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Atomic force microscopy on polymers and polymer related compounds

4. Polytetrafluoroethylene and polycarbonate*

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SUMMARY

Surface morphology and molecular arrangement have been recorded by atomic force microscopy (AFM) on polytetrafluoroethylene (PTFE) and on polycarbonate (PC) films. In a thin layer of PTFE deposited by rubbing polymer on hot glass substrate unidirectional orientation of polymer has been revealed. Individual polymer chains have been visualized. An interchain distance of .53 nm and several periodicities along the chain contours have been found - .44 nm, .62 nm and .82 nm - in accordance with a 13/6 helix.

The monitoring of surface changes during thermal treatment of amorphous - bis-phenol A - PC film has been realized by AFM. Different types of surface morphology were revealed. Spherulites are formed during polymer crystallization. In most cases, however, numerous nanocrystallites appeared after thermal treatment. On their surfaces well-ordered atomic scale AFM images have been received. The arrangement of AFM patterns can be characterized by periodicities of .50 nm and .52 nm in the orthogonal directions. Polycarbonate oligomers - as the product of surface degradation - effectively might form the observed nanocrystallites.

INTRODUCTION

Atomic force microscopy (AFM) [1] is the new scanning probe technique, which offers an unique capability for surface analysis of polymer samples. It can be efficiently used in combination with conventional electron microscopy methods - scanning electron microscopy (SEM) and transmission electron microscopy (TEM), especially in its energy specific imaging mode (ESI), which allows element specific imaging. In the examination of polymer surface morphology AFM is the complementary to SEM. Both methods have their advantages and disadvantages. Sample preparation for AFM measurements is less time-consuming and the contrast in the AFM image has direct correspondence to surface corrugations. However, rough surfaces can be better studied by SEM. The unique possibility of AFM to reveal the pecularities of surface molecular arrangement in the atomic scale is the basis of its enormous potential. Molecular structure has been usually studied by diffraction techniques, and in some cases TEM can be applied. However, most of structural methods provide information concerning bulk. Thus, with AFM,

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*Prof. Dr. G. Zachmann zum 60. Geburtstag herzlichst gewidmet

**Permanent address: Institute of Chemical Physics, USSR Academy of Sciences, ul. Kosygina 4, Moscow 117977, USSR methods of surface structure studies acquire an excellent companion.

Validity of AFM as structural method had been already proved in several cases, when morphology and surface molecular arrangement have been detected in linear and cyclic alkanes, cold-extruded polyethylene, epitaxially crystallized polypropylene, and polydiacytelene [2-5]. At scales from microns to angstroms fibrils, lamellae, individual polymer chains and atom groups on lamellar surfaces have been visualized in AFM images.

The results of AFM studies on surfaces of polytetrafluoroethylene (PTFE) and polycarbonate films (PC) will be presented below [+]. PTFE is a highly crystallizable polymer, and due to its specific chain structure it has tendency to form extended chain crystals. It also exhibits low friction, which is explained by the inherently low cohesive forces between adjacent polymer chains [6]. The rod-like monocrystals of virgin polymer have been examined by the sophisticated high resolution TEM technique [7]. The linear ordering of polymer chains with interchain spacing of .49 nm was detected. Thus, a study of PTFE by AFM is interesting from different points of view.

In the development of AFM applications to polymers the examination of semicrystalline surfaces seems to be extremely interesting. For this purpose (bis-phenol A) polycarbonate (PC) was chosen. The structure of this polymer in amorphous and crystalline states is under discussion since a long time [8-9]. Specific conformation of polymer chain probably retards its crystallization [10], which is rather slow even at optimal temperatures. The various morphological structures have been registered by electron microscopy on the surface of thin PC films during thermal treatment [9, 11].

EXPERIMENTAL

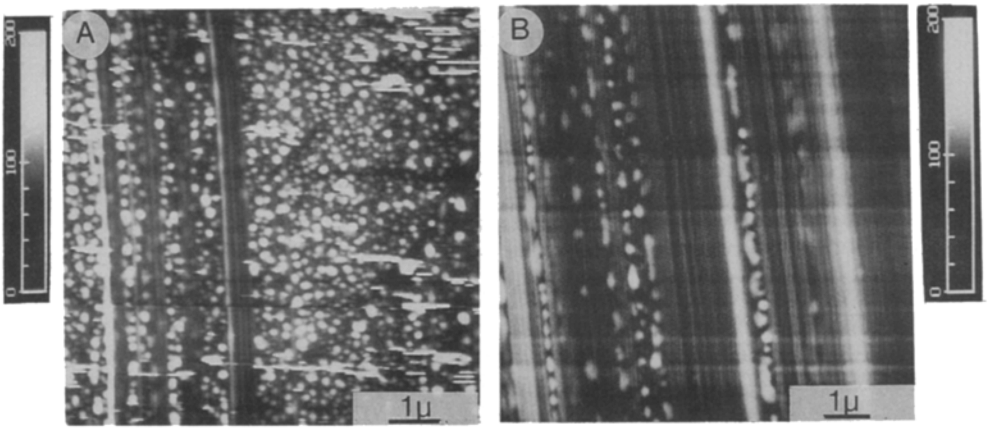
A sample of PTFE was prepared in a simple way. A glass microscope slide was heated up to 200C and polymer layer was deposited by rubbing a piece of material on the hot support. Polycarbonate (Lexan 165) has been used in the experiments. Thin films of PC were casted from 1% CH_2Cl_2 solution on a glass support. After two days of solvent evaporation in vacuum films were subjected to thermal treatment at 145C, 159C and 177C in vacuum. The time of treatment was varied from 1 to 12 days.

AFM measurements were carried out with a 'Nanoscope II' (Digital Instruments, Inc., Santa Barbara, Cal., USA) at ambient conditions. The images of areas larger than 100 x 100 nm^2 were collected in the height imaging mode. At smaller scales force and height imaging modes were applied. V-shaped cantilevers with force constants of .06 N/m and .12 N/m were used. The variations of interacting repulsive force have not led to evident changes of images. AFM 'A' and 'D' heads were used to areas from 10 x 10 nm^2 - 600 x 600 nm^2 and 200 x 200 nm^2 - 15 x 15 μ^2, respectively. There are several reasons, which influence the accuracy of geometrical parameters, calculated from AFM images. Thermal drift during measurements at ambient conditions, the possible inclination of a sample with respect to the tip and non-linear effects of piezodrive lead to the deviations of data up to 10%. Further experimental details are presented in [2-5].

RESULTS AND DISCUSSION

Polytetrafluoroethylene

Large scale AFM images of PTFE film are presented in Fig. 1A-1B. Only few long polymer fibrills are distinguished on surface of the amorphous glass substrate in Fig. 1A. The latter is visualized as an array of randomly distributed AFM patterns with diameters in a range of 150 - 250 nm. In another place (Fig. 1B) the polymer film covers a bigger area, and it also shows up the fibrillar morphology aligned along rubbing direction. The cross-section size of individual PTFE fibrills varies from 80 to 200 nm, and their length is bigger than the maximal range (15 μ) of applied 'D' head of the instrument. The linear AFM patterns, oriented in the same way, have been registered in smaller scale images, Fig. 2A-2B. There are places with different order in the force map in Fig. 2A. The found imperfections can be assigned to surface defects with a size of 5 - 10 nm. At higher magnifications (Fig 2B) in addition to rows of AFM patterns the definite structure along the chains also is distinguished. The averaged periodicity in the direction perpendicular to the observed linear structures - .53 ± .02 nm - correlates with the expected value of



Figures 1 A - 1 B: Top view AFM images • Morphology of oriented PTFE

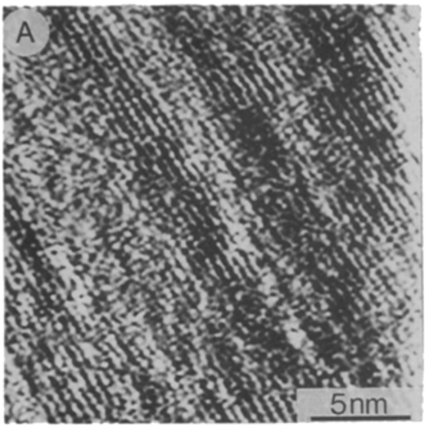
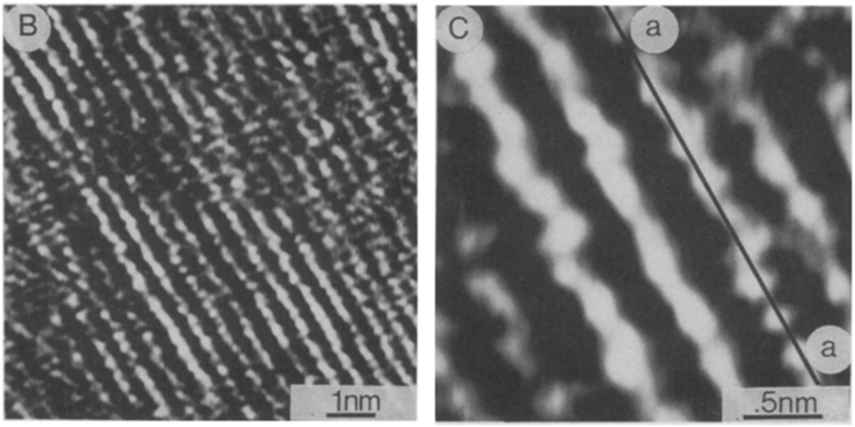
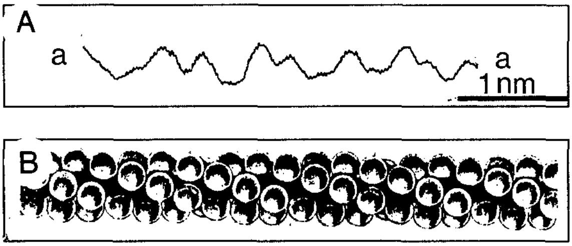


Figure 2 A: Top view AFM image of same sample • PTFE chain structure

For all Figures: A vertical grey scale bar in a large scale AFM image indicates the corrugations - in nm - in z-direction, perpendicular to the examined surface • In an atomic scale image a grey scale bar corresponds to changes in force in the range of .1 nN • Scales are indicated by bars



Figures 2 B - 2 C: Atomic resolution AFM top-views of polytetrafluoroethylene

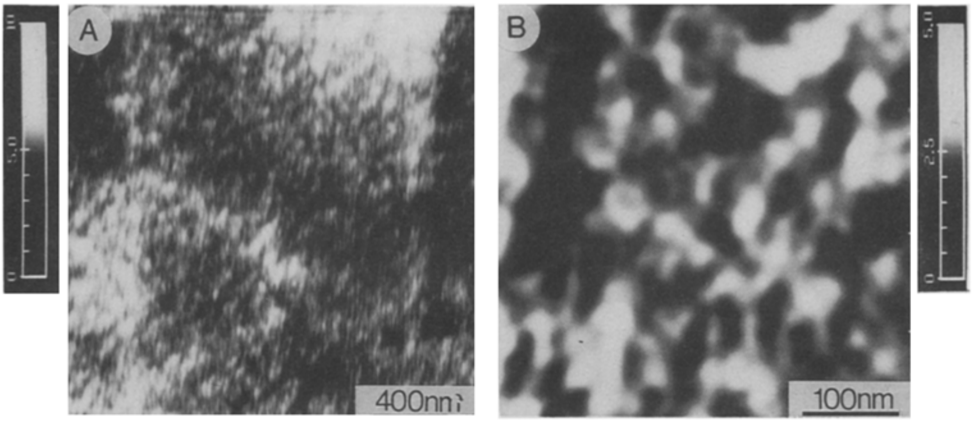


Figures 3: A • Contour along line in Figure 2 C
B • 13/6 helical chain conformation • Identical scale

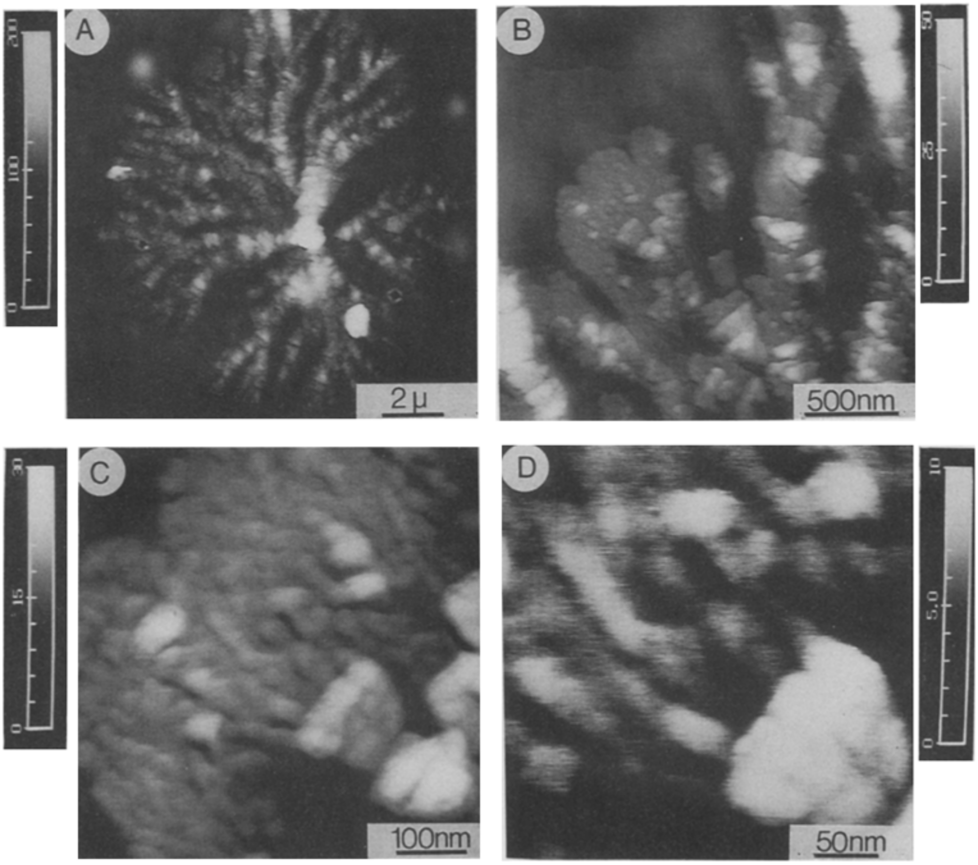
interchain distance in PTFE. The interchain parameter of .566 nm was determined in the diffraction experiments [6]. The smaller value of .49 nm was registered in the high resolution TEM experiment [7]. Thus, we can interprete the AFM image as the visualization of arrays of polymer chains. The periodicites along chain patterns might be estimated from the contours along the chains as indicated in the zoomed image Fig. 2C. Distances between elevated AFM patterns of .44 nm, .62 nm and .82 nm have been found along such contour, Fig. 3A. It is known that PTFE chain exists in two different helical conformations - 15/7 and 13/6 - at temperatures above and below 19C, respectively. In Fig. 3B the polymer molecule in one of its possible conformations, 13/6, is illustrated. In this case the repeat distance along the polymer chain is 1.69 nm. The elevated bright patterns in the force map (Fig. 2C) might be assigned to positions of highest atoms of polymer chain. There is a correspondence between periodicities along chains in the AFM image and interatomic distances in 13/6 conformation macromolecule. This result and the visualization of the polyethylene chain in all trans conformation [2] make evident that there is a definite perspective to apply AFM to the conformational analysis of polymer chains.

Polycarbonate

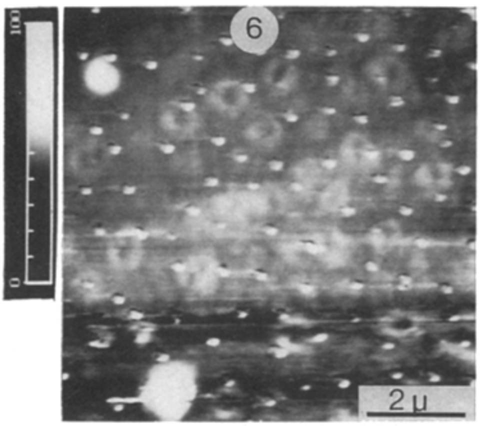
In the AFM image the surface of amorphous polycarbonate film was observed as an array of randomly distributed patterns with diameters in the range 50-100 nm, Fig. 4A-4B. The surface corrugations are small, ca. 5 nm in height. These structures probably are formed during solvent evaporation.

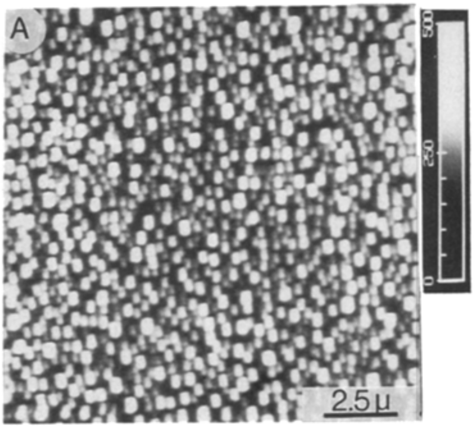


Figures 4 A - 4 B: Amorphous PC film with randomly distributed patterns



Figures 5 A - 5 D: Spherulitic structures on polycarbonate film after 36 hours treatment at 145C





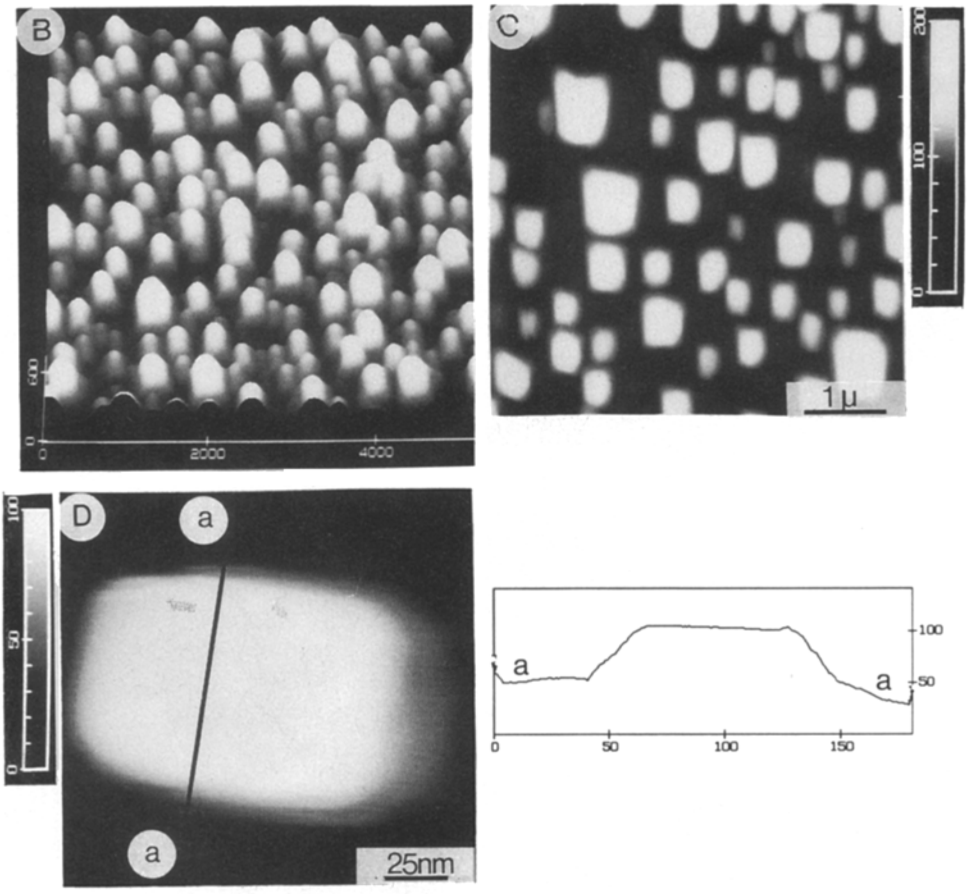
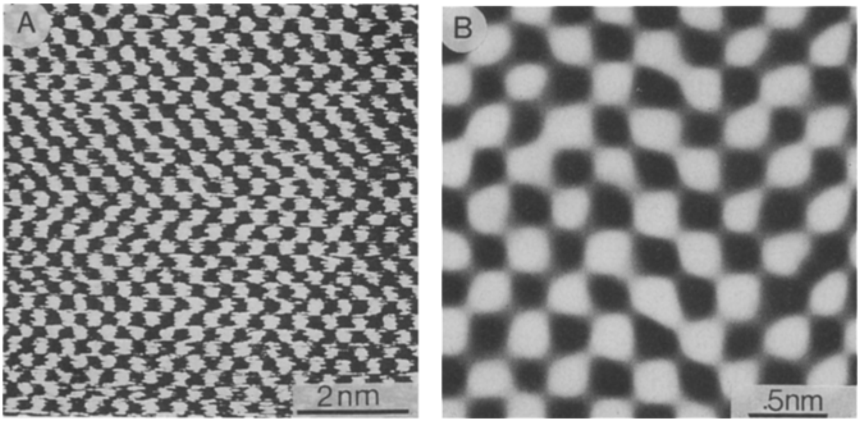
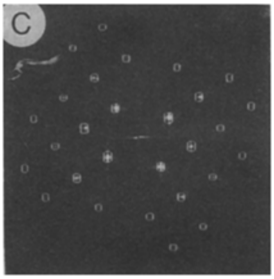


Figure 6: Top-view on film with round shaped PC platelets grown at 145C

Figures 7: PC elongated platelets grown at 159C • A - B after 10 days
C - D after 5 days • E • Surface profile of the pattern in Fig. 7D





Figures 8: Atomic scale AFM top-view images from platelet in Fig 7D
A • without data treatment
B • after 2D-FT noise reduction procedure
C • 2D-Fourier transform of Fig. 8A Spots marked by boxes were engaged for Fig. 8B image construction

Thermal treatment at 145C induces several types of surface morphology in the PC film. The most interesting were spherulitic structures found on polymer surface after 36 hours of treatment. In a sequence of images (Fig. 5A-5D) morphological features are shown with increasing magnification. The substructure of spherulite appeared to consist of round-shaped patterns of 30-50 nm diameter. However, we have not succeeded to achieve atomic resolution on this surface. The observed spherulitic morphology was not the dominant one found during treatment at 145C. In Fig. 6 the surface regions with small round-shape patterns, ca. 50 nm in diameter, are shown. The number of such patterns increased with time.

Monitoring of morphology changes after heating at 159C and 177C reveals similar tendency. Spherulitic structures have not been observed, however. The characteristic large scale images are presented in Fig. 7A-7C. In images of smaller areas, Fig. 7D, AFM patterns have the shape of elongated platelets with characteristic dimensions of ca. 50 x 150 nm^2. These patterns can be assigned to nanocrystalites, which are formed during thermal treatment. This suggestion was fully supported by atomic scale images, presented in Fig. 8A-8B, and the corresponding 2D Fourier transform in Fig. 8C. They show perfect order of AFM patterns, which can be characterized by main periodicities of .50 nm and .52 nm in the perpendicular directions, as indicated in Fig. 8B. These periodicities generally correlate with the crystalline phase structure parameters of this polycarbonate. It was found that its unit cell exhibits the parameters a=1.23 nm, b=1.01 nm, c=2.05 nm, and γ=84° [12]. The AFM repeat distances in orthogonal directions correspond to b/2 and c/4, respectively. Another probable interpretation of the origin of observed nanocrystallites is connected with the possibility of polymer thermal degradation. Then, the nanocrystallite can be assigned to oligomer PC. The competition between degradation and crystallization at surface of the examined PC film may be favorable for the first process. Only at lower temperature spherulitic structures of crystalline polymer have been found occasionally.

CONCLUSIONS

The development of AFM approach to polymer surfaces shows that this technique can be succesfully applied to crystalline and semicrystalline materials. The AFM resolution of surface structure details is higher than that acheived by TEM. Details of conformational order have been revealed in polymer chains. It was shown that by AFM nanometric scale crystalline structures on the surface of semicrystalline polymers can be characterized.

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\+ These results were given by us first in a lecture in Baltimore, at the 5th ISPAC Symposium on May 31, 1991, and in a lecture in Santa Barbara, at the Nanoscope Users Meeting on June 25, 1991

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