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The Effect of the Chain Length and the End-Groups on the Epitaxial Growth of Long-Chain Molecules

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Five paraffins (C_{30}—C_{44}) and three linear compounds with polar end-groups,such as hydroxyl, methyl-ester, and carboxyl groups, were deposited on the cleavage surface of an alkali halide crystal in vacuo. Paraffin films deposited on the substrate took the same crystal structure and molecular orientation, independent of the number of carbon atoms in the chain. In the case of derivatives, the morphology and orientation of the crystals, however, differed with the end-groups. The (110) planes of paraffins, alcohol,and methyl-ester crystals were oriented parallel to the substrate (001) plane, and their *c*-axes were parallel to the [110] direction of the substrate crystal. On the other hand, the (001) plane of the acid crystal lay parallel to the substrate surface, so that the *c*-axis of the crystal was oblique to the substrate surface. The epitaxial growth of linear molecules with different end-groups was explained by the difference in the interaction between the end-groups and the substrate.

In recent years, attempts have been made to prepare many organic compounds in the form of an ultrathin film and study the relation between the physical properties and molecular arrangements in the films. The main methods of preparing oriented thin films are the Langmiur-Blodgett method and the physical vapor deposition (PVD) method. The former has been widely applied to amphiphilic linear molecules. The orientation of their films, however, is a single-molecular arrangement normal to the substrate and it was reported, on the basis of microscopic observation, that the uniformity of the molecular packing was incomplete even in the first monolayer.[1] On the other hand, the PVD method has been applied to planar and linear molecules and could give an alternative molecular orientation, depending on the evaporation conditions.[2-10] In the case of linear molecules such as paraffin,[11] they took two orientations on the cleavage surface of alkali halide. The films deposited on the substrate 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, while their fiber axes were parallel to the [110] direction of the substrate crystal. On the other hand, the films deposited on the substrate kept at temperatures near or above their melting points were composed of discrete, disk-like crystals, and their fiber axes were perpendicular to the substrate.

The linear polar molecules such as methyl triacontanoate also took two similar orientations.[12] The crystal morphology, however, was different from that of paraffin, although methyl triacontanoate molecules were oriented parallel to the substrate surface. It seems that the epitaxial growth of linear molecules from the vapor phase depends on the kind of end-group as well as on their crystal structures. It is well-known that paraffins have many polymorphic forms. Their polymorphs depend on even and odd number of carbon atoms,[13,14] as well as the crystallization conditions. It seemed that it would be interesting to investigate the effects of end-groups and the number of carbon atoms on the morphology and orientation of linear molecular crystals.

In this paper, paraffins containing an even or odd number of carbon atoms and their derivatives with different polar end-groups, such as hydroxyl, methyl-ester, and carboxyl groups, were evaporated on alkali halide crystals. The epitaxial growth and growth mechanisms of these linear molecules were then studied by using an electron micrograph and by electron-diffraction.

Experimental

The materials used were five paraffins ($C_{30}H_{62}$, $C_{35}H_{72}$, $C_{36}H_{74}$, $C_{40}H_{82}$, and $C_{44}H_{90}$) and three linear polar compounds containing 30 carbons($C_{30}H_{61}OH$, $C_{29}H_{59}COOCH_3$, and $C_{29}H_{59}COOH$). These materials, obtained from the Tokyo Chemical Industry Co., Ltd., were of a purity higher than 99%. These samples were sublimated from a quartz crucible heated with a tungsten coil onto the clean surface of an alkali halide in a vacuum of 1.33×10^{-3} Pa. Single crystals of alkali halide, NaCl and KCl, were cleaved in air and mounted on a metal block equipped with an electric heater as well as a thermocouple for the temperature measurement of the substrate crystal. After being heated to a higher temperature, the substrate was kept at a temperature between 20 and 100 °C. About 5 mg of each material was deposited vertically onto the substrate surface, which faced downwards on a horizontal plane separated from the crucible by about 10 cm. The rate of sublimation was about 1.5 nm min^{-1}. The temperature of the evaporation source was kept in the range from 180 to 200 °C. The thickness of the deposited films was estimated to be in the range from 80 to 100 nm by using a quartz crystal microbalance. The specimens used for electron microscopy were prepared by the dissolution of the substrate in water after they had been reinforced with evaporated carbon film. The orientation of the deposited crystal relative to the substrate crystal was determined by chromium shadowcasting along the [100] direction of the substrate crystal. Thallium(I) chloride, prepared by evaporation, was used as the standard calibration material for spacing measurements.

Results and Discussion

Crystal morphology and molecular orientation have a close relation to the surface treatment, mainly

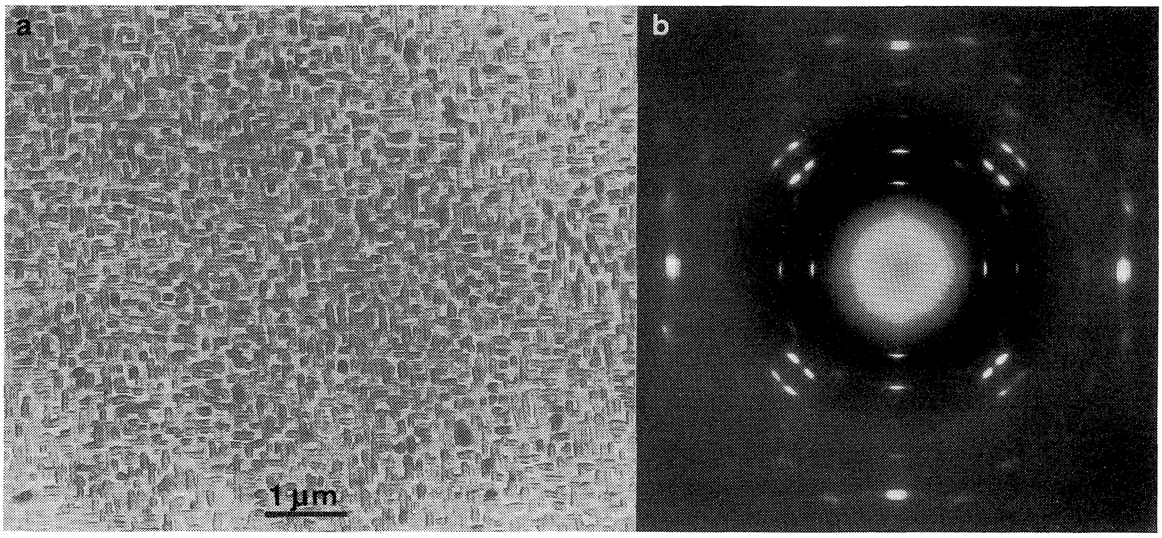

Fig. 1. Electron micrograph (a) and electron-diffraction pattern (b) of triacontane film vacuum-deposited on the (001) plane of KCl kept at 20°C after being preheated at 150°C.

depending on the bake-out procedure. When these compounds were evaporated onto a cleavage surface of alkali halide without any heat-treatment, the films were composed of granules with various orientations. The triacontane film vacuum-condensed on the substrate which had been heated at 150 °C for 1 h in advance and then kept at 20 °C was composed of small rod-like crystals crossing each other orthogonally, as is shown in Fig. 1(a). The needle axis of the deposited crystals was parallel to the substrate [110] direction. Corresponding to such a configuration of the film, the diffraction pattern shown in Fig. 1(b) also had an orthogonal appearance. This pattern is a superposition of two identical fiber diagrams rotated at 90° to each other. The crystals vacuum-condensed on the KCl and NaCl surfaces had the same morphology and showed identical diffraction patterns.

Crystals of such linear molecules as paraffin and its derivatives generally have a lamellar structure. They are composed of stacked layers which consist of chain molecules lying with their axes parallel to each other. In order to generalize the similarity detected among the crystal structures of chain molecules, Vand has introduced the concept of a subcell which is determined by the position of the methylene groups.[15] The most widely encountered type of subcell is an orthorhombic one occupied by two C_2H_4 groups. The diffraction pattern shown in Fig. 1(b) is composed of reflections situated at the reciprocal lattice points hkl_s of the sublattice and a series of $00l$ reflections in the small-angle region; the suffix s indicates the subcell lattice. A triacontane crystal has an orthorhombic subcell with dimensions of a_s=0.733, b_s=0.492, and c_s=0.2546 nm.[16] On the basis of the dimensions, the reflection spots in Fig. 1(b) were indexed as is shown in Fig. 2, in which the open circles represent the basic single-crystal pattern. The total pattern is overlapped by rotating the pattern at 90°. This pattern is similar to the pattern obtained from hexatriacontane film grown epitaxially. From the same consideration as that applied to the orientation of the hexatriacontane crystal, the (110) plane of the triacontane crystal is found also to be oriented parallel to the substrate (001) plane, while its c-axis lies parallel to the [110] direction of the substrate crystal. The crystals of the other paraffins vacuum-condensed on alkali halide surfaces had the same morphology and showed the diffraction pattern of the identical subcell independent of the carbon atoms. This suggests that all the paraffin crystals used are composed of the same subcell and take the same orientation when they grow epitaxially on alkali halide. In addition to the reflection spots of the identical subcell, a series of reflections was found on the equator in the small-angle region. Figure 3 shows the series of $00l$ reflections corresponding to the long-spacings from each paraffin crystal. In the case of molecules with an odd number of carbon atoms, the

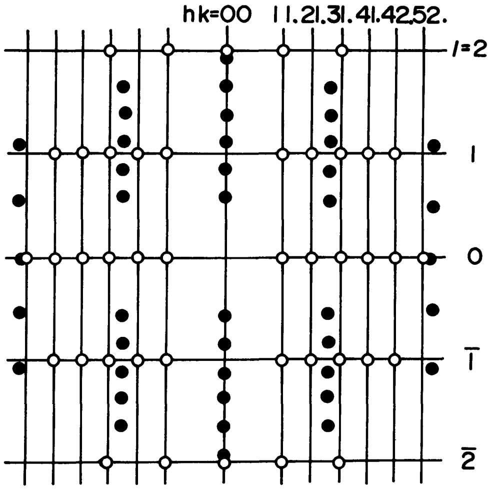

Fig. 2. The interpretation of the diffraction pattern shown in Fig. 1(b). The open circles represent the basic single crystal pattern.

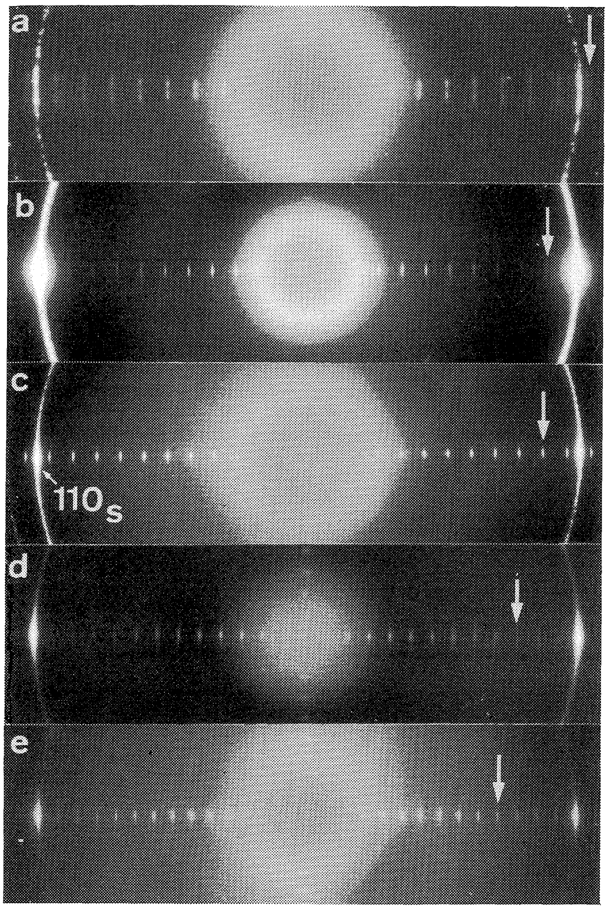

Fig. 3. Electron-diffraction patterns of the long-spacings of (a) $C_{30}H_{62}$, (b) $C_{35}H_{72}$, (c) $C_{36}H_{74}$, (d) $C_{40}H_{82}$, and (e) $C_{44}H_{90}$. Arrow indicates the tenth reflection spot.

Table 1. Long-Spacings of Paraffins

Sample	Observed Value/nm	Calculated Value/nm
$C_{30}H_{62}$	3.993	4.002
$C_{35}H_{72}$	4.634	4.639
$C_{36}H_{74}$	4.769	4.766
$C_{40}H_{82}$	5.305	5.275
$C_{44}H_{90}$	5.829	5.784

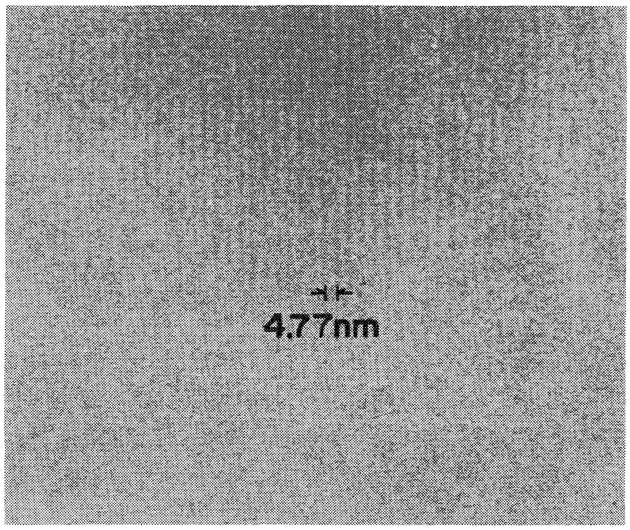

Fig. 4. The 001 lattice image of $C_{36}H_{74}$ crystal.

long-spacings indicate the thickness of two molecules because of the crystal symmetry. Considering the extinction law for the crystal symmetry, l is integer for the molecules with an even number of carbon atoms, while it is even for the molecules with an odd number of carbon atoms. It is noted that the reflections can be clearly observed over the tenth order. Consequently, it seems that the crystallinities of the evaporated paraffin films are very high. These $00l$ reflections demonstrate the lamellar structure of paraffin crystals directly. The individual long-spacings obtained from the $00l$ reflections are given in Table 1. In the crystal of the orthorhombic form, the chain is perpendicular to the basal plane and the length of one zig-zag of a chain is estimated to be 0.2546 nm. The long-spacings may be expressed by an equation of this type;

$$d\,(\mathrm{nm}) = 0.1273 \times m + 0.183$$

m is the number of carbon atoms.[14] The long-spacings calculated from the equation are given in Table 1. The observed values from C_{30} to C_{44} coincide with the calculated values within the error of measurement. Figure 4 shows the high-resolution electron micrograph of hexatriacontane film. A periodicity of 4.77 nm corresponding to the molecular length is observed, although the paraffin crystal is very sensitive to the radiation damage by an electron beam. This finding indicates directly that hexatriacontane molecules lie parallel to the substrate surface.

The 1-triacontanol film vacuum-deposited on the substrate kept at 20 °C was composed of rod-like crystals crossing each other orthogonally, as is shown in Fig. 5(a). The electron-diffraction pattern from the film shows a pattern similar to that of triacontane film. It is well-known that linear alcohols, like other linear molecules, exhibit polymorphism.[17,18] The alcohols have a hexagonal high-temperature form (α) which is stable just below the melting point. The alcohols with an even number of carbon atoms possess two low-temperature forms; the one form is orthorhombic (β), with its chains normal to the (001) plane, while the other is monoclinic (γ), with chains inclined to the plane. In all forms, the long-spacings indicate the thickness of two molecules. The experimental formulae for the long-spacings of the three forms were classified as follows,

$$l_\alpha = 0.252n + 0.45$$
$$l_\beta = 0.252n + 0.55$$
$$l_\gamma = 0.215n + 0.32$$

n is the number of carbon atoms.[17]

The long-spacing obtained from the $00l$ reflections shown in Fig. 5(c) was 8.10 nm. This value coincided with the spacing calculated by the formula for the β form. The subcell dimensions of the β form are a_s=0.733, b_s=0.504, and c_s=0.252 nm.[17] Con-

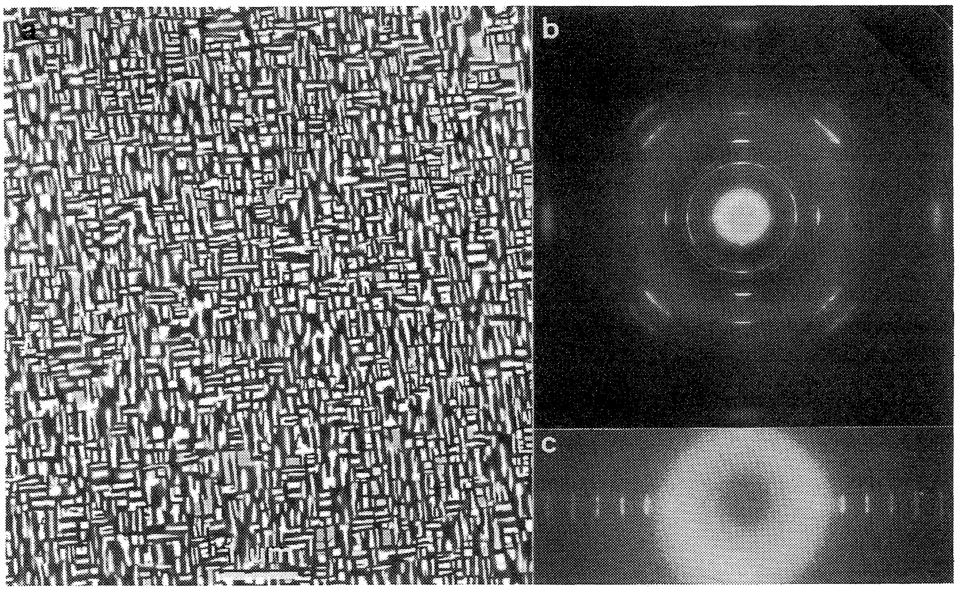

Fig. 5. Electron micrograph (a), electron-diffraction pattern (b), and the long-spacings (c) of 1-triacontanol film.

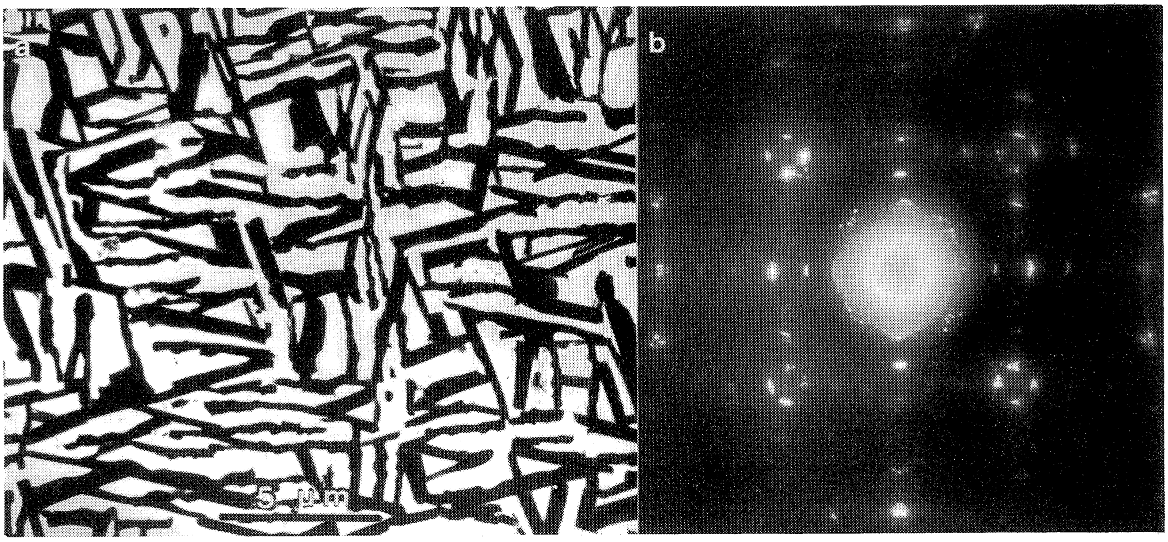

Fig. 6. Electron micrograph (a) and electron-diffraction pattern (b) of methyl triacontanoate film.

sequently, the crystal form of 1-triacontanol deposited on the substrate was assumed to be of the orthorhombic form, with dimensions of $a_s(=a)=0.733$, b_s $(=b)=0.504$, $c_s=0.252$, and $c=8.10$ nm. On the basis of these subcell dimensions, the reflection spots in Fig. 5(b) were indexed so as to be similar to the diffraction pattern of the triacontane film shown in the previous section. Therefore, it seems that the epitaxial overgrowth of 1-triacontanol molecules vacuumcondensed on the substrate is similar to that of triacontane molecules.

Figure 6(a) shows the electron micrograph of the methyl triacontanoate film deposited on the substrate kept at 30 °C. 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 6(b) shows the electron-diffraction pattern from the film. As has been described in a previous paper,[12] the (110) planes of the two crystals related by mirror symmetry, whose mirror plane corresponds to the (110) plan of KCl, are oriented parallel to the substrate surface. Their c-axes are parallel to the [110] direction of the substrate KCl.

The crystal morphologies differed with the end-groups when the linear molecules grew epitaxially on KCl. The epitaxial overgrowth of paraffins and 1-triacontanol crystals on the surface of KCl is represented schematically in Figs. 7(a) and (b). The (110) planes are oriented parallel to the substrate surface. The c-axes are parallel to the [110] direction of KCl. Figures 7(c) and (d) show the schematic representation of the relative orientation and the epitaxial over-

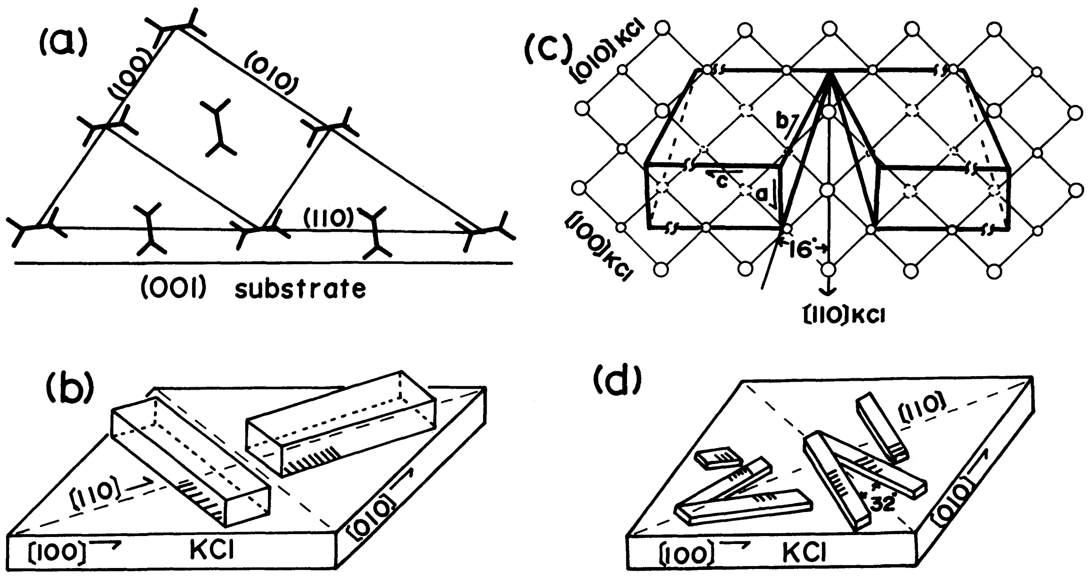

Fig. 7. (a): The relation between paraffin and alcohol molecules and the substrate surface. (b): Orientation of the deposited paraffin and alcohol crystals on the substrate surface. The chain molecules are shown in the crystals. (c): Schematic diagram of the relative orientation of methyl ester crystals and KCl (001) surface. (d): Orientation of the deposited methyl triacontanoate crystals on the substrate surface.

growth of the methyl triacontanoate crystals on the KCl (001) surface. The [110] direction of the methyl triacontanoate crystals crosses the [110] direction of the substrate crystal at 16°. The morphology of the deposited methyl triacontanoate is V-shaped, and these V-shaped crystals grow epitaxially, crossing each other orthogonally, corresponding to the C_{4v} symmetry of the substrate crystal.

The triacontanoic acid film deposited on the substrate at 20 °C was composed of randomly-oriented rod-like crystals and lamellar crystals filling in the space among the former, as is shown in Fig. 8(a). The high-resolution electron-diffraction pattern from the film showed the arc reflection spots on the ring pattern, as is shown in Fig. 8(b). This pattern was similar to the pattern obtained from hexatriacontane film, in which the crystal *c*-axis was oriented perpendicular to the substrate.[11] However, not all spots were indexed to the series of *hk*0 reflections. When the film was tilted about 40° around the *a*-axis of the crystal, the pseudo-hexagonal net-pattern appeared, as is shown in Fig. 8(c). The normal-chain carboxylic acids are known to possess several crystalline modifications. The crystals of even-numbered acids have three forms which are called the A-, B-, and C-form respectively, in order of the decrease in long-spacings.[19] The chain molecules in the B-and C-forms tilt to the basal (001) plane at angles of 62.76° and 51.54° respectively; these angles correspond to the β angle in respective monoclinic form. The B- and C-forms have the same subcell dimensions; a_s=0.740 nm and b_s=0.496 nm,[20,21] and the long-spacing of the C-form triacontanoic acid crystal is 6.52 nm.[22] The crystal parameters of the C-form triacontanoic acid crystal are a=0.936, b=0.496, c=6.52 nm, and β=128.4°. The net pattern in Fig. 8(c) was indexed with *hk*0 reflection series of the C-form. Therefore, the triacontanoic acid crystal deposited on the substrate is the C-form, and its *c*-axis tilts at an angle about 50° to the basal plane. Consequently, the (001) plane of the triacontanoic acid crystal is

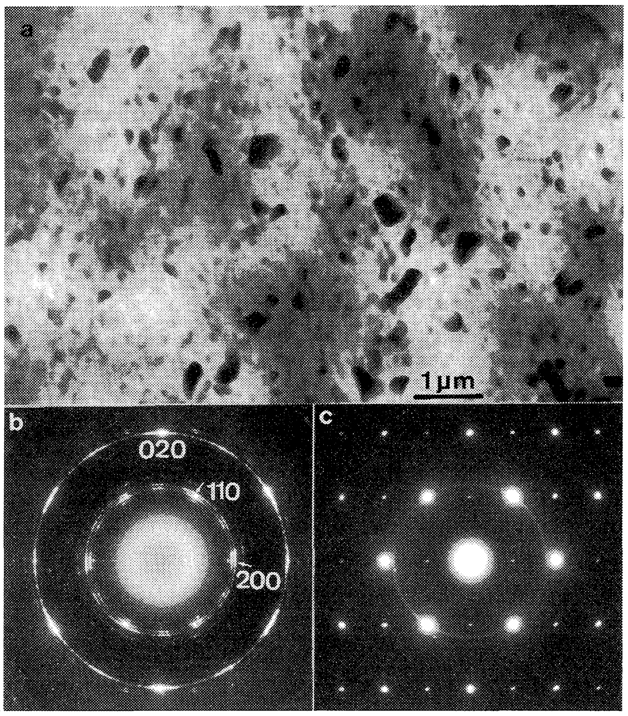

Fig. 8. Electron micrograph (a) and electron-diffraction patterns (b) (c) of triacontanoic acid film. Electron-diffraction pattern (c) was obtained from the film tilted about 40° around the *a*-axis of the crystal.

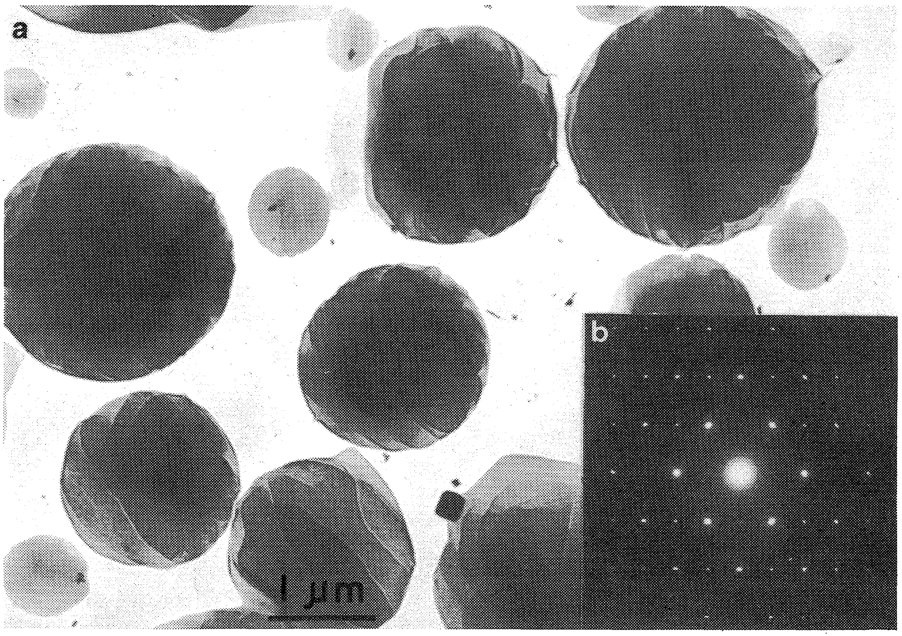

Fig. 9. Electron micrograph (a) and electron-diffraction pattern (b) of triacontane film deposited on the substrate kept at 100°C.

oriented parallel to the substrate (001) plane; as a result of such an orientation, the *c*-axis tilts at an angle of 51.54 ° to the substrate.

When the substrate was kept at a temperature higher than the melting point of each linear molecule, each sample vacuum-condensed on the surface formed discrete, disk-like crystals which were composed of overlapping lamellae, as is shown in Fig. 9(a). The electron-diffraction patterns from these crystals shows a single net-pattern of higher-order reflections of 100_s and 010_s, as is shown in Fig. 9(b); this indicates that the *c*-axes of the crystals are perpendicular to the substrate surface. Therefore, when linear molecules are evaporated on a substrate which is kept at a temperature above their melting points, the liquid deposit condenses in droplets due to the surface energy. On cooling, the deposited molecule probably crystallizes independently of the molecule-substrate interaction and forms the disk-like crystals composed of lamellae.

Paraffins, 1-triacontanol, and methyl triacontanoate crystals took their *c*-axes parallel to the substrate surface. On the other hand, the triacontanoic acid crystals took their *c*-axes perpendicularly to the substrate surface. It seems that the epitaxial overgrowth of long-chain molecules is dependent on the interaction between the end-groups and the substrate. Mauritz et al. pointed out that the non-polar aliphatic long-chain was oriented parallel to the alkali halide surface to minimize the total energy of molecular interaction and that the dispersion-repulsive force was most sensitive to orientation and was greater in magnitude than the electrostatic forces.[23] On the contrary, the polar end-groups probably have a tendency to come in contact with ionic species by means of dipole–dipole interaction. If the dipole–dipole interaction is strong and the interaction between the deposited molecule and the substrate is rather weak, the molecule comes into close contact with the ionic species on the substrate by the end group; the resultant orientation of the crystals is a standing *c*-axis one in order to maintain their molecular configuration. The adsorption strength of long-chain molecules with polar end-groups on metal increases in the following sequence: ester$<$alcohol $<$acid.[24] This order on metal may be applied on such ionic substrates as KCl. The more strongly the polar end-groups interact with the substrate, the more the tendency turned the standing *c*-axis orientation increases. It seems that the standing *c*-axis orientation of the triacontanoic acid crystal is caused by the strong interaction between the end-group and the substrate. If long-chain acid molecules have more carbon atoms than that of triacontanoic acid, it is probable that the influence of the polar end-group decreases and its *c*-axis becomes parallel to the substrate.

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