Dual Morphology of Islands and Fractal Holes in Block Copolymer Thin Films

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The fractal growth phenomenon has attracted many investigators due to its intriguing *self-similar* structure usually originating from the diffusion-limited motion of interfaces.[1–3] Examples of this nonequilibrium pattern formation include dendritic solidification in an under-cooled medium,[4] viscous fingering,[5] and electrodeposition.[6] Recently, Koneripalli et al.[7] added one more example to a broad class of this patterning process; they reported the fractal hole growth in conformationally strained block copolymer thin film composed of $^3/_2$ lamellar bilayers.

It is well-known that symmetric diblock copolymers form lamellar microdomains on the order of their radii of gyration due to the constraint of chemical junction points between the two polymer blocks limited to the interface.[8] When spun-cast into thin films, the lamellae preferably align parallel to the substrate with *symmetric* or *asymmetric* wetting depending on the interplay between the substrate interaction and the surface tension of each block. This further causes the formation of island or hole structures with their heights quantized in $(n + 1/2)L_0$ for the asymmetric wetting or in nL_0 for the symmetric wetting since the block copolymer lamellae tend to maintain their equilibrium lamellar period L_0.[8–11] Up until now, only islands or holes have been observed in block copolymer thin films, which are thermodynamically stable structures.

In this communication, we report, for the first time, the *dual morphology* of islands and *fractal holes* in a block copolymer thin film with an initial thickness of $1.5L_0 < t_0 < 2.0L_0$, which represents a kinetically trapped metastable structure. To this end, lamellar-forming polystyrene-*block*-poly(2-vinylpyridine) (PS–P2VP) diblock copolymer thin film with a thickness of $t_0 = 1.8L_0$ was spun-cast from *N,N*-dimethylformamide (DMF)[12] onto Si substrate coated with ultrathin poly-(allylamine hydrochloride) (PAH) sublayer. The resultant film contains a small amount of residual solvent due to a high boiling point of DMF (T_b = 153 °C). Optical (OM) and atomic force microscopies (AFM) were combined together to investigate the complex thin film morphology of block copolymers originating from the competition between the lamellar ordering and the slow evaporation of the residual solvent during the annealing process.

PS–P2VP copolymer having a PS weight fraction of 0.37, which was determined by H NMR, was synthesized by sequential anionic polymerization in tetrahydrofuran (THF) at −78 °C using *sec*-butyllithium as an initiator. The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, were determined to be 111 kg/mol and 1.16, respectively, by GPC using PS standards. Small-angle X-ray scattering (SAXS) measurements carried out at 4C1 beamline in Pohang Light Source (PLS), Korea, revealed that our PS–P2VP forms lamellar microdomains in bulk over a wide range of temperature covered in this work. Equilibrium bulk lamellar period of the block copolymer was measured to be 50 nm at 180 °C from the relationship of $L_0 = 2\pi/q_{max}$, where q_{max} is the wavenumber at the first-order peak.

To prepare block copolymer thin films (ca. 89 nm thick), ultrathin film (2 nm thick) of PAH ($M_w \sim$ 70 000, Aldrich Chem. Co.) was first prepared by spin-coating 10 mM aqueous solution of PAH at 4000 rpm onto a Si wafer, which was pretreated with RCA solution (H_2O_2: NH_4OH:H_2O = 1:5:1) at 60 °C for 20 min and washed with deioninzed water. A 4 wt % solution of PS–P2VP in DMF was then spun-cast at 2000 rpm onto the PAH-coated substrate. Film thickness was measured using a Gaertner ellipsometer with a He–Ne laser having λ = 632.8 nm.

The specimens were annealed in a vacuum oven at 180 °C, which is well above the glass transition temperatures T_g's of both blocks, for a given period time, and then quenched to room temperature for observations with OM and AFM. OM was carried out using a Nikon OPTIPHOT-2POL in reflection mode. AFM measurements were performed using a Digital Instruments Nanoscope IIIa in a tapping mode with a Si_3N_4 tip.

Figure 1 shows optical micrographs in reflection mode for a PS–P2VP thin film with t_0 = 89 nm ($\sim 1.8L_0$) after annealing at 180 °C in a vacuum for (a) 10, (b) 30, (c) 43, and (d) 55 h. Typical images with smooth surface but different heights can be clearly seen. The dark green region is higher than the brown region, and the brown region is higher than the light yellow region, as will be revealed by the AFM measurement below. Asymmetric wetting occurs in our system since PS wets the surface due to its lower surface energy while P2VP wets the PAH substrate due to its higher affinity. In this case, *interconnected* island structures are expected for the thickness ratio of t_0/L_0 = 1.8.[13] Indeed, these spinodal-like interconnected island structures[14] in a dark green color[15] are observed with brown backgrounds at the initial stage of annealing as shown in Figure 1a. Further annealing, however, leads to the abnormal formation of light yellow fractal-like spots within a brown region as shown in Figure 1b. These spots correspond to fractal holes and grow in size with annealing time as shown in Figure 1c,d. The typical size of fully grown fractal holes exceeds 50 μm, which is quite large.

AFM was also carried out since OM does not provide accurate information on the height profile of the film. Figure 2 shows an AFM height image and a cross-sectional height profile of a fractal hole in a PS–P2VP thin film with $t_0 = 1.8L_0$ after annealing at 180 °C for 55 h in a vacuum. Three flat regions with different heights are clearly indicated in the image, implying that the fractal region corresponds to the hole with the lowest height. The cross-sectional height profile in the upper part of Figure 2 shows that both the step height of islands and the step depth of holes are about 55 nm. This value is consistent with the bulk lamellar period of L_0 = 50 nm at 180 °C obtained from SAXS measurements. The slight difference in L_0 between the two

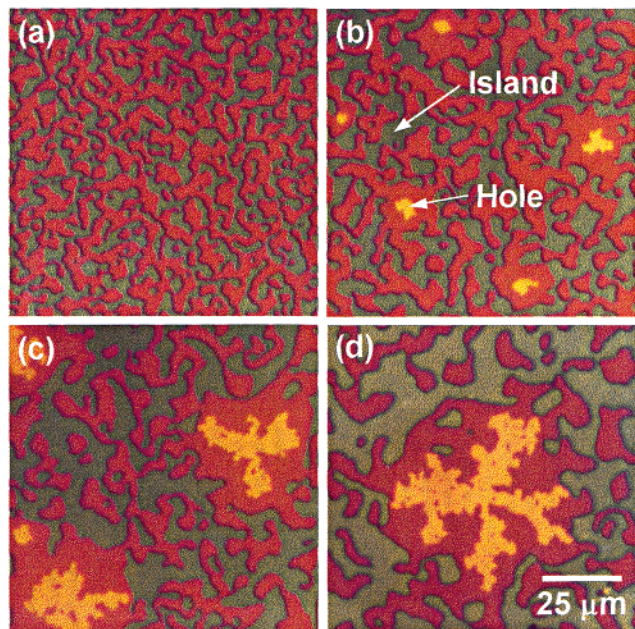* To whom correspondence should be addressed. E-mail: khchar@plaza.snu.ac.kr.

Figure 1. Optical micrographs in reflection mode for a PS–P2VP thin film with $t_0 = 1.8L_0$ after annealing at 180 °C in a vacuum for (a) 10, (b) 30, (c) 43, and (d) 55 h.
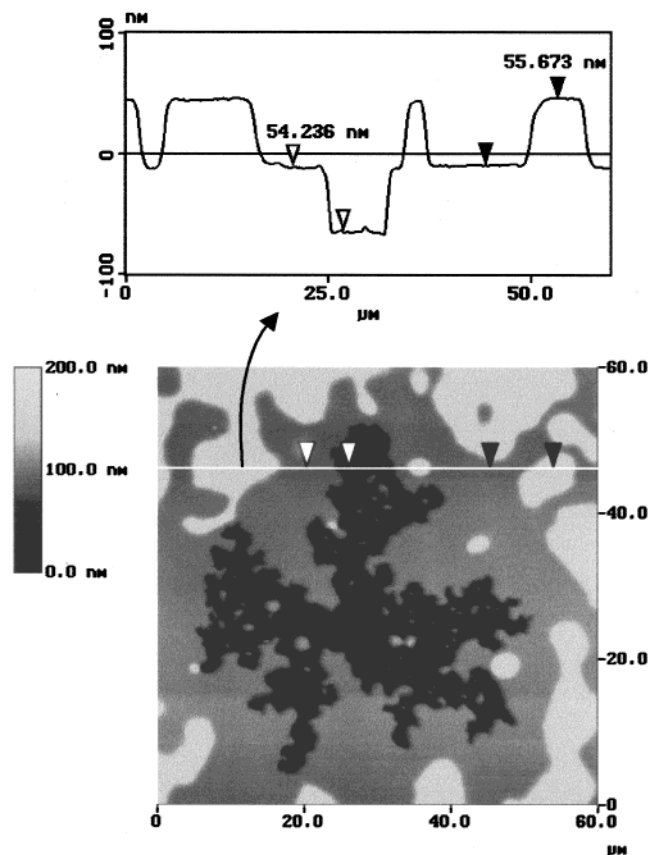

Figure 2. An AFM height image and a cross-sectional height profile of a fractal hole in a PS–P2VP thin film with $t_0 = 1.8L_0$ after annealing at 180 °C for 55 h in a vacuum.
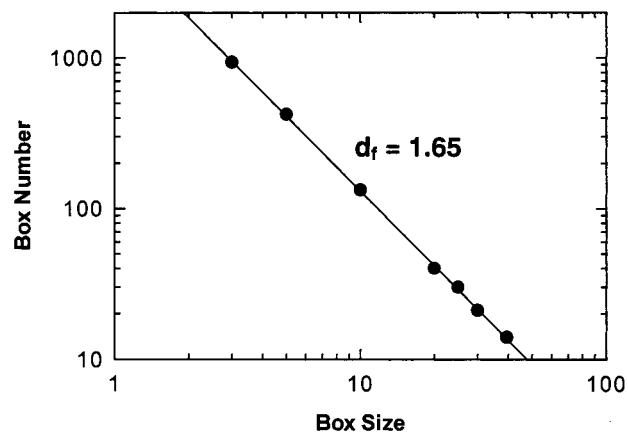

Figure 3. Fractal dimension analysis of a fully developed hole (shown in Figure 2) by using the box count method.

carried out for the samples at an equilibrium temperature. It should also be noted here that the bottom of the fractal hole region is not the bare Si substrate. The AFM image of the scratched surface near a fractal hole (not shown here) revealed that the hole has the height of 24 nm, comparable to $0.5L_0$. This implies that interconnected islands are 2.5 bilayer high and fractal holes 0.5 bilayer high with respect to the substrate. This is in complete agreement with the asymmetric wetting behavior as mentioned above.

Fractals in our system are quite similar in shape to nonequilibrium patterns observed in other systems, particularly such as metal dendrites grown by electrodeposition,[6] two-dimensional crystallites grown on a rough surface,[4] and viscous fingering patterns in a radial Hele-Shaw cell.[5] As a result, we performed the fractal dimension analysis for a fully developed hole shown in the lower part of Figure 2 by using the box count method,[1-3] and the results are shown in Figure 3. The fractal dimension d_f of the hole can be obtained from the scaling relationship of $N(l) \sim l^{-d_f}$, where $N(l)$ is the number of boxes of size l that occupy the hole region. From the slope in Figure 3, $d_f = 1.65$ was obtained for the fractal hole in our system. This is in agreement with the mean-field theory for the diffusion-controlled cluster formation proposed by Muthukumar.[17] Based on his derivation of $d_f = (d^2 + 1)/(d + 1)$ where d is the Euclidian dimension of space, $d_f = 5/3$ is easily obtained in two dimensions ($d = 2$), which is exactly the case for our system. In addition, this is also completely consistent with the result reported by Koneripalli et al.[7] on the fractal hole growth in strained block copolymer lamellae. They first prepared laterally strained $3/2$ bilayers of a symmetric PS–P2VP diblock copolymer with a thickness of $1.45L_0$ by the confinement technique followed by annealing. Subsequent annealing after removing the confinement layer led to the development of fractal holes quite similar in form to ours. They attributed this fractal hole formation, which is governed by the Laplace equation with moving boundary conditions, to the heterogeneous nucleation by tiny dust particles in laterally strained lamellae. The important difference between the present work and the work by Koneripalli et al.[7] is that the fractal holes develop in the presence of interconnected islands in our system. We attribute this abnormal dual morphology to the fact that our block copolymer thin film contains a small amount of residual solvent after spin-casting due to its very high boiling point, as will be depicted below. This
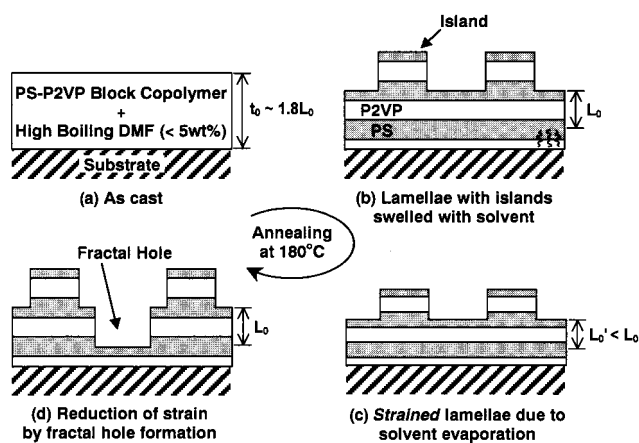
different measurements comes from the fact that the interaction between PS and P2VP segments becomes more repulsive in thin films due to the effects of the substrate and the surface, enabling block copolymers more stretched perpendicular to the interface.[16] The difference can also arise from the fact that AFM was performed for the quenched samples while SAXS was

Figure 4. Schematic of the fractal hole formation in block copolymer thin film induced by slow evaporation of high-boiling solvent.

kinetically trapped nonequilibrium dual morphology in our block copolymer thin films was found to be stable during prolonged annealing at 180 °C up to 8 days, indicating *metastability*.

Figure 4 illustrates a schematic of the fractal hole formation in our block copolymer thin film with $t_0 \sim 1.8L_0$ induced by slow evaporation of a high-boiling solvent. As-cast film contains a small amount of DMF solvent (typically below 5%) due to its high boiling point (Figure 4a). Immediately after annealing at 180 °C, parallel lamellae with interconnected island structure quickly develop in the thin film in the presence of residual high-boiling solvent due to high mobilities of both PS and P2VP segments since the annealing temperature is much higher than the T_g's of both segments (Figure 4b). Further annealing causes the residual solvent to evaporate completely. This induces a slight reduction in the total layer thickness, thus making the lamellae strained laterally similar to the case of Korneripalli et al.[7] (Figure 4c). Strains imposed on the island layer can be easily removed by adjusting their step height L_0' to the equilibrium domain period L_0 since the sides of the islands are free surfaces. On the other hand, the strained layer beneath islands cannot easily attain their equilibrium domain period without a rupture of the layer since it requires the diffusion of the block copolymer chains in the direction normal to the lamellar layer, which is highly restricted. The easiest way to reduce strains imposed on the layer is the development of the defects such as holes (Figure 4d). This hole growth process follows the fractal growth with diffusion-limited annihilation.

To check the schematic shown in Figure 4, we investigated the effect of the amount of residual solvent in the film on the rate of fractal hole development. We preannealed the as-cast specimen at 95 °C for 3.5 days in a vacuum in order to remove the residual solvent completely. The preannealing condition does not affect the initial surface morphology since the temperature is lower than the T_g's of both block segments, as evidenced by OM. About 2% reduction in the film thickness was observed by ellipsometry after preannealing. A corresponding increase of the refractive index value was also observed after the removal of solvent, since the refractive index of DMF ($n = 1.428$ at 25 °C) is lower than that of the block copolymer ($n = 1.58-1.59$). This implies that the as-cast specimen contains about 2% of residual solvent. It should be mentioned here that the

thin-film samples for the determination of the amount of residual solvent were cut from the same specimen as that used in the above OM and AFM measurements without preannealing in order to avoid any experimental uncertainty. We also prepared film specimens with shorter preannealing time in order to reduce the solvent content. It was found from the ellipsometry that the film contains about 1% of residual solvent after preannealing at 95 °C for 12 h. Subsequent annealing of the specimen at 180 °C revealed quite interesting results; the fractal hole growth in the preannealed film starts at 97 h, as observed by OM (not shown here), which is much longer than 30 h for as-cast films without preannealing (Figure 1b). This dramatic retardation of the fractal hole growth comes from the fact that the decrease of residual solvent content in the film by preannealing causes the reduction of strains imposed on the film.

Although the lateral stress induced by slow evaporation of residual solvent is believed to trigger the formation of fractal holes within the island morphology, the development of many fractal holes throughout the whole specimen with longer annealing time can be explained by combining *autophobic dewetting* behavior.[16,18,19] Autophobic dewetting in our system, however, is slightly different since it occurs at a height of $0.5L_0$ between the ordered PS brush attached to the substrate and another ordered PS brush in direct contact with it, while autophobic dewetting of macroscopic disordered droplets from substrate-induced dense *brush* layer of ordered copolymers has been reported in other block copolymer thin film systems.[16,18] In addition to the amount of residual solvent in the film, initial film thickness, the composition asymmetry of the block copolymer and the brush density in the $L_0/2$ layer adjacent to the substrate will also affect the fractal hole growth process in our system. The detailed discussion of these effects, however, is beyond the scope of this article and will be dealt with in a future publication.

In summary, we have shown for the first time the abnormal *dual morphology* of interconnected islands and *fractal holes* in block copolymer thin films with an initial thickness of $1.5L_0 < t_0 < 2.0L_0$. The development of fractal holes is initiated by the lateral strains induced by postevaporation of a small amount of residual high-boiling solvent after fast formation of parallel lamellae with interconnected islands. Thin films created in the present work are believed to be a promising candidate for nonglossy coating materials due to their intriguing self-similar micropatterns.

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