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Solvent dependence of the evolution of the surface morphology of thin asymmetric diblock copolymer films

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Abstract

The evolution of surface morphology of thin films of asymmetric diblock copolymers with spherical microdomains was studied using atomic force microscopy (AFM). The investigated polymer was poly(styrene-*block*-2-ferrocenylethyl methacrylate) (PS-*b*-FEMA), and the molecular weight ratio of PS and FEMA blocks was 7:1. Different solvents were used for film preparation to investigate the solvent influence to surface topography and evolution of the islands. It was found that the effects of solvent used persist after annealing and that the films prepared from different solvents show markedly different surface topographies. Furthermore, the solvent used influences the mechanical adhesion of the film to the substrate, and thusly affects the annealing temperature, which would cause delamination of the film from the substrate. Finally, some recommendations are given on solvent choice and film preparation in order to improve surface quality of the films, which is necessary for successful pattern transfer over a large area.
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1. Introduction

Self-organization of the block copolymers into ordered nanostructures with sizes in 10–100 nm range (determined by the molecular size) offers a great potential for nanotechnology applications since it enables fabrication of the structures with sizes beyond the limit of the conventional lithography. Unlike e-beam and scanning probe lithographies, which are serial and hence time-consuming techniques, diblock copolymer patterning is fast and inexpensive. Successful nanopatterning of substrates and/or fabrication of nanostructures using diblock copolymers were reported [1–9]. Diblock copolymer patterning technique is based on the principle that incompatible segments in a block copolymer molecule can exhibit phase separation in a controlled and reproducible manner. The phase separation in the bulk of the copolymer film is determined by the polymer structure and the volume ratio between different blocks (Flory–Huggins parameter). The domains formed can be spheres, cylinders, bicontinuous (gyroid), perforated layers (HPL), and lamellae [10]. However, the nanostructures formation and ordering are influenced by other factors as well, such as the substrate used [11], film thickness [6,12], presence of external electric field, and even solvent used for the film preparation [13]. The component, which is preferentially solvated by the solvent used, will have stronger tendency to appear on the surface [13]. It was also shown that perpendicular, parallel, and mixed domain orientations can be obtained for different solvent evaporation rates in triblock copolymer films [14,15].

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Symmetric diblock copolymers have been extensively studied, both theoretically and experimentally. Symmetric diblock copolymers prefer to separate in lamellar structure [16–21]. In attempting to minimize the total energy, diblock copolymers tend to form island or holes on the surface if the thickness of the film is different from nL for symmetric wetting or $(n+1/2)L$ for asymmetric wetting, where n is an integer and L is the repeat period of the polymer morphology in the bulk [16,17,19,21]. The island formation on the surface of the symmetric diblock copolymer films of poly (styrene-*b*-butylmethacrylate) was studied in detail by Coulon et al. [16]. They reported three mechanisms present in evolution of surface morphology: growth of individual island (hole), coalescence of neighboring islands (holes), and disappearance of the smallest islands (holes) [16]. They also found that for longer annealing time at 170 °C, holes or islands in the film, which is between $2L$ and $3L$ thick, tend to be eliminated [16]. Evolution of the surface morphology with annealing time and dependence of surface morphology on film thickness for very thin poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) films above order–disordered transition temperature was also studied [18]. Surfaces with spinoidal pattern, holes, or droplets were found depending on film thickness and annealing time [18]. For a detailed review on block copolymer thin films (dealing with symmetric block copolymers), see Refs. [19,20].

Although asymmetric block copolymers are of far greater interest for practical applications in fabrication of nanostructures, there have been fewer studies of asymmetric block copolymer thin films than studies of symmetrical ones. Majority of the studies of asymmetric block copolymers focus on the polymers expected to exhibit cylindrical microphase separation [7,12,22–28]. Theoretical studies on asymmetric block copolymer thin films predicted the existence of various phases (parallel cylinders, perpendicular cylinders, lamellae, perforated lamellae [22,23], and spheres [23]). Coexistence of different phases in thin films of asymmetric block copolymers was experimentally confirmed for thin films of diblock [26,27] and triblock [12,28,29] copolymers. It was also shown that spherical and cylindrical microphase separation can be obtained for the same copolymer for different annealing temperatures [24]. Nearly symmetric (f=0.55) and asymmetric (f=0.77) films of PEP–PEE diblock copolymers were studied [25], and it was found that in asymmetric diblock copolymer films bulk morphology (hexagonal cylinders) is different from lamellar-like near the surfaces—the surfaces are smooth before and after annealing, but with no observable periodic pattern on the surface [25]. The asymmetric diblock copolymer films (film thickness ~640 nm) studied in their work, unlike the symmetric ones, exhibited no large island formation [25]. In contradiction with their result, Kim and Russel [26] studied the evolution of free surfaces of PS-*b*-PMMA thin films and found that the islands with height of one period form on the surface. The islands consist of PMMA cylinders with parallel orientation, while on the edges of the islands they observed features, which they attributed to cylinders with perpendicular orientation [26]. For thin films of poly(styrene–butadiene–styrene) (SBS) triblock copolymer, it was found that perpendicular or parallel orientation of the cylinders can be obtained for different film thickness [28]. However, recent study found that observation of hexagonal array of dots on the film surface does not necessarily imply perpendicular cylinders [29]. It should be pointed out that the sample preparation in Refs. [26,29] is different (thermal annealing vs. solvent vapor treatment), which may account for the observed differences. Solvent treatment can result in large changes, dependent on the solvent used, in the film morphology [30]. Coexistence of different morphologies (parallel and perpendicular cylinders, wetting layer, and perforated lamellae) under identical experimental conditions was also demonstrated for thin SBS films on Si substrates after exposure to chloroform vapor [12]. Spheres, cylinders, and perforated lamellae have been found to co-exist in the same sample by depth profiling the morphology in islands of thin poly(styrene-*b*-butadiene) thin films. There have been few systematic studies on the behavior of asymmetric block copolymers with spherical phase separation [31,32]. Yokoyama et al. [31,32] found that large islands or holes form poly(styrene-*b*-2-vinylpyridine) thin films, which are thinner than six layers of spheres, while for thicker films, strain due to difference between actual film thickness and inherent period of the block copolymer is released by defects in layering of spheres inside the film [31]. The studies on asymmetric block copolymer films clearly demonstrate the complexity of the phenomena determining the morphology in thin films. It is very difficult to establish which phenomena are general for thin films of block copolymers and which are specific to certain block copolymer/substrate system. In addition, differences in sample preparation techniques can contribute to different phenomena observed in the same block copolymer/substrate system.

In this work, we focus on the study of island formation in thin poly(styrene-*b*-2-ferrocenylethyl methacrylate) (PS-*b*-FEMA). Influence of the solvent and the substrate used for the film preparation was investigated. The island formation and their evolution with annealing time were studied by surface probe microscopy. The majority of the films studied here are below $2L$ thick, since such films are of interest for nanofabrication applications. For nanopatterning applications, it is very important that the film exhibits uniform thickness and flat surface so that the generated patterns can be successfully transferred from block copolymer film to the substrate. Therefore, study of island formation and evolution in asymmetric diblock copolymer films is of interest for large area nanopatterning applications. We have chosen to study a polymer where one block contains iron atoms, because an iron-containing block is more resistant to oxygen plasma reactive ion etching and hence would enable one-step pattern transfer from the diblock to the substrate. The paper is organized as follows. In the following section,

experimental details are given. In Section 3, obtained results are presented and discussed. Finally, conclusions are drawn.

2. Experimental details

2.1. Polymer synthesis

The diblock copolymer, poly(styrene)-*block*-poly(2-ferrocenylethyl methacrylate) (PS-*b*-PFEMA) was prepared using the atom-transfer radical polymerization (ATRP) [12] from the polystyrene-Br (PS-Br) macro-initiator and 2-ferrocenylethyl methacrylate (FEMA) [13] in the presence of the catalyst (2,2′ -bipyridine (bipy) and CuBr with PS-Br/CuBr/bipy=1:1:3), which is shown in Fig. 1. The resulting PS-*b*-PFEMA was separated from PS-Br by silica gel flash column chromatography (methylene chloride/ethyl acetate, 8:1). It was characterized by ^{1}H and ^{13}C NMR, IR, and GPC. Its IR spectrum exhibited a strong CO stretching absorption at about 1727 cm^{-1}. No vinyl proton resonances were observed in the ^{1}H NMR spectrum of the diblock copolymer, which is consistent with its ^{13}C NMR results. The PS/PFEMA ratio is about 1:3, based on ^{1}H NMR analyses.

2.2. Substrate preparation

Substrates used were Si wafers with a native oxide layer or hydrogen-passivated Si wafers. The wafers were cleaned ultrasonically for 10 min in toluene, acetone, and ethanol, or toluene, acetone, and ethanol, and deionized (DI) water. The cleaning cycle was repeated until the wafers were clean. The films on wafers with different last step in the cleaning cycle were prepared and compared. Hydrogen passivation was performed by dipping in HF solution and rinsing in deionized water.

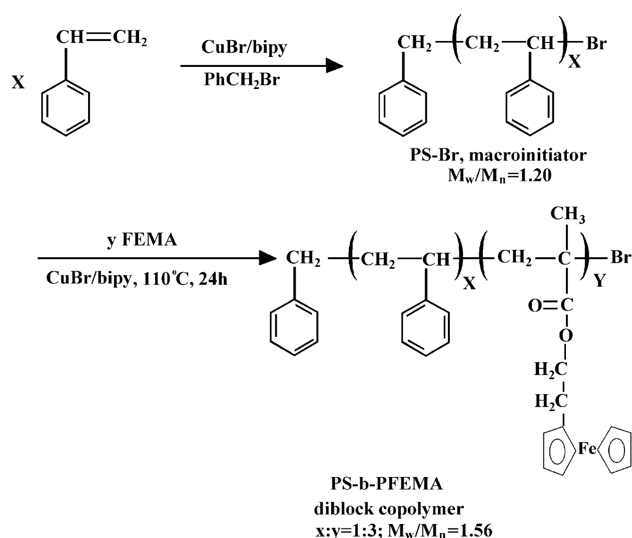

Fig. 1. Reaction scheme for PS-*b*-FEMA synthesis.

2.3. Film preparation

The polymer film samples were prepared by spin-coating from 1% to 3% (w/v) solutions. Spinning speeds used were in the range 500–1000 rpm. The solvents used were tetrahydrofuran (THF) (boiling point: 66 °C, vapor pressure: 0.215 bar), toluene (boiling point 111 °C, vapor pressure 0.034 bar), and xylene (boiling point ~140 °C, vapor pressure 0.011 bar). The films were annealed in a vacuum oven or vacuum-sealed glass tubes at different temperatures (120 and 140 °C) for up to 24 h. Annealing in air and in N_2 for comparison was also performed.

2.4. AFM characterization

Film thickness was measured by atomic force microscopy (AFM) of the step in the film produced by mechanical scratching using a thin metal wire. As the polymer film is significantly softer than the Si substrate, light scratching did not damage the substrate. Average step height from the film surface to the surface of the substrate was used as an estimate of the film thickness.

AFM images in topography and phase-contrast mode were recorded using Park Scientific Instruments Autoprobe CP (commercial silicon cantilevers with spring constant ~1.6 N m^{-1}), Seiko SPI 3800 N probe station and SPA 300HV SPM (commercial silicon cantilever with spring constant 14 N m^{-1}), and NTMDT Solver P47 (boron doped silicon tips with force constant in the range 28–91 N m^{-1}). The AFM was operated in ambient. Images for the samples shown in Fig. 3a–d were obtained using contact mode on Autoprobe CP AFM instrument in order to obtain good quality and cover very large area (50×50 μm) images. Remaining images were obtained using dynamic mode AFM in dynamic mode with either Solver P47 (Fig. 3f) or Seiko SPM (all other figures). Resonant frequency of the tip used for Solver P47 AFM was 290 kHz, scanning speed was 1 Hz, and set point amplitude was 80% of the free amplitude. For Seiko SPM, the tips were used at their fundamental resonance frequency, which typically ranged between 110 and 150 kHz. The lateral scan speed was 0.5 Hz for image size above 10 μm and 1 Hz for images of 2 μm. The driving amplitude and set-point ratio were systemically varied to produce accurate, reproducible topography, and phase images [33]. The set-point amplitude was 75–95% of free oscillation amplitude.

3. Results and discussion

We have found that, for the polymer studied in this work, hydrogen passivation of the silicon substrate does not significantly influence the surface topography of the polymer films prepared from THF solution. Moreover, no significant differences were observed for annealing in air, vacuum, or nitrogen. However, substrate surface cleaning

procedure and the solvent used for the film preparation had significant influence on the film properties, which persisted even after 24 h annealing. It is known that solvent can have significant influence on the surface composition and fast evaporation rate can prevent reaching the equilibrium [13]. In this work, we have chosen THF as a non-selective solvent for the two blocks, as preferential solvent would cause more soluble component to preferentially appear at the surface [13]. In addition to THF, we have also investigated two good solvents for polystyrene (toluene and xylene), but not for PFEMA. These solvents have been chosen due to their lower vapor pressure and hence slower evaporation rate compared to THF.

Fig. 2 shows the AFM images of ~50-nm film spin-coated from toluene solution before annealing and after 2, 6, and 12 h annealing. It can be observed that the films show relatively smooth surface. No phase separation can be observed on the surface with the exception of sample annealed for 6 h (Fig. 2c). The phase-separated areas on the surface disappear with prolonged annealing time. The

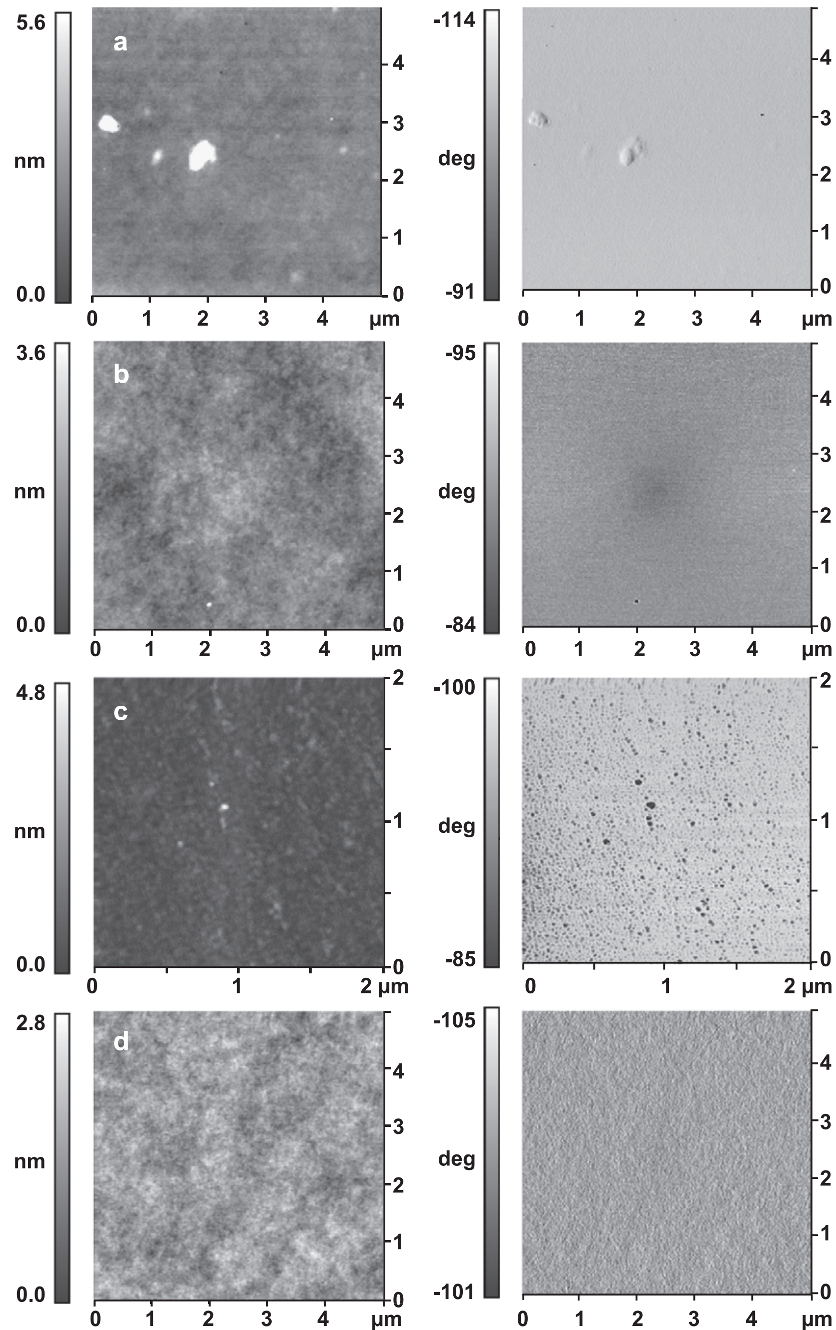

Fig. 2. Topography (left) and phase-contrast (right) AFM images of the film spin-coated from toluene solution (a) as spin-coated, (b) annealed at 140 °C for 2 h, (c) annealed at 140 °C for 6 h, (d) annealed at 140 °C for 12 h. Images were obtained using Seiko SPI 3800 N in dynamic mode.

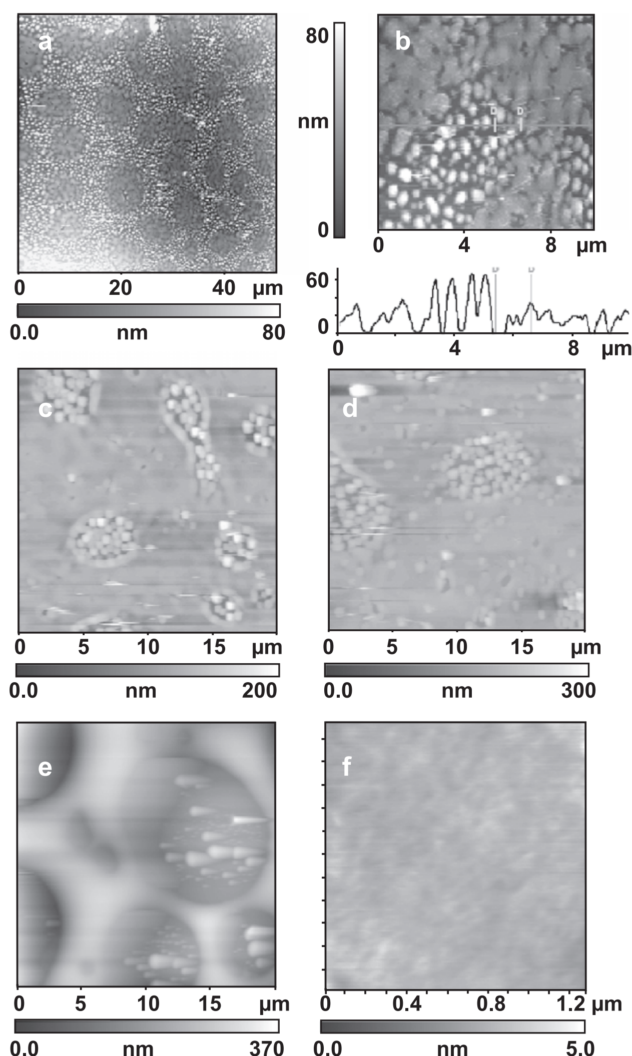

Fig. 3. Topography AFM images of the film spin-coated from THF solution (a) as spin-coated, 50-nm-thick film (Autoprobe CP, contact mode), (b) as spin-coated, 50-nm-thick film with height profile shown (Autoprobe CP, contact mode), (c) 50-nm-thick film annealed in vacuum at 120 °C for 1 h (Autoprobe CP, contact mode), (d) 50-nm-thick film annealed in vacuum at 120 °C for 6 h (Autoprobe CP, contact mode), (e) 180-nm-thick film annealed at 140 °C for 6 h (Seiko SPI 3800 N, dynamic mode), (f) 50-nm-thick film (no annealing) exposed to toluene vapor for 5 min (Solver P47, dynamic mode).

films show no delamination for annealing at 140 °C for 24 h.

The films prepared from THF show markedly different behavior. The film surface before annealing is rough, showing islands of varying heights. Films prepared from THF were annealed at 120 and 140 °C, as some delamination occurred after annealing at 140 °C. Fig. 3a shows the large area (50×50 μm) AFM image of the ∼50-nm-thick samples. Existence of two different types of domains, one with higher oval islands with sharp boundaries and the other with lower, more diffuse islands, can be observed. Fig. 3b shows the topography of the same sample (10×10 μm area) with the height profile corresponding to the horizontal line shown in the image. Differences between the two types of domains are clearly shown. This demonstrates that higher islands can be formed even before previous polymer layer is fully completed. After annealing (Fig. 3c for 1 h, Fig. 3d for 6 h), it can be observed that there are large areas of the sample that show slightly rippled surface (<10 nm). From phase-contrast images (not shown as no significant variation can be observed), it can be concluded that the film is dominantly covered with one component, the block with lower surface energy. On 20×20 μm images of the sample after 1 h annealing (Fig. 3c), we can observe that there are areas showing large islands surrounded by a rim. After 6 h annealing (Fig. 3d), the rims disappear but the island areas are still visible though not exhibiting as sharp contrast with the featureless areas as for shorter annealing time. We also attempted to anneal the sample at 140 °C. It was found that some delamination occurred after annealing at this temperature. Thicker films (with thickness in the range 180–200 nm) were prepared, but delamination was also observed. In areas where the film was still present on the substrate after 12 h annealing, oval areas of lower thickness with oval islands can be observed, similar to thinner films (Fig. 3e). Exposure to toluene vapor for 5 min for ∼50-nm-thick film results in large areas with featureless surface, as shown in Fig. 3f.

Fig. 4 shows the AFM images of the samples prepared from xylene solution. The films are smooth and phase-contrast images are featureless in all cases, indicating that

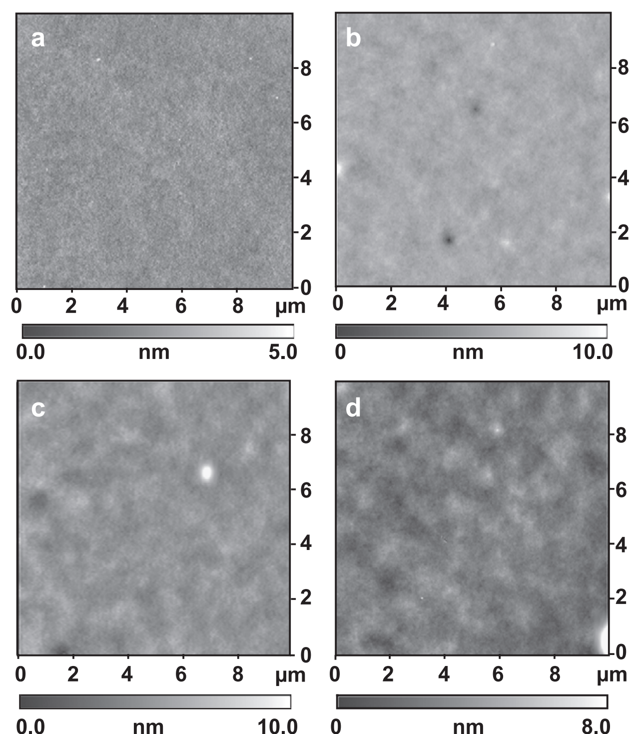

Fig. 4. Topography AFM images of the film spin-coated from xylene solution (a) as spin-coated, (b) annealed at 140 °C for 2 h, (c) annealed at 140 °C for 6 h, (d) topography of the film annealed at 140 °C for 12 h. Images were obtained using Seiko SPI 3800 N in dynamic mode.

the surface is covered by a component with lower surface energy. After annealing, some islands can be observed, but the island density is low. The films prepared from xylene solution are thinner (25–30 nm) and the film thickness showed small variation on the spinning speed (in the range 500–1000 rpm). The studies in literature on the evolution of the islands in the diblock copolymer films are contradictory. It was reported that, for PS-*b*-PMMA films with cylindrical phase separation, large islands form only after annealing and the height of the islands after 24 h annealing corresponds to one period of the diblock copolymer [26]. Coulon et al. [16] reported growth and coalescence of the islands (holes) in symmetric films of poly(styrene-*b*-butylmethacrylate) and disappearance of the smallest islands (holes) with increased annealing time. Growth of the islands, but no coalescence, was reported for PS-*b*-PMMA films [17]. On the other hand, Yokoyama et al. [31] reported that the island profile (sharp vs. diffused) depends upon the film thickness. It was demonstrated that thick films do not form islands or holes [31]. Similarly, Karim et al. [25] observed no island or hole formation in their asymmetric block copolymer films (results shown for 640 nm film). Relatively thin film in their study (135 nm) had rippled surface before and smooth surface after annealing [25]. It is hard to establish which of the reported phenomena represents general behavior of the diblock copolymer films. One of the generally accepted rules is that the thickness of the block copolymer film is quantized to nL for symmetric wetting (same block located at both interfaces) or $(n+1/2)L$ for asymmetric wetting (different blocks at two interfaces), and that islands or holes are formed if the thickness deviates from these values. However, based on the data reported in the literature, it can be concluded that island formation behavior is also likely to be dependent on the polymer investigated (i.e., asymmetric PS-*b*-PMMA [26] exhibiting different behavior from symmetric poly(styrene-*b*-butylmethacrylate) [16]), while the results of Yokoyama et al. [31] clearly demonstrate that island profile is thickness-dependent and no islands will form in thicker films. In this work, we show that the island formation and evolution is dependent on the solvent used for film preparation.

The effects of solvent on the topography and surface roughness of dip-coated and spin-coated polystyrene films were studied [34–36]. Study on 18 different solvents found that the roughness increases monotonically with vapor pressure [34]. A study of 8 different solvents and 3 solvent mixtures also found that the solvents with small vapor pressure yield smooth films whose roughness is correlated to the roughness of the substrate [35]. RMS surface roughness increased with increasing vapor pressure (with exception of cyclohexane and cyclohexane containing mixtures), while no obvious trends on the solvent viscosity were observed [35]. It was also reported that spin-coating and solution casting yield similar quality films, and that the quality of the films is mainly dependent on the substrate and the solvent used [36]. It was also found that the solvent with lower vapor pressure (toluene) resulted in smoother films compared to a solvent with higher vapor pressure (dichloromethane) [36]. For diblock copolymers, surface topography dependence on the solvent is more complex as solvent selectivity needs to be considered. In this work, we investigated one non-selective high vapor pressure solvent (THF) and two selective low vapor pressure solvents (toluene and xylene). We found that the films prepared from THF exhibited fundamentally different behavior from the films prepared from toluene or xylene. Since it is expected that THF would evaporate fast, rough film surface was not surprising. However, it is not fully clear why the effects of solvent used for film preparation persist after prolonged annealing. Possible reasons would be differences in adsorption of block copolymers from selective and non-selective solvent, as well as differences in the speed of solvent evaporation. In order to double-check whether poor quality of the diblock copolymer films prepared from THF is a general phenomenon, we also compared PS-*b*-PMMA films prepared from toluene and THF solutions. It was found that the films prepared from THF exhibit significantly rougher surface initially and different behavior after annealing compared to films prepared from toluene. However, a study on polystyrene-poly(4-vinylpyridine) films found that the films dip-coated from a non-selective solvent (chloroform) exhibited smooth surface, while the surface of films prepared by dip-coating from selective solvents for PS block (THF and toluene) exhibited rough surface [37]. The difference between their results and ours may be due to different polymer used, different substrate, and different film preparation method (spin-coating in our work, dip-coating followed by solvent washing to remove excess material in Ref. [37]). Therefore, it can be concluded that non-selectivity of the solvent is not a sufficient condition for producing smooth films of diblock copolymers. The obtained result that surface roughness of films is significantly lower for low vapor pressure solvents is in agreement with the previous studies on polystyrene films [34–36]. However, definite guidelines for solvent choice for diblock copolymer films require further study.

We have also investigated the influence of the substrate cleaning procedure on the topography and mechanical quality of the films. We have found that the substrate cleaning procedure plays a role in reduction of defects, improvement of mechanical adhesion of the film, and obtaining large areas of smooth, defect-free surfaces. The last step in the cleaning procedure before spin-coating was found to be a significant factor even after thorough drying of the substrates in an oven. For the polymer investigated in this work, the best results were obtained for films spin-coated from toluene solution with toluene as the last cleaning step. The films with DI water as the last cleaning step produced from the same solution exhibited inferior surface and mechanical quality, which is possibly due to small amount of water chemically attached to the substrate surface and immiscibility of toluene and water. For xylene solution, better result is obtained when DI water is

the last step compared to toluene as the last step in the cleaning procedure. Therefore, in order to produce smooth films with good substrate adhesion and low number of defects, it is important to optimize the solvent choice and the substrate cleaning procedure for the polymer used. It can be expected that the solvents with slower evaporation rate will produce better quality films than fast evaporating solvents. Roughness of the films prepared from THF was found to persist after 24 h annealing, while exposure to toluene vapor for shorter period of time (5–30 min) can result in significant smoothening of the surface.

4. Conclusions

We have studied the evolution of the surface morphology with annealing time for the thin films of poly(styrene-*b*-2-ferrocenylethyl methacrylate) prepared from different solvents on Si (hydrogen-passivated and -unpassivated) substrates. It was found that the influence of the solvent used on the film topography persists even after 24-h annealing. Spin-coating from THF solution, which is a non-selective solvent for both blocks, resulted in rough film surface and inferior mechanical adhesion to the substrate causing delamination after annealing at temperatures at which films prepared from other solvents were stable. Films prepared from toluene showed smooth surface before and after annealing. Films prepared from xylene showed smooth surface. After annealing, some islands can be observed, but the island density was not very large (less than 10 islands on 20×20 μm). The surface roughness of films prepared from THF solution was attributed to high vapor pressure of THF. It was also found that the surface cleaning procedure had significant influence on the topography and number of defects in the films.

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