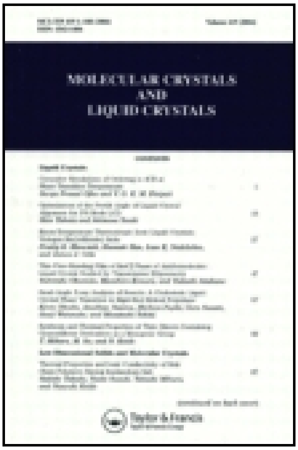

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Relaxation of the Stress Produced by Photopolymerization of a Diacetylene Crystal

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Relaxation of the Stress Produced by Photopolymerization of a Diacetylene Crystal

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A single crystal of diacetylene monomer, 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD), is polymerized by photo-irradiation keeping the *b*-axis of polymer crystals parallel to that of monomer crystals on which some amount of stress is introduced in the lattice of polymer crystals. In the present study, morphological changes on the surfaces of DCHD polymer crystal were observed by atomic force microscopy in order to examine the relaxation mechanism of such stress. On polymerization, nodule-like structures were formed on the surface, aligning along the direction of nearly 60° with respect to the *b*-axis of monomer crystal. The alignment of nodules is concluded to correspond to a mechanical slip direction in the monomer crystal.

Keywords: 1,6-di(N-carbazolyl)-2,4-hexadiyne; stress relaxation; photopolymerization; atomic force microscopy

INTRODUCTION

Solid state polymerization of diacetylenes has been investigated since the report by Wegner in 1969 [1]. The polymerization occurs through topochemical reaction due to crystal structure dependent 1,4-addition of neighboring monomer. In the case of 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD) (Figure 1), the crystal structures of the monomer and polymer crystals have been analyzed by X-ray method [2,3] and found that the *b*-axis of the produced polymer crystal is parallel to that of the original monomer crystal. Recently, the detailed polymerization process was investigated by high resolution cryogenic transmission

electron microscopy (cryo-TEM) [4]. According to the results, the nucleation of polymer crystal induced by heat treatment is different from that by electron irradiation. In addition, as the polymerization proceeds, the internal stress produced by the differences in the lattice constants of the polymer and monomer crystals was expected to be relaxed by changing the orientation of molecules in polymer crystallites. Such relaxation process is important practically in the fabrication of thin polymer films.

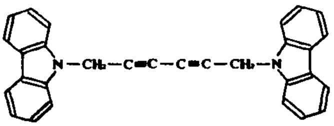

FIGURE 1 Chemical formula of DCHD

In this study, we directly observed surfaces of DCHD monomer and polymer crystals during thermal or photo-induced polymerization with an atomic force microscope (AFM), and the relaxation mechanism of internal stress generated in polymer crystal will be discussed from the view point of the morphological changes of the polymer crystals.

EXPERIMENTAL

DCHD monomer single crystals with needle-like shapes (1mm x 1mm x 10mm), recrystallized from acetone solution, were used. From X-ray analysis, the *b*-axis was concluded to correspond to the direction of the needle axis. On thermal polymerization, DCHD crystal was heated in a glass ampule at 150°C for ca. 25h after degassing, while photopolymerization was performed by UV irradiation with a mercury lamp (75W). The surfaces of polymerizing crystals were observed with AFM in course of the polymerization time in both polymerization processes. DCHD crystal changed its color on polymerization from colorless to dark brown with metallic luster, due to the formation of one-dimensional conjugated system in the polymer chain.

The AFM observation was carried out on the (101)-plane of DCHD crystal, which was confirmed by X-ray method, at room temperature with a NanoscopeIIIa in tapping mode.

RESULTS AND DISCUSSION

Figure 2 shows an AFM image of DCHD monomer crystal before polymerization. The direction of the *b*-axis is indicated with an arrow in the figure. The surface of DCHD monomer is flat with several edge lines along the *b*-axis. As already reported [5], the (101)-plane of

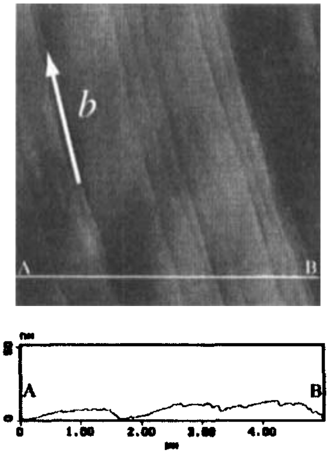

FIGURE 2 An AFM image of DCHD monomer crystal (5μm x 5μm) and the cross-section profile.

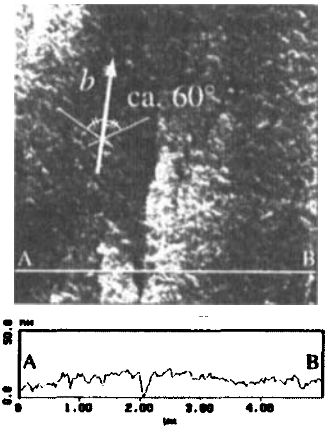

FIGURE 3 An AFM image of DCHD polymer crystal by photo-irradiation (5μm x 5μm) and the cross-section profile.

polymer matches up to the same plane of monomer. An AFM image shown in Figure 3 exhibits, therefore, the (101)-plane of DCHD polymer crystal produced by photo-irradiation for ca. 2h. The *b*-axis is indicated with an arrow in the figure and coincides with that of monomer crystal. In the figure, nodule-like structures with the size of 50~100 nm are found to form on the surface, which align nearly along the direction of 60° away from the *b*-axis. In the case of DCHD polymer crystal produced by thermal polymerization, long striations along the *b*-axis were observed instead of the nodules. Therefore, we can expect that the nucleation in photopolymerization occurs at random at various points differing from the case of thermal polymerization.

The formation of the nodules can be interpreted as follows. Figure 4 schematically shows the relative orientation of the DCHD monomer and polymer crystals. The solid and dotted lattices indicate the (010)-planes of monomer and polymer crystals, respectively. The structure of DCHD crystal changes keeping the (101)-plane as the common plane on polymerization [5]. Accordingly, stress should be induced in the (101)-plane of polymer crystal. As the result, the polymerized crystallites with nodule-shape slip mutually to relax the stress. Figure 5 shows DCHD monomer crystal projected onto near (101)-plane where the carbazole groups located at both ends of DCHD are nearly overlapped. A slip

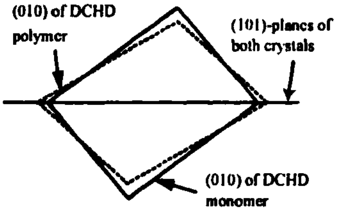

FIGURE 4 Relative orientation between DCHD monomer and polymer crystals.

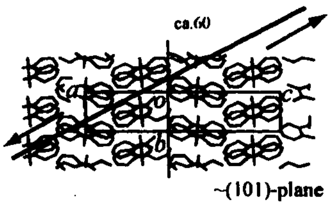

FIGURE 5 DCHD monomer crystal projected to near (101)-plane.

anticipated from the alignment of monomer molecules is induced along the arrows (nearly $[12\bar{1}]$), relating to the direction of ca. 60° away from the *b*-axis. On photopolymerization, the internal strain caused by such differences in lattice constants is relaxed so as for the DCHD crystals to slip along the above direction. When the DCHD crystal was elongated mechanically along the *b*-axis direction, the similar morphology with 60° off axial alignment of small crystallites was observed. This fact clearly designates the existence of $[12\bar{1}]$ direction slip.

From the present AFM observation, morphological changes produced by both the polymerization processes found to be clearly distinguishable. Therefore, there can be different relaxation mechanisms for internal stress at the interface of monomer and polymer. On thermal polymerization, a small number of nuclei begin to grow in needle-like crystals revealed by cryo-TEM experiment [4] and drastic orientation change occurs at crystallite's surface; *i.e.* the needle-like domains at surface vary their orientation from that expected from topochemical reaction, which leads to the striation formation as observed by AFM. On photopolymerization, however, numerous nuclei are formed randomly, which results in the formation of nodule-like domains. The nodules adjust their mutual orientation along the slip direction along $[12\bar{1}]$ in order to relax the stress.

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