

Phase Separation, Wetting and Dewetting in PS/PVME Blend Thin Films: Dependence on Film Thickness and Composition Ratio

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Abstract The effects of film thickness and composition ratio on the morphology evolution of polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend thin films were investigated. Diverse morphology evolutions including droplet-matrix structure, hole emergence, bicontinuous structure formation, percolation-to-droplet transition could be observed under annealing in two-phase region, depending on film thickness and composition ratio. The mechanism for these morphology variations was related to the complex effects of phase separation, dewetting and preferential wetting. The comparison between the thickness of bottom PVME layer and the twice of gyration radius $2R_g$ (PVME) played a dominant role in morphology control. Only when the PS/PVME film had specific film thickness and compositional symmetry, phase separation and dewetting could happen in sequence.

Keywords Phase separation; Dewetting; Wetting

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INTRODUCTION

Polymer thin film has attracted a lot of attention in recent years due to its wide application in many fields, including soft lithography, biological and automotive industries. Usage of the thin film directly relates to its stability. For one polymer component film on a solid substrate, it may become unstable if its thickness decreases to a certain value, leading to a breakup process named as dewetting^[1–4].

Even if the film thickness (d) is too thick to trigger a dewetting, sometimes other factors such as heat loading, can lead to the occurrence of dewetting^[5]. One main rupture mechanism is spinodal dewetting which occurs when the thermal fluctuation is amplified by van der Waals intermolecular forces^[6–8]. The other different pathway for dewetting is nucleation and growth process. According to the origin of rupture, the latter pathway can be classified as homogeneous thermal nucleation^[8, 9] and heterogeneous impurities induced nucleation^[10, 11]. Besides these, autophobicity^[12], density fluctuation^[13] and Marangoni flow^[14] are the other possible mechanisms for dewetting^[15].

Polymer blend thin films with partial miscibility is expected to result in a more complicated interplay between phase separation and dewetting. Our previous study^[16] on the PS/PVME blend thin film with thickness of ~ 100 nm found that, the interplay between phase separation and dewetting is closely dependent on the molecular weight of PS component.

In the film with $M_w(\text{PS}) \gg M_w(\text{PVME})$, the middle PS/PVME layer dewets firstly from the bottom PVME layer, and then phase separation occurs in the dewetted network which leads to the formation of volcano crater in the final dewetted droplet with a large scale. However, in the film with $M_w(\text{PS}) \approx M_w(\text{PVME})$, spinodal decomposition and subsequent percolation-to-droplet transition (PDT) occur firstly. During the retraction of phase separated droplets, the dewetting of bottom PVME layer happens onto quartz substrate.

Besides the molecular weight, phase separation and dewetting also have a strong dependence on film thickness. In PS/PVME blend film with a wide thickness range of 65 μm to 42 nm^[17], the morphology evolution can exhibit bicontinuous structure, irregular structure or dewetted droplet structure. The interplay of spinodal decomposition and dewetting in two-phase region plays a main role in morphology evolution, which is also related to the composition fluctuation or capillary fluctuation. In another report^[18], the mechanism for structure evolution in PS/PVME film can change from spinodal decomposition in thick (180 nm) film to nucleation and growth in thin (30 nm). This transition correlates with the maximum wavelength of concentration fluctuations and the diffusion of component with lower free surface energy.

Composition also is an important factor for morphology evolution control of polymer blend thin films. Composition variation in PMMA/SAN films can produce significant influences on its gradient in composition fluctuation, and accordingly accelerates (or suppresses) dewetting^[19, 20]. Karim *et al.* reported that in the PS/PVME films with

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thickness of ~100 nm, bicontinuous structure and droplet-matrix structure are found in the films with near-critical composition and off-critical composition, respectively, which is due to the surface tension variations within the film accompanying phase separation^[21].

The main objective of this paper is to study the effects of film thickness and composition ratio on morphology evolution of PS/PVME thin films with $M_w(\text{PS}) \approx M_w(\text{PVME})$ (molecular weight symmetry). Special attention is put on the successive occurrence of phase separation and dewetting manifested by the sequence of bicontinuous structure and hole formation of bottom PVME layer. The corresponding mechanism is explored in terms of comparison between the thickness of bottom PVME layer and the twice of gyration radius $2R_g(\text{PVME})$.

EXPERIMENTAL

PVME ($M_w = 5.45 \times 10^4$, PDI = 2.6) was purchased from Tokyo Chemical Industry in this study. The molecular weights of PS provided by Sigma-Aldrich Co has a bimodal distribution ($M_{w1} = 9.6 \times 10^4$, PDI₁ = 2.14 and $M_{w2} = 1300$, PDI₂ = 2.37) and the average molecular weight is $M_w = 3.8 \times 10^4$ measured by TOSOH HLC-8320 (GPC). PS and PVME with compositional symmetry (50/50 *W/W*) were dissolved in toluene with concentrations of 0.005, 0.01, 0.02 and 0.04 g/mL. After filtering with 0.22 μm pore size membrane, the PS/PVME/toluene solution was spin-coated onto a quartz substrate to get blend thin films. Prior to use, the spin-coated PS/PVME films were placed in a vacuum oven at room temperature for 24 h.

A spectroscopic ellipsometer (RISE-Zenith, Syscos Instruments, Shanghai) was used to determine the film thickness of PS/PVME blend thin films and layer thickness in detail by the aid of tri-layer mode.

A home-made small angle light scattering (SALS) with He-Ne laser source ($\lambda = 632.8 \text{ nm}$) equipped with a CCD camera and a hot stage (Linkam LTS350, UK) was employed to measure the cloud point of PS/PVME (50/50) blend films with different thicknesses. The heating rate was kept at 0.5 °C/min.

In situ surface morphology (in-plane direction) observation of PS/PVME blend films was performed by an optical microscope (BK-POL-TR) equipped with a CCD camera and a hot stage. A 3D measuring laser microscope (OLS4100, Olympus) also assisted for morphology observation.

RESULTS AND DISCUSSION

Film Thickness Measurement

The principle of reflection in spectroscopic ellipsometer is described as follows^[22]. The ratio of the reflection coefficients of the in-plane (R_p) and out-of-plane (R_s) polarized light is related to the amplitude attenuation Ψ and the phase difference Δ between the p and s waves:

$$R_p/R_s = \tan \Psi \exp(i\Delta) \quad (1)$$

For a single layer on a substrate the reflection coefficients for

p or s polarization are

$$R = [r_{01} + r_{12} \exp(-i\beta)]/[1 + r_{01}r_{12} \exp(-i\beta)] \quad (2)$$

$$\beta = 4\pi n_1 d_1 \cos(\phi_1)/\lambda \quad (3)$$

in which the subscripts 0, 1, 2 denote air, film, and substrate, respectively. n_1 and d_1 in Eq. (3) represent the refractive index and thickness of the film, respectively. ϕ_1 is the incident angle, and λ is the wavelength. The Fresnel coefficients (r_{ij}) for p or s polarization relative to the refractive index n and incident angles ϕ in each medium are given as

$$r_{i,j(p)} = (n_j \cos \phi_i - n_i \cos \phi_j)/(n_j \cos \phi_i + n_i \cos \phi_j) \quad (4)$$

$$r_{i,j(s)} = (n_i \cos \phi_i - n_j \cos \phi_j)/(n_i \cos \phi_i + n_j \cos \phi_j) \quad (5)$$

where the subscripts i and j represent either of air, film or substrate. All these equations are used together to define an algebraic relationship for the reflection coefficients in Eq. (1), which is then solved numerically to give the simulated profiles of Ψ and Δ . Iterative schemes can be used to build up reflection equations for multilayer systems^[23].

Fig. 1 displays the $\Psi \sim \lambda$ and $\Delta \sim \lambda$ data of PS/PVME (50/50) blend thin films prepared by PS/PVME/toluene solutions with different concentrations. A tri-layer structure composed of top PVME layer, middle PS/PVME blend layer and bottom PVME layer is employed to analyze the ellipsometer data. The formation of the tri-layer (sandwiched) structure is attributed to the lower surface free energy of PVME and higher wettability between PVME and the substrate^[16, 24]. The simulation results based on the tri-layer model are displayed as solid lines, which perform a good fit to the experimental data for Figs. 1(b)–1(d). Schematic description for the tri-layer structure is given as Fig. 2(a).

Combining the above equations and ellipsometer data, the thickness d and refractive index n are shown in Table 1 after simulation. It is obvious that the film thickness increases with the increase of solution concentration. The total film thicknesses for blend thin films prepared by solution with concentration of 0.005, 0.01, 0.02 and 0.04 g/mL are about ~40, ~80, ~170 and ~400 nm, respectively. It should be noted that when the solution concentration is increased to 0.04 g/mL, the top PVME and bottom PVME layers are minus by simulating the experimental data with tri-layer mode. Finally the thickness is obtained by the simulation of single layer mode as what Fig. 2(b) describes. This result may be related to the relatively lower mobility of polymer chain in the solution with rather higher concentration. During spin-coating, the polymer chains are frozen fast due to the higher concentration before the formation of tri-layer structure, resulting in a single blend layer of PS/PVME (50/50) right after preparation.

Cloud Point Determination

The scattering intensity variations with the temperature increase of the PS/PVME (50/50) blend thin films prepared by different solution concentrations are displayed in Fig. 3. In the homogeneous region the scattering intensity is constant, while it increases rapidly with temperature once some structures appear. A cloud point (T_c) can be determined

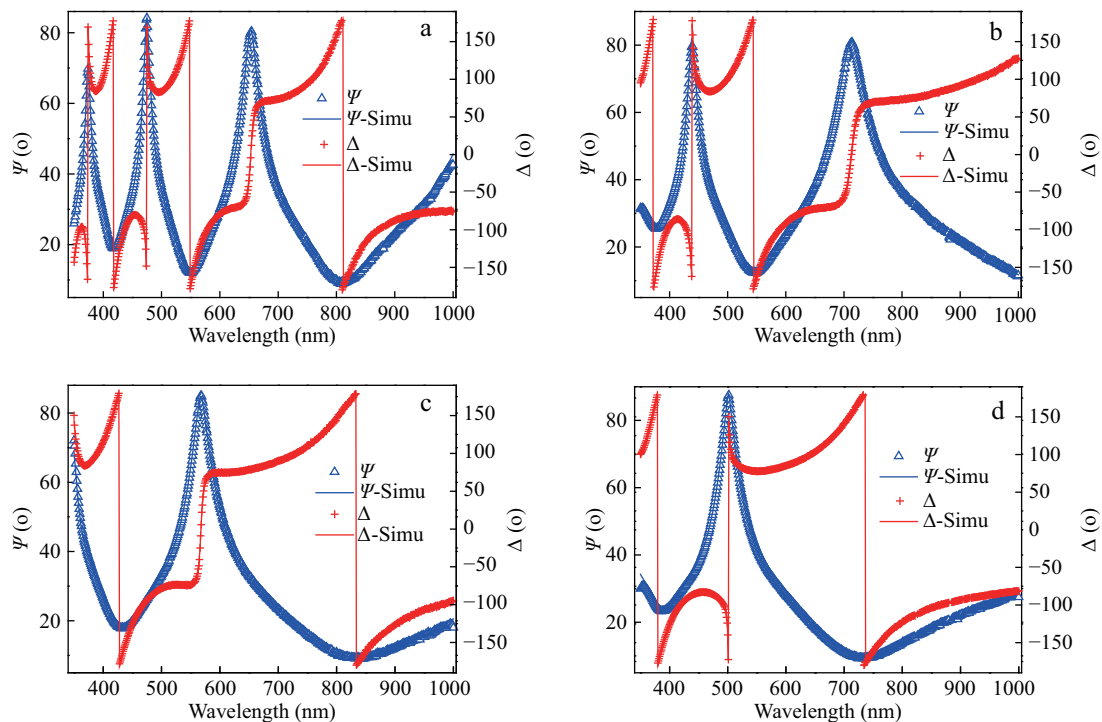


Fig. 1 $\Psi \sim \lambda$ and $\Delta \sim \lambda$ measured by spectroscopic ellipsometer for PS/PVME (50/50) blend films prepared by different solution concentrations of (a) 0.04 g/mL, (b) 0.02 g/mL, (c) 0.01 g/mL and (d) 0.005 g/mL

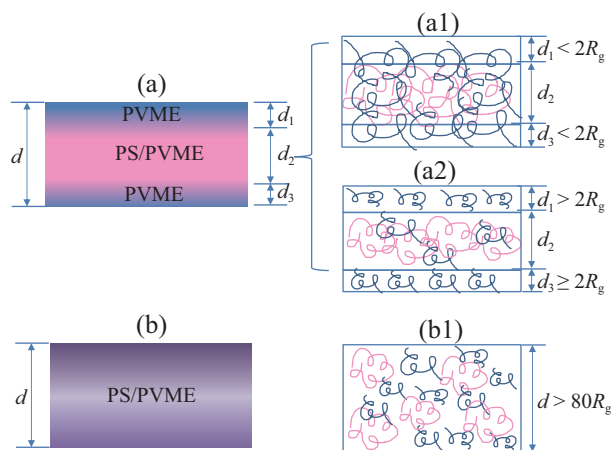


Fig. 2 Schematic description for (a) tri-layer structure and (b) single blend layer in PS/PVME blend films prepared by different solution concentrations. The blue curves and pink curves in (a1), (a2) and (b1) indicate PVME chains and PS chains, respectively.

as the starting point of the increase in scattering intensity. Strictly speaking, this T_c cannot be regarded just as phase separation temperature since the structure formation causing the rapid increase in scattering intensity may also be caused

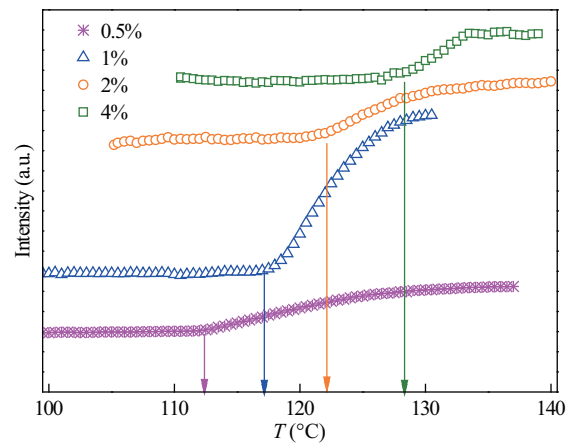


Fig. 3 Cloud point determination of different PS/PVME (50/50) films by light scattering intensity variation with temperature increase rate of 0.5 °C/min

by dewetting. It is obvious that T_c increases with film thickness (d) monotonously. T_c s of the PS/PVME (50/50) blend thin films with thickness of ~40, ~80, ~170 and ~400 nm are 112, 117, 122 and 127 °C, respectively. This dependence of the cloud point on film thickness is consistent

Table 1 Thickness d and refractive index n of each layer in PS/PVME (50/50) blend thin films prepared with different solution concentrations

c (g/mL)	Top PVME layer		Middle blend layer		Bottom PVME layer	
	d_1 (nm)	$n@550$ nm	d_2 (nm)	$n@550$ nm	d_3 (nm)	$n@550$ nm
0.005	8	1.48	30	1.58	5	1.48
0.01	18	1.48	50	1.58	11	1.48
0.02	31	1.48	130	1.58	20	1.48
0.04	/	1.48	400	1.56	/	1.48

with previous reports on PS/PVME blend thin films^[18, 25]. The lower cloud point for the thinner film may be ascribed to the earlier formation of dewetted structure.

Morphology Evolution and Mechanism

Dependence on film thickness

To provide sufficient driving force for morphology evolution and the same thermal mobility for all the polymeric components, PS/PVME blend thin films are annealed under 140 °C. The morphology evolution of PS/PVME blend thin films with different thicknesses is displayed in Fig. 4. For the film of ~400 nm, the PS/PVME film experiences a typical spinodal decomposition (SD) phase separation as shown in Fig. 4(a). Before 10 min, the film exhibits a typical co-continuous structure and grows in size. Becke line test^[26] suggests that the dark phase is mainly composed of PS since the Becke halo is moving toward it (PS has a higher refractive index) when the distance between lens and sample is decreased. With a further coarsening of phase structure, the PS-rich phase loses its continuity and leads to an occurrence of percolation-to-droplet transition (PDT). Finally, the dispersed PS-rich phase retracts into spherical shape to reduce the interfacial free energy. Under the condition of compositional symmetry (50/50) and molecular weight symmetry ($M_w(\text{PS}) \approx M_w(\text{PVME})$), PS/PVME film demonstrates a typical spinodal decomposition behavior when the film is thick enough to ~400 nm.

With decrease of film thickness to ~170 nm, the morphology evolution of PS/PVME (50/50) film is complex. From Fig. 4(b), we can know that PS/PVME (50/50) film with ~170 nm thickness experiences a spinodal decomposition followed by PDT. However, during the

retraction of PS-rich phase, the bottom PVME layer dewets quartz substrate. Consequently, PS-rich droplets are encapsulated in PVME-rich long bands. The dewetting behavior after spinodal decomposition is elucidated by the competitive effects of drag force generated between PS-rich droplets and the matrix (bottom PVME layer)^[16] and the preferential wetting of bottom PVME layer on substrate. The final PS-rich droplets encapsulated in PVME-rich “shell” is similar to the structure of PMMA/SAN blend films formed by solvent annealing to some extent^[27, 28], in which SAN-rich droplets are on the top of PMMA-rich mimic-films. The different solubility of polymers in solvent provides different chain mobility between PMMA and SAN, while the preferential interaction between PMMA and substrate impels PMMA chains to diffuse downward. Under the complex factors of composition fluctuation, vertical phase separation and dewetting, the top SAN/bottom PMMA structure forms eventually^[27].

When the thickness is decreased to ~80 nm, the morphology evolution process is similar to that in ~170 nm thick PS/PVME (50/50) film. Comparing Fig. 4(b) and Fig. 4(c), it can be found that the structure size is smaller and the density is higher in 80 nm film than those in ~170 nm film. Combining Fig. 4(c) and Fig. 5, it is found that the dewetted holes can form at 5 min annealed under 140 °C even at the initial stage of SDSP during which the co-continuous structure still exists. The earlier appearance of dewetted holes on the bottom PVME layer in thinner ~80 nm film than that in 170 nm film indicates the strong dependence of dewetting on film thickness.

Fig. 4(d) reveals that PS/PVME (50/50) film with

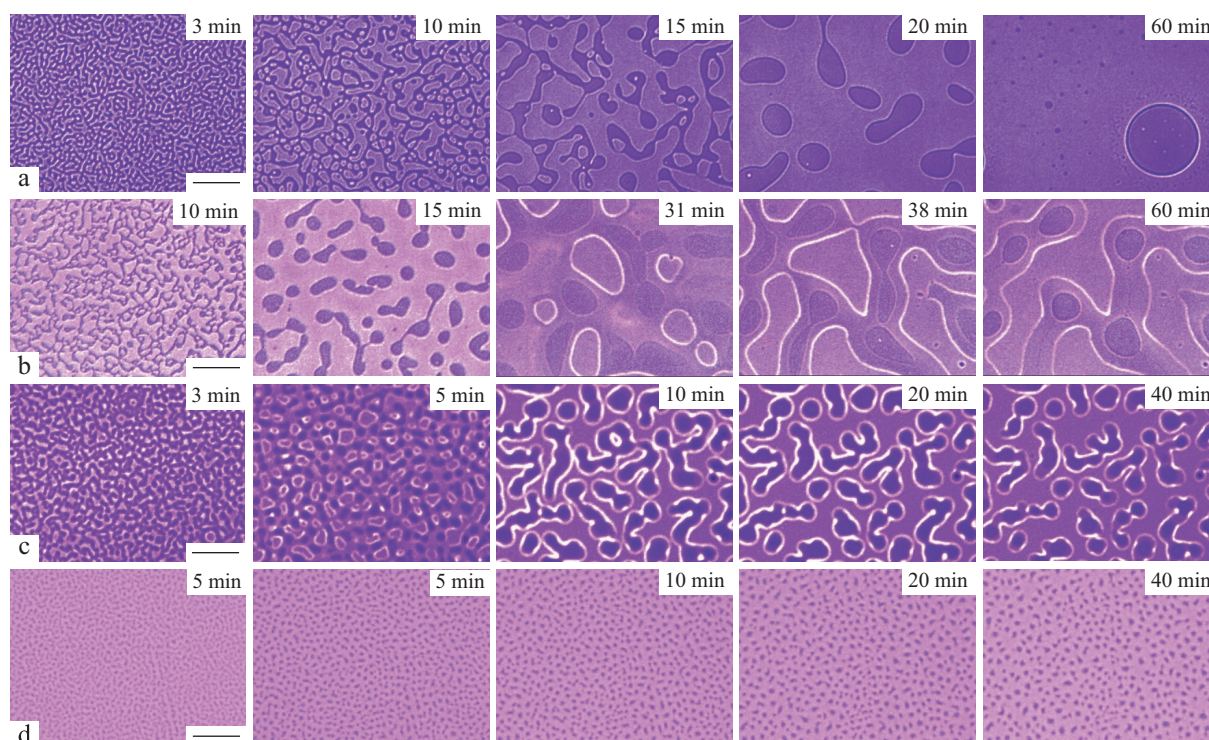


Fig. 4 Morphology evolution of PS/PVME (50/50) blend thin film with different thicknesses of (a) ~400 nm, (b) ~170 nm, (c) ~80 nm and (d) ~40 nm after temperature jump to 140 °C. The scale bar denotes 50 μm.

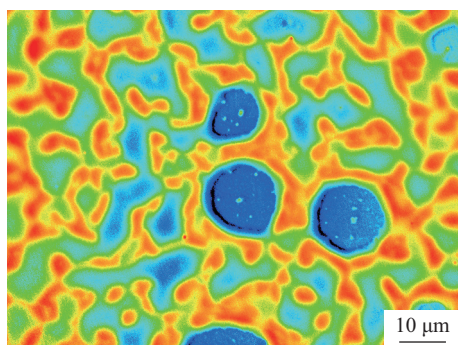


Fig. 5 PS/PVME (50/50) blend film with thickness of ~ 80 nm measured by laser scanning confocal microscopy after annealing for 5 min under 140°C

thickness of ~ 40 nm dewets instantaneously once annealing under 140°C for less than 5 min, leading to numerous dispersed dewetted droplets with almost uniform size, which accords with the characteristic of spinodal dewetting^[9, 29]. After 5 min, the dewetted droplets coalesce each other slowly into droplets with larger size. To verify that film dewets substrate as a whole, the water “annealing” experiment lasts for about one week, and no change is found on the bottom matrix, which is an indication of substrate exposure after the dewetting of whole film induced by annealing in two-phase region.

Fig. 4 results indicate that the morphology evolution is closely related to the film thickness. The unique characteristic of morphology evolution for these PS/PVME (50/50) films provides the possibility to distinguish the sequence of phase separation and dewetting, which is manifested by breakup of bottom PVME layer. Only when the film thickness is in the range of 80–170 nm, we can distinguish the sequence of phase separation and dewetting of bottom PVME layer on substrate. The question how the film thickness influences the stability of bottom PVME layer comes out. According to Table 1, the thicknesses of bottom PVME layer for the film with total thickness of ~ 170 , ~ 80 and ~ 40 nm are 20, 10 and 5 nm, respectively.

The radius of gyration of an unperturbed polymer chain (R_g) is calculated by^[18]

$$\langle R_g^2 \rangle^{1/2} = \frac{A}{\sqrt{6}} \left(\frac{C_\infty b^2}{M_0} \right)^{1/2} M^{1/2} \quad (6)$$

where A , C_∞ , b , M_0 , and M are the expansion factor, the characteristic ratio, the bond length, the average molecular weight per backbone bond, and the polymer molecular weight, respectively. For PVME in this study, $A \approx 1$, $C_\infty = 7.1$, $b = 1.53 \text{ \AA}$, $M_0 = 58$ and $M = 5.45 \times 10^4$. For PS in this study, $A \approx 1.73$, $C_\infty = 10$, $b = 1.53 \text{ \AA}$, $M_0 = 104$ and $M = 3.8 \times 10^4$. The twice of gyration radii ($2R_g$) for PVME and PS are 10.2 and 21.4 nm, respectively, which are calculated by Eq. (6).

Table 1 reveals that the thickness of middle blend layer is larger than either $2R_g(\text{PVME})$ or $2R_g(\text{PS})$, thus special attention is paid on the thickness of bottom PVME layer since it is liable to dewet substrate.

In the film with conditions of $d = \sim 40$ nm, $d_1 < 2R_g(\text{PVME})$ and $d_3 < 2R_g(\text{PVME})$, PVME chains are constraint

in both top and bottom layers, as described by Fig. 2(a). Usually a flexible polymer chain constrained in ultrathin space ($< 2R_g$) is in a nonequilibrium state, as the conformation entropy of an individual chain is reduced in comparison with that in a three dimensional solid state^[25]. T_g s of PS and PVME in this study measured by DSC (TA, Q20) are approximately 64 and -26°C , respectively. In term of this view, the two-dimensional top and bottom PVME layers cannot exist stably even under room temperature due to the flexibility of PVME chains. However, the frozen PS chains whose T_g ($\sim 64^\circ\text{C}$) is higher than room temperature can prevent the diffusion of PVME chains. Thus, the tri-layer structure shown in Fig. 2(a) can have a stable existence after spin-coated under the coupling effects of geometric confinement and the restraint of frozen PS chains. Once the film is annealed at 140°C , the thermal molecular motions of both PS and PVME chains are so vigorous that phase separation and dewetting occur simultaneously, which leads to the breakup of the film as a single layer.

In the films with $d = \sim 80$ nm and $d = \sim 170$ nm, $d_1 > 2R_g(\text{PVME})$ and $2R_g(\text{PVME}) \leq d_3 \leq 4R_g(\text{PVME})$ indicate that PVME chains locate in top and bottom layers coil in three dimensions as displayed in Fig. 2(a). During the spinodal decomposition process, the bottom PVME layer can exist for a certain time due to the preferential wettability between PVME and substrate. Our previous study proposed that the retraction of elongated ribbons or droplets induced by phase separation might generate a drag force between PS-rich droplets and the matrix (bottom PVME layer), which overcame the preferential wetting between bottom PVME layer and substrate, resulting in the breakup of bottom PVME layer. The dewetting between PVME and substrate happens earlier in the film whose bottom PVME layer has smaller thickness during phase separation process due to the less wetting affinity.

For the films with $d \geq 400$ nm ($d \geq 80R_g$), the thickness of bottom PVME layer is great enough to overcome the drag force induced by phase separation between PS and PVME. Thus, the blend film only displays a spinodal decomposition process without the occurrence of dewetting on substrate even annealing for 12 h under 140°C .

Concluded above, film thickness of PS/PVME blend thin films can bring complex effects on wettability between PVME and substrate, dewetting between the whole film with substrate, and phase separation between PS and PVME, which plays a dominant role in their morphology evolution control.

Dependence on composition ratio

Morphology evolution of PS/PVME blend thin films with different composition ratios under 140°C is shown in Fig. 6. The concentration of polymer blend solution is kept as 0.01 g/mL to exclude the total film thickness (~ 80 nm) on the morphology evolution. Figs. 6(a) and 6(b) show that PS/PVME (10/90) and PS/PVME (30/70) films possess a typical dewetting process. Both of them dewet instantaneously, leading to numerous dispersed droplets with almost uniform size. After the fast Fourier transform (FFT) of the dewetted structures, we can see a scattering ring presented at the right bottom of the images. This analysis

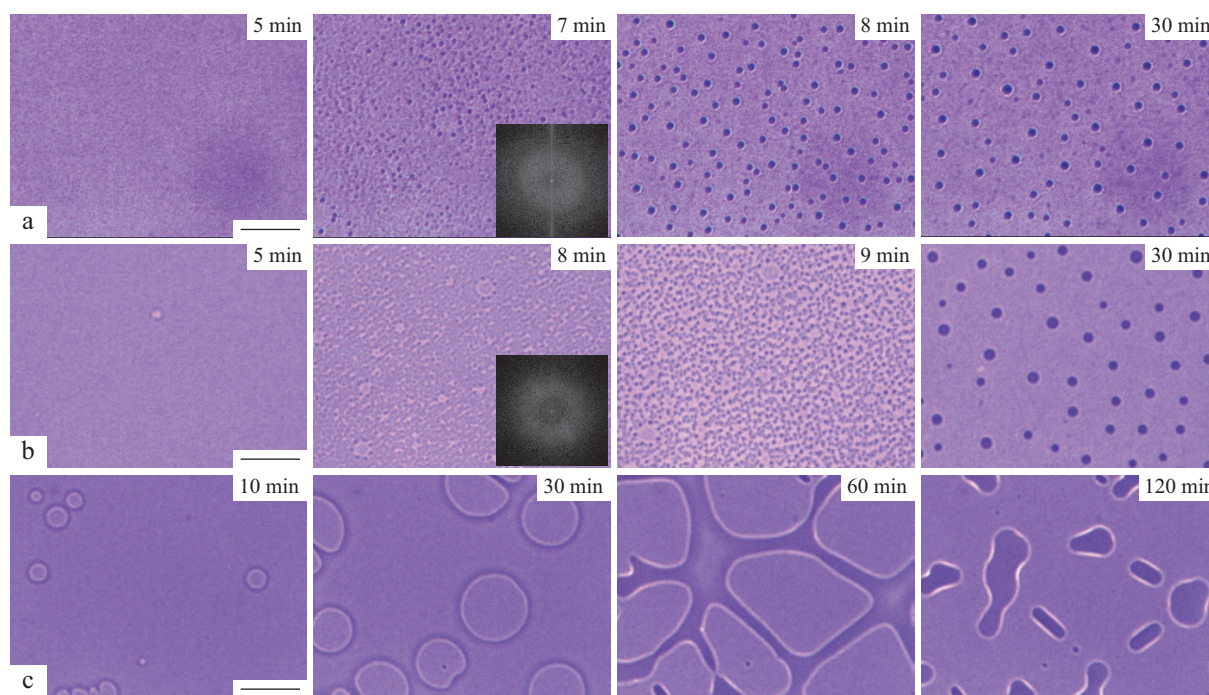


Fig. 6 Morphology evolution of PS/PVME blend thin film with different composition ratios of (a) 10/90, (b) 30/70, (c) 70/30 after temperature jump to 140 °C. Film thickness is about 80 nm. The scale bar denotes 50 μm .

implies a spinodal dewetting process happened in PS/PVME (10/90) and PS/PVME (30/70) films, and the instantaneity of film breakup also accords with the characteristics of spinodal dewetting. After 7 min, the droplets coalesce with each other into larger droplets to reduce the interface free energy. As the majority of PS component, the final droplets have similar refractive index of PS which is confirmed by Becke line test.

In PS/PVME (70/30) film, holes emerge once annealing for 10 min under 140 °C. Then it experiences a classical process including hole growth (10–30 min), irregular ribbon formation induced by holes coalescence (30–60 min), and the decay of ribbons into droplets (60–120 min). The feature of morphology evolution in PS/PVME (70/30) film satisfies the heterogeneous dewetting^[9, 29]. Due to the preferential wetting between PVME and substrate and the lower surface energy of PVME, the dispersed droplets should be composed of outer PVME-rich layer and inner PS-rich core.

It is worth exploring the nature of matrix (light region in Fig. 6). Considering the susceptibility of PVME to moisture, the annealed PS/PVME films (corresponding to Fig. 6) are exposed in the air for about one month to investigate the morphology change. As shown in Figs. 7(a) and 7(b), the

appearance of round holes on matrix clearly suggests the occurrence of dewetting behavior on substrate. A possible reason for the phenomenon is that the absorption of moisture contained in the air by the bottom PVME layer induces a dewetting *via* “solvent” annealing^[30]. This confirms the existence of bottom PVME layer on substrate in PS/PVME (10/90) and PS/PVME (30/70) films. Different from Figs. 7(a) and 7(b), the matrix (blue region) in Fig. 7(c) keeps smooth all the time, indicating that the droplets are dispersed on substrate rather on PVME layer.

It is taken for granted that the PVME ratio is directly related to the thickness of top and bottom PVME layers if the solution concentrations prepared for the films are kept the same. Fig. 8 shows the $\Psi \sim \lambda$ and $\Delta \sim \lambda$ data for PS/PVME films measured by spectroscopic ellipsometry. Based on the tri-layer model, the layer thickness can be derived from simulated results. According to Table 2, the total thickness of PS/PVME (10/90), (30/70) and (70/30) are 82, 74 and 76 nm, respectively.

Main following attention is put on the comparison between thickness of bottom PVME layer (d_3) and twice of gyration radius ($2R_g$) of PVME. For PS/PVME (10/90) and

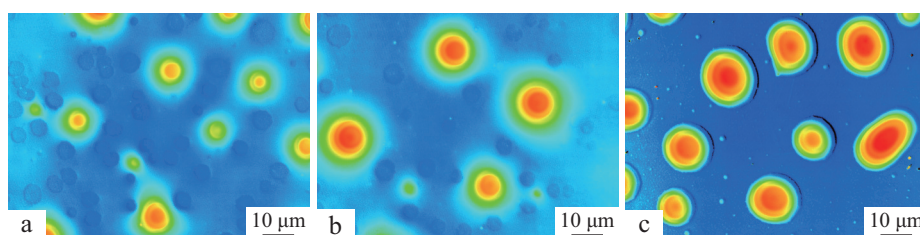


Fig. 7 (a) PS/PVME (10/90), (b) PS/PVME (30/70) and (c) PS/PVME (70/30) blend thin films with thickness of ~ 80 nm measured by laser scanning confocal microscopy after being exposed in the air for one month.

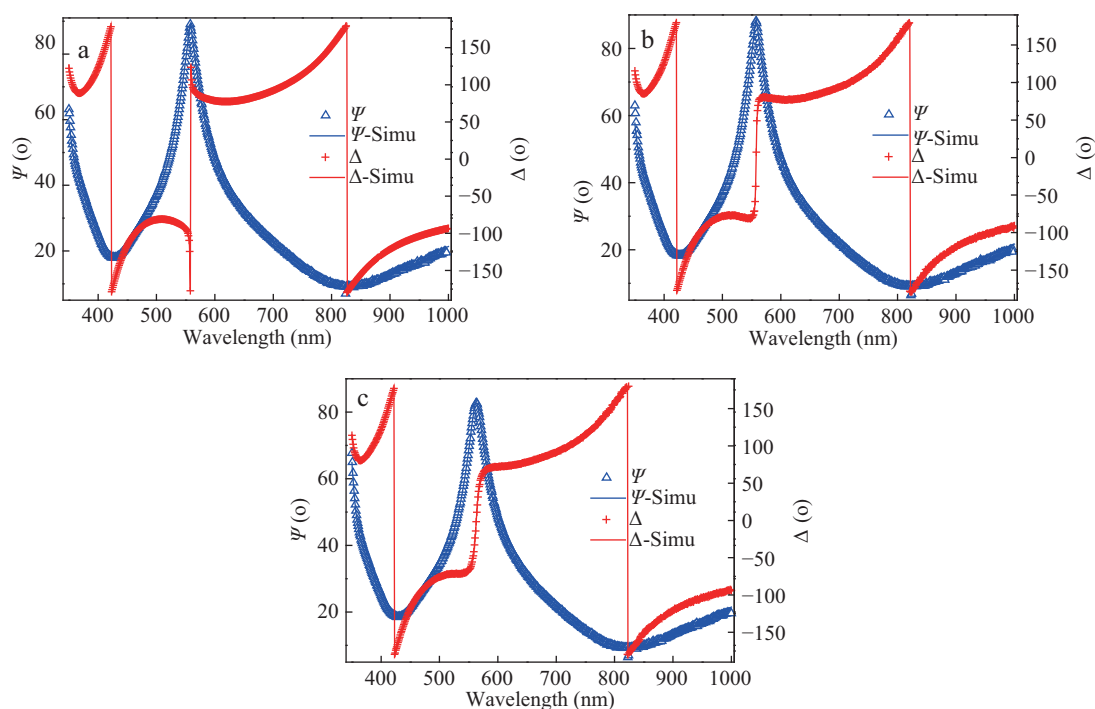


Fig. 8 $\psi \sim \lambda$ and $\Delta \sim \lambda$ measured by spectroscopic ellipsometer for PS/PVME blend thin films prepared by solution concentration of 0.01 g/mL. The PS/PVME composition ratios are (a) 10/90, (b) 30/70 and (c) 70/30.

Table 2 Thickness d and refractive index n of each layer in PS/PVME blend thin film prepared with different PS/PVME ratios but the same solution concentration

Composition ratio	Top PVME layer		Middle blend layer		Bottom PVME layer	
	d_1 (nm)	$n@550\text{nm}$	d_2 (nm)	$n@550\text{nm}$	d_3 (nm)	$n@550\text{nm}$
10/90	27	1.48	30	1.50	25	1.48
30/70	19	1.48	42	1.55	15	1.48
70/30	4	1.48	68	1.60	4	1.48

PS/PVME (30/70) films, $d_1, d_2, d_3 > 2R_g(\text{PVME})$ and $d_2 > 2R_g(\text{PS})$ suggest that PS and PVME chains are coiled in three dimensions. Due to the preferential wetting affinity between bottom PVME layer and substrate, the spinodal dewetting occurs at the interface between middle PS/PVME blend layer and bottom PVME layer, and the top PVME layer always covers on the dewetted droplets. Even the dewetted droplets retract into round shape at the final stage of morphology evolution, the bottom PVME layer can keep stable on substrate. Since PVME is the majority in these two blend films, the final droplets are composed of PS-rich phase, which is also confirmed by Becke line test.

When PS composition increases to 70 wt%, $d_1 < R_g(\text{PVME})$ and $d_3 < R_g(\text{PVME})$ reveal that both top and bottom PVME layers are under the thermodynamical nonequilibrium state right after film preparation. Thus, the morphology of PS/PVME (70/30) blend thin film evolves as a single layer during annealing at 140 °C which is above both T_g s of PS and PVME. It should be noted that the process of heterogeneous dewetting resembles the viscoelastic phase separation (VPS), including hole appearance and growth, a network formation of PS-rich phase, and the final breakup of PS-rich network into dispersed droplets. The only difference between them is the matrix at the final stage of morphology evolution is whether the substrate or the PVME-rich phase.

The large T_g difference between PS ($T_g = 64$ °C) and PVME ($T_g = -26$ °C) makes PS/PVME blend be a dynamically asymmetric system. The morphology evolution in PS/PVME (70/30) blend thin film relates to the interplay of wetting and dewetting, both of which are relevant to the dynamic asymmetry and the compositional asymmetry.

Until now, we know that the stability of bottom PVME layer in PS/PVME blend thin films is closely related to both film thickness (d) and composition ratio. Schematic description of the structure formation in PS/PVME blend thin films with different film thicknesses and composition ratios is concluded in Fig. 9. The final morphology due to heat annealing exhibits two types, dispersed droplets on PVME layer and dispersed droplets on substrate, reflecting that the main difference of these morphology evolutions is the stable existence of bottom PVME or not.

In the case of $d \geq 400$ nm, PS/PVME (50/50) film shows spinodal decomposition and percolation-to-droplet transition, resulting in the morphology of PS-rich droplets on PVME-rich matrix. In the range of $\sim 170 \text{ nm} \geq d \geq \sim 80$ nm, the successive occurrence of spinodal decomposition and bottom PVME layer dewetting can be distinguished in the PS/PVME (50/50) film, in which the thickness of bottom PVME layer is comparative to $2R_g$ – $4R_g$ of PVME. The drag force between PS-rich phase and the matrix (bottom PVME layer)

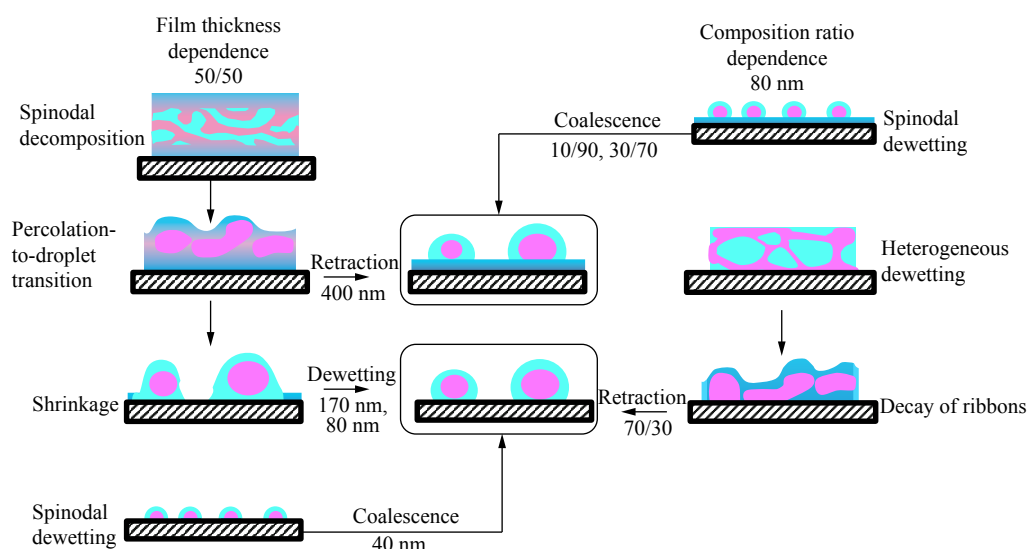


Fig. 9 Schematic description of the structure formation in PS/PVME blend thin films with different film thicknesses (left part) and composition ratios (right part). The pink and blue regions indicate PS-rich phase and PVME-rich phase, respectively

induced by phase separation is relatively strong due to the same viscous nature of PS and PVME. The preferential wetting between PVME layer and substrate is rather weak in case of such small thickness, which can be overcome by the drag force, and leads to the breakup of PVME layer as a dewetting process. When the thickness decreases to $d \leq 40$ nm, the bottom PVME layer is too thin to exist stably once annealing under 140 °C, and thus the film dewets substrate as a single layer directly.

As PS composition increases, the thickness of bottom PVME layer due to its preferential wetting with substrate will decrease. In the PS/PVME films with composition ratios of 10/90 and 30/70, spinodal dewetting occurs at the interface between the middle blend layer and bottom PVME layer, which is thick enough to exist stably even at the late stage of spinodal dewetting. As for the composition ratio of 70/30, the film experiences heterogeneous dewetting, decay of ribbons and then retraction into spheres. Owing to the rather thin top and bottom PVME layers, PS/PVME (70/30) film dewets as a single layer, leading to the exposure of substrate.

CONCLUSIONS

Morphology evolution process in PS/PVME blend thin films shows a strong dependence on film thickness and composition ratio. The diverse morphology evolutions of PS/PVME films are resulted from the complex effects of phase separation, dewetting and preferential wetting, in which composition asymmetry and dynamic asymmetry play essential roles. There are two final morphologies in different films after annealing, both of which display a droplet-matrix structure. The only difference between them is the stable existence of bottom PVME layer on substrate or not. Special attention is put on the comparison between the twice of gyration radius $2R_g(\text{PVME})$ and the thickness of bottom PVME layer measured by spectroscopic ellipsometry. Only

when the PS/PVME film has compositional symmetry (50/50) and the film thickness satisfies the condition of $2R_g(\text{PVME}) \leq d \leq 4R_g(\text{PVME})$, phase separation and dewetting of the bottom PVME layer can happen in sequence during annealing in two-phase region, manifested by the coexistence of bicontinuous or droplet-matrix structure and holes on the bottom PVME layer.

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