Mushroom-shaped Morphology Formed in Thin Films of Cylinder-forming Block Copolymer

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Abstract The morphology of the film of polystyrene-block-poly(methyl methacrylate)(PS-b-PMMA) block copolymer having polystyrene(PS) cylinder forming composition spin-coated on a neutral brush modified silicon substrate has been investigated in this report. A mushroom-shaped morphology formed in the film with one period to two periods(L_0-2L_0) in thickness, which was spin-coated under a low humidity condition(RH *ca.*13%) and then thermally annealed at an extreme high temperature(230 °C). The results suggest that the spin-coating condition together with the confinement conditions plays a crucial role in the interesting morphology formation.

Keywords Block copolymer; Film; Morphology

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1 Introduction

The phase behavior of block copolymers has been studied for several decades and continues to be an active area of researches in both experimental and theoretical points of view. The ordered microstructures of block copolymers in thin films have been successfully used in "bottom-up" nanofabrication such as templates for inorganic composites or lithographic processes on hard substrates^[1-3]</sup>. Although the bulk phase behavior of block copolymers has been well described in terms of two parameters of the composition and the degree of segregation between the blocks^[4], the thin film ordered structures and their orientations are more complicated due to the film preparation conditions and film confinement conditions such as the wetting properties of each block on the substrate surface and at the air/film interface^[5-16]. Hence, to design and process such materials, it is essential to understand their behavior in thin films in detail.

In most of the researches on thin block copolymer films, lamella-forming systems have been considered^[5-8], and the effects of wetting conditions^[5-6] and the energetic/chemical nature of the surfaces^[7-9] on lamellae ordering are relatively well understood. However, these findings are only partially confirmed for compositionally asymmetric block copolymers forming cylindrical and spherical domains^[5,6]. For cylinderforming block copolymers, theoretical work suggests that the preferential wetting of one block in the thin films may induce layer-like domain structures in a region close to the planar surface^[9,10] and has been confirmed by a few studies^[9,11]. Nevertheless, the components of block copolymers generally have different surface tensions, and the microstructure of the block copolymer thin film depends strongly on which component(majority component or minority component) prefers the substrate. Extensive researches have been focused on the microstructure of the block copolymer thin films with the minority component having higher surface tension^[9,12–14]. For cylinder systems in which the minority component has a lower surface tension, such as polystyrene-polybutadiene(SB) block copolymer with polybutadiene(PB) cylinder forming composition, Harrison *et al.*^[15] noted that the near surface regime was composed of a planar wetting layer, this surface effect was also seen in free standing films^[16].

In this work, we studied the polystyrene(PS, with lower surface tension) cylinder orientation as a function of the surface field on the substrate and the free surface of the film in the thin films of PS cylinder-forming polystyrene-block-poly(methyl methacrylate)(PS-b-PMMA) block copolymer. An attractive finding is that the PS cylinders are mushroom shaped. From our study, it appears that such mushroom-shaped PS cylinders can be explained *via* constraint conditions of the film formation during preparation process. A direct observation of the mushroom-shaped morphology dominated nanostructure shown in this work will offer a good example to refine the input parameters to the theory and simulation and to test the predictions against the results under other conditions in block copolymer researches. The study may lead to an effective approach to improve the order and make the morphology robust.

2 Experimental

2.1 Materials and Sample Prepararion

An asymmetric diblock copolymer used in this paper, PS₄₅₆-b-PMMA₁₄₀₄(the numbers in subscript refer to the number-average degree of polymerization of each block), with a polydispersity index of 1.10 was purchased from Polymer Source Inc., and used as received. In bulk state, this block copolymer adopts hexagonally packed PS cylinders with a center-to-center distance(the period L_0) of about 66 nm embedded

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in a PMMA matrix, confirmed by small-angle X-ray scattering (SAXS). A hydroxy end-functionalized random copolymer of styrene and methyl methacrylate, denoted as PS-*r*-PMMA, with a styrene fraction of 0.6 and M_w 7400 g/mol and a polydispersity of 1.80, was used to prepare energetically neutral brush for the block copolymer.

For the preparation of the block copolymer film, two kinds of substrates were used. One was bared silicon wafer with a native oxide layer of 100 nm. It was cleaned in a mixture of H_2SO_4 and $H_2O_2(70:30$, volume ratio) for 30 min at 120 °C, followed by thorough rinsing with distilled water. Then the cleaned wafers were dried in a stream of nitrogen. The other one was the above cleaned silicon wafer modified with the random copolymer brush. It was prepared by spin-coating PS-*r*-PMMA onto the cleaned silicon wafer followed by annealing at 180 °C under vacuum for 2 d. This procedure permitted the coupling reaction between the hydroxyl group of PS-*r*-PMMA and the oxygen group in the silicon oxide layer. A thin layer(*ca.* 6 nm) of PS-*r*-PMMA remained on the surface after rinsing with toluene.

Block copolymer thin films with 30–200 nm in thickness were prepared by spin-coating dilute toluene solutions onto the bared or the neutral brush modified silicon wafers under low or high humid conditions(the relative humidities of low and high humidities were RH *ca.* 13% and >75%, respectively). The thickness of the block copolymer film, controlled by the concentration of the solutions with mass fraction of 1% or 2% and the spin-coating speed with 1000–3000 r/min, was determined by ellipsometry and atomic force microscopy(AFM) after scratching with a blade. After being dried at room temperature under vacuum for 24 h to remove residual solvent, the films were annealed under vacuum at 180 °C for 2 d or 230 °C for 5 h followed by quenching to room temperature.

2.2 Instruments

The morphologies of the block copolymer films were investigated by tapping mode scanning probe microscopy(SPM) (Dimension 3100, Nanoscope from Digital Instruments Corp.), field emission scanning electron microscopy(FESEM, Hitachi, S-4800, operated at 3 kV), and transmission electron microscopy(TEM, Hitachi, S-7600, operate at 100 kV). The samples for FESEM were exposed to RuO₄ vapor for 3 h at room temperature to selectively stain PS to enhance the mechanical stability of PS followed by UV etching for 80 min and acetic acid rinsing for 30 min and washing with distilled water. The samples were then coated with platinum and dried in vacuum for 24 h. For TEM, the films were floated onto the surface of a 5% (mass fraction) HF solution, transferred to a water bath, and then collected on TEM copper grid. Before checking, the samples were exposed to RuO₄ vapor for 20 min at room temperature to selectively stain PS to enhance the contrast between PS and PMMA, the PS nanodomains were dark and the PMMA nanodomains were bright.

3 Results and Discussion

Fig.1 shows the typical morphology of the block

copolymer thin film with *ca*. 110 nm in thickness spin-coated under RH *ca*. 13% and subjected to thermal anneal at 230 °C for 5 h. Fig.1(A) shows scanning probe microscopy(SPM) phase image of PS-b-PMMA film. Because the PMMA block is harder than PS block at room temperature, the PMMA phase looks brighter in an SPM phase image^[17,18]. Therefore, the dispersed phase looking darker in the SPM phase image in Fig.1(A) should be PS phase, and the content of the PS nanodomains(with sizes ranging from 43 nm to 200 nm) on the film surface was calculated to be 46%, larger than that in the bulk (27%). Fig.1(B) shows TEM image of this film, where PS nanodomains being darker because of selective staining are seen as dispersed phase, which is consistent with SPM phase contrast image in Fig.1(A).



Fig.1 Morphology of block copolymer film on neutral brush modified silicon substrate with *ca*. 110 nm in thickness and subjected to thermal anneal at 230 °C for 5 h

(A) SPM phase image; (B) TEM image of the film before removal of PMMA; (C) and (D) plane-view and cross-sectional FESEM images of the film after UV removal of PMMA, respectively. The white circles in (A), (C) and (D) indicate the connection of the mushroom caps, which look like parallel PS nanodomains at the film surface.

Fig.1(C) and (D) give plane-view and cross-sectional FESEM images of the film respectively after PMMA matrix has been removed. Vertical mushroom-shaped PS cylinders consisting of larger sized caps(with size ranging from 43 nm to 200 nm) and smaller sized stems(with size ranging from 37 nm to 43 nm) are observed. From the comparison of the film surface structure as shown in images (A) and (C) with the film internal structure as shown in image (D) in Fig.1, it is rationally to expect that the short parallel-like PS nanodomains on the film surface marked by white circles in images (A), (C) and (D) in Fig.1 are formed by connection of the mushroom caps.

It is of interest to note that the vertical PS cylinders in the film are not straight but mushroom-shaped. Generally, the morphology of a block copolymer thin film prepared by thermal anneal strongly depends on the film confinement conditions, the film thickness and the preference to which component of the substrate and the free surface due to the two components having different surface tensions. To explore the film confinement on the mushroom-shaped morphology formation, the morphologies of films with different thicknesses on different substrates followed by thermal anneal at different temperatures under vacuum were investigated. For the block copolymer film(*ca*. 110 nm in thickness) prepared on bared silicon wafer, there were seldom residual PS nanodomains(not shown) after thermal anneal under vacuum at 230 °C for 5 h followed by the UV removal of PMMA matrix, indicating that the PS nanodomains were not attached to the substrate. As is known, the silicon wafer with the oxide layer strongly prefers to the PMMA block and accordingly there is a layer of PMMA on the substrate after thermal anneal^[7,8]. After UV etching and acetic acid rinsing, the PMMA is removed and hence there is seldom residual nanodomains on the substrate. Therefore, it is reasonably to conclude that the neutral brush on the silicon wafer is prerequisite in the mushroom-shaped PS cylinder formation.

At the same time, the effect of the confinement conditions of the film free surface on the mushroom-shaped PS cylinder formation was examined at different thermal anneal temperatures because the surface tension difference between PS and PMMA decreases with increasing temperature^[19,20] and accordingly the preferential affinity of the film free surface for a certain component can be manipulated. Fig.2 shows the morphology of the film with a thickness of ca. 110 nm spin-coated under RH ca. 13% on the neutral brush modified substrate and annealed at 180 °C for 2 d. The SPM phase image of the original film in Fig.2(A) shows that the content of PS which is looked darker on the film surface is about 65%, larger than that in the film annealed at 230 °C[ca. 46% as shown in Fig.1(A)], indicating that more PS nanodomains form parallel cylinders. The FESEM image after the UV removal of the PMMA matrix in Fig.2(B) shows that the PS nanodomains are perpendicular near the bottom of the film but parallel near the free surface of the film, which is consistent with the SPM phase image in Fig.2(A). Near the bottom of the film, there exists a neutral brush and it is possible to have a perpendicular orientation of PS cylindrical nanodomains due to the balanced interaction between each block and the neutral brush. However, near the free surface of the film, since the higher surface tension of PMMA decreases more rapidly with temperature than the lower surface tension of PS, the PS block has more tendency to locate at the film free surface at lower temperature(180 °C) than that at higher temperature (230 °C) to minimize the free energy of the film and hence the volume fraction of PS on the film surface at 180 °C(ca. 65% in Fig.2) is larger than that on the film surface at 230 °C(ca. 46% in Fig.1). However, the high



Fig.2 Morphology of block copolymer film on neutral brush modified silicon substrate with *ca*. 110 nm in thickness subjected to thermal anneal at 180 °C for 2 d

(A) SPM phase image before removal of PMMA;(B) FESEM image after UV removal of PMMA.

temperature can not mediate the surface tension at all and accordingly PS still preferentially locates on the film surface. The content of PS on the film surface(*ca*. 46%) is still higher than that in film bulk(*ca*. 27%). That is, mushroom-shaped PS rods consisting of large-sized caps and small-sized stems formed. The result indicates that the preferential affinity of the film free surface for PS block decreased by the extreme high temperature at 230 °C plays a key role in the vertical mushroom-shaped PS cylinders formation.

Another crucial factor of the film confinement conditions, film thickness, on the mushroom shaped PS cylinder formation was also examined. Fig.3 shows the cross-sectional FESEM micrographs of the block copolymer films with 30 nm(ca. 1/2 L_0), 65 nm(ca. L_0), and 200 nm(3 L_0) respectively in thickness spin-coated on the neutral brush modified substrate at RH ca. 13% followed by thermal anneal at 230 °C under vacuum for 5 h. Obviously, when the film thickness is ca. $1/2L_0$ as shown in Fig.3(A), the PS block forms only hemispheres displayed on the neutral brush after the UV removal of the PMMA matrix. The film thickness increases to ca. L₀, the PS nanodomains form vertical mushroom-shaped cylinders, as shown in Fig.3(B). And when the film thickness is $ca. 3L_0$, the PS nanodomains form a trinary structure consisting of vertical mushroom-shaped cylinders near the top of the film, vertical cylinders near the bottom of the film, and vertical and horizontal cylinders in mixed orientation at the middle of the film. That is, the mushroom shaped morphology can not span the film.



Fig.3 FESEM images of block copolymer films with different thickness on neutral brush modified silicon substrate subjected to thermal anneal at 230 °C for 5 h after UV removal of PMMA

(A) ca. $1/2L_0$; (B) ca. L_0 ; (C) ca. $3L_0$.

It is noteworthy that at the bottom of the film there exists a neutral brush which makes it possible to have a vertical orientation of PS cylindrical nanodomains because of the balanced interaction between each block and the neutral brush^[8,21]. And on the free surface there also exists a "neutral" environment manipulated *via* the extreme high temperature which makes the PS component can not cover the whole free surface in spite of having lower surface tension. As is known, the confinements of both substrate and free surface extend into the bulk with a decay length of one microdomain spacing respectively^[9,22]. Combining both two up-bottom("neutral" free surface) and bot-tom-up(neutral brush) effects, the controllable film thickness in our case is expected to be about two nanodomain spacings($2L_0$). The results in the present case indeed confirm that when the film thickness is less than $2L_0$, *ca.* 110 nm, as shown in Fig.1, we can clearly observe the PS cylinders formed vertical mushroom-shaped morphology, when the film thickness is *ca.* $3L_0$, it is difficult to observe vertical mushroom-shaped PS cylinders, but a trinary structure as shown in Fig.3(C). The above results indicate that the confinement of the film indeed plays a crucial role in the mushroom-shaped morphology formation in the present PS-b-PMMA with PS cylinder forming composition.

For this interesting mushroom-shaped morphology, it is also necessary to mention the importance of the low humid condition, RH ca. 13%, during spin-coating the dilute block copolymer solution onto solid substrate. For the film prepared under high humid condition(RH ca. 75% and 90%), no vertical PS cylinders formed even after high temperature thermal annealing, suggesting that the humid condition during spincoating process may also be a crucial effect on the vertical mushroom-shaped PS cylinder formation. In general, different humid condition results in different solvent evaporation rate and accordingly different amounts of residual solvent remain in the film. Higher humidity will result in a larger amount of residual solvent in the film. For the film prepared under a high humid condition, the high amounts of residual solvent make both two blocks have enough time to relax to minimize the free energy of the film and hence form a layer of PS covering the film surface due to its comparatively lower surface tension and its more dissolvable in toluene than PMMA, as shown in Fig.4(A) and (B). This estimation can be confirmed by the water contact angle of the film, ca. 84°, a typical water contact angle of PS homopolymer. In this case, the fact that the PS nanodomains have already located on the film surface(stable state) makes it difficult to induce them to orient vertically to the film surface. Thus, it is expected that it is this layer of PS that constrains the vertical mushroom-shaped PS cylinders formation. On the contrary, there are both components of PS and PMMA on the surface of the as-spun film prepared under a low humid condition, RH ca. 13%[Fig.4(C) and (D)]. The contact angle of this film is ca. 79°, which is very similar to the value of the as-thermal-annealed film in Fig.1(A) and (B). In this



Fig.4 Plane-view[(A) and (C)] and cross-sectional[(B) and (D)] FESEM images of the as-spun film prepared under different humid conditions after UV removal of PMMA

> (A) and (B) Prepared under high humid condition (RH *ca.* 90%); (C) and (D) prepared under low humid condition(RH *ca.* 13%).

case, it is easy to induce the PS nanodomains to orient vertically to the film surface by high temperature, say, *ca.* 230 °C.

In summary, we have studied mushroom-shaped morphology of the film of PS-b-PMMA block copolymer having PS cylinder forming composition with the thickness L_0-2L_0 by thermal anneal of the film at an extreme high temperature(230 °C). The results suggest that the spin-coating condition together with the confinement condition plays a crucial role in the interesting morphology formation. The low content residual solvent in the film spin-coated under a low humid condition results in the two components of PS and PMMA sharing the film surface and hence the PS nanodomains can form mushroom-shaped morphology with mushroom cap locating near the top and the mushroom stem locating near the bottom of the film in virtue of the extreme high annealing temperature.

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