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Molecular weight effects on the phase morphology of PS/P4VP blend films on homogeneous SAM and heterogeneous SAM/Au substrates

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Abstract

The effects of the molecular weight of polystyrene (PS) component on the phase separation of PS/poly(4-vinylpyridine) (PS/P4VP) blend films on homogeneous alkanethiol self-assembled monolayer (SAM) and heterogeneous SAM/Au substrates have been investigated by means of atomic force microscopy (AFM). For the PS (22.4k)/P4VP (60k) system, owing to the molecular weight of PS component is relatively small, the well-aligned PS and P4VP stripes with good thermal stability are directed by the patterned SAM/Au surfaces. With the increase of the molecular weight of PS component (for the PS (582k)/P4VP (60k) system), the diffusion of P4VP is hindered by the high viscosity of PS during the fast spin-coating process. The phase separation behavior of PS/P4VP on the SAM/Au patterned substrates is similar to that on the homogeneous SAM and cannot be easily directed by the patterned SAM surfaces even though the characteristic length of the lateral domain morphology is commensurate with the stripe width. This indicates that the relative viscosity of the PS is one of the dominant factors in obtaining well-aligned pattern by the phase separation of polymer blends.

Keywords: PS/P4VP blend films; Molecular weight; Patterned substrates

1. Introduction

Surface-directed phase separation in thin polymer blend films can lead to pattern replication, which is expected to play an important role in future technological applications (e.g. plastic-based electronic devices and template in lithographic processes) [1]. Therefore, in recent years, there has been an increasing interest in controlling the phase separation morphology of the thin blend films on the patterned surfaces [1–8]. The results of Böltau et al. [2] showed that patterned stripes of gold and SAMs of CH_3-terminated alkanethiols on gold could direct the phase separation of PS/poly(vinyl pyridine) (PVP) blend. Karim et al. [3] obtained stable and well-aligned stripes of deuterated polystyrene/polybutadiene (dPS/PB) blend film phase separation on a microcontact printed (μCP) alkanethiol patterns with hydrophobic and hydrophilic end groups ($-CH_3$ and $-COOH$). Cyganik et al. [4] investigated P2VP/dPS and P2VP/brominated polystyrene (PBrS) blends on SAM stripes of alkanethiols with $-CH_3$ and $-COOH$ end groups. It has been shown that the transfer of the pattern from the substrate (with alternating stripes of equal width w and different surface energy) to the phase-domain structure of a thin polymer blend film depends on a wide variety of parameters [1]. The complete ordering of the polymer phases can occur only for pattern size comparable to the characteristic length of the lateral domain morphology on the respective homogeneous substrate [2–6,9,10]. The final morphology also depends on the results of the competition between the surface and interfacial energy [5,6], that is, to obtain a well-aligned phase separation pattern, substrate/polymer interactions should be adjusted carefully in experiments [4]. The results of Cyganik et al. [4] also showed that a large surface energy difference between two types of alternating stripes did not improve the transfer of the substrate pattern. Computer simulations of Kielhorn and Muthukumar [5] investigated the effect of a patterned surface on the phase separation kinetics of a thin polymer blend film using the Cahn–Hilliard–Cook model. Shou and Chakrabarti [6] simulated the effects of different substrate pattern widths and surface interaction strengths on the phase

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morphology. However, hydrodynamic interactions, which exist in experimental situation, are not included in the above experiments and computer simulations. Whether viscous flows, which have an important influence on the surface structures during the process of spin coating or phase separation, would allow for a better film alignment is still an important, unanswered question [6].

When the phase separation of a binary blend (A/B) in the presence of a patterned surface takes place, to minimize the system's energy, the material of component A rushes to the respective stripes which attract component A. A flux of component B in the opposite direction will carry through. To form a well-aligned phase separation pattern, it is thought that the diffusion properties of molecules or aggregates in solution are very important. In this work, the PS/P4VP system, which the Flory–Huggins interaction parameter ($0.30 < \chi_{\mathrm{S,4VP}} < 0.35$) [11] is much larger than the value ($\chi_{\mathrm{S,2VP}} = 0.1$) of the PS/P2VP system [12], was chosen as a model system. The molecular weight of the P4VP is fixed and the molecular weights of the PS component are varied from 22.4 to 582k. The morphology formation of a thin PS/P4VP film on a homogeneous SAM substrate was studied firstly. Furthermore, the effects of the relative viscosity of PS components on the pattern replication of PS/P4VP blend onto patterned substrates were investigated.

2. Experimental section

2.1. Materials

Polystyrene (PS-2), poly(4-vinylpyridine) (P4VP) and hexadecanethiol were purchased from Aldrich Chemical Company and used as received. The other polystyrene samples (PS-1, and PS-3) were obtained from Nanjing University, China. Their characteristics are shown in Table 1. Chloroform, ethanol and tetrahydrofuran (THF) were analytical grade. The viscosity of PS in CH_3Cl at 25 °C was calculated by $[\eta] = 7.16 \times 10^{-3} M^{0.76}$ [ml/g] [13]. The glass transition temperature (T_g) of a polymer was measured by DSC.

2.2. Film preparation

Polymer solutions were prepared by dissolving the polymer mixtures with different ratios of PS and P4VP (weight/weight) in chloroform. The polymer solutions were filtered with 0.22 μm Millipore membrane before used.

Prior to spin coating, the silicon wafer was cleaned with a mixed solution of concentrated H_2SO_4 and H_2O_2 (30%) (70/30 v/v) at 110 °C for 1 h, then the wafer was rinsed in deionized water for several times and dried with nitrogen gas. The substrates were first covered with about 2 nm thick chrome layer, followed by the evaporation of a 30 nm thick gold (Au) layer. To produce homogeneous SAM surfaces, a self-assembled hexadecanethiol monolayer was deposited onto the substrate surfaces by immersing gold-covered silicon wafers overnight in a 0.285% (w/w) solution of hexadecanethiol in an ethanol/THF (5/2 w/w) [14]. Patterned SAM surfaces were produced using micro contact-printing procedure (μCP) [15,16]. A patterned PDMS elastomer stamp printed the 'ink' of hexadecanethiol molecules in 2 mM ethanol solution onto gold surface. Fig. 1 shows the PDMS stamps geometries used in this study. The dimensions of SAM/Au stripe patterns were 10.3 μm/8.7 μm, and 18.5 μm/18.5 μm, respectively.

The films were prepared from the PS/P4VP solutions (typically 1.5 wt% polymer) with KW-4A Precision Spin-Coater (Chemat Technology, Inc.) in a glove box. The spin coating was carried out at 2000 rpm for 30 s at room temperature. All spin-cast films were dried in a vacuum for 10 h at 50 °C to remove any remaining solvent.

2.3. Atomic force microscopy

The AFM measurements of the blend films were performed on SPA300HV with an SPI3800 controller, Seiko Instruments Industry, Co., Ltd. The images were taken with the contact mode and friction force microscopy (FFM) image was performed simultaneously with topographical imaging. The FFT analysis was performed using the software provided by Seiko Instruments Industry, Co.

3. Results and discussion

To understand the phase morphology of PS/P4VP blend films spin coated on the patterned substrates, it is instructive to discuss first phase morphology taking place for the same blend on homogeneous SAM substrates.

3.1. Surface morphologies of PS/P4VP blend films on homogeneous SAM surfaces

Fig. 2(a)–(f) shows the AFM topographical images of the PS-1/P4VP (70/30, 50/50, 30/70, w/w) blend films as spin coated and treated with cyclohexane for 5 min (the PS-rich phase was removed [14,17]) on the hexadecanethiol SAM-covered substrates. The bright and dark parts in Fig. 2(a)–(c) are corresponding to the P4VP- and PS-rich phases, respectively. With 70% PS/30% P4VP, the surface

Table 1
Characteristics of PS and PMMA

Polymer	M_w	M_n	M_w/M_n	$[\eta]$ [ml/g]	T_g (°C)
P4VP	60k	–	–	–	155
PS-1	22.4k	21.6k	1.03	14.49	98
PS-2	129k	121k	1.06	54.82	107
PS-3	582k	522k	1.11	172.29	107

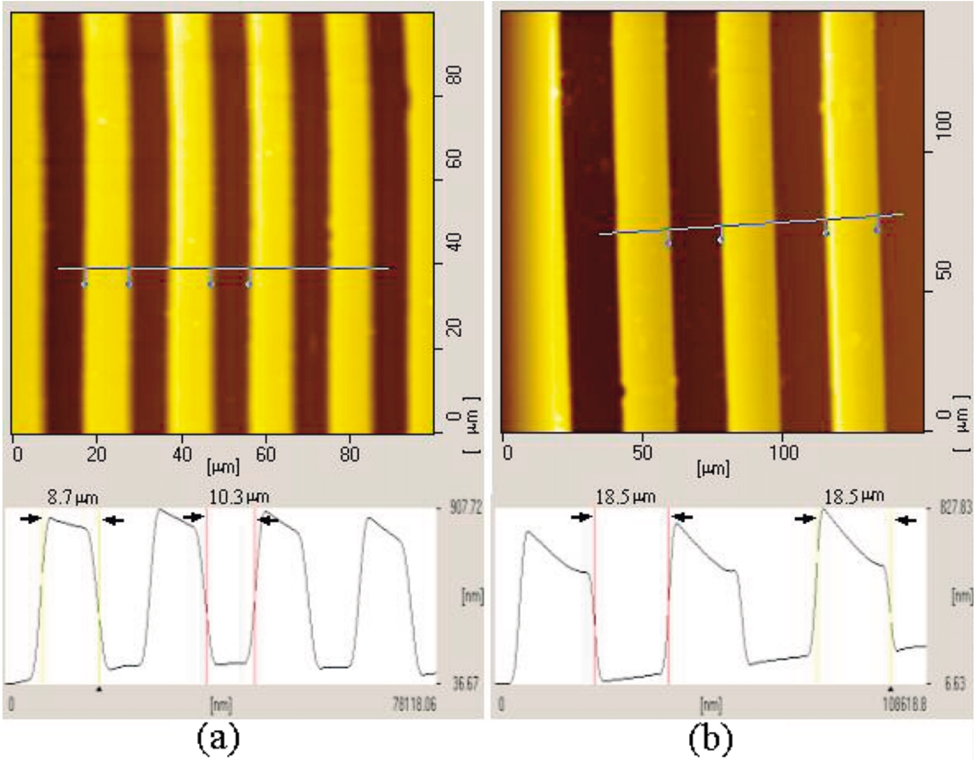

Fig. 1. Two-dimensional and cross-sectional AFM images of PDMS molds. The dimensions of SAM/Au stripe patterns were 10.3 μm/8.7 μm (a), and 18.5 μm/18.5 μm (b), respectively.

shows the sea-island structure. When the blend composition varies to 50% PS-1/50% P4VP, the islands begin to coalesce and form continuous structures. When the content of P4VP increases to 70%, the PS-rich phase on the surface changes from a continuous structure to an island structure.

However, when the molecular weight of PS component increases to 582k, as shown in Fig. 3, the surface morphology development of PS-3/P4VP films with different proportions of the polymers is different from that of PS-1/P4VP. With 70% PS-3/30% P4VP, the surface shows a continuous layer with many holes. After treatment the film with cyclohexane, the droplets composed of P4VP-rich phase appear at the positions of the holes (Fig. 3(a)), that is, the top layer is mainly composed of PS-rich phase and P4VP-rich phase is below the average height of the PS-rich phase layer. When the blend composition is changed to 50% PS-3/50% P4VP, Fig. 3(b) shows that the protruded P4VP islands disperse in PS-rich phase matrix. While, for 30% PS-3/70% P4VP, the P4VP islands tend to coalesce and form large and continuous domains.

Compared Fig. 3(f) with Fig. 2(f), one can see that the surfaces of P4VP-rich phase domains are very glossy when the PS molecular weight is 22.4k. However, the surfaces of the P4VP-rich phase domains are relatively rough when the PS molecular weight is 582k. The higher magnification AFM image displayed in Fig. 3(g) reveals that the continuous P4VP-rich phase domains in Fig. 3(f) are composed of small P4VP particles. This result clearly indicates that if the molecular weight of the PS component is too large, the aggregating process of the small P4VP-rich phase domains during spin-coating will be hindered seriously. It is speculated that the viscosity of the PS component will play an important role in the structure formation. Strawhecker et al. [18] has reported the effect of solvent evaporation on film roughness of a homopolymer and discussed the role of solution viscosity. It is well known that the zero-shear viscosity (η_0) of the flexible linear polymers has established two regions, which are separated by a characteristic molecular weight M_c ($\eta_0 \sim cM^{\alpha}$, the exponent α is related to the concentration and the molecular weight of the polymer [19]). In melt or concentrated solution, low molecular weight PS ($M < M_c$ (35k)) moves independently, but the movements of high molecular weight PS ($M > M_c$) are retarded by entanglements. At the third and the fourth stages of spin-coating, the solution film thins gradually dominated by viscous forces and solvent evaporation. It is during the third and the fourth stages that phase separation occurs for immiscible polymer blends. The depleted P4VP-rich phase first formed the small particles; the small P4VP particles collide via Brownian motion and adhere to each other to form aggregates. As solvent evaporates (the solvent evaporation rate is supposed to be constant for the PS/P4VP solutions with different PS molecular weights [20]), the viscosity of the film will increase to a point where the instabilities or phase separation are no longer created [18]. For PS-1/P4VP system, owing to

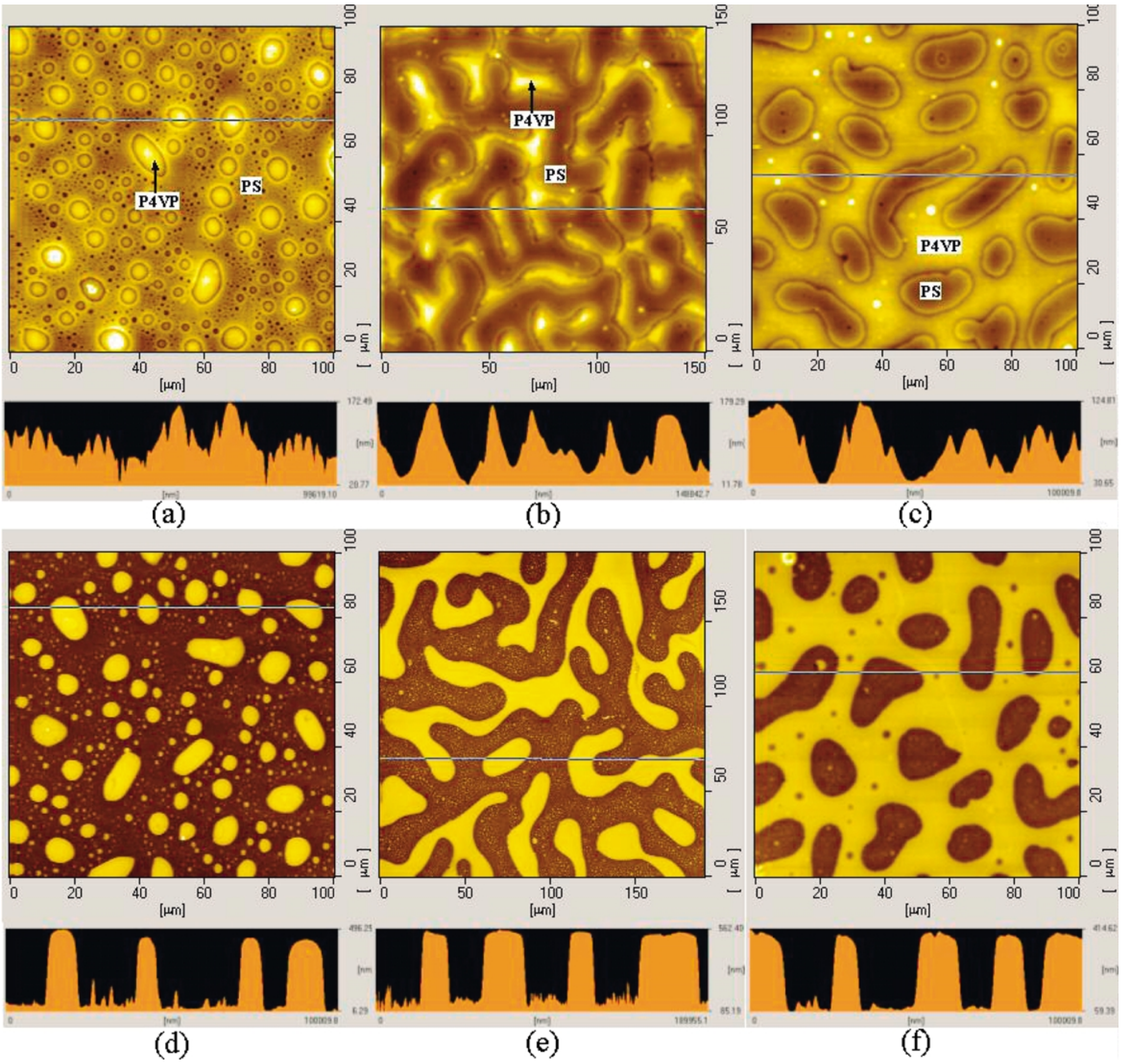

Fig. 2. AFM topographical images and sectional view along the lines in the AFM images for the PS-1/P4VP blend films with different compositions. PS-1/P4VP (w/w): (a), (d) 70/30; (b), (e) 50/50; (c), (f) 30/70. (Top: as spin-coated; bottom: PS-rich phase was removed by treated with cyclohexane for 5 min).

the viscosity of PS component is relative small, P4VP molecules have longer diffusion time and the P4VP-rich phase can also coalesce and form bicontinuous structures very quickly by local surface flow (the driving force is the attractive interactions between aggregates). This may be similar to the first stage of phase separation of the colloidal suspensions system [21], in which a particle network formed initially. Therefore, continuous P4VP-rich phase domains are easily formed in Fig. 2(b). When the M_w is increased to 58.2×10^4, owing to the large viscosity of PS component, the time for the viscosity of the film increasing to the point where the instabilities or phase separation are no longer developed [18] is shortened. Although the phase separation took place early [22,23], the P4VP aggregates cannot coarsen further to form larger structure easily by local surface flow at the late stage of spin-coating. Therefore, the surfaces of P4VP domains in Fig. 3(f)–(g) are rough.

3.2. Surface morphologies of PS/P4VP blend films on patterned SAM surfaces

The AFM images of the spin-coated PS-1/P4VP (= 50/50 w/w) films on the SAM patterned surfaces by μCP with two different stripe widths are shown in Fig. 4(a)–(d), respectively. For Au/SAM stripes with the stripe widths of 8.7 μm/10.3 μm, AFM image (Fig. 4(a)) shows that the narrow and elevated stripes alternate with wider and lower regions. It has been demonstrated that the more polar P2VP is favored on the gold surface and the PS is on the SAM surface [2,8]. Similar to P2VP, P4VP should also be favored on the gold surface. After treatment with cyclohexane to remove the PS component [14,17], one can determine that the brighter parts in Fig. 4(a) were corresponding to the P4VP-rich phase (which is on the Au stripes) and the darker parts were corresponding to the PS-rich phase (which is on the SAM stripes) (Fig. 4(b)). This

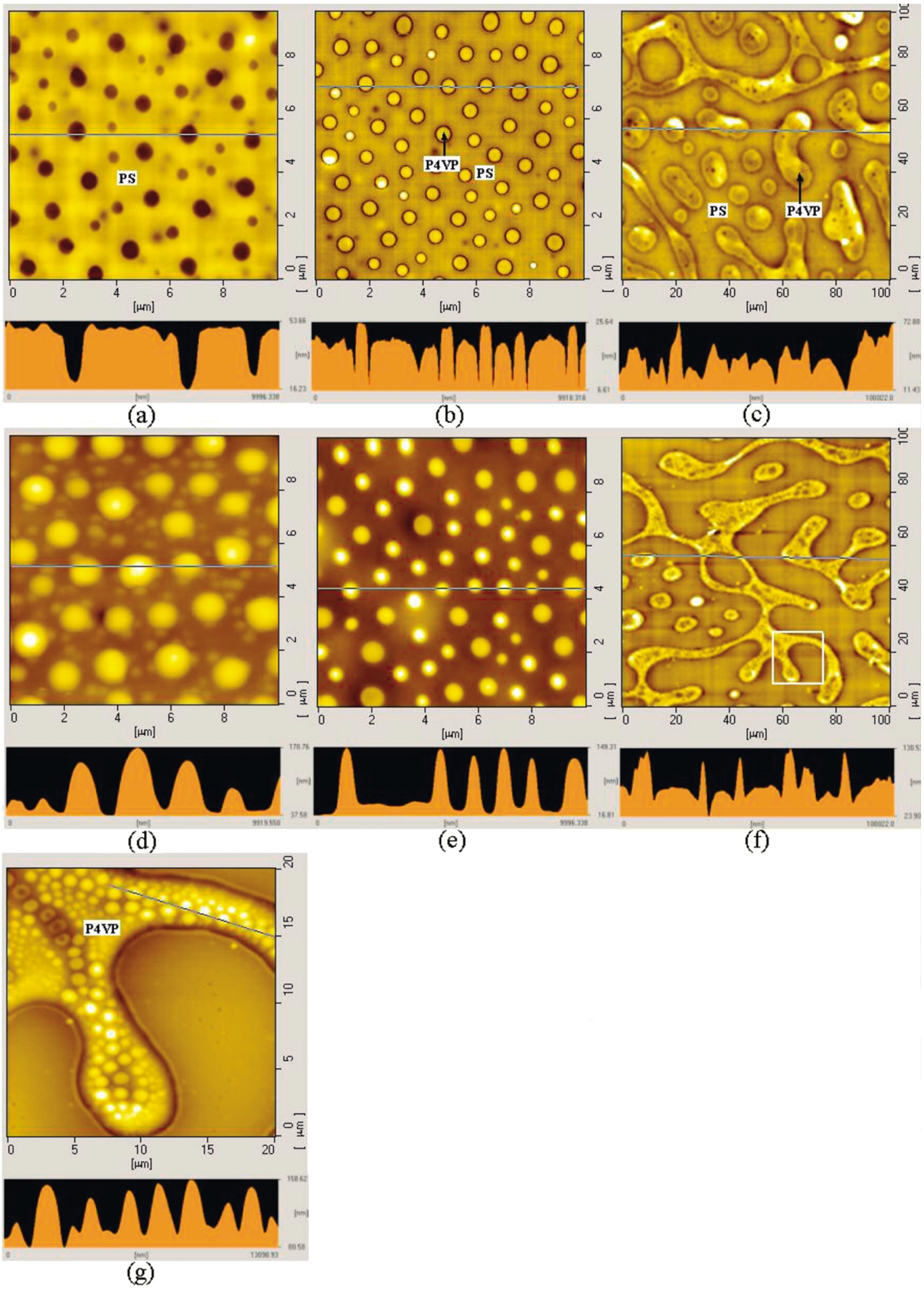

Fig. 3. AFM topographical images and sectional view along the lines in the AFM images for the PS-3/P4VP blend films with different compositions. PS-3/P4VP (w/w): (a), (d) 70/30; (b), (e) 50/50; (c), (f) 30/70. (Top: as spin-coated; middle: PS-rich phase was removed by treated with cyclohexane for 5 min). (g) AFM image of the detail of (f) indicated by the white box.

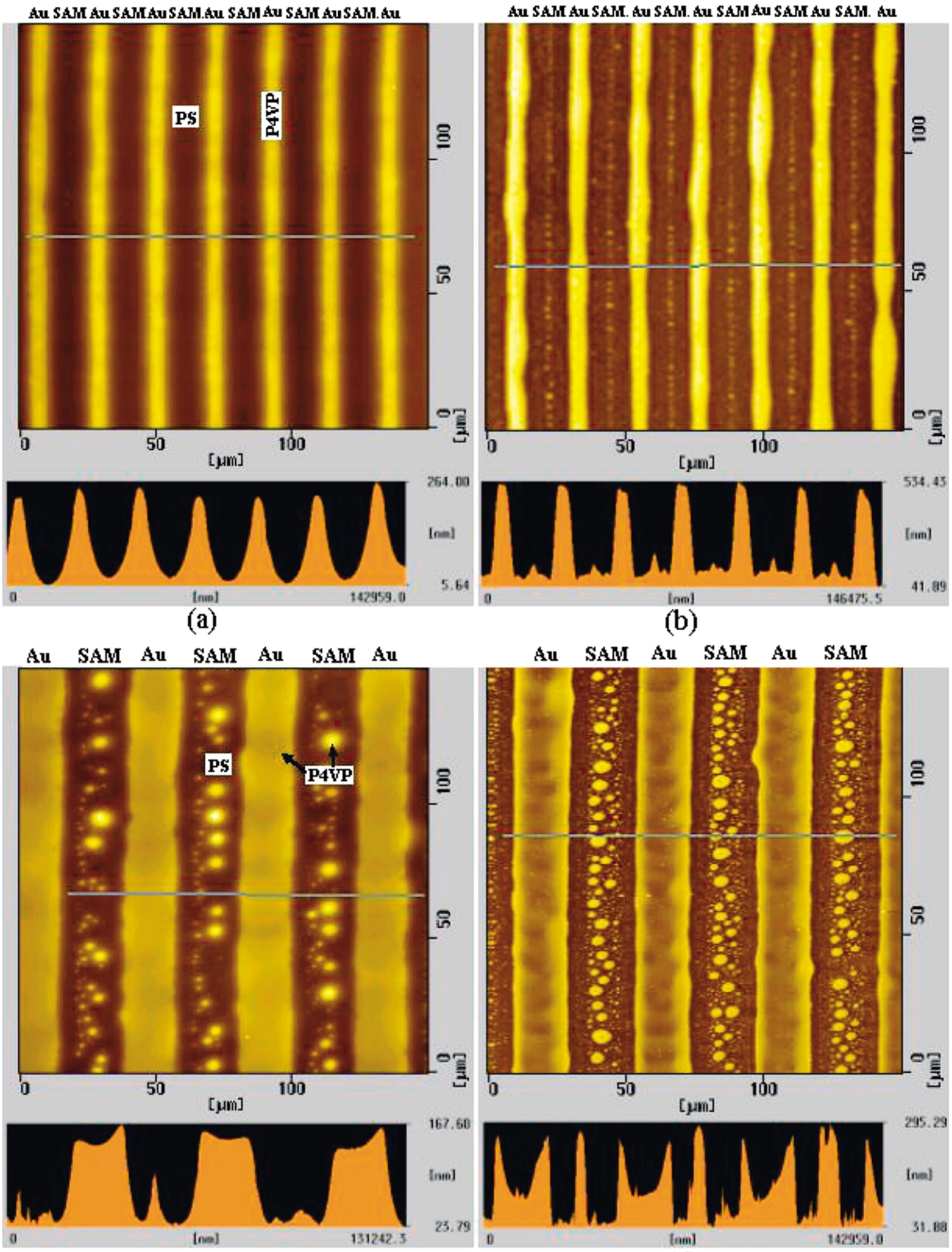

Fig. 4. AFM topographical images of the PS-1/P4VP (50/50, w/w) blend films on the patterned substrates with different stripe widths. SAM stripe/Au stripe: 10.3 μm/8.7 μm for (a) and (b); 18.5 μm/18.5 μm for (c) and (d). The films in (b) and (d) had been treated with cyclohexane for 5 min to remove the PS-rich phase.

indicates that, on the time scale of the spin-coating process, the phase separation was almost completed and phase separation pattern was well aligned with sharp interfaces between the P4VP- and the PS-rich phases. This is because the characteristic length of the lateral domain morphology (8.7 μm) obtained by fast Fourier Transition (FFT) could match with the gold stripe widths. It is consistent with the conclusion that the complete ordering of the polymer phases can occur only for patterns size comparable to the characteristic length of the lateral domain morphology on the respective homogeneous substrate [1,5,6,10].

When the stripe widths of the SAM/Au strips were 18.5 μm/18.5 μm (it did not match with the characteristic length of the lateral domain morphology of PS-1/P4VP blend), it was found that the directing effects of the μCP-patterned surfaces made most P4VP-rich phase aggregate align along the gold stripes (Fig. 4(c)). In the central part of a SAM stripe region, the small P4VP particles were dispersed in the PS matrix. It has been shown that the attraction of one blend component to one substrate region is the main force driving pattern replication [1,4,9]. Since the substrate/polymer interaction is short ranged, the blends away from the substrate does not feel this interaction and the phase separation at early times is as in the bulk fashion [6]. One can see from Fig. 4(c) and (d) that on the border of the SAM stripes, the P4VP-rich phase had diffused to the gold stripes and formed the depletion regions. An increase in the distance from the gold stripe, the driving force making the P4VP molecules diffuse to gold stripe become weak. As a result, the P4VP molecules on the central part of a SAM stripe did not feel or feel little attraction from gold substrates and the phase separation occurs as it is on the homogeneous SAM substrate. The small droplets in the central region of a SAM stripe can be explained as follows. The strong interaction between the gold substrate and the P4VP molecules will make the P4VP molecules diffuse to the striped gold surfaces once the polymer solution is deposited on the substrate. At the same time, the PS component will diffuse to the striped SAM surfaces to minimize the system's energy. Hence the P4VP content in solution on the SAM striped surfaces will be less than the original value. Therefore, the droplets of the P4VP-rich phase are form and frozen in the PS-rich phase matrix at the central part of a SAM stripe during spin-coating. From Fig. 4(c) and (d) one also can see that the stripe width of 18.5 μm has exceeded the upper limit on the scale at which the surface patterning can be controlled completely [3]. From above discussion, one can clearly see that though the stripe width did not match with the characteristic length of the lateral domain morphology, due to the relatively small viscosity of the PS component, the P4VP molecules can diffuse and aggregate on the gold stripe surfaces.

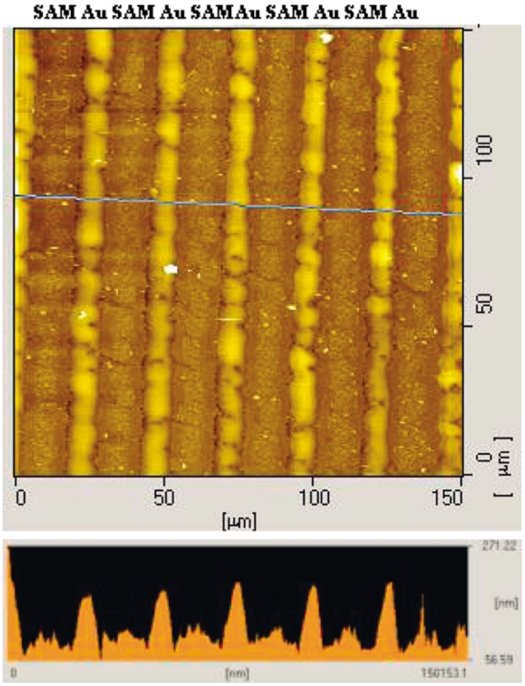

Fig. 5. AFM topographical image and sectional view along the line in the AFM image for the PS-2/P4VP (50/50, w/w) blend film on the patterned substrate with the stripe width of 10.3 μm/8.7 μm. The films had been treated with cyclohexane for 5 min to remove the PS-rich phase.

When $M_{w,PS}$ or the relative viscosity of PS component is very high, the aggregate of the P4VP-rich phase during the spin-coating process into large domains will become more and more difficult on homogeneous substrates (Fig. 2(f) and (g)). This effect also plays a significant role in the phase separation of polymer blend taking place on the μCP-patterned surfaces. When the molecular weight of PS is increased to 129k, an ordering of surface pattern was observed on the patterned substrate with the gold stripe width of 8.7 μm (Fig. 5). However, one can see from Fig. 5 that, the pattern surfaces of the P4VP-rich phases on gold stripes was rough and had many defects. When the molecular weight of PS was increased to 582k, no matter what the blend composition was, any directing effects of the μCP-patterned surfaces with two stripe widths on the phase separation were not observed during spin-coating process. The observed morphologies are similar to the surface morphologies of PS-3/P4VP on homogeneous SAM surfaces. One possible reason is that the stripe width does not match with the characteristic length of the lateral domain morphology. However, the main reason is because of the large viscosity of the PS component. The time for the solution film becoming glassy (the point where the instabilities are no longer developed [18]) become very short, that is, the P4VP molecules have shorter diffusion times and the further coarsening or aggregating into ordered domains on the gold stripe surfaces become very difficult during spin-coating. When the diffusion time is prolonged, for example, the PS-3/P4VP films on the μCP-patterned substrates were prepared by dip-coating, the situation is improved clearly (Fig. 6). This indicates that the relative viscosity of the PS becomes one of the dominant factors in

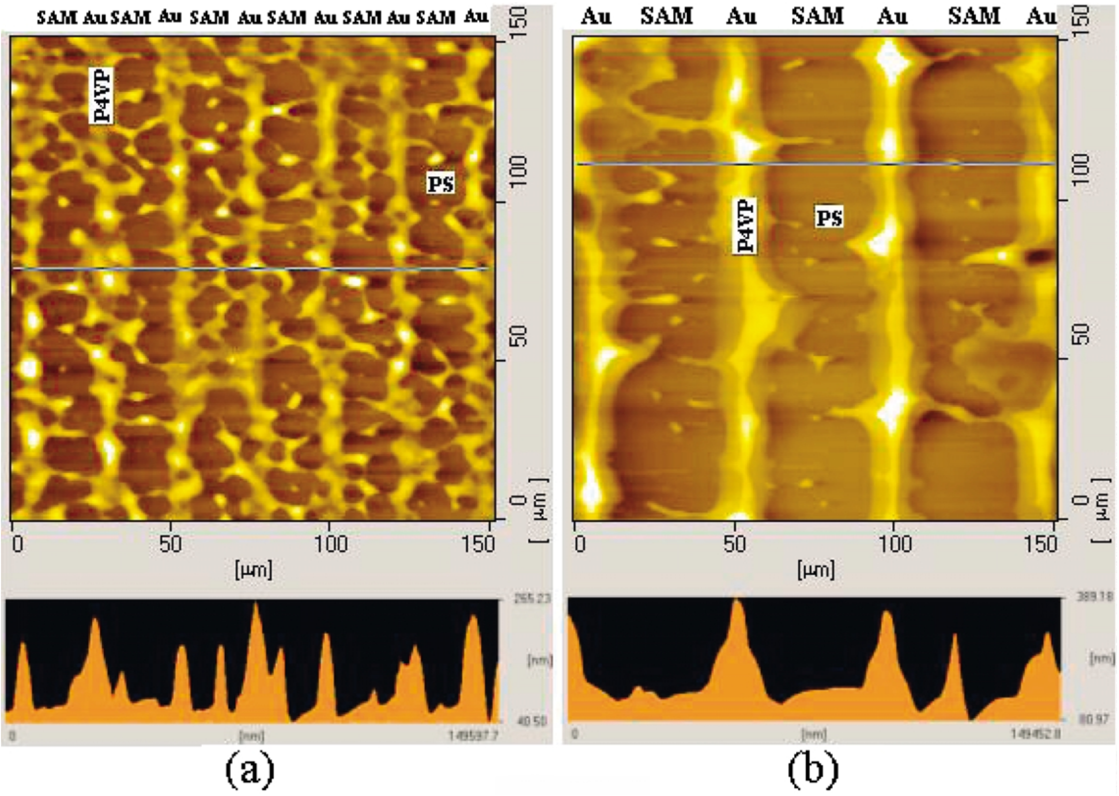

Fig. 6. AFM topographical images and sectional view along the lines in the AFM images for the PS-3/P4VP (50/50, w/w) blend film on the patterned substrate with the stripe width of 10.3 μm/8.7 μm. The films were prepared by dip-coating.

obtaining well-aligned pattern by the phase separation of polymer blend during spin-coating.

3.3. The stability of the aligned PS/P4VP stripes

It is usually thought that the thermal stability of SAMs of alkanethiols on Au may be problematic (alkanethiols had limited thermal stability at 100 °C [24]) because the polymer systems must often be annealed at high temperatures to increase mobility and induce self-assembly [25]. The stability of the films with aligned PS/P4VP stripes needs to be investigated. Fig. 7 clearly shows that a well-aligned pattern is much stable at high temperature once it is formed during spin-coating. When the film was annealed at 146 °C (which is higher than the glass transition temperature of PS and less than that of P4VP) for 25 h, the AFM image shown in Fig. 7(a) is almost identical to the morphology at room temperature (Fig. 4(a)). When the aligned film was annealed at 170 °C (which is well above the glass transition temperatures of PS and P4VP) for 36 h, the surfaces of the P4VP stripes became slightly rough and small particles along central line of the PS stripe (lower regions) appeared (Fig. 7(b)). One can see from the FFM image that these small particles are corresponding to P4VP, which is formed via secondary phase separation during annealing [26–28].

4. Conclusions

The effects of the molecular weight of PS component on the surface morphologies of strongly incompatible PS/P4VP blend films on homogeneous and patterned SAM surfaces were investigated by means of AFM. When the molecular weight of PS component was relatively small (for the PS (22.4k)/P4VP (60k) system), the P4VP droplets can form large aggregates or bicontinuous structures easily during spin coating process. On patterned SAM surfaces, the phase separation of PS-1/P4VP blend can be directed and a well-aligned pattern, which has a good thermal stability, was obtained. The directing effects of the μCP-patterned surfaces also could be observed even if the stripe width did not match with the characteristic length of the lateral domain morphology. However, if the molecular weight of PS component was very large (for the PS (582k)/P4VP (60k) system), the aggregate of the P4VP-rich phase will be suppressed due to large solution viscosity. Therefore, the phase separation of PS-3/P4VP blend cannot be easily directed even though the characteristic length of the lateral domain morphology is commensurate with the stripe width. On the basis of our results, to obtain a well-aligned phase separation pattern, the effect of the molecular weight or solution viscosity of the polymers is one important factor and should be chosen properly in experiments.

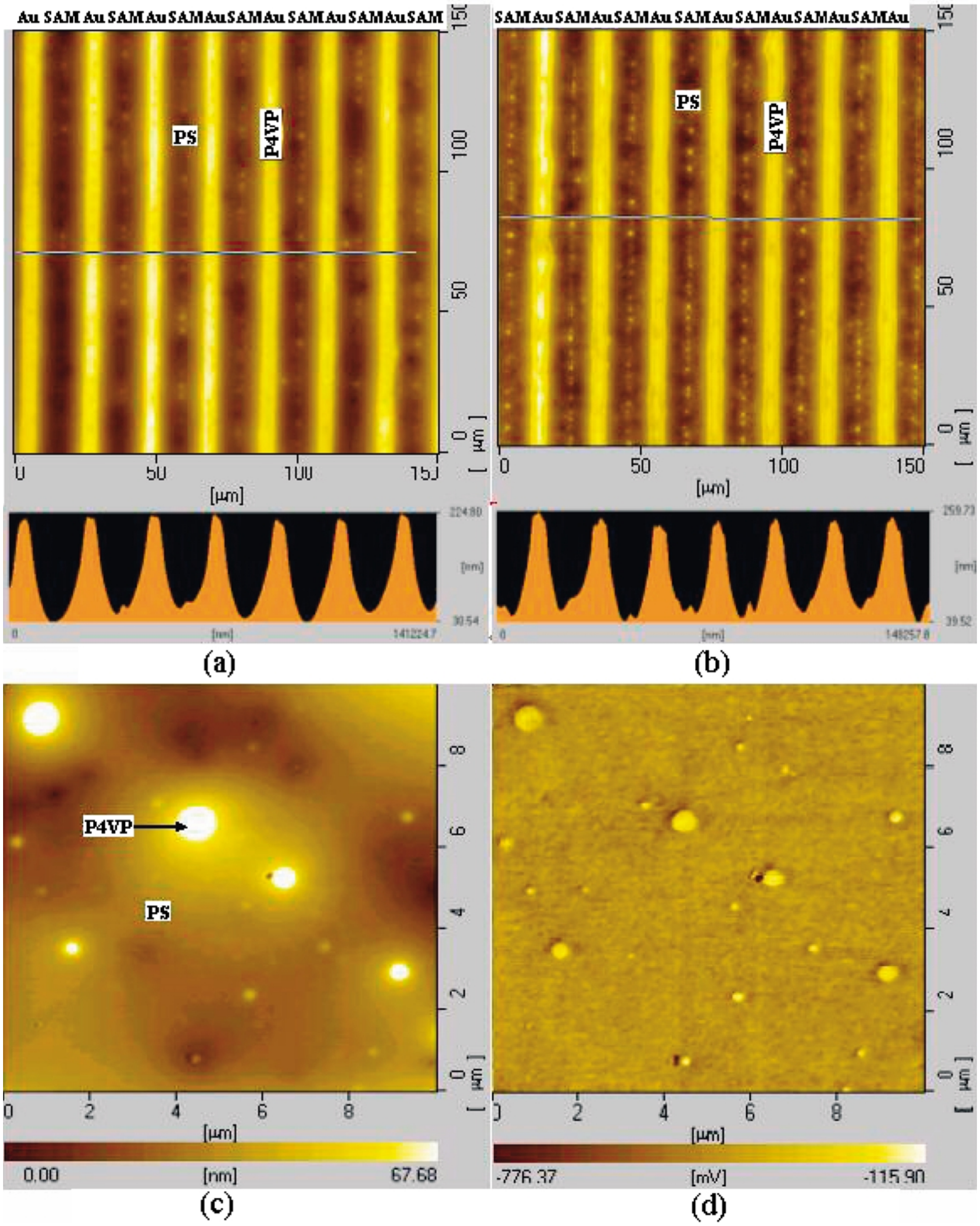

Fig. 7. AFM topographical images of the aligned PS-1/P4VP (50/50, w/w) blend films on the patterned substrates with the stripe width of 10.3 μm/8.7 μm after annealing at 146 °C for 25 h (a) and 170 °C for 36 h (b). (c) and (d) are the AFM and FFM images scanned at the lower regions of (b).

Acknowledgements

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