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Templated Sub-100-nm-Thick Double-Gyroid Structure from Si-Containing Block Copolymer Thin Films

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The directed self-assembly of diblock copolymer chains (poly(1,1-dimethyl silacyclobutane)-block-polystyrene, PDMSB-b-PS) into a thin film double gyroid structure is described. A decrease of the kinetics of a typical double-wave pattern formation is reported within the 3D-nanostructure when the film thickness on mesas is lower than the gyroid unit cell. However, optimization of the solvent-vapor annealing process results in very large grains (over 10 μm^2) with specific orientation (i.e., parallel to the air substrate) and direction (i.e., along the groove direction) of the characteristic (211) plane, demonstrated by templating sub-100-nm-thick PDMSB-b-PS films.

AB-type block copolymers (BCPs) self-assemble into periodic structures at the nanometer scale with a range of controllable morphologies, including lamellae (L), cylinders (C), spheres (S), and unique network morphologies.^[1–3] The complex network nanostructures are an orthorhombic O^{70} phase with optical anisotropy and a double gyroid (DG) morphology with a cubic unit cell. The noncubic network with an $Fddd$ symmetry was recently predicted by Tyler and Morse^[4] as an equilibrium phase occurring within a narrow region located between the lamellar and the DG phases, and was experimentally observed two years later by Takenaka et al.^[5] The DG structure is also an accepted equilibrium phase, first identified in strontium saturated soaps by Luzzati and Spegt in 1967.^[6] The DG-forming BCP with space group $Ia\bar{3}d$ was independently identified no prior to 1994 by Hajduk et al.^[7] and Schulz and co-workers.^[8] In this exceptionally rich year, Matsen and Schick theoretically demonstrated that the DG-forming BCP is a stable phase, localized between the lamellar and the cylinder phases.^[2]

Order-order transitions (OOTs) between the different BCP domain structures occur by changing the temperature, or by imposing an external field, such as a flow field or an electric field. For instance, the C to DG (C–DG) transition has received considerable attention since Rançon and Charvolin have demonstrated an epitaxial relationship during the phase transformation in surfactant system.^[9] Using the self-consistent field theory (SCFT), Matsen^[10] proposed the C–DG transition proceeds epitaxially by a nucleation and growth mechanism, implying the (100) plane of the hexagonal C phase and the (211) plane of the DG structure, which is supported by experiments.^[8,11–13]

The self-assembly of BCP into a thin-film DG structure offers a unique route to tailor nanoscale materials requiring an architecture consisting of two interwoven continuous networks in 3D space. This 3D nanostructure is characterized by complex patterns, such as wagon wheel and double-wave patterns, and small domain dimensions, which are highly challenging to achieve by traditional top-down lithography. The DG-forming BCP is consequently one of the most appealing morphologies to provide a significant advancement in technological applications, since new transport characteristics can be achieved due to its unique texture in 3D space, providing well-defined, continuous pathways. Most notably, functional applications using DG metal-oxide replicas for dye-sensitized solar cells or for efficient electrochromic devices have demonstrated its potential to outperform existing technologies.^[14–17] Harvesting nonlinear optical effects from DG-templated PbSe networks obtained from a BCP scaffold also offers promising avenues for the development of carrier multiplications solar cells, as theoretically demonstrated by Khlebnikov and Hillhouse.^[18] Inorganic replicated porous

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DG structures provided as well enhanced catalytic efficiency or ultrafiltration performance.^[19–24] The DG-forming structure was further exploited for the development of antireflection coatings, photonic crystals, and optical metamaterials, in which light-matter interactions are strongly affected by such complex morphology.^[25–27]

For all aforementioned applications, thin-film DG structures forming very large grains with tunable orientation and direction of crystallographic planes are highly desired. To control the plane orientation within the 3D nanostructure, the solvent-vapor annealing (SVA) approach is an effective methodology, since SVA provides avenues to order structures, which are unattainable through thermal annealing.^[28–34] Additionally, large-grain areas with a preferential plane direction can be achieved by the use of topographical substrates to guide the BCP self-assembly.^[35–37] The template methodology is more effective for thinner polymeric layers, since surface and topographic fields induced by this direct self-assembly (DSA) approach are stronger for sub-100-nm-thick BCP film. However, the stability of sub-100-nm-thick gyroid layers on templates is another challenge that is of crucial importance, because the 3D-nanostructure cannot properly develop when the film thickness is lower than the DG unit cell dimension, making this fascinating morphology becomes unstable. Consequently, limited examples of the thin-film gyroid morphology have been reported.^[38–40] For instance, Ross and co-workers demonstrated the thin-film morphology of a polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) BCP can form spheres, cylinders, perforated lamellae, or two interwoven continuous networks, depending on the film thickness, its commensurability with the microdomain period, and the ratio of solvents used for the SVA process, while this PS-*b*-PDMS self-assembles into a DG morphology in bulk.^[41]

In this work, we report for the first time on templated sub-100-nm-thick gyroid layers enabling the production of large grains with size over 10 μm^2 , in which the characteristic (211) plane oriented parallel to air surface is also aligned along the groove direction. To produce such a long-range, ordered, double-wave pattern, a tetrahydrofuran (THF)-vapor-swelling, approximately two times the poly(1,1-dimethyl silacyclobutane)-*block*-polystyrene (PDMSB-*b*-PS) thin films, was used. We also demonstrated the kinetic of the DG structure formation is decreased with the film thickness and, especially, if the polymer thickness is locally lower than the gyroid unit-cell size. This phenomenon is due to the fact that an intermediate structure, having its plane oriented parallel to the air surface, which is epitaxially related to the (221) plane of DG structure, becomes a long-lived nonequilibrium state when the film thickness is decreased. This intermediate state is finally converted to the DG structure after a sufficient SVA time.

The PDMSB-*b*-PS diblock copolymer used in this study has a molecular weight of 24.3 kg mol^{-1} and PDMSB volume fraction, Φ_{PDMSB} , of 0.38. To prepare well-defined PDMSB-*b*-PS chains with a narrow dispersity ($\bar{D} = 1.07$), a sequential anionic polymerization of (1,1-dimethyl silacyclobutane) (DMSB) and styrene was performed.^[42,43] From a previous study, the Flory–Huggins interaction parameter, χ_{DS} , between PDMSB and PS was estimated to be 0.07.^[44] PDMSB-*b*-PS

thin films were spin-coated on smooth and templated silicon substrates using a 2 wt% copolymer solution, in a mixture of tetrahydrofuran and propylene glycol monomethyl ether acetate (THF/PGMEA: 2/1). The film thickness, t , was controlled by varying the spin-coating speed (2–5 krpm). The self-assembly of PDMSB-*b*-PS thin films was achieved by exposing samples during different times (ranging from 1 to 17 h) to a continuous stream of THF vapor produced by bubbling nitrogen gas through the liquid solvent, as described previously.^[45] This continuous flow system was used to control the THF vapor pressure in the chamber by dilution with a separate N_2 stream, so that the solvent vapor consisted of 16 sccm THF vapor and 4 sccm N_2 (total 20 sccm) swelled the films without dewetting. The film thickness evolution was monitored during the swelling process using a spectroscopic reflectometer. Solvent-annealed PDMSB-*b*-PS thin films were quenched in air by quickly removing the lid of the chamber then, a CF_4/O_2 reactive ion etch (RIE) treatment was subsequently applied to preferentially remove PDMSB domains (plasma conditions are 40 W, 17 sccm CF_4 , and 3 sccm O_2) prior to perform grazing incidence small angle X-ray scattering (GISAXS) measurements, and to take atomic force microscopy (AFM) images.

The AFM phase image presented in **Figure 1** shows a solvent-annealed (1 h, THF) 180-nm-thick PDMSB-*b*-PS film (24.3 kg mol^{-1} , $\Phi_{\text{PDMSB}} = 0.38$) treated by a CF_4/O_2 RIE plasma from which the characteristic (211) crystallographic plane of the DG structure oriented parallel to the air surface can be observed. This typical DG pattern is referred to the “double-wave pattern” since it consists of small- and large-amplitude oscillations. GISAXS data associated to this sample well matches with (121) and (220) Bragg diffraction spots as reported previously by Ree and co-workers,^[46] which confirms that a preferential orientation of (211) planes is produced within the PDMSB-*b*-PS layer (see Figure 1). For this 3D nanostructure, the unit-cell dimension, a_{G} , was determined to be 63.4 nm, while the period of the (121) plane was

Figure 1. a) AFM topographic view and its associated b) GISAXS pattern of a solvent-annealed (1 h, THF) PDMSB-*b*-PS thin film ($t \approx 180 \text{ nm}$) treated by a CF_4/O_2 RIE plasma, where PS (bright) and etched PDMSB (dark) domains are arranged in a double-wave pattern. Scale bar: 200 nm.

estimated to be 24.7 nm. For sub-100-nm-thick PDMSB-*b*-PS films, the SVA conditions (17 h, THF) induces the splitting of the polymer layer into terraces during the swelling process, which impinges on the formation of the DG structure on terraces with a thickness, t , lower than the DG unit-cell dimension, $t < a_G$. For instance, in-plane cylinders with a period of 22 nm are formed on lower terraces, where $t = 50 \text{ nm} < a_G$ while the DG structure properly develops on upper terraces (see Figure S1, Supporting Information). Interestingly, an orientational match between the cylinder and the gyroid phases, as well as a match in their domain size could be observed in Figure S1 (Supporting Information). Indeed, the intersmall amplitude oscillation distance is commensurate with the cylinder period.

In order to control the grain orientation and improve their size within the 3D nanostructure, topographical gratings in silica were used. These guiding patterns fabricated by interference lithography with a period of 500 nm consisted of 250-nm-width, 45-nm-deep trenches separated by 250-nm-width mesas. Importantly, the thin morphology is very sensitive to the nature and the ratio of solvents used for the SVA process, since highly ordered in-plane cylinders (period $\approx 24 \text{ nm}$) oriented along the groove direction were produced from templated 180-nm-thick PDMSB-*b*-PS layers placed under a vapor, consisting of a mixture of THF and methanol (THF/MeOH: 2/1), during 1 h (see Figure S2, Supporting Information). By contrast, AFM images presented in **Figure 2** show a templated 180-nm-thick PDMSB-*b*-PS layer self-assembled into a DG structure with (211) plane oriented along the groove direction when a THF vapor is used for the SVA process. Here, the film thickness is larger than the lattice parameter, a_G , of the 3D nanostructure allowing a complete development of the gyroid texture after exposing the sample during 1 h under THF vapor. However, the use of self-assembled BCP-thick-films lessens the influence of topographical substrates, as reported previously.^[47] This phenomenon leads to the observation of four preferential directions of (211) planes, which are predominately oriented parallel (0°), diagonal (-45° , 45°), and orthogonal (90°) to the grating direction.

To improve the control of the (211) plane direction, templated PDMSB-*b*-PS films with a sub-100-nm thickness have

Figure 2. ($2 \times 2 \mu\text{m}$) AFM a) topographic and its associated b) phase views of a solvent-annealed (1 h, THF) 180-nm-thick PDMSB-*b*-PS film deposited on a topographical substrate, followed by a CF_4/O_2 RIE treatment. Inset: ($0.75 \times 0.75 \mu\text{m}$) AFM phase image showing that the (211) plane of the DG structure is oriented along the groove direction. Scale bars: 200 nm.

Figure 3. ($2 \times 2 \mu\text{m}$) AFM a) topographic and its associated b) phase views of a solvent-annealed (1.5 h, THF) 95-nm-thick PDMSB-*b*-PS film deposited on a topographical substrate, followed by a CF_4/O_2 RIE treatment. Insets: ($0.75 \times 0.75 \mu\text{m}$) AFM topographic and phase images. Sketches: patterns of the planes oriented parallel to air substrate for (top) the DG and (bottom) the intermediate structure. Scale bars: 200 nm.

been produced in order to strengthen the influence of the grating substrate. A templated 95-nm-thick PDMSB-*b*-PS layer treated by a THF vapor during 1 h 30 min is shown in **Figure 3**. Two morphologies consisting of an intermediate phase and the DG structure having its (211) planes oriented along the grating direction can be clearly differentiated in the AFM images. The plane oriented parallel to the air surface of the intermediate phase presents some similarities (epitaxial relations) with the (211) plane of the DG structure, which occupies smaller regions. Indeed, the pattern of the intermediate phase exhibits similar small-amplitude oscillations oriented along the groove, compared to those observed on the double-wave pattern (see Figure 3). The main difference is that the thick- and large-amplitude oscillations of the double wave pattern are replaced by periodically distributed spots having the same height as the small amplitude oscillations, so that a pattern with wavy lines and dots is observed. This pattern is very

similar to the metastable state, which appears in an SCFT study proposed by Matsen, where the C to DG transition proceeds epitaxially by a nucleation and growth mechanism.^[10] In another study, Ji et al. have used SCFT calculations to show that the lamellar to DG transition can occur from a metastable cylinder-like state having a (211) plane with a pattern similar to the one observed in Figure 3.^[48]

In general, we also observe that the “wavy line and dot” pattern presents more defects/imperfections on regions located on mesas than in trenches, indicating that the film thickness plays an important role on the development of the intermediate phase. To get some insights on the kinetic of the DG structure formation, the variation profile of the polymer-film thickness deposited on the grating has been determined. The AFM topographic profile obtained from a solvent-annealed (1.5 h, THF) PDMSB-*b*-PS thin film deposited on a 500-nm pattern revealed a peak-valley amplitude of ≈ 10 nm, which corresponds to a continuous film of thickness ≈ 90 nm in the trenches and ≈ 55 nm above the mesas (see Figure S2, Supporting Information). From this result, it appears that the film thickness on the mesas is lower than the gyroid unit cell dimension ($t_{\text{mesa}} = 55 \text{ nm} < a_G = 63.4 \text{ nm}$) after the solvent annealing process (dry state). This should stabilize the intermediate structure and delay/impinge on the epitaxial phase transition; although, in the swollen stage, the film thickness reaches approximately two times its initial thickness, as monitored by spectral reflectometry (see Figure S3, Supporting Information). To highlight the importance of the film thickness on the stability of the intermediate state, it could be observed in some regions of a templated 95-nm-thick PDMSB-*b*-PS layer treated by a THF vapor during 5 h that the double wave pattern is well-defined only in trenches (i.e., where the film is thicker), while the mesas are still occupied by the “wavy line and dot” pattern (Figure 4). By contrast, AFM images

Figure 4. ($2 \times 2 \mu\text{m}$) AFM a) topographic and its associated b) phase views of a solvent-annealed (5 h, THF) 95-nm-thick PDMSB-*b*-PS film deposited on a topographical substrate followed by a CF_4/O_2 RIE treatment. Inset: ($0.75 \times 0.75 \mu\text{m}$) AFM topographic and phase images showing a region of the templated film where the DG and the intermediate structure occupy the trenches and the mesas, respectively.

Figure 5. ($1.5 \times 1.5 \mu\text{m}$) AFM a) topographic and its associated b) phase views of a solvent-annealed (17 h, THF) 95-nm-thick PDMSB-*b*-PS film deposited on a topographical substrate followed by a CF_4/O_2 RIE treatment. Inset: the 2D-FFT exhibits sharp spots, indicating the double-wave pattern is highly ordered.

presented in Figure 5 show that the development of a complete gyroid structure could be achieved both on in trenches and on mesas when a similar PDMSB-*b*-PS layer is swollen during 17 h by THF vapor. These results definitely assert that the kinetics of the DG-phase formation is delayed if the condition $t_{\text{mesa}} < a_G$ is fulfilled, since the double-wave-pattern formation is not reached both in trenches and on mesas after 5 h of SVA treatment, while a complete development of the DG texture is achieved after exposing the sample during 1 h when $t_{\text{mesa}} \gg a_G$ (see Figure 2).

DSA of solvent-annealed (17 h, THF) sub-100-nm-thick PDMSB-*b*-PS layers on guiding patterns has revealed to be a very efficient methodology to control the grain orientation and improve their size, since long-range-ordered grains with size over $10 \mu\text{m}^2$ and having the (211) plane of the DG structure oriented along the groove direction were produced. This point is illustrated on low magnification AFM topographic images presented in Figure 6, from which apparent lines (at such magnifications) corresponding to large-amplitude oscillations of the double-wave pattern are found to be oriented along the groove direction. In addition, characteristic spots of the double-wave pattern formed on the (211) plane are clearly visible on the associated bidimensional fast Fourier transform (2D-FFT). Such behavior demonstrates that the use of topographical substrate in combination with suitable SVA conditions enables the formation of very large grains, in which both the orientation and the direction of the (211) plane are controlled.

In summary, highly ordered, double-wave patterns with a $\approx 63 \text{ nm}$ unit cell dimension have been achieved for the first time from templated sub-100-nm-thick double gyroid films. This long-range ordered, fascinating nanostructure within very large grains (size $>10 \mu\text{m}^2$) opens up appealing applications in nanotechnology requiring well-defined complex 3D patterns with small dimensions. For instance, next-generation solar cell may require

Figure 6. (10 × 10 μm) AFM topographic view of a solvent-annealed (17 h, THF) 95-nm-thick PDMSB-*b*-PS film deposited on a topographical substrate, followed by a CF₄/O₂ RIE treatment. Typical large wave amplitudes observed on the (211) plane of the gyroid structure appear at this magnification as lines aligned with the groove direction. Inset: the 2D-FFT exhibits sharp spots, indicating highly ordered domains within a single grain orientation.

a control of the double gyroid plane orientation to achieve an effective infiltration of hole-transporting materials, while long-range-ordered patterns aligned along a preferential direction enable optimized charge generation and collection through direct “nontortuous” pathways and limited grain boundaries. Further works on this BCP will target the use of this DG structure as scaffold for the definition of inorganic or metallic replica through the selective removal of the PS domains. The long-range structural ordering demonstrated in this study is envisioned to promote their inherent functional photonic, electronic, or transport properties.

Experimental Section

Synthesis of PDMSB-*b*-PS: DMSB (Sigma-Aldrich, 95%) and styrene (Across Organic, 99.9%) were successively distilled over CaH₂ and di-*n*-butylmagnesium at 35 and 60 °C, respectively. THF and heptane were first distilled over CaH₂ and then over sodium/benzophenone and living polystyrene, respectively. In order to obtain the PDMSB-*b*-PS block copolymer used in this study, anionic polymerization was performed by sequential addition of the DMSB and S monomers in a THF/heptane mixture (50/50 in volume) at −50 °C using sec-BuLi as an initiator. The macromolecular characterization of the PDMSB-*b*-PS was performed by using a combination of size-exclusion chromatography using the universal calibration technique for the determination of the molecular weight, and ¹H-NMR spectroscopy for the block copolymer composition.

Directed Self-Assembly of PDMSB-*b*-PS Thin Films: Untemplated and templated PDMSB-*b*-PS thin films were spin-coated (2–5 krpm) using a 2 wt% copolymer solution in a mixture of THF/PGMEA (2/1). The self-assembly of PDMSB-*b*-PS thin films was

promoted by exposing samples to a continuous stream of THF vapor produced by bubbling nitrogen gas through the liquid solvent, as described previously.^[45] Templated and untemplated film thicknesses have been determined from scratched polymer area and using a Filmetrics F20-UV instrument, respectively.

Topographical Grating Fabrication: The periodic topographical gratings were fabricated using a Lloyd’s mirror interferometer with a 325-nm He-Cd laser beam. To transfer the interference lithography pattern into the Si/45 nm SiO₂ layer, a trilayer resist stack methodology was used. This trilayer was obtained by inserting a hard mask layer consisting of an SiO₂-thick-film between a chemically amplified negative resist resin and an antireflection coating (ARC) layer. After development of the resist, the pattern was transferred into the hard mask then into the ARC, and finally into the SiO₂ by a series of RIE steps to form a grating.

AFM Characterization: AFM (Dimension FastScan, Bruker) was used in tapping mode to characterize the surface morphology of PDMSB-*b*-PS thin films. Silicon cantilevers (Fastscan-A) with a typical tip radius of ≈5 nm were used. The resonance frequency of the cantilevers was about 1.25 kHz. Prior to AFM measurement, PDMSB-*b*-PS thin films were etched with a fluorine-rich RIE treatment in PE-100 chamber (RIE, Plasma Etch) to remove preferentially the PDMSB phase (plasma conditions are: 40 W, 17 sccm CF₄, and 3 sccm O₂).

GISAXS Measurement: GISAXS experiments were performed on the Dutch-Belgian Beamline at the European Synchrotron Radiation Facility (ESRF) station BM26B in Grenoble (12 keV).^[49] The incidence angle was set in the range of 0.1°–0.14°, which is between the critical angle of the PDMSB-*b*-PS film and the silicon substrate, to illuminate (by the beam) the samples with a typical size of 150 mm². 2D scattering patterns were collected with a PILATUS 1 m detector and the sample-to-detector distance was set to 3200 mm. PDMSB-*b*-PS samples for GISAXS measurements were spin-coated onto Si substrates from a 2 wt% copolymer solution in a mixture of THF/PGMEA (2/1), then exposed to a THF vapor to promote the PDMSB-*b*-PS thin film self-assembly.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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