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Perpendicular oriented cylinders via directional coalescence of spheres embedded in block copolymer films induced by solvent annealing

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ABSTRACT

Polystyrene-b-poly(methyl acrylate) (PS-b-PMA) block copolymer with PS volume fraction of 25.2 vol% was synthesized by atom transfer radical polymerization. Non-pretreated silicon wafers were used as the substrates to prepare perpendicular oriented PS cylinders in PMA matrix via solvent annealing which could induce the transformation of spheres to vertically oriented and hexagonally packed cylinders. The spherical microdomains were formed after the evaporation of solvents from the solutions of the block copolymer in selective solvents mixed from methanol, acetone and dichloromethane. The thickness of films could be as thick as 1000 nm, which were much thicker than usual cases and the cylinders came from the directional coalescence of the spheres, thus any pre-treatments of the substrates were not required for perpendicular orientation. The structures were characterized by small angle X-ray scattering (SAXS), transmission electron microscope (TEM), atom force microscopy (AFM) and grazing incidence small angle X-ray scattering (GISAXS).

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1. Introduction

Incompatibility between two blocks of a block copolymer (BCP) can drive the micro-phase separation, forming a variety of morphologies, including spheres, cylinders, bicontinuous gyroids and lamellae etc. [1–5] in tens of nanometers as a function of composition. During past decades, much attention has been given to this field, because of the compelling applications such as photonic band gap materials, selective separation membranes and templates for advanced nanotechnology [1,6–24]. The key to these potential applications is to control the perpendicular orientation and lateral ordering of the microdomains. To fabricate materials with long-range order and precisely controlled nanoscale structures, diverse approaches have been developed, including shear flow [25],

applied electric fields [24,26], thermal gradients [27], chemically patterned substrates and balancing interfacial interaction [28]. Continuous attentions have been given to develop methods to achieve perpendicular orientation of cylindrical microdomains in BCP films. Such films have long been recognized potential in a broad range of applications. Specifically, vertically aligned cylinders which penetrate through the films and are in uniform diameter of several nanometers can be selective removed by chemical rinsing or plasma etching. The resultant nano-porous membranes are highly considered for selective transports, size-selective separations and transferable templates for nanotechnology [14–18,29–31].

In our previous work, we reported a directional coalescence of spherical nanostructures in the direction perpendicular to the film surface could be applied to vertically align cylindrical microdomains, because of the memory of the chemical potential gradient [32]. Nonequilibrium spherical nanostructures formed from the minor block species of a BCP in a selective solvent for the major

component could be transferred and trapped in the film after casting and solvent evaporation, and subsequent thermal annealing of the sample over glass transition temperatures of both blocks induced the directional coalescence of nonequilibrium spheres, forming perpendicular orientation of cylindrical microdomains. Using this strategy, we successfully realized the vertical alignment of polystyrene (PS) cylindrical microdomains in the poly(ethylene–butylene) (PEB) matrix with film thickness of about 1 mm, which was much thicker than the thickness limit as we mentioned above. However, in our previous work, we demonstrated that this mechanism can only be applied to the films with a thickness over 10 μm. Thus, developing a common and facile method that could be used to prepare vertically aligned cylinders in films with various thicknesses scales is a key point to realize those potential applications.

Herein we continuously demonstrate that the strategy could be applied to prepare perpendicular oriented cylinders in BCP films using a different annealing method. In our previous study, the thermal annealing was applied to form the perpendicular oriented cylinders in BCP thick films, while in this study the solvent annealing was firstly reported to induce the directional coalescence of sphere in both thick and thin films. Polystyrene-*b*-poly(methyl acrylate) (PS-*b*-PMA) block copolymer with PS volume fraction of 25.2 vol% was synthesized by atom transfer radical polymerization (ATRP). Dissolving PS-*b*-PMA BCPs in mixture of acetone, methanol and dichloromethane and after spin cast, the spherical microdomains can be formed during the evaporation of dichloromethane which makes the mixed solvent more selective for PS. Subsequently, solvent annealing induced directional coalescence of nonequilibrium spheres to form hexagonally packed cylinders vertical to the surface of substrate. Herein, it is easy to understand that the surface properties of substrates, e.g. hydrophilic, hydrophobic, have little influence on the morphology and orientation behaviors, because the thickness of films was thicker than those usual cases (30–50 nm) and the preferential interactions of the blocks with the substrate have been overcome, thus the spherical microdomains could be maintained inside the films after spin cast and solvent evaporation. Any pre-treatments, such as oxidization, chemically patterning of substrates, pre-spin cast or pre-grafting of a random block copolymer on substrates, are not required in our study. This strategy could provide a novel and simple methodology to fabricate highly perpendicular cylinders or nano-channels in BCP films with various thickness scales, which would play a vital role in practice usage.

2. Experimental section

2.1. Materials

Bis(2-dimethylaminoethyl)methylamine and (1-bromoethyl) benzene were purchased from Sigma–Aldrich Co., LLC. Styrene, methyl acrylate, CuBr, CuBr$_2$, anisole, acetone, methanol, dichloromethane (CH$_2$Cl$_2$), tetrahydrofuran (THF) and toluene were purchased from Nacalai Tesque. Styrene and methyl acrylate monomers were purified by mixing it with aluminum oxide granules to remove inhibitors before polymerization. Other reagents were used as received (analytically pure). Silicon wafers with resistivity <0.2 Ω cm purchased from the Nilaco Corporation and coverslips purchased from Matsunami Glass Ind., Ltd. Company were washed by toluene and dried in air before use.

2.2. Synthesis of PS-*b*-PMA block copolymer

ATRP has been proved to be a powerful tool to synthesize various block copolymers, as comprehensively reviewed elsewhere [33,34]. Here in a typical procedure, styrene, (1-bromoethyl)benzene, CuBr,

CuBr$_2$, ligands and certain amount of anisole were added into a round-bottomed flask. The flask was degassed by three freeze–pump–thaw cycles, sealed in vacuum, and immersed into oil bath at 90 °C to start the polymerization. After a prescribed time, the flask was exposed to air and the solution was diluted with toluene. Active aluminum powders were added into the solution and stirred for several hours to remove the catalysts. Subsequently, polystyrene macroinitiator was precipitated in large amount of methanol followed by filtration and dried under reduced pressure at room temperature. Chain extensions were performed in a similar process. Methyl acrylate monomers, PS macroinitiators, CuBr, CuBr$_2$, PMDETA and certain amount of anisole were added into a round-bottomed flask. After three freeze–pump–thaw cycles, the flask was sealed in vacuum and immersed into oil bath at 100 °C to start the polymerization. After a prescribed time, the block copolymer of PS-*b*-PMA was precipitated in a large amount of methanol and dried under reduced pressure at room temperature. The PS-*b*-PMA BCPs with PS volume fraction of 25.2 vol% were synthesized in this method, and details were summarized in Table 1 and Figs S1 and S2.

2.3. Preparation of thick and thin films

Polymer solutions were prepared by dissolving the BCPs in selective solvents mixed from CH$_2$Cl$_2$, methanol and acetone in a volume ratio of 0.37:0.21:0.42, of which solubility parameters are 9.7, 14.5, and 10 (cal/cm^3)$^{1/2}$, respectively. And the solubility parameter of the mixed solvents is calculated as 10.8 (cal/cm^3)$^{1/2}$ which is good solvent for PMA (10.7 (cal/cm^3)$^{1/2}$) but poor solvent for PS (8.6 (cal/cm^3)$^{1/2}$) [35]. It is a slightly difficult to dissolve BCPs in the mixture of methanol and acetone. Thus, to enhance solubility, CH$_2$Cl$_2$ which is good for both PS and PMA, was used as the co-solvent. Dichloromethane can volatilize rapidly at room temperature from the mixed solution. After complete evaporation, most methanol and acetone still remain in solution. Firstly, the copolymer was dissolved in CH$_2$Cl$_2$ under magnetic stirring, after totally dissolved, methanol and acetone were added into the CH$_2$Cl$_2$ solution. The mixture solution was stirred overnight prior to film preparation in order to make sure the total dissolution. Unless otherwise stated, the polymer concentration in the mixed solutions was about 5 and 10 wt%. To prepare thick films, polymer solutions were poured into a polytetrafluoroethylene (PTFE) Petri dish, after complete evaporation of solvents which usually took about one week at room temperature, an as-cast film with the thickness of about 1 mm was obtained. Subsequently, the thick film was cut into small pieces, thermal annealed in a vacuum oven at 180 °C for about 48 h and solvent annealed in a box full of THF vapor for several hours. Thin films were obtained by a spin-casting method at 3000 rpm for 30 s on a silicon wafer with one square centimeter in size. After that, the thin films were placed into a box full of CH$_2$Cl$_2$ vapor for several minutes to perform solvent annealing.

2.4. Characterization

Size exclusion chromatography (SEC) was carried out for determination of molecular weight and its distribution of the synthesized polymers in the following conditions: in THF (1 mL/min) at 313 K on four polystyrene gel columns (Tosho TSK) gel GMH

Table 1
Characteristics of PS-*b*-PMA synthesized by ATRP.

PS M_n (kg/mol)[a]	PS M_w (kg/mol)[a]	PS PDI[a]	BCP M_n (kg/mol)	BCP M_w (kg/mol)[a]	BCP PDI[a]	PS volume fraction (vol%)[b]
9.1	9.9	1.09	42.6[a] 38.1[b]	59.1	1.39	25.2

[a] Determined by SEC columns calibrated with polystyrene standards.
[b] Determined by ^{1}H NMR.