Reports

Orientational Ordering of Polymers by Atomic Force Microscope Tip-Surface Interaction

ON MAN LEUNG AND M. CYNTHIA GOH*

Results of studies on the interaction between the tip of an atomic force microscope and polystyrene molecules in a film spread on a surface are reported. The tip produces a persistent deformation on the film; some of the polymer molecules are eventually pulled up by the tip. Nanometer-size structures are induced, resulting in a pattern that is periodic and is oriented perpendicular to the scan direction.

THE ATOMIC FORCE MICROSCOPE (AFM) (*1*) has found application in a variety of surface studies including atomic scale friction (*2, 3*), elasticity (*4*), and surface forces (*4, 5*) but has mainly been used for imaging the surface topography of nonconducting surfaces with high resolution (*6*). In these investigations, one monitors the deflection of a tip, caused by its interaction with the surface when a scan is made, to map out the surface topography. Typically, imaging is done under conditions that minimize the force between the tip and the surface molecules. Calculations indicate that the operating force for studies of biological samples should not exceed 10^{-11} N (*7*) and that forces of the order of 10^{-8} N can lead to large deformations of the surface (*8*). When one attempts to image adsorbate on a surface with an AFM, the process of scanning can drag or push molecules around and lead to distorted or disappearing images. The results of our study show how interesting surface structures can be created by the interaction between an AFM tip and a polymer film.

We undertook this study to investigate whether the force between the AFM tip and the surface molecules could be exploited for the creation of structure on a nanometer scale (*9*). In a recent report of theoretical considerations and molecular dynamics simulation, Landman *et al.* (*10*) showed how the interaction between an Ni tip and an Au surface in an AFM created an atomic scale instability that pulled Au atoms toward the Ni, eventually coating the tip. They then measured the force as a function of separation between the tip and the surface and found the results to be in agreement with their simulation.

We chose mica as the substrate for deposition of the polymer layer because it can be cleaved easily to yield large flat areas. We prepared dilute solutions of polystyrene (obtained from Aldrich Chemical) (*11*) by dissolving 25 mg of the polymer in 25 ml of benzene (*12*) at 20°C. In a typical experiment, the desired polymer was deposited from a previously prepared, well-stirred solution onto freshly cleaved mica with a 1-μl pipette; the solvent was then allowed to evaporate before the scan. The solvent evaporation is quite rapid, typically a few seconds. The deposited film was amorphous and is estimated to be of the order of a micrometer thick.

The AFM used was a Nanoscope II (Digital Instruments), which is capable of scanning a region of up to 12 μm by 12 μm. We intentionally operated at comparatively large forces (in the vicinity of 10^{-7} N) to enhance the tip-surface interaction. All the tips we used for this study were made of microfabricated Si_3N_4 (Digital Instruments). They were attached onto 100-μm cantilevers with a force constant of about 0.58 N/m.

The AFM tip can be positioned in one particular spot a few nanometers above the sample. This distance should be sufficiently small, such that there is enough interaction to allow the tip to track the topography of the sample when it is scanned in the *x* and *y* directions (*13*). We obtained the images presented here by performing a raster scan, where the cantilever was held stationary in the *x* and *y* directions, and the sample was moved first along the horizontal (*x*) direction and then an increment in the vertical (*y*) direction. They were neither filtered nor processed in order to avoid possible artifacts.

One can measure the operating force by holding the cantilever stationary while moving the sample toward and away from the tip repeatedly along the *z* direction and monitoring the cantilever deflection. As the sample was brought closer to the tip, the interaction was increased. We used this "force mode" of operation of the AFM to examine the interaction between the tip and the polymer molecules. The AFM tip was positioned above a film of polystyrene (molecular weight = 95,800) and held stationary for 30 s (Fig. 1A) and for 10 min (Fig. 1B). In the beginning, the film appeared quite homogeneous on this scale (similar to that of Fig. 2A), with a surface roughness of less than 1 nm. When the tip was held stationary at one spot, a lump developed under the tip. This lump was noticeable after only a few seconds. Both the vertical and lateral dimensions of this lump increased with time; after 10 min, it was about 20 nm high and 300 nm in diameter. The asymmetry of the lump possibly reflects the shape of the tip. Obviously, there was an interaction between the tip and the polymer molecules, which caused a deformation of the surface.

On the basis of information supplied by the manufacturer, the tip is pyramidal in shape with a contact surface area of about 10^{-15} m^2. Thus, the force per contact area on the polymer surface is large, of the order of 10^6 N/m^2. It is likely that the tip will deform the surface so that some of the polymer molecules are pulled up. This is analogous to the simulation of Landman *et al.* (*10*). The main difference is that their

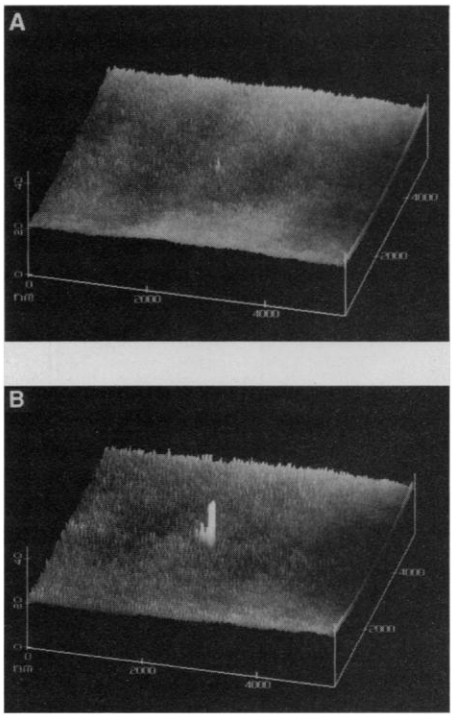

Fig. 1. AFM images of the polystyrene surface taken after the tip had been held fixed at the center of the scan for 30 s (**A**) and for 10 min (**B**). All of these images are taken from the same area.

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

*To whom correspondence should be addressed.

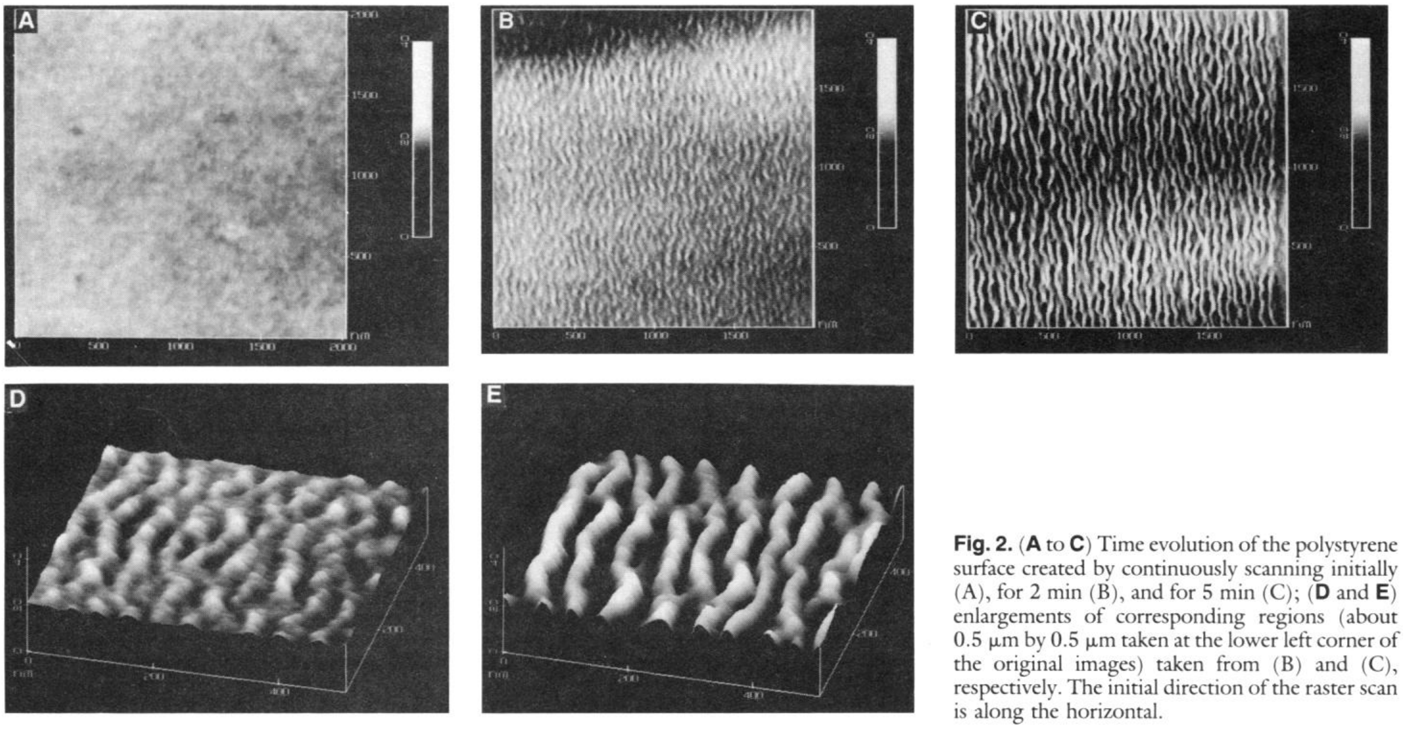

Fig. 2. (**A** to **C**) Time evolution of the polystyrene surface created by continuously scanning initially (A), for 2 min (B), and for 5 min (C); (**D** and **E**) enlargements of corresponding regions (about 0.5 μm by 0.5 μm taken at the lower left corner of the original images) taken from (B) and (C), respectively. The initial direction of the raster scan is along the horizontal.

simulation shows a plastic deformation of the surface followed by the formation of a connective junction between the tip and the Au surface, resulting in the coating of the Ni tip by Au atoms. In our experiments, the polymer molecules forming the surface film were entangled through their long chains, which means that the tip cannot easily pull molecules off the surface; rather, one polymer molecule can drag several chains with it, which in turn are likely to pull other chains (*14*), producing a lump in the surface. The deformation produced by the tip-surface interaction in this case is apparently long-lived (*15*). In the course of the deformation, different configurations of the entangled polymer chains could have been generated, which then persisted over the long time scales that are characteristic of polymer relaxations (*16*), resulting in a surface structure that is retained for a long time.

We then investigated the effect of moving the tip slowly across the surface, scanning at a speed of about 17 μm/s. We took images of polystyrene (molecular weight = 95,800) as a function of time while scanning continuously and maintaining a constant force (*17*) (Fig. 2). An image taken immediately after deposition and solvent evaporation (Fig. 2A) showed that the surface coverage was homogeneous and smooth to within 1 nm at this scale. After 2 min (Fig. 2B), the roughness of the surface had increased. Structures about 50 nm wide became evident at this point. With further scanning, these structures were better defined and increased in width (x) and thickness (z) (Fig. 2C). At this point, there appeared to be distinct oriented bundles on the surface. The increase in surface roughness and the formation of distinct "bundles" could be seen more clearly (Fig. 2, D and E). The z scale is the same in these two images. Comparing the two images, one can see that the lumps in Fig. 2D would eventually form the more distinct bundles seen in Fig. 2E. The sequences of these images were always reproducible. Furthermore, we had studied a range of molecular weight of polystyrene (from 32,000 to 573,000) corresponding to different sizes and found no obvious changes in the dimensions and patterns of these structures.

The "bundles" seen in the figures are definitely not individual polymer molecules:

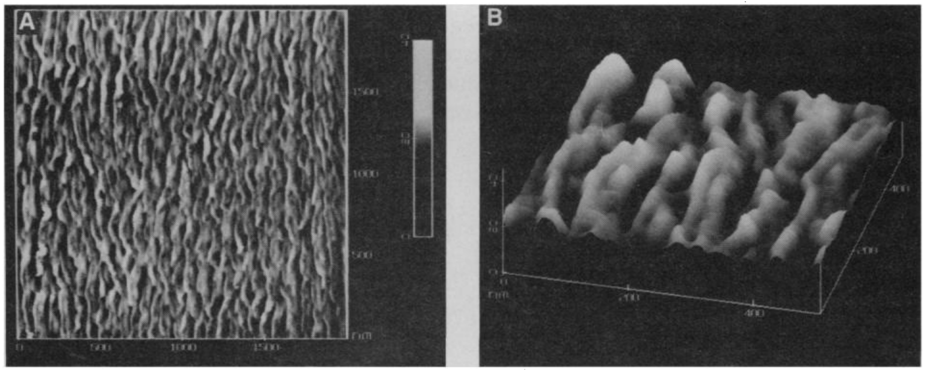

Fig. 3. Image taken from the same experimental run as those in Fig. 2. (**A**) The result of scanning for 2 hours. (**B**) Surface view of the enlarged image from (A). Enlargement was done in the same way as those in Fig. 2, (D) and (E).

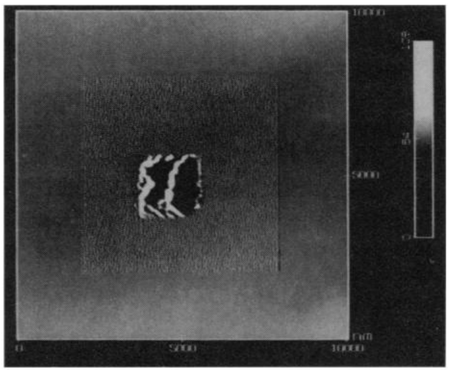

Fig. 4. This image is the result of three consecutive steps. A region 1.5 μm by 1.5 μm has been scanned for 4 hours. Then, a zoom-out area of 6 μm by 6 μm was scanned for another 5 min. Finally, a zoom-out image of 10 μm by 10 μm was taken at the first scan.

the distances involved are much too large. The bundles thus correspond to aggregates of molecules. The existence of superstructures and aggregates has been reported in a variety of polymer systems (although not in polystyrene at room temperature), especially those of biological importance, but the underlying cause of the aggregation is not clear (*18*). In our experiments, we were able to easily induce the formation of clumps of polystyrene molecules in the surface films; by understanding the origin of the time-dependent patterns we create while scanning the surface, we hope to learn more about this process of aggregation.

There are two interesting aspects of the pattern of structures formed in our experiments: (i) the uniformity of the structures makes the images appear periodic, and (ii) the bundles formed are elongated such that the long axis is perpendicular to the scan direction (*19*). We can check that the orientation of the bundles is indeed perpendicular to that of the scan direction by simply rotating the scan direction after several minutes. In this case we found that the direction of the bundles rotated as well.

As the tip was allowed to scan for a longer time, we observed that the aggregation process continued and that the bundles grew in size (Fig. 3A). From a comparison of Figs. 3B and 2E, it appears that the bundles that were distinct after 5 min of scanning had begun to aggregate to form larger bundles. These results are summarized in Fig. 4, which also shows that the polymer film did not aggregate simply as a result of the elapsed time. A smaller region (1.5 μm by 1.5 μm) was scanned continuously for 4 hours; then the scan size was increased to 6 μm by 6 μm, and this larger region was scanned for 5 min. The overall image was then taken at the first scan of the 10 μm by 10 μm area. The patterns formed are consistent with Figs. 2 and 3, and the boundaries between the regions are quite sharp.

Three conditions were necessary for the formation of surface structures: (i) there must be a reasonable balance between tip–surface molecule forces versus surface molecule–surface molecule forces, (ii) the deformation should be plastic, and (iii) there must be enough molecules on the surface. We realized these conditions in our experiments by using a polymer deposited onto a surface as a multilayer from a dilute solution. Because the polymer chains were weakly interacting in solution and the solvent evaporated rapidly, chains that were entangled but loosely bound were presumably formed at the surface. Otherwise, the tip-polymer interaction may not be strong enough to cause a deformation (*20*).

One of the interesting aspects about being able to produce these structures is the possibility of obtaining novel properties from the material. Although the maximum scan size of our AFM is 12 μm by 12 μm, by translating the sample and making further scans, we are able to produce macroscopic areas of aligned structures.

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11. In dilute solutions, the polymer chains are well separated and noninteracting.
12. We also used toluene and chloroform as solvents; similar results were obtained.
13. We define the coordinates such that the z axis is perpendicular to the surface plane and the x axis is horizontal in all the images presented here.
14. We do not rule out the possibility that some polymer molecules may jump and coat the tip as well. (We found indirect evidence for this: after scanning the surface for a long time, the images get worse, but, if the tip is washed with a solvent that dissolves the polymer, it functions as well as a new tip.) However, there is enough polymer in the deposited film, and eventually the entanglement is expected to lead to the situation described.
15. The lump persisted for at least several hours. However, we were unable to follow the behavior for a longer time for technical reasons: if the sample is removed from the microscope, it is very difficult to find the location of a 10-nm structure within a sample 1 cm square.
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17. The shading of the images reflects the surface topography (z) and was maintained in the different images that are being compared: Figs. 2A, 2B, 2C, and 3A; Figs. 2D, 2E, and 3B.
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19. The individual polymer molecules may be oriented along the scan direction, as one would generally expect. However, the formation of the aggregates is quite rapid and we were unable to resolve the orientation of the individual polymer molecules within the bundles.
20. We were unable to produce oriented bundles in polyethylene oxide, which was deposited from crystallites; rather, we saw small crystalline structures similar to those observed with optical and electron microscopes. Furthermore, if we reduced the operating force by imaging polystyrene film deposited on mica under water, the interaction between the tip and the polymer was reduced, and we were unable to produce the alignment.
21. This work was supported in part by the Natural Science and Engineering Research Council of Canada. We thank M. Moskovits and T. Dickson for helpful discussions and reading of the manuscript.

8 August 1991; accepted 31 October 1991

Luminescent Colloidal Silicon Suspensions from Porous Silicon

JULIE L. HEINRICH, CORRINE L. CURTIS, GRACE M. CREDO,
KAREN L. KAVANAGH,* MICHAEL J. SAILOR*

A procedure for generating colloidal suspensions of Si that exhibit luminescence, attributed to quantum confinement effects, is described. Samples of n- or p-type Si that have been electrochemically etched to form porous Si can be ultrasonically dispersed into methylene chloride, acetonitrile, methanol, toluene, or water solvents, forming a suspension of fine Si particles that luminesce. Transmission electron microscopy analyses show that the Si particles have irregular shapes, with diameters ranging from many micrometers to nanometers. Luminescent, composite polystyrene/Si films can be made by the addition of polystyrene to a toluene suspension of the Si nanoparticles and casting of the resulting solution onto a glass slide.

SMALL COLLOIDAL SEMICONDUCTOR particles (typically ~10 nm in diameter) have properties that deviate substantially from those of the bulk material. As the particle size in semiconductors approaches the exciton diameter, the particles are referred to as quantum-size particles (*1–3*). A number of colloidal semiconductors exhibiting quantum confinement effects in either their emission or their absorption spectra have been synthesized, including Si (*4, 5*), GaAs (*6, 7*), and many of the I-VII and II-VI semiconductors (*2*). The study of

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J. L. Heinrich, C. L. Curtis, G. M. Credo, M. J. Sailor, Department of Chemistry, The University of California at San Diego, La Jolla, CA 92093.
K. L. Kavanagh, Department of Electrical and Computer Engineering, The University of California at San Diego, La Jolla, CA 92093.

*To whom correspondence should be addressed.