CHARACTERIZATION OF POLYMER SURFACES WITH ATOMIC FORCE MICROSCOPY

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ABSTRACT

Applications of state-of-the-art atomic force microscopy methods to the elucidation of the surface and near-surface structure of polymeric solids are described. Contact, tapping, force modulation, frictional force, and other modes of atomic force microscopy are described, and recent results are summarized. Conformational and chain order, crystalline order, polymer crystals, lamellar structures, lamellar surfaces, fold surfaces, and fibers and films with highly oriented molecules all yield important information. Controlled deformation of polymer surfaces, both reversible and irreversible, with the atomic force microscope, provides a wealth of information about mechanical properties on a nanometer scale. The observation of phase-separated regions and of polymer crystals lying below a smooth surface shows that not only topography but also elastic inhomogeneity can be observed in great detail with the atomic force microscope. This is a rapidly developing field, and some indications of future developments are presented.

PROBING SURFACES WITH AFM

Scanning probe microscopy constitutes a family of advanced techniques for surface analysis (1a,b,c). Although scanning tunneling microscopy (STM) was invented first, the current progress in scanning probe microscopy of polymers is largely in the development of atomic force microscopy (AFM). The universal character of the repulsive forces between the tip and the sample, which are

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employed for surface analysis in AFM, enables the examination of a practically unlimited range of materials. After being introduced as the analogue of STM for the high-resolution profiling of nonconducting surfaces, AFM has developed into a multifunctional technique suitable for characterization of topography, adhesion, mechanical, and other properties on scales from hundreds of microns to nanometers. Polymeric materials, which play an important role in modern technology, have been examined by AFM (2a,b,c). An increasing technological interest in polymer properties at the nanometer scale emphasizes the importance of AFM applications to polymers.

AFM Experiment

In the atomic force microscope, the sample surface is scanned with a probe consisting of a miniature cantilever and a sharp tip. The tip apex is in continuous contact with the surface when imaging is performed in AFM contact mode, or it is in intermittent contact with the sample in the tapping mode (3a,b) (Figure 1*a*,*c*). In this mode, the probe is driven into an oscillation at its resonant



Figure 1 (a) Schematic describing the operation of atomic force microscope. (b) Scanning and detection of the normal and lateral force variations in the contact mode using differential signals (A + B) - (C + D) and (A + C) and (B + D), respectively. To increase the lateral force sensitivity, scanning is performed sidewise as shown. (c) Tapping mode cantilever oscillation amplitude in free air and during scanning.



Figure 1 (Continued)

frequency by a small piezoelectric element. The microscopic tip is situated at the end of the cantilever, and the bending of the cantilever (contact mode) or damping of its oscillation amplitude (tapping mode) in response to the repulsive or attractive forces between the sample and the tip is monitored by an optical lever. A laser beam focused on the cantilever is reflected onto a four-quadrant photodetector, with the pairs of sectors (A, B) and (C, D) arranged to detect bending deflection, bending oscillation, and torsion of the cantilever (Figure 1b). The sample is moved in a raster pattern under the tip by the piezoelectric drive in a horizontal plane, while the vertical motion is controlled by a feedback mechanism. In contact mode, the feedback raises or lowers the sample and keeps the cantilever deflection at the set-point value. In tapping mode (Figure 1c), the oscillation amplitude, which is reduced from the amplitude of the freely oscillating probe (A_0) by tip-to-sample repulsive interactions that occur each cycle, is kept at the set-point value (A_{sp}) by adjusting the vertical (z-axis) position of the sample with the piezoelectric drive. Such operation modes, called constant force, are the most common in AFM. The variations of the z-position of the sample during scanning are plotted as a function of the x,y position of the tip to create the height image, in which gray or color contrast is used to show the z-variations.

In the following we first consider operating modes relevant to the contact mode and then discuss some pecularities of the tapping mode.

Contact Mode

Although AFM was introduced for high-resolution surface profilometry, the height image records the surface topography exactly only when the tip-tosample force is too small to deform the surface. A priori, it is difficult to say whether the tip-to-sample force is small or large enough to induce surface deformation. Therefore, measurements at different forces can be helpful in the interpretation of the image features that involve sample stiffness. This is illustrated by the height images recorded in contact mode on the surface of a microlayer polyethylene (PE) sample (Figures 2a,b). This sample is composed of alternating layers of low- and high-density polymers (for layer M, $\rho = 0.92$ g/cm³, for layer N, $\rho = 0.86$ g/cm³). The weight ratio and, consequently, the width of the M and N layers is 2:1. The height image obtained with a tip-to-sample force of 20 nN (Figure 2a) reveals a number of surface features, including traces of the ultramicrotome knife used for the surface preparation. In the height image recorded at a force of 150 nN (Figure 2b) the sample surface is seen as a microlayer pattern with alternating stripes of different contrast. The bright stripes, $2-3 \ \mu m$ in width, can be assigned to the M layers, which represent the minor component of this material. The broad dark stripes are related to low-density N layers, which are depressed more by the tip than the high-density layers.



Figure 2 AFM height images recorded in the contact mode at different tip forces: (*a*) 20 nN, (*b*) 150 nN, on the surface of the microlayer PE sample consisting of M and N components. The contrast covers height variations in the 0-380 nm range in both images.

This example shows that the magnitude of the tip-to-sample force interactions are of primary interest in AFM (4a,b). The applied forces are classified as low or high by comparison with the stiffness of a sample under investigation. The amount of deflection for a given force also depends on the tip-to-sample contact area. Measurements at different tip-to-sample forces can be obtained not only by varying the force level of the set-point but also by choosing cantilevers with different spring constants, by operating in different imaging modes, and by using different ambient media (vacuum, air, or liquid). Quantitative estimates of the force in the contact mode are based on the spring constant of the particular cantilever used. In the commercially microfabricated Si and Si₃N₄ probes with cantilevers of different shapes (triangular and diving-board) (lengths 100-450 μ m, and thickness 1–4 μ m), the spring constants vary from 0.01 to 50 N/m. The soft cantilevers are used for the contact mode and the more rigid ones for the tapping mode. In the latter mode, cantilever stiffness is required to withdraw the tip from the surface in every oscillation cycle. The magnitude of the tip-to-sample force in the contact mode at ambient conditions is between 10 and 100 nN, and it can be increased by increasing the set-point deflection values. Immersing the tip and the sample surface in liquid (water, alcohol, etc) minimizes capillary forces and is useful for low-force imaging in both the contact and tapping modes. Under liquid, forces of around 1 N/m or less can be achieved with most soft cantilevers with spring constants below 0.1 N/m.

The main use of AFM is for the observation of surface topography by recording height images, but this technique has several other important capabilities:



b

Figure 3 (*a*) Force-versus-distance curve showing the deflection of the cantilever when the sample is moved toward the AFM probe and retracted from it. (*b*) Amplitude-versus-distance curve in the Tapping mode, which escribes the changes of the amplitude of the oscillating cantilever when the sample is moved toward the probe and retracted from it.

 The dependence of the vertical deflection of the cantilever from its rest position on the vertical position of the piezodrive at a particular point on the sample is often presented in a force-versus-distance curve (often called the force curve) (Figure 3). Such curves are used for monitoring and for adjusting the tip-to-sample force. They can also be employed for characterization



Figure 4 AFM height (*a*) and force volume (*b*) images of thin lube sputter textured surface of a hard disk. The contrast covers height variations in the 0–720 nm range in (*a*) and the local force variations in (*b*). (*c*) Force plot illustrating force-versus-distance curves obtained at places indicated with the arrows on elevated (marked with *) and flat (unmarked) regions of the disk. The force variations are measured as the difference between cantilever deflections in the force curves at the z_0 position shown in (*c*). (Image is courtesy of K Kjoller, Digital Instruments, Inc.)

of mechanical properties of the surface and for observation of the adhesion or stickiness between the sample surface and tip. The pull-out force required to retract the tip from the surface can be used as a quantitative measure of the tip-to-sample adhesion (Figure 3*a*). At strong forces (left part of the force curve in Figure 3*a*), the tip may deform the surface of a soft sample. A more detailed consideration of the tip-induced surface deformation is given below.

In the recently introduced force volume mode, the force curves are collected at (64×64) mesh points on the scanned area. This technique produces maps of surface stiffness and adhesion. These capabilities are illustrated in Figures 4 and 5. The results shown in Figure 4 were obtained on the surface of a computer hard disk coated with a lubricant. Height image shows that the surface topography is characterized by flat areas with bumps of 80–120 nm in height, which have a technological function. Force curves of two types were recorded during scanning of this area, and they exhibit substantially different pull-out forces. The force volume image, which shows the variations of this difference as a function of position on the surface, reveals that the bumps are less sticky than the flat regions. In another experiment, force



Figure 5 AFM height (*a*) and force volume (*b*) images of the microlayer PE sample consisting of K and L components. The contrast covers height variations in the 0–320 nm range in (*a*) and the local force variations in (*b*). (*c*) Force plot illustrating force-versus-distance curves obtained on soft layer (marked with *) and hard layer (unmarked) in the places indicated with arrows in the height image in (*a*). The force variations were measured as the difference between the cantilever deflections in the force curves at the z_0 position shown in (*c*).

volume measurements were performed on the surface of the microlayer PE sample described above. These measurements were conducted at relatively low force, so the height image (Figure 5*a*) does not reveal the microlayer pattern. The force curves recorded on this surface are of two types, as shown in Figure 5*c*. Both exhibit similar pull-out forces but have different slopes in the repulsive force region (left part of the force curves). The force volume image (Figure 5*b*) presents the map of differences in the deflection of the cantilever at the z_0 vertical tip position, which is seen as alternating bright and dark stripes. Such a map of local stiffness shows the location of soft and hard PE layers.

2. The (A + C) - (B + D) difference signal is related to the cantilever torsion and gives a measure of the lateral force experienced by the tip. Depending on the scanning direction (often called trace and retrace), the signal changes its sign and has reversed contrast in the lateral force images recorded in the trace and retrace directions, (Figure 1*b*). Such effects, which were attributed

 height.lof
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 Image: state sta

Figure 6 AFM height image (*a*) and lateral force images in trace (*b*) and retrace (*c*) directions recorded on the microlayer PE sample. The applied force was 30 nN. (*d*) AFM height images (*d*) and lateral force images in trace (*e*) and retrace (*f*) directions at the same place as in (*a*) to (*c*) but with the applied force of 50 nN. The contrast covers height variations in the 0–400 nm range in (*a*) and (*d*), and it is proportional to the force in relative units in (*b*) to (*c*) and (*e*) to (*f*).

to differences in local friction and adhesion (5, 6) were observed for many samples. However, such observations are not necessarily indications of differences in the chemical nature of the surface regions. The lateral force imaging of the multilayer PE sample shows that the different contrast in images recorded in the trace and retrace scans can originate from different local stiffness (Figure 6a-f). In the experiment conducted at higher tip-tosample force, the soft PE layers appeared darker than hard layers in the trace image and the contrast is reversed in the retrace image (Figure 6e, f). The lateral force images recorded at small tip-to-sample force do not show such contrast variations (Figure 6b,c). This contrast behavior means that soft PE layers exhibit higher friction than the hard ones. It is natural to expect that a higher lateral force is needed to move the tip across the soft layer, due to the larger penetration of the tip into the sample. This result shows that the lateral force depends on surface stiffness and that the surface deformation caused by the tip-to-sample force should be considered in the lateral force imaging.

3. The mechanical response of the surface can be examined with AFM by forming images in the contact force mode at different force levels. With a



Figure 7 Diagram of force modulation mode showing probe scanning a low elastic modulus material from left to right. Signal amplitude increases when the tip encounters higher elastic modulus (stiffer) sites.

high force between the tip and the sample, the image contrast may depend more on variations of surface stiffness than on surface topography. To examine mechanical properties of the surface, one can also utilize the force modulation mode (7). In this mode, a periodic z-modulation is applied to the cantilever with a bimorph piezoelement, while the tip scans the sample in the contact mode (Figure 7). Such experiments are typically conducted at the resonant frequency of the driving bimorph element (8–10 kHz), and oscillation amplitudes of 1 to 5 nm are applied vertically to the base of the cantilever. In contrast to the tapping mode (Figure 1*c*), the whole probe is moving vertically. The amplitude of the cantilever bending caused by interaction of the tip and the sample is recorded with the photodetector. The observed deflection amplitude is larger when the tip interacts with hard surface regions than when it interacts with the soft surface regions. Two



Figure 8 Height (*a*) and amplitude (*b*) images recorded in the force modulation mode on the surface of composite materials consisting of carbon fibers embedded in epoxy matrix. The contrast covers height variations in the 0-150 nm scale in (*a*) and the amplitude variations in the 0-1 nm scale in (*b*). (Images are courtesy of P Maivald, Digital Instruments Inc.)

examples are chosen to demonstrate the force modulation mode. The height and amplitude images of a composite material consisting of carbon fibers embedded in an epoxy matrix are shown in Figures 8a,b. The contrast in the height image, which shows the surface topography, is much less than in the force modulation image, which shows the stiffness of the surface. The oscillation amplitude image shows more pronounced contrast between the hard carbon fiber (darker: higher amplitudes) and soft epoxy matrix (brighter: lower amplitudes). In another example, the amplitude image recorded on the surface of a tri-block copolymer (styrene-butadiene-styrene) sample reveals morphology often observed when phase-separation occurs, which is barely distinguished in the height image (Figures 9a,b). The force modulation and relevant modes are potentially important for studies of materials with frequency-dependent mechanical properties, although only a few reports are available (8a,b).

Tapping Mode

In AFM applications to soft materials, such as polymers and biological samples, it was found that high tip-to-sample forces in the contact mode and, especially the presence of lateral forces, often led to mechanical deformation of the surface. The need to avoid surface damage was one of major motivations for the development of the tapping mode, a popular AFM technique (3a,b). In this mode, short, intermittent contacts between the tip and the surface minimizes the



Figure 9 Height (*a*) and amplitude (*b*) images recorded in the force modulation mode on the surface of tri-block (styrene-butadiene-styrene) copolymer. The contrast covers height variations in the 0-5 nm scale in (*a*) and amplitude variations in the 0-6 nm scale in (*b*). (Images are courtesy of J Thornton, Digital Instruments Inc.)

inelastic deformation of the sample. Numerous examples confirmed that the effective forces experienced by the sample in the tapping mode are smaller than in the contact mode (9a). Comparison of contact mode and tapping mode images of 3-nm wide nanofibrils, in stretched PE tape, showed that these nanofibrils are damaged less during imaging with the tapping mode (9b).

A broad range of soft materials, especially biological samples, became accessible for imaging (10) with the advent of the tapping mode. The operation at small forces does not totally exclude the possibility of surface deformation during scanning. Measurements at different force levels are an indispensible part of tapping mode imaging. In this mode, variation of the tip-to-sample force can be achieved by changing the driving amplitude and the set-point amplitude A₀ and A_{sp}. The effective tip-to-sample force increases with the increase of A_0 and/or the difference, $A_0 - A_{sp}$ (11). In the tapping mode, in contrast to the contact mode, the height images show minor, and for many samples, barely detectable variations with changes in the force. The frequency and phase of the oscillating cantilever are more sensitive to the tip-to-sample interaction force. The description of the vibrating probe as a harmonic oscillator shows that repulsive tip-to-sample force interactions cause a shift of the resonant frequency to high frequencies and related phase changes (12). Attractive forces decrease the resonant frequency. The images of frequency shifts and phase changes provide new information about surface topography and other properties (13a,b). The frequency shift images are not widely used in measurements at ambient conditions because the low Q-factor of the cantilever in air makes it difficult to track the small negative frequency shifts and to use them for the feedback required for imaging in the attractive force regime. Such an operation works well in ultra high vacuum (UHV) where the Q-factor of the oscillating probe is extremely high. Atomic-scale defects of several semiconductor lattices were observed in this mode (14).

In routine AFM applications at ambient conditions, the phase images are very useful. The phase images, which are often recorded simultaneously with the height images, show the variations, at different points on the surface, of the phase of an oscillating probe determined at v_0 , the fundamental resonant frequency of the freely oscillating probe. Before the tip engages the sample, the phase of the freely oscillating probe was adjusted to zero. Phase images provide the best contrast of fine morphological and nanostructural features due to their high sensitivity to surface imperfections such as steps, cracks, and the like. On surfaces with local variations of mechanical properties, the phase changes are even more informative (15). The interpretation of the phase images of multicomponent surfaces is facilitated by analysis of phase curves, which are plots of phase versus A_{sp}/A_0 (Figure 10*a*,*b*). In these measurements, probes with force constants of around 40 N/m were applied. The phase curves obtained on mica at different A_0 show that at small amplitude the phase behavior is different from that at high amplitudes (Figure 10a). This is most likely due to the liquid contamination layer existing on any surface in air. The phase shift determined on materials with elastic moduli above about 100 GPa (mica, Si, sapphire, etc) exhibits almost identical behavior: Phase shift increases with decrease of the A_{sp}/A_0 ratio and saturates at A_{sp}/A_0 values below 0.3 (Figure 10b). In the experiments on PE samples with different density, the phase shift behavior was found to depend substantially on polymer density, which is related to elastic modulus (Figure 10c, d). [In addition to the pair of M and N polymers mentioned earlier, we identify another pair of polyethylenes with different densities as K $(\rho = 0.96 \text{ g/cm}^3)$ and L $(\rho = 0.92 \text{ g/cm}^3)$.] The K and L polymers were used for preparation of another microlayer K/L sample, which was also examined with AFM. At high A_{sp}/A_0 ratios (0.8 to 0.9), the phase shifts determined on different components have similar magnitude. At light tapping, when the tipto-sample force interactions are small, the phase differences between materials with different stiffness are also small. Therefore, the phase images emphasize surface nanostructure of the microlayer K/L sample, which is barely seen in the height image (Figure 11*a*,*b*). With decrease of A_{sp}/A_0 , the phase curves of different PE samples behave differently. For the high-density material K, the phase curve resembles those for materials with high elastic moduli (Figure 10c). The phase curves for L and M exhibit similar behavior, but at A_{sp}/A_0 in the 0.8 to 0.3 range (moderate tapping), the positive phase shifts are smaller than those for K. At moderate tapping, the phase curves for N (PE with large concentration of short-chain branches) are characterized mostly by negative shifts (Figure 10*d*). This observation can be explained tentatively either by adhesion between the tip and the sample caused by increasing of the tip-to-sample contact area or by viscoelastic effects.

The comparison of the phase curves of different PE samples at moderate tapping indicates that they are directly related to material density and elastic modulus. This finding is consistent with the expected correlation between the positive frequency shift that is a measure of the sample stiffness. In other words,



Figure 10 (*a*) Phase shift versus A_{sp}/A_0 determined on mica at different A_0 . (*b*) Phase shift versus A_{sp}/A_0 determined on different materials with $A_0 = 140$ nm. (*c*) Phase shift versus A_{sp}/A_0 determined on the different PE layers (L and K) with $A_0 = 100$ nm. (*d*) Phase shift versus A_{sp}/A_0 determined on the different PE layers (M and N) with $A_0 = 100$ nm.



Figure 10 (Continued)

the force interaction with harder materials leads to large positive frequency and phase shifts, both measured with respect to the frequency and phase of the freely oscillating cantilever, as compared with the interaction with soft material (13b). As a result, the phase images shows surface areas with different stiffness as seen in Figure 11*c*, where K layers are brighter (larger phase shifts) than L layers. A similar effect was found in the phase image of the microlayer M/N sample (Figure 12*a*,*b*).

The correlation between the phase contrast and stiffness of the surface areas at moderate tapping is reversed when imaging is performed at A_{sp}/A_0 below 0.2 (hard tapping). High-density layers in the K/L and M/N samples are darker than low-density layers (Figure 11*c*, Figure 12*d*). This effect is also consistent with the behavior of the corresponding phase curves at A_{sp}/A_0 below 0.3. It is





Figure 11 Height and phase images recorded on the microlayer PE sample consisting of K and L components. The images in (*a*) and (*b*) were recorded at $A_{sp}/A_0 = 0.9$, the images in (*c*) and (*d*) at $A_{sp}/A_0 = 0.5$ and 0.1, respectively. The contrast covers height variations in the 0–250 nm range in (*a*) and (*c*), and the phase variations in the 0–120 degree range in (*b*), and in the 0–80 degree range in (*d*).

worth noting that the height images of the K/L microlayer sample obtained at moderate and hard tapping are identical to those in Figure 11*a* and therefore are not shown. Although the reversal of the phase contrast at small A_{sp}/A_0 values is not fully understood, larger frequency and phase shifts in hard tapping on a soft surface might be related to the fact that both the average time the tip spends in contact with the sample and the tip-to-sample contact area become substantially larger on a soft surface than on a hard surface. The increased contact area led to the effective increase of the stiffness of soft layers.



Figure 12 Height (*a*,*c*) and phase (*b*,*d*) images recorded on the multilayer PE samples consisting of M and N components. The images in (*a*) and (*b*) were recorded at $A_{sp}/A_0 = 0.9$, the images in (*c*) and (*d*) at $A_{sp}/A_0 = 0.5$. The contrast covers height variations in the 0–170 nm range in (*a*), and the phase variations in the 0–20 degree range in (*b*), in the 0–80 degree range in (*c*), and in the 0–50 degree in (*d*).

To conclude, phase detection in the tapping mode allows extension of the mechanical studies with AFM to soft samples, which are not accessible in the force modulation mode. The stiffness-related contrast of the phase images offers new possibilities for imaging multicomponent polymer samples. This is confirmed by the phase images of several polymer systems (Figures 11,12). Such an approach can be generalized, because by choosing an appropriate probe material, the elastic moduli in other ranges can be examined in a similar manner. For example, for phase detection of metals and their alloys, probes with higher spring constants than those used in the present study should be used.

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To extract comprehensive data about surface topography, adhesion, and mechanical properties, measurements should be performed at different operating conditions. Minimizing the applied force helps to avoid surface deformation and also to reduce the tip-to-sample contact area. Increasing contact area adversely affects the AFM resolution for imaging of partially or poorly ordered structures. This is especially important for probing surface structures with dimensions in the 1 to 100 nm range, because the estimated diameter of the tip-to-sample contact area during imaging of organic surfaces with a force of few nN is in the range of several nanometers (16). Although the usefulness of AFM to examine adhesion and mechanical behavior of polymers at submicron scales is well established, only the first steps toward quantative studies have been undertaken. Further progress of these areas requires the close interplay of experimental and theoretical approaches. Macroscopic theories need to be modified to describe the tip-to-sample interactions at the nanometer scale.

IMAGING POLYMER LATTICES AND CHAINS

The primary goal of the invention of AFM was to observe surface structures at the atomic scale. This capability was demonstrated in the contact mode studies of crystalline surfaces of inorganic and organic crystals, semiconductors, and the like (1a,b,c). It was also found that unlike STM images, which often reveal atomic-scale defects, in most cases the AFM images show perfect lattices, even of samples whose STM images indicate the presence of many defects. These findings raised questions about the nature of atomic-scale AFM imaging and led to a further search for methods that provide true atomic resolution (14, 17). In the contact-mode AFM operating at tip-to-sample forces in the nN range, the contact involves tens of atoms on the tip and a similar number on the sample. The multi-atom contact does not exclude the possibility of atomic-scale imaging from periodic modulation of the tip motion by a surface lattice (18). In such a case, the AFM images reveal surface lattices, but local atomic- and molecularscale defects are averaged. A possibility for reducing the tip-to-sample contact area to atomic-scale dimensions, and thereby allowing the detection of atomicscale defects, was recently demonstrated using the analogue of the tapping mode in UHV (14). For practical applications at ambient conditions, the ultimate resolution of the AFM is often limited by the nature of the sample. The smallest features resolved unambiguously in images of partially ordered surfaces are limited by the size of the tip-to-sample contact area.

Observations of Surface Lattices

In the first AFM applications to polymers, it was a challenge to achieve molecular-scale resolution. Such studies were performed on the surfaces of polymer



Figure 13 AFM force image of cyclic alkane $C_{48}H_{96}$ crystal. The contrast covers force variations in the relative units.

and monomer crystals and on highly oriented polymer samples. The images of the surfaces composed of ends of linear $C_{36}H_{74}$ or folds in cyclic $C_{48}H_{96}$, which are considered as model compounds for polyethylene (PE), were obtained in early AFM images (19). The patterns of these images are in good agreement with the crystallographic positions of end methyl groups and $-(CH_2)-(CH_2)$ molecular folds. The image obtained of the surface composed of ends of molecules in the platelet-shaped crystal of $C_{48}H_{96}$ is shown in Figure 13. Individual bright spots that form a periodic lattice in the image can be assigned to $-(CH_2)-(CH_2)-$ groups. The topmost H-atoms were not separately resolved due to their high mobility (in case of $-CH_3$), or the inadequate resolution of the contact AFM mode.

The arrangement of molecular folds on the lamellar surfaces of singlepolymer crystals has long been debated (20). Although the structure of these crystals is well known from diffraction studies, there are several models suggesting either ordered adjacent re-entry or various disordered structures of the lamellar surface.

AFM was applied to clarify morphological and structural features of polymer single crystals. Well-ordered arrays of folds were observed in height mode AFM observations of fold surfaces of some PE crystals (Figure 14*a*) (21), but in



general the images of PE fold surfaces are not as clear. More typically, images such as those shown in Figure 14*b* are obtained after the removal of spatial frequencies higher than 0.25 nm^{-1} , which amounts to ignoring features in the image that are smaller than the diameter of a molecule. Such images suggest that the folds adjacent to a particular fold are found at levels that differ up or down in a random way by distances around 0.25 nm, which is one c-axis repeat distance in the PE single crystal.

Also, because the chain axis in a PE lamellar crystal is tilted with respect to the normal to the fold surface owing to the hollow pyramidal growth habit of PE, a fold that protrudes above its neighbors will have its high point, which is observed by the AFM tip, moved both sideways and upward with respect to the fold surface. The roughness of fold surfaces with folds at differing heights, the unknown but probably too large radius of the AFM tips currently available, the chain tilt with respect to the fold surface, as well as the uncertainty in the angle between the normal to the fold surface and the direction of the line along which the tip is carried as the cantilever bends, all combine to make it impossible to unambiguously interpret images such as Figure 14*b*.

AFM images showing periodic lattices are rarely obtained from the fold surfaces of lamellar crystals of polymers. A lower magnification image of the fold surface shows larger scale structures, which are patches containing a hillock with an altitude of up to one nanometer, that are sometimes observed on the fold surface of PE crystals, particularly at the sector boundaries (Figure 15). Images of the lateral surfaces of oriented polymers (2c) often show higher resolution of adjacent polymer molecules, presumably because these lateral surfaces are smoother on a local scale than the fold surfaces.

Polyethylene oxide (PEO) crystallizes into lamellae in which the chain axis is along the normal to the fold surface. Recently, Nie et al obtained an AFM image of the fold surface of a lamella of PEO (Figure 16) (22). The folds all appear to be at the same level. The Fourier transform of the image shows that the spacing is about 0.65 nm, which is close to that expected from the crystal structure of PEO.

Polydiacetylenes (PDA) are a class of polymers that can be obtained in crystalline form by solid-state polymerization of their monomers. Consequently, such crystals possess well-defined surfaces that facilitate recording of

Figure 14 (*a*) AFM image of the fold surface of a lamellar PE crystal, with high resolution. (Reprinted from *Polymer*, with permission from Elsevier Science, Ltd.) (*b*) Typical height mode image of the fold surface of a lamellar PE crystal, filtered to remove high spatial frequencies. The contrast covers height variations in the 0–0.5 nm range.

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Figure 15 AFM height image obtained on the lamellar surface of PE single crystal. The contrast covers height variations in the 0-1 nm range.

molecular-scale AFM images in the contact mode. Such images were obtained on both the largest planes of lozenge-shaped crystals of poly-2,4-hexadienylenebis(p-fluorobenzenesulfonate) (pFBS) and its monomer. The images exhibit similar patterns, which are consistent with the crystallographic lattices of these compounds (23). The difference between the atomic-scale pattern within the unit cell of the AFM images and surface molecular structure derived from the crystallographic data may be due to surface changes induced by the tip.

Conformational and Chain Order in Polymers

Observations of chain packing and conformational order of oriented polymers were reported by several research groups. Molecular-scale images were obtained on lateral surfaces of oriented samples of PE (24a,b), polytetrafluoroethy-lene (PTFE) (25a,b), polypropylene (26a), and polybutene-1 (PB-1) (26b). Images showing the arrangement of polymer chains in stretched PE tape and in



Figure 16 (*a*) AFM height mode image with lattice resolution of chain folds obtained on the lamellar surface of PEO single crystal. The inset shows the Fourier transform of the image. (*b*) AFM height mode image, at low magnification, of the lamellar crystals from which the lattice resolution was obtained. (Reprinted from *Polymer Communications*, with permission from Elsevier Science, Ltd.)

an oriented PTFE layer prepared by rubbing are shown in Figure 17*a,b*. The interchain distances derived from these images are consistent with the results obtained by X-ray and electron diffraction. The difference between the 0.5-nm interchain distance of PE and the 0.56-nm interchain distance for PTFE reflects the larger size of the CF₂ groups. The periodicity along the chains found in such images confirms the all-*trans* conformation of PE chains and the helical conformation of PTFE chains. A more complicated molecular-scale lattice pattern was observed by Jandt et al (26b) on a thin oriented film of PB-1 (Figure 17*c*). This pattern is characterized by a repeat distance of 0.7 nm along the stretching direction and by a repeat distance of 1.2 nm in the periodicity of 0.65 nm found by the X-ray diffraction of oriented films. Although the fine structures distinguished within the unit cell are related to the conformation of PB-1 chains, the location to individual molecular groups is not precisely defined by the AFM images (26b).

AFM also complements electron microscopy and diffraction methods in studies of epitaxially grown polymer crystals. The recording of lattice images of lateral surfaces of isotactic polyproylene crystals allows the sense of the helicity of the polymer chains to be observed (27a,b). A similar approach has been used to determine the helicity of isotactic polypropylene chains in the oriented samples (28).

Individual biological and synthetic polymers molecules can be observed when they are deposited from dilute solutions as isolated and extended chains on flat substrates. Many STM and AFM studies have been performed on



Figure 17 Molecular-scale AFM images obtained on the surfaces of the stretched PE tape (a), an oriented layer of PTFE (b), and melt-drawn PB-1 film (c). The contrast covers force variations in the relative units in (a) and (b), and height variations in the 0–1 nm scale in (c). [Image in (c) is courtesy of M Miles, Bristol University.]



Figure 18 AFM height image showing DNA strands on mica. The contrast covers height variations in the 0–1 nm range. (Image is courtesy of M Allen, Digital Instruments, Inc.)

single biological macromolecules, especially DNA (29). Images showing DNA strands (Figure 18) and their nanostructural features can be routinely obtained, but important aspects still need to be critically evaluated. The evident problem, besides the possible force-induced surface deformation, in structural characterization of such objects is related to the influence of the tip shape on images of single polymer strands.

AFM may also be used to examine some aspects of polymer chain dynamics. Kumaki et al (30) studied the organization in ultrathin poly(styrene-bmethylmethacrylate) [p(s-b-MMA)] films collected on mica from the water sub-phase. In samples having less than a monolayer of coverage, patches consisting of grains, about 30 nm in diameter, of hydrophobic styrene blocks, which are phase separated from hydrophilic MMA segments, were observed. The MMA segments form a thin, compact layer surrounding the styrene particles. When the sample was exposed to a relative humidity of 80%, the MMA strands unfolded and adopted a more extended chain conformation. This example illustrates the ability of AFM to monitor conformational changes. Possible influences of tip-to-sample force interactions on such dynamic processes must be kept in mind.

EXPLORING STRUCTURAL HIERARCHY

Visualization of the molecular-scale polymer features in AFM images recorded in the contact mode is attractive, and it can be used in combination with data obtained by X-ray diffraction and electron microscopy techniques to characterize the chain conformations and their packing in ordered systems. Unfortunately, the inability of contact-mode AFM to detect local molecular-scale defects at ambient conditions limits the analysis of structural imperfections, which strongly influence the physical properties of polymers. Further progress in the molecular-scale imaging can be expected with oscillatory modes, which provide atomic-scale resolution in UHV (31).

AFM applications to polymer surfaces are providing interesting images of nanometer-scale and micron-scale polymer structures, many of which are barely accessible by other microscopic techniques.

Crystalline Order and Structures up to 100 µm

After a discussion of conformational and chain order, polymer structures on the nanometer scale revealed in AFM images of different samples are described.

The folding of molecular chains into a lamellar struc-LAMELLAR STRUCTURES ture is one of the unique features of polymers. Lamellae are a common nanostructural element of many polymeric materials. In dilute solutions, lamellar folding is associated with the growth of single crystals. Lamellar crystals also grow from the melt. PE single crystals exhibit a hollow-pyramidal shape in solution that collapses to a flat but often wrinkled or torn shape on a flat substrate. Single crystals of PE with growth spirals, which were deposited on mica, are shown in Figure 19*a*,*b*. Note that the phase image emphasizes the edges of single crystals and growth spirals. There are no phase differences between surfaces of PE single crystals and substrate (mica) because the modulus of PE along the chain is relatively high (220 GPa for c-axis of PE single crystals, 170 GPa for mica) and is not detected with the probe whose spring constant is about 40 N/m. Phase contrast between the surface of mica and the fold surface of a PE single crystal was observed when scanning was performed with a probe whose stiffness was about 150 N/m. Imaging of the lamellar surfaces with AFM



Figure 19 AFM height (*a*) and phase (*b*) images showing aggregates of PE single crystals. The contrast covers height variations in the 0-120 nm range in (*a*) and phase variations in the 0-80 degree range in (*b*).

showed nanoscale features of single crystals, among which are 15–20-nm wide rows of patches or hillocks, with a height of about 1 nm, along the diagonals of the lozenge-shaped PE crystals. These diagonals divide the PE crystal in four sectors or fold domains in which the pattern of the folds is oriented differently (32a). In another AFM study, thickness differences of a few tenths of nanometers were found in adjacent growth sectors of PE crystals with different crystallographic facets (32b). Patches that were up to a nanometer higher and about 10–20 nm in diameter are distinguished on all sectors of most PE single crystals examined (Figure 16).

Lamella are generally produced when a polymer is cooled from the melt, but the shape of such lamella is different from the usual lozenge shape. In semicrystalline polymers, lamellar structures often coexist with uncrystallized material, which accumulates at the surface of the sample and between the lamellae. These structural features are demonstrated in Figure 20a,d, where the height and phase images of the surface of a low-density linear PE film are shown. With light tapping, the height image (Figure 20a) reveals the smooth corrugated topography of this film. The phase image (Figure 20b) shows only faint traces of lamellar structures in one of the elevated areas. With hard tapping, the corrugations seen in the height image (Figure 20c) become more pronounced and the lamellar structure is evident. The phase image (Figure 20d) distinctly reveals that lamellae are a dominant structural element in this sample and that the topmost layer consists of material with no structure on the nanometer scale. An increase of the tip-to-sample interactions causes the



Figure 20 AFM height and phase images of PE tape recorded in light (*a,b*), and hard tapping, (c,d). The contrast covers height variations in the 0–200 nm range in (*a*)) and in the 0–250 nm range in (*c*) and phase variations in the 0–25 degree range in (*b*) and (*d*).

underlying lamellar structures to appear in both the height and phase images. The reverse situation, with lamellar structures a minor component embedded in a structureless matrix, is shown in Figure 21*a,b*. These images were recorded on the microlayer PE (M/N) sample after annealing at 190°C and cooling to room temperature. Although the N component is a non-crystallizable polymer, the phase image (Figure 21*b*) distinctly shows the presence of crystalline structures in this layer. The height image (Figure 21*a*) is not helpful in this case. The lamellar structures entered the N layer from the interface between the M (dark) and N (bright) layers. Dendritic structures (dark) were observed within the N layer. This observation indicates diffusion of the high-density M component



Figure 21 AFM height and phase images obtained on microlayer PE sample (M/N) after thermal treatment (2 h at 190° C). The contrast covers height variations in the 0–270 nm range in (*a*) and phase variations in the 0–17 degree range (*b*).

into the low-density N layer, where it crystallized in the form of dendritic structures. The dendrite branches are in the form of lamellar crystals about 20 nm wide, and the darker color in the phase image reflects the higher stiffness of these regions as compared with the stiffness of the structureless surrounding.

AFM observations of lamellar crystals and their nanometer-scale structure were reported by several groups. These studies are aimed at a better understanding of the lamellar organization in spherulites and at understanding crystal growth (?,b). Observations of lamellar crystals by microscopic methods sometimes requires etching away the structureless topmost layer. For a number of systems, this procedure can be avoided by utilization of phase imaging, which also provides information about the thickness of the topmost layer (SN Magonov et al, in preparation).

NON-LAMELLAR ORDERING In the examination of surfaces of polymers, one finds structures of different size, which do not necessary resemble lamellae. Several examples are given below.

Morphology and nanostructure of extruded samples of pure copolyester (CPEST, Kodar) and CPEST blended with polycarbonate (PC), on the surface perpendicular to the extrusion plane were examined with AFM (SN Magonov et al, in preparation). Figure 22*a* shows the ultramicrotomed surface of the microlayer PC/CPEST (2:3) sample. The CPEST layers consist of slightly larger grains than are present in the neighboring PC layers. The phase image (Figure 22*b*) shows almost no differences between PC and CPEST layers, which indicates equal stiffness of these layers. This finding is consistent with



Figure 22 AFM height, (*a*) and phase (*b*) images of the interface between the PC and CPEST layers in the microlayer sample. The contrast covers height variations in the 0-100 nm range in (*a*) and the phase variations in the 0-120 degree range in (*b*). The extrusion direction is from lower left to upper right.



Figure 23 AFM height and phase images of microlayer PC/CPEST sample after 2 h annealing at 195° C. The contrast covers height variations in the 0–100 nm range in (*a*) and phase variations in the 0–120 degrees range in (*b*).

the almost equal density of CPEST, $\rho = 1.192 \text{ g/cm}^3$, and PC, $\rho = 1.194 \text{ g/cm}^3$ (36). CPEST can be partially crystallized, whereas PC is non-crystallizable. The AFM images of the ultramicrotomed surface of the PC/CPEST sample, annealed at 195°C, reveal elongated spherulite-like patterns in the CPEST layers (Figure 23*a*,*b*). The phase image (Figure 23*b*) indicates that these patterns are harder than the surrounding material, thus they can be assigned to CPEST

crystallites, which have a nanostructure different from the PE lamellar dendrites found on the ultramicrotomed surface of the microlayer M/N sample.

Similar crystalline, spherulite-like patterns were found in the extruded samples of pure CPEST and melt-blended PC/CPEST material after annealing for 2 h at 195°C. Phase images (Figure 24b,c) show that CPEST crystallites in the melt-blended sample consist of slightly bent stacks. Spherulite patterns with cross-hatched nanostructure were found in pure CPEST. These examples demonstrate that AFM can produce new data about the crystallization of copolyesters.

A similar approach can be applied to describe ordering of polymer dendrimers, a new class of materials in which large macromolecules are formed through repeated chemical branching (37). Although the chemical structure of these polymers excludes the possibility of lamellae folding, crystal-like structures are often observed for such materials. In Figure 25*a*, *b*, crystallites found in deposits of fourth generation dendrimer (38) on mica show rectangular platelet structures as well as more fully developed spherulites. Ordering of these large macromolecules into crystal-like structures likely resembles the assembly of micelles of low-molecular weight amphiphiles into supramolecular aggregates, which was recently observed with AFM (39). In another example, the ordering of a carbosilane dendrimer observed in ultrathin films on mica is shown in Figure 26a. The polymer layer lying directly on the substrate is 3.5 nm thick and almost totally covers the mica surface, leaving only a few holes. Numerous droplets with a pedestal and onion-like top part were found on the first layer. This polymer is soft, and it cannot be examined in the contact mode without being destroyed. Even more, it is one of a rare class of materials that are deformed by the small tip-to-sample forces used in the tapping mode. The height profile across two elevated patterns in the upper part of Figure 26a shows that the height of the structure decreases substantially with an increase of the applied force (Figure 26b).

To explain the organization of dendrimers, strong intermolecular interactions and partial interpenetration of neighboring macromolecules should be considered. The observation of a similar structure for two other dendrimer systems (40) indicates the existence of common features of this ordering.

Oriented Polymer Materials

Stretching of polymers is one of the most common methods for preparation of high-performance materials with outstanding mechanical properties. The optimization of mechanical behavior of oriented polymer samples requires understanding the structure-property relations, based on many different experimental techniques. Surface features of oriented polymers, from molecular-scale lattices to large-scale morphologic patterns, can be examined with AFM. The imaging of polymer nanostructures and their modification during stretching is







Figure 25 (*a*) and (*b*) AFM height images obtained on different parts of 4th generation dendrimer adsorbate on mica. The contrast covers height variations in the 0-10 nm range in (*a*) and in the 0-90 nm range in (*b*).

often a primary goal of AFM studies of oriented polymers. Several aspects of such imaging are discussed below.

The morphology and nanometer-scale structure of polymers are often studied by electron microscopy techniques: TEM and SEM. Because these methods require elaborate sample preparation, AFM is more convenient for such studies. With AFM, one can observe nanoscale structural features near the surface of a thick sample that are not as accessible by TEM and SEM. One example, see Figure 27a,b, shows height and deflection images recorded in the contact mode, with 2 nN force, on stretched ultrahigh-molecular weight PE tape (41). The images show nanofibrils that are oriented parallel and perpendicular to the stretching direction. The parallel nanofibrils are 5–7 nm in width; the transverse nanofibrils are 3–4 nm in width. These features are found only in the topmost layers, which can be removed by the scanning tip with applied force larger than 5 nN. After removal of these layers, wider nanofibrils (diameters of ~20–30 nm) with periodic contrast changes (repeat distance of ~25 nm) along the stretching direction are observed (Figure 28*a*). The molecular-scale image in Figure 28*b* shows that brighter places along the nanofibrils are related

Figure 24 (*a*) Height image of a crystalline pattern in the melt-blended PC/CPEST sample. (*b*, *c*) Phase images with different magnification recorded in the central part of the crystalline pattern shown in (*a*). The contrast covers the height variations in the 0-150 nm range in (*a*) and the phase variations in the 0-12 degree range in (*b*) and (*c*). The extrusion direction in these images is from lower left to upper right.



Figure 26 (*a*) AFM height image of carbosilane dendrimer adsorbate on mica. The contrast covers height variations in the 0–60 nm range. (*b*) Cross-section profiles determined across two elevated patterns in (*a*). The upper profile is determined from the height image measured with $A_{sp}/A_0 = 0.75$, the middle profile is from the height image measured with $A_{sp}/A_0 = 0.5$, and the lower profile is from the height image measured with $A_{sp}/A_0 = 0.25$.

to harder surface areas with well-defined chain packing, whereas darker places correspond to softer areas, which are depressed more by the tip-to-sample force. Similar periodic contrast with repeat distances in the 15–25 nm range were obtained in the AFM images of stretched, isotactic polypropylene and nylon samples. These findings are consistent with the X-ray diffraction data obtained from oriented polyolefins. The data show periodic density variations (repeat distances are ~10–30 nm), which are known as the long period.

The example given shows that by AFM imaging, using different applied forces, structural information about both outer layers and the core structure of fibrils can be obtained. The topmost layers are important for evaluation of the sample adhesion, whereas the tensile characteristics of oriented materials are largely determined by the structural organization in the core part. The



Figure 27 AFM height (*a*) and deflection (*b*) images obtained on the stretched PE tape. Stretching direction is from lower left to upper right. The contrast covers height variations in the 0-25 nm range in (*a*) and force variations in relative units in (*b*). These images were obtained in the contact mode under water.



Figure 28 (*a*) and (*b*) AFM height images obtained on the stretched PE tape. The contrast covers variations in the 0-50 nm range in (*a*) and in the 0-2 nm range in (*b*).

experience accumulated in studies of stretched PE tapes was applied in the characterization of commercial ultrahigh-molecular weight PE fibers (42).

The use of the tapping mode and phase imaging for studies of oriented samples also can be rewarding. The height and phase images obtained from the highly oriented PE sample produced by extrusion are shown in Figure 29a,b. The phase image shows stiffness variations along the nanofibrils.



Figure 29 AFM height (*a*) and phase (*b*) images obtained on the surface of extruded PE sample with extrusion ratio 60. The contrast covers height variations in the 0-25 nm range in (*a*) and phase changes in the 0-4 degree range (*b*).

Another application of AFM studies of oriented polymers is monitoring of structural changes that accompany deformation processes. The combination of microtensile devices with an AFM is useful for this purpose (43a,b). Detailed information about the transformation of crystalline morphology and lamellar structure into nanofibrillar architecture can be obtained by analyzing the same areas of polymer sample as the stress and strain are increased.

Thermally Induced Structural Changes

The evaluation of the performance of polymeric materials often requires a knowledge of thermotropic structural changes accompanying melting, crystallization, or glass transition. AFM improves the characterization of thermally induced structural rearrangements by imaging at different temperatures. Mechanical properties of polymer samples are temperature dependent. These materials usually become softer at elevated temperatures, so tapping mode measurements in a broad temperature range are very instructive. The high sensitivity of AFM phase images to differences in density of the polymer is useful, and one of the first examples of such studies is given below (44).

Poly(diethylsiloxane) (PDES) is a polymer with a flexible inorganic backbone $[-Si(C_2H_5)_2-O-]_n$. PDES exists in different structural states (45), i.e. at temperatures below 280 K, PDES is in a crystalline state, and above 320 K it is in an amorphous state. At room temperature, PDES is a mixture of partially ordered (mesomorphic) and amorphous materials, and it is too soft to be examined with the AFM contact mode. For AFM studies, a polymer layer was



Figure 30 AFM height and phase images of PDES patches deposited on Si substrate by rubbing. The contrast covers height variations in the 0-600 nm range in (*a*) and phase changes in the 0-80 degree range (*b*).

deposited on a Si substrate by rubbing. The height and phase images recorded at room temperature are shown in Figure 30a,b. The height image shows PDES patches 200 to 300 nm high lying on the Si substrate. More distinctive features are seen in the phase image, where the bright areas correspond to stiff substrate regions, and the dark areas correspond to the amorphous polymer. Arrays of elongated structures found within the amorphous layer have a contrast that is closer to that of hard regions than to the amorphous polymer. These structures can be assigned to PDES in a mesomorphic state. The phase images in Figure 31a,b emphasize the nanostructure of one such set of elongated elements. It is evident that the single element consists of several 30–40-nm wide linear strands attached together with softer amorphous material between the strands. These linear strands can be assigned to PDES lamellae.

With the decrease of temperature to 273 K, all the PDES transforms into the mesomorphic state, and in many areas, a more compact lamellar packing is observed. These lamellae are oriented perpendicular to the rubbing direction and lie along a backbone that is parallel to the rubbing direction (lower left to upper right in Figure 31). PDES crystallization below 273 K is accompanied by further changes of sample morphology and nanostructure. The height image of crystalline PDES (Figure 32*a*) shows oriented morphology with patterns whose shape reveals their monoclinic crystalline structure. The phase image in Figure 32*b* reveals a linear substructure with 50-nm wide stripes oriented along the rubbing direction. The phase image in Figure 32*c* was recorded during the process of crystallization, and it shows the crystallization front moving from the lower



Figure 31 (*a*) and (*b*) Phase images with different magnification obtained on the PDES patches also seen within the dark area of Figure 30*b*. The contrast covers phase variations in the 0-90 degree range in (*a*) and in the 0-100 degree range in (*b*).

left toward the upper right. This example demonstrates the capability of AFM for monitoring thermally induced structural transitions in polymer samples.

CHARACTERIZATION OF POLYMER MECHANICAL PROPERTIES

AFM studies of polymers reveal that in certain circumstances the image contrast correlates with mechanical properties of the sample. In the near future, quantitative estimates of polymer mechanical characteristics from AFM data should become more reliable. This possibility, to access materials properties at the micron and submicron scale, is a unique feature of AFM, and it will be rewarding to check the relationship between mechanical characteristics at large and small scales. Definite problems need to be solved before quantitative evaluation of elastic and storage moduli from the contact mode and tapping mode experiments is straightforward. The main difficulties are related to precise measurements of the tip-to-sample forces and the sample deformation. The measurement of the forces requires a precise determination of the spring constant of the cantilever and of the instrumental sensitivity during the experiment. Poor knowledge of the geometry of the apex of the tip presents serious difficulties for evaluation of the tip-induced sample deformation and tip-to-sample contact area, which are indispensible for the quantitative determination of elastic moduli. A close look at this problem is given below. Our description is restricted to discussion of elastic deformation of polymer samples, but a broadened application of AFM to polymers must also include the examination of viscoelastic behavior (8).





Figure 32 Height (*a*) and phase (*b*) images obtained on the PDES patches crystallized at -5° C. (*c*) Phase image showing the front of crystallization. This image was obtained at the same area as those in (*a*) and (*b*). The contrast covers height variations in the 0–182 nm range in (*a*) and phase variations in the 0–15 degree in (*b*) and in the 0–50 degree range in (*c*).

Surface Deformation and Elastic Modulus

The tip-to-sample force interactions are a key issue in AFM. The surface deformation caused by the tip-to-sample force can be observed on different scales. The deformation of PE microlayers with different density was documented in Figure 2. Image contrast related to the long period was detected in the highforce images of stretched polyolefin tapes (Figure 28), providing an example of the surface deformation on the nanometer scale. Tip force-induced conformational changes were recently observed on protein crystals (46). In AFM images recorded at different force levels in the contact mode on layered crystals of transition metal compounds, the tip-induced depression of individual atoms was observed (46). These deformation effects are caused by different local "hardness" of atoms, which depends on their structural and chemical bonding environment. In addition to macroscopic surface deformation resulting from the tip-to-sample force, which is predicted by continuum theory, the force from the tip also induces stiffness-dependent surface corrugations on an atomic scale (47). The atomic-scale corrugations can be qualitatively modeled with crystallographic data and interatomic potentials. The macroscopic surface deformation can be treated in the framework of different continuum mechanics deformation theories.

The simple Hertz approach (48) describes elastic deformation z of the flat surface by a spherical tip with radius R:

 $z = \alpha (F^2/R * \mathrm{E}^2)^{1/3},$

where $E = elastic modulus of the sample, \alpha$ is a coefficient, and *F* is the applied force. Account is taken of the fact that the elastic moduli of polymer samples are smaller than those of the Si tip and that the Poisson ratio of the polymer samples is close to 0.5. Analysis of the tip-to-sample forces should include the possible contribution of adhesion, and there are several relevant theories. The effect of adhesion may be neglected when the sample and the surface regions have similar adhesion and also in high-force AFM studies when the tip behavior is mostly governed by the mechanical properties of the subsurface part of the sample.

The analysis of the Hertz equation for a Si probe on a Si wafer shows that at a tip-to-surface force of 10 nN, the contact radius is around 0.1 nm. In such a case, the accuracy and reproducibility of the AFM measurements of surface features less than a nanometer high are essentially dependent on the profile of the tip apex. Polymer samples with elastic moduli in the MPa to GPa range can be deformed much more by the Si tip. (Under common experimental conditions, using the Si tip, contact-mode AFM performed on the surface of a bulk polymer surface engenders tip-to-sample force of 10 to 20 nN, stress of several GPa at the tip, and surface indentations in the 10 to 100 nm range.) For a thin polymer

films on a rigid substrate, the mechanical response to deformations exceeding 10% of the film thickness depends on the modulus of the substrate.

Hertz theory can be used to relate the force dependence of the apparent step height between the hard and soft PE layers, discussed above, and the force curves obtained on the same sample. The difference in the indentation of materials with different elastic moduli (subscripts: h is hard, s is soft) is expressed as

$$z_{\rm s} - z_{\rm h} = rac{lpha}{R^{1/3}} \left(rac{1}{{
m E}_{\rm h}^2} - rac{1}{{
m E}_{\rm s}^2}
ight) F^{2/3}.$$

The experimental force dependence of the apparent step height between the M and N layers in the microlayer PE sample can be approximated using this expression. However, the knowledge of $\beta = \alpha/R^{1/3} * (1/E_{\rm h}^2 - 1/E_{\rm s}^2)$ does not provide us with moduli values. Reasonable guesses about the tip radius and one of these two moduli are required. If available, macroscopic moduli of one of the materials can be used for a first approximation. The tip diameter of a commercial Si_3N_4 and Si probe is often determined with electron microscopy, and it is typically in the 10-30 nm range. It is better to characterize the tip diameter of the particular probe used in the experiment. The force-versusdistance measurements on a sample with known elastic moduli can be used to determine the tip radius under the assumption that the deformation is purely elastic (49). The elastic modulus of the sample can also be determined from the force-versus-distance curves recorded in the contact-mode AFM. Figure 33 shows differences between the cantilever deflections in the force-versusdistance curves measured on the soft (M) and hard (N) PE layers and on the glass surface. In the measurement on the glass surface, the cantilever deflection is by the cantilever spring constant because the depression of the glass by the tip is negligible. This is not true for the polymer samples. In the force-versusdistance curves recorded on the M and N layers, the piezoscanner travel (z_s and $z_{\rm h}$), which causes the sample to bend the cantilever to the deflection D_o, are larger than the travel, z_{α} , for the glass sample. This is caused by depression of the polymer samples by the tip. The ratio of the tip-induced depressions, z_s and $z_{\rm h}$, of the M and N PE layers is related to the elastic moduli of these materials:

 $z_{\rm s}/z_{\rm h} = ({\rm E}_{\rm h}/{\rm E}_{\rm s})^{2/3}.$

The z_s/z_h ratio determined from the force-versus-distance curves in Figure 33 at high forces is 2 to 2.4. Therefore, the elastic modulus of the hard layer is three to four times higher than that of the soft layer. This value is much smaller than the ratio (about 100) of elastic moduli of similar polymers determined from tensile tests on macroscopic samples (50). The origin of this discrepancy is not yet clarified. One possibility is that the mechanical behavior of the M and N materials in the confined geometry of the microlayer blend differs



Figure 33 (*a*) Force curves recorded on the surfaces of soft (N) and hard (M) PE layers and on the glass substrate with Si probe (spring constant 0.9 N/m). (*b*) The force curves adjusted to the same coordinates.

from that in macroscopic samples. The second possibility is in the use of the Hertz equation, which is strictly applicable only for elastic surface deformations smaller than the tip radius. The large surface deformations of bulk polymer samples produced by the sharp tip are more reliably described in terms of the Sneddon model (51). However, even this approach has limitations, as seen from analysis of nanoindentation data.

Nanoindentation

Examination of the mechanical properties of solid samples by producing indentation marks is a routine procedure for metals and ceramics. Commercial instruments such as the Nanoindenter (52) evaluate the elastic and plastic response of materials using indentation with depth resolution of 0.4 nm and force resolution of 300 nN. Information about microhardness testing of polymers and about the relationship between microhardness and other mechanical properties such as viscoelasticity and microstructure can be found elsewhere (53a,b,c). The use of AFM for indentation tests is definitely attractive. First, the indentation measurements can be performed at small scale and with high spatial and force resolution. In such experiments, the depth resolution is typically 0.1 nm, and the force resolution is less than 50 nN for the stiffest probes, with a spring constant of 500 N/m. Additionally, an advantage of indentation with the AFM is that the geometry of the indentation can be observed with the same probe by scanning the indentation mark and the surrounding area at a lower force.

In order to produce the indentation mark, the sample is moved toward the tip until the tip deflection indicates that the desired force level is attained. The character of the force-versus-distance curve recorded during indenting and in load-unload cycles helps to estimate the amount of plasticity and the elastic These force-distance curves are similar to those routinely used in moduli. the contact-mode AFM, which were described above. After the indentation is done, the topographic measurements are performed in the tapping mode at much smaller tip force. The image records the lateral size of the indentation mark and its depth. Although the indentation is accompanied by elastic and plastic recovery, the knowledge of the lateral dimensions of the indentation mark and the tip geometry help to reconstruct the initial shape of the indentation and to estimate the hardness of the material. Figure 34 shows indentation marks produced by a Si probe on the surface of a microlayer M/N sample. As expected, the larger marks were produced on the soft microlayer. Measurements of the depths of indentation marks on both layers show that the deformation recovers in time. The time dependence of the depth recovery after indenting the hard layer is shown in Figure 35. Such delayed recovery reveals information about the viscoelastic nature of the sample.

AFM indentation studies were performed using different commercial probes on a number of polymers (polyurethanes with different density, cross-linked PDES, cross-linked epoxy networks, polyetheretherketone) whose elastic moduli are in the 0.5 MPa to 3GPa range (MR Van Landingham, thesis in preparation). As expected, the slope of the force-versus-distance curves was steeper for the stiffer samples. For each cantilever probe, however, the steepness changes leveled off above a certain modulus value (approximately 0.5 GPa for probes with 30 to 40 N/m spring constant, 0.05 GPa for the probes with 2 to 3 N/m, and 1 to 20 MPa for probes with 0.5 to 0.6 N/m spring constant). These results are in agreement with the results from the stiffness-related phase changes observed with the tapping mode. It was shown that the phase changes detected using probes with 30 to 40 N/m spring constant level off for materials with



Figure 34 Height image of the microlayer M/N sample with indentation marks produced at the same force. The contrast covers height variations in the 0–200 nm range.

moduli around 1 GPa. These data indicate that whereas stiff commercial Si probes (spring constant 30–40 N/m) can be used for AFM mechanical studies on many polymer materials (contact mode, tapping mode, indentation), the examination of engineering plastics requires stiffer probes. The possible candidates for such applications are stainless steel cantilevers (spring constant 200 to 300 N/m) with diamond tips, which are in use for indentation and wear test studies of high-technology coatings used in semiconductor and data storage applications.

Nanoindentation measurements complement other types of AFM studies of mechanical properties of polymers. The force-versus-distance curve obtained in the indentation experiments gives mechanical information from the bulk material, whereas the behavior of force-versus-distance curves recorded in the contact-mode AFM is determined by material closest to the surface. When the tip penetrates deeply into material, the resulting deformation should be treated in terms of the Sneddon model. In this model the relationship between



Figure 35 Time dependence of the indent depth marked by * on the image in Figure 34.

indentation depth z, and load P is given as

 $\mathbf{P} = \xi \mathbf{E} z^{\mathbf{m}}$

where ξ is a constant depending on the geometry of the contact, and E is the sample modulus. The parameter *m* is determined from a curve fit of P as a function of *z*, and it equals 2 for a cone-shaped indentor. The experimental data obtained with conical indentors, however, are described by unloading indenting curves with *m* in the range 1.2 to 1.5. This effect likely is caused by plastic deformation in the vicinity of the tip apex that effectively increases the contact area. In general, the problem is the same as in analysis of the contact-mode AFM data. The function ξE , which describes the relation between the load and the indentation depth, contains both the geometric factors and the sample modulus. Both variables are unknown, and either an independent measurement of the contact area or a reasonable guess of elastic modulus is needed to solve this problem.

The use of AFM for small-scale indentation expands the possibilities for such applications. Further theoretical and experimental efforts are required for quantitative analysis of the data. At present, the AFM mechanical measurements can be performed on the comparative level. Examination of a series of materials with the same probe could provide data useful for comparison of the elastic moduli or other mechanical properties of a set of polymeric materials.

FURTHER PERSPECTIVES

In early AFM applications to polymers, the imaging of molecular-scale features, e.g. the implementation of the unique capability of this technique, was emphasized. Although the observation of periodic lattices showing atomic and molecular order on polymer surfaces still attracts the interest of many research groups, current AFM applications are much broader. This technique is finding increasing use in academic and industrial research. The spectrum of AFM applications is substantially widened with the development of new operating and imaging modes. In addition to elucidating topography and nanostructure, one can employ AFM for investigation of mechanical, adhesive, and hydrophilic/hydrophobic properties. These properties can be examined at micron and submicron scales that are much less accessible by other methods.

In a low-force experiment, the surface topography remains unchanged and is correctly reproduced in the AFM height images. In such experiments, weak surface forces, which are responsible for adhesion, for example, may contribute to the image contrast. With broader AFM studies, the number of practical applications will continue to increase. In high-force images, the contrast is related more closely to variations of surface stiffness than to variations of topography. The interplay between experimental studies and theoretical approaches will continue to optimize AFM imaging and to improve correlation of the image contrast to stiffness, adhesion, etc. The discovery of such correlations makes possible the recognition of individual components in multicomponent systems. Also, the viscoelastic nature of many polymer systems can be observed as a function of position in the sample. Systematic studies of viscoelastic behavior will require further instrumental developments based on a combination of relaxation and AFM techniques.

AFM is a growing family of operating and imaging modes that complement each other, as well as the results of other microscopic, mechanical, and thermal techniques. The novelties of AFM are definitely attractive for researchers. AFM demands thorough and innovative approaches in order to avoid artifacts and to gain the maximum information from the measurements. A researcher can select the appropriate modes to suit the material under examination and the properties of interest. The combined use of several modes and different experimental conditions is the basis for a comprehensive examination of polymer samples with the AFM.

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Literature Cited

- Chen CJ. 1993. Introduction to Scanning Tunneling Microscopy. Princeton: Princeton Univ. Press
- Bonnell DA, ed. 1993. Scanning Tunneling Microscopy and Spectroscopy. New York: VCH
- Magonov SN, Whangbo M-H. 1996. Surface Analysis with STM and AFM. Weiheim: VCH
- Albrecht TR, Dovek MM, Lang CA, Grutter P, Quate CF, et al. 1988. J. Appl. Phys. 64:117
- Patil R, Kim S-J, Smith E, Reneker DH, Weisenhorn AL. 1991. Polym. Commun. 31:455
- 2c. Magonov SN. 1996. Polym. Sci. B 38:143
- Zhong Q, Innis D, Kjoller K, Elings VB. 1993. Surf. Sci. Lett. 290:L688
- 3b. Elings V, Gurley J. 1996. U.S. Patents 5412980, 5519212
- Weisenhorn AL, Hansma PK, Albrecht TR, Quate CF. 1989. Appl. Phys. Lett. 54:2651
- Burnham NA, Colton RJ. 1989. J. Vac. Sci. Technol. A 7:2906
- Overney R, Meyer E, Frommer J, Brodbeck D, Lüthi R, et al. 1992. *Nature* 359:133
- Noy D, Frisbie CD, Rozsnyai LF, Wrighton MS, Lieber CM. 1995. J. Am. Chem. Soc. 117:7943
- Maivald P, Butt H-J, Gould SAC, Prater CB, Drake B, et al. 1991. Nanotechnology 2:103
- Radmacher M, Tillmann RW, Gaub HE. 1990. Science 2:257
- O'Shea SJ, Welland ME, Pethica JB. 1994. Chem. Phys. Lett. 223:336
- 9a. Wong TMH, Descouts P. 1995. J. Microsc. 178:7
- Wawkuschewski A, Crämer K, Cantow H-J, Magonov SN. 1995. Ultramicroscopy 58:185
- Hansma PK, Cleveland JP, Radmacher M, Walters DA, Hillner P, et al. 1994. Appl. Phys. Lett. 64:1738

- Höper R, Gesang T, Possart W, Hennemann O-D, Boseck S. 1995. Ultramicroscopy 60:17
- 12. Dürig U, Zuger O, Stadler A. 1992. J. Appl. Phys. 72:1778
- Babcock K, Dugas M, Manalis S, Elings V. 1995. MRS Symp. Proc. 355:311
- 13b. Vairac P, Cretin B. 1996. Appl. Phys. Lett. 68:461
- 14. Sugawara Y, Ohta M, Ueyama H, Morita S. 1995. *Science* 270:1646
- Magonov SN, Elings V, Whangbo M-H. 1996. Surf. Sci. Lett. In press
- Weihs TP, Nawaz Z, Jarvis SP, Pethica JB. 1991. Appl. Phys. Lett. 59:3536
- Ohnesorge F, Binnig G. 1993. Science 260:1451
- Landman U, Luedke WD, Nitzan A. 1989. Surf. Sci. 10:L177
- Stocker W, Bar G, Kunz M, Möller M, Magonov SN, Cantow H-J. 1991. Polym. Bull. 26:215
- Bassett DC. 1981. Principles of Polymer Morphology. New York: Cambridge Univ. Press
- 21. Patil R, Reneker DH. 1994. *Polymer* 35:1909
- 22. Nie H-Y, Motomatsu M, Mizutani W, Tokumoto H. 1996. *Polymer* 37:183
- Magonov SN, Bar G, Cantow H-J, Bauer H-D, Möller I, Schwörer M. 1991. *Polym. Bull.* 26:223
- 24a. Magonov SN, Qvarnström K, Elings V, Cantow H-J. 1991. Polym. Bull. 25:689
- 24b. Magonov SN, Sheiko SS, Deblieck R, Müller M. 1993. Macromolecules 26:1380
- Magonov SN, Kempf S, Kimmig M, Cantow H-J. 1991. Polym. Bull. 26:715
- Hansma HG, Motamedi F, Smith P, Hansma PK, Wittman JC. 1992. Polymer 33:647
- 26a. Snetivy D, Vansco GJ, Rutledge GC. 1992. Macromolecules 25:1380
- 26b. Jandt KD, McMaster TJ, Miles MJ,

Petermann J. 1993. *Macromolecules* 26: 6552

- 27a. Lovinger AJ, Lotz B. 1996. Polym. Prepr. 37:428
- Stocker W, Lovinger AJ, Schumacher M, Graff S, Wittmann JC, Lotz B. 1996. *Polym. Prepr.* 37:548
- 28. Vansco GJ. 1996. Polym. Prepr. 37: 550
- Bustamante C, Vesenka J, Tang CL. 1992. Biochemistry 31:22
- Kumaki J, Nishikawa Y, Hashimoto T. 1996. J. Am. Chem. Soc. 118:3321
- Sugawara J, Ohta M, Ueyama H, Morita S. 1995. Science 270:1646
- 32a. Crämer K, Wawkuschewski A, Cantow H-J, Magonov SN. 1995. Polym. Bull. 35:457
- 32b. Nakagawa Y, Hayashi H, Takahagi T, Soeda F, Ishitani A, et al. 1994. Jpn. J. Appl. Phys. 33:3771
- Crämer K, Schneider M, Mulhaupt R, Cantow H-J, Magonov SN. 1994. *Polym. Bull.* 32:637
- 33b. Deleted in proof
- 34. Deleted in proof
- Deleted in proof
- Joseph EA, Lorenz MD, Barlow JW, Paul DR. 1982. Polymer 23:112
- 37. Dvornic PR, Tomalia DA. 1996. Curr. Opin. Coll. Interface Sci. 1:221
- Percec V, Chu P, Ungar G, Zhou P. 1997. J. Am. Chem. Soc. 118:In press
- Tuzov I, Crämer K, Pfannemüller B, Magonov SN, Whangbo M-H. 1996. New J. Chem. 20:37
- Mate CM, Friedenberg M, Devonport W, Hawker C. 1996. Am. Chem. Soc. Symp.,

Scanning Probe Microsc. Polymers, Orlando, FL

- Wawkuschewski A, Cantow H-J, Magonov SN. 1994. Adv. Mater. 6:476
- Wawkuschewski A, Cantow H-J, Magonov SN, Hewes JD, Kocur MA. 1995. Acta Polym. 46:168
- 43a. Hild S, Gutmannsbauer W, Luth R, Fuhrmann J. et al. 1996. J. Polym. Sci. Polym. Phys. 34:1953
- Coulon G, Astelein G, G'Sell C. 1996. Polym. Prepr. 37:555
- Magonov SN, Elings V, Papkov VS. 1997 Polymer. 38:297
- Papkov VS, Kvachev Yu P. 1989. Prog. Coll. Polym. Sci. 80:221
- 46. Müller ĎJ, Büldt G, Engel A. 1995. *J. Mol. Biol.* 249:239
- Bengel H, Cantow H-J, Magonov SN, Monconduit L, Evain M, et al. 1994. Surf. Sci. Lett. 321:L170
- 48. Hertz H. 1882. J. Reine Angew. Math. 92:156
- Weisenhorn AL, Khorsandi M, Kansas S, Gotzos V, Butt H-J. 1993. Nanotechnology 4:403
- Sehanobish K, Patel RM, Croft BA, Chum SP, Kao CI. 1994. J. Appl. Polym. Sci. 51:887
- 51. Sneddon IN. 1965. Int. J. Eng. Sci. 3:47
- 52. Nanoindenter is the trademark of Nanoindenter Inc., Knoxville, TN
- 53a. Balta Calleja FJ. 1985. Adv. Polym. Sci. 66:117
- Lorenzo V, Perena JM, Fatou JG. 1990. J. Mat. Sci. Lett. 9:1011
- 53c. Alba S, Lobet JL, Vovelle L. 1993. J. Adhes. Sci. Technol. 7:131



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