

# Self-assembly of functional nanostructures from ABC triblock copolymers

SABINE LUDWIGS, ALEXANDER BÖKER, ANDREJ VORONOV, NICOLAUS REHSE, ROBERT MAGERLE AND GEORG KRAUSCH\*

Lehrstuhl für Physikalische Chemie II and Bayreuther Zentrum für Kolloide und Grenzflächen (BZKG), Universität Bayreuth, 95440 Bayreuth, Germany

\*e-mail: georg.krausch@uni-bayreuth.de

Published online: 26 October 2003; doi:10.1038/nmat997

The spontaneous formation of nanostructured materials by molecular self-assembly of block copolymers is an active area of research, driven both by its inherent beauty and by a wealth of potential technological applications<sup>1–4</sup>. Thin films of block copolymers have attracted increasing interest, particularly in view of possible applications in nanotechnology<sup>5–9</sup>. Although much of the work has concentrated on block copolymers consisting of two components, the insertion of a third block greatly enlarges the structural diversity and allows incorporation of additional chemical functionality<sup>10,11</sup>. Here we describe a highly ordered hexagonally perforated lamella structure based on an ABC triblock copolymer thin film. By suitable choice of the three blocks a versatile structure is formed. The perforated lamella can serve as a lithographic mask, it can be chemically converted into an amphiphilic structure without losing its order, and after selective removal of one of its constituents it could be used as a responsive membrane. Intriguingly, the particular choice of the blocks ensures that the structure is formed irrespective of the chemical nature of the solid substrate. The experimental results are supported by mesoscale computer simulations.

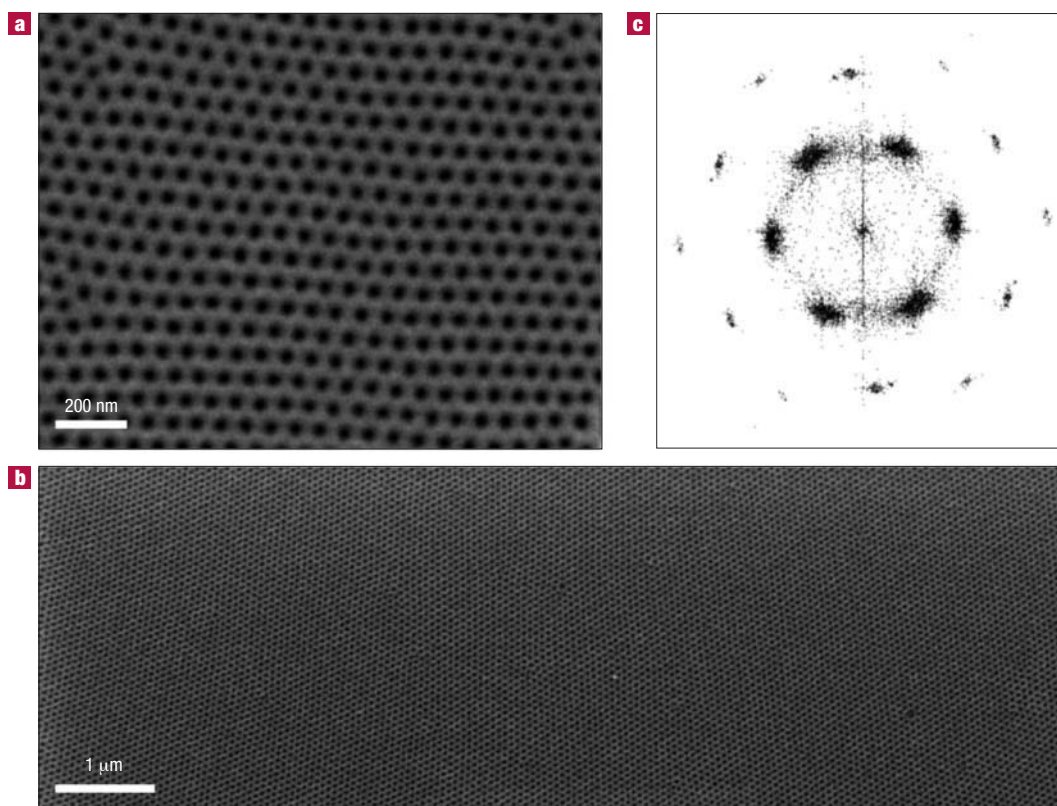
Most studies on block copolymer thin films have focused on binary systems, that is, on block copolymers composed of two different materials A and B. In films used for nanolithography, the copolymers may form a spherical or cylindrical mesostructure. In the latter case, the cylinders tend to lie parallel to the surfaces of the film. Considerable effort has been taken to overcome this tendency and stabilize a perpendicular orientation, which is desired for many applications<sup>12,13</sup>. The cores of perpendicular cylinders can be removed by selective degradation of the core material, thereby leaving a nanoscopically patterned mask for further etching, material deposition or other uses<sup>6,14</sup>.

If three, instead of two, different polymeric components are linked together to form what is then called an ABC triblock copolymer, the structural variety is significantly increased<sup>10</sup>. Although potentially more versatile than binary block copolymers because of the increased chemical complexity, these materials have been much less studied in the context of nanotechnology applications. Here, we describe the thin-film self-assembly of a linear triblock copolymer, polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(*t*-butyl methacrylate) (PS-P2VP-PtBMA). The polymer was synthesized by anionic polymerization following standard procedures<sup>15</sup>. The weight-averaged molecular mass of the polymer is 140,000 ( $M_w = 140K$ ), the polydispersity amounts to

$M_w/M_n = 1.02$  (where  $M_n$  is the number-averaged molecular mass) and the volume fractions of the three blocks are 16%, 21% and 63% for the PS, P2VP and PtBMA blocks, respectively. In the bulk, the material has a structure of hexagonally packed cylinders embedded within the PtBMA matrix material<sup>16</sup>. The experimental data are compatible with the notion of a core-shell structure, where the minority PS block forms a cylindrical core surrounded by a P2VP shell. Thin films of this material were prepared on various substrates (silicon wafers covered with native oxide, carbon-coated silicon wafers, NaCl surfaces) by spin-coating from chloroform solution. To increase mobility and aid equilibration, the samples were annealed in a well-controlled atmosphere of chloroform vapour. After drying, the thin-film microdomain structure was investigated by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and scanning force microscopy (SFM). For TEM investigations, films were prepared on NaCl substrates, which were subsequently dissolved in water. The freely floating films were picked up on a TEM grid for further investigation.

Figure 1a,b shows FE-SEM images of a PS-P2VP-PtBMA film (thickness:  $37 \pm 3$  nm) after storage in chloroform atmosphere and subsequent drying. The images are characterized by a hexagonal arrangement of dark dots with a characteristic nearest-neighbour distance of  $70 \pm 5$  nm. The large-scale image (Fig. 1b) shows that this structure is formed with only a small number of defects over an area of about  $12 \times 4 \mu\text{m}^2$ . This impressive degree of order is also reflected in the Fourier transform (Fig. 1c).

To establish the microdomain structure responsible for the hexagonal array of dots observed in the FE-SEM images, the samples were investigated by nanotomography<sup>17</sup> (not shown here). In short, the sample was eroded in an oxygen plasma and SFM images were taken after each erosion step. The results of these experiments are consistent with a perforated lamella structure within the thin film. This structure can be visualized as a P2VP/PS/P2VP sheet perforated by PtBMA channels, which connect between two outer PtBMA layers (see Fig. 2e for a sketch). Further experimental evidence for this model is given in Fig. 2a and b, where we show two SFM images of a thin PS-P2VP-PtBMA film before and after ultraviolet irradiation (UV-B, 150 W, 60 min). This treatment preferentially removes the acrylate matrix phase. On ultraviolet irradiation the originally rather flat surface develops a highly ordered hexagonal array of hollows, as the PtBMA is removed from the perforations in the P2VP/PS/P2VP layer.



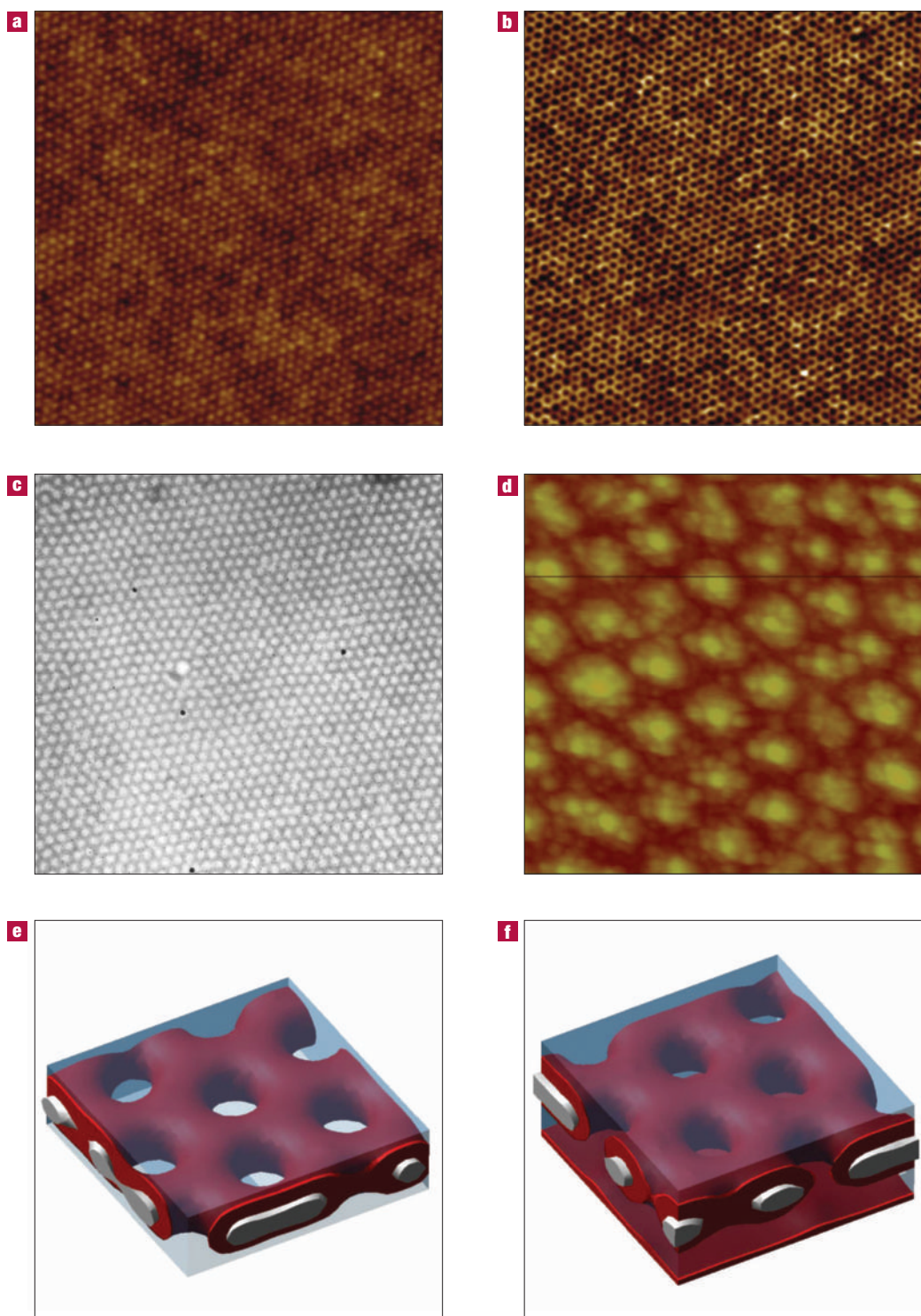
**Figure 1** Highly ordered microstructure of a block copolymer. **a, b**, FE-SEM images of a 37-nm-thick PS-P2VP-PtBMA film after solvent vapour treatment (partial pressure  $P_{\text{CHCl}_3}$  was reduced from 0.94 saturation pressure,  $P_{\text{sat}}$ , to below  $0.3 P_{\text{sat}}$  within 100 h) and subsequent drying. **c**, Fourier transform of an FE-SEM image of size  $5 \times 5 \mu\text{m}^2$ .

This finding suggests that the perforated lamella structure could be used for lithographic applications, as can be done with perpendicularly oriented poly(methyl methacrylate) (PMMA) cylinders in PS-PMMA block copolymer thin films<sup>6,14</sup>. But the perforated layer remaining after PtBMA removal consists of the PS core with its surface covered by a layer of P2VP, which can easily be modified chemically. In particular, quaternization of P2VP will lead to a water-soluble coverage of the PS core, thereby circumventing well-known wettability problems occurring when the holes in the polymer structure are to be filled in a subsequent electrochemical processing step<sup>8,14</sup>. Moreover, the thickness of the quaternized layer will depend on the pH of the surrounding medium, suggesting that the resulting structure could be of use as a (pH-) responsive membrane. The limited thickness of the perforated lamella structure may be a disadvantage in lithography. It is, however, desirable in membrane applications, where a high density of well-defined nanoscopic holes within a sheet ~50 nm thick is needed for optimal permeability. Because free-standing films are needed for membrane applications, the film must be mechanically stable. We have therefore studied thin films prepared on polished NaCl substrates. After preparation, the substrates are dissolved in water and the free-standing block copolymer films are picked up on TEM grids. Figure 2c shows a TEM image taken from such a film, clearly showing both that the quality of the nanostructure is preserved and that the free-standing films, which contain a single layer of perforated lamella, have sufficient mechanical stability.

As an alternative to PtBMA removal by ultraviolet radiation, the matrix phase can be converted into poly(methacrylic acid) (PMAA) by hydrolysis in HCl. Figure 2d shows an SFM image of a copolymer film, which was prepared on a polished silicon wafer as described above and

subsequently exposed to an atmosphere of HCl and water vapour (concentrated HCl at 60 °C) for hydrolysis. SEM images (not shown here) indicate that the overall nanostructure is not affected by this treatment. If the film surface is imaged in water, however, we observe a hexagonal array of protrusions (about 15 nm high). Because PMAA swells considerably in water, the protrusions will form on top of the perforations of the P2VP/PS/P2VP lamella, where more PMAA material is present. Evidently the PS core is stable enough to withstand the forces exerted on the majority PMAA blocks during swelling in water. Again, the height of the protrusions is expected to vary with the pH, resulting in a responsive nanostructure.

The perforated phase is generally believed not to be a bulk equilibrium phase in binary block copolymer systems<sup>18</sup>. But recent experimental and simulation results on binary systems<sup>19</sup> show that the perforated lamella phase can be stabilized by surface interactions in thin films of cylinder-forming block copolymers. If both boundary surfaces prefer the majority phase, cylinders tend to orient parallel to the boundary surfaces. In case of strong-enough preference, the bulk of the thin film may be depleted of the majority component and the cylindrical cores of the minority phase may connect to a perforated sheet<sup>20</sup>. For the ternary copolymer studied here, the bulk equilibrium structure is also a hexagonally packed cylindrical structure. The PtBMA majority phase has the lowest surface energy and therefore is attracted to the free surface of the film. If the substrate attracted the PtBMA majority phase as well, one would expect the stabilization of a perforated lamella similar to the binary cylindrical systems mentioned above<sup>19</sup>. In the case of a polar substrate like  $\text{SiO}_x$ , on the other hand, strong physisorption of the polar P2VP middle block is expected<sup>21</sup>. Because of the particular stoichiometry of the block copolymer, however, such a physisorbed



**Figure 2** Exploring the microstructure of block copolymer films. **a, b**, Tapping-mode SFM topography images of the block copolymer film before (**a**) and after (**b**) exposure to ultraviolet radiation ( $3 \times 3 \mu\text{m}^2$ , same film as in Fig. 1). **c**, TEM image of a block copolymer film prepared on a polished NaCl substrate, floated onto  $\text{H}_2\text{O}$ , and picked up onto a TEM grid ( $2 \times 2 \mu\text{m}^2$ ; preparation:  $P_{\text{CHCl}_3} = 90.0 p_{\text{sat}}$ ,  $t = 15 \text{ h}$ ). **d**, Tapping-mode SFM image of a block copolymer film after hydrolysis of the PtBMA blocks into PMAA. The image was taken in  $\text{H}_2\text{O}$  using the liquid cell of the Multimode SFM ( $0.5 \times 0.5 \mu\text{m}^2$ ). **e, f**, Results of MesoDyn simulations assuming symmetric (**e**) and asymmetric (**f**) boundary conditions. The block copolymer was modelled by an  $\text{A}_3\text{B}_4\text{C}_{12}$  gaussian chain with interaction parameters  $\epsilon_{\text{AB}} = 7.0$ ,  $\epsilon_{\text{AC}} = 8.0$ ,  $\epsilon_{\text{BC}} = 6.0$  (all in  $\text{kJ mol}^{-1}$ ). The film interfaces were treated as hard walls with interaction parameters  $\epsilon_{\text{AM},1} = 8.0$  (4.0 in **f**),  $\epsilon_{\text{BM},1} = 6.0$  (6.0),  $\epsilon_{\text{CM},1} = 0$  (-2.0),  $\epsilon_{\text{AM},2} = 8.0$  (6.0),  $\epsilon_{\text{BM},2} = 6.0$  (-8.0) and  $\epsilon_{\text{CM},2} = 0$  (4.0) (M1 indicates free surface; M2 indicates substrate). The size of the simulation box is  $32 \times 32 \times (H + 2)$  with walls at  $z = 0$  and  $H + 1$ . The film thickness  $H = 9$  and 14 grid points in **e** and **f**, respectively. All other parameters are as reported elsewhere<sup>19</sup>.

layer will have a PtBMA-rich surface. In consequence, a perforated lamella would again be stabilized between two surfaces both preferentially attracting the PtBMA majority phase. It is a particularly intriguing property of the material under study that the perforated lamella phase is stabilized irrespective of the chemical nature of the substrate, as any polar substrate will self-adjust its surface energy by firm physisorption of a thin block copolymer layer terminated by PtBMA as soon as the surface is brought into contact with the copolymer solution, before the film is formed. This notion is in line with our experiments. We used three different substrate materials ( $\text{SiO}_2$ ; Figs 1 and 2a,b; NaCl; Fig. 2c; carbon-coated silicon wafer: not shown here) and in all cases the perforated lamella phase was formed. Moreover, experiments with varying film thickness (not shown here) clearly show the existence of an adsorbed layer underneath the perforated lamella.

In addition, we examined the concept of a self-adjusting surface energy of the substrate by dynamic density functional theory (DDFT) simulations using the MesoDyn code<sup>22–24</sup>. The polymer was modelled as an  $\text{A}_3\text{B}_4\text{C}_{12}$  triblock copolymer confined between symmetric walls attracting the C-block (see Fig. 2 for details). Figure 2e shows a result of such a simulation. The core-shell perforated lamella is clearly seen in the centre of the film, which is terminated by continuous C-layers (transparent) at both boundary surfaces. For comparison, in Fig. 2f we show the results of a MesoDyn simulation with all parameters kept the same as in Fig. 2e, except that the bottom boundary now attracts the B middle block and the film thickness is 5 grid points thicker. As a result, a thin B wetting layer is formed at the bottom boundary (red), which terminates with a C-rich layer (transparent), on which the perforated lamella structure is again formed. Indeed, the perforated lamella is formed irrespective of the preference of the substrate. This property establishes a major advantage over other systems, where considerable experimental effort is needed to adjust the substrate surface energy in order to achieve the desired orientation of the nanostructure<sup>12</sup>.

We finally turn to the high degree of order formed spontaneously in the structure. We have not undertaken any particular measures (such as topographic patterning of the substrate surface<sup>25</sup>) to improve the order. It is known that suitable treatment can indeed improve the order of a block copolymer mesostructure<sup>26</sup>. But whenever our PS-P2VP-PtBMA films do not show the perforated lamella structure (for example, owing to different thickness) they have a lower degree of long-range order. We are therefore led to assume that the bicontinuous nature of the perforated lamella phase is essential for long-range order to occur in this system. Indeed, as the perforated lamella phase is continuous in all three components, chain diffusion within the film should be aided. In consequence, defect removal through diffusion should be considerably enhanced compared with other, non-continuous microdomain structures. This finding is in agreement with our own results on other block copolymer systems and with earlier results by others (U. Wiesner, personal communication).

Received 3 July 2003; accepted 12 September 2003; published 26 October 2003.

## References

- Bates, F. S. & Fredrickson, G. H. Block copolymer thermodynamics: theory and experiment. *Annu. Rev. Phys. Chem.* **41**, 525–557 (1990).
- Klok, H. A. & Lecommandoux, S. Supramolecular materials via block copolymer self-assembly. *Adv. Mater.* **13**, 1217–1229 (2001).
- Adrington, A. C. *et al.* Polymer-based photonic crystals. *Adv. Mater.* **13**, 421–425 (2001).
- Bockstaller, M., Kolb, R. & Thomas, E. L. Metallo-dielectric photonic crystals based on diblock copolymers. *Adv. Mater.* **13**, 1783–1786 (2001).
- Mansky, P., Chaikin, P. & Thomas, E. L. Monolayer films of diblock copolymer microdomains for nanolithographic applications. *J. Mater. Sci.* **30**, 1987–1992 (1995).
- Park, M. *et al.* Block copolymer lithography: Periodic arrays of similar to 10(11) holes in 1 square centimeter. *Science* **276**, 1401–1404 (1997).
- Cheng, J. Y. *et al.* Formation of a cobalt magnetic dot array via block copolymer lithography. *Adv. Mater.* **13**, 1174–1178 (2001).
- Jeoung, E. *et al.* Fabrication and characterization of nanoelectrode arrays formed via block copolymer self-assembly. *Langmuir* **17**, 6396–6398 (2001).
- Kim, H.-C. *et al.* A route to nanoscopic  $\text{SiO}_2$  posts via block copolymer templates. *Adv. Mater.* **13**, 795–797 (2001).
- Bates, F. S. & Fredrickson, G. H. Block copolymers: designer soft materials. *Phys. Today*, **52**, 32–38 (1999).
- Krausch, G. & Magerle, R. Nanostructured thin films via self-assembly of block copolymers. *Adv. Mater.* **14**, 1579–1583 (2002).
- Mansky, P. *et al.* Controlling polymer-surface interactions with random copolymer brushes. *Science* **275**, 1458–1460 (1997).
- Thurn-Albrecht, T. *et al.* Overcoming interfacial interactions with electric fields. *Macromolecules* **33**, 3250–3253 (2000).
- Thurn-Albrecht, T. *et al.* Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates. *Science* **290**, 2126–2129 (2000).
- Giebler, E. & Stadler, R. ABC triblock polyampholytes containing a neutral hydrophobic block, a polyacid and a polybase. *Macromol. Chem. Phys.* **198**, 3815–3825 (1997).
- Ludwigs, S. *et al.* Phase behavior of linear polystyrene-block-poly(2-vinylpyridine)-block-poly(tert-butyl methacrylate) triblock copolymers. *Polymer* **44**, 6815–6823 (2003).
- Magerle, R. Nanotomography. *Phys. Rev. Lett.* **85**, 2749–2752 (2000).
- Hajduk, D. A. *et al.* Stability of the perforated layer (PL) phase in diblock copolymer melts. *Macromolecules* **30**, 3788–3795 (1997).
- Knoll, A. *et al.* Phase behavior in thin films of cylinder-forming block copolymers. *Phys. Rev. Lett.* **89**, 035501 (2002).
- Huinink, H. P. *et al.* Asymmetric block copolymers confined in a thin film. *J. Chem. Phys.* **112**, 2452–2462 (2000).
- Tassin, J. F. *et al.* Kinetics of adsorption of block copolymers revealed by surface plasmons. *J. Phys. Chem.* **93**, 2106–2111 (1989).
- Fraaije, J. G. E. M. Dynamic density-functional theory for microphase separation kinetics of block-copolymer melts. *J. Chem. Phys.* **99**, 9202–9212 (1993).
- Fraaije, J. G. E. M. *et al.* The dynamic mean-field density functional method and its application to the mesoscopic dynamics of quenched block copolymer. *J. Chem. Phys.* **106**, 4260–4269 (1997).
- Sevink, G. J. A. *et al.* Dynamics of surface directed mesophase formation in block copolymer melts. *J. Chem. Phys.* **110**, 2250–2256 (1999).
- Segalman, R. A., Yokoyama, H. & Kramer, E. J. Graphoepitaxy of spherical domain block copolymer films. *Adv. Mater.* **13**, 1152–1155 (2001).
- Kim, G. & Libera, M. Morphological development in solvent-cast polystyrene-polybutadiene-polystyrene (SBS) triblock copolymer thin films. *Macromolecules* **31**, 2569–2577 (1998).

## Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for financial support (SFB 481), and A. Knoll, G.J.A. Sevink, C. Abetz and M. Hund for help. A modified version of the MesoDyn Code for asymmetric boundary conditions was kindly provided by G. J. A. Sevink and A. V. Zvelindovsky. A.V. acknowledges financial support through the Humboldt Foundation and R.M. acknowledges financial support through the VolkswagenStiftung.

Correspondence and requests for materials should be addressed to G.K.

## Competing financial interests

The authors declare that they have no competing financial interests.