Pattern guided structure formation in polymer films of asymmetric blends

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Abstract

Two off-critical blends of poly(2-vinylpyridine) and polystyrene, 2:3 and 3:2 (w:w) PVP:PS, were spin-cast (with varied domain scale R) onto periodically (λ = 4 μm) patterned substrate. The pattern consisted of two alternating symmetric stripes: Au attracting PVP and neutral self-assembled monolayer. The resulting droplet-type morphologies were recorded with Scanning Force Microscopy and examined with integral geometry approach. PVP-rich islands of the 2:3 PVP:PS films form, for a wide R/λ range, strongly anisotropic morphologies. They show up, for R/λ ~ 0.5, a weak λ/2-substructure of smaller PVP droplets in addition to the domains periodic with λ. The 3:2 blend exhibits morphologies with dominant λ-structure of PVP ribbons, which encircle PS droplets. For R/λ ~ 0.5, smaller PS domains are also present but no λ/2-substructure is formed. The $|z_E|$-values of droplet surface density are reduced, as compared to homogeneous substrate, for the 3:2 blend (with $|z_E| \rightarrow 0$ for R ~ λ). This effect is absent for the 2:3 mixture.

Keywords: Atomic force microscopy; Soft-lithography; Pattern replication; Self-assembly; Polymer films; Thin film structures

1. Introduction

Simple, low cost methods for the reliable replication of (sub-)micrometer size patterns are of considerable technological interest [1,2]. As a reply to this demand novel techniques were developed in the last decade, focused mainly on the replication into homopolymer films of the periodic (with λ) patterns defined by the master [3–6] or its elastomer replica (soft-lithography) [7–12]. They were successfully applied to form specific functional elements of photonic or opto-electronic devices [13].

Alternative approaches were proposed for multi-component polymer films, simultaneously allowing for the surface pattern-guided alignment of various (micro-)phase domains, which might form various functional elements of potential hi-tech devices [14]. Long-ranged ordered microphase structures were obtained for symmetric [15] and asymmetric [16] block copolymers positioned on the pattern. In turn, experimental [15,17–28] and theoretical [19,29–32] studies reported on pattern-directed structure formation in spin-cast (solvent-quenched) [15,17,18,23,24,28] or temperature-quenched [17,19–22] binary blend films correspond exclusively to symmetric (or critical [19–21]) homopolymer mixtures. Droplet-type morphologies, often required by photonic [33] or electro-optical [34] devices, are not characteristic for such blends. This limits domain patterns available for potential applications. Only very recently a brief comparison between pattern transposition in symmetric and asymmetric blend films has been presented [27]. Pattern-guided morphologies of multi-component polymer film are usually produced by a sequence of different
procedures [35,36] (e.g., involving blend film annealing [17,19–22]). In contrast, spin-casting offers one-step process to deposit and align various phase domains.

The aim of the present study is to understand similarities and differences in pattern-directed structure formation during spin-casting of asymmetric (and off-critical) binary blends (2:3 and 3:2) of the same model polymer system (poly(2-vinylpyridine)) PVP/deuterated polystyrene PS with different ratio of its components (PVP:PS). To this end we have examined with Scanning Probe Microscopy (SPM) film topographies reflecting overall phase domain structures [18,24,25,37,38]. They were formed on the same pattern for different casting conditions that varied the inherent structural scale $R$. $R$ was determined with Fast Fourier Transform (FFT) analysis [24,25] to be in the range $0.2\lambda \leq R < 1.8\lambda$. The recorded morphologies were analyzed quantitatively with the recent extension [39–41] of integral geometry approach [42,43].

The symmetric substrate pattern used, with one of two alternating stripes neutral and the second stripe attracting one component of the system (PVP), is compositionally incommensurate [29] for asymmetric blends. In this work we investigate how this problem affects domain structures when the phase driving the pattern transposition constitutes minor (2:3) and major (3:2) mixture component. The morphology of the former blend exhibits (for $R/\lambda \sim 0.5$) a weak $\lambda/2$-substructure in addition to the domains in register with underlying periodic substrate pattern. In turn, only the domain ordering of the latter mixture reacts strongly when the structural scale $R$ is comparable to pattern periodicity $\lambda$. For the mixture 3:2 (but not 2:3) the domain surface density is reduced for polymer films on the pattern as compared to the films on homogeneous substrate.

2. Experimental section

2.1. Preparation of polymer films

The substrates used in the experiment were Au-covered Si wafers with two, patterned and homogeneous, regions covered with self-assembled monolayer (SAM) of hexadecanethiol [HS(CH$_2$)$_{15}$CH$_3$]. To produce the substrate half of the wafer was patterned with alternating symmetric stripes (width of ca. 2 $\mu$m and period $\lambda = 4.0(1)\mu$m [24,25]) of pure Au and SAM using the micro-contact printing method [7], and then the other part of the wafer was immersed in hexadecanethiol solution [44]. The substrates of control samples were homogeneous SAM. The polymers used in this work were poly(2-vinylpyridine) (PVP, molecular weight $M_w = 115$ kDa, polydispersity index $M_w/M_n = 1.02$) and deuterated polystyrene (PS, $M_n = 174$ kDa, $M_w/M_n = 1.03$), purchased from Polymer Standards Service, Mainz and used as obtained. The critical PVP weight fraction $\Phi_C$ of this couple is equal to 0.54. Pure polymers were used to prepare two asymmetric (and off-critical) PVP:PS blends with PVP weigh fraction $\Phi$ equal to 0.40 (blend 2:3) and 0.60 (blend 3:2). The polymers were dissolved in analytic grade tetrahydrofuran (THF) and the blend films were prepared by spin-coating with coater KW-4A, Chemat Technology, controlled by coating speed $\omega = 5800$ rpm (for the control samples different values were also used) and polymer concentration 4 $\leq c_p \leq 18$ mg/mL. The average film thickness, determined from AFM images taken after partial film removal [38] from the control and selected experimental samples, ranged from 14 to 130 nm.

2.2. Surface characterization

Topography and friction SPM images of the cast thin films were collected in air at room temperature by atomic (AFM)- and lateral (LFM)-force modes of CP Park Scientific Instruments microscope (scan range up to 80 $\times$ 80 $\mu$m) working in contact mode with a Si$_3$N$_4$ tip and a typical load of 4 nN. LFM resolves domains rich in PS and PVP [38,45]. The LFM data illustrate overall phase domain structure, as confirmed by a composition mapping mode of dynamic secondary ion mass spectrometry (dSIMS) [25] and by AFM combined with selective dissolution of PVP and PS by ethanol and cyclohexane, respectively [38,45]. All structures shown in the images were reproducible, independent of scan direction or scan range. Images with different range were collected to provide data optimal for image analysis. SPM pictures of two regions, with homogeneous and patterned substrate, were recorded for each sample as pairs of isotropic and anisotropic morphologies, respectively, formed in the same spin-casting experiment.

2.3. Image analysis

The topographic (AFM) images were examined numerically with integral geometry approach [39,41] and Fourier analysis [24,25] using the software developed in our laboratory. For each AFM image of the surface (with bimodal height $h$-distribution centered at $\langle h_1 \rangle$ and $\langle h_2 \rangle$), the Euler characteristic $\chi_E$ (connectivity) of elevated regions (i.e., with local height $h > \langle (h_1) + (h_2) \rangle/2$) was calculated [39,41] using the algorithm of Ref. [43] (simpler but equivalent to that of Ref. [42]). $\chi_E$ is defined as the difference between the number of separated elevated and depressed regions normalized by the analyzed area. For each AFM image its 2-dimensional Fast Fourier Transform (FFT) was computed [24,25]. FFT spectrum of isotropic and anisotropic morphology is characterized by an isotropic diffuse ring with $|k| = k^*$. The radial average $P(k)$ of the squared FFT amplitudes was used to determine (Lorentz line fit) the radius $k^*$ of the ring at its maximum and the inherent domain scale $R = 1/k^*$.

3. Results and discussion

3.1. Asymmetric blends on homogeneous SAM

To study pattern transposition in thin films, which is based on phase separation and pattern-guided selective
ceters\textsuperscript{45,49,50,55}. In addition, the process might involve coarsening regimes) of thermodynamic and kinetic parameters, evaporation and resulting rapid variations (across different R\textsuperscript{[45]} of AFM images used to determine R from ring radius (FFT scales correspond to AFM scan ranges).

These commonly accepted features must be specified to describe the studied film blends PVP:PS (Fig. 1). PVP, which is less soluble in a common solvent (THF)\textsuperscript{[18]}, solidifies during solvent evaporation earlier than PS\textsuperscript{[37,40,61]}, leading to the collapse of the initially THF-swollen PS-rich areas below the level of PVP phase. Therefore in the final solvent-free film (Fig. 1), PVP and PS domains are elevated and depressed, respectively, and the phase morphology is mirrored by film topography\textsuperscript{[18,24]}. The compositional dependence of film topography (recorded for homogeneous SAM substrate) reveals two droplet-type morphologies, dominated by PVP-rich islands (blend 2:3, PVP fraction \( P = 18 \text{ mg/mL} \)) and PS-rich holes (blend 3:2, \( \Phi = 0.60 \), Fig. 1(b) and (d)). They are separated by bicontinuous structures at intermediate compositions\textsuperscript{[40,53,54]} and plausible, however, that the latter precedes the former (as deduced very recently for another blends\textsuperscript{[40,53,54]} and manifests in different film morphologies when the former cannot develop during extremely rapid formation of very thin films\textsuperscript{[27,62]}. In turn, the (hydrodynamic, convective) instability of the free film surface is clearly evident in films thicker (i.e., formed longer) than those considered in this study\textsuperscript{[45]}.

### 3.1.1. Film structure formation

The phase separation\textsuperscript{[37–40,44–55]} that occurs during spin-casting\textsuperscript{[55–58]} is a complex process that cannot be described using quasi-static models\textsuperscript{[45]} due to fast solvent evaporation and resulting rapid variations (across different coarsening regimes) of thermodynamic and kinetic parameters\textsuperscript{[45,49,50,55]}. In addition, the process might involve various interfacial instabilities\textsuperscript{[40,44,45,51–54,60]} and leads often, due to the lack of sufficient equilibration, to long-lived metastable morphologies\textsuperscript{[48]}. While the multiple mutually coupled effects, that cannot be observed directly, are not completely resolved, the salient features of the consecutive stages of spin-casting have been recognized\textsuperscript{[55,56]}: First, most of polymer solution is spun-off leaving a uniform homogeneous film\textsuperscript{[56]}. Second, radial liquid flow that is caused by a balance between centrifugal and viscous forces, decreases film thickness and controls its final average value \( h \)\textsuperscript{[25,38,56–58]}.

It is during this stage that phase separation, initiated by evaporating solvent\textsuperscript{[48–50,55]}, takes place in a certain range of decreasing solvent concentration and terminates when polymer molecules are no longer mobile. Third, lateral domain structure, although frozen in place, is reflected by surface topography since the rate of solidification due to solvent evaporation as well as polymer swelling in the remaining solvent is different for various polymer-rich phases\textsuperscript{[44,48]}. The phase separation in the cast films can follow different evolution patterns\textsuperscript{[45]} (or their combinations\textsuperscript{[40,44,45]}): (i) Bulk coarsening is confined by film geometry into two dimensions\textsuperscript{[37–39,46–50]}; (ii) Horizontal phase structure is formed due to interfacial (capillary, dewetting) instability breaking up transient multilayer phase arrangement\textsuperscript{[40,45,48,51–54]}; (iii) Lateral compositional variation is driven by hydrodynamic (convective) instability\textsuperscript{[44,45,60]} (due to solvent concentration\textsuperscript{[59]} or temperature\textsuperscript{[60]}-gradient across the film).

3.1.2. Adjustable structural scale \( R \)

The processes of film thinning due to radial flow of solution and phase separation along the solvent-quench path coexist side by side (the second casting stage). The former governs film thickness \( h \sim c_p/\sqrt{\omega} \) and is controlled by spinning speed \( \omega \) and polymer concentration \( c_p \) in the solvent, as shown for pure polymers\textsuperscript{[56–58]} and polymer blends (composed of PVP and PS)\textsuperscript{[25,38]}. The latter process results in lateral domain structures. They are larger for thicker films since solvent drying and phase coarsening takes place during a longer period of time. As a result self-similar growing morphologies were observed for series of films cast with decreasing \( \omega \)\textsuperscript{[48]} and increasing \( c_p \)\textsuperscript{[24,38]}.

![AFM images of film blends 2:3 (a,c) and 3:2 PVP:PS (b,d) spin-cast onto homogeneous SAM substrate from THF solutions with constant spinning speed \( \omega = 5800 \text{ rpm} \) and varied polymer concentration \( c_p \): (a,b) \( c_p = 4.1 \text{ mg/mL} \), (c,d) \( c_p = 18 \text{ mg/mL} \). Insets display 2-dim FFT analysis of AFM images used to determine \( R \) from ring radius (FFT scales correspond to AFM scan ranges).](Image 1)
For asymmetric PVP:PS blends, self-similar isotropic structures are always formed in the 3:2 films (Fig. 1(b) and (d)). In the 2:3 layers the self-similarity of the morphology shown in Fig. 1(a) is somewhat affected for the longest film formation time (Fig. 1(c)) when first effects of free surface instability [45,62] modify PVP domain coalescence on a scale larger than the domains. Such effects are weaker for PS droplets in films 3:2 cast in similar conditions (Fig. 1(d)).

In addition, a simple scaling relation between horizontal and vertical lengths of the film structure was concluded for the system studied here. For the binary [62] and ternary [38] blends composed of PVP and PS the observed lateral domain scale \( R \sim h \) is related linearly with the film thickness \( h \). To present directly how the characteristic domain scale \( R \), which is a key parameter in this study, depends on the spin-casting conditions (and having in mind the relations \( R \sim h \) and \( h \sim c_P/\omega^{1/2} \)) we have plotted \( R \) as a function of \( c_P/\omega^{1/2} \) (Fig. 2). Two data sets correspond to \( R \)-values, determined with FFT analysis for asymmetric film blends 2:3 (open circles) and 3:2 (solid circles) cast on homogeneous SAM. Both data sets are scattered (due to limited reproducibility in \( \omega \) and \( c_P \)) along the linear relation marked by solid line. The corresponding linear coefficient \((29.5 \pm 1.4) \mu m/mL rpm^{1/2}/mg\) is close to that \((28.6 \pm 0.8) \mu m/mL rpm^{1/2}/mg\) evaluated (from similar plot) for the blend 1:1 [27]. This might suggest similar solvent-quench paths and drying times when casting conditions are fixed. Final phase evolution regime of the same spinodal-decomposition-type can be concluded for continuous (\( \Phi = 0.50 \)) and droplet (\( \Phi = 0.40, 0.60 \)) morphologies [63].

3.2. Asymmetric mixtures on Au/SAM pattern

While neither PVP nor PS wets the free surface or the SAM-covered substrate, PVP exhibits strong affinity to the Au surface [18,24–26]. This drives the organization of lateral domains of PVP:PS blends (Fig. 3(b)–(e)) on the substrate with Au/SAM pattern (see LFM image in Fig. 3(a)) [18,24,25]. Such ordering process is compositionally incommensurate for the symmetric pattern (Fig. 3(a)) and the asymmetric film blends 2:3 and 3:2. PVP-rich phase

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**Fig. 2.** Inherent scale of lateral domains \( R \) formed by PVP:PS film blends 2:3 (open circles) and 3:2 (solid circles) on homogeneous SAM substrate as a function of \( c_P/\omega^{1/2} \), reflecting spin-casting conditions.

**Fig. 3.** LFM image of the substrate pattern (with periodicity \( \lambda = 4 \mu m \)) Au/SAM (a). Micrographs of PVP:PS film blends 2:3 (b,d) and 3:2 (c,e) spin-cast (\( c_P = 7 mg/mL, \omega = 5800 \) rpm) onto the pattern prior (b,c; LFM) and after (d,e; AFM; different spots) selective dissolution of PVP. Light regions correspond to original Au-stripes in (a) (covered with HS(CH2)15COOH to improve contrast) as well as to PVP in (b,c) and PS in (d,e).
(with higher friction [25,38,45]) corresponds to brighter regions in LFM images (Fig. 3(b) and (c)) as confirmed by AFM combined with selective dissolution of PVP (Fig. 3(d) and (e)). PVP forms on the Au-stripes isolated droplets (films 2:3), or continuous ribbons which can intrude elsewhere to separate PS droplets (films 3:2). The compliance of both droplet-type morphologies (Fig. 1) with the substrate pattern is described below for two topographic sequences of spin-cast films ‘frozen’ for increasing both the drying time (i.e., thickness $h \sim c_p/\sigma^{1/2}$) and inherent size $R$ of coarsening lateral domains. Such a sequence resembles structures evolving during quasi-2-dim phase coarsening [25] (but the surface/interface instability effects can be also relevant).

3.2.1. Blends 2:3

A series of blend films spin-cast ($\omega = 5800$ rpm) from solutions with polymer concentration $c_p$ ranging from 4.0 to 18 mg/mL is illustrated in Fig. 4. First AFM image of this series (Fig. 4(a)) illustrates practically isotropic domains of size $R/2 \sim 0.1 \lambda$ (0.4 µm) with some weak traces of linear domain arrays. The next figure (Fig. 4(b)), corresponding to $R \sim 0.5 \lambda$, show elongated PVP droplets in register with underlying pattern with periodicity $\lambda$. In addition, we observe (located between them) slightly smaller droplets of a weak $\lambda/2$-substructure. The coalescence of PVP droplets is more effective along the Au-stripes, resulting in primary $\lambda$-structure. Another PVP droplets appear with inter-domain spacing $R \sim \lambda/2$ away from the primary structure, forming the substructure. This secondary ordering effect is enhanced by the strips depleted in PVP, adjacent to the primary structure and separating it from the substructure. For longer drying times (Fig. 4(c) and (d)) the coalescing PVP droplets forming the primary structure become much more distinct than droplets formed on neutral SAM stripes. The cross-section (Fig. 4(f)) of AFM image recorded for $R/\lambda \sim 1$ (Fig. 4(d)) shows periodic PVP-rich elevations with the base comparable to the Au-stripe width (2 µm) and the regions between them disturbed by weak undulations. In turn, the situation corresponding to $R \sim 1.8 \lambda$ and the longest film formation time used is presented in Fig. 4(e). It shows large elongated PVP domains, comparable in size to those observed on the homogeneous SAM substrate (for the same casting conditions – see Fig. 1(c)) but with the domains aligned along the Au-stripes.

To examine quantitatively the formed anisotropic morphologies the integral geometry approach [39,41] was applied. This method yields the Euler characteristic $\chi_E$ (formally the difference between surface density of distinct elevated and depressed regions), which is especially apt to measure the droplet coalescence. The surface density of PVP-rich elevated droplets, expressed for the blend 2:3 by $\chi_E$, is presented in Fig. 5(a) as a function of domain scale.

Fig. 4. AFM images of film blends 2:3 spin-cast ($\omega = 5800$ rpm) on the substrate pattern from solutions with polymer concentration $c_p = 4.0$ (a), 4.1 (b), 7 (c), 9 (d), 18 mg/mL (e). Inherent domain scale $R$ equals to 0.20 $\lambda$ (a), 0.47 $\lambda$ (b), 0.92 $\lambda$ (c), 1.07 $\lambda$ (d,f), 1.66 $\lambda$ (e). The cross-section (f) corresponds to the solid white line in (d).
The $V$-values determined for the film regions on the pattern (solid squares) and on homogeneous SAM (open squares) seem both to be scattered along the same scaling relation $V = C R^{-2}$ [39,42]. This indicates that overall phase coarsening is not much affected by the substrate pattern. For each pair of isotropic and anisotropic morphologies island density is indeed quite similar, irrespectively of casting conditions (Fig. 6). In addition, the Euler characteristic $\nu_E$ (Fig. 5(a)) does not reflect any reaction of domain ordering for the domain scale $R$ comparable to the pattern period $\lambda$.

3.2.2. Blends 3:2

A sequence of film blends 3:2 cast ($\omega = 5800$ rpm) from solutions with $c_P = 4.0 - 18$ mg/mL is shown in Fig. 7. This series starts, for $R \sim 0.3 \lambda$ (Fig. 7(a)), with almost isotropic morphology dominated by polydisperse (in size) PS-rich holes (cf. Fig. 1(b)) surrounded by continuous elevated PVP-rich ribbons. Weak sporadic alignment along parallel lines can be noticed. The next AFM image (Fig. 7(b)), corresponding to $R \sim \lambda/2$, shows the Au-stripes coated in their center by PVP ribbons intruding elsewhere to enclose larger PS droplets. In addition, the Au-substrate regions are covered to their complete lateral extension by small PS-droplets surrounded by PVP-rich elevations. Superfluous PVP material (major blend component) forms numerous bridges between the elevations lined in register with the Au-stripes. However, no $\lambda/2$-substructures are formed midway between them. The alignment of such linear elevations is improved for larger $R$-values (Fig. 7(c) and (d)). Simultaneously, the number of the bridges is reduced (Fig. 7(c) and (d)) to reach minimum for the domain scale $R$ almost matching the pattern periodicity $\lambda$. Corresponding cross-section (Fig. 7(f)) of AFM image (Fig. 7(d)) shows superfluous PVP material up-lifted above the Au-stripes forming periodic high elevations separated by V-shaped valleys. When the inherent scale $R$ of domain structure is larger than pattern periodicity $\lambda$ (Fig. 7(e)) the bridges, linking the PVP elevations above the Au-stripes, are formed again and the periodic elevations become less ordered.

The results of integral geometry analysis [39,41] performed for the film blends 3:2 are presented in Fig. 5(b). The Euler characteristic $\nu_E$ is negative as the morphologies are dominated by the (PS-rich) holes. For all casting conditions the surface density $|\nu_E|$ of separate PS domains is reduced for the sample regions on the pattern Au/SAM (solid squares) as compared to those on homogeneous SAM (open squares). This is evident from AFM images recorded for the pairs of isotropic and anisotropic morphologies, corresponding to various casting conditions and different values of inherent domain scale $R$ (Fig. 8). This effect is much weaker for the morphologies with larger scale $R > \lambda$ (Fig. 8(b) and (d)). The scaling relation $|\nu_E| \sim 1/R^2$ [39,42] is roughly reproduced by the morphologies on SAM (solid line and open squares in Fig. 5(b)). However, different situation is observed for the films on the pattern (solid symbols and the dashed line) with the $|\nu_E|$-values showing minimum $|\nu_E| \rightarrow 0$ for $R \sim \lambda$ (see the inset in Fig. 5(b)). This reflects strong reaction of domain ordering to the matched inherent dimensions of domain structure $R$ and substrate pattern $\lambda$. The modification of lateral phase
Coarsening by the patterned substrate was reported earlier [23] for nanoscopic pattern inhibiting phase separation. An opposite effect is observed here (Fig. 8) with the macroscopic pattern enhancing phase coarsening, most effectively for $\lambda > R$. Most probably the relevant mechanism includes the transport of PVP material to the layers wetting Au-stripes through continuous PVP-rich tubes, driven by the curvature of phase boundaries between PVP-rich and PS-rich phases. This is analogous to hydrodynamic flow [64]-driven wetting of blend surfaces, reported earlier [65–67]. Perfectly aligned PVP stripes wetting Au-stripes are formed when the width $\lambda/2$ of the latter fits the inherent domain size $R/2$. This alignment is lost and the bridges between the PVP regions on the Au-stripes are re-introduced for the domains larger than the stripe width (i.e., for $R > \lambda$).

4. Summary and conclusions

We present experimental results on thin film morphology of two asymmetric (and off-critical) homopolymer blends, 2:3 and 3:2 PVP:PS, forming PVP- and PS-rich isolated droplets, respectively, on homogeneous SAM substrate. The blends are spin-cast (with varied domain scale $R$) on the symmetric substrate pattern. One of two alternating (with micrometer periodicity $\lambda$) substrate stripes is neutral (SAM) and another (Au) attracts preferentially PVP.

For both blends optimal pattern replication is obtained when $R \sim \lambda$ (Figs. 7(d), 4(d)). However, when PVP forms the majority phase (3:2 PVP:PS), the compliance of film structure with the pattern is so strong that (PS) droplet morphology is almost completely transformed into the elongated continuous domains. This is due to the hydrodynamic flow-driven wetting of the Au-stripes involving transport of PVP through continuous tubes of its majority phase. In contrast, ordered droplet-type morphologies are obtained for 2:3 PVP:PS as a result of pattern-guided
growth of isolated PVP droplets (minority phase). As a consequence droplet density is reduced on the pattern, as compared to homogeneous SAM substrate, for 3:2 but not 2:3 PVP:PS films. Different film morphologies are obtained also for \( R \sim \lambda/2 \) (see Figs. 7(b) and 4(b)). In 3:2 PVP:PS the Au-stripes are coated by PVP ribbons (intruding elsewhere to enclose larger PS droplets) and small PS-domains (encircled by PVP-rich elevations). However, no \( \lambda/2 \)-substructures are formed between the periodic PVP elevations. In contrast, in 2:3 PVP:PS the smaller PVP droplets locate midway between the PVP domains in register with Au-stripes. \( \lambda/2 \)-substructures are formed due to a weak secondary ordering effect.

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