

Imaging organic compound assemblies. Oligomers, polymers and alkane derivatives in scanning force microscopy

Introduction

Scanning force microscopy (SFM), also known as atomic force microscopy (AFM), is a surface imaging technique based on a purely mechanical imaging process. During its development over the last 20 years it has become a key instrument in nanoscience and nanotechnology. In AFM a very sharp tip attached to a cantilever is brought into very close proximity to the surface and then scanned line by line to probe the surface texture of the sample.

Scanning force microscopy allows in-situ measurements which do not require staining or coating of the sample as is necessary in electron microscopy techniques. Depending on sample parameters, contact mode or dynamic modes (e.g. IC mode) can be used to obtain high resolution images even on very soft samples. In contact mode the tip is scanned continuously in very close proximity across the sample. In dynamic mode tip sample interaction can be minimized by using a vibrating cantilever. In addition, the dynamic mode provides qualitative information about sample parameters by observing the phase signal.

Why is it useful to have a scanning force microscope for polymer research?

AFM achieves a higher resolution compared with the traditional microscopy techniques such as light microscopy (LM) and confocal laser scanning microscopy (CLSM). Electron microscopy techniques (EM) are also often used in polymer research and AFM can be used as a complementary tool to study such polymer preparations which are too sensitive to be studied with an electron beam.

AFM sample preparation is comparably easy, there is neither a conductive coating required, nor any sample staining. The samples can be kept at ambient conditions, and imaging in liquid or in organic solvents is possible, too. Exchanging the liquid is also possible during the experiment using a perfusion liquid cell. The temperature

can be controlled over a wide range, normally between 0 and 240 °C.

Combining different imaging techniques saves time and leads to more reliable and meaningful scientific results. During AFM imaging, the sample can be observed optically in both reflected light and transmitted light. All modern contrast enhancing transmitted light techniques as provided by inverted optical microscopes can be used together with AFM, and all fluorescence microscopy techniques (confocal, CLSM, TIRF) and polarized light applications are also available.

AFM Instrumentation and samples

All images shown in this report were obtained with a JPK NanoWizard® AFM. The JPK Polymer stage and the JPK LifeScience stage was used, depending on the application and sample mounting. The Life Science stage was mounted onto a Zeiss Axiovert 200 inverted optical microscope. Cantilevers used for imaging were from NanoWorld, Mikromasch and Appnanotech.

The samples we studied for this report were organic compounds, both natural and synthetic examples, such as alkanes, alkane derivatives and aromates. The compounds are of both technical and academic interest. The molecular weight of the samples studied in this report ranges between 300 and 130.000 g/mol.

Oligomer imaging

Hexacontane

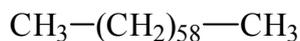


Fig. 1 Chemical formula of hexacontane, MW 843.62 g/mol.

Hexacontane belongs to the alkanes. It is a saturated and non-branched C chain with 60 carbon atoms (Figure 1). The length of a C-C single bond is 154 pm, the C-C-C angle is 104°. The melting point of the compound is between 94 and 96 °C. Hexacontane is soluble in warm xylene. For the experiment a concentration of 0.001 - 0.01 to g/L or $\sim 10^{-5}$ - 10^{-6} mol/L is needed. This low concentration was reached with a dilution series. 2 mg of hexacontane were dissolved in 2 mL warm xylene (heated to 60 °C, the boiling point of xylene ~ 140 °C). 30 μL of this solution was diluted with 870 μL xylene to a concentration of 0.03 mg/mL. 30 μL of this solution was then diluted with 870 μL of xylene to an end concentration of 0.001 mg/mL. A home-made spin coater (1800 rev./min) was used for sample preparation [1].

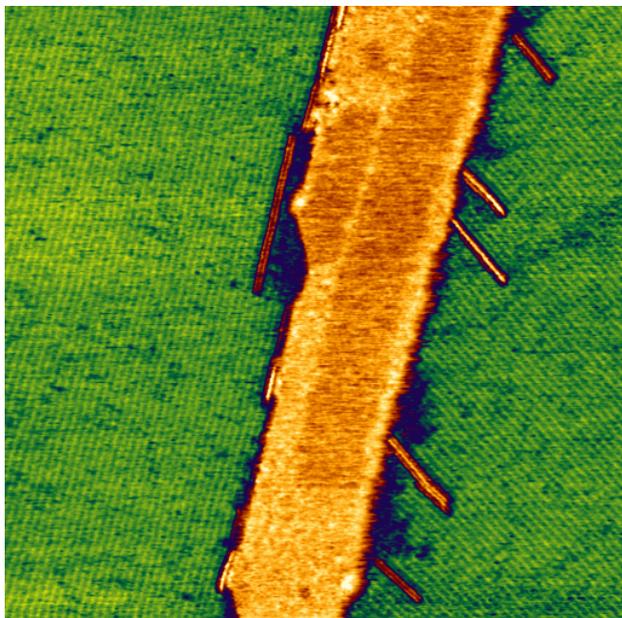


Fig. 2 AFM image of a preparation of hexacontane on HOPG. The stripes represent monomolecular layers of hexacontane, lying next to each other. The width of one stripe corresponds to the length of the hexacontane molecule.

A piece of freshly cleaved HOPG (highly ordered pyrolytic graphite) was used as a sample substrate. One drop of the diluted solution was dropped onto the substrate and spun for 30 – 60 s. For a mechanically more stable sample preparation the sample can be heated onto a heating plate to 140 °C for about 10 min. The sample then was imaged in dynamic mode with a NanoWorld® SSS (super sharp silicon) tip. Best images were obtained in “soft” dynamic mode, meaning a relatively weak damping of the amplitude where the setpoint is near the free amplitude.

Comparing the two green areas in Figure 2 shows that both of them exhibit a pattern of parallel stripes with different orientations. The angle between the stripes in the two domains is 60°. Figure 3 shows higher resolution images within one of the striped domains. The 7.5 nm width of the lamellae stripes corresponds with the length of an extended hexacontane molecule.

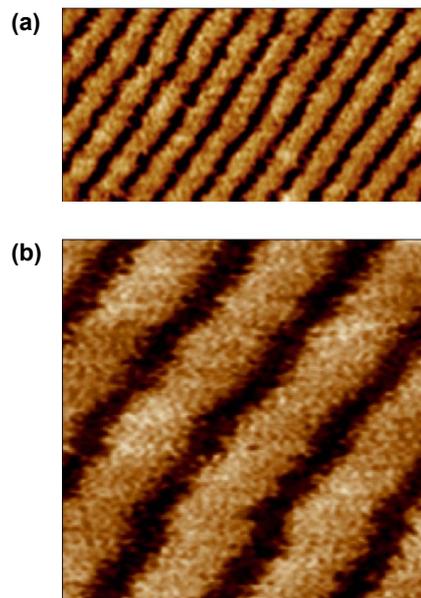


Fig. 3 Hexacontane, prepared on HOPG. One lamellum has a width of 7.5 nm. (a) image size 95 x 50 nm. (b) zoom, image size 30 x 30 nm

In Figure 4 a schematic diagram shows the arrangement of the hexacontane molecules within the the lamellar structures. The lateral self-assembly of the molecules forms the striped patterns seen by the AFM.

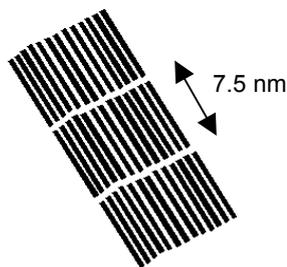


Fig. 4 Self-assembly of hexacontane molecules on HOPG leads to lamellar structures with 7.5 nm width.

Higher resolution can also be achieved using AFM. Atomic lattice resolution has been achieved under ambient conditions on some crystalline condensed matter samples such as HOPG (highly ordered pyrolytic graphite) and mica surfaces, as shown in Figure 5.

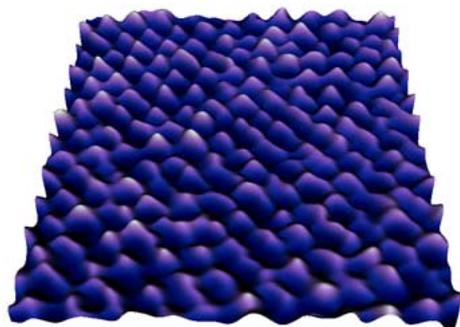


Fig. 5 Atomic lattice resolution of a mica surface. Height image. Image size 6.6 nm x 6.6 nm, z-range 0.4 nm. NanoWizard® AFM was installed on an optical inverted microscope.

p-Hexaphenyl (p-6P)

The organic compound used in this study is para-hexaphenyl, which can be seen as coming from a benzene structure. The conjugated polymer is poly-para-Hexaphenylene. The oligomer p-Hexaphenyl consists of a linear chain of six benzene rings, as shown in Figure 6.

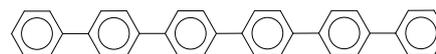


Fig. 6 Chemical structure of p-Hexaphenyl. C₃₆H₂₆, molecular weight 458.60 g/mol.

Sample preparation was done in a vacuum sublimation process. Hexaphenylene molecules were evaporated in vacuum (10⁻⁷ mbar) at temperatures above 330 °C onto two different surfaces, a cleaved mica surface, and a gold-coated mica surface. In both cases, the samples were heated afterwards by a focused Ar ion laser beam [2,3]. On both mica and gold the p-6P forms nanofibers. Depending on the substrate, the arrangement of the compound leads to very different fiber patterns. On mica surfaces p-6P exhibit needle-shaped aggregates, as seen in Figure 7.

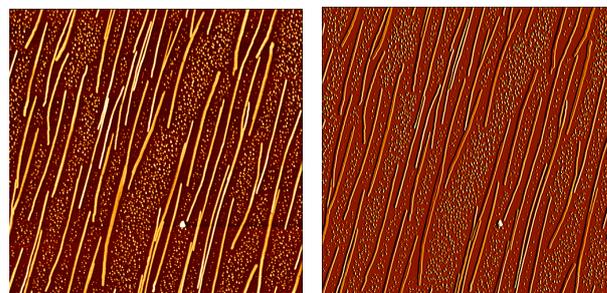


Fig. 7 p-Hexaphenyl nanofibres prepared on clean mica. Height (left) and amplitude (right) images. Image size 25 µm x 25 µm.

The height and width distribution is quite uniform, with a typical height around 50-70 nm, and a typical width of 350 nm. Their widths can be in the order of several hundred nanometers with heights of a few ten nanometers and lengths of several tens to several hundreds of microns. Areas covered by needles aligned in the same direction can reach 1 cm².

Between the needles, a huge number of small dots can be observed. Their density decreases in the near of the rods. They consist of the organic material from which the rods are grown. The forces that drives the growth are the electric dipole fields on the mica surface. A freshly cleaved muscovite mica surface has a surface dipole field of 107 V/cm and the p-6P molecules grow parallel to the direction of this field.

When irradiated with UV light (360 nm) the needles show a deep blue fluorescence at 425 nm, as can be seen in Figure 8(c). One future application for these nanofibres may be to use them as nano-lightguides.

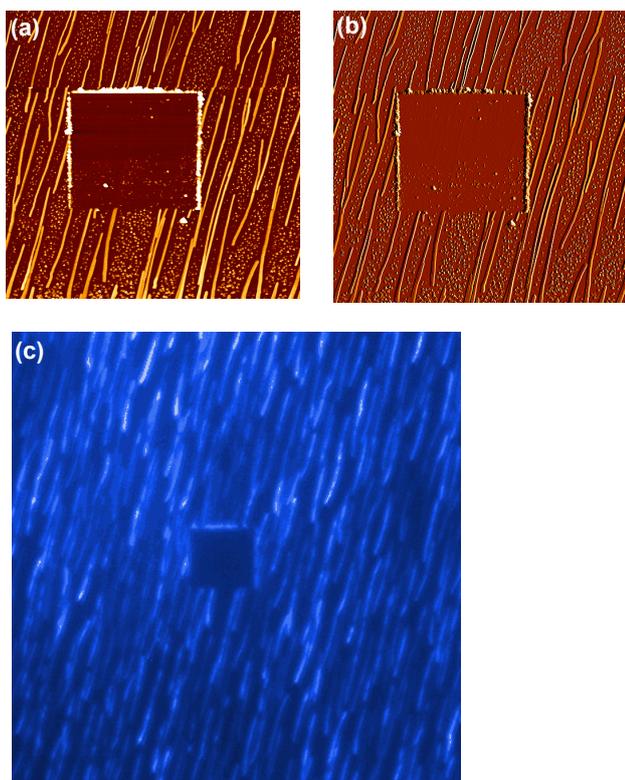


Fig. 8 Micromanipulation on nanofibres. The AFM tip was used to scratch nanofibres off the mica surface. The AFM images (a) height, and (b) amplitude have a scan size of 25 µm x 25 µm. The scratched area had a size 10 µm x 10 µm. The fluorescence image (c) has a size of 70 µm x 70 µm.

Since the AFM and fluorescence microscopy can be performed simultaneously, both optical and AFM imaging can be used in-situ to study these types of nanofibres and their optical properties.

Here the AFM tip was used to scratch the nanofibres from a region of the mica surface, as shown in Figure 8. A cantilever with a relatively high spring constant (40 N/m) was used as a tool for manipulation of the sample. Therefore a dynamic imaging mode (IC mode) was used for imaging at low force without disturbing the fibres. The instrument was used in contact mode for manipulation, using an applied force of 100 nN.

Preparing p-hexaphenyl on gold-coated mica leads to a net-like pattern as shown in Figure 9. In this case, mica's strong dipole field is insulated by the gold cover. Gold itself does not exhibit such a high surface dipole field. Therefore the needles form a network on the surface and are not aligned in parallel lines.

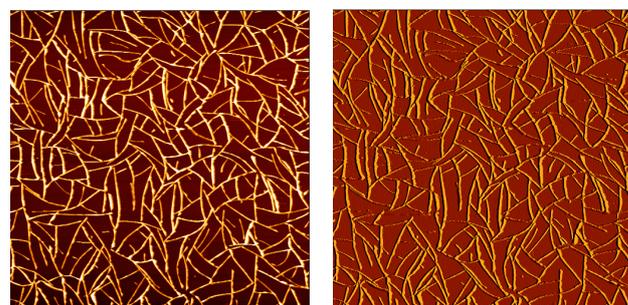


Fig. 9 p-hexaphenyl nanofibres prepared on gold-coated mica. Needles form a net-like structure. Image size 20 µm x 20 µm. Height (left) and amplitude (right) images.

Polymer Imaging

Polystyrene-PMMA block copolymer

The first block-copolymers were synthesized in the 1950s. They contain at least minimum two different "blocks" in each individual polymer chain, where the backbone is composed of different monomers. Their advantage compared with traditional polymers is their improved and controllable physical properties.

The monomers of the di-blockcopolymer polystyrene-block-polymethyl-methacrylate (PS-b-PMMA) consist of linked chains of polystyrene und PMMA, with a molecular weight of 39,000 g/mol. For AFM imaging this sample was prepared in a spin-coating process on a silicon substrate. In the height image in Figure 10, the cylinders (width 10-15 nm, height 1 nm) lying on a flat surface are clearly resolved. The rods are lying in parallel but curved lines, and each rod can be up to several micrometers long. In this case, the flat cylinders consisting of PMMA are lying in a polystyrene matrix. In the phase image of Figure 10, the contrast between the PMMA rods (black) and the polystyrene matrix (green) is more clearly resolved.

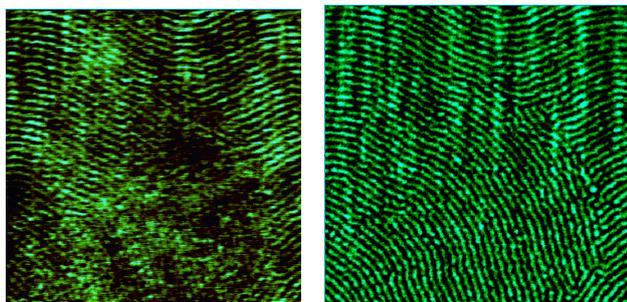


Fig. 10 PS-b-PMMA block copolymer. Image size 1 x 1 μm . Height (left) and phase image.

SBS styrene-butadiene-styrene triblock copolymer

A well-known tri-block copolymer is SBS (styrene-butadiene-styrene). SBS belongs to the group of thermoplastic elastomers and is made by anionic polymerisation. In the SBS case one starts with the anionic polymerization of styrene, and adds butadiene, after all styrene monomers have been reacted. Starting the reaction leads to a negatively charged ion. These reaction solutions are called "living polymers" because in an environment free of water and protic solvents negatively charged organic ions remain there, also after all monomers are polymerized.

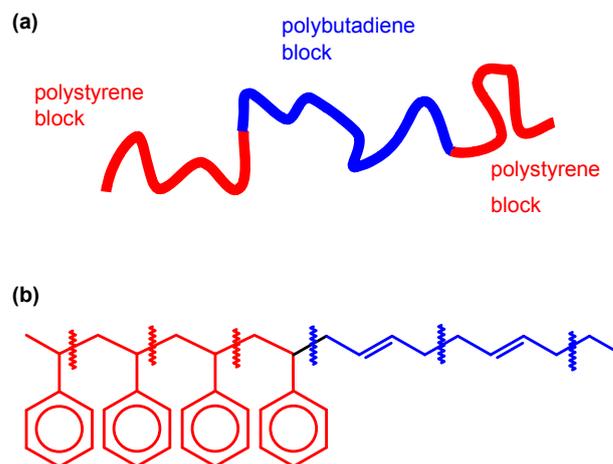


Fig. 11 (a) Very simple schematic view of the SBS block copolymer molecule. (b) Chemical structure of the polystyrene and polybutadiene sections. Parts formed from styrene monomers (red) and butadiene monomers (blue) are marked.

Pure polystyrene is a brittle and tough hard plastic, and this gives SBS its durability. Polybutadiene is rubbery, and this gives SBS its rubber-like properties and prevents the polystyrene from breaking. During the reaction the lengths of the styrene or butadiene chains can be controlled individually. Copolymers with a short soft butadiene-chain are highly transparent, shiny and impact resistant. The polymer is used for food and cosmetics packaging and shrinking foil, those with longer butadiene chains for shoe soles and tire treads. The molecular weight of the sample used here was 130,000 g/mol.

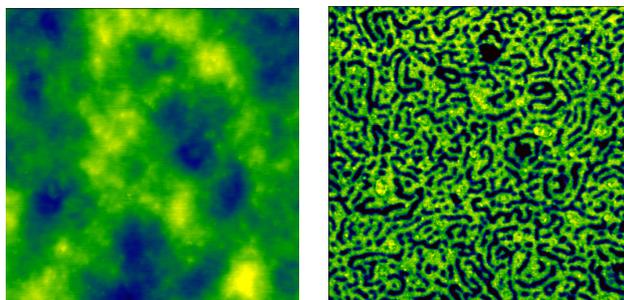
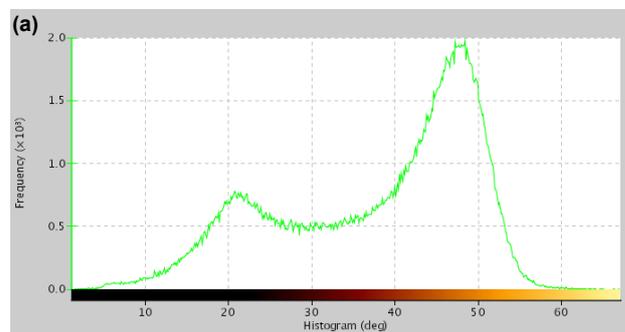


Fig. 12 SBS block-copolymer imaged in IC mode. Image size $1\ \mu\text{m} \times 1\ \mu\text{m}$. Left: height image, right: phase image. In the phase image dark areas correspond to polybutadiene, bright areas to polystyrene.

For AFM measurements SBS had to be prepared on a solid support. First, SBS was dissolved in toluene to a final solution of 5 % w/v. The thin films supported by a glass cover slip were prepared on a spin coater (1800 rev./min). Vacuum annealing of SBS at temperatures above $100\ ^\circ\text{C}$ ($190\ ^\circ\text{C}$ in this case) leads to nano-phase separation.

In contrast to the AFM height images of PS-b-PMMA (Figure 10), the height image in Figure 12 exhibits a relatively featureless surface, with pits of 80 nm in diameter and 3 - 4 nm in depth. The phase image exhibits a strong contrast from 10-15 nm wide dark rods in a bright matrix, where the rods are 60 nm or longer. The histogram analysis of the phase image in Figure 13 (a) clearly resolves the two species.

In this case the sample is a styrene-rich SBS. Some block-copolymers show de-mixing phenomena due to the insolubility of polybutadiene in polystyrene. From transmission-electron-microscopy (TEM) data it is known that butadiene forms hexagonally packed cylinders, embedded in a styrene matrix, as shown schematically in Figure 13. This means that in the phase image of Figure 12, the dark areas correspond to polybutadiene and bright areas to polystyrene.



(b)

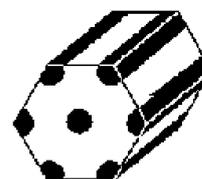


Fig. 13 (a) Histogram of the values in the phase image of Figure 12. (b) In a styrene-rich SBS the minority phase (polybutadiene) forms a hexagonally close-packed cylinder structure.

Biaxially-oriented Polypropylene

Like the copolymers also biaxially-oriented polypropylene (BOPP, a newer abbreviation is PP-BO) belongs to the polymers that are common in everyday use. The name comes from the manufacturing process in which a polypropylene foil is stretched in two directions. The AFM image in Figure 14 reveals a fiber-like structure [4]. Fibres are not completely separate and are oriented from the upper left to the bottom right side of the image. Connecting fibres also can be seen spreading from left to right.

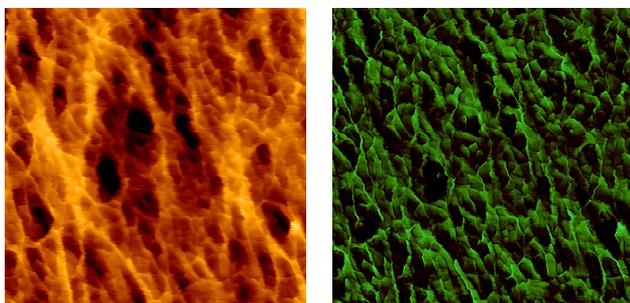


Fig. 14 Biaxially-oriented polypropylene foil. Image size 800 nm x 800 nm, height range 33 nm. Height (left) and phase (right) images.

Compared with standard polypropylene foils PP-BO has got an increased transparency and brilliance but also added better mechanical parameters such as added tear and scratching resistance as well as a high stiffness, a good low temperature resistance and impermeability for liquids and gases. PP-BO is widely spread, also for household use (bags, foils). Monoaxially-oriented polypropylene which is only stretched in one direction is often used for adhesive foils. Since 10 years, an increasing number of countries (Australia, Romania and others) issue their banknotes made out of PP-BO due to their wear-resistance and higher number of options to add security features.

Spherulites

Some bacteria use poly-hydroxybutyrate (PHB) as a food-storage molecule. By changing the feedstock they can also be forced to produce a copolymer named PHB-PHV consisting of poly-hydroxybutyrate-poly-hydroxyvalerate that contains ω-hydroxy valeric acid monomers.

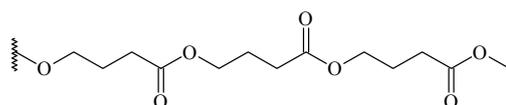


Fig. 15 Chemical formula of poly-hydroxybutyrate. It is synthesized in a polycondensation reaction of ω-hydroxy butyric acid monomers.

Many polymers tend to fold along the chain length to form large flat crystals, with a thickness much smaller than the lateral dimensions. These lamellae are often formed parallel to each other and form layered crystal sheets. The sheets also can form larger arrangements, where the lamellae grow approximately radially out from the center of a polymer spherulite. The images displayed in Figure 16 show the central section of one these spherulite structures.

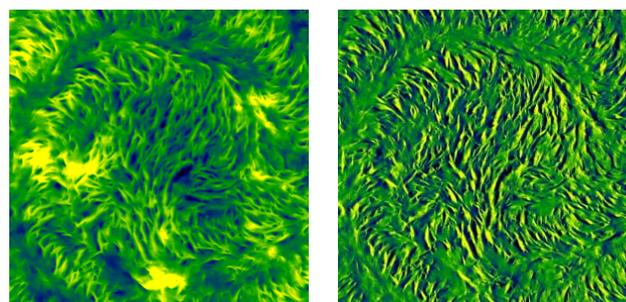


Fig. 16 Height image (left) and phase image (right) of a spherulite structure in a PHB-PHV film. Image size 8 μm x 8 μm, height range 140 nm.

Self-assembled monolayers of phosphonic acid with long alkyl chain

Octadecylphosphonic acid (OPA) is an amphiphilic molecule with a C-18 alkyl chain and a phosphonic acid group on one end (Figure 17). It is used for modification of oxidic metal surfaces (passivation). On aluminum surfaces it serves as a corrosion protector and it has also been used for chemical modification of titanium implant surfaces [5].

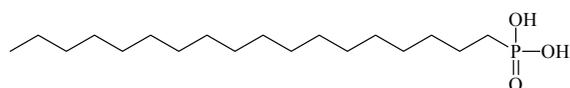


Fig. 17 Octadecylphosphonic acid (OPA), $\text{CH}_3(\text{CH}_2)_{17}\text{PO}_3\text{H}_2$, molecular weight 334,5 g/mol.

Preparing OPA on mica leads to robust self-assembled monolayers [6]. For the preparation of OPA monolayers on mica, OPA is dissolved in ethanol (0.25 mM) and the solution is spread onto a freshly cleaved sheet of mica (8 x 8 mm). The OPA is allowed to adsorb for 10 s, then the excess solution is removed with a stream of dry nitrogen.

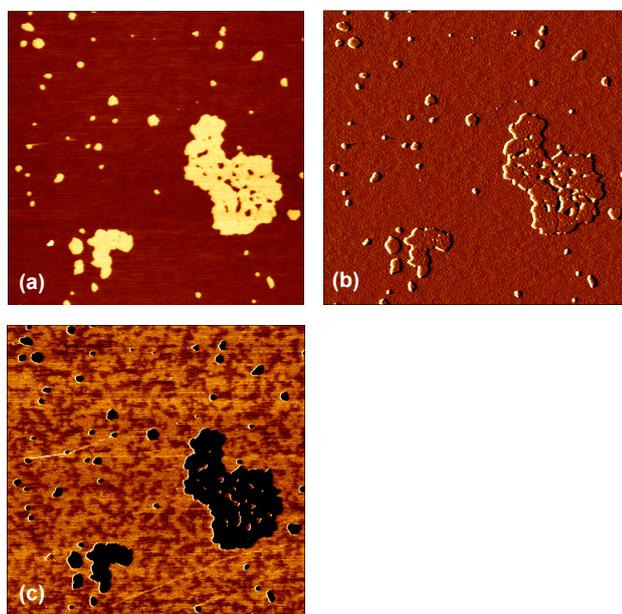


Fig. 18 OPA prepared on mica leads to monomolecular layers. Scan size 2 x 2 μm . Height (a), error (b) and lateral force (c) images.

AFM imaging was performed in contact mode with a very soft cantilever (spring constant 40 mN/m) for lateral force mode. In the height images small round dots with diameters in the 100 nm range are clearly resolved. But also larger curvilinear plaques with diameters up to 1 μm can be observed. The cross section displayed in Figure 19 indicates that the average height step is 2.3 nm. The histogram analysis of the height image also shows this uniform height distribution. The height of the plaques corresponds with the length of a single OPA molecule.

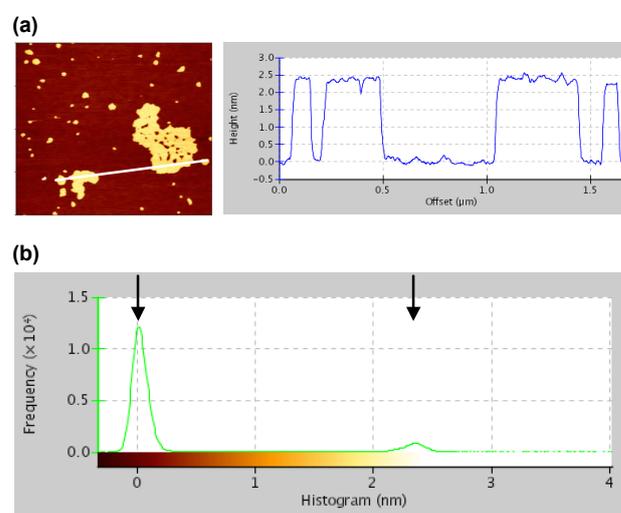


Fig. 19 (a) The cross-section indicates the height of the OPA monolayer. (b) Histogram analysis of the OPA height image. Two peaks are clearly resolved.

In the lateral force image in Figure 18 (c), the plaques indicate a relatively low lateral deflection and thus a lower friction compared with the friction on the pure mica surface. On the areas uncovered by OPA a pattern of brighter and darker domains is resolved which is invisible in the vertical deflection image.

Conclusions

In this report we presented AFM-based studies on samples made from alkanes, alkane derivatives, aromates and polymers. Information about the sample surface properties could be obtained on a micrometer and a nanometer range. Molecule assemblies could be resolved up to the length of single molecules. Phase separation phenomena also could be studied, not only depending on the pure surface properties alone. In case of fluorescent samples we successfully combined fluorescence microscopy with AFM. For a report on temperature-dependent polymer properties see JPK's application report "Temperature control for polymer crystallization studies".

Acknowledgements

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