Observation of modification and recovery of local properties of polyethylene oxide

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By applying large forces to the surface during an atomic force microscopy scanning, crystallized polyethylene oxide (PEO) films were modified and showed a new structure in which there are the formation of a nanometer-scale bundle structure and an increase of elastic stiffness. The modified part was removed by dropping benzene onto a rotating surface through a peeling process for the case of thin modified layers, while for thick layers, the local properties were recovered by absorbing benzene into the modified parts. In the course of these measurements, the thickness of the modified layers was estimated. © *1997 American Vacuum Society.* [S0734-211X(97)03004-7]

I. INTRODUCTION

Recently, there has been increasing interest in characterizing[1] as well as locally modifying polymers with atomic force microscopy (AFM).[2–5] It was reported that bundles were formed on a polyacetylene surface due to scanning an AFM tip on the surface.[2] We have demonstrated that the morphology and mechanical properties of a crystallized polyethylene oxide (PEO) film with spiral and layered structures prepared on mica surfaces can be locally modified by applying forces at 20 nN during scanning in an AFM.[5] The modification in morphology is a formation of bundles with spacing distances of about 15 nm on the PEO surface. The modification in mechanical properties is an increase in elastic modulus as estimated from the measurement of force-distance curves or in elastic stiffness as imaged by the force modulation technique.[4–7] This modification is believed to be due to the rearrangement of the PEO molecular chains caused by the interaction between them and the AFM tip. However, as far as we know, there has been no report on the depth and surface property variation of the modified polymer structure.

The modified structure can be removed by dropping benzene, which is a good solvent for PEO, onto the rotating sample surface, from which the depth information is obtained. There are two reasons for rotating the sample during the benzene dropping action, i.e., controlling the amount of benzene absorbed into the PEO film to prevent its dissolution and providing a centrifugal force to remove the modified PEO structure mechanically from the sample surface. Based on the experimental observations of removed parts and complete recovery of the modified PEO structures, we clarify that the depth of the modified structure is dependent on the applied forces and the change in the mechanical properties is limited to the modified PEO structures. These results are unique in contributing to the understanding of the local modification of polymers caused by tip-surface interaction in the AFM. We will also discuss the mechanism for the observed removal and recovery of the modified PEO structure by considering possible differences in benzene absorption due to structure changes of the molecular chains in the modified PEO.

II. EXPERIMENT

The crystallized film of PEO was prepared by coating a PEO solution in benzene onto a cleaved mica surface mounted on a spin coater followed by annealing the sample in a moderate vacuum at 90 °C for 24 h (PEO's melting temperature is 66 °C).[8] The thickness of the sample was about 200 nm. To map the mechanical properties, we modified a commercial AFM system (SPA 300, Seiko Instruments Inc.) so as to oscillate the sample height with a peak-to-peak amplitude of 1 nm at 5 kHz and to record the response of the cantilever with a lock-in amplifier. The response of the cantilever to an oscillation of the sample height corresponds to the slope of the force-distance curve available after the tip mechanically contacts with the sample surface. This slope is not only determined by the elastic modulus (Young's modulus) of the sample, but also by the spring constant of the cantilever and the applied force between the tip and sample surface.[5] The response of the cantilever to the oscillation of the sample height can qualitatively express the elastic stiff-

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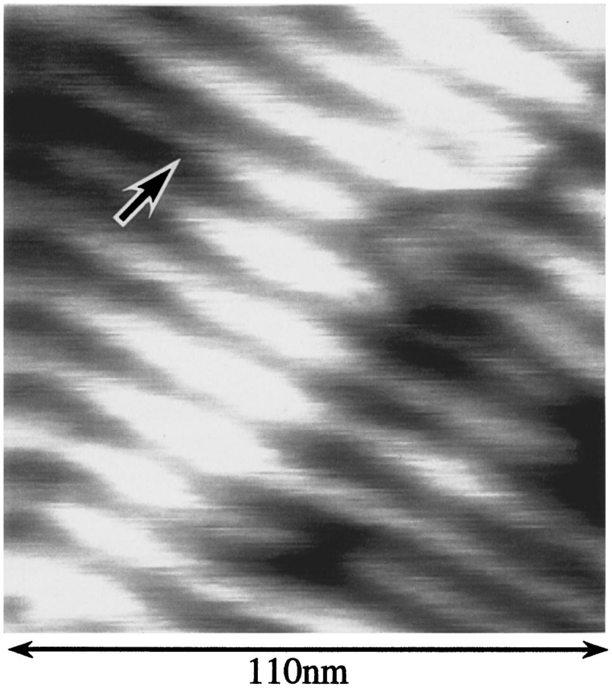

FIG. 1. An AFM image of a bundle structure of PEO crystallized surface formed by scanning a tip at 20 nN. The imaging area is 110×110 nm^2 and the grey scale is from 0 to 15 nm.

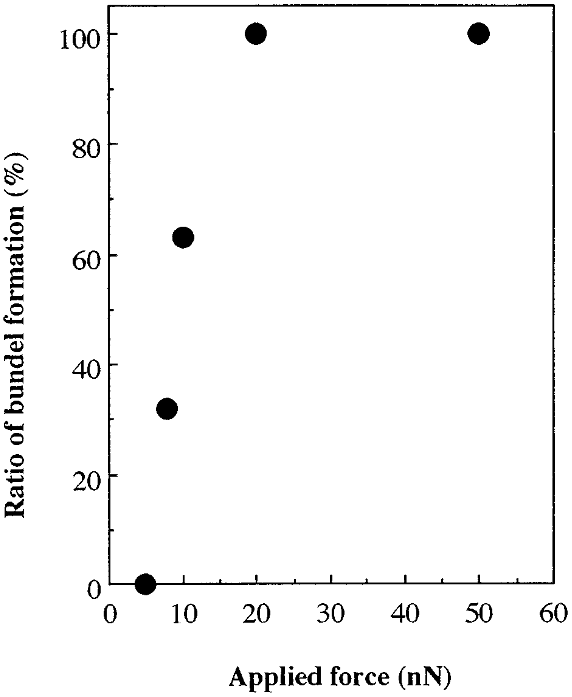

FIG. 2. The ratio (%) of the area with bundle structure to the entire area scanned by a tip at various forces.

ness for the sample surface. Using this technique we can map the elastic stiffness distribution simultaneously with topography of the sample surface. Details of the technique were described elsewhere.[5] A rectangular shaped silicon cantilever with a spring constant of 0.75 N/m and a resonance frequency of 88 kHz (Olympus Opt. Inc.) was used in this study. The cantilever is 0.8, 40, and 100 μm in thickness, width, and length, respectively. The tip is 2.8 μm long and the radius of the apex is about 20 nm. All measurements were performed in air at room temperature with a relative humidity of 50%–60%.

Here, we describe procedures for the modification of the crystallized PEO film and for the removal of the modified PEO structure. A large area of 8 μm square was first imaged with small forces of 5 nN under which there was no detectable degradation on the surface. Then a smaller area of 5 μm square was modified by scanning the tip with large forces (for example, 50 nN). The modification was confirmed by observing both the bundle structures and the increase in the elastic stiffness. To probe the depth of and surface property variation on the modified PEO structure, we replaced the sample onto the spin coater and dropped benzene onto the sample surface while rotating at a rate of 1000 rpm. Although the accurate quantity of benzene absorbed into the PEO films could not be estimated, we gave a rough qualitative description for the amount of benzene in terms of the number of drops of benzene. Then the sample was placed in a moderate vacuum at room temperature for 12 h to evacuate residual benzene. After the above treatments the sample was remounted on the AFM scanner for topography and elastic stiffness measurements.

In order to exactly observe the same area, we prepared a marker by scratching crossed lines on the backside surface of the mica substrate and placed the AFM tip around there with the help of an optical microscope through the transparent mica substrate and thin PEO film.

III. RESULTS

Figure 1 shows a typical AFM image (110 nm square) of a bundle structure on the PEO surface formed by scanning the AFM tip at 20 nN. The structure is seen as regular white bundles perpendicular to the scanning direction (indicated by an arrow) of the large force scanning. The spacing between the bundles is about 15 nm and the corrugation height is about 3 nm. The length of the bundles is on the order of 100 nm.

We found that there was a threshold force for the formation of bundles when scanning the AFM tip on the PEO surface. We imaged (at 5 nN) a series of topography of areas modified at various forces and calculated the ratio of the bundled area to the entire area that experienced the large force scanning. The result is summarized in Fig. 2, showing the existence of a threshold at ~10 nN. We noted that the surface of PEO showed an aging effect in the modification, that is, a fresh surface needs small applied forces while an aged one needs larger applied forces for being modified. For example, aged PEO surfaces kept in air for about one month could never be modified even at the applied forces as large as 50 nN. This effect is tentatively attributed to a lubricant effect on the PEO surface due to adsorption of water.[9]

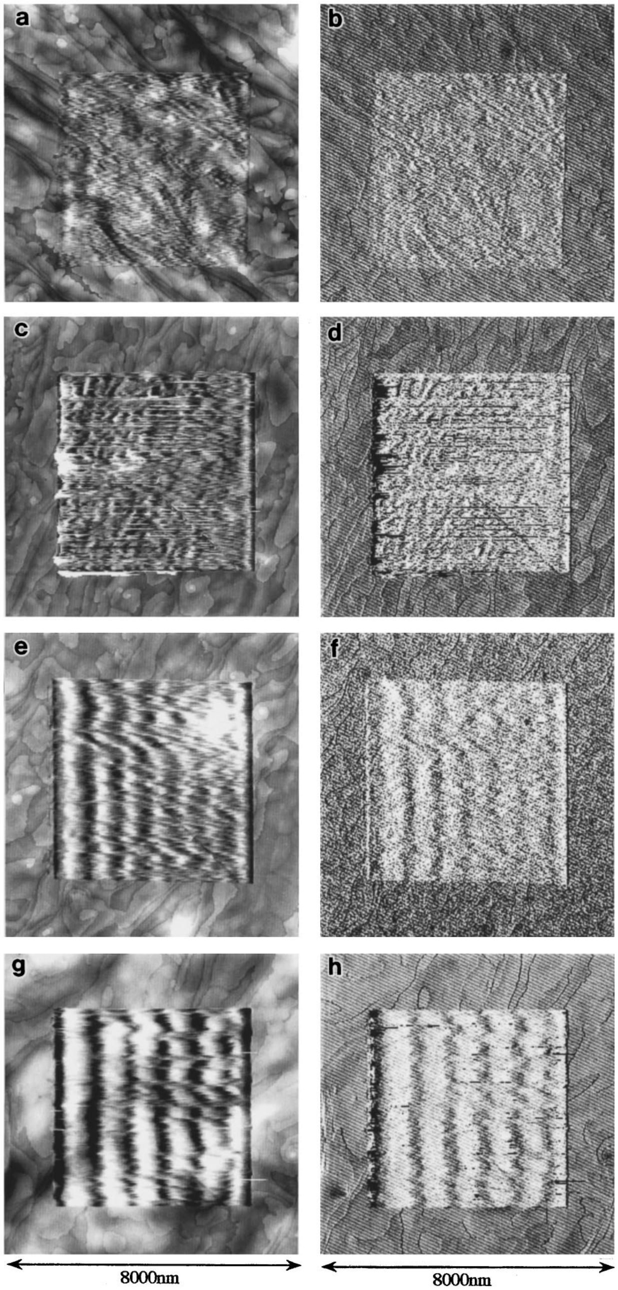

FIG. 3. Simultaneously obtained topographic (left-hand side) and elastic stiffness distribution (right-hand side) images of PEO surfaces modified by scanning a tip at large forces of 25, 50, 100, and 150 nN at the central areas ($5000\times5000\ \text{nm}^2$). The grey scales (from the dark to the white of the image) for the topographic images of (a), (c), (e), and (g) are from 0 to 56, 85, 95, and 174 nm, respectively. Data in elastic stiffness images are a direct record from a lock-in amplifier of the response of the cantilever to the oscillation of the sample height at 5 kHz with a peak-to-peak amplitude of 1 nm. The average increase of the elastic stiffness on the modified PEO shown in (b), (d), (f), and (h) is 1.8%, 2.8%, 3.0%, and 3.3%, respectively.

We extensively studied the modified PEO structure as a function of the applied forces above the threshold force. Figure 3 shows the results of modification in topography (left-hand side) and elastic stiffness (right-hand side) of PEO surfaces by scanning an AFM tip over 5000 nm square at 25 [(a), (b)], 50 [(c), (d)], 100 [(e), (f)], and 150 [(g), (h)] nN, respectively. All images were obtained at 5 nN and the sample height was oscillated in a peak-to-peak value of 1 nm for imaging the elastic stiffness distribution.

The morphology of all of the modified areas in Fig. 3 is seen as being scratched by the tip. The modified surfaces in Figs. 3(a) and 3(c) are seen as a hammered-out plate, while those in Figs. 3(e) and 3(g) show an undulation character. When the applied force is increased, the undulation character becomes clear. As shown in Figs. 3(e) and 3(g), there are seven and six bundles in the area of 5000 nm square, respectively. This micron-scale bundle structure is similar to that reported in Ref. 3, whose spacing distance is dependent on the applied forces. By magnifying all of the modified areas shown in Figs. 3(a), 3(c), 3(e), and 3(g), we confirmed the existence of nanometer-scale bundles perpendicular to the scanning direction (not shown), which is similar to that shown in Fig. 1. Although the modified PEO surfaces caused by various applied forces show different surface morphology on a micron-scale, there is an identical nanometer-scale bundle formation on all of the modified areas shown in the topographic images in Fig. 3. Therefore, two types of structure exist on the modified PEO surface. One of them is a bundle structure with spacing distances of about 15 nm, which is formed when scanning a tip at forces over the threshold value of ~ 10 nN. The other one is the micron-scale bundle structure which is formed when scanning tip at forces over about ten times of the threshold value. We noted that the spacing distance of the micron-scale bundles is dependent on the applied forces while that of the nanometer-scale bundles is not.

The simultaneously obtained elastic stiffness distribution is shown on the right-hand side in Fig. 3 in which the elastic stiffness is expressed in a manner where the brighter contrast corresponds to the larger elastic stiffness. It is clear that there is an increase in the elastic stiffness on the modified areas as shown in Figs. 3(b), 3(d), 3(f), and 3(h). The elastic stiffness imaging is thus effective to qualitatively measure the elastic stiffness distribution on a surface. For a quantitative analysis on the elastic modulus, however, force-distance curves should be measured.[5] In this article we only show a change in the elastic stiffness due to the modification. From cross sectional analysis for the images shown in those figures, we found a relative increase of 1.8%, 2.8%, 3.0%, and 3.3% in the elastic stiffness on the modified areas caused by an applied force of 25, 50, 100, and 150 nN, respectively.

Figures 4(a) and 4(c) show topographic images for the samples modified at 25 and 50 nN and then treated by dropping five and ten drops of benzene onto the surface as described in the experimental section, respectively. The images shown in Figs. 4(a) and 4(c) are exactly the same areas as those for Figs. 3(a) and 3(c), respectively. It is clear that certain parts of the modified PEO structures are removed and the underlying PEO surfaces are visible. We also see that some single bundles still remained in Fig. 4(a) but not in Fig. 4(c). There are no bundles detected on the newly appeared underlying PEO surfaces that look to be identical to the pristine PEO surfaces. The simultaneously obtained elastic stiff-

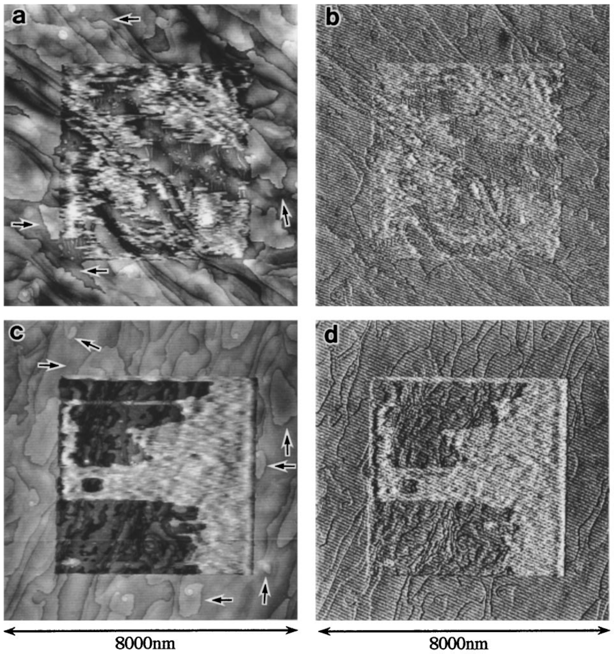

FIG. 4. Simultaneously obtained topographic [(a) and (c)] and elastic stiffness distribution [(b) and (d)] images of the 25 and 50 nN modified PEO surfaces at the same locations as those in Figs. 3(a) and 3(c), respectively, after benzene dropping action. Arrows in (a) and (c) indicate slight reduction of edges by benzene. In (b) and (d) the newly appeared underlying PEO surfaces exhibit the same elastic stiffness as the pristine ones and some of the modified structures still remain and show a larger elastic stiffness similar to that in Figs. 3(b) and 3(d), respectively. The grey scale for the topographic images in (a) and (c) are from 0 to 56 and 125 nm, respectively.

ness distribution images in Figs. 4(b) and 4(d) show that the remaining modified PEO parts have larger elastic stiffness than the underlying PEO. It also shows that the elastic stiffness distribution on newly appearing underlying PEO surfaces is the same as that on the pristine PEO, indicating that the elastic stiffness change is limited to the modified layers.

This type of experiment for removing the modified PEO parts is useful to obtain depth information for the modification. From cross sectional analysis of the images shown in Figs. 4(a) and 4(c), we estimated average height differences of about 10 and 40 nm, respectively, between the remaining modified parts and the newly appeared underlying PEO surfaces. From these results, we find that the thickness of the modified layer at 25 nN is about 10 nm, which corresponds to the thickness of the topmost layer of the crystallized PEO. When the applied force increased to 50 nN, the PEO film was modified into a depth of about 40 nm, corresponding to four layers of PEO. The removal of the modified PEO structures caused by relatively smaller applied forces, especially by 25 nN, shows a good reproducibility. Based on the morphology as shown in Figs. 4(a) and 4(c) the removal process of the modified PEO is considered as a mechanical peeling of the modified PEO layers during dropping benzene onto the rotating surface.

By carefully comparing Figs. 3(a) and 3(c) with Figs. 4(a) and 4(c), we note that there are some small changes in the morphology of the pristine PEO after the benzene dropping action, i.e., the edges of layered structures are observed to be removed slightly as indicated by arrows in Figs. 4(a) and 4(c). As the amount of benzene dropped onto the surface increases from five to ten drops, by comparing Figs. 4(a) with 4(c) we can see that the reduction of edges becomes clear. The results shown in Figs. 4(a) and 4(c) indicate that the removal of the pristine PEO caused by the benzene dropping action is limited to the edges. This experimental result indicates that the rotating surface of the crystallized PEO film cannot absorb benzene effectively, while the edges of the layered structures can trap some benzene. Therefore, when we drop benzene onto the rotating PEO sample surface, benzene starts to attack the pristine PEO from the edges but not surfaces.

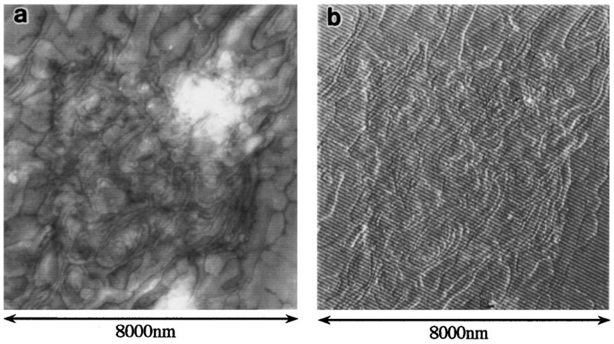

FIG. 5. Simultaneously obtained topographic (a) and elastic stiffness distribution (b) images of the 100 nN modified PEO surface at the same location as that in Fig. 3(e) after dropping 20 drops of benzene onto the rotating surface. The modified PEO surface was recovered. The grey scale for the topographic image is from 0 to 95 nm. No elastic stiffness difference between the pristine and the once-modified surface was detectable.

For the modified PEO structures under applied forces of 100 and 150 nN shown in Figs. 3(e) and 3(g), respectively, we did not observe any removal of the modified PEO structures by dropping ten drops of benzene onto the rotating surface. When we increased the number of benzene drops, we observed a recovery of the modified PEO structures to layered crystalline structures. Figures 5(a) and 5(b) show resulting changes in both topography and elastic stiffness distribution after dropping 20 drops of benzene at the same area shown in Fig. 3(e). In the topographic image we can see some footprint, whereas in the elastic stiffness image, no contrast difference between the pristine and the once-modified PEO is detectable. It is clear that the modified area is recovered to being similar to the pristine one. This recovery process is considered to be due to a swelling effect of molecular chains in the modified PEO, which is a relaxation process of polymer molecular chains upon absorbing solvents. We noted that the benzene dropping action has a relatively weak influence on the pristine part of PEO, which may have originated from the difference in surface structure for the modified and pristine PEO. When benzene is absorbed adequately into the modified PEO layers, the molecular chains thoroughly swell, resulting in a recovery both in surface morphology and elastic stiffness. The experimental result strongly indicates that the modified parts of PEO directly

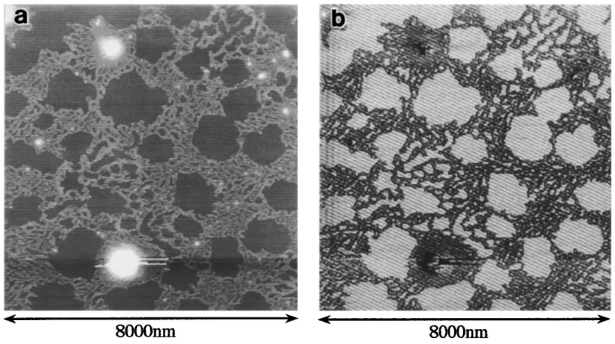

FIG. 6. Simultaneously obtained topographic (a) and elastic stiffness distribution (b) images after dropping 40 drops of benzene onto the rotating surface. The PEO film was dissolved by benzene and only a monolayer PEO network remained. The mica substrate surface is visible and shows an elastic stiffness of 10% larger than that of the PEO. The grey scale for the topographic image is from 0 to 80 nm. Data in elastic stiffness image are a direct record from a lock-in amplifier of the response of the cantilever to the oscillation of the sample height at 5 kHz with a peak-to-peak amplitude of 1 nm.

contribute to the increase of the elastic stiffness, which may be caused by the compact molecular chains arrangement due to the pressure induced by the tip.

When we dropped 40 drops of benzene onto the surface, we observed that the PEO films were finally dissolved into benzene and the surface of the mica substrate appeared as shown in Fig. 6. In Fig. 6(a) only a monolayer network of PEO molecules with a thickness of about 10 nm remains and the remaining parts are assigned to the mica substrate due to the larger elastic stiffness[4] expressed in Fig. 6(b) as a contrast of 10% larger than that on the PEO films. We confirmed that dropping several drops (for example, five drops) onto a nonrotating surface also caused a result similar to that in Fig. 6, which indicates that a rotating surface hinders the absorption of benzene into the film and hence results in the mechanical peeling.

We also confirmed that after annealing the sample at 90 °C (the temperature at which we prepared the sample), the modified area was completely recovered and there was no detectable difference in both morphology and elastic stiffness between the pristine PEO and the once-modified surfaces. At a high temperature of 90 °C, PEO melts and recrystallizes so that the modified and pristine molecular chains could not be distinguished.

IV. DISCUSSION

The relationship between the depth of the modified PEO layers and the applied forces is revealed through the peeling process of the modified PEO parts obtained by dropping benzene to the rotating surface. The PEO layers near the surface can be modified by the tip pressure. When the applied force is 25 nN, only the topmost layer is modified. When the force increases to 50 nN, four layers can be modified. This means that when the applied force increases to 50 nN, it can influence the PEO films up to four layers. Since the contact area of the tip and the sample surface is small, the pressure can be very large, e.g., 0.1 GPa if we assume a contact area of $500\ \text{nm}^2$, which is calculated from the Hertzian contact between the tip with a radius of 20 nm and PEO film with a Young's modulus of 0.3 GPa[5] under an applied force of 50 nN. Under a large pressure, the PEO molecular chains can be rearranged to form bundles and hence to contribute at least partly to the increase of the elastic stiffness. For the modification by forces of 100 and 150 nN as shown in Figs. 3(e) and 3(g), more than four layers of the PEO layers are expected to be modified. However, in this case we could not peel off the modified region so the exact depth of the modified PEO could not be obtained. Here we discuss a possible model for the behavior in the removal of the modified PEO layers as a function of applied forces.

In our experiment we changed the amount of benzene dropped onto the surface while keeping the sample rotation speed constant at 1000 rpm. This means that we controlled the interaction time between benzene and the surface. When $\sim$20 drops of benzene were dropped, molecular chains in the modified PEO are easier to swell than in the pristine PEO as seen in Fig. 5, indicating a difference in absorbing benzene for the two kinds of PEO structures. This difference is thus considered to result in different interaction times for the modified and pristine layers. The change in surface structure caused by tip-surface interaction during the large force scanning should correspond to the different interaction time. For the modified PEO surface, the modification possibly induces cracks or defects, which may serve as effective paths for benzene to penetrate into the PEO films so that benzene has sufficient time to swell molecular chains. For the pristine PEO surface which is crystallized, there are almost no paths for benzene to penetrate into the PEO films on the time scale under consideration. Thus benzene dropped could not have enough time to be effectively absorbed from the surface but could be trapped by the edges of the layered or spiral structures, resulting in slight removal of edges to be observed as indicated by arrows in Figs. 4(a) and 4(c).

By dropping benzene onto the rotating sample surface, we observed a peeling of certain parts of the modified PEO layers for those caused by 25 and 50 nN. Using the concept of the interaction time of benzene and the surface as discussed above, we explain the variation in peeling of the modified PEO as a function of the applied forces. For the modified PEO layers caused by 25 and 50 nN, the interaction time corresponding to dropping five or ten drops of benzene allows benzene to penetrate to the interface of the modified and underlying PEO layers to weaken the interaction there but not to swell all of the modified PEO. Because the sample was rotating at 1000 rpm during the benzene dropping action, the weakened parts of the modified PEO layers were peeled off by the centrifugal force due to the rotation.

However, we did not observed any peeling processes for the modified layers made by 100 and 150 nN in our experiment. For these modified PEO layers, because of a deeper modification, it needs a much larger amount of benzene to penetrate to the interface of the modified and underlying layers to swell the molecular chains or weaken the interaction between the modified and the underlying PEO layers. The interaction time corresponding to dropping five or ten drops of benzene may be too short to allow benzene to penetrate to the interface. When increasing the interaction time to that corresponding to dropping 20 drops of benzene, the modified layers near the surface may start to swell and recover by absorbing benzene, which in turn prevents benzene from further penetrating to the interface. Therefore, no peeling of the deeply modified PEO layers can be realized. It is obvious that when the interaction time is extremely large the modified PEO and also the pristine PEO will be dissolved into benzene, as shown in Fig. 6. The condition for that is to drop enough of an amount of benzene (for example, 40 drops) onto the rotating surface. An alternative way to make the PEO films dissolve into benzene is to drop a small amount of benzene (for example, five drops) onto the nonrotating surface.

V. CONCLUSIONS

By applying five and ten drops of benzene onto rotating sample surfaces at 1000 rpm, we removed parts of the PEO layers modified by applied forces of 25 and 50 nN and estimated depths as 10 and 40 nm, respectively. In contrast, under the same conditions of benzene dropping action, we could not remove the PEO layers modified by forces of 100 and 150 nN. When dropping 20 drops of benzene, the modified parts completely recovered by absorbing benzene into the modified PEO parts. By simultaneously imaging elastic stiffness distribution with topography, we confirmed that the elastic stiffness change due to the modification is limited to the modified structure. An adequate amount of benzene dropped into the PEO finally results in complete dissolution of both the modified and pristine PEO surfaces so that the mica substrate surface appeared.

A model is proposed to explain the observed removal and recovery of the modified PEO structures by considering whether benzene can penetrate to the interface between the modified and underlying layers. For relatively thin modified layers ranging from 10 to 40 nm, benzene can penetrate to the interface of the modified and underlying PEO layers to weaken the interaction there. Then the weakened modified PEO parts can be peeled off by the centrifugal force due to the rotation. For the modified layers with a thickness larger than 40 nm, benzene can swell the layers near surface before it penetrates into the interface and recovers the modified PEO parts. This process in turn prevents benzene from penetrating further into the underlying modified PEO layers. Therefore, no peeling process can be realized, at least under the condition in our experiment.

The results reported are expected to contribute to a better understanding of the modified PEO layers by investigating not only the changes in the structure and mechanical properties, but also the thickness as a function of the applied forces. However, much work remains to be done to completely understand the local change in the modified structure. For example, in the PEO layers modified by relatively large forces of 150 nN [Fig. 3(g)] the valley is softer than the protruding bundle, which indicates that the molecular chains become compact in the protruding bundle but not in the valley. Furthermore, a quantitative analysis of changes in the elastic modulus in the modified PEO surface as a function of applied forces is highly required.

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