Atomic Force Microscopy Study of Environmental Responses on Poly(vinyl alcohol)-*graft*-polystyrene Surfaces[†]

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An environmentally induced surface rearrangement occurring on poly(vinyl alcohol)-*graft*-polystyrene (PVA-PS) surfaces has been studied by means of an atomic force microscopy technique. In a dry state, the graft copolymer film surfaces were covered by a thin flexible layer of PS component on a PVA sublayer. The topmost PS layer became unstable when the film was immersed in water. A dewetting process took place to generate a "hole-with-rim" pattern for the graft copolymers with 12−23 mol % PS content. The number of the "hole-with-rim" structure increased along with the immersion time, while their sizes were not appreciably varied. The dewetting process for the graft copolymers with 26−41 mol % PS content, on the other hand, produced a "wormlike" pattern, which corresponds to the microphase separation morphology observed in dry state. The graft copolymer film recovered from water and dried at 120 °C reproduced the original smooth surface morphology, while film dried at ambient temperature maintained a notably rough surface morphology.

Introduction

Graft copolymers as well as block copolymers, comprised of covalently connected immiscible polymer segments, generally result in microphase separation structure in bulk, but their surfaces tend to be covered by one component with the lower surface energy over the sublayer of another component with the higher surface energy.[1] In addition, these copolymer surfaces are known to undergo a notable restructuring by responding to the change of the contacting medium from air to water within a short time scale.[2,3]

We have so far reported on surface formation and environmentally induced surface rearrangement occurring on poly(vinyl alcohol), PVA,[4−7] and polyurethane-based[7−11] graft copolymers having uniform size polysiloxane, polyether, polyamine, and polystyrene (PS) graft segments, prepared by means of a macromonomer technique.[12] In particular, the PVS-PS graft copolymer exhibited note-
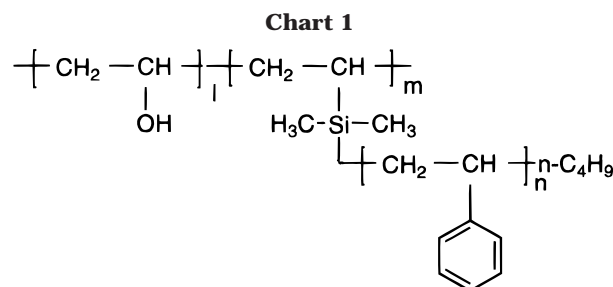
Chart 1

Table 1. Poly(vinyl alcohol)−polystyrene Graft Copolymer Samples

sample	M_n of polystyrene graft[a]	polystyrene content (mol %)[b]	MW ($\times 10^{-3}$)[c]
A1	5900	4.2	23.3
A2	5900	12.2	21.0
A3	5900	23.7	17.5
B1	4000	4.6	23.4
B2	4000	12.9	19.2
B3	4000	23.2	14.7
C1	3500	41.4	10.9
D1	2400	5.2	16.7
D2	2400	26.5	8.1

[a] See also Chart 1. [b] $n/(l+n) \times 100$ in Chart 1. [c] By gel permeation chromatography measurements of poly(vinyl acetate)−polystyrene graft copolymers.

worthy behavior.[6] Thus during the film preparation by casting, the PS component was favored to accumulate on the topmost surface due to its lower surface energy, which was confirmed by X-ray photoelectron spectroscopy (XPS) as well as contact angle measurements. Remarkable was that by immersion into water the contact angle of an air bubble at the surface gradually changed from the value characteristic for the PS homopolymer to one closer for the PVA homopolymer within a few hours.

Atomic force microscopy (AFM) is a powerful means to observe microscopic polymer surface morphology not only in the dry state but also in water. Thus the AFM study on block and graft copolymer as well as polymer blend

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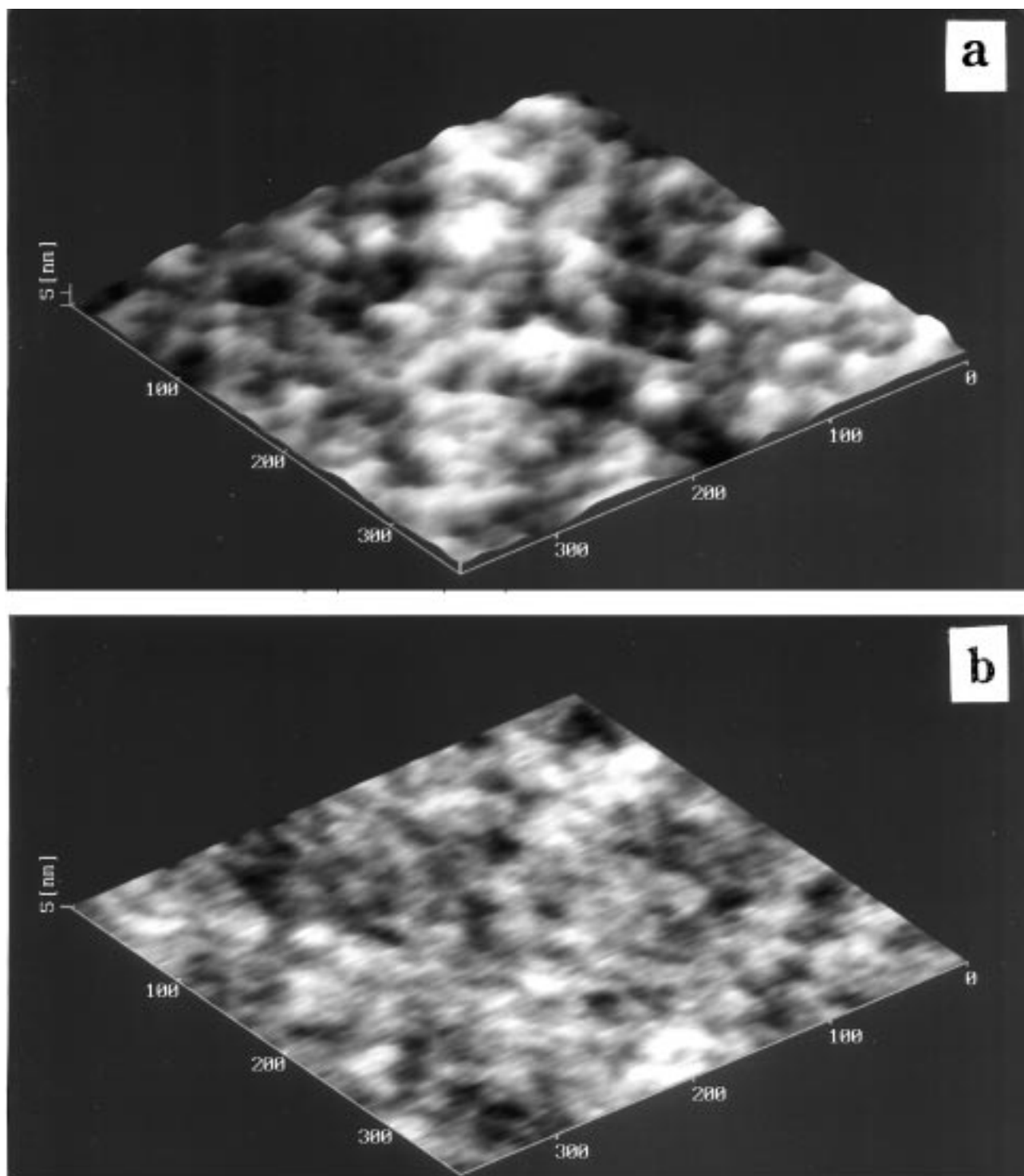(12) Yamashita, Y., Ed. *Chemistry and Industry of Macromonomers*; Huthig & Wepf: Basel, 1993.

Figure 1. Three-dimensional AFM height images of the surfaces of (a) PVA homopolymer (sample PVA-1, see Experimental Section) and (b) PS homopolymer (sample, see Experimental Section) in a dry state. The scan sizes are 375 nm × 375 nm. The contrast covers 8.7 nm for (a) and 1.5 nm for (b).

surfaces has become an area of intense current interest.[13-22] So far, a contact-mode AFM study on styrene–

ethylene/butylene–styrene block copolymer revealed a "wormlike" morphology at the subsurface or the near surface corresponding to its microphase-separation struc-

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tures in bulk.[14] This implies that the contact-mode AFM technique can detect the subsurface or the near surface morphology by ignoring the presence of the topmost thin flexible polymer layer at the block copolymer surface. Thus indeed, an alternative and more surface-sensitive tapping-mode AFM experiment on styrene-butadiene-styrene triblock copolymer surfaces allowed one to observe, with an optimal force variation, not only a "wormlike" structure near the structure but also a smooth topmost polymer layer.[15]

In the present study, we have applied an AFM technique to study on the surface morphology, both in dry state and in water, of a series of PVA-PS graft copolymers with different graft lengths and contents. We demonstrate that the AFM is capable of observing the surface dynamics of these graft copolymers induced by water immersion. The obtained AFM results are subsequently compared with previous observations obtained by the XPS as well as the contact angle measurements.[6]

Experimental Section

1. Samples. A series of PVA-PS graft copolymer samples (Chart 1) was prepared according to the method detailed before[23] and is listed in Table 1. A PS homopolymer sample was synthesized by a living polymerization technique, by terminating with methanol. The molecular weight was 33 500 with the polydispersity (M_w/M_n) of 1.10. A PVA homopolymer sample was prepared through a radical polymerization of vinyl acetate, followed by the saponification with NaOH/methanol. The molecular weight was 18 000 with reference to the poly(vinyl acetate) precursor. The sample is referred as PVA-1. Other two PVAs, i.e., PVA-2 (M_w 13000−23000) and PVA-3 (M_w of 89000−98000) both from Aldrich, were also used for a comparison purpose.

PVA-PS graft copolymer film samples were prepared on a clean glass plate by casting from a dimethyl sulfoxide solution (2 wt %), followed by drying at room temperature by reducing the pressure to 100 mbar for 2 h. Thereafter, the sample film was evacuated at 40 °C for 24−36 h and subsequently annealed with gradual heating under vacuum at 80−110 °C for 72 h. A PS film sample was prepared likewise, but from a THF solution. The sample film was subsequently dried in an ambient condition for 24 h and evacuated at 40−60 °C for 48 h. Six types of PVA film samples were prepared, i.e., three from a dimethyl sulfoxide solution and three from an aqueous solution. The subsequent drying and annealing treatments were performed similar to those for the graft copolymer samples. The sample films were finally evacuated at 40 °C for several hours just prior to the AFM experiments. The thickness of PVA-PS graft copolymer film samples as well as of PVA and PS homopolymer film samples was ca. 300 μm.

2. Atomic Force Microscopy (AFM) Measurements. AFM experiments were performed on a scanning probe microscope (SPA300, Seiko). The contact-mode measurements were carried out using a triangular microcantilever OMCL-TR-400 PSA (Olympus) with a silicon nitride tip, 200 μm long with 0.02 N/m spring constant. The tapping-mode observations were performed with Seiko SI-DF3 cantilevers, with 3.2 N/m spring constant and 34 kHz resonance frequency. As the precise tip geometry in atomic scale is not under absolute control by the manufacturer, special attention has been devoted to ensure reliability and reproducibility of the observed AFM images. Only those images that were reproducible at least by two different cantilevers were taken in account for the subsequent discussion. In the measurements in dry state, adhesive and capillary forces ranging from 0.5 to 2.2 nN were exerted between the sample surface and the tip.[19] Nevertheless, AFM images were reproducible in most cases and the follow-up overview did not show any traces of the previous scanning. The measurements in water, on the other hand, allowed reduction of such secondary forces as small as 0.1 nN.
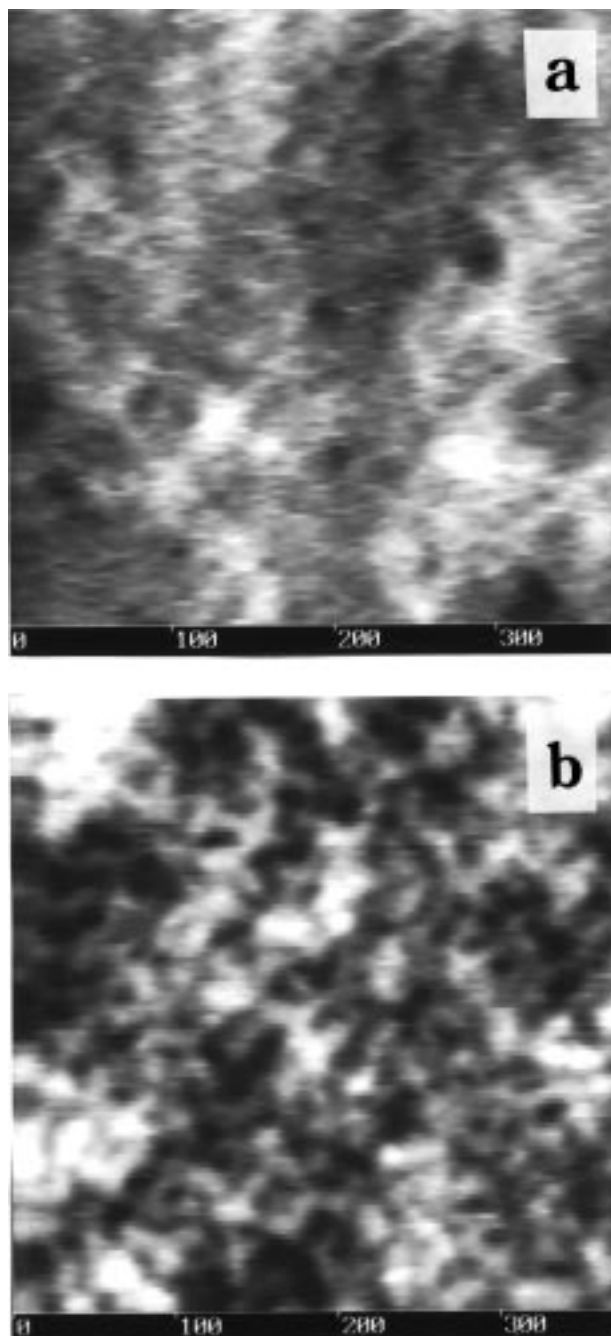
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Figure 2. AFM height images of the surface of PVA-PS graft copolymer of (a) 4.2 mol % and (b) 26.5 mol % PS content in dry state (samples A1 and D2 in Table 1). The scan size is 375 nm × 375 nm. The contrast covers 4.4 nm for (a) and 4.7 nm for (b).

Results and Discussion

1. PVA and PS Homopolymer Surfaces. Three different PVA homopolymer sample surfaces were examined by contact-mode AFM technique in a dry state. A rugged surface in height range of 8−12 nm, as shown in Figure 1a was commonly observed for all PVA samples regardless of the molecular weight and of the casting solvent. The rugged surface morphology is presumably corresponding to crystalline-amorphous domains present at the subsurface or the near surface region of the sample film. In water, on the other hand, the PVA homopolymer surfaces failed to provide reproducible AFM images, presumably due to the sample surface swelling. The recovery of the sample film from water and subsequent
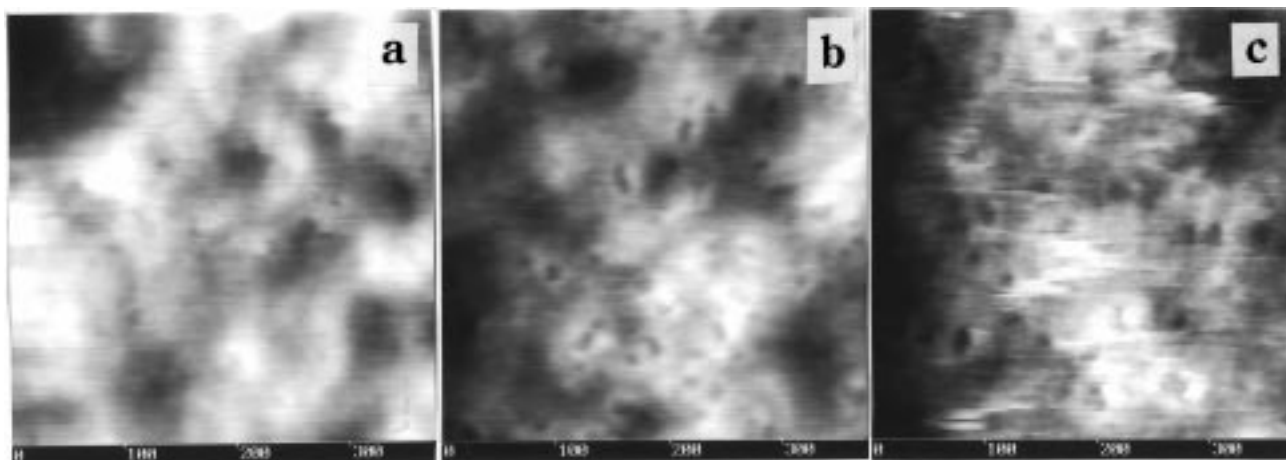
Figure 3. AFM height images of the surface of PVA-PS graft copolymer of 12.9 mol % PS content (sample B2 in Table 1) in water for (a) 20, (b) 425, and (c) 1320 min. The scan size is 375 nm × 375 nm. The contrast covers 7.5 nm for (a), 7.3 nm for (b), and 8.1 nm for (c).

drying at 30 °C again showed a characteristic morphology of the PVA homopolymer surface described above.

A PS homopolymer sample was examined both by a contact- and a tapping mode AFM techniques. A very smooth surface in contrast to the PVA surface, in height range of as small as 1.5 nm was observed by both techniques as seen in Figure 1b. And in water, the surface of the PS homopolymer film sample remained stable, showing a similar surface feature as observed in the dry state.

Thus the surfaces of the PVA homopolymer and that of the PS homopolymer can be distinguished both in dry state and in water by the AFM technique.

2. PVA-PS Graft Copolymer Surfaces. 2-1. In Dry State. The preceding XPS and contact angle studies on PVA-PS graft copolymer surfaces revealed[6] that the topmost surface of the graft copolymer is covered by the PS component, which is presumed to be flexible even at temperatures lower than its bulk T_g. In the present AFM examination for a series of PVA-PS graft copolymers in the dry state, two distinct surface images were observed depending on their PS contents. The graft copolymer sample with 4.2 mol % PS content (A1 in Table 1) showed isolated dark spherical domains dispersed in a bright matrix (Figure 2a). In contrast, the graft copolymers with 26.5 mol % PS content (D2 in Table 1) showed a "wormlike" pattern (Figure 2b). The relevant "island in sea" or "wormlike" morphology were observed for a variety of block copolymer systems[14-17] and was ascribed to the microphase separation morphology at the subsurface region.

Although the topmost surface of the block and graft copolymer is covered by a lower surface energy component at equilibrium after annealing, the AFM, in particular with the contact-mode measurement, is unable to sense it when the topmost layer is thin and flexible. The tapping-mode measurement, on the other hand, is reported to detect the topmost layer of the block copolymer films.[15-17] However, the tapping-mode AFM measurements with various applied forces on the PVA-PS graft copolymers failed to detect the topmost PS layer. This is presumably because the force applied on the sample surface by the tip in our AFM instrument could not be reduced below 1−2 nN owing to the contribution of adhesive and capillary forces. The presence of the topmost PS layer on the graft copolymer film samples, on the other hand, appears to reflect on their smoother surfaces in height range of ca. 5 nm compared to the PVA homopolymer surface in height range of 8−12 nm.
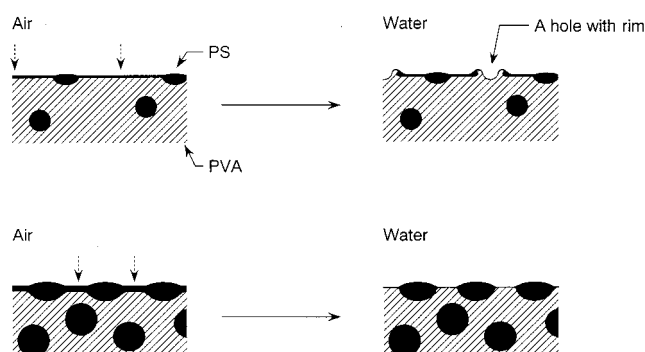

Figure 4. Schematic picture of the environmental response on the surface of PVA-PS graft copolymers of (top) low and (bottom) high PS contents.

2-2. In Water. The surfaces of PVA-PS graft copolymers with up to 5 mol % PS content (samples A1, B1, and D1 in Table 1) failed to show, as in the case of the PVA homopolymer, reproducible AFM images in water. These graft copolymer surfaces are considered to undergo an extensive structural rearrangement to form a PVA-like surface within a short time scale, although no noticeable swelling of the sample films was observed during the immersion into water.

The surfaces of the graft copolymers with 12−23 mol % PS content (sample A3, B2, and B3 in Table 1), on the other hand, showed reproducible AFM images in water. A "hole-with-rim" pattern as shown in Figure 3 was commonly observed on their surfaces after immersion into water. The holes are similar in their sizes, i.e., 15−20 nm in diameter and 5−8 nm in depth. With the prolonged immersion time, the number of the "hole-and-rim" structures slowly increased, while their sizes remained almost unaffected.

The "hole-with-rim" structure is routinely observed at an initial stage of a dewetting process, where a thin liquid layer on solid substrate becomes unstable to rupture itself.[24-27] The dewetting proceeds with enlarging the size of holes, and with grouping the rims to form two-dimensional foams. The walls of the foam then break up

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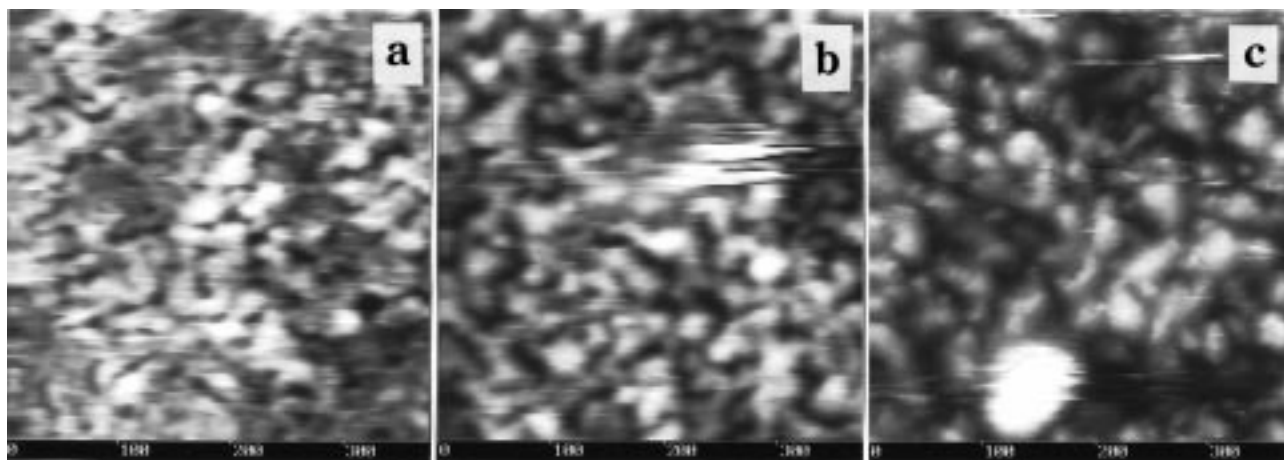(27) Muller-Bushbaum, P.; Stamm, M. *Macromolecules* **1998**, *31*, 3686.

Figure 5. AFM height images of the surface of PVA-PS graft copolymer of 26.5 mol % PS content (sample D2 in Table 1) in water for (a) 4, (b) 35, and (c) 1150 min. The scan size is 375 nm × 375 nm. The contrast covers 8.4 nm for (a), 10.5 nm for (b), and 10.8 nm for (c). The bright spots with scanning traces observed in (b) and (c) correspond to a droplet on the surface.

into isolated droplets. As schematically shown in Figure 4, the topmost PS layer on the present graft copolymer surfaces likewise undergoes the dewetting by the immersion into water. The thin PS layer becomes unstable to rupture itself to form a "hole-with-rim" structure. The dewetting process will be further promoted by the surface swelling of the PVA domain, which comprises the sublayer matrix. On the other hand, the dewetting process is hindered by geometric confinement of the PS segment covalently linked to the PVA segment. Thus these "hole-with-rims" are to be covered by the PVA component, since the formation of PVA−water interface is apparently a major driving force of this surface rearrangement process. The PS component, on the other hand, covers the remaining surface area. These will explain the formation of "hole-with-rim" patterns on the surfaces of PVA−PS graft copolymers with certain PS contents.

The surfaces of graft copolymers with 26−41 mol % PS contents (samples C1 and D2 in Table 1) showed different AFM images, i.e., a "wormlike" pattern as shown in Figure 5, corresponding to their microphase separation morphology observed in the dry state (see Figure 2b). Here, the dewetting of the PS layer appears to complete to produce the "wormlike" surface structures with restructuring the topmost PS layer present in the dry state (Figure 4). Also many droplets, presumably of the PS component, were observed on these graft copolymer surfaces in water (parts b and c of Figure 5). These droplets are similar in their sizes, i.e., ca. 30 nm in diameter and 10−13 nm in height. They were observed within 5 min after the immersion into water, indicating a rapid surface rearrangement occurs. On the other hand, a "hole-with-rim" pattern was not observed on these surfaces.

The previous contact angle measurements for these graft copolymer surfaces indicated an extensive surface rearrangements along with the immersion into water.[6] Although the time scale of contact angle variations and that of morphological evolutions monitored by AFM are only qualitatively comparable, both techniques evidently showed the environmentally induced surface rearrangement.

Also the previous contact angle analysis showed distinct disagreement between the two graft copolymer surfaces prepared by different treatments after recovery from water, i.e., one with simple drying at ambient temperature and another with annealing at high temperature (above T_g of both polymer component).[6] The present AFM study could show that the annealing at 120 °C, after the

immersion into water for 20 h, reproduced the initial AFM image before the water immersion. This coincides with the contact angle result, where the contact angle on the annealed sample surface is almost identical to that on the initial one. On the other hand, the sample surface simply dried at an ambient condition showed a notably rough AFM image. Thus the surface morphology, once rearranged by the immersion into water, is thought to be preserved at least in certain extent. This is unique for the PVA-PS graft copolymer surfaces but is not applicable for the relevant graft copolymer having polysiloxane graft segments, where the contact angle was completely reversible during in the dry state and in the water process.

Conclusions

An environmentally induced surface rearrangement occurring on PVA-PS graft copolymer surfaces has been monitored by means of an AFM technique. In the dry state, the graft copolymer film surfaces were covered by a thin flexible layer of the PS component, but the topmost PS layer formed on the PVA sublayer became unstable when the film was immersed into water. A dewetting process took place to generate a "hole-with-rim" pattern for the graft copolymers with 12−23 mol % PS content. The number of the "hole-with-rim" patterns increased along with the immersion time, while their sizes were not appreciably changed. The dewetting on the surfaces of the graft copolymers with 26−41 mol % PS content produced a "wormlike" pattern, corresponding to their microphase separation morphology in the dry state. The graft copolymer film recovered from water and annealed at 120 °C reproduced the initial surface image, while the film dried at ambient temperature preserved the rough surface image.