Long-Range Ordering of Block Copolymer Gyroid Thin Films Driven by Solvent Annealing

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Abstract

This work presents an approach to achieve long-range ordering of polystyrene-block-poly(L-lactide) (PS-PLLA) gyroid thin films on a PS-OH and PLLA-OH functionalized (i.e., neutral) substrate using solvent annealing. Interesting morphological evolution from disorder to gyroid and finally cylinder can be found while using a partially selective solvent for PS to anneal the PS-PLLA thin film. To acquire a thin-film sample with thermodynamically stable gyroid morphology, a non-preferential solvent should be used for solvent annealing to enable long-range ordering of gyroid thin film. The ability to achieve long-range ordering of PS-PLLA gyroid thin films with uniform surface opens up appealing applications in nanotechnology. By taking advantage of degradable character of PLLA, nanoporous PS with well-defined texture can be fabricated by hydrolysis and used as a template for synthesis of various nanohybrids and nanoporous materials.

Keywords - Solvent annealing, Thin films, Degradable block copolymers, Orientation

Introduction

Block copolymers (BCPs) have been extensively studied because of their ability to self-assemble into various ordered nanostructures resulting from the incompatibility of their constituent blocks and the constrain of chemical junction. Among all of the nanostructures formed by the self-assembly of BCPs, the double gyroid is one of the most appealing morphologies for practical applications because of its unique geometry, comprising a matrix and two continuous but independent, interpenetrating networks in three-dimensional space. For such nanostructured materials to prove useful in applications, thin-film samples with oriented nanostructures over large area must be formed. The use of solvent vapor to induce the orientation of BCP nanostructures (i.e., solvent annealing) has become one of the most commonly used approaches.

Here, we aim to achieve long-range ordering of PS-PLLA gyroid thin films on a neutral substrate using solvent annealing. As illustrated in Fig. 1, to create a neutral substrate, a Si wafer with SiO$_2$ surface was functionalized using PS-OH and PLLA-OH brushes as reported in our previous studies, giving a non-preferential substrate for the PS-PLLA. For the development of complete gyroid texture, the thickness of the spin-coated thin film should be controlled over the lattice constant (L$_0$) of 100 nm for the gyroid-forming PS-PLLA in bulk. As a result, thin film with thicknesses of 200 nm was prepared onto the functionalized Si wafer by spin coating using PS-PLLA solutions. The formation of the microphase-separated morphology from spin coating is attributed to the selectivity of the solvent, and the disorder-like texture results from fast evaporation of the solvent that gives kinetically trapped morphology instead of the equilibrium gyroid phase.

Fig. 1. Fabrication of long-range ordering of nanoporous gyroid thin films using solvent annealing.

Experiments

Thin-film samples with thickness of 200 nm was prepared on a functionalized SiO$_2$ by spin-coating using chlorobenzene solution of PS-PLLA, and then annealed with chloroform vapor. To investigate the morphological evolution of the PS-PLLA gyroid thin films during solvent annealing, scanning probe microscope (SPM) and transmission electron microscope (TEM) were used to observe the morphologies after solvent annealing followed by fast solvent evaporation.

Results and Discussion

Morphologies of Spin-coated BCP thin films. To create a neutral substrate, a Si wafer with SiO$_2$ surface was functionalized using PS-OH and PLLA-OH brushes as reported in our previous studies, giving a non-preferential substrate for the PS-PLLA. For the development of complete gyroid texture, the thickness of the spin-coated thin film should be controlled over the lattice constant (L$_0$) of 100 nm for the gyroid-forming PS-PLLA in bulk. As a result, thin film with thicknesses of 200 nm was prepared onto the functionalized Si wafer by spin coating using PS-PLLA solutions. The formation of the microphase-separated morphology from spin coating is attributed to the selectivity of the solvent, and the disorder-like texture results from fast evaporation of the solvent that gives kinetically trapped morphology instead of the equilibrium gyroid phase.

Morphological evolution as a function of solvent annealing time. Starting from the disorder-like, microphase-separated morphologies, a good solvent, chloroform, was used for solvent annealing to give required BCP chain mobility for ordering of the disorder-like textures. Thin films with initial thickness of 200 nm was annealing for 50, 100, 200, and 400 s, respectively,
followed by instantaneous removal of solvent from the cast films.

After solvent annealing for 50 s, the morphology remains as disorder-like texture due to insufficient time for ordering. Interestingly, as the annealing time increases to 100 s, characteristic crystallographic plane of (211)G can be observed in thin films. As the annealing time increases from 100 to 200 s, a characteristic crystallographic plane of (110)G can be found in addition to the (211)G plane. These results suggest that the final morphologies of the PS-PLLA thin film (i.e., the forming nanostructures and corresponding orientation) is very sensitive to the annealing time.

As a result, we speculate that it is possible to acquire the formation of gyroid nanostructure with controlled orientation by taking advantage of the phase transitions from disordered phase to ordered phase. Consequently, the transitional gyroid phase can be trapped after quickly removal of the solvent and it is expected to give the cylinder phase after long enough time for solvent annealing. Fig. 2 shows the results of PS-PLLA thin-film sample with solvent annealing for 80 s (< 100 s). Well-ordered (211)G plane is obtained (Figure 2(a)). The TEM projection as shown in Figure 2(b) further demonstrates the forming gyroid phase in the thin film. The corresponding cross-sectional image (Figure 2(c)) shows the <110> projection of the gyroid phase extending from the film surface to the substrate, reflecting the oriented (211)G plane to the air surface.

Fig. 2. (a) Tapping-mode top-view SPM height, (b) TEM, and (c) cross-sectional TEM images of PS-PLLA thin film with the thickness of 200 nm on functionalized SiO2 substrate after solvent annealing for 80 s using chloroform vapor.

Annealing with a non-preferential solvent. With the use of the non-preferential solvent and the neutral substrate, it is reasonable to expect that the PS-PLLA gyroid thin film with (211)G plane oriented parallel to the air surface and also the substrate can be formed after long-time solvent annealing. A neutral solvent, 1,2-dichloroethane,4 was thus used for solvent annealing. Furthermore, characteristic crystallographic planes of (211)G can be clearly identified after solvent annealing using non-preferential solvent, 1,2-dichloroethane. As annealing time increases to 200 s or even longer (e.g. 400 s), the oriented (211)G plane parallel to the air surface remains without further phase transformation. As a result, stable equilibrium morphology with the (211)G plane oriented parallel to the air surface can be obtained. Consequently, nanoporous PS can be simply obtained by hydrolysis of PLLA in the PS-PLLA thin film, as evidenced by FESEM (Fig. 3(a)) and SPM (Fig. 3(b)), reflecting the open-cell character with characteristic (211)G plane at the surface of the thin film. The characteristic (211)G plane after hydrolysis can be clearly identified from the enlarge view of FESEM image as shown in the inset of Fig. 3(a). GISA XS 2D pattern with the characteristic (211)G plane parallel to the thin film plane can be acquired (Fig. 3(c)); the diffraction results are consistent to the results of SPM and FESEM. Also, in contrast to the results of the GISAXS from the PS-PLLA thin film, the diffraction spots from the nanoporous PS can be clearly identified due to the increase on electron density contrast from the replacement of PLLA fraction to the air. As a result, nanoporous PS thin film with well-defined co-continuous nanochannels and uniform surface can be successfully prepared after removal of the PLLA.

Fig. 3. (a) FESEM and (b) Tapping-mode SPM height images of PS-PLLA thin film and (c) 2D GISAXS patterns with the thickness of 200 nm on functionalized SiO2 treated in 1,2-dichloroethane vapor for 400 s after hydrolysis for 30 mins. The inset shows the enlarge view for (a).

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References