Atomic Force Microscopy of Photolysis of Azobisisobutyronitrile in the Solid State

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The formation of regular nanostructures by photolysis of azobisisobutyronitrile (AIBN) in the solid state is investigated using atomic force microscopy (AFM) and known crystal packing data. AFM reveals that the crystal face (001) of AIBN yields both craters and volcanoes. All the experimental results are correlated with the crystal structure. Molecular interpretation of the AFM features of AIBN is given.

Atomic force microscopy (AFM) is a versatile tool. Recently, it has been applied to the submicroscopic investigation of chemical reactions on crystal solid.[1,2]

Presently, there are eight basic types of surface features depending on different crystal and different crystallographic faces of the same crystal.[1-4] These surface features are due to long-range molecular movements which are strictly guided by the crystal structures according to three-stage sequences of i) phase rebuilding, ii) phase transformation and iii) crystal disintegration.[5] Kaupp et al. have studied dimerization of some mono-olefin or diolefin derivative crystals using AFM and known crystal packing data.[1,2] It is of particular interest to extend these studies to photolysis of azobisisobutyronitrile (AIBN) in the solid state. In this article we present our first AFM mechanistic observation of regular nanostructures generated by photolysis of AIBN. Molecular interpretation of the AFM features of AIBN is given.

A Digital Instruments NanoScopeIII was used with commercial standard silicon nitride cantilevers and tips. The spring constant was 0.12 N/m. The forces were set at 10-30 nN throughout in constant height mode in ambient atmosphere. Flat and smooth crystal of AIBN was glued to adhesive tab on the AFM support as horizontally as possible with the desired crystallographic face on top. The experiment at room temperature and in the ambient atmosphere was performed by removing the whole support with the sample immediately after the initial measurement and placing it under a high pressure mercury lamp, which was irradiated for a given time. Thereafter the support was again mounted on the AFM and measurements were done as closely as possible to the original site as judged with a microscope viewing the unchanged shape of the crystal. The AFM scans were repeated at various time intervals. 10 µ scans were usually recorded at 1.0 Hz. The experiment was reproduced at least thrice. In all cases AFM measurements were extended to other sites of the same face in order to prove uniformity of the feature.

Crystal packing drawing was generated from published X-ray crystal structure data using Cambridge Structural Database System (Laboratory of Computer Chemistry, Chinese Academy of Science, China).[6]

Single crystals were obtained as described[7] and irradiated on the AFM stage directly from 25 cm distance with a 400 w high pressure mercury lamp through a water-cooled Solidex filter. Miller indice was determined by X-ray diffraction while using the known crystal data.

A. B. Jaffe et al. have reported that crystalline AIBN undergoes photolysis to yield a nitrogen molecule and a pair of CIP radicals.[8]

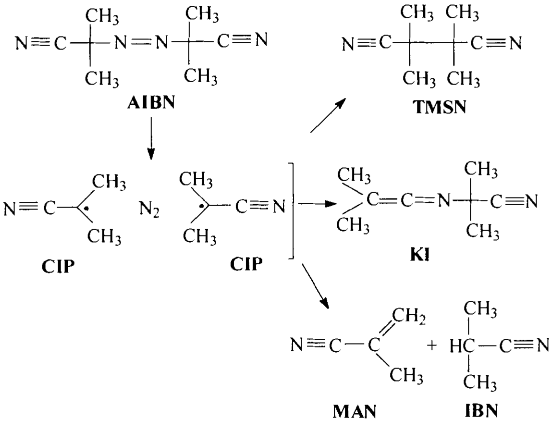

Figure 1 shows clearly the features of the main crystal face (001) of AIBN. After 2 min irradiation both craters and volcanoes are formed on the initially smoother (001) face (R_{ms} = 0.452 nm) (Figure 1a). Both craters and volcanoes are about 0.9-1.4 µm wide and 200-320 nm deep (craters) or high (volcanoes) (Figure 1b). On further irradiation, both width and height of them increase. For instance, after 5 min irradiation both craters and volcanoes are about 1.0-2.0 µm wide and 400-800 nm deep (craters) or high (volcanoes) (Figure 1c). The nanostructure formed seems to indicate that the phase transformation has taken place in the photolysis of AIBN. The phenomenon appears to correlate with the crystal structure of AIBN.

In Figure 2 is given the stereoscopic view of the molecular packing of AIBN on (001). It can be easily seen from Figure 2 that in the AIBN molecule all atoms except those of the methyl groups are planar. The molecules are most easily visualized as nearly planar S-shaped N≡CCN=NCC≡N backbones with methyl groups above and below the plane because of the eclipsed conformation. The packing of the molecules in the crystal lattice is the molecular close-packing. The outmost atoms of the molecule are N and H and the neighbouring molecules contact through these. After the irradiation, the intermediate radicals CIP are produced in the crystal, and thus the original crystal lattice will become extremely distorted. Moreover, the products of photolysis TMSN, KI, IBN and MAN, once formed, can not fit in with the original lattice of AIBN. They must therefore try to relieve stress by lifting themselves uphill. Due to this movement the photolysis of AIBN can continue. Thus, the (001) surface gives rise to volcanoes, which were seen experimentally by AFM (Figure 1). The crater formation is probably due to the photoelimination of

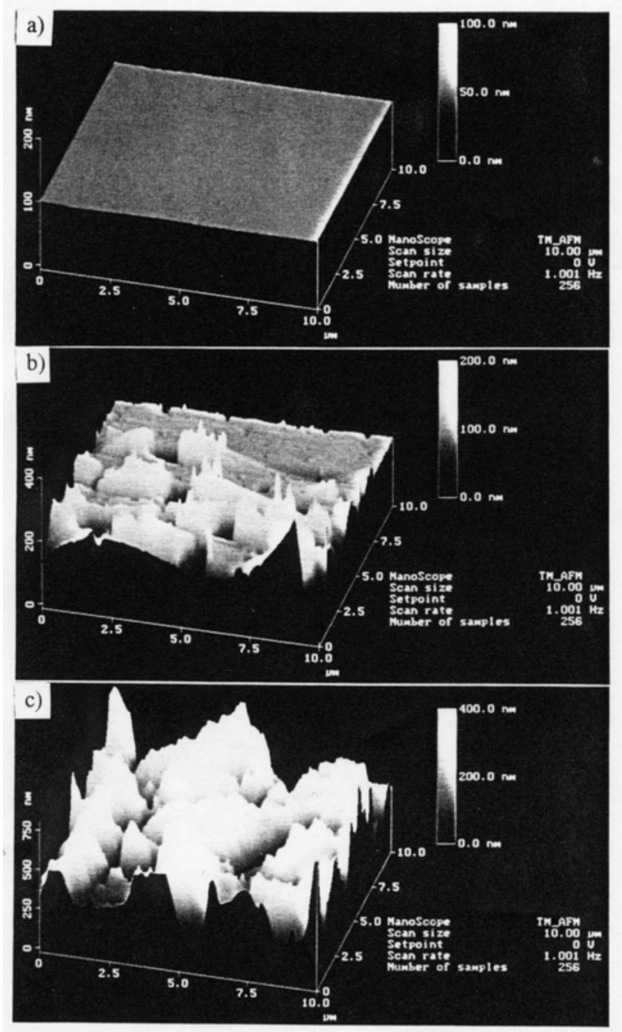

Figure 1. AFM surface of **AIBN** on its main face (001): a) Fresh. b) After 2 min irradiation. c) After 5 min irradiation.

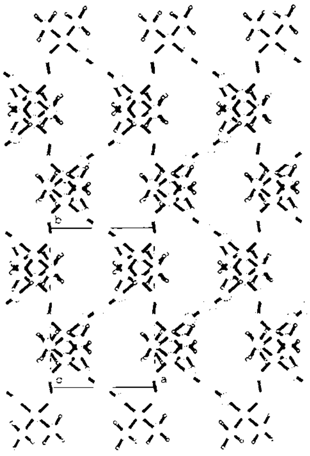

Figure 2. Stereoscopic view of the molecular packing in the crystal of **AIBN** on (001).

nitrogen molecule from crystalline AIBN. The craters will help to release the nitrogen molecule which is formed inside the crystal.

AFM provides new answers for elucidation of organic chemical reactions of crystals. The observed AFM surfaces are correlated with known X-ray crystal structures and lead to an improved interpretation of experimental results that could not be accommodated by previous methods and theories.

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