

Surface Analysis of Polymeric Materials by Atomic Force Microscopy

S.N. Magonov *
H.J. Cantow

Appearance of atomic force microscopy (AFM) will strongly improve the surface characterization of polymeric materials. The possibility of this scanning probe method to registrate the surface morphology and molecular arrangement substantially increases the knowledge about polymeric surfaces. Below we are presenting short overview of AFM applications to polymeric systems. More information can be found in the original publications [1-6].

All results were obtained with a "Nanoscope II" scanning probe microscope (Digital Instruments Inc. Santa Barbara, USA) at ambient conditions. Preparation of sample surfaces is the important question of AFM measurements on polymers. However, sample preparation is less elaborative task in the comparison with the conventional electron microscopical techniques. Monocrystals of oligomers and polymers can be examined without any preparation. Solution or spin cast polymers are also suitable for examination. Flat surfaces of bulk samples of rigid polymers can be prepared by ultramicrotomy at room temperature. Cutting and milling at liquid nitrogen temperature also can be a challenge for preparation of rubber materials and their composites. However, in both cases the observed sample morphology might bear features associated with cutting procedure. Imaging of polymer surfaces are carried out in constant force or constant height regimes. Three-dimensional surface profiles or maps of interatomic forces are presented by AFM images. In the nearest future this information will be accompanied by surface elasticity and friction maps, which will be very important, especially, for composite materials.

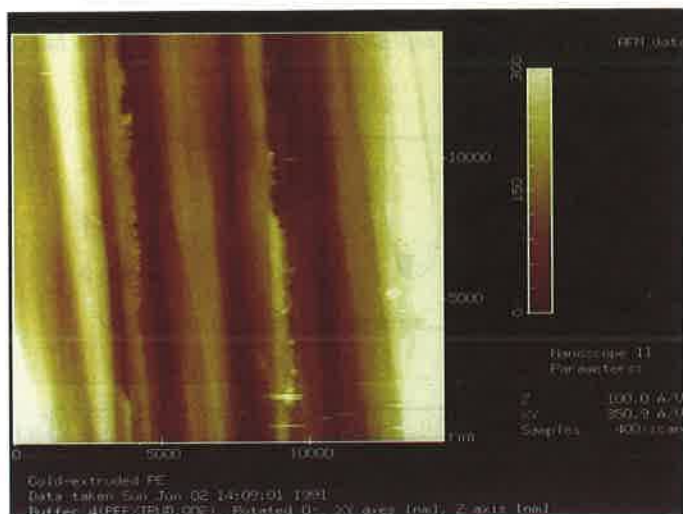


FIGURE 1a. - AFM image of cold-extruded polyethylene (Freiburger Materialforschungszentrum FMF).

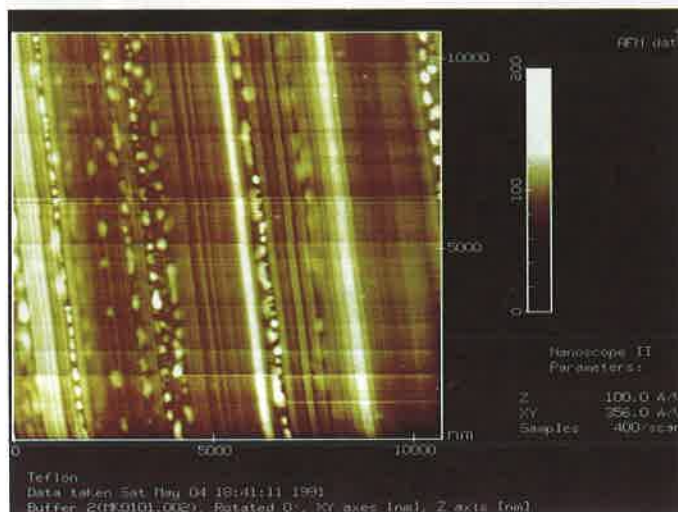


FIGURE 1b. - AFM image of thin film of polytetrafluoroethylene (Freiburger Materialforschungszentrum FMF).

Surfaces of highly crystalline polymers - polyethylene (PE) and polytetrafluoroethylene (PTFE) - can be easily characterized by AFM. These polymers have tendency to form extended chain crystalline structures. Fibrillar morphology of PE and PTFE samples was demonstrated in figures 1a-1b. Glancy surface of cold-extruded PE was prepared by microtomy of rod-like sample along the extrusion direction. The imaged PTFE film was obtained by rubbing the material on a heated glass substrate. In the other case PE was crystallized in a contact with anthracene monocrystal and the epitaxial crystalline surface is demonstrated in figure 2a. Polymer lamellae are aligned along the two main directions of organic monocrystals. Another morphology of PTFE was discovered on the surface of thicker polymer film deposited by rubbing (figure 2b). The equidistantly separated morphological units were detected along the main fibrils of polymer. They might be assigned to individual PTFE lamellae. The interpretation of morphological features is substantially supported by AFM images at higher magnifications, which reveal surface molecular arrangement. AFM patterns representing the individual polymer chains of PTFE (figure 3a) are oriented along the main direction of fibrils. The interchain spacing of 0.55 nm is in a good correspondence with the crystallographic data. The arrangement of extended PE chains with interchain separation of ca. 0.50 nm (cold-extruded sample) is shown in figure 3b. In some places the periodicity along the chain was 0.24 nm in correspondence with the repeat distance of 0.25 nm in the extended PE chain.

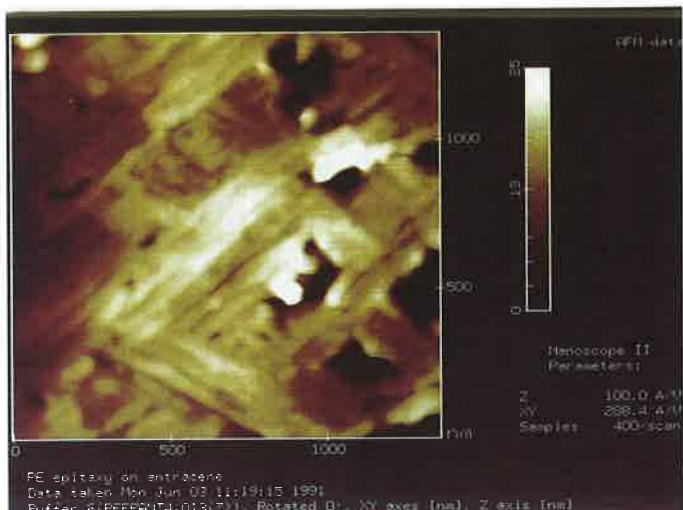


FIGURE 2a. - AFM image of polyethylene surface crystallized in contact with anthracene monocrystal.

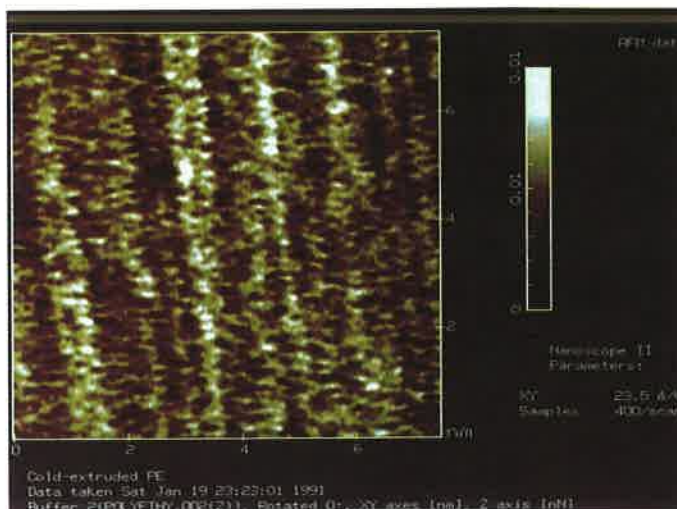


FIGURE 3b. - AFM images of cold extruded polyethylene (Freiburger Materialforschungszentrum FMF).

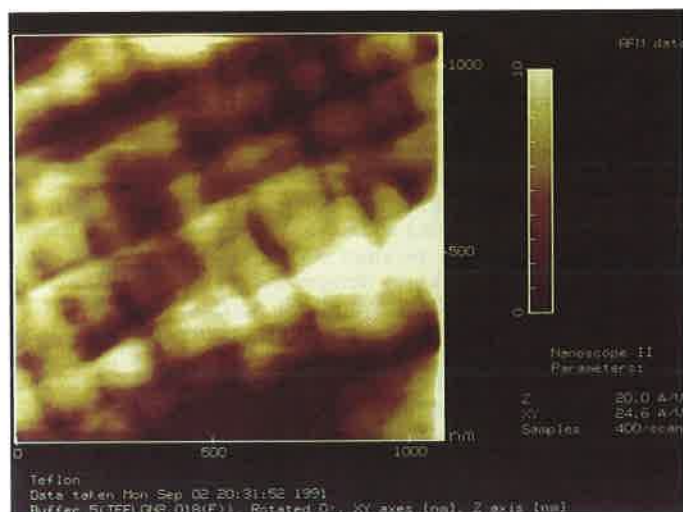


FIGURE 2b. - AFM image of thick film of polytetrafluoroethylene (Freiburger Materialforschungszentrum FMF).

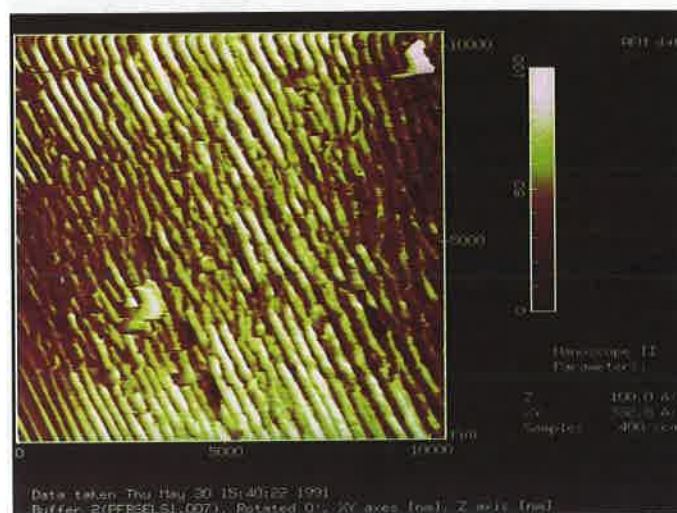


FIGURE 4a. - AFM images of surface (the bc plane) of polydiacetylene (2,4-hexadiynylene bis(p-fluorobenzenesulfonate)) monocrystal (Freiburger Materialforschungszentrum FMF).

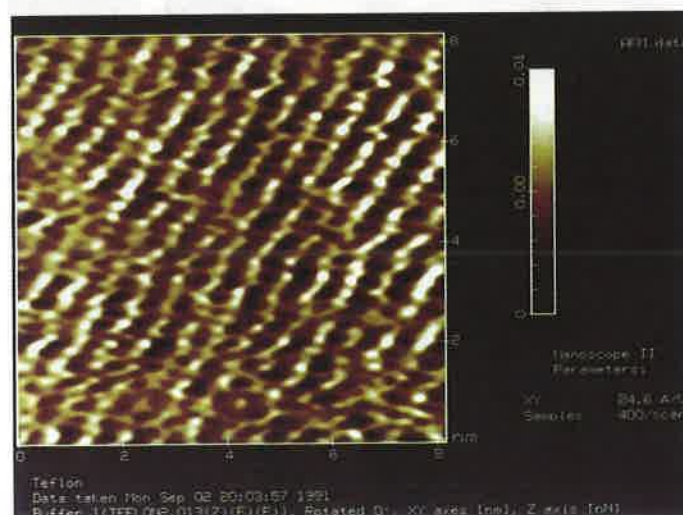


FIGURE 3a. - AFM images of polytetrafluoroethylene (thick film) (Freiburger Materialforschungszentrum FMF).

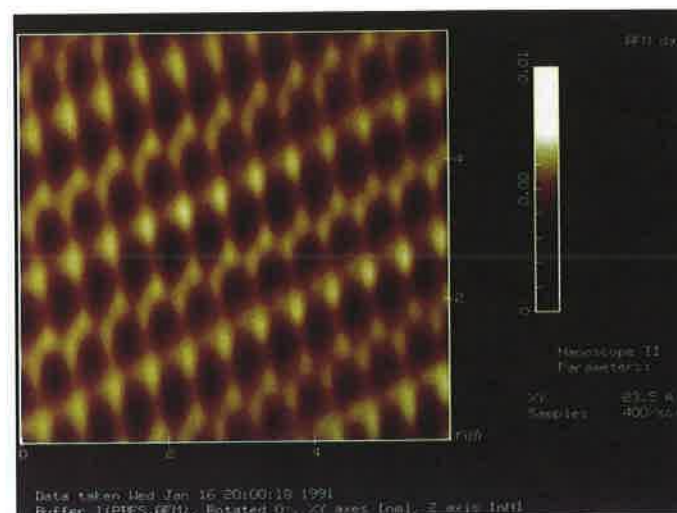


FIGURE 4b. - AFM images of surface (the bc plane) of polydiacetylene (2,4-hexadiynylene bis(p-fluorobenzenesulfonate)) monocrystal at a different scale (Freiburger Materialforschungszentrum FMF).

AFM images of polydiacetylene (bis(p-fluorobenzenesulfonate) monocrystal, figures 4a-4b, demonstrate its fibrillar morphology and surface arrangement of side chain substituents on the bc crystallographic plane. Several surface defects are distinguished in the large scale image. The comparison of the AFM pattern arrangement on the bc plane with the molecular structure, reconstructed from the crystallographic data, reveals surface reconstruction.

Many of polymeric materials are semicrystalline and amorphous compounds. Tendency of amorphous material to dominate in the surface layers of semicrystalline polymers due to lower surface energy is known. Absence of order at large scales of nanometers or microns as well as absence of surface molecular ordering will lead to AFM images, which will be difficult to separate from the instrumental noise and to characterize. These difficulties are expected in the AFM analysis of surfaces of amorphous and semicrystalline polymers. However, there are cases, when surface of semicrystalline polymer can be tested by AFM.

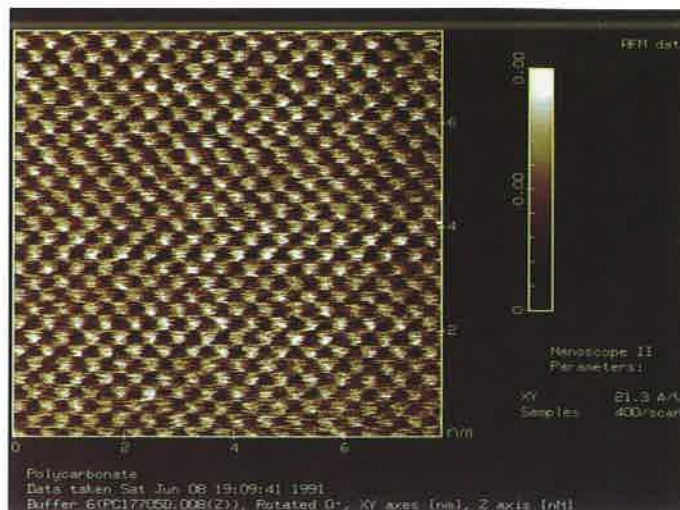


FIGURE 5c. - AFM images of bis-phenol A polycarbonate film after thermal treatment : 5 days at 178 °C (Freiburger Materialforschungszentrum FMF).

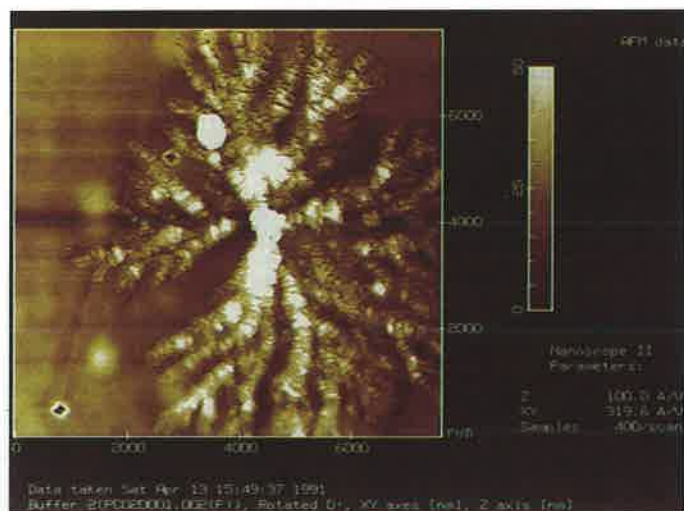


FIGURE 5a. - AFM images of bis-phenol A polycarbonate film after thermal treatment : 36 hours at 145 °C (Freiburger Materialforschungszentrum FMF).

Bis-phenol A polycarbonate was chosen as an example. Solution cast amorphous film was thermally treated in the range of 145 °C - 180 °C. AFM image of surface of amorphous film shows only some randomly distributed corrugations, probably associated with a solvent evaporation. In AFM images two processes are visualized. Crystallization and polymer degradation seem to compete during tempering at elevated temperatures. Spherulitic morphology typical for polymer crystallization was found after thermal treatment at lower temperature (145 °C), figure 5a. Numerous nanocrystalites covered the surface of polymer film after treatment at higher temperatures, figure 5b. They have been assigned to monocrystals of PC oligomers, which appeared as the result of thermal degradation. Perfect molecular organization on the surface of such monocrystalite is shown in figure 5c.

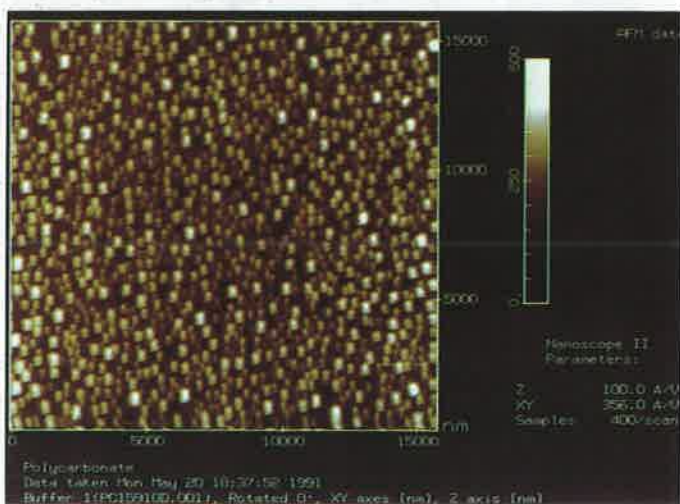


FIGURE 5b. - AFM images of bis-phenol A polycarbonate film after thermal treatment : 5 days at 178 °C (Freiburger Materialforschungszentrum FMF).

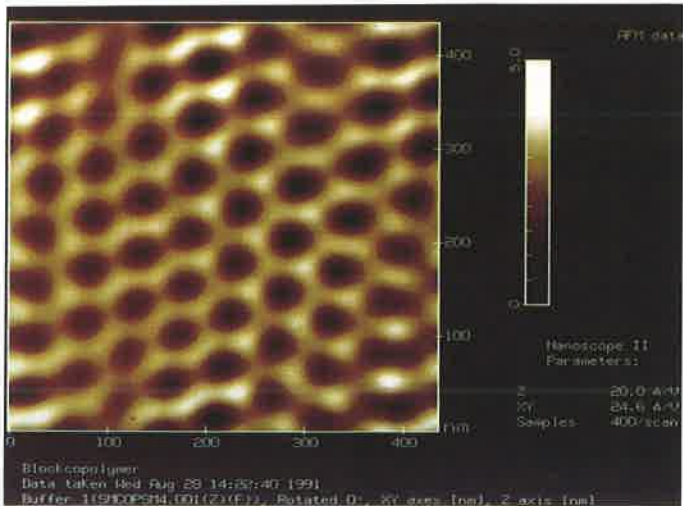


FIGURE 6. - AFM image of solution cast film of poly(styrene-methylmetacrylate) (Freiburger Materialforschungszentrum FMF).

Among amorphous polymeric materials block copolymers in many cases demonstrate the well organized morphology due to phase separation phenomenon. These structures can be revealed

by AFM, which in this respect competing with traditional electron microscopy methods. One of the examples of well defined morphology found in copolymer of styrene and methylmethacrylate is presented in *figure 6*. AFM image was obtained on the surface of co-polymer film casted from acetone/cyclohexane. Though the interpretation of this image is under way, the ability of AFM for topographical characterization is well demonstrated.

References

[1] S.N. Magonov, K. Qvarnström, V. Elings, H.J. Cantow, *Polym. Bull.*, **1991**, *25*, 689.

[2] B. Lotz, J.C. Wittmann, W. Stocker, S.N. Magonov, H.J. Cantow, *Polym. Bull.*, **1991**, *26*, 209.

[3] W. Stocker, G. Bar, M. Kunz, M. Möller, S.N. Magonov, H.J. Cantow, *Polym. Bull.*, **1991**, *26*, 215.

[4] S.N. Magonov, G. Bar, H.J. Cantow, H.D. Bauer, I. Müller, M. Schwoerer, *Polym. Bull.*, **1991**, *26*, 233.

[5] S.N. Magonov, H.J. Cantow, submit to *J. Appl. Polym. Sci.*, *Appl. Polym. Symp.*, **1991**.

[6] S.N. Magonov, S. Kempf, M. Kimmig, H.J. Cantow, *Polym. Bull.*, to be published.