

- [7] W. W. Lee, P. S. Ho, *MRS Bull.* **1997**, 22, 19.
- [8] *Handbook of Multilevel Metallization for Integrated Circuits* (Eds: S. R. Wilson, C. J. Tracy, J. L. Freeman, Jr), Materials, Technology, and Applications, Noyes Publications, Park Ridge, NJ **1993**.
- [9] P. G. Harison, *J. Organomet. Chem.* **1997**, 542, 141.
- [10] Ch. X. Zhang, F. Babonneau, C. Bonhomme, A. F. Yee, *J. Am. Chem. Soc.* **1998**, 120, 8380.
- [11] R. M. Laine, A. Sellinger, V. Chu, C. Viney, *J. Polym. Sci.: Part A, Polym. Chem.* **1994**, 32, 3069.
- [12] P. A. Agaskar, *Inorg. Chem.* **1991**, 30, 2707.
- [13] T. E. Gentle, A. R. Bassindale, *J. Inorg. Organomet. Polym.* **1995**, 5(3), 281.
- [14] G. Cerveau, R. J. P. Corriu, B. Dabien, *J. Mater. Chem.* **2000**, 10, 1113.
- [15] G. Cerveau, R. J. P. Corriu, *Coord. Chem. Rev.* **1998**, 178, 1051.
- [16] D. A. Loy, J. P. Carpenter, T. M. Alam, J. H. Small, K. J. Shea, *J. Am. Chem. Soc.* **1999**, 121, 5413.
- [17] Damage category of cross cutting based on EN ISO 2409. For check of adhesion of the film a grid system surface must be scratched on the film: with a sharp knife six parallel and six vertical lines are scratched at a distance of 1 mm into the surface. Then a tape is stuck over the grid system and taken off evenly. The surface can be evaluated to place the material in the appropriate damage category.
- [18] R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, 95, 1409.
- [19] H. S. Yang, S. Y. Choi, S. H. Hyun, H. H. Park, J. K. Hong, *J. Non-Cryst. Solids* **1997**, 221, 151.
- [20] Y. Abe, K. Kagayama, N. Takamura, T. Gunji, *Mater. Res. Soc. Symp. Proc.* **1999**, 565, 247.
- [21] C. Maddalon, K. Barla, E. Denis, C. Lair, E. Dehan, *Microelectron. Eng.* **2000**, 50, 33.
- [22] J. K. Lan, Y. L. Wang, Y. L. Wu, H. C. Liou, Y. L. Cheng, *Thin Solid Films* **2000**, 377, 776.
- [23] J. K. Lee, K. Char, H. W. Rhee, D. Y. Yoon, *Copolymer* **2001**, 42, 9085.
- [24] R. F. Cook, E. G. Liniger, D. P. Klaus, S. A. Cohen, *Mater. Res. Soc. Symp. Proc.* **1998**, 511, 31.
- [25] J. F. Remenar, C. J. Hawker, J. L. Hedrick, D. Y. Yoon, *Mater. Res. Soc. Symp. Proc.* **1998**, 511, 69.
- [26] S. J. Ding, P. F. Wang, D. W. Zhang, W. W. Lee, *Mater. Lett.* **2001**, 49, 154.
- [27] S. M. Kim, D. Y. Yoon, *Mater. Res. Soc. Symp. Proc.* **1998**, 511, 39.
- [28] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, 62, 7512.

A Rapid Route to Arrays of Nanostructures in Thin Films**

By Zhiqun Lin, Dong Ha Kim, Xiaodong Wu,
Laurie Boosahda, Daria Stone, Luanne LaRose, and
Thomas P. Russell*

Numerous self-assembling methods have been used to obtain well-ordered arrays of nanoscopic structures in thin films. However, to fully utilize the well-defined structures that are

produced, it is apparent that self-assembly processes alone are not sufficient. Rather, directed self-assembly is necessary where an external field is used to direct the orientation of structures formed.^[1–4] Diblock copolymers, polymers comprised of two chemically distinct chains covalently linked at one end, self-assemble into well-ordered morphologies ranging from spherical to cylindrical to lamellar, depending upon the volume fraction of the components. The size of the domains is dictated by the size of the molecules and, hence, is nanoscopic. In the bulk, mechanical shear can be used to control the spatial orientation of the domains,^[5–7] whereas in thin films, electric fields^[1–4] and controlled interfacial interactions^[8–18] have been used to this end. It is, also, possible to trap copolymers in a non-equilibrium state with a desired orientation by solvent-casting.^[17–21] However, producing well-ordered thin films can take hours to achieve or there are restrictions on the film thickness. Both present barriers to their end-use. Here, a very rapid route is described by which the cylindrical microdomains of an asymmetric diblock copolymer of polystyrene (PS) and polyethyleneoxide (PEO) denoted P(S-b-EO) can be oriented normal to the surface of a film over very large areas. Results are shown where, within seconds, arrays of nanoscopic cylindrical domains of PEO are produced in a glassy PS matrix in films with thickness several times the period of the copolymer. This was found over a wide range in molecular weight, allowing control over the size of the cylindrical domains and the areal density of the arrays. In addition, since PEO is water soluble, the oriented arrays of nanoscopic cylinders open a novel route towards water permeable membranes with well-defined channel sizes.

Shown in Figure 1 are phase atomic force microscopy (AFM) images of 25 K and 90 K P(S-b-EO) asymmetric block copolymers obtained after spin coating onto silicon oxide substrates. In both cases, arrays of nanoscopic, cylindrical domains of PEO are seen at the surface of the film. The average center to center distance of the cylindrical domains, λ_{C-C} , for the 25 K copolymer is 40 nm with an average cylinder diameter, D , of 24 nm. In the bulk $\lambda_{C-C} = 33.7$ nm, as measured by small angle X-ray scattering (SAXS). For the spin-coated film of the 90 K copolymer, $\lambda_{C-C} = 85$ nm with $D = 58$ nm. Bulk SAXS measurements of the 90 K copolymer were not possible due to instrumental resolution. From the results of the 25 K copolymer, λ_{C-C} for the spin-coated film is larger than that seen in the bulk, indicating, as would be expected, that the spin-coated films are trapped in a non-equilibrium state due to the high glass-transition temperature of the PS matrix. For both copolymers, the cylindrical PEO domains appear dark in the AFM phase images, indicating that PEO is softer than the PS matrix. Consequently, PEO has not crystallized upon spin coating.

Shown in Figure 2 are the height and phase images of a folded 25 K film (see Experimental). In the height image (Fig. 2a) both the top and bottom of the film appear flat, due to the expanded height scale of the image. However, a film thickness of 0.14 μm can easily be determined, in agreement with that measured by optical ellipsometry. The phase image

[*] Prof. T. P. Russell, Z. Q. Lin, Dr. D. H. Kim, Dr. X. D. Wu
Department of Polymer Science and Engineering
University of Massachusetts
Amherst, MA 01003 (USA)
E-mail: russell@mail.pse.umass.edu
L. Boosahda
Peck Middle School
Holyoke, MA 01040 (USA)
D. Stone
Chestnut Accelerated Middle School
Springfield, MA 01107 (USA)
L. LaRose
Greenfield Middle School
Greenfield, MA 01301 (USA)

[**] This work was funded by the National Science Foundation supported Materials Research Science and Engineering Center at the University of Massachusetts (DMR98-09365) and the Department of Energy, Office of Energy Sciences (DE-FG-96ER45612).

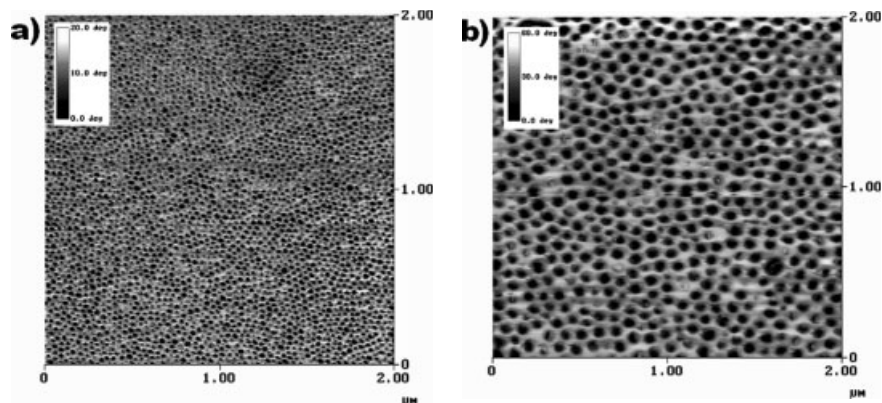


Fig. 1. AFM phase images of PS-b-PEO with cylindrical microdomains oriented normal to the film surface obtained after spin coating onto silicon substrate. a) 25K P(S-b-PEO) with a film thickness of 140 nm. b) 90 K P(S-b-PEO) with a film thickness of 150 nm. The phase scale is shown in the inset. Image sizes are $2 \mu\text{m} \times 2 \mu\text{m}$.

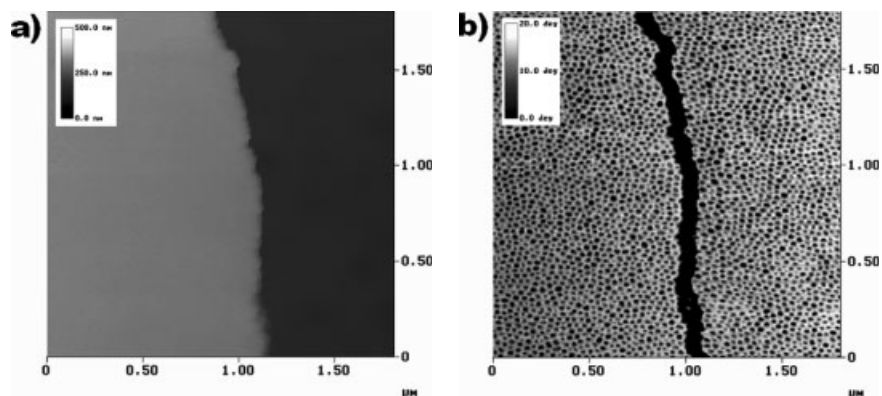


Fig. 2. AFM height (a) and phase (b) images of a folded 25 K P(S-b-PEO) thin film. The height and phase scales are shown in the inset. Image sizes are $1.8 \mu\text{m} \times 1.8 \mu\text{m}$.

(Fig. 2b) shows that the cylindrical PEO domains are present on both the top and bottom of the film after spin-coating and λ_{C-C} and D are identical for both surfaces. Similar results were obtained for the 90 K copolymer. This suggests that the cylindrical domains span the entire thickness of the film. Confirmation that this occurs is obtained from transmission electron microscopy. Shown in Figure 3 is a cross-sectional TEM image of a thin section of a 25 K film stained with RuO_4 . The lighter cylindrical domains of the PEO are seen to span across the entire film thickness. Thus, simply by spin coating, a film

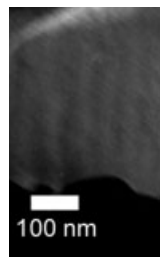


Fig. 3. Cross-sectional transmission electron microscopy image of a spin-coated, 25 K P(S-b-EO) film on a gold substrate after staining with RuO_4 . The PS domains are stained preferentially and appear dark.

of P(S-b-EO) is obtained containing an array of nanoscopic, cylindrical domains of PEO that span across the film.

As expected from the results of others,^[22–25] the PEO within the cylindrical domains crystallized. Shown in Figure 4a is an AFM phase image of the 90 K copolymer after extended annealing at room temperature. Crystallization of the PEO is evidenced by the enhancement of the phase within the cylindrical domains. Heating the sample to 165°C , well above the glass-transition temperature of the PS and the melting point of the PEO, produced a film that was featureless (Fig. 4b). Near the edges of the film, optical microscopy showed evidence of terracing of the film. These observations indicate that, at equilibrium, the cylindrical morphology orients parallel to the surface^[26] of the film due to preferential interactions of the PEO block with the substrate and the lower surface energy PS block ($\gamma_{\text{PS}} = 33 \text{ mN/m} < \gamma_{\text{PEO}} = 43 \text{ mN/m}$). The non-equilibrium structure of the copolymer achieved during spin coating can, however, be preserved by crosslinking the PS matrix with UV radiation. Figure 4c shows a spin-coated film that was initially cross-linked, then heated to 85°C for 3 days. As seen, the spin-coated structure is retained, whereas without crosslinking, it is lost, even under these mild conditions.

Since PEO is water soluble, while PS is not, it should be possible to preferentially swell the PEO domains while retaining the lateral structure of the film. Shown in Figure 5 are AFM height and phase images of a film of the 25 K copolymer after immersion in water for one day. The height image shows that the cylindrical domains are slightly higher than the surrounding PS matrix. The phase image in Figure 5b, on the other hand, shows that the cylindrical domains are much softer than the PS matrix. While quartz oscillator measurements are being performed to quantify the extent of water uptake, these results show that swelling has occurred and that a water-permeable membrane can be produced where the size of the channels can be controlled by the molecular weight of the copolymer.

A mechanism can be suggested by which spin coating can produce an array of cylindrical domains oriented normal to the surface. The preferential interactions of the blocks with the substrate and air surfaces would promote an orientation of the cylindrical microdomains parallel to the surface. The initially spin-coated copolymer film, however, is phase-mixed, as opposed to microphase-separated, due to the presence of benzene, a good solvent for both blocks. As the

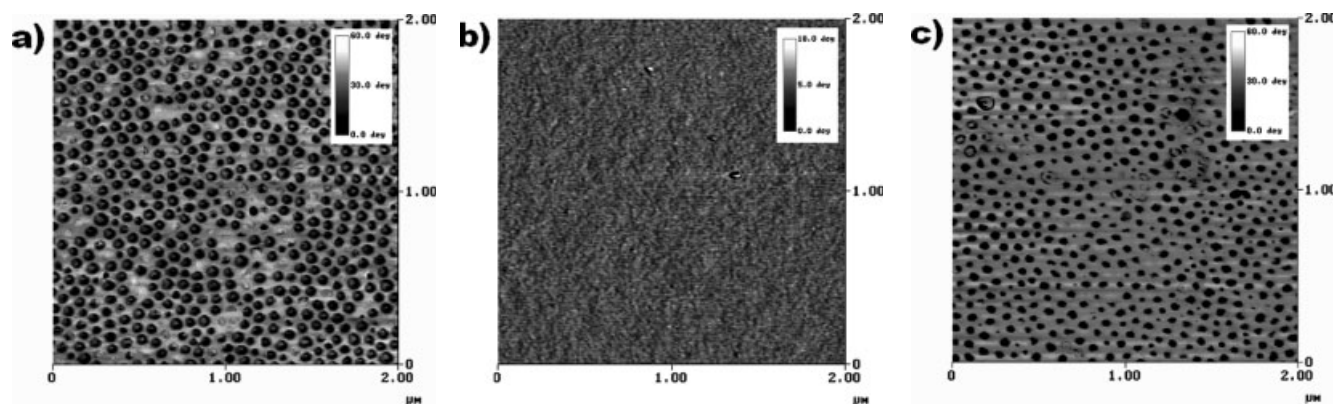


Fig. 4. AFM phase images of 90K P(S-b-PEO) thin films. a) As-cast and annealed at room temperature for two months. b) Annealed at 165 °C for three days. c) Annealed at 85 °C for three days after crosslinking with UV radiation for 35 min. The phase scale is shown in the inset. Image sizes are 2 $\mu\text{m} \times 2 \mu\text{m}$.

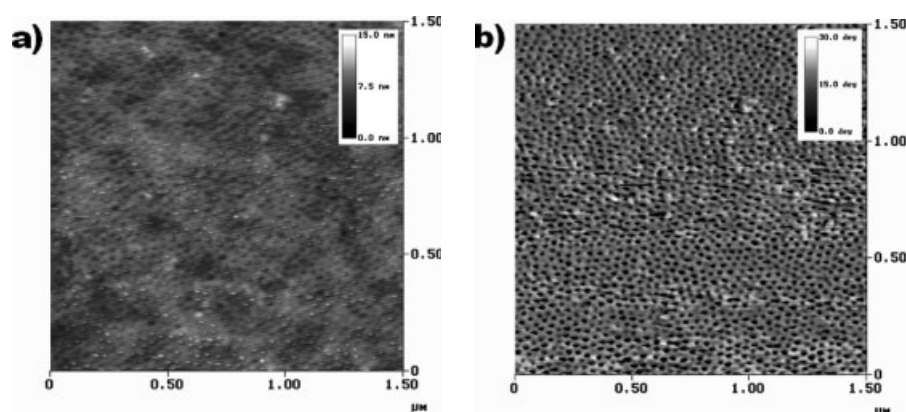


Fig. 5. AFM height (a) and phase (b) images of 25K P(S-b-PEO) thin films after immersion in H_2O for a day. The phase scale is shown in the inset. Image sizes are 1.5 $\mu\text{m} \times 1.5 \mu\text{m}$.

solvent concentration decreases, the block copolymer undergoes a transition from the disordered to ordered state. In a thin film, however, solvent evaporation is not uniform throughout the film. Rather, the solvent must diffuse through the film, producing a gradient in the solvent concentration normal to the film surface. As solvent is removed from the surface, the gradient progresses through the film. This concentration gradient translates into an ordering front that propagates from the substrate to the air surface. Interfacial interactions are, however, strongly mediated, since benzene is a good solvent for both the PS and PEO blocks.^[27,28] This markedly reduces any preferential affinity of the blocks to the substrate tending to align the copolymer chains parallel to the substrate surface and, consequently, the orientation of the morphology normal to the surface. Concurrently, the glass-transition temperature of the PS matrix increases above room temperature, locking in the oriented morphology. As the ordering front moves away from the substrate, the microphase separation is templated by the existing domains and the domains orient normal to the surface.

The behavior seen here has also been observed in solution cast films of poly(styrene-*b*-butadiene-*b*-styrene)^[17] from toluene and in spin coated films of poly(styrene-*b*-ferrocenyl-

silane) from toluene.^[21] In each of these cases, as in the P(S-b-EO) results reported here, a good solvent for two highly immiscible blocks was used^[29] and the glass-transition temperature of at least one of the blocks was well above room temperature. In cases where these conditions are not satisfied, as with P(S-b-MMA), a highly oriented, ordered morphology is not observed. The general applicability of these conditions to other systems is currently under study.

In conclusion, we have shown a rapid route by which the morphology of block copolymers can be oriented

normal to the surface of a film where the total film thickness is many times the period of the copolymer. This structure in the film is far removed from the equilibrium structure which can be achieved by thermally annealing the film. A simple explanation is proposed to describe this observation. By crosslinking the matrix of the copolymer, the orientation of the microdomains can be preserved and a reorganization of the film retarded. The preferential swelling of the nanoscopic, cylindrical domains of the copolymer with water points to a viable route by which solid, water-permeable membranes can be obtained in a simple, rapid manner.

Experimental

Asymmetric diblock copolymers of PS and PEO, denoted P(S-b-EO), having molecular weights of 25 300 (25 K) and 89 600 (90 K) with PEO volume fractions of 0.25 and 0.35, respectively, were used in this study. Solutions of the copolymers (2 % w/v) in benzene were spin coated onto silicon substrates. The spinning speed was used to vary the thickness of the films and films up to 0.3 μm were investigated in this study.

AFM images were obtained in both height and phase contrast mode using a Digital Instruments Dimension 3000 scanning force microscope in the tapping mode. AFM images were obtained on the surface and bottom of the films. To accomplish the latter, ~100 nm of silicon oxide was evaporated onto a Si wafer. The P(S-b-EO) film was spin coated directly onto this surface. The P(S-b-EO) film was floated onto the surface of a 5 wt.-% hydrofluoric acid (HF) solution

and transferred to a water bath. Using a glass microscope slide, the copolymer film was transferred onto the slide and then, prior to full transfer, the direction of motion of the slide was rapidly reversed causing the film on the surface to fold on top of the film on the substrate. Consequently, one portion of the transferred films had the original surface of the film on top and another portion of the transferred film had the bottom of the original film on the top.

A 50 nm layer of gold was evaporated onto 1.5 mm thick film of poly(ether ether ketone) (Ultem, GE) at a pressure of 10^{-7} mmHg. A solution of the copolymers (2 % w/v) in benzene was spin coated onto gold surfaces. The cross-sectional specimens of the thin film were microtomed using Leica Ultramicrotome at room temperature. Transmission electron microscopy studies were performed on a JOEL 100CX transmission electron microscope, operating at 100 kV accelerating voltage. Ruthenium tetroxide (RuO_4) was used to stain preferentially the polystyrene phase.

Received: April 18, 2002
Final version: July 15, 2002

A Series of Organic Conductors, $\kappa\text{-(BETS)}_2\text{FeBr}_x\text{Cl}_{4-x}$ ($0 \leq x \leq 4$), Exhibiting Successive Antiferromagnetic and Superconducting Transitions**

By Emiko Fujiwara, Hideki Fujiwara, Hayao Kobayashi,*
Takeo Otsuka, and Akiko Kobayashi*

Recently, there has been an increasing interest in the development of bi-functional molecular systems such as magnetic organic conductors. For example, $\beta''\text{-(BEDT-TTF)}_4(\text{H}_2\text{O})\text{-[Fe(C}_2\text{O}_4)_3\text{](C}_6\text{H}_5\text{CN)}$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) has received much attention as the first paramagnetic organic superconductor.^[1] More recently, the first molecular ferromagnetic metal, $(\text{BEDT-TTF})_3[\text{MnCr(C}_2\text{O}_4)_3]$, which is regarded as a possible candidate for a dual-action material, was discovered.^[2,3] About a decade ago, we started to try to develop organic metals with magnetic anions such as FeCl_4^- and FeBr_4^- , in order to study the interplay of conduction electrons and localized magnetic moments in organic conductors.^[4] Considering the lack of direct contact between magnetic transition metal ions and the S (or Se) atoms of TTF-like π donors in Bechgaard type salts consisting of organic π donors and inorganic magnetic anions, the π -d interaction will be weak. Therefore, the stabilization of the metallic state down to low temperatures is of key importance in order to observe the bi-functional properties that originate from the interplay of π - and d-electron systems. We adopted bis(ethylenedithio)tetrathiafulvalene (BETS) as a donor because of its strong tendency to form a stable metallic band.^[5] Although the isostructural non-magnetic GaX_4^- ($\text{X} = \text{Cl, Br}$) salts exhibit rather simple superconducting transitions,^[6] BETS conductors containing magnetic Fe^{3+} ions were found to show a variety of electromagnetic properties.^[7] For example, $\lambda\text{-(BETS)}_2\text{FeCl}_4$ with a triclinic structure shows a π -d coupled antiferromagnetic insulating transition at ambient pressure,^[8,9] but becomes a superconductor at high pressure.^[10] Furthermore, under high magnetic fields, the antiferromagnetic insulating state changes to the field-induced metallic state with ferromagnetically oriented Fe^{3+} spins above 11 T,^[8c] and then to a novel magnetic-field-induced superconducting state above 17 T.^[11] In addition, by mixing magnetic Fe^{3+} and non-magnetic Ga^{3+} ions, an unprecedented superconductor-to-insulator transition was discovered.^[12]

[*] Prof. H. Kobayashi, Dr. E. Fujiwara, Dr. H. Fujiwara
Institute for Molecular Science and the
Graduate University for Advanced Studies
Myodaiji, Okazaki 444-8585 (Japan)
E-mail: hayao@ims.ac.jp
Prof. A. Kobayashi, Dr. T. Otsuka
Research Centre for Spectrochemistry
Graduate School of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
E-mail: akiko@chem.s.u-tokyo.ac.jp

[**] This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Areas (B) of Molecular Conductors and Magnets (No. 11 224 101 and 11 224 211) from the Ministry of Education, Culture, Sport, and Technology, Japan.

- [1] T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky, T. P. Russell, *Science* **1996**, 273, 931.
- [2] P. Mansky, J. DeRouchey, T. P. Russell, J. Mays, M. Pitsikalis, T. Morkved, H. Jaeger, *Macromolecules* **1998**, 31, 4399.
- [3] T. Thurn-Albrecht, J. DeRouchey, T. P. Russell, H. M. Jaeger, *Macromolecules* **2000**, 33, 3250.
- [4] T. Thurn-Albrecht, J. Schotter, G. A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russell, *Science* **2000**, 290, 2126.
- [5] G. H. Fredrickson, F. S. Bates, *Annu. Rev. Mater. Sci.* **1995**, 1.
- [6] Z. R. Chen, J. A. Kornfield, S. D. Smith, J. T. Grothaus, M. M. Sattowski, *Science* **1997**, 277, 1248.
- [7] J. H. Laurer, B. S. Pinheiro, D. L. Polis, K. I. Winey, *Macromolecules* **1999**, 32, 4999.
- [8] M. Muthukumar, C. K. Ober, E. L. Thomas, *Science* **1997**, 277, 1225.
- [9] C. De Rosa, C. Park, E. L. Thomas, B. Lotz, *Nature* **2000**, 405, 433.
- [10] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. J. Hawker, *Science* **1997**, 275, 1458.
- [11] E. Huang, L. Rockford, T. P. Russell, C. J. Hawker, *Nature* **1998**, 395, 757.
- [12] L. Rockford, Y. Liu, P. Mansky, T. P. Russell, M. Yoon, S. G. J. Mochrie, *Phys. Rev. Lett.* **1999**, 82, 2602.
- [13] L. Rockford, T. P. Russell, M. Yoon, S. G. J. Mochrie, *Macromolecules* **2001**, 34, 1487.
- [14] R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, 13, 1152.
- [15] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, 276, 1401.
- [16] C. Harrison, M. Park, P. Chaikin, R. A. Register, D. H. Adamson, N. Yao, *Macromolecules* **1998**, 31, 2185.
- [17] G. Kim, M. Libera, *Macromolecules* **1998**, 31, 2569.
- [18] M. A. van Dijk, R. van den Berg, *Macromolecules* **1995**, 28, 6773.
- [19] P. Mansky, C. K. Harrison, P. M. Chaikin, R. A. Register, N. Yao, *Appl. Phys. Lett.* **1996**, 68, 2586.
- [20] R. G. H. Lammertink, M. A. Hempenius, J. E. van den Enk, V. Z.-H. Chan, E. L. Thomas, G. J. Vansco, *Adv. Mater.* **2000**, 12, 98.
- [21] K. Temple, K. Kulbaba, K. N. Power-Billard, I. Manner, A. Leach, T. Xu, T. P. Russell, C. J. Hawker, *Adv. Mater.* **2002**, 14, in press.
- [22] Y. L. Loo, R. A. Register, A. J. Ryan, *Phys. Rev. Lett.* **2000**, 84, 4120.
- [23] Y. L. Loo, R. A. Register, A. J. Ryan, G. T. Dee, *Macromolecules* **2001**, 34, 8968.
- [24] G. Reiter, G. Castelin, J. W. Sommer, *Phys. Rev. Lett.* **2001**, 87, 226101.
- [25] P. Huang, L. Zhu, S. Z. D. Cheng, Q. Ge, R. P. Quirk, E. L. Thomas, B. Lotz, B. S. Hsiao, L. Liu, F. Yeh, *Macromolecules* **2001**, 34, 6649.
- [26] G. Coulon, T. P. Russell, V. R. Deline, P. F. Green, *Macromolecules* **1989**, 22, 2581.
- [27] N. F. Brockmeier, *Macromolecules* **1972**, 5, 130.
- [28] C. Booth, *Polymer* **1972**, 12, 309.
- [29] L. Zhu, S. Z. D. Cheng, B. H. Calhoun, Q. Ge, R. P. Quirk, E. L. Thomas, B. S. Hsiao, F. Yeh, B. Lotz, *Polymer* **2001**, 42, 5829.