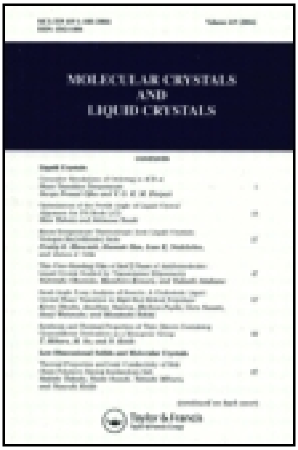

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Atomic Force Microscopy Studies of Crystals That Undergo Solid State Reaction Initiated by Ultraviolet or Ionizing Radiation

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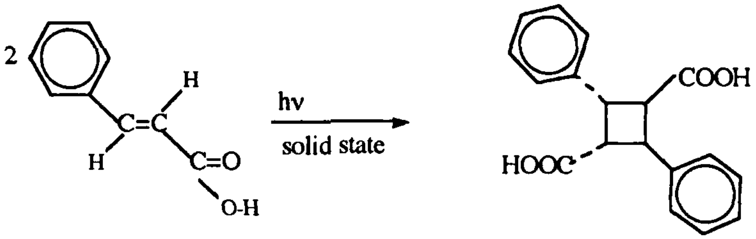
Abstract. Using atomic force microscopy(AFM), conical surface eruptions are observed on the major faces of crystals of the dialkylurethanes of 5,7-dodecadiyn-1,12-diol and α- cinnamic acid as these crystals undergo solid state reaction in the presence of air initiated by ionizing radiation and ultraviolet light, respectively. These eruptions are not observed when the irradiations are carried out in the absence of air under our experimental conditions. The eruptions formed on α- cinnamic acid are significantly smaller than those found on the polymerizing diacetylene crystals. The α- cinnamic acid single crystals were mounted on AFM slides and irradiated in the presence of bulk crystals, and the bulk conversion of the irradiated samples was estimated by proton NMR spectroscopy.

INTRODUCTION

Atomic force microscopy(AFM)[1] has become a major tool in the study of the surface morphology of organic molecular and polymeric materials[2-4], both as single crystals and thin films of materials that are electrical insulators. AFM is particularly well suited for the study of crystals undergoing solid state reaction[5] initiated by ultraviolet(UV) light or ionizing radiation, such as ^{60}Co γ radiation, because reaction will initiate near the crystal surface.

We have recently reported[6] that AFM studies of single crystals of diacetylene(DA) monomers that are dialkylurethanes of 5,7-dodecadiyn-1,12-diol reveal anisotropic surface eruptions on the [100] faces of these crystals when they are irradiated with ^{60}Co γ radiation or electron beams in the presence of air, but not in its absence. The eruptions on the average are 0.5 microns at the base and about 700 Å in height. They appear after about 1 Mrad of radiation at a dose rate of 1 Mrad/hr. in a process requiring about 50 Mrad for complete conversion to polymers that are thermochromic and reported[7] to be photochromic for the case of the bis-n propylurethane(PUDO). Crystals having surface eruptions are irreversibly converted from their blue form to a red form at room temperature on exposure to a single pulse of 532 nm light while crystals lacking the eruptions do not undergo this change. Hence the interaction of laser light with these crystals is critically dependent on the details of the surface morphology of the crystals.

In view of the role of air in the surface eruption process, we wondered if other materials undergoing solid state reaction would exhibit related behavior. In view of our continuing interest[8,9] in mechanistic and spectroscopic aspects of the solid state dimerization of cinnamic acids, we chose to investigate α-cinnamic acid. The solid state dimerization of α-cinnamic acid to truxillic acid is illustrated in Scheme 1.



Scheme 1. Solid state dimerization of α-cinnamic acid to truxillic acid.

EXPERIMENTAL SECTION

Cinnamic acid was obtained from Aldrich Chemical Company and recrystallized from benzene or ethanol. The crystals were identified as α phase[10] from their X-ray powder pattern with the aid of the program "Micro D-space", Materials Data, Inc., Livermore, California. AFM imaging was carried out using a Park Scientific Instruments Autoprobe cp scanning probe microscope under ambient conditions. The images were obtained in the noncontact mode using silicon cantilevers(2μm ultralevers, Park Scientific, force constant = 25 N/m) at a resonant frequency of about 200 kHz. The tip radius was specified to be about 250 Å by Park Scientific as seen from high resolution scanning electron micrographs. An 80 μm scanner was used. The AFM images did not change when irradiated samples were examined at a time more than 24 hours after initial imaging. Irradiation at 370 nm was carried out using four 15 watt Sylvania 2051 sources as previously described.[9] The peak output of these lamps is 370 nm but they emit a broad range of wavelengths. For AFM study, single crystals were placed on mounts so as to expose the largest face and these were irradiated along with loose crystals. Irradiations were carried out in a cell with a quartz window either in the presence of air or under static argon. Circulating water controlled the temperature of the cell to 20°C, and the lamp-to-sample distance was 8 cm. After irradiation, the degree of dimerization of the bulk sample was determined by proton nmr spectroscopy using a Bruker instrument at 250 MHz in acetone- d_6 solution. The amount of conversion of cinnamic acid to truxillic acid dimer in the sample was estimated from the relative areas of the vinylic protons of cinnamic acid at δ 6.5-6.6 and the aliphatic protons of the truxillic acid dimer at δ 3.8 and 4.4.

RESULTS AND DISCUSSION

Samples of cinnamic acid were irradiated at 370 nm for 48 hours in the presence of air. Study of the bulk irradiated samples by proton NMR revealed that the cinnamic acid in the samples was 5.0-7.6% converted to truxillic acid. AFM examination of the main face of irradiated crystals revealed eruptions that were 0.2 microns in diameter at the base and approximately 200 angstroms in height. These eruptions are somewhat smaller than those found on the polymerizing DA monomers[6] discussed above. The AFM image of a pristine cinnamic acid crystal is displayed in Figure 1, and the image of a crystal irradiated in air is shown in Figure 2. The appearance of these eruptions is qualitatively similar to those previously observed[6] in diacetylene polymerizations. Eruptions are also observed on cinnamic acid crystals irradiated in air using 254 nm light. These observations of a substantially changed crystal surface are in general accord with a previous report concerning UV irradiation of α-cinnamic acid in the presence of air.[11]

Somewhat different observations were made when cinnamic acid crystals were irradiated at 370 nm under a static argon atmosphere. Figure 3 shows the AFM image of a crystal taken from a batch where the bulk conversion was 10.6% irradiated under argon for 48 hours. Note that while the surface is significantly rougher than the pristine surface shown in Figure 1, this image lacks the features of the erupted surface shown in Figure 2. Hence, under the conditions described herein, the surface morphologies of α-cinnamic acid crystals are different depending on whether or not air was present during irradiation. An earlier study[11] reported that the same features were observed on the [010] face of α-cinnamic acid independent of whether UV irradiation was carried out in air or under vacuum.

Examination of crystals of α-cinnamic acid irradiated under argon by optical microscopy on the AFM stage and elsewhere revealed a range of behavior. While some crystals revealed virtually no change upon irradiation, others revealed extensive cracking along the long dimension of the crystal.

In summary, we have observed that, like DA crystals of the dialkylurethanes of 5,7-dodecadiyn-1,12-diol, crystals of α-cinnamic acid show different surface morphologies depending on whether or not the crystals are irradiated in the presence of air.

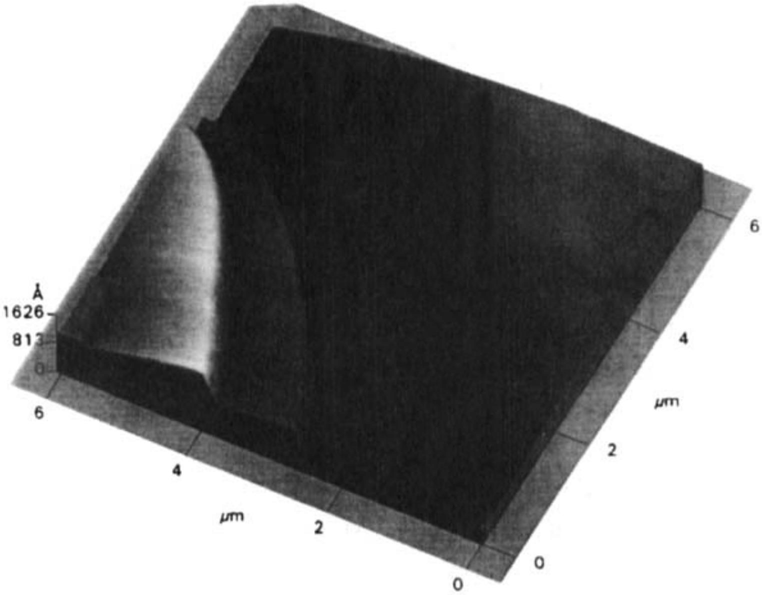


Figure 1. AFM image of the main face of a pristine cinnamic acid crystal.

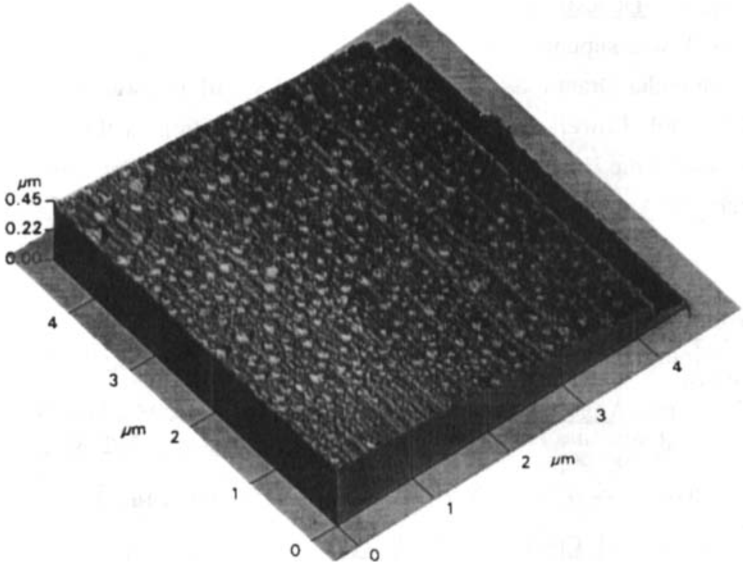


Figure 2. AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm in the presence of air. Note the conical eruptions covering the surface.

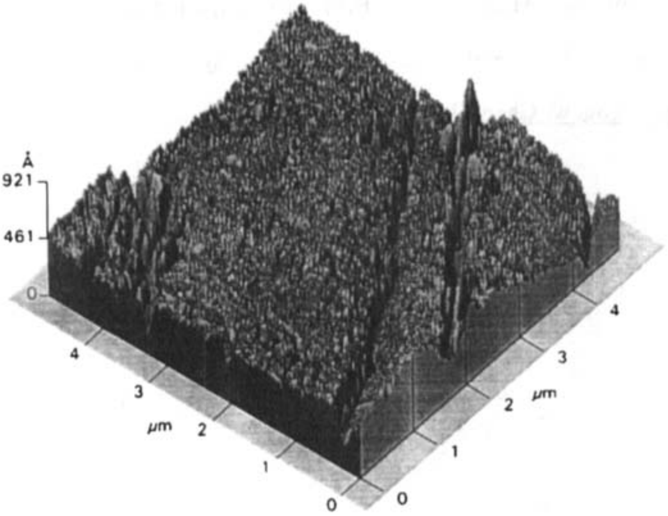


Figure 3. AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm under argon. Note the development of cracks.

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