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The Epitaxial Growth of the Methyl Triacontanoate Crystal

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Methyl triacontanoate (MT) was deposited on the cleavage face of the KCl crystal in vacuo. The MT film was composed of V-shaped crystals growing along two directions crossing at 32°, and these crystals intersected at right angles to each other. The bisectional direction of the V-shaped crystals corresponds to the [110] direction of the substrate crystal. The electron-diffraction pattern from the film consisted of the reflection spots corresponding to the $(hkl)_s$ planes of the subcell and the series of 00*l* reflections in the small-angle region. The crystal structure of the deposited MT crystal was monoclinic in form. The (110) plane of the MT crystal was oriented parallel to the substrate (001) plane, and its *c*-axis was parallel to the [110] direction of the substrate crystal. The V-shaped crystal was explained by the molecular arrangement in the epitaxial growing crystals. When the substrate was kept at a higher temperature than the melting point of MT, the deposit coagulated to disk-like crystals whose *c*-axis was perpendicular to the substrate.

Recently organic thin films have attracted a good deal of attention for use in new systems which enable one to draw out various functions by the design of the molecular construction and various combinations. Their electronic, photoelectronic, and optical properties can be expected to improve those of metals and inorganic compounds. These properties are probably controlled by the molecular arrangement in the films. The techniques for preparing organic films can be divided into two types of processes: dry and wet. The Langmuir–Blodgett (L–B) method has been well developed as a wet process, and the properties of L–B films have been reported by many workers.[1] However, the L–B method can be applied only to amphiphilic molecules. In the case of vacuum-evaporation as a dry process, on the contrary, there have been many reports on the structures and nucleation mechanisms of metals and inorganic compounds, but few reports on those of organic compounds.[2–5]

Ashida and his co-workers have studied the epitaxial growth from the vapor phase of polycyclic aromatic[6–8] and linear molecules, such as paraffins,[9] polyethylene[10] and polypropylene.[11] Paraffin molecules took two orientations on the cleavage surface of alkali halide, depending on the evaporation conditions. The films deposited on the cleavage face of alkali halide crystals kept at room temperature were found to be composed of raft-like crystallites. The (110) plane of these crystals was oriented parallel to the substrate (001) plane, and their fiber axes were parallel to the [110] direction of the substrate crystal. When paraffins were deposited on the substrate kept at temperatures near or above their melting points, the films were composed of discrete disk-like crystals and their fiber axes were oriented perpendicular to the substrate. The linear polymers, such as polyethylene and polypropylene, were decomposed thermally to compounds of a low molecular weight during the evaporation process; these compounds also took an orientation similar to that of the paraffin crystals. The crystals composed of linear molecules probably exhibit a distinguished anisotropy of electrical and mechanical properties as a result of interaction between long-chain molecules. It is well-known that these crystals exhibit polymorphs depending on the crystallization temperature. It is interesting to investigate the effect of end group on the morphology and orientation of linear molecular crystals. In this work, the epitaxial overgrowth of methyl triacontanoate (MT) film evaporated on the potassium chloride (001) surface was studied by using an electron micrograph and electron diffraction.

Experimental

MT ($C_{29}H_{59}COOCH_3$, mp, 71.0 °C) was obtained from the Tokyo Chemical Industry Co., Ltd.. The purity of the MT was 99.5%. The single crystal of potassium chloride used as the substrate was cleaved in air and immediately placed in the evaporation chamber. After the substrate had been baked out at 200 °C for one hour in 1.33×10^{-3} Pa, the MT was evaporated vertically from a quartz crucible heated with a tungsten coil onto the substrate surface, which was kept at a temperature between 20 and 90 °C. The average thickness of the deposited film, monitored by means of a quartz crystal microbalance, was 100 nm. The specimen used for electron microscopy was prepared by the dissolution of the substrate in water after the film had been reinforced with evaporated carbon film. The orientation of the deposited crystal related to the substrate crystal was determined by shadowcasting the chromium metal along the [100] direction of the substrate crystal. Thallium(I) chloride prepared by evaporation was used as a standard calibration material for the spacing measurements.

Results and Discussion

The features and orientation of the deposited crystallites depend on the evaporation conditions. The crystalline size increases generally with an elevation of the substrate temperature, whereas the crystal shape and the molecular orientation have a close relation to the substrate treatment, mainly the bake-out procedure of the substrate. When MT was evaporated onto a cleavage surface of potassium chloride without heat treatment, the film was composed of randomly-oriented granules about 100 nm in diameter. When, on the other hand, the substrate was heated at 200 °C

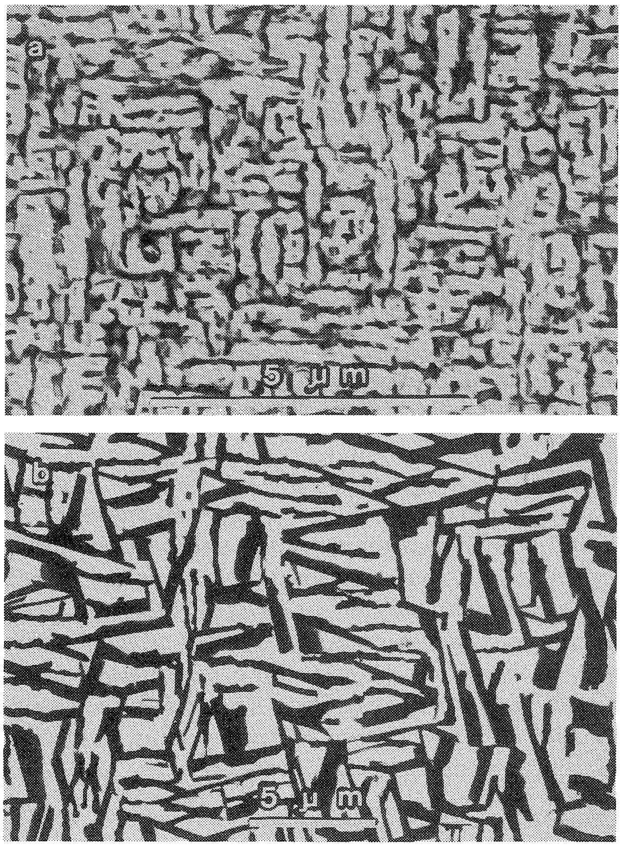

Fig. 1. Electron micrographs of MT films vacuum-deposited on the (001) plane of KCl kept at 20°C (a) and 30°C (b) after being preheated at 200°C.

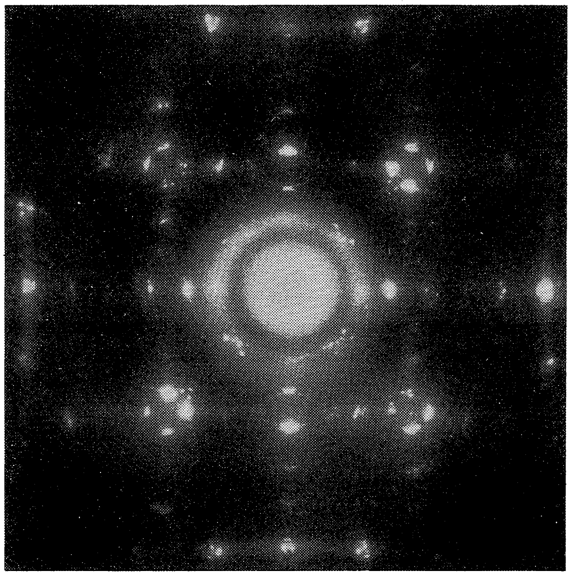

Fig. 2. Electron diffraction pattern of MT film shown in Fig. 1 (b).

for 1 h in advance and then kept at about 20 °C, the MT film vacuum-deposited on the substrate was composed of string-like crystals, as is shown in Fig. 1 (a). Although these crystals appeared to cross each other at right angles, careful observation showed that each string-like crystal was composed of many small rod-like crystals. A slight elevation of the substrate temperature to 30 °C caused a considerable growth of the crystallites, as is shown in Fig. 1 (b). The film was composed of V-shaped crystals growing along two directions crossing at 32°, and the [110] direction of the substrate crystal corresponded to the bisectional direction of the V-shaped crystals. These crystals intersected at right angles to each other. Figure 2 shows the electron-diffraction pattern from the film. This diffraction pattern as well as the intensity appeared identical to the diffraction pattern from hexatriacontane film reported in a previous paper.[9] Although the crystal structure of MT has not been reported, it seems that the evaporated films of MT and paraffin are similar in crystal structure and take the same orientation. In order to generalize the similarity detected among the crystal structures of chain molecules, Vand has introduced the concept of a subcell determined by the positions of the methylene groups.[12] The most widely encountered type of subcell is the orthorhombic paraffin cell. The crystals, composed of chain molecules, have long spacings which are defined as the distance between the basal planes of the crystal lattice passing through the end groups of the chain molecules. These distances are of the order of a chain length of one molecule. Francis and Piper have measured the long spacings of a series of methyl esters of fatty acids containing carbon atoms from 16 to 38.[13] The long spacings of these esters fall accurately on two individual straight lines corresponding to their carbon number. The line for the esters containing an odd number of carbon atoms lies about 0.5 Å above the line of the even. Malkin found that methyl esters containing an even number of carbon atoms have only one crystal form, in which the chains are tilted 63° relative to the basal plane.[14] Because the MT molecule contains 30 carbon atoms, it seems that the MT crystal belongs to the same crystal form as those crystals with even carbon atoms and that its long spacing is 150 Å. Among the homologous series of methyl esters with the even number of carbon atoms, the crystal structure of methyl stearate (C_{18}) is investigated in detail. The crystal form is monoclinic, with dimensions of a=5.61, b=7.33, c=106.6 Å, and β=116° 47′.[15] The carbon chains are arranged in an orthorhombic packing, $O\perp(101)$, and the subcell dimensions are a_s=5.07, b_s=7.33, c_s=2.53 Å, and β_s=89°, the suffix s indicates the subcell lattice. On the basis of these results, it is assumed that the crystal dimensions of MT are a=5.61, b=7.33, c=150 Å, and β=116° 47′, including the subcell of a_s=5.07, b_s=7.33, c_s=2.53 Å, and β_s=89°. The relationship between the unit cell and the subcell is represented schematically in Fig. 3. The (001) plane of the unit cell corresponds to the (101) plane of the subcell, and the (110) plane is held in common between the unit cell and the subcell. The electron-diffraction

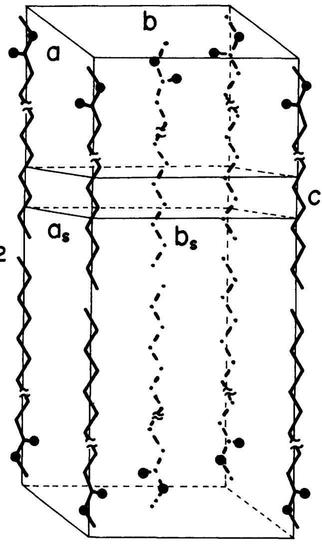

Fig. 3. The relationship between the subcell and the unit cell of MT crystal. Closed circles indicate the oxygen atoms.

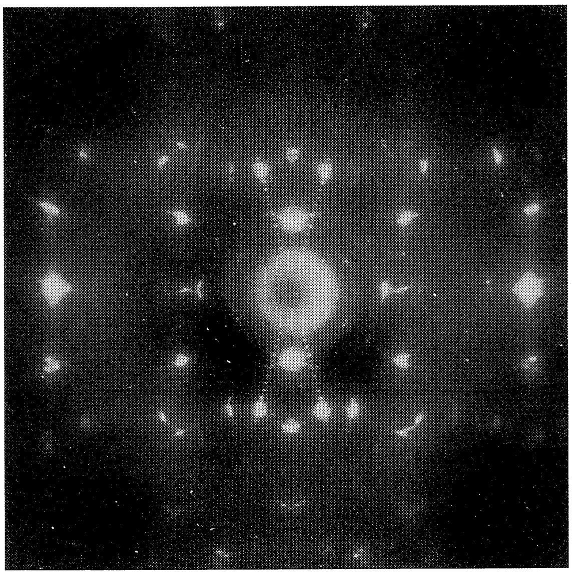

Fig. 5. Electron diffraction pattern of MT film tilted about 23° around c_u-axis of the B-set crystals.

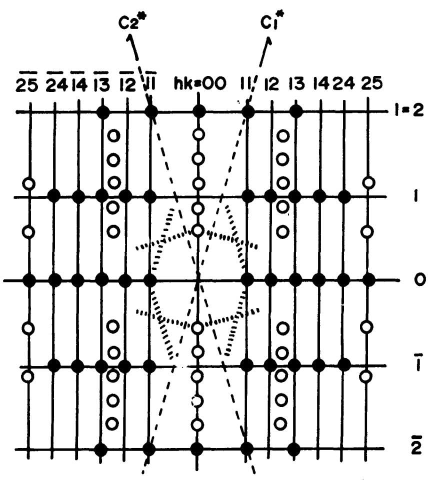

Fig. 4. The interpretation of the diffraction pattern shown in Fig. 2. Closed circles are representation of the basic single crystal pattern. The dotted lines indicate the reciprocal c_u*-axis of the crystals.

pattern shown in Fig. 2 showed the reflection spots corresponding to hkl_s of the sublattice and a series of $00l$ reflections in the small-angle region. On the basis of the subcell dimensions, the reflection spots in Fig. 2 were indexed as is shown in Fig. 4, in which the closed circles represent the basic single-crystal pattern. The total pattern is overlapped by rotating the pattern at 90°. All the crystals are classified as A- or B-set, corresponding to the reflection spots indicated by the closed and the open circles. As a result of the finite thickness of the layers, the reflection spots are elongated in the direction perpendicular to the layer surface. They intersect at the points and/or in the elongated intensity regions of the reciprocal lattice with the Ewald sphere. From a consideration of the observed and calculated spacing as well as the intensities, the reciprocal lattice points, 250_s and 002_s, were found to lie directly on the Ewald sphere. The direction of the c_S-axis corresponds to the [110] direction of the substrate crystal. Consequently, the a_s-, b_s-, and c_s-axes of the subcell lattice are inclined to the normal of the substrate surface at angles of about 30°, 120°, and 90° respectively. On the other hand, the normal of the (110) plane is inclined to the a_s-, b_s-, and c_s-axes at angles of about 34°, 124°, and 90° respectively. When the two sets of angles are compared, it is found that the (110) plane of the MT crystal is oriented parallel to the substrate (001) plane and that its c-axis lies parallel to the [110] direction of the substrate crystal. From a consideration of the molecular arrangement, these findings indicate that the close-packed layer of molecules lies parallel to and adjacent to the substrate face and that the chain molecules are aligned along the lines of the same charge in the substrate [110] direction. The $00l$ reflection spots of hexatriacontane crystals were clearly observed on the line between the point of origin and the 001_s reflection spot; they divide the space into half the number of its carbon atoms, as has been described in a previous paper.[9] In the case of the MT crystal, the lines of the $00l$ reflection spots intersect the equator by an angle of about 74°, the spot intensities on the line through the point of origin are very weak, while those on the line through the 110_s reflection spot are relatively strong. The crossing angle between c_u*- and c_s*-axes, in which the suffix u indicates the unit lattice, is calculated to be about 16° when these axes are projected on the (110) plane. Therefore, the direction of the $00l$-reflection-spots line corresponds to the direction of the reciprocal c_u*-axis of the crystal, indicated by a dotted line in Fig. 4.

In order to determine the molecular orientation of

MT, the film was tilted against the incident beam. When the film was tilted about 23° around the [110] axis of the substrate crystal, that is, the c_u-axis of the B-set crystals, so that the incident beam became perpendicular to the reciprocal c_u^*-axis of the A-set crystals, $00l$ reflection spots clearly appeared on the line through the point of origin and intersected the equator at about 74°, as is shown in Fig. 5. Because the order of $00l$ reflection spots appeared to be more than 50th, it seems that the crystallinity of the evaporated MT film is very high. The reflection spots were indexed as is shown in Fig. 6. The diffraction pattern from the A-set crystals contained hkl_s spots of the sublattice and the series of $00l$ reflection spot crossing each other at about 32°, while that from the B-set crystals shows the net pattern of 110_s and 001_s reflection spots. The reflection spots of the A-set crystals show a mirror symmetry, whose mirror plane corresponds to the (110) plane of the substrate crystal. Therefore, two MT crystals (A_1- and A_2-sets), related with mirror symmetry, and oriented so as to cross each other at about 32°. The long spacing was found to be 75.0 Å by the measurement of the distance of the $00l$ reflection spots. Because of the symmetry of the MT crystal, $00l$ reflections are absent when l is odd. The observed intensities of the $00l$ reflection spots are strong when l is $4n$, while they are very weak when l is $2n$. The calculated values of the structure factor of the $00\cdot4n$ reflection are several times higher than those of the $00\cdot2n$ reflection. This phenomenon was also observed in the methyl stearate crystal.[15] These facts suggest that the longer the aliphatic chain length, the less the effect of the end groups on the structure factor. Considering the rule of the absent reflection, the long spacing $(=c\times\sin\beta)$ of the MT crystal is determined to be 150.0 Å. This value agrees well with the one calculated as has been described in a previous section. Since the $12l$ and its higher-order reflection spots from the A-set crystals appeared strongly, the reciprocal lattice points, 120_s and 001_s, were found to lie nearly on the Ewald sphere. The intersection angle between the normal of the (110) plane and the zone axis [210] of the $(001)_s$ and $(120)_s$ planes is calculated to be about 21°. This value coincides well with the tilting angle of the film against the incident beam.

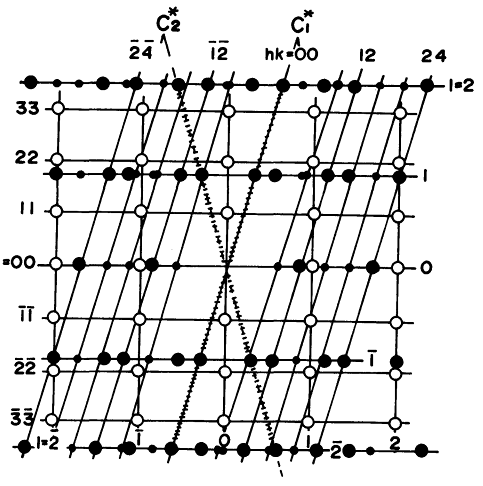

Fig. 6. The interpretation of the diffraction pattern shown in Fig. 5.

On the other hand, the diffraction pattern from the B-set crystals shows the single net pattern of the higher-order reflections of 110_s and 001_s. Each reflection spot has a very strong intensity and shows a streak to the reciprocal c_u^*-axis of the crystal. Figure 7 shows schematically the relationship of the B-set reflection

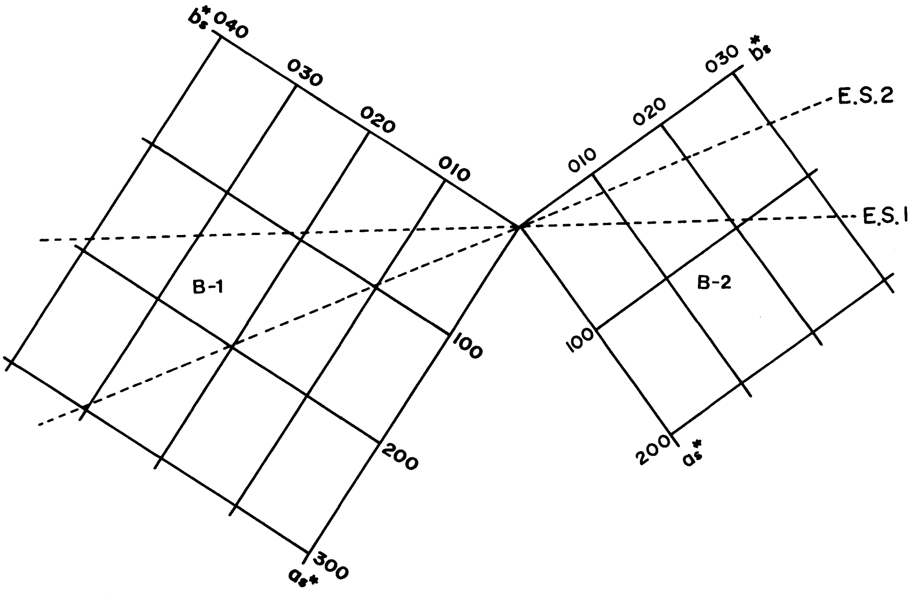

Fig. 7. Schematic diagram of the reciprocal B-set lattice points and Ewald spheres corresponding to Figs. 2 and 5. The lines of E.S.1 and E.S.2 represent the cross sections of Ewald sphere before and after tilting the film.

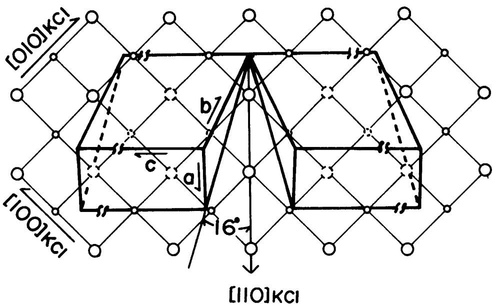

Fig. 8. Schematic diagram of the relative orientation of MT crystals and KCl (001) surface.

spots before and after tilting the film by 23°. The lines of E.S.1 and E.S.2 represent the cross-sections of the Ewald sphere before and after tilting the film. Before tilting the film, the 120_s and 130_s lattice points of the crystals related to the mirror symmetry in the B-set (B_1-and B_2-sets) and situated near the E.S.1. After tilting the film, on the other hand, 110_s and its higher-order reflection spots of the B_1-set crystal came to lie directly on the E.S.2.

The epitaxial overgrowth of MT crystals on the surface of potassium chloride is represented schematically in Fig. 8. The (110) planes of the two crystals related by mirror symmetry, whose mirror plane corresponds to the (110) plane of potassium chloride, are oriented parallel to the substrate surface. Their *c*-axes are parallel to the [110] direction of potassium chloride. Consequently, the [110] direction of the MT crystals crosses the [110] direction of the substrate crystal at 16°. The longitudinal directions of the deposited MT crystals cross at 32°, corresponding to such a molecular orientation. Therefore, the morphology of the deposited MT is V-shaped and these V-shaped crystals grow epitaxially, crossing each other orthogonally corresponding to the C_{4v} symmetry of the substrate crystal.

When the substrate was kept at a temperature between 80 and 90 °C, the MT vacuum-deposited on the substrate formed discrete, disk-like crystals, as is shown in Fig. 9 (a). The electron-diffraction pattern from these crystals shows the single net pattern of higher-order reflections of 100_s and 010_s, as is shown in Fig. 9 (b), which indicates that the *c*-axes of the crystals are perpendicular to the substrate surfaces. This diffraction pattern is similar to the pattern obtained from solution-grown crystallites of linear molecules. It is well-known that the crystals of linear molecules containing MT grow in lamellae from organic solutions. This fact suggests that this crystal habit of linear molecules is the most stable form thermodynamically.

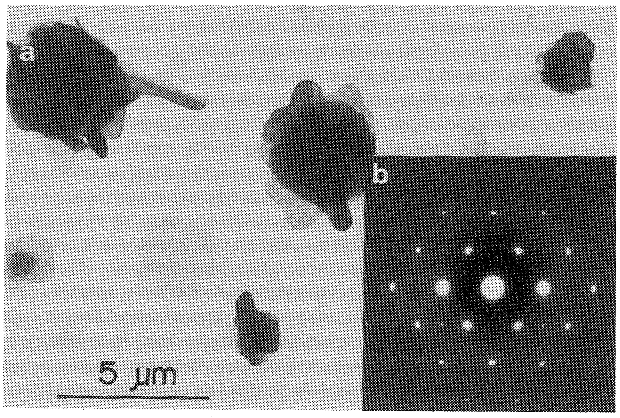

Fig. 9. Electron micrograph (a) and electron diffraction (b) of MT crystals deposited on KCl at 80°C.

When the substrate is kept at a higher temperature than the melting point of MT, the deposit melts completely on the substrate and crystallizes independently of the molecule-substrate interaction on cooling.

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