a space of 1000 nm, is far removed from the equilibrium morphology of any block copolymer. Despite this, the block copolymer chains conform to the underlying pattern. Even the central circle, which was patterned to be 24 nm in diameter, is faithfully reproduced in the block copolymer film as a single PS cylinder surrounded by PMMA. For the smallest circle in our pattern, the per-chain bending energy is $0.67 \pm 0.26 k_B T$ units.

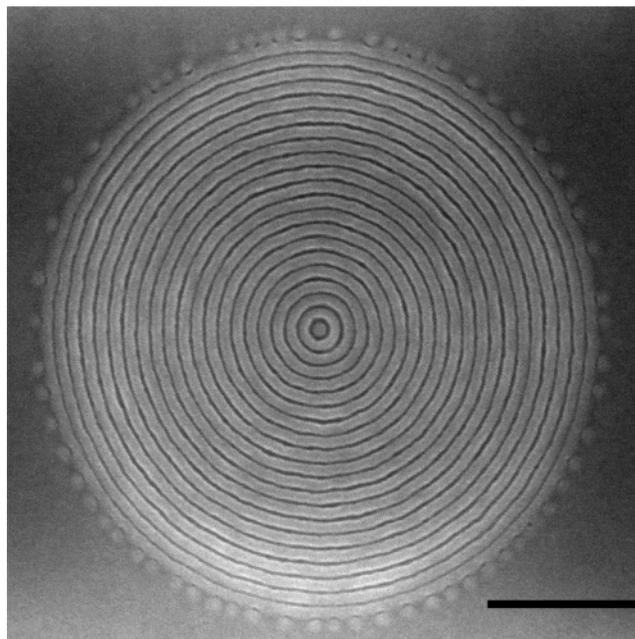


Figure 3. SEM micrograph of poly(styrene-*block*-methyl methacrylate) diblock copolymer on a silicon wafer with concentric circles patterned into the polystyrene brush. Scale bar is 500 nm.

For the patterns in the polymer brush to be transferred to the block copolymer, the favorable interactions between the brush and diblock must be greater than the free energy cost for bending the lamellae. For a randomly arranged PS-PMMA film on a patterned brush of 50% duty cycle, on average half of the diblock PMMA segments will be in contact with the PS brush, and half of the diblock PS segments at the interface will be contacting the plasma-treated brush. In a film with perfect registry between the block copolymer and the patterned brush, all PS segments of the diblock will be contacting the polymer brush, and all PMMA segments will be contacting the plasma-treated brush. Assuming that the plasma-treated regions of the brush are chemically equivalent to PMMA, the difference in interfacial energy between these two arrangements on a per chain basis, Δf_{int} , is given by²⁷

$$\Delta f_{\text{int}} = \frac{\gamma_{\text{MS}} N v}{2t} \quad (4)$$

With the interfacial energy between PS and PMMA, $\gamma_{\text{MS}} = 0.9 \pm 0.5 \text{ erg/cm}^2$,^{28,29} and polymer film thickness, $t = 49 \text{ nm}$, $\Delta f_{\text{int}} = 0.27 \pm 0.15 k_B T$ units, which is comparable in magnitude to the curvature energy for the smallest circle in Figure 3.

In related work, Nealy et al. showed that bent block copolymer lamellae could be obtained by lithographically directed assembly if polystyrene and poly(methyl methacrylate) homopolymers were added to the PS-PMMA diblock copolymer.¹⁷ While this approach does lead to faithfully patterned block copolymer films,³⁰ the presence of homopolymers leads to an increase in the natural domain spacing by a factor of about 2. Our work demonstrates that the addition of homopolymers is not necessary for bending block copolymer nanostructures.

In summary, the lithographically directed assembly of block copolymers can be successfully applied even if the desired patterns are very different from the equilibrium morphology. Our work establishes the possibility of obtaining lithographically directed patterns with widely different curvatures within close proximity in a block copolymer thin film. To our knowledge,

the inner circle in Figure 3 represents the smallest curved feature that has been faithfully located and reproduced in a polymer film.

Acknowledgment. This work was supported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under the Department of Energy Contract No. DE-AC02-05CH11231.

Supporting Information Available: Scanning electron micrographs of self-assembled block copolymer thin films on concentric circle patterns drawn over a range of electron beam dose.³⁰ This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Harrison, C.; Adamson, D. H.; Cheng, Z. D.; Sebastian, J. M.; Sethuraman, S.; Huse, D. A.; Register, R. A.; Chaikin, P. M. *Science* **2000**, *290*, 1558–1560.
- Kim, D. H.; Kim, S. H.; Lavery, K.; Russell, T. P. *Nano Lett.* **2004**, *4*, 1841–1844.
- Segalman, R. A. *Mater. Sci. Eng. R* **2005**, *48*, 191–226.
- Fasolka, M. J.; Mayes, A. M. *Annu. Rev. Mater. Res.* **2001**, *31*, 323–355.
- Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. *Nature (London)* **2003**, *424*, 411–414.
- Thomas, E. L.; Reffner, J. R.; Bellare, J. J. *Phys., Colloq.* **1990**, *51*, C7, 363–374.
- Angelescu, D. E.; Waller, J. H.; Adamson, D. H.; Deshpande, P.; Chou, S. Y.; Register, R. A.; Chaikin, P. M. *Adv. Mater.* **2004**, *16*, 1736.
- Rockford, L.; Liu, Y.; Mansky, P.; Russell, T. P.; Yoon, M.; Mochrie, S. G. J. *Phys. Rev. Lett.* **1999**, *82*, 2602–2605.
- Xu, T.; Zhu, Y. Q.; Gido, S. P.; Russell, T. P. *Macromolecules* **2004**, *37*, 2625–2629.
- Xiang, H. Q.; Lin, Y.; Russell, T. P. *Macromolecules* **2004**, *37*, 5358–5363.
- Xiang, H.; Shin, K.; Kim, T.; Moon, S. I.; McCarthy, T. J.; Russell, T. P. *Macromolecules* **2005**, *38*, 1055–1056.
- Xiang, H.; Shin, K.; Kim, T.; Moon, S. I.; McCarthy, T. J.; Russell, T. P. *Macromolecules* **2004**, *37*, 5660–5664.
- Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401–1404.
- Cheng, J. Y.; Mayes, A. M.; Ross, C. A. *Nat. Mater.* **2004**, *3*, 823–828.
- Li, H.-W.; Huck, W. T. S. *Nano Lett.* **2004**, *4*, 1633–1636.
- Edwards, E. W.; Montague, M. F.; Solak, H. H.; Hawker, C. J.; Nealey, P. F. *Adv. Mater.* **2004**, *16*, 1315–1319.
- Stoykovich, M. P.; Müller, M.; Kim, S. O.; Solak, H. H.; Edwards, E. W.; de Pablo, J. J.; Nealey, P. F. *Science* **2005**, *308*, 1442–1446.
- Leibler, L. *Macromolecules* **1980**, *13*, 1602–1617.
- Mansky, P.; Russell, T. P.; Hawker, C. J.; Pitsikalis, M.; Mays, J. *Macromolecules* **1997**, *30*, 6810–6813.
- Peters, R. D.; Yang, X. M.; Kim, T. K.; Sohn, B. H.; Nealey, P. F. *Langmuir* **2000**, *16*, 4625–4631.
- de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Clarendon Press: Oxford, 1993.
- Wang, Z.-G.; Safran, S. A. *J. Chem. Phys.* **1991**, *94*, 679–687.
- Wang, Z.-G. *J. Chem. Phys.* **1994**, *100*, 2298–2309.
- Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639–4647.
- Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: New York, 1996; pp 335–340.
- The symbols in Figure 1 denote the radii of curvature of the circles corresponding to the unmodified polystyrene regions. The estimated errors were calculated using the uncertainties in the polymer parameters L , a , and N , given in the text and using an error in radius of curvature of ± 2 nm, the pixel size of the electron beam lithography tool.
- Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press Limited: London, 1985.
- Wu, S. *J. Phys. Chem.* **1970**, *74*, 632–638.
- Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
- Typical results obtained as a function of electron beam dosage are given in the Supporting Information. For the particular experiment shown there, the faithful reproduction of the concentric circles pattern requires dosages between 824 and 1100 $\mu\text{C}/\text{cm}^2$. In 70% of the experiments, we were able to find regions where the polymer film was faithfully patterned. The dosage range over which faithful reproduction of the pattern was observed, however, varied from experiment to experiment. In 30% of the experiments, only imperfect patterns were found at all locations on the polymer film. The failure of these experiments may be related to poor formation of the polymer brush layer, irregularities in the lithography or plasma etching, or polymer degradation during annealing. Experiments are underway to better understand and improve the reproducibility of the process.

MA0526443