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Surface-induced Phase Separation of Binary Polymer Blends on the Chemically Patterned Substrate

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Summary

The patterned substrate with alternating SiO_2 and octadecyltrichlorosilane (OTS) self-assembled monolayers (SAM) was used to induce phase separation of PS (polystyrene) and PVP (poly2-vinylpyridine) binary polymer blend films. The PS- and PVP- phase were situated on the OTS and SiO_2 domains, respectively. It revealed that even though the characteristic length scales (D) of phase separation were different from the periods of prepatterned substrates (λ), if the surface interaction between each component and substrate is strong enough, the lateral growth of phase separation domains is significantly constrained and the domains replicate the surface patterns.

Introduction

In recent years, there has been an increasing interest in controlling morphology of phase separation of thin polymer blend films due to their important applications in diverse fields, such as opto-electronic devices and templating in lithographic processes [1, 2]. Experimental techniques have been developed to create surfaces patterned with imprinted structures, which can be used to guide structure formation in thin films of polymer mixtures [3, 4]. The presence of those surfaces can significantly alter the phase decomposition (PD) of polymer blends thin films owing to break the symmetry of polymer mixture and preferentially attract one of the blend components [5-7]. Many groups [3, 8, 9] studied the phenomena for PVP/dPS or PVP/PBrS blends films spin-cast onto the Au substrate patterned with self-assembled monolayers $HS(CH_2)_{15}COOH$ or $HS(CH_2)_{15}CH_3$. It revealed that most effective pattern transfer was achieved when the characteristic size D of the phase domains were commensurate with the pattern periodicity (λ). Simulation [10-12] results showed that the competition between the interfacial energy and the substrates potential became more pronounced when the blend thin film was cast on a chemically patterned substrate. If the surface interaction was strong enough, the lateral growth of domains was significantly constrained and the domains followed the surface imprints. In our work, we revealed the simulation results through experiments. We used the silicon wafers patterned with OTS SAM by μCP [13] to induce the phase separation of PS and PVP polymer blend

thin film. The patterned substrates featured alternating stripes or lattices of SiO_2 and OTS monolayers. The morphology formation of PS/PVP films on a homogeneous OTS SAM, silicon substrate were investigated first, and then the replication of PS/PVP blend films onto the patterned substrates were studied. The transformation of the diverse patterns onto the film surfaces took place after PS/PVP spin-cast onto substrates immediately. Different periodicity patterned substrates all induced ordered patterns very well due to the drastically large surface tension difference between SiO_2 surface and OTS monolayers.

Experimental

Materials

The polished test grade silicon (100) wafers (p-type) were purchased from Silicon Company of China. Octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$, 95%), PS and PVP were purchased from Aldrich Chemical Company. The characteristics of the PS and PVP are shown in Table 1. Tetrahydrofuran (THF) (99.9%, anhydrous) was from Beijing Chemical, China and used without further purification.

Table 1. Characteristics of PS and PVP.

Polymer	M_w ($\times10^4$)	M_n ($\times10^4$)	M_w/M_n	density(g/cm^3)
PS	11.4	11.1	1.03	1.05
PVP	1.5	1.4	1.05	1.12

Microcontact printing of OTS

The silicon wafers were cut into 1×1 cm^2 pieces. Then, they were placed into a mixed solution of concentrated H_2SO_4 and H_2O_2 (70/30) (v/v) at 393k for 1h. After cleaned with purified deionized water for several times, they were dried in a stream of high-purity N_2 (99.99%) gas. This treatment removed the residual hydrocarbon impurities and a ultra thin oxidization layer (SiO_2) ca. 4 nm (by spectroscopic ellipsometry) yielded. The oxidization layer had a strong hydrophilic character.
Micro-contact printing procedure [13] was used to create OTS SAMs strips featured parallel and squared wells on the silicon wafers. First, a patterned PDMS elastomer mold was made. The details of how to make a PDMS elastomer mold have been described elsewhere [14]. Casting prepolymer, Sylgard 184 on a prepatterned substrate created by lithographic process, and then curing at 65 ^{o}C for 4 h, after peeled off, the PDMS molds with relief structures as negative replicas of the prepatterned substrate were formed. Next, the micro-contact printing procedure was done in a homemade glove box with a nitrogen atmosphere and the humidity was 40±1%. A PDMS stamp was soaped with a 1.0 wt % solution of OTS in toluene and blew dry with nitrogen and kept contact with the pre-cleaned silicon wafers for 30-60s. Then the pattern was transferred onto the underlying substrate.
Figure 1 shows the typical images of the patterned elastomer stamps used in our work. The patterned elastomer stamp printed the “ink” of OTS molecules in 1.0% w/w toluene solution onto the silicon wafer surfaces. The thickness of the OTS molecules was

ca. 4 nm by spectroscopic ellipsometry. Thus, the patterned substrates were prepared with alternating stripes or lattices of SiO_2 and OTS monolayers, respectively. Figure 2 present the AFM images of the prepatterned substrates produced by μCP. The brighter domains are OTS, the darker domains are SiO_2, respectively.

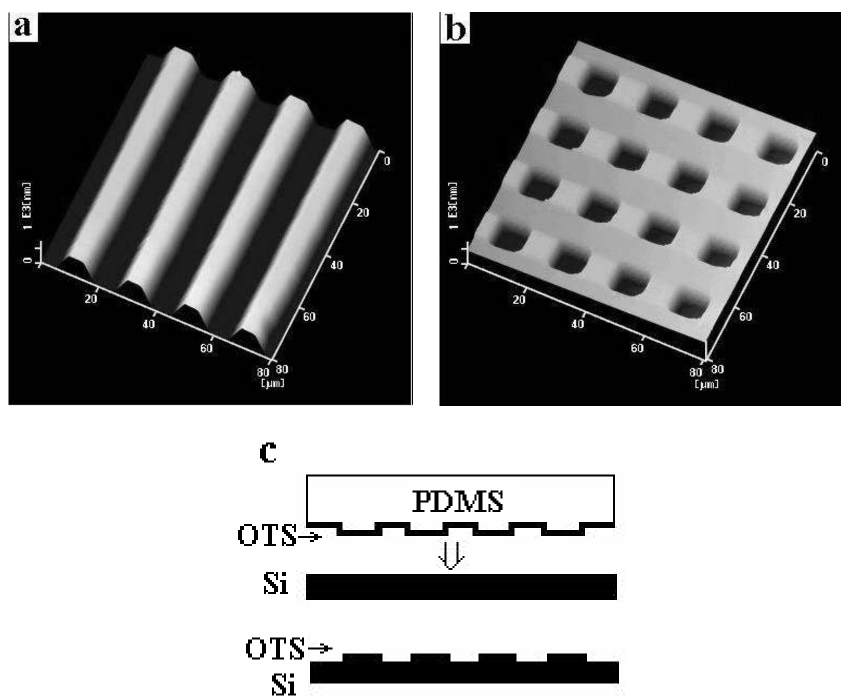
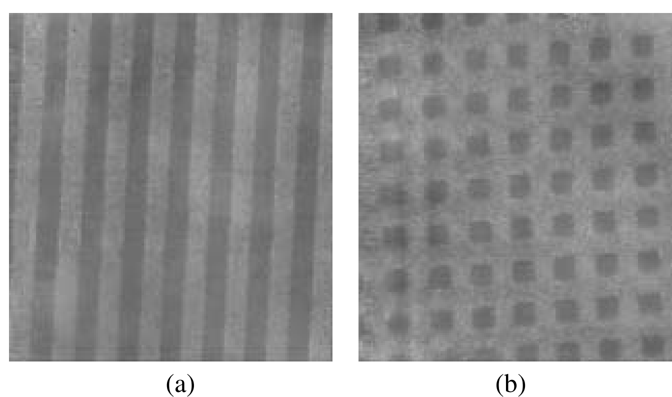


Figure 1. Typical AFM images of the patterned elastomer stamps. (a) Parallel stripes. with width of 10 μm. (b) Squared well with the side length of 10μm (c) A patterned elastomer stamp prints the "ink" of OTS molecules in 1.0% (w/w) toluene solutions onto the silicon wafer surface.



(a) (b)

Figure 2. AFM images of the prepatterned substrates produced by μCP. The scale is 150 μm × 150 μm.

Sample preparation

The polymer solutions were prepared by dissolving a mixture of PS and PVP (weight/weight=1:3.4) [15] in THF at the total polymer concentration of 1.0%w/w. Prior to spin coating, the polymer solutions were filtered with 0.22 μm Millipore membrane. Then, they were spin-cast onto the substrates at a speed of 2000 rpm. All the spin-coated films were dried in a vacuum for 10 h at 50 °C.

Atomic force microscopy

Atomic force microscopy (AFM) measurements were performed on SPA300HV with an SPI 3800 controller, Seiko instruments industry, Co. Ltd. The topographical images were taken with contact mode and tapping mode at room temperature, respectively. The tip type of contact mode is SN-AF01, made of Si_3N_4 with a typical spring constant of 0.01 N/m. The scan rate was about 1.0 Hz. The overall phase domain morphology was determined by selective dissolution of PS-rich and PVP-rich phase by immersing the films in cyclohexane and ethanol, respectively.

Results

The surface morphologies of PS/P2VP spin-cast onto the OTS SAM and silicon substrates.

Figure 3(a) shows the 3D topographic AFM image of PS/PVP (w/w=1:3.4) spin-cast onto the OTS SAM substrate. The thickness of the film is about 85 nm. Figure 3(b) is the corresponding 3D topographic image of the remaining PVP phase after the PS-rich phase is removed by immersing the sample in the cyclohexane for 5 min. It can be concluded that the higher and wider phase domain is PVP. Since THF is better solvent for PS, PVP phase is more quickly depleted of the solvent and turns solid earlier than PS [16]. We can see the height difference between the higher domain and lower domain increases drastically after cyclohexane treatment. From Figure 3, it can be seen that the

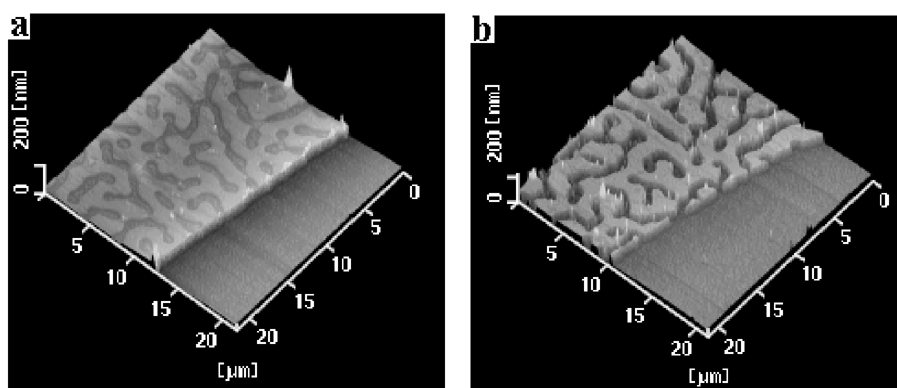


Figure 3. 3D topographic AFM images of PS/PVP (1:3.4 w/w) spin-cast from a THF solution (1 wt%) onto the OTS SAM substrate. (a) as cast. (b) after the PS phase was removed by immersing the sample in cyclohexane.

laterally disordered domains composed of PS- and PVP-rich phase adjacent to air and substrate interfaces formed.

Figure 4(a) is the topographic image of PS/PVP spin-cast onto the SiO_2 substrate. The thickness of the film is about 75 nm. Smooth surface formed. Figure 4(b) is the remained image after the samples was treated by cyclohexane. Similar smooth surface emerged. Line profiles of Figure 4 (below) show the thickness contrast of the samples before and after cyclohexane immersion. The film thickness changed form the 75 nm to 50 nm. From Figure 4(a) and (b), it can be seen that, different from on the OTS SAM substrate, a bilayer film composed of PS-rich and PVP-rich laminated domains adjacent to air and substrate interfaces, respectively, is observed for PS/PVP blend spin-cast on silicon substrate. These results indicate that more polar PVP is favored at the SiO_2 surface, while apolar PS is excluded onto the surface of the PVP.

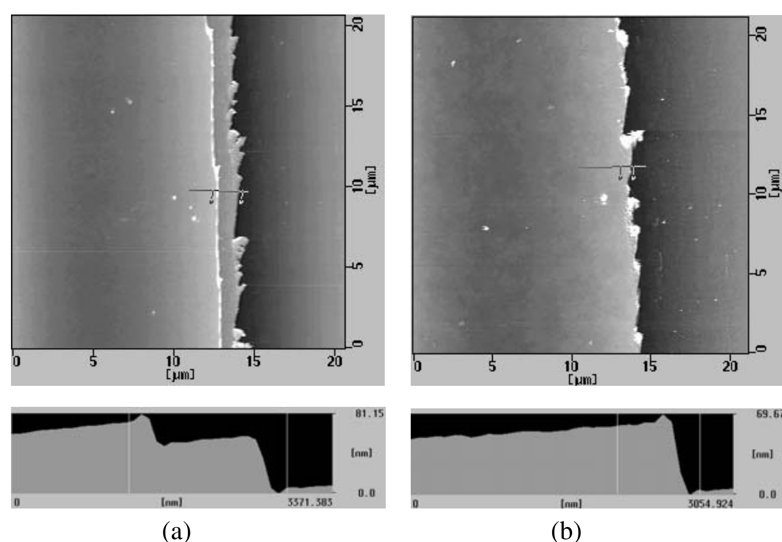


Figure 4. (top) Topographic AFM images of PS/PVP (1:3.4 w/w) from a THF solution (1 wt%) spin-cast onto the SiO_2 substrate. (a) as cast. (b) after cyclohexane treatment. (below) Line profiles along the lines in the top images.

The surface morphologies of PS/PVP spin-cast onto the patterned silicon substrates.

Figure 5(a-d) show the film topographies after PS/PVP (w/w=1:3.4) spun-cast onto the patterned substrates from THF solution. The thickness of the film is about 85 nm. The patterned substrates featured alternating stripes and lattices, respectively. The width of stripes is 5μm (in Figure 5(a)) and 10μm (in Figure 5 (b)). The lattices patterns featured square (the side width of the little lattice is 5μm) Figure 5(c) and rectangular (the side width×length=5×10μm) Figure 5(d). The cross sections taken along the lines in the images were shown below in Figure 5. The line profiles of AMF images indicate that the brighter stripes are higher. It can be seen from the cross sections, the width of the bump parts and the groove parts are nearly equal to that of patterns on the substrates, i.e. the sizes of phase domains are commensurate with the pattern periodicity. Selective dissolution was used to determine the phase domains on the substrates. Figure 6 is the remained topography after the PVP was removed by ethanol corresponding to Figure 5.

From the above results, we can see that the PVP-rich phase situates on the SiO_2 domains of the patterned substrates. The PS-rich phase is on the OTS SAM domains. Those images show that the phase separation patterns effectively replicate the substrate patterns.

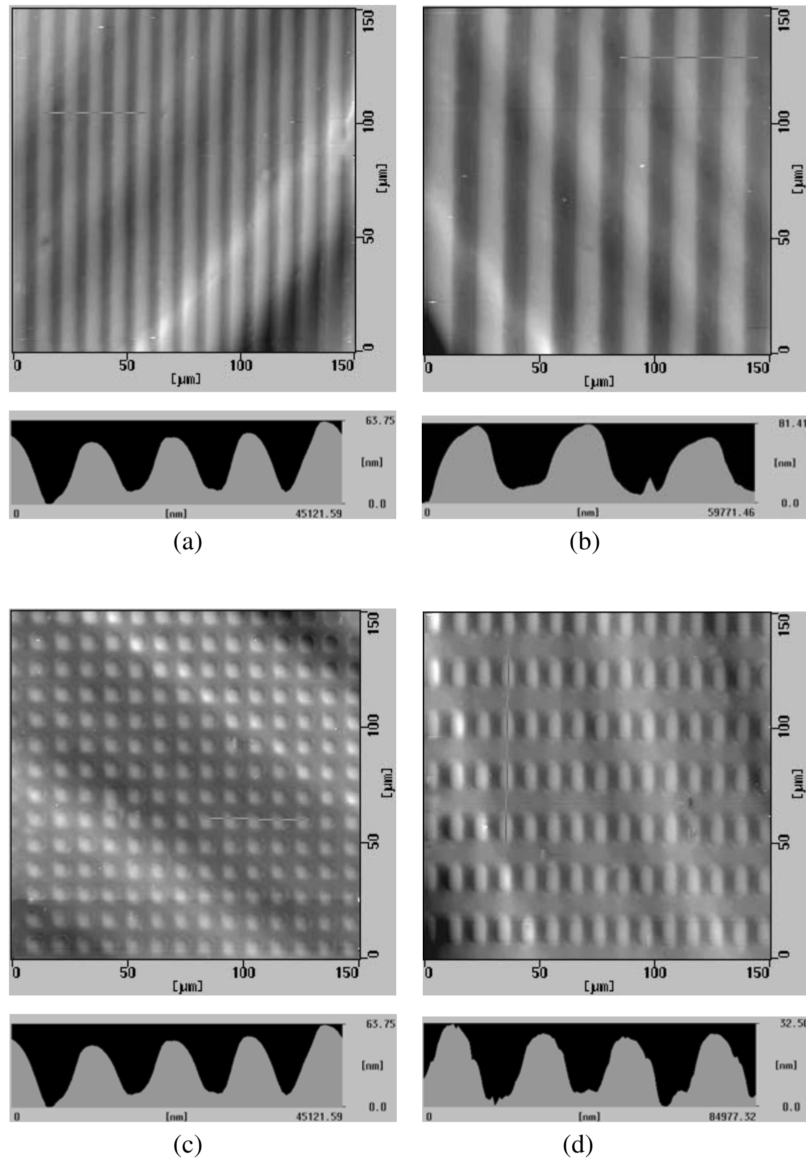


Figure 5. (top) AFM images of PS/PVP blend (1:3.4 w/w) spin-cast from a tetradrofurane (THF) solution (1 wt%) onto the patterned silicon wafers which featured with stripes and lattices of SiO_2 and OTS SAMs. (a) The width of the stripes is 5µm. (b) The width of the stripes is 10µm. (c) The sides of the lattices are 5µm × 5µm. (c) The sides of the lattices are 5µm ×10µm. (below) Line profiles along lines in the top images.

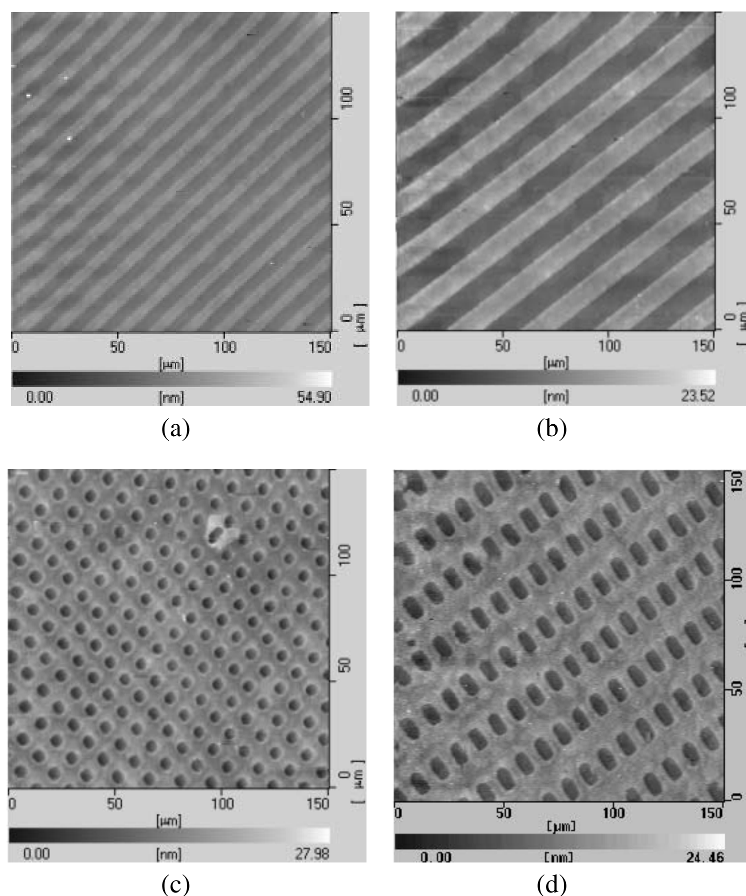


Figure 6. AFM image of Figure 5 after the PVP was removed by ethanol.

Discussion

For thicker blends films, bulk-like phase separation will occur, which leading to the formation of an isotropic, disordered phase morphology with a characteristic length scale. But for thin blend films (usual thickness is less than 100 nm), since the surface-area-to-volume ratio is relatively large, both air/polymer and polymer/substrate interfaces play an important role in determining the morphology of phase separation due to the presence of wetting/dewetting behavior of each polymer component to the air or substrate. Multilayer films will emerge originating from the surface-directed phase separation [5] when each phase strongly wet the substrate. PS and PVP are strongly incompatible ($\chi \approx 0.1$). When they were dissolved in a common solvent and spin-cast onto the substrate, phase separation of two polymer components occurred. For PS/PVP blend phase separation on SiO_2 substrate, owing to PVP phase preferentially wetting the SiO_2 substrates, bilayer film with a PS layer on the top of the PVP layer formed. Meanwhile, since γ (PS) (39.8mN/m) < γ (PVP) (45.1mN/m) [17], bilayer film structure decreased the surface free energy of whole system. But when the phase separation took place on the OTS SAM substrate, an isotropic and disordered phase

morphology was observed. It was due to the presence of no preferential wetting for the OTS SAM substrate. Both PS and PVP phase were adjacent to air and substrate interfaces.

Drastically changed morphology was observed for PVP/PS blend spin-cast onto the patterned substrate composed of OTS SAM and SiO_2. The patterns were transferred to the blend films very well. Phase separation in polymer mixtures was altered by the presence of patterned substrate with lateral pattern of surface energy. The PVP assembled on the SiO_2 domains by the adsorption action between the PVP and SiO_2. At the same time, the PS was pushed to the OTS SAM domains. This process was completed on the time scale of the spin-coating process and the phase separation domains were well aligned with sharp interfaces between the PVP- and the PS-rich phases. Importantly, diverse patterns with different periods (λ) were replicated to blend films with characteristic length scale (D). To determine the characteristic length scale of phase separation domains, two-dimensional fast Fourier transforms (FFT) in Figure 3 (a) were calculated. The characteristic length scale (D) was about 3.0 μm.

Krausch et al. [3, 8, 9] have studied the different factors determining the phase domain morphology and surface topography of thin polymer films undergoing phase decomposition during spin-coating onto the patterned substrates. For PS and PVP blend film spun-cast on Au / ($HS(CH_2)_{15}CH_3$) SAM substrate, they obtained that the optimum conditions of pattern transfer were the characteristic size D of the phase domains equaled to the pattern periodicity. But in our work, the transfer of the substrate patterns into the film took place for diverse patterns periodicity and different shape substrates (i.e. $D \neq \lambda$). In addition, the final morphology also depends on the competition between surface and interfacial energy. [8] The complete ordering of the polymer phases can occur only when substrate/polymer interactions dominate over the interfacial tension between the two polymers. Many groups studied the phase separation of thin polymer blend film on a chemically heterogeous surface through computer simulations [10, 11, 12]. Simulations clearly demonstrate that when the surface pattern width is increased and a strong surface interaction is chosen, an almost perfect match between the film morphology and the substrate pattern is observed. The competition between the interfacial energy and substrate potential becomes more pronounced when the blend thin film is cast on a chemically patterned substrate. If the surface interaction is strong enough, the lateral growth of domains is significantly constrained and the domains follow the surface imprints. We demonstrated the simulations results in the experiments. The static water contact angles of the substrates are shown in Table 2. It can be seen that SiO_2 surface is 0°, drastically less than the static water contact angle of the Au surface. The static water contact angles of the hexadecanethiol and OTS SAM surface are nearly equal. Thus the surface tension difference between SiO_2 surface and OTS SAM surface is drastically larger than the surface tension difference between Au

Table 2. Static water contact angles of substrate surfaces.

Substrate	Θ (deg) (°)
Au	65[a]
SiO_2	0[b]
OTS	105[c]
($HS(CH_2)_{15}CH_3$)	108[d]

[a] Ref. [16] [b] Ref. [18] [c] Ref. [19] [d] Ref. [20]

surface and hexadecanethiol SAM surface. In addition, the interfacial tension of the PVP/PS used in our work resembles that of the PVP/PS used by other Groups [3, 8, 9]. So the transfer of the good ordered patterns from the substrates to the film surface is due to the drastically larger surface tension difference between SiO_2 and OTS SAM.

Conclusions

We used the silicon wafers patterned with OTS SAM to induce PS/PVP blend thin film phase separation. In contrast to homogeneous substrates, good-ordered patterns were transferred from the substrates to the film surface on the patterned substrates. It revealed that if the surface interaction between each component and substrate is strong enough, the lateral growth of phase separation domains is significantly constrained and the domains replicate the surface patterns.

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15. The critical volume of phase separation can be calculated by $\varphi_c = \left[\sqrt{\frac{N_A}{N_B}} + 1\right]^{-1}$. N_A and N_B are the repeat unit number. The repeat unit number of PS (A) ($M_n=11.1\times10^4$) and PVP (B) ($M_n=1.4\times10^4$) is about 1000 and 100, respectively. Then the critical volume of PS ($\varphi_{c(A)}$) is about 24% and the critical volume of PVP ($\varphi_{c(B)}$) is about 76%. The critical weight ratio of PS and PVP is 1:3.4.
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