Instability and Pattern Formation Induced in Thin Crystalline Layers of a Conducting Polymer P3HT by Unstable Carrier Films of an Insulating Polymer

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ABSTRACT: We investigate the stability, self-organized morphology, and kinetics of dewetting in a thin polymer bilayer (~100 nm) of P3HT/polystyrene (PS) supported on Si wafers. The thin film of the conducting polymer, P3HT or regioregular poly(3-hexylthiophene), is driven to microstructure formation by dewetting of the unstable PS underlayer. Eventually, dewetting results in the formation of an undulating P3HT conducting skin covering the isolated islands of PS. The characteristic length scale of the structure is linearly proportional to the thickness of the PS underlayer. The kinetics of hole growth shows that the slippage behavior of the P3HT/PS bilayer which is different from the no-slip seen without the presence of the P3HT over layer. The bending elasticity and slippage induced by confinement of the PS layer by the P3HT layer strongly influence the length scale and kinetics of the dewetting process.

INTRODUCTION

The processes occurring during dewetting of thin (<100 nm) liquid films have been widely investigated because of their technological applications and fundamental scientific importance of highly confined systems. Some previous papers have reported that dewetting of thin polymer films, which can form almost regular structures with a characteristic length scale, 1,2 also provides an effective pathway to self-organize ultrathin polymer films and fabricate ordered micro-/nanopolymer patterns with many potential applications. 3–12 Recently, the dewetting processes in polymer bilayers have shown a rich variety of dynamics and morphologies. 13–22 For example, a large variety of microstructures including periodic arrays of open and closed micro-/nanochannels, 13–22 encapsulated micro-/ nanodroplets, and membranes like structures can be obtained from the dewetting of polymer bilayer. 12–14 Self-organization in a bilayer provides a far greater potential for tailoring of more complex micro/nanostructures compared to a single-layer system. The instability phenomenon is governed by the effective molecular interactions among the three interfaces that separate the four media: substrate, bottom layer, top layer, and surrounding gas (air). The attractive van der Waals forces promote instability in the films, whereas the interfacial tensions at the interfaces and the effective repulsive van der Waals forces stabilize them.

The patterning of conducting-insulating polymeric multilayer thin films has attracted much attention due to its potential applications. The regioregular poly(3-hexylthiophene) (P3HT), which is one of the most investigated π-conjugate polymers, has stimulated much interest. 23–31 However, self-organization of P3HT films by dewetting poses special challenges because the melting temperature of P3HT is high and close to its degradation temperature. Below the melting temperature of P3HT, its crystalloid behavior limits its mobility and thus inhibits its dewetting on a solid substrate. Thus, owing to its semiflexible, crystalline nature, it becomes difficult to process a P3HT film.

Here, we investigate a novel possibility of self-organizing P3HT microdomains or dots by employing a thin unstable carrier layer underneath the P3HT film. To this end, we investigate the dewetting processes in a bilayer of P3HT/polystyrene (PS) supported on Si wafers. The two polymers chosen are not miscible, and the amorphous PS layer underneath the P3HT film can be driven to dewetting by annealing beyond the glass transition temperature of PS, even though P3HT is not degraded. We thus investigate the possibility of self-organized pattern formation in the P3HT layer controlled by the instability of its PS substrate layer. It is found that the dewetting of the PS underlayer can indeed produce microstructures of a conducting P3HT skin encapsulating the insulating PS islands. The characteristic length scale of these structures can be tuned by changing the thickness of the thin PS carrier layer. We thus provide an effective pathway to produce the ordered structures of the P3HT conducting layer.

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EXPERIMENTAL SECTION

The system under investigation is a polymeric bilayer of polystyrene of varying molecular weights (PS, $M_w = 3.7 \text{ kg/mol}$, 10 kg/mol, 30 kg/mol, and $M_w = 97 \text{ kg/mol}; M_w/M_n < 1.1$; obtained from Aldrich) and regioregular poly(3-hexylthiophene) (P3HT, $M_w = 15−45 \text{ kg/mol}; M_w/M_n < 2$ and $T_m = 238 \degree C$; obtained from Aldrich). The bilayers were formed on the Si wafers without the oxide layer. First, PS films were spin coated from a toluene solution onto the Si wafers. The P3HT solution was filtered through the filters with 0.2 μm holes in order to remove large crystalline aggregates. P3HT films were separately spin coated from its chloroform solution onto the mica wafers. The bilayer films were prepared by floating P3HT films on the surface of deionized water and shifting on the PS film. The bilayer films were annealed at 170 °C. The characteristic length scale of dewetting with the PS film thickness is shown in Figure 1.

Figure 1. (a–h) Optical images of the P3HT films ($h_{\text{P3HT}} = 25 \text{ nm}$) on PS ($M_w = 30 \text{ kg/mol}$) layers of different thickness on the Si wafers without the oxide layer at annealed at 170 °C: (a) $h = 32 \text{ nm}$, (b) $h = 39 \text{ nm}$, (c) $h = 52 \text{ nm}$, (d) $h = 68 \text{ nm}$, (e) $h = 82 \text{ nm}$, (f) $h = 105 \text{ nm}$, (g) $h = 136 \text{ nm}$, (h) $h = 175 \text{ nm}$. (i) Variation of the characteristic length scale of dewetting with the PS film thickness. The size of all images is 225 μm (height) × 225 μm (width).

Figure 2. (a–c) Optical microscopy images of the P3HT films of different thickness on PS ($M_w = 30 \text{ kg/mol, 36 ± 3 nm}$) films annealed at 170 °C: (a) $h_{\text{PS}} = 25 \text{ nm}$, (b) $h_{\text{PS}} = 50 \text{ nm}$, (c) $h_{\text{PS}} = 75 \text{ nm}$. The size of all images is 225 μm (height) × 225 μm (width).

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films. The thicknesses of the polymer films were measured by ellipsometry. To initiate the dewetting process, the samples were heated to a temperature above the glass transition temperature of PS. The surface morphology was observed by optical microscopy (OM) in the reflection mode. We obtained the contact angles of two different liquids on the solid surface by drop shape analysis at room temperature, and used the measurements to calculate the surface energy of the solid substrate and polymer film by the method of harmonic mean.

## RESULTS AND DISCUSSION

During the dewetting process, the thickness of liquid film is the main parameter that determines the characteristic length scale of the instability. We first show the influence of the thicknesses of the PS and P3HT layers on the characteristic wavelength of the instability. Parts a–h of Figure 1 displays a series of OM images and shows the influence of the thickness of PS ($M_w = 30$ kg/mol) underlayer on the characteristic length scale of the instability. Figure 1i shows the plot of the characteristic length scale of the instability and the thickness of PS ($M_w = 30$ kg/mol) layer. As shown in Figure 1i, the characteristic length scale of the instability increases almost linearly with the increase in the thickness of PS underlayer. When the PS film thickness reaches about 175 nm (see Figure 1h), the bilayer became stable in the annealing process.

Figure 2 displays the influence of the thickness of the P3HT upper layer on the characteristic length scale of instability. From Figure 2, we observe that the characteristic wavelength of the instability is nearly independent of the thickness of the P3HT film. Thus, in the range investigated here, the characteristic wavelength of the instability depends more strongly on the thickness of the PS layer and is nearly independent or weakly dependent on the thickness of P3HT film. The annealing temperature ($170 \, ^\circ C$) is far lower than the melting temperature of P3HT ($238 \, ^\circ C$), and P3HT film is not molten. Thus, the solid elastic P3HT film should be largely stable against local variations in its thickness along its length because creation of an uneven thickness elastic film requires much more energy than its simple bending. Indeed, AFM imaging of the P3HT surface after dewetting of the PS layer did not show rupture or even any appreciable roughness on the length scales smaller than the dewetting wavelength. The instability of the P3HT-PS interface is fueled by the instability and rupture of the PS under layer, and the P3HT film simply bends to conform to the buried interface. Thus, dewetting of the PS layer produces an undulating P3HT conducting layer and rupture of the PS underlayer, and the P3HT instability of the P3HT-PS interface is fueled by the instability length scales smaller than the dewetting wavelength. The characteristic wavelength of the instability increases almost linearly with the increase in the thickness of PS underlayer.

Another important factor to be considered is the possibility of slipping of the PS film on its substrate. We observed the slippage effect in the kinetics of holes growth in the case of high molecular weight PS ($M_w = 30$ kg/mol) even without the P3HT top layer. This molecular weight is beyond the chain entanglement limit for PS. Interestingly, as discussed below, the presence of the P3HT top layer can induce slippage even in the relatively lower molecular weight PS films. Previous theoretical predictions indeed show that slip can also reduce the exponent, which in an extreme case can be as small as 1.25, reduced from its no-slip value of 2. Thus, both the slippage effect and the confinement offered by the elastic P3HT
layer may influence the wavelength. Regardless of the relative influence slippage has on the wavelength of the bilayer studied here, the slippage effect induced by the presence of P3HT is an interesting aspect of the viscous–elastic bilayer. In what follows, this slippage effect is clearly demonstrated in the discussion below.

We investigated the kinetics of hole-growth in the PS layer to gain insights into the possibility of slippage of the bilayer on the Si substrate. From Figure 4, it is found that the two lower molecular weight PS underlayers are unstable \( (M_w = 3.7 \text{ kg/mol}, \text{ and } 10 \text{ kg/mol}, \text{ thickness, } h = 160 \pm 5 \text{ nm}) \) evidently because of their sufficient mobility for reorganization. However, at the same annealing temperature of 170 °C, the two higher \( M_w \) PS underlayers \( (M_w =30 \text{ kg/mol and 97 kg/mol}, \text{ all } h = 160 \pm 5 \text{ nm}) \) are stable because of persistent chain entanglement and residual elasticity.

Figure 5 summarizes the kinetics of hole-growth in different PS films annealed at different temperatures. It is known that the radius of hole increases with time as \( R \approx t^n \), where the exponent \( n \) is close to 1 for nonslipping films but close to \( 2/3 \) for strongly slipping films.50–52 At the annealing temperature of 170 °C, the kinetics of hole-growth in the PS layer without the P3HT top layer is shown in the Figure 5a. It is found that the radius of holes grows linearly with time in the two cases of PS3.7K and PS10K, which are lower than the chain entanglement molecular weight (about 20 kg/mol). These results are consistent with previous studies.50–52 Thus, slippage of lower molecular weight PS without P3HT is ruled out. However, during the dewetting of the PS film with the P3HT top layer, even the low \( M_w \) PS layers \( (M_w = 3.7 \text{ kg/mol and } 10 \text{ kg/mol}) \) show strong slip (see Figure 5b). At higher annealing temperature of 195 °C, dewetting of the high molecular weight PS30K (beyond the entanglement limit) without the P3HT top layer proceeds as \( R \approx t^{2/3} \). We thus observe some signature of slippage in the case of high molecular weight PS30K only but not for low molecular weight PS layers without P3HT. The lowest molecular weight PS layer (3.7 kg/mol) does show slip even after it is confined by the P3HT layer. However, the higher molecular weight PS layers (10 and 30 kg/mol) capped with P3HT top layers display signatures of slip. The above results on slippage of PS layers buffered by P3HT films are rather intriguing and point to the role of P3HT in promoting PS slippage, as discussed below. Even in the case of the lowest \( M_w \) PS \( (M_w = 3.7 \text{ kg/mol}) \), which is far lower than the entanglement molecular weight of PS (about 20 kg/mol), there is strong slip observed at 170 °C. This annealing temperature is much in excess of the \( T_g \) of the PS (about 74 °C for PS3.7 kg/mol) but is much lower than the \( T_m \) of the P3HT (238 °C). Thus, slippage of the PS layer in the absence of an

Figure 4. (a–h) Optical microscopy images of P3HT films \( (h_{\text{P3HT}} = 50 \text{ nm}) \) on different PS underlayers \( (h = 160 \pm 5 \text{ nm}) \): (a) \( M_w = 3.7 \text{ kg/mol at } 170 ^\circ\text{C} \), (b) \( M_w = 10 \text{ kg/mol at } 170 ^\circ\text{C} \), (c) \( M_w = 30 \text{ kg/mol at } 170 ^\circ\text{C} \), (d) \( M_w = 97 \text{ kg/mol at } 170 ^\circ\text{C} \), (e) \( M_w = 3.7 \text{ kg/mol at } 195 ^\circ\text{C} \), (f) \( M_w = 10 \text{ kg/mol at } 195 ^\circ\text{C} \), (g) \( M_w = 30 \text{ kg/mol at } 195 ^\circ\text{C} \), (h) \( M_w = 97 \text{ kg/mol at } 195 ^\circ\text{C} \). The size of all images is 600 μm (height) × 450 μm (width).

Figure 5. Variation of the hole-radius with time in the dewetting of PS \( (h = 160 \pm 5 \text{ nm}) \) films resting on the Si wafers stripped of their oxide layers: (a) without P3HT top layer; (b) with P3HT top layer \( (h_{\text{P3HT}} = 50 \text{ nm}) \).
over layer of P3HT can be ruled out and was indeed not observed without a P3HT overlayer. Thus, the slippage is likely because of the complex rheological behavior (soft solid) of the P3HT upper layer much below its melting coupled to the greater PS chain entanglements and chain adhesion between the PS and P3HT chains. For π-conjugated polymers as P3HT with rigid-conjugated backbone and long hexyl side chains, its mobility is significantly different from the flexible-chain polymers. Previous works have reported that during the annealing process the attraction between the benzene rings in the PS and the thiophene rings in the P3HT enables the PS and P3HT chains to be close to each other due to similar π-conjugated electrons in the both rings, and there is also the attraction between the carbon backbone of PS and the alkyl side chain of P3HT.

As shown, slippage is not observed in the dewetting of the lower M_w PS under layers (PS3.7K and PS10K) without the P3HT top layer. Also, as shown, the presence of the top layer induces slippage. The top solidlike layer has a propensity to slip. The slippage induced in the PS layer by the top layer should be encouraged by a stronger adhesion between PS and P3HT layers. Thus, there can be increased physical adhesion and slippage between the PS chains and the P3HT chains at lower temperatures and higher molecular weights as both of these favor lower chain mobility and entropy, as well as higher viscosity and elasticity (more solidlike behavior). Indeed, at the lower temperature of 170 °C, the dewetting of the high molecular PS film (M_w = 30.0 kg/mol) is completely inhibited owing possibly to its high viscosity (low mobility) and residual elasticity. When the annealing temperature is increased to 195 °C, the slippage is observed in dewetting kinetics. With the increase in the molecular weight of PS, interchain adhesion is likely to be stronger between the PS and the P3HT chains. In the case of the higher M_w PS (M_w = 30 kg/mol), we have observed the slippage effect in the kinetics of holes growth of PS film on Si wafer without P3HT top layer. This implies that the PS chains have had an entanglement effect in the system even without P3HT top layer. Higher molecular weights thus promote slippage because of greater chain entanglements and possibly, a greater interchain adhesion.

From parts a1–c1 of Figure 6, it is seen that the color of the residual film in the hole floor is similar to the color of the P3HT film on the Si wafer. To further confirm the absence of PS layer from the dewetted areas and the presence of bilayer in other areas, the dewetted structures were treated by cyclohexane, which is a selective solvent for dissolution of PS but not for P3HT. In the (hypothetical) situation where P3HT film dewets on the PS film (schematic Figure 7I), the whole film will be etched out after exposure to cyclohexane. However, it is found that the solvent could not remove the residual (P3HT) film in the holes and destroyed selectively only the non-dewetted region containing PS (see parts a2–c2 of Figure 6). Thus, the residual film in the holes is P3HT, and it is the PS film that dewets between the Si substrate and P3HT film (schematic Figure 7II). To further confirm the location of P3HT after dewetting, we used a 2D scanning electron microscopy/energy dispersive X-ray microscopy (SEM-EDX) to map the distribution of sulfur which is present only in P3HT. Figure 8a is a 2D SEM morphology image of P3HT (50 nm)/PS (M_w = 10 kg/mol, 160 nm) film after dewetting by thermal annealing at 170 °C. The light region is dewetted (hole-floor), and the left gray part is the accumulated bilayer (PS particle/P3HT). Figure 8b is the SEM-EDX image showing the mapping of sulfur element at many spots across both the regions of the image 8a. It is seen that the sulfur signal (white dots) distributes homogeneously in both the dewetted and nondewetted regions. This indicates the presence of a P3HT overlayer covering the whole surface after dewetting of the PS underlayer.
CONCLUSIONS

We show that a flat crystalline conducting thin film of P3HT can be self-organized into undulating microdomains at temperatures much lower than its melting (and degradation) point by coating it on top of a thin unstable carrier polymer layer such as polystyrene, which can be induced to dewet by thermal annealing. The PS underlayer dewets between a solid substrate and the thin semisolid regioregular poly(3-hexylthiophene) film thus producing PS droplets sheathed by P3HT. The domain size and the distance between these domains can be controlled as they increase almost linearly with the PS film thickness. Interestingly confinement of PS with P3HT can induce or greatly enhance the slippage of the PS during dewetting in the confined space compared to PS dewetting in air. Elastic nature of the P3HT layer and entanglement or adhesion of PS chains with P3HT chains may be responsible for slippage. The anomalous dependence of the instability of the PS van der Waals potential by the presence of P3HT film. The bilayer strategy presented here may be useful for the physical self-assembly in thin films of other crystalline functional polymers that are not easily amenable to dewetting and in microfabrication of ordered structures by directed self-organization on physicochemically patterned templates.3−12,57−62

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Notes
The authors declare no competing financial interest.

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REFERENCES

(2) Sharma, A.; Reiter, G. J. Colloid Interface Sci. 1996, 178, 383−399.
(10) Sarkar, J.; Sharma, A. Langmuir 2010, 26, 8464−8473.
(34) Sarkar, J.; Sharma, A. Langmuir 2010, 26, 8464−8473.
(38) David, M. O.; Reiter, G.; Sitthai, T.; Schultz, J. Langmuir 1998, 14, 5667−5672.
(41) Sharma, A. Langmuir 1993, 9, 861−869.