Polymer Bulletin 26, 223–230 (1991)

Polymer Bulletin

Atomic force microscopy on polymers and polymer related compounds

3. Monocrystals of monomer and polymer 2,4-hexadiynylene bis(*p*-fluorobenzenesulfonate)*

S. N. Magonov[1,], G. Bar[1], H.-J. Cantow[1,2,]***, H.-D. Bauer[3], I. Müller[3], and M. Schwoerer[3]**

[1]Freiburger Material-Forschungszentrum FMF and [2]Institut für Makromolekulare Chemie,
Universität, Stefan-Meier-Strasse 31, W-7800 Freiburg, Federal Republic of Germany
[3]Bayreuther Institut für Makromolekülforschung BIMF and Physikalisches Institut, Universität
Bayreuth, P.O. Box 101251, W-8580 Bayreuth, Federal Republic of Germany

SUMMARY

The largest surfaces of lozenge-shaped monocrystals of polymer 2,4-hexadiynylene bis(p-fluorobenzenesulfonate), (pFBS), and its monomer have been studied by Atomic Force Microscopy (AFM). Tridimensional maps of interatomic forces between probe and surface have been recorded at areas from hundreds of nanometers down to the atomic scale. The examined surfaces, which generally correspond to the crystallographic [100] plane, are built from end groups of substituents, benzene rings, with main planes being perpendicular to the surface. Large scale AFM images reveal a fibrillar structure of the polymer surface in contrast to a not well-defined morphology of the monomer surface. The atomic scale maps of polymer and monomer [100] surfaces look quite similar. They can be characterized by alternating rows of 'hills', one of which shows zig-zag type arrangement. The repeat distances along the rows are .53 ± .04 nm for the polymer and .61 ± .06 for the monomer. In the close to perpendicular direction - $\alpha = 89.5 \pm 3.0^\circ$ for the polymer and the monomer - the repeat distances are 1.62 ± .16 nm for the polymer and 1.47 ± .08 nm for the monomer. These values are in general agreement with the crystallographic parameters, b = .4914 nm, c = 1.4103 nm (polymer), and b = .5187 nm, c = 1.4093 nm (monomer). The appearance of alternating rows in AFM images does not exactly correspond, however, to the surface atomic arrangement in the [100] plane, which has been reconstructed from the crystallographic data. Though the AFM patterns might be assigned to -CF-CH- groups of substituents, the differences found between images and diffraction data are discussed.

INTRODUCTION

Nowadays, characterization of surface structure of organic compounds is significantly improved by AFM. Spatial resolution of individual surface atoms and molecular groups provided by this technique opens unique perspectives for science and technology. At first stage well-ordered surfaces of inorganic and organic monocrystals have been probed by AFM [1-3]. Correspondence of structure of AFM images to main crystallographic parameters can be regarded as experimental support for validity of the new method as a tool for structural analysis. This method has definite advantages in comparison with the

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*Dedicated to Prof. Dr. Takeo Saegusa on the occassion of his retirement celebration

**Permanent address: Institute of Chemical Physics of the USSR Academy of Sciences, Kosygin ul. 4, SU-117977 Moscow, USSR

***To whom offprint requests should be sent conventional diffraction methods. Local surface molecular defects and ordering in relatively small molecular domains can be visualized by AFM. However, due to several reasons - e. g. thermal sample drift - the precision of AFM measurements is not as high as in diffraction techniques.

The first AFM image of a polymer, revealing individual chains, was obtained from a polyaniline layer on mica [1]. A possibility to visualize even conformational order of polymer chains has been demonstrated by experiments with cold-extruded polyethylene [4]. The arrangement of end groups and parts of molecular folds, which form lamellae surfaces in monocrystals of normal and cyclic alkanes, was well resolved in the corresponding AFM images [5].

One of the main requirements for successful AFM imaging is flatness of an examined surface. Thus, we can expect that cleaved surfaces of macroscopic monocrystals of different types of polydiacetylenes (PDA) might be appropriate for AFM analysis. Interest on testing those compounds is also based on perspectives of imaging different surface defects and on on-line studies of molecular events during polymerization. The bulk structure of different PDA's is known [6], and this may be helpful for the interpretation of AFM images. The present communication is based on first results of AFM surface imaging of polymer and monomer monocrystals of a symmetrically substituted PDA.

EXPERIMENTAL

AFM studies of polymer and monomer monocrystals at ambient conditions were carried out with a commercial scanning probe microscope 'Nanoscope II' (Digital Instruments, Inc., Santa Barbara, CAL, USA). Type 'A' AFM head was used. It allows measurements at areas from 700 x 700 nm down to the atomic scale. Cantilevers with force constants of .06 and .12 N/m were usually applied. During experiment an examined surface was scanned by a cylindrical piezodrive under a sharp microscopic Si_3N_4 probe. An initial positioning of a probe on a flat surface region was carried out with an optical stereomicroscope. The tridimensional contour of constant interatomic force was recorded in AFM experiments. Top-view images with grey scale coded height are mainly used to present AFM information. The 'hills' in the z-direction - z being the direction perpendicular to the examined surface - correspond to surface spots with higher repulsive force. Only low frequency filtering was applied to the received images, unless specifically mentioned. More experimental details concerning AFM can be found in the previous publications [1,4,5].

A symmetrically substituted diacetylene, 2,4-hexadiynylene bis(p-fluorobenzenesulfonate) - pFBS - was chosen for our examination. This compound was synthesized according to [7]. Monocrystals of monomer were grown from solution at 10° C. The largest surface of the lozenge-shaped monocrystal corresponds to the crystallographic [100] plane, the c-direction being parallel to the longest diagonal [8]. Polymerization was conducted thermally (120 hours at 60° C). The good quality surfaces were prepared by cleavage. In addition to the examination of the main [100] plane, an attempt was done to image other surfaces. A surface, which in accordance with [8] might be indentified as the [102] plane, was prepared by cutting with a razor blade.

The modified molecular graphics program 'Schakal' [9] was used for the reconstruction of molecular arrangement on different crystallographic planes of monomer and polymer monocrystals. The results of crystallographic analysis of these compounds [10] were taken as the basis.

RESULTS AND DISCUSSION

AFM images reveal morphology details from large scales available by conventional optical and electron microscopy down to nanometers. The comparison of large scale AFM images of monomer and polymer monocrystals have demonstrated well pronounced differences. An imaging of the monomer surface has not revealed a defined morphology, Fig. 1A. Several flat terraces are presented in this image. Their size depends on quality of cleavage. In contrast to monomer the polymer surface has fibrillar morphology, as can be seen from Fig. 1D. A linear type of structure also was found at smaller scale, Fig. 1E. The diameter of microfibrils varies from 10 to 30 nm. They are aligned along the b axis. Observed morphological changes between monomer and polymer surfaces can be explained as the direct consequence of polymerization process. Even under an optical microscope one can observe a splitting of surface material into numerous macroscopic filaments after cleavage of a polymer crystal.

Molecular ordering has been revealed in smaller scale AFM images of monomer and polymer surface. One of surface regions of monomer is shown in Fig. 1B. Periodical AFM patterns, distinguished in this image, are ordered in rows. In some places defects like protrusions have been observed. Such case is shown in the zoomed part of the image discussed, Fig. 1C. The defects of the same type have been also observed on polymer surfaces, Fig. 1F.

It should be noted that, at present, the quality of atomic scale AFM in many cases is not as good as the one achieved in imaging of conductive monocrystals by scanning tunneling microscopy. Perhaps, with development of instrumentation and with more experimental experience in choosing of object-oriented imaging conditions, this situation will be improved. However, at the moment we have used different filtration procedures, incorporated in the 'Nanoscope II' software, for treatment of raw data. Atomic scale AFM images of PDA monocrystals and its monomer have lower contrast than images taken from normal and cyclic alkanes, and Fast Fourier Transform (FFT) was used in some cases in order to improve the pictures. The procedure is demonstrated in Fig. 2A-2E. The as-received atomic scale AFM image of the polymer surface having the best contrast, Fig. 2A, can be characterized by the two-dimensional FFT picture, Fig. 2E. Brighter spots correspond to well pronounced periodicities found in this image. If only these patterns have been used for the restoration of surface image by the reverse procedure, then one obtains the image shown in Fig. 2B. Images of monomer surface have been also improved in the same manner, Fig. 2C, 2D. It is necessary to underline that this treatment leads to an idealized structure in the restored AFM image. Thus, for

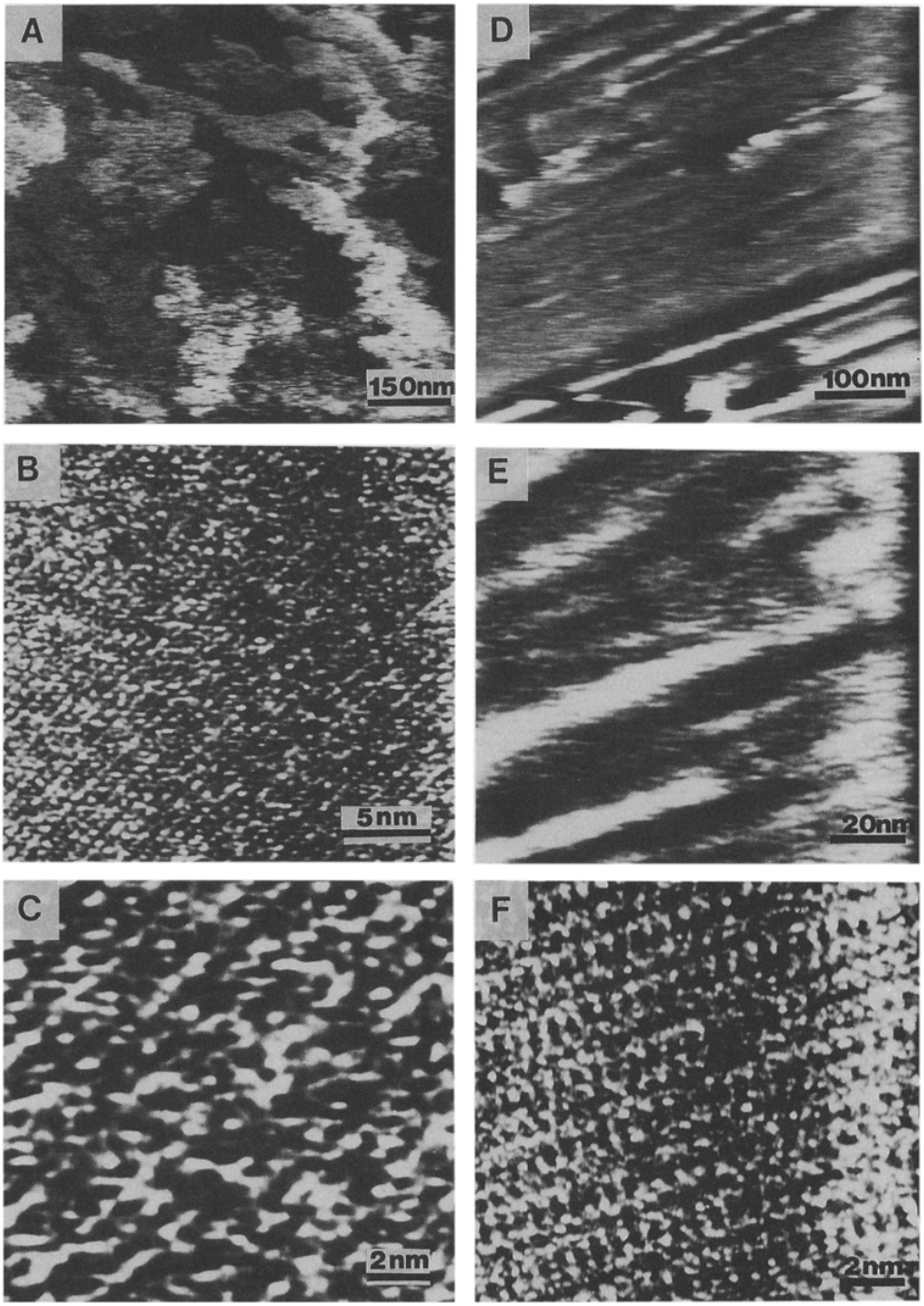


Figure 1: AFM images of the [001] surface of monomer (A - C) and polymer (D - F) pFBS monocrystals

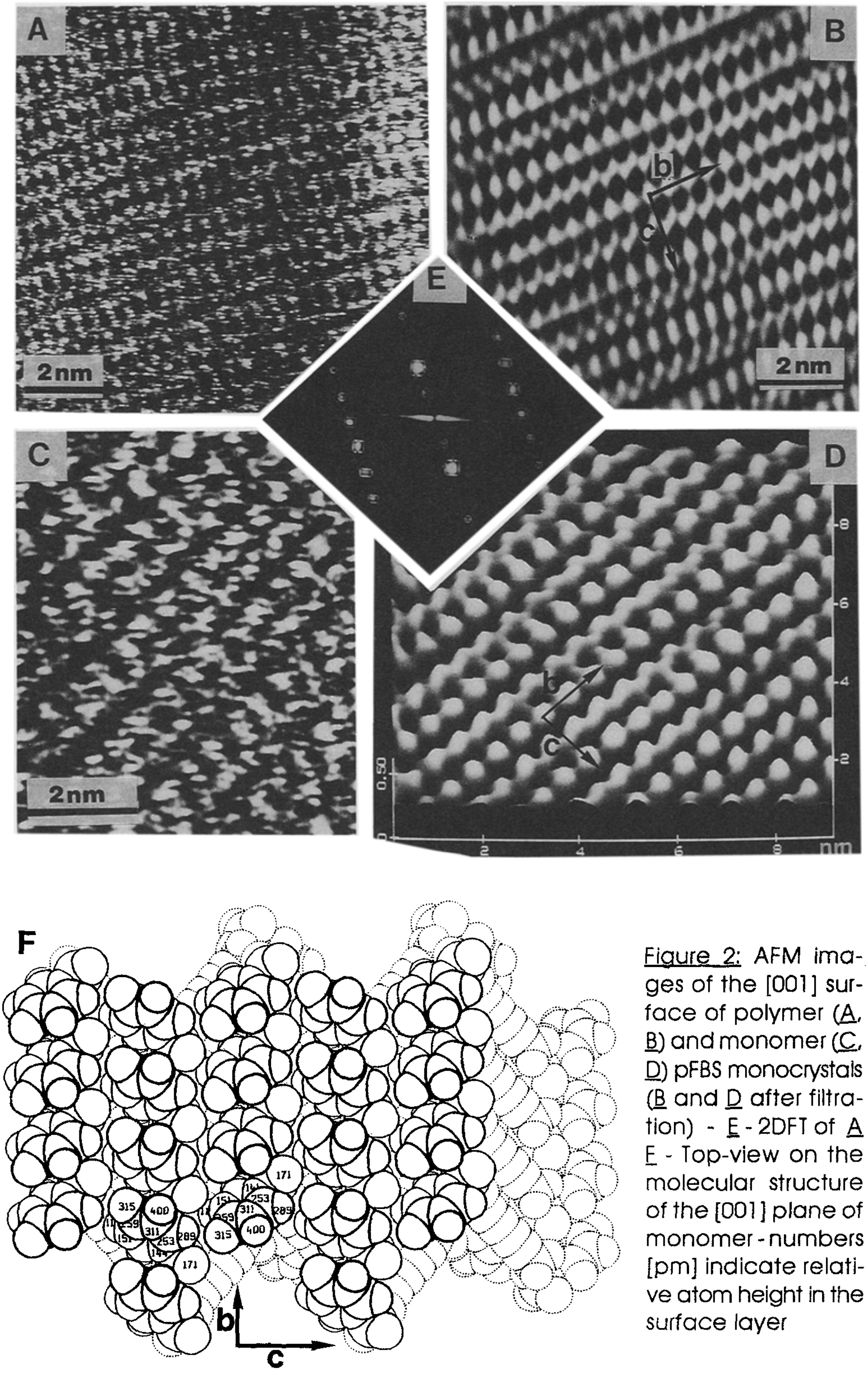


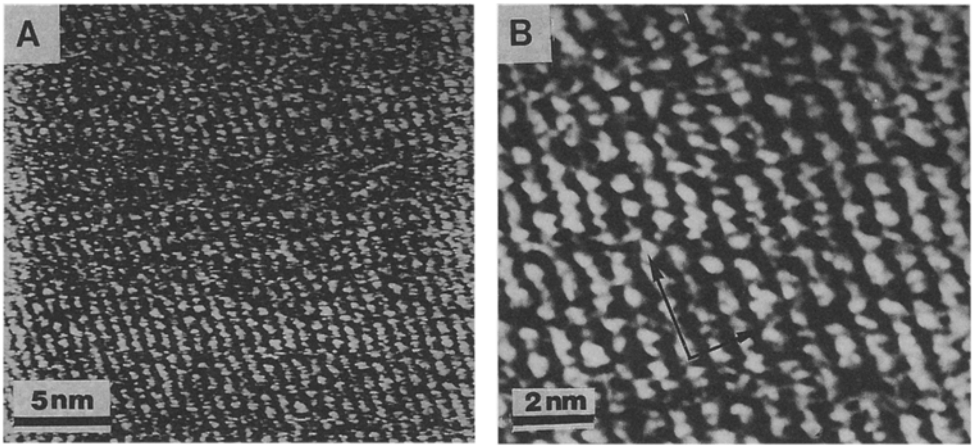
Figure 2: AFM images of the [001] surface of polymer (A, B) and monomer (C, D) pFBS monocrystals (B and D after filtration) - E - 2DFT of A F - Top-view on the molecular structure of the [001] plane of monomer - numbers [pm] indicate relative atom height in the surface layer

visualization of local surface defects the above-mentioned procedure is not suitable. In the reconstructed image well distinguished alternating rows of AFM patterns are arranged along the same direction as microfibrils. One row of zig-zag type is different from the other one, which consists of larger patterns. Filtered images with higher contrast than initial ones were used for numerical treatment. It was detected that due to thermal drift the AFM images recorded during scanning in different directions (up or down) even after tens of minutes since a beginning of an experiment still have slightly different geometrical parameters. That's why the averaged periodicities of AFM patterns are usually calculated for the examined surfaces. The arrangement of AFM images of polymer can be characterized by the main periodicities along the rows, in the b-direction, $b_{AFM} = .52 \pm .04$ nm and in the almost perpendicular direction ($\alpha = 89.9 \pm 3.0^{\circ}$), $c_{AFM} = 1.60 \pm .16$ nm. The distance between neighbouring patterns in the zig- zag rows is .32 ± .02 nm. In contrast to large scale images, the atomic scale AFM pictures of polymer and monomer crystals look quite similar. In the AFM images of a monomer surface the same main features were observed and the repeat distances - $b_{AFM} = .58 \pm .05$ nm, $c_{AFM} = 1.52 \pm .12$ nm - do not differ much from the ones registered for polymer.

Though, it was known that the examined surface of monocrystals corresponds to the crystallographic [100] plane, for the detailed assignment of AFM images the molecular arrangement on this surface was reconstructed from the crystallographic data. Fig. 2F demonstrates atoms in the surface layer of .4 nm in thickness. This layer is formed from rings of subsituents, with main plane being perpendicular to the surface. The molecular arrangement on this plane is almost identical for polymer and monomer. The slight differences in periodicities of molecular structure in polymer and monomer monocrystals [10] are small enough to be distinguished in AFM images. Thus, it is clear why the AFM images of polymer and monomer look quite the same. However, the obtained atomic scale AFM images are only in a general agreement with the crystallographic arrangement. The repeat distances correspond to the surface unit cell parameters. However, the difference between AFM images and the reconstructed crystallographic molecular arrangement is evident when stacks of benzyl groups are compared with the rows of AFM patterns. From crystallographic data the planes of benzyl rings of neighbouring stacks inclined to the b axis at the same angles of different sign. In AFM images individual patterns of neighbouring alternating rows are different. One of the rows is formed from elongated individual patterns, the other one consists on more resolved 'hills', which are arranged zig-zag. This tendency of alternating rows has been detected in many images obtained on several polymer and monomer monocrystals. It might be reasonable to assign the individual AFM patterns to edges of benzyl rings, consisting of -CH-CF- groups. During AFM imaging of the [001] plane of tetracene [11] the elongated elevations were also assigned to the similar molecular groups. It can happened that in one of the observed rows the orientation of benzyl group is so that the discussed AFM patterns have been resolved.

Thus, we can state that the substituents positions in the surface layer of pFBS and its monomer, as ruled out from AFM maps, are different from the crystallographic arrangement [10]. There are two possible explanations. It might be that on the surface of a monocrystal - due to different molecular environment - benzyl planes of neighbouring rows are arranged in another manner than in bulk. This situation does not look too artificial, because it can be realized by rotation of cyclic substituents along flexible bonds. This type of rearrangement has been previoulsy found in two temperature-dependent crystallographic modifications in one of PDA, which is structurally similar to the examined one [12]. Another less probable explanation might be based on differences in molecular structure between the examined compound and that used for the crystallographic analysis.

The examined surface of monocrystals is a good example of AFM application. However, an interesting process of molecular rearrangement during polymerization takes place in the [102] plane. In a first approach cuts from the surface of a



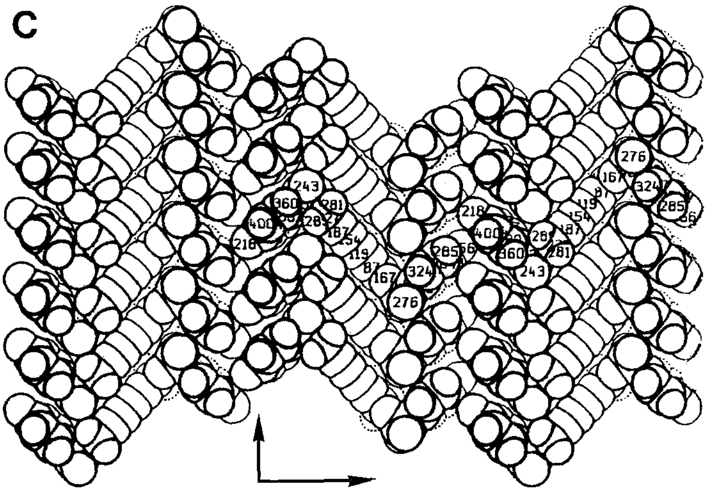


Figure 3: AFM images A and B of the [102] (?) surface of monomer pFBS - B is zoomed from A - C - top-view on the molecular structure of the [102] plane of monomer - numbers [pm] indicate relative atom height in the surface layer

monomer monocrystal, which might be parallel to the [102] plane, were prepared and examined by AFM. The best image obtained is reproduced after filtration, Fig. 3A-3B. It differs from the ones presented above. No direct correspondence has been found between this image and the molecular arrangement on the [102] plane (Fig. 3C), which was reconstructed from the crystallographic data. In most ordered regions of AFM image main periodicities in the orthogonal directions are .96 and .71 nm. However, the molecular arrangement on the [102] plane has different repeat distances, .514 and 3.37 nm, in the directions indicated in Fig. 3C.

Further investigations, including parallel AFM and X-ray diffraction experiments, should help us to clarify this problem.

CONCLUSION

The AFM results of surface examination of monocrystals of symmetrically substituted PDA and its monomer show unique perspectives of this method. It is clear that different questions concerning structure and molecular behaviour in PDA can be solved with the help of AFM. First of all, this technique can be extremely useful for the localization and classification of surface defects, which have been detected by various indirect methods. The question concerning possible differences of surface and bulk structure arised in first experiment can be clarified soon. Surface images of unsymmetrically substituted PDA may give a definite answer concerning statistical or correlated distribution of different substituents. On-line visualization of polymerization processes in monomer crystals induced by light or heat may be realized in near future.

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Accepted March 21, 1991 C