Ailoring Spatial Orientations of Microphase-Separated Cylinders and Lamellae of Block Copolymer Thin Films

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Abstract

In the study, I investigated microphase-separated nanostructures of PS-P2VP thin films by annealing in binary solvent vapors of chloroform and methanol. Ordered microphase-separated nanostructures were achieved by controlling solvent annealing conditions. One of the key parameters is the compositions of binary co-solvent vapors. We also discuss the thermodynamic properties of perpendicularly-oriented nanocylinders. Firstly, I discuss different morphologies achieved in thin films upon exposure to binary solvent vapors of various fractions of chloroform and methanol. By an atomic force microscopy (AFM) and grazing-incident small-angle X-ray scattering (GISAXS), I identified that the nanostructures were comprised of perpendicularly-oriented cylinders with hexagonal lattice, the coexistence of parallel-oriented cylinders and perforated lamellae, and parallel-oriented lamellae with gradually increasing the proportion of methanol in the cosolvent vapors. In particular, when PS-P2VP thin films were annealed in chloroform for a long time period vertically-oriented cylinders were obtained. By contrast, parallel-oriented lamellae were obtained when post-annealing was carried out twice in chloroform vapor, we would obtain a spherical morphology. Besides, we use theoretical calculation to explain the influence of added methanol vapor on the thin film stability.

Keywords –PS-P2VP, co-solvent annealing, self-assembly

Introduction

The self-assembly behavior in thin films of block copolymers (BCP) has been widely studied because BCP thin films have morphologies more diverse than those of bulk samples1–3. Fabricating BCP thin films by spin coating combined with annealing under a solvent vapor becomes a simple, robust and effective way to produce nanodomains with long-range lateral order or ordered patterns with diverse morphologies4–5. The swelling of BCP thin films with a solvent to a particular extent to decrease the glass transition temperature Tg of polymers imparts a chain mobility during the solvent annealing; highly ordered arrays are thus achievable with solvent annealing at low temperatures. For BCP that thermally degrades easily at high temperatures, solvent annealing offers an alternative route to promote highly ordered arrays of nanodomains. Another advantage of solvent annealing is that, whereas thermal annealing inevitably leads BCP thin films to have equilibrium nanodomains, solvent annealing causes the formation of metastable nanostructures that can be preserved on the vitrification of constituted blocks after rapid evaporation of the solvent.

We investigated the structural evolution of polystyrene-block-poly-2-vinylpyridine P(S-b-2VP) thin films with solvent annealing in mixed vapors of chloroform and methanol. Our objective was to acquire an improved understanding of the self-assembly behavior of thin films under solvent annealing in mixed vapors of binary immiscible solvents.

Experiment

Polystyrene-block-poly-2-vinylpyridine P(S-b-2VP), Mn = 66.5 kg/mol, the volume fraction of PS and P2VP blocks being fPS=71% and fPEO=29%, PDI=1.05 was purchased from Polymer Source, Inc. and used as received. Bare silicon wafers (SiOx/Si) were cleaned in a piranha solution (3:1 v/v 30 % H2O2,H2SO4) for 40 min, rinsed with deionized water, and dried under flowing N2. P(S-b-EO) was dissolved in O-xylene. P(S-b-2VP) films of varied thickness were prepared via spin coating from polymer solutions of 1.5 mass % at 1000 rpm for 60 s. In an attempt to control the ordering and spatial orientation of nanodomains with solvent annealing, each film was then placed in a sealed jar with chloroform/methanol vapor for 5 h of solvent annealing. Chloroform is a non-selective, nonpolar solvent for the PS and P2VP block whereas methanol is the most selective solvent for the P2VP block. Chloroform (Psat=160 mmHg at 25 °C) is more volatile than methanol (Psat=126.9 mmHg at 25 °C).

To observe nanodomains and dewetted morphologies, we investigated the surface of thin films with an atomic-force microscope (AFM, SPA400 Seiko) in the tapping mode. We used aluminum-coated silicon cantilevers of length 125 μm, width 30 μm and thickness 4 μm. The force coefficient was approximately 42 N/m and the resonance frequency used was 160 kHz. For optical microscopy (OM, Olympus BX-BL2A) measurements we used the reflection mode. Measurements of grazing-incidence small-angle X-ray scattering (GISAXS) were performed with synchrotron source (λ= 1.55 Å at 8 keV) at beamline BL23A of National Synchrotron Radiation Research Center (NSRRC).

Results & Discussion

The solvent-annealing process of PS-P2VP using chloroform and methanol, we found that the content of methanol has a great impact on nanostructures. With gradually increasing the proportion of methanol, the nanostructures were comprised of perpendicularly-oriented cylinders (The content of methanol is 0%) with hexagonal lattice, the coexistence of parallel-oriented cylinders and perforated lamellae (The content of methanol is 25%), and parallel-oriented lamellae (The content of methanol is 33% and 40%) (Seeing Fig.1). It is worth mentioning that the 1st layer structure of parallel-oriented lamellae is parallel cylinders, because of the
interfacial energy of substrates. Fig.2 shows the GI-SAXS result of 2D pattern and 1D in-plane scattering profile. The 2D pattern of perpendicularly-oriented cylinders displays five sharp diffraction features at \(\mathbf{q}/\mathbf{q}^{\perp}\) ratios \(1:2:4:8:16\), and the other morphologies of PS-P2VP displays more than three sharp diffraction features. From the above information, the ordering and types of PS-P2VP nanostructures can be controlled through this solvent annealing process.

In particular, when PS-P2VP thin films were annealed in chloroform for a long time period vertically-oriented cylinders were obtained. By contrast, parallel-oriented lamellae were obtained when post-annealing was carried out twice in chloroform vapor, we would obtain a spherical morphology. We can understand that spherical morphology is thermodynamically stable state and vertically-oriented cylinders is thermodynamically metastable state.

References


