

## Advantages of scanning probe microscopy in polymer science

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**W**E INTRODUCE THE ATOMIC FORCE microscope (AFM) and its capabilities with special regard to its use in polymer science. It shows several advantages over other analytical techniques, such as scanning electron microscopy, differential scanning calorimetry, and dynamic mechanical analysis. Its main advantage is that the samples need not be prepared specially and can therefore be studied in their native environment. Furthermore, the AFM can be used to detect physical properties locally on a molecular scale, which may be of interest for characterizing polymer blends or structured polymers.

### Introduction

Polymer surfaces and thin polymer films or coatings, as well as their technological application, are important fields of current research. Polymers are widely used as components in industrial products, for example as water or oil repellents, stabilizers, lubricants or adhesives. They are also of increasing importance in the nanotechnology sector, where they are used as templates for molecular devices, sensor technology or patterned surfaces for microelectronic developments. Many molecular concepts in nanotechnology rely on interfacial organization and self-assembly of molecules, yielding well-defined structures in thin films over large areas. Exact control of the molecular organization on the nanoscale has set new demands on chemistry as well as on characterization methods such as microscopy. The macromolecular structure, which includes the degree of polymerization, chain architecture, polymer functionalities and the composition all have to be controlled.

The development of scanning probe microscopes allows all these factors to be analysed on a molecular scale without damaging the sample.

In 1981, Binnig and Rohrer<sup>1</sup> introduced the scanning tunnelling microscope (STM) as the first member of the family of scanning probe microscopes (SPM). The STM measures a tunnelling current between an atomically sharp probe and a sample surface that are separated by only a few angstroms. The STM can image the surface topography with atomic resolution.

It is, however, of limited use for non-conductive materials like polymers, since it relies on the measurement of a tunnelling current that flows through an electronic gap between a conductive tip and a conductive sample.

For this reason the atomic force microscope (AFM) was introduced by Binnig *et al.* in 1986.<sup>2</sup> This instrument measures the atomic forces acting between the sample and a silicon probe and can be used to investigate both conductive and non-conductive sample surfaces equally, under ambient conditions.

In addition to the requirement for relatively uncomplicated imaging conditions and the high resolution that can be achieved, AFM offers a variety of new contrast mechanisms. These allow, for example, the distinction between different chemical and physical structures and therefore extend the microscope's capabilities beyond morphological studies. Mechanical properties, such as viscoelasticity, friction, and adhesion can be characterized quantitatively on a nanometre scale. Furthermore, the measurement of molecular forces and manipulation of single macromolecules is now possible.

All SPMs use an atomically sharp probe (typical tip radius <10 nm), which is scanned across the sample surface, to sense different types of interactions in the near field of the surface. These interaction forces are measured for every point on the raster pattern, which results in a three-dimensional topographical image. The lateral resolution depends mainly on the tip diameter.

SPMs have few limitations regarding

imaging conditions, because samples need not be prepared in any special way, as is required for electron microscopy (for instance, etching and metal coating). Hence, they can be used to visualize the native structure of a surface. Most SPMs can operate in vacuum,<sup>3</sup> in air and in liquid,<sup>4</sup> which allows *in situ* observation of biological systems in their natural medium.

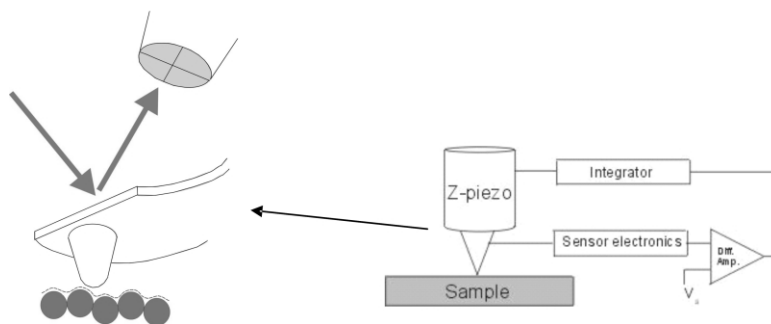
Depending on the probe type, one can distinguish between scanning tunnelling microscopy (STM), scanning force microscopy (SFM), scanning near field optical microscopy (SNOM)<sup>5</sup>, and other SXM techniques, where X refers to the physical properties measured by the probe, such as the magnetic field, electrostatic charge or temperature.

### Operating and imaging modes of the AFM

The operating mode of all SPMs is similar; in all cases the forces acting between the probe and the sample are measured. Depending on the probe and the operating mode, different properties of the sample can be recorded. The following sections describe how the interaction forces are detected and how the different operation modes work.

### Signal detection

The up- or downward movement of the probe as it follows the surface structure of the sample is measured by the distortion of a laser beam. The probe is mounted on a soft cantilever that can easily bend as the probe follows the surface. The cantilever reflects the laser beam into a segmented photodiode. Vertical movement of the cantilever displaces the reflected laser beam in the photo-detector. The feedback electronics then adjust the voltage to the vertical (z) piezo actuator to compensate for this change by moving the probe up or down until the reflected laser beam is back at its original position in the photo-detector. This detection system is schematically illustrated in Fig. 1.



**Fig. 1.** The detection system of an SPM. The laser beam is reflected from the cantilever into a photodiode. Movement of the reflected laser beam activates the feedback electronics, which regulates the vertical position of the probe.

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### Contact mode

In contact mode the probe is so close to the sample that the interaction forces between the atoms of the sample and the atoms of the tip of the probe are repulsive. During scanning, this force is kept constant by an electronic feedback mechanism. This adjusts the voltage to the *z*-piezo and hence moves the probe up or down, according to the displacement of the reflected laser beam. If the distance between the probe and the sample decreases, repulsive forces increase and the cantilever is bent upwards. The *z*-piezo must be retracted, so that the cantilever returns to its original position. The voltage required for this movement of the cantilever is plotted for every scan-point, resulting in a three-dimensional topographic image of the surface.

It has to be kept in mind though, that the image represents the charge density on the surface, which is not necessarily the same as the topography. If, instead of the vertical distortion of the cantilever the lateral distortion is detected, then an image of the friction of the sample surface is obtained.

Contact mode is preferably used on hard surfaces, where the probe will not indent the surface too much. Thus damage to the surface is avoided.

### Non-contact mode

In the non-contact mode,<sup>6</sup> the distance between probe and sample is larger than in the contact mode, so that the interaction forces are attractive (van der Waals forces). The probe is mounted on a stiffer cantilever, with a spring constant of 20–70 N m<sup>-1</sup>. The cantilever is oscillated above the surface at its resonance frequency by applying an appropriate a.c. voltage to the *z*-piezo. As the probe scans across the surface, any change in distance between probe and sample will result in a change in the amplitude. The voltage required to compensate for this frequency shift by moving the *z*-piezo up or down is plotted for every point, which results in a three-dimensional topographic image.

A phase image can be recorded simultaneously by plotting the phase shift for every image point. This image shows material contrasts on the sample surface because different materials absorb energy from the oscillation differently and therefore cause different phase shifts in the oscillating signal. This is plotted for every scan point and results in an image that displays the material composition of the sample.

The non-contact mode is used for soft samples, whereas in contact mode the

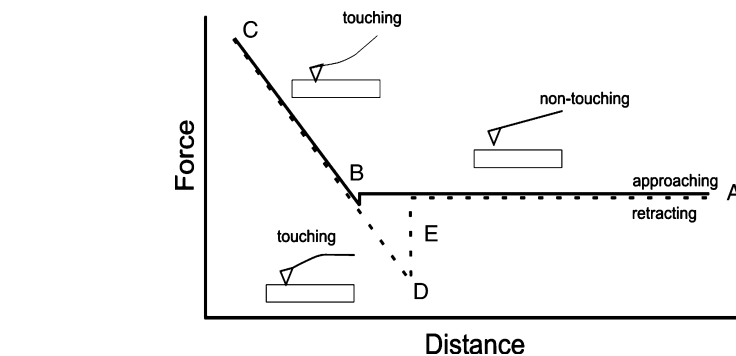


Fig. 2. Schematic force–distance relationship of the cantilever deflection and the vertical distance.

probe might damage the surface.

For all topographic images the voltage values needed to correct the *z*-position of the probe are converted into nanometre distances, and then allocated a value between 0 and 255. This represents the grey scale, or colour image, where the lighter parts are higher than the darker areas.

### Force versus distance curves

Besides imaging, the AFM can be used to probe physical properties locally, at specific points on the sample surface. The most common method is to record a force–distance curve.<sup>7,8</sup> Here, the deflection signal obtained by the distortion of the laser beam is plotted as a function of the vertical distance as the probe is lowered onto the surface and retracted again. This is shown schematically in Fig. 2.

The cantilever is lowered from a certain height above the surface until it touches the surface (A to B). In this region no force is acting on the probe and the cantilever is not distorted. At B the probe jumps into contact with the sample and, from there onwards, the probe is in contact with the sample surface and the cantilever is therefore bent upwards (B to C). The gradient of this part is greater for harder sample surfaces.

As the probe is retracted, it will stay in contact with the surface, because of an adhesive force acting between the sample and the probe (C to D). At D the cantilever finally comes loose and is no longer distorted. The distance from point D to the base line (E) is a measure of the adhesive force acting between the probe and the sample. The adhesive force can be calculated by multiplying the deflection E by the spring constant of the cantilever.

### Experimental setup

In our experiments we used two different instruments: an Explorer AFM from Topometrix and a Multimode AFM from Veeco, as described below.

### Topometrix Explorer

The Explorer can be used on any flat sample surface, since the tip (and not the sample) is moved by the *x*- and *y*-piezo actuators. The only requirement is that the sample is securely fixed and does not move. The maximum scan size is 100  $\mu\text{m}^2$  with a maximum scan height of about 7  $\mu\text{m}$ . Most images of polymer surfaces shown in this article were acquired with a scan size of approximately 2  $\mu\text{m}$  and a lateral resolution of approximately 50–80 nm.

The Explorer can image sample topographies in the contact and non-contact modes. The latter is generally used for soft polymer surfaces, since these would otherwise be disturbed in contact mode. The instrument can be operated in a self-built vacuum chamber, at pressures ranging from about 10<sup>-3</sup> mbar to ambient conditions. This chamber is equipped with a heating/cooling stage, which allows temperatures ranging from about -10°C to 120°C. The heating/cooling stage consists of two serial Peltier elements mounted on an *x/y* translator table, to allow for easy positioning of the sample. The setup is displayed in Fig. 3.

### Veeco Multimode SPM

The Multimode SPM is somewhat limited in terms of sample size, because

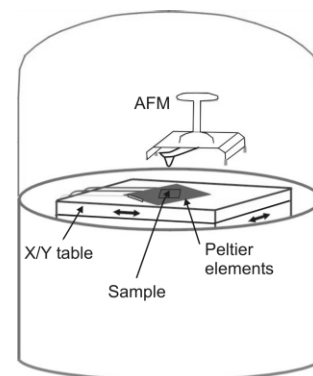


Fig. 3. Experimental setup of the vacuum chamber and the AFM: the sample is fixed on a heating/cooling stage, which is mounted on an *x/y*-translator. The AFM is then placed above the sample.

the sample holder (and not the probe) is moved in the  $x/y$ -direction and the probe is controlled only in the vertical direction. The maximum sample size that can be handled is approximately  $1 \times 1 \times 0.5 \text{ cm}^3$ . Topographic images can be acquired in contact and non-contact mode and material contrast can be identified in the phase image, which is simultaneously acquired with the non-contact topography image.

The maximum scan size for our experiments was  $10 \mu\text{m}^2$  and the resolution in typical images with a size of  $2 \mu\text{m}^2$  was about 10–20 nm. This is considerably better than the resolution achieved with the Explorer.

Force versus distance curves, as described above, can be acquired, which yield information about the hardness of the sample and adhesive forces between the tip and the sample.

The non-contact probes used for both instruments were Si probes, mounted on rod-shaped cantilevers manufactured by Nanosensors, with a resonance frequency of about 170 kHz and a spring constant of typically  $50 \text{ N m}^{-1}$ .

For contact mode measurements Si probes mounted on V-shaped cantilevers with spring constants of about  $0.2\text{--}0.5 \text{ N m}^{-1}$  were used.

For some force versus distance measurements, hydrophilic  $\text{Si}_3\text{N}_4$  probes mounted on rod-shaped cantilevers with a spring constant of  $0.2 \text{ N m}^{-1}$  were used to measure the hydrophilicity of the sample.

### Characterization of polymers

A few practical applications of the AFM in polymer science are described below. These are mainly the results of research projects carried out at the Institute for Polymer Science over the past two years. Besides these, there are many more applications and polymeric systems that can be studied.

#### Imaging of latex particles

Latexes form the basis of adhesives, lubricants and paints. It is important to understand their behaviour with changing temperature, pressure and humidity. For paint, for example, it is important to know at which temperature film formation of the latex particles happens — this should preferably be below room temperature — and how film formation takes place.

The fact that for analysis by AFM the samples need not be fixated or prepared in any way, as is the case for analysis by, for example, scanning electron microscopy (SEM), allows physical processes, such as drying or film formation, to be investi-

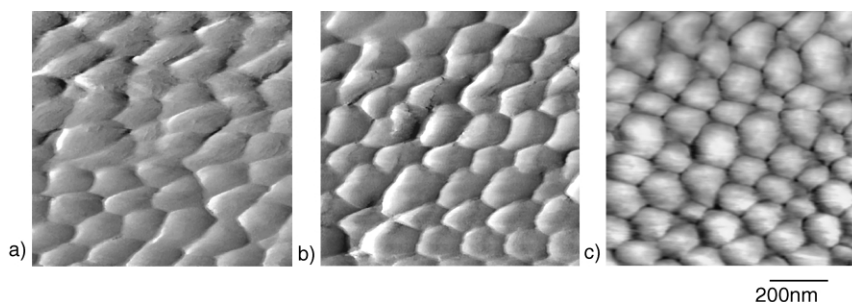


Fig. 4. Drying of latex particles: a) the particles protrude from the surface as the water evaporates, b) the particles become ordered, c) the spheres are closely packed and deformed into hexagons.

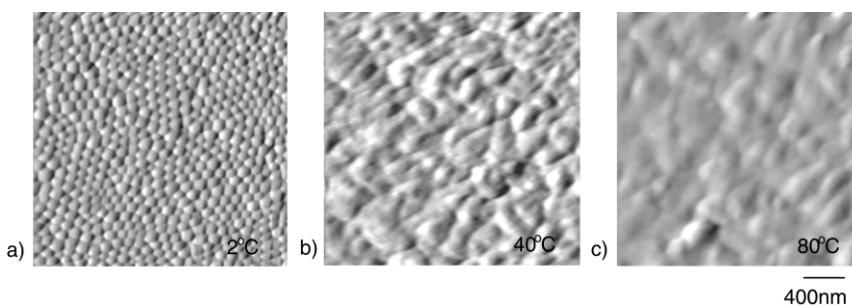


Fig. 5. The different stages of latex film formation: a) ordered, individual spherical particles, b) particles interdiffuse; c) a flat film is formed.

gated as a function of time, temperature or other conditions.

For instance, the process of drying and film formation of latex particles has been observed by AFM. A wet sample was cast on a silicon substrate at a temperature below its glass transition temperature ( $T_g$ ). This is the temperature at which chain segments of the polymer are able to move and molecules can interdiffuse.

To accelerate the drying process and to avoid condensation on the surface of the sample, the AFM measurements were performed in the vacuum chamber at a pressure of about 1 mbar. Figure 4 shows how the latex particles protrude from the water surface and create a two-dimensional ordered array as the interstitial water evaporates. Finally, the capillary pressure forces them into close contact, they lose their spherical shape and are deformed into hexagons.

Figure 5 shows how individual latex particles change into a flat film as the temperature is increased above the  $T_g$  of the latex. The particles start to deform and interdiffuse, finally forming an interlinked flat film.

Information such as the deformation parameter can be obtained from these image sequences by measuring the particle diameter and plotting it as a function of time or temperature. In this way polymers can be compared in terms of their different film formation behaviours. Such information is important as film formation behaviour can influence the choice of the form of latex used for com-

mercial products. The measurements performed here revealed, for example, that small particles form a film faster than larger particles, and that the particle structure influences the film formation behaviour.<sup>9</sup>

AFM also allows the detection of the internal structure of latex particles. For example, core-shell polymers consisting of a high- $T_g$  core surrounded by a low- $T_g$  shell were imaged at temperatures below and above the shell  $T_g$ . Figure 6 shows how the high- $T_g$  cores become visible at the surface at temperatures where the softer shell polymer starts to flow. The original core-shell particles have a diameter of about 80 nm, whereas the diameter of the cores is only about 50 nm. This confirms two things: that the polymer does indeed have a core-shell structure and that the cores are of the theoretically calculated size.

#### Imaging physical properties

Physical properties of polymers, such as hardness, adhesion or friction, can also be imaged with the AFM. Figure 7 shows a topographic image (a) and phase image (b) of hard filler particles in a soft polymeric matrix. Both images were acquired simultaneously. In the topographic image no distinction between the two different polymer phases can be made, only differences in height are represented. In the phase image the harder particles can clearly be seen as light areas within a uniformly grey background, which represents the soft polymer matrix.

Other systems, where it might be desirable to image material contrasts are, for example, drug-releasing polymers. The drug is embedded in a polymeric matrix that is slowly dissolved in the stomach and releases the drug at a constant rate over a certain time. Figure 8 shows the topography (a) and phase image (b) of a blood pressure-regulating drug (lighter parts in Fig. 8b) dispersed in a polymer matrix (dark background in Fig. 8b). Again, the material contrast can be clearly seen in the phase image, whereas in the topography image it is not possible to distinguish between the two phases.

In both cases the important additional information that can be obtained from the phase image is the distribution of one material in a matrix of another material. AFM images can be used to verify that the achieved distribution is even, and that the percentage of the materials is correct.

Probing

A Si<sub>3</sub>N<sub>4</sub>-coated probe was used to study the hydrophobicity of polydimethylsiloxane (PDMS) samples with different additives, which under certain conditions become hydrophilic. The different adhesive forces acting between the hydrophilic probe and hydrophobic PDMS samples are shown in Fig. 9a. The difference between the deflection and retracting curves (part E of the force distance-curve; see above) represents the adhesive force, which in this case is a measure for the hydrophilicity of the sample. The larger the adhesive force, the more hydrophilic is the sample surface. The difference between the samples can be clearly seen. Figure 9b shows the different gradients of the approaching curves, indicating the different hardness of the surface layer of the samples. The inset in Fig. 9b displays the different gradients of the force-distance curves for the different samples and shows clearly the differences in hardness.

Again, these parameters can be measured by AFM on a native system and, therefore, it is possible to detect changes over time or as a function of ageing using temperature, pressure and so on.

Besides hardness and adhesive forces, it is also possible to detect thermal properties of polymers on a molecular scale. We developed a technique to measure glass transition and melting temperatures of polymers using the AFM.<sup>10,11</sup> The instrument is operated in the non-contact mode with the cantilever oscillating stationary above the sample surface at its resonance frequency. This frequency is measured

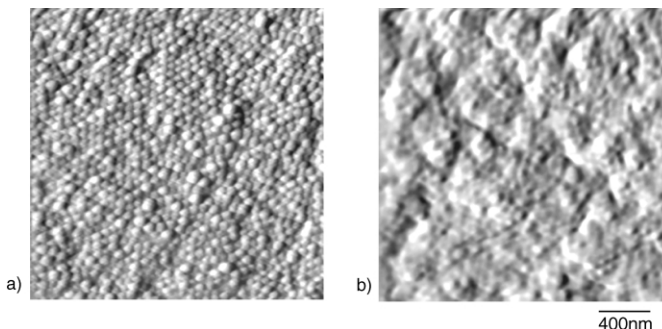


Fig. 6. Core-shell particles: a) below the shell T<sub>g</sub> and b) above the shell T<sub>g</sub>. The cores become visible as the shell polymer starts to flow.

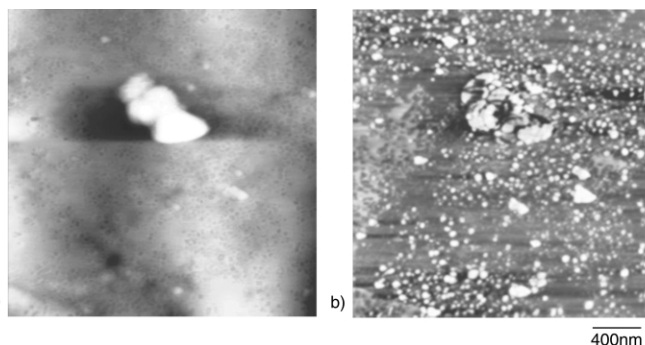


Fig. 7. Topography (a) and phase image (b) of hard filler particles embedded in a soft polymer matrix. Image size: 2 μm.

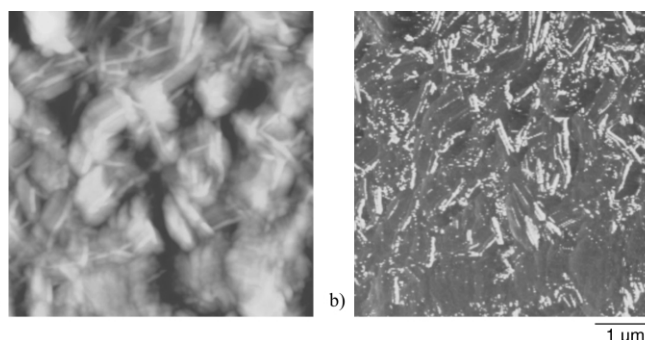


Fig. 8. Topography (a) and phase image (b) of drugs dispersed in a polymer matrix. Image size: 6 μm.

as a function of temperature, which is increased from a point below the transition temperature to one above it at a constant heating rate of about 2°C min<sup>-1</sup>. Transitions in the polymer appear as a plateau (T<sub>g</sub>) or as a sharp kink (melting point) in the otherwise linear decreasing function, as displayed in Fig. 10.

This method is especially useful for the characterization of structured polymers or polymer blends. It is difficult to detect individual transition points of such polymeric systems with conventional techniques, such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). For the study of more

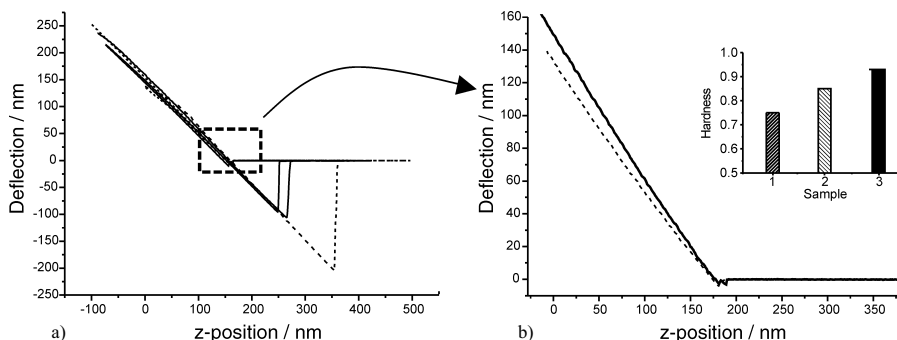


Fig. 9. Force-distance curves of different polymers showing: a) difference in hydrophilicity and b) difference in surface hardness.

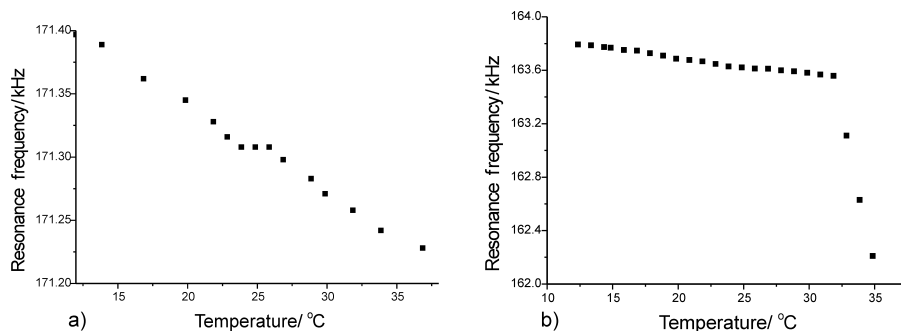


Fig. 10. a) Glass transition of an unstructured copolymer and b) melting point of octadecene. Both transitions are measured at the theoretically predicted temperatures.

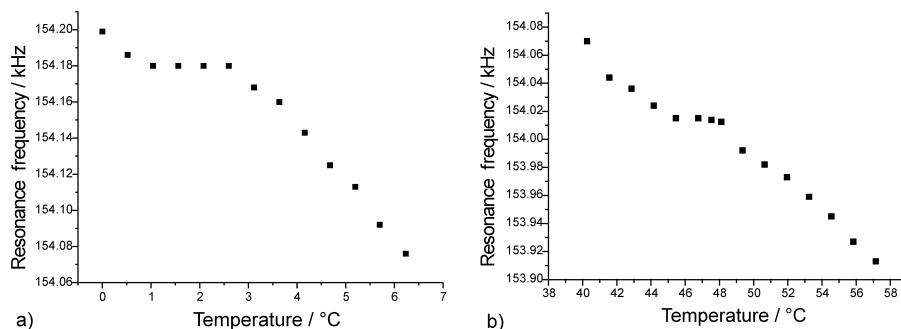


Fig. 11. Glass transition of a) the soft (low  $T_g$ ) shell polymer at around 2°C; and b) the hard (high  $T_g$ ) core polymer at around 49°C.

complicated systems, like core-shell polymers, the AFM proved to be far more appropriate than DSC, or DMA. AFM resolved individual  $T_g$ s reliably, as shown in Fig. 11. Core-shell particles containing a hard core surrounded by a soft shell were studied and both  $T_g$ s could be determined at the expected temperatures (around 2°C and 49°C in this case).

### Conclusions

The AFM is clearly a versatile tool for characterizing polymeric surfaces: it can be used to determine and visualize the

surface morphology as well as physical properties, such as adhesion, friction and material contrasts.

Apart from imaging, it can also be used to probe certain properties, such as adhesive forces, hardness or thermal transitions locally. Owing to its relatively simple setup and the fact that no preparation of the sample is necessary, it is also possible to determine changes of these properties over time or with changing external conditions, such as temperature and pressure.

This combination of visualization of the

surface on a molecular scale with the measurement of physical properties makes the AFM a unique tool for polymer characterization.

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### On devising the wheel

The use of tools has often been regarded as the defining characteristic of *Homo sapiens*.... But, in the light of abundant and increasing evidence that subhuman primates and even lower animals can use tools, the view is now gaining ground that what is characteristic of human beings is not so much the devising of tools as the communication from one human being to another of the know-how to make them. It was not so much the devising of a wheel that was distinctly human, we may suggest, as the communication to others, particularly in the succeeding generation, of the know-how to make a wheel. This act of communication, however rudimentary it may have been..., marks the beginning of technology, or the science of engineering.

Peter Medawar  
(Technology and Evolution)

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