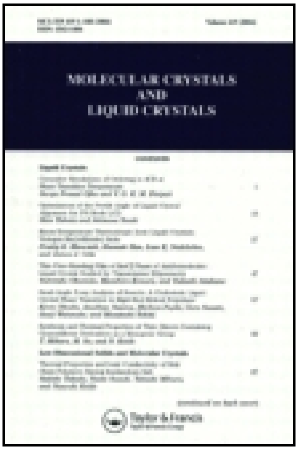

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Epitaxial Growth of Vapor-Deposited 1,4-BIS[β-Pyridyl-(2)-Vinyl] Benzene Film and its Photo-Polymerization

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EPITAXIAL GROWTH OF VAPOR-DEPOSITED 1,4-BIS[β-PYRIDYL-(2)-VINYL] BENZENE FILM AND ITS PHOTO-POLYMERIZATION

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Abstract 1,4-Bis[β-pyridyl-(2)-vinyl] benzene (P2VB) grew epitaxially on a cleavage surface of KCl crystal from vapor phase. By photo-irradiation P2VB monomer in the film converted to poly-P2VB containing cyclobutane rings. The photopolymerization mechanism of P2VB film was discussed from the electron microscopic observation.

INTRODUCTION

Since Hasegawa and Suzuki reported [1] that 2,5-distyrylpyrazine (DSP) was polymerized to high crystalline polymer by photo-irradiation in the solid state, photopolymerization of diolefine compounds in solid state has attracted much attention, so that these polymers can be utilized as electronic and optical materials [2]. The interest for photopolymerization of such compounds has led to investigate on thin films in order to study the relation between the physical properties and molecular arrangement in the films. In previous papers [3-5], we investigated the epitaxial growth and photopolymerization of DSP film, vapor-deposited onto a KCl (001) surface. The present study is concerned with the epitaxial growth of 1,4-bis[β-pyridyl-(2)-vinyl] benzene (P2VB) from vapor phase and the structural change of the film by photo-irradiation.

EXPERIMENTAL

P2VB was vapor-deposited onto a cleavage surface of KCl from a fused silica crucible heated by a tungsten filament in a vacuum of 1.33×10^{-3} Pa. The P2VB film on the KCl substrate was irradiated with a 500 W high-pressure mercury lamp at room temperature. The film on KCl was examined by a JASCO A302 infrared spectrometer. After reiforcement with evaporated carbon film, the P2VB film was stripped off from the substrate on a water surface and placed on an Au-coated micro grid. Electron microscope used here was a JEM-200CX with a minimum exposure device. The gold film on the micro grid was used as a standard calibration material for lattice spacing measurements.

RESULTS AND DISCUSSION

Figure 1 shows the IR absorption spectra of the original P2VB powder and of the vapor-deposited P2VB films before and after photo-irradiation. Because the spectra of the original P2VB powder and the film vapor-deposited onto KCl show the same absorption bands, no structural change of P2VB occurs during the evaporation. By photo-irradiation absorption peaks at 1630 and 976 cm^{-1} assigned to aliphatic C=C and trans-vinylene C-H stretching vibrations, respectively, decreased and at the same time a new absorption peak at 930 cm^{-1} attributed to cyclobutane group appeared. Therefore , P2VB monomers converted to a polymer , linked by cyclobutane rings, by the photochemical reaction.

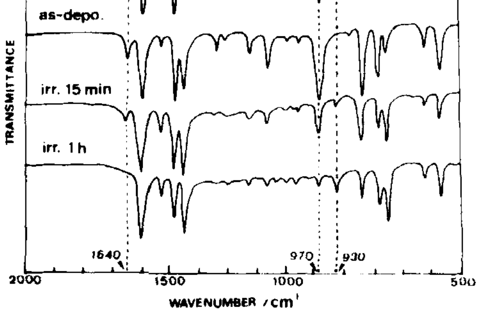

Fig.1 IR spectra of the original P2VB powder and of the vapor-deposited P2VB films before and after photo-irradiation

A P2VB film vapor-deposited on the kCl substrate without any preheat treatment was composed of randomly-oriented small granules, tabular crystallites , and laminate ones, as is shown in Fig.2. Electron diffraction patterns of these three kinds of crystallites displayed single crystal patterns with the diffraction spots corresponding to lattice spacings of 2.07 and 0.48, and 2.10 and 0.36, and 0.48 and 0.73 nm, respectively. These patterns coincided the net patterns plojected along the a-, b-, and c-axes of P2VB crystal, respectively , whose unit cell dimensions are a=2.106, b=0.9567 , c=0.7311 nm and the space group is Pbca [6].

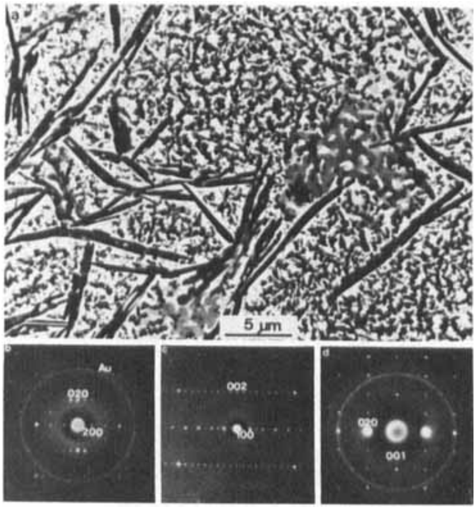

Fig.2 Electron micrograph of P2VB film evaporated on the KCl substrate without preheat treatment (a) and electron diffraction patterns of small granule (b), of tabular crystallite (c), and of laminate one (d)

When the substrate was kept at 80°C after preheating at 150°C for 1h, the film was composed of tabular crystallites grown epitaxially, as is shown in Fig.3. The longitudinal directions of the crystallites (c-axis) made an angle of 10° with respect to the $[110]_{KCl}$ direction. Sometimes a small number of crystallites aligned along the direction crossing at 2° to the $[110]_{KCl}$ direction. The electron diffraction pattern of the film showed the superposition of the single crystal pattern

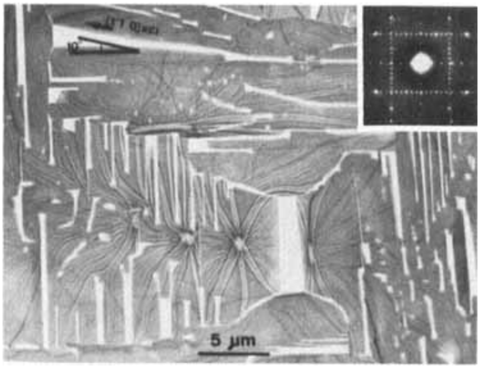

Fig.3 Electron micrograph and electron diffraction pattern of P2VB film evaporated on the KCl substrate kept at 80 °C after being preheated at 150 °C

projected along the b-axis of P2VB crystal. The molecular arrangements in the P2VB crystal are explained by Nakanishi et al [6]. From the mutual relations between the deposited and substrate crystals, it was concluded that the molecules are arranged on the substrate as represented schematically in Fig. 4. When the c-axis of the crystal makes an angle of 10° to the $[110]_{KCl}$ direction, the benzene ring of a molecule, which is electron-rich moiety , comes into contact closely with Cl^- ion of the substrate. At the same time, the electron-deficient pyrazine rings settle on K^+ ions of the substrate. Therefore, the long axis of the molecule lies parallel to the substrate surface and aligns along the $[120]_{KCl}$ direction. Minor orientation formed with the interaction between the electron-rich nitrogen atom and K^+ ion and between the electron-deficient carbon atom and Cl^- ion.

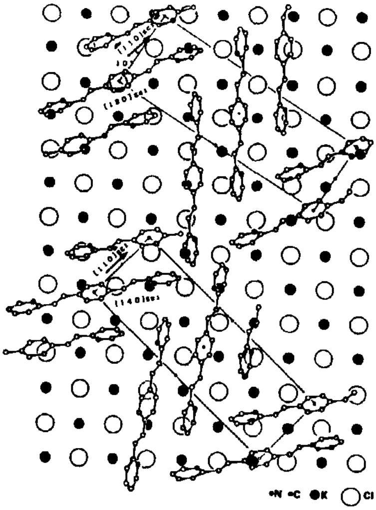

Fig.4 Mutual orientations of both crystal lattices of a KCl substrate and P2VB molecules on the (010) plane of the crystal

When the P2VB film was photo-irradiated, the fissures occured along the c-axis in the tabular crystallites, as is shown in Fig.5. The electron diffraction patterns from the crystallites after photo-irradiation showed single crystal patterns whose lattice spacings were slightly different from those before photo-irradiation. As the irradiation time prolonged, the diffraction spots became diffuse. The electron diffraction pattern after photo-irradiation for 1 h coincided the single crystal pattern projected along the b-axis of poly-P2VB crystal whose unit cell parameters are a=

1.89, b=1.05, and c=0.753nm and space group is Pbca [6] Thus an epitaxial film of poly-P2VB was obtained by the photo-irradiation of an epitaxially grown P2VB film.

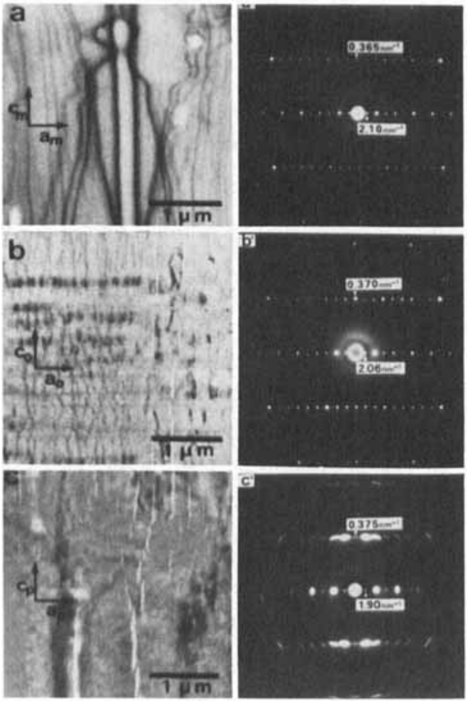

Fig.5 Electron micrographs and electron diffraction patterns of tabular crystallites before (a,a') and after photo-irradiation for 15 min (b,b') and 1 h (c,c')

Figure 6 shows continuous changes in lattice spacings of P2VB film during photo-irradiation . This result leads to the conclusion that the photopolymerization of P2VB film proceeds as a stepwise mechanism.

Figure 7 shows highly magnified images of tabular and laminate crystals before and after photo-irradiation. Before photo-irradiation lattice fringes of 1.05 and 0.48nm spacings are observed in the tabular and in the laminate crystals, respectively , as is shown in Figs. 7 (a) and (b). The former periodicity coincides with the 200 lattice spacing and the latter with the 020 lattice spacing of the monomer crystal. Defect structures are scarcely observed in the films, that is , the monomer films have a high crystalline order.

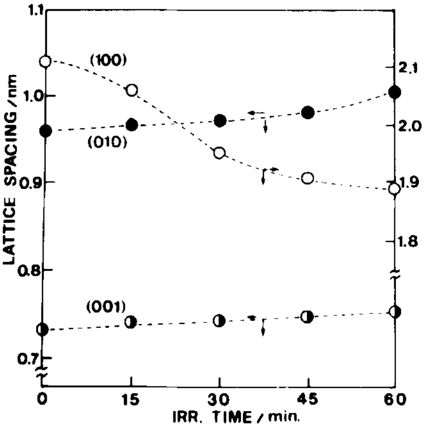

Fig.6 Plots of lattice spacings against the photo-irradiation time

After photo-irradiation those lattice fringes which

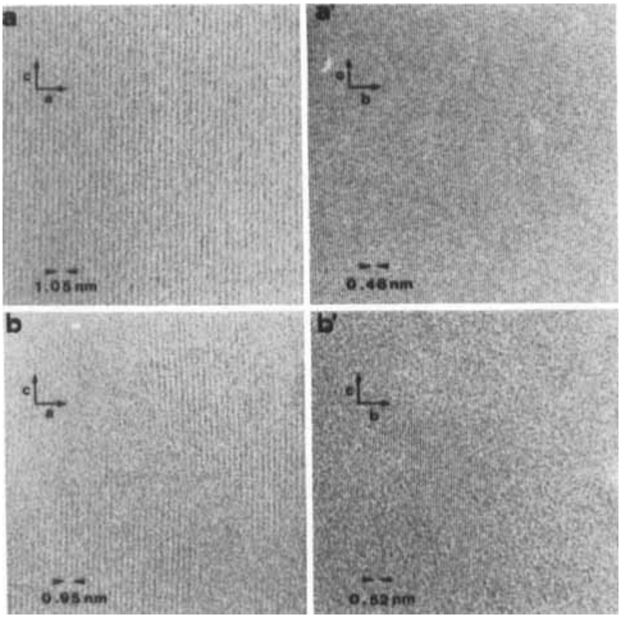

Fig.7 Lattice images of tabular (a) and of laminate (a') crystals before photo-irradiation, and after photo-irradiation for 1 h (b', b')

coincide with the 020 and 200 lattice spacings of the poly-P2VB crystal change to 0.52 and 0.95 nm spacings, respectively, as shown in Figs. 7 (a') and (b'). Although the well ordered lattice fringe patterns are cut to smaller areas and interrupted by somewhat disordered regions, the lattice fringes are aligned in the same direction as the original crystal. The directions of the crystallographic axes of the polymer crystal coincide with those of the monomer crystal. These findings indicate that the monomer crystal converts to the polymer crystal under maintaining the space group, and that the photopolymerization of a vapor-deposited P2VB film is a topotactic reaction. Consequently, it is concluded that the photopolymerization of P2VB film occurs within the monomer matrix and that it proceeds through a direct rearrangement of molecules from monomer to polymer in crystal state.

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