

Polymerization Process of 1,6-di(N-carbazolyl)-2,4-hexadiyne Epitaxially Grown Films Studied by Cryo-TEM

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Thin films of 1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD) grown epitaxially on (0 0 1) surface of KCl through vacuum-deposition were examined on their polymerization process induced by heat treatment. The structural changes due to polymerization in the films were investigated by electron diffraction and high resolution (HREM) cryo-TEM.

Keywords: 1,6-di(N-carbazolyl)-2,4-hexadiyne / polymerization process / low temperature high resolution imaging

Since Wegner has demonstrated in 1969 that solid-state polymerization of diacetylenes can be characterized as a diffusionless and lattice controlled process[1], many solid-state reactions in diacetylene derivatives have been examined on their unique features[2,3]. As for 1,6-di(N-carbazolyl)-2,4-hexadiyne (hereafter abbreviated DCHD), Enkelmann *et al.*[4] has reported in 1977 that DCHD monomer crystals can be topochemically polymerized by heat treatment or γ -irradiation. In the present study, the high resolution electron microscopic work was performed by cooling the specimen at a low temperature with a cryo-specimen-holder and employing a minimum electron irradiation system for image recording. The structural correlation of thin poly-DCHD film with the monomer film grown epitaxially on a substrate are examined by high resolution imaging to elucidate the polymerization process.

A small amount of the DCHD powder was heated and

sublimed on KCl substrate at 50°C in the vacuum of 5×10^{-5} Pa. The polymerization of DCHD was carried out by heating at 150°C in a nitrogen atmosphere.

A high resolution image of polymer crystal obtained by heating a monomer film on the KCl substrate at 150°C for 5 h is shown in Fig.1(a). The high resolution image shows a part of a needle-like crystal. At inner part of the crystal (the right part of the image), lattice fringes of 0.43nm are observed along two directions. The angle between these lattice fringes is about 59° and the angle of the fringe with the *b*-axis is about 60°, which agrees well with values calculated from the polymer crystal, assuming that the lattice fringes come from the (1 1 1)- and (1 $\bar{1}$ 1)-planes. The area, therefore, can be assigned as a projection of polymer crystal along the [1 0 $\bar{1}$]. At the edge of the crystal, lattice fringes of 0.83nm are running along the *b*-axis, which corresponds to the spacings of (0 0 2). This lattice plane could not satisfy the Bragg condi-

STATES AND STRUCTURES — Crystal Information Analysis —

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development on high resolution energy filtered imaging as well as electron energy-loss spectroscopy.



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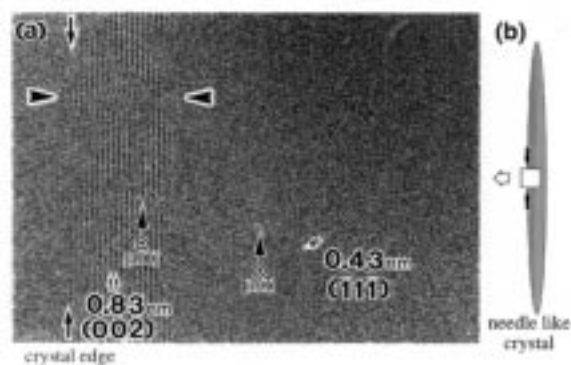


Figure 1. High resolution image of fully polymerised film by thermal treatment for 5 h at 150°C, where the vertical arrows indicate the crystal edge.

tion if the polymerization of monomer crystal occurs topochemically. When the poly-DCHD changes its orientation from the topochemical one by rotating about 28° around the *b*-axis, the (002) lattice fringes become observable in HREM. The poly-DCHD crystals seem to grow in many cases by changing drastically their orientation at the crystal edge, because such rotation is needed probably to relax a stress produced during the polymerization. In addition to this orientation change, crystal distortion is observed at the edges indicated by the two black arrowheads in Fig.1(a). This distortion may be introduced by collision of two growing polymer crystals from the opposite sides along the *b*-axis. Thus the DCHD molecules change their orientation, especially at the crystal edge where it is easy to expand the volume and to change orientation.

To examine the process of polymerization, it is necessary to observe intermediate stages of the polymerization. A high resolution image at such intermediate stage of polymerization is shown in Fig.2(a) as a projection nearly along $[1\ 0\ \bar{1}]$ axis of polymer. Various lattice fringes having different spacings can be found in the crystal, which are corresponding to those of (202). From this micrograph it becomes clear that the polymer and the monomer crystallites coexist as small domains in partially polymerized crystal. The regions of d ~ f and h show intermediate lattice spacings between those of monomer and polymer, so that these regions are considered to be a mixed crystal or a solid solution of monomer and polymer molecules. Since all values of lattice spacings observed in the image are between those of (202)-spacings of monomer and polymer crystals, it can be concluded that various transient states of crystal structure coexist at microscopic level in partially polymerized crystal. This result supports the previous X-ray study on bulk specimen[5], and gives new information. That is, the transient state is an aggregation of very small crystal-

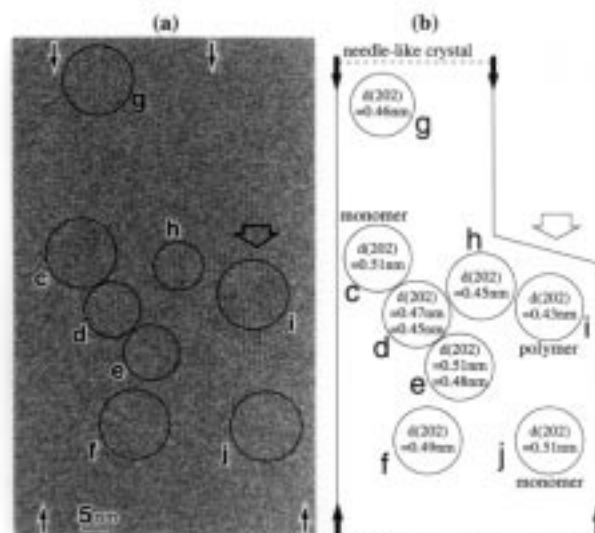


Figure 2. (a) High resolution image of partially polymerised film for 3 min at 150°C. (b) Schematic illustration corresponding to (a).

lites having slightly different lattice spacings in the needle-like crystal which was originally a single crystal of monomer. In addition to this, it is interesting that the almost polymerized region i is found at a crystal edge indicated by the wide white arrow, where the monomer crystal was ended along the *b*-axis. On the other hand, at the inner parts of the crystal, polymerization did not start or did not complete as indicated by the lattice fringes with different spacings in the figure. Then the thermal polymerization could start from such a defect at crystal edge. As polymerization proceeds, the small domains of solid-solution may coalesce coherently each other along the chain axis, resulting in a large fibrous domain as observed in Fig.1.

Finally the large domain at edges of needle-like crystal, considered to be a domain fully polymerized at an early stage, may change its orientation drastically, probably to relax a stress produced by polymerization at inner part of the crystal.

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