the model reactions at higher temperatures some trace amounts of unidentified products were observed in the HPLC records. Their UV response corresponded to up to 5% of the total absorption, which may well have included the product of the assumed deactivation reaction.

Conclusions

The network formation theory, based on the theory of branching processes, in which branched and cross-linked structures are assembled from structural fragments, seems to describe well real systems composed of a macrodiol and diisocyanate. The two gel points corresponding to sol → gel and gel → sol transitions predicted by the theory were observed experimentally. With increasing temperature, the latter transition is shifted to a lower excess of isocyanate groups and the region where the gel exists becomes narrower. This is due to a decrease in stability of allophanate and biuret groups. At higher temperatures, the experimental gel fractions are smaller than the theoretical ones. This fact is explained by some unidentified side reaction in which NCO groups are deactivate but their intensity is rather low.

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Comparative Study on the Folded-Chain Structure in Polyethylene and Cycloparaffins. 1. TEM Study on Molecular Orientation of Polyethylene on a Decorated Surface of Polyethylene and Cycloparaffin Single Crystals

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ABSTRACT: The folded-chain structure of polyethylene (PE) was compared with that of cycloparaffins by using the vapor-deposition method of PE on the fold surface of their single crystals. The vapor-deposited PE molecules orient in the direction parallel to the *b*-axis of monoclinic cycloparaffins, $(CH_2)_{36}$ and $(CH_2)_{60}$, which is parallel to the "folding direction". When the fold surface of a PE single crystal was decorated as above, the deposited PE molecules orient parallel to the (110) growth face in each (110) sector of the single crystal. This fact strongly supports the (110) fold in the (110) sector of PE single crystal. Decoration with vapor-deposited PE on the surface of a lozenge-shaped single crystal of orthorhombic cycloparaffin, $(CH_2)_{120}$, also showed identical morphology to the case of a PE single crystal. This fact evidences the (110) fold of the $(CH_2)_{120}$ crystal, although there still remains the question whether the fold structure of $(CH_2)_{120}$ is the same as that of PE. The orientational relationship between the deposited PE and various substrates is also discussed by analyzing their electron diffraction patterns. For example, the 002 reflection from deposited PE was arced for PE and $(CH_2)_{120}$ substrates, but it was not arced for $(CH_2)_{36}$ and $(CH_2)_{60}$ substrates. This result suggests that there exists some orientational distribution of the molecular axis of PE deposited on PE and $(CH_2)_{120}$ single crystals.

1. Introduction

The folded-chain structure of polyethylene (PE) has been studied extensively, since it was found in the single crystals grown from a solution in 1957.[1] Some models of the structure were proposed: regular sharp fold model, loose loop model, and random reentry model.[2] It is the current belief that the folded-chain structure is somewhat regular,[3,4] which means adjacent reentry, although there still remain problems, such as distribution in the folding direction and the size of fold parts.

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Table I
Lattice Constants of Various Cycloparaffins and PE

lattice const	$(CH_2)_{24}$[a]	$(CH_2)_{36}$[b]	$(CH_2)_{48}$[b]	$(CH_2)_{60}$[b]	$(CH_2)_{72}$[b]	$(CH_2)_{120}$[c]	PE[28]
cryst[d] system	mono	mono	mono	mono	mono	ortho	ortho
a, nm	1.017	1.033	1.033	1.033	1.033	0.746	0.740
b, nm	0.803	0.824	0.819	0.817	0.817	0.498	0.493
c, nm	3.10	4.63	6.20	7.73	9.26	7.77	0.254
β, deg	120.2	119.4	118.7	118.6	118.8	90.0	90.0
Z[e]	4	4	4	4	4	1	(2)

[a] The lattice constants of this cycloparaffin were converted from the data reported by Groth.[10] [b] The lattice constants of these cycloparaffins were converted from the data reported by Trzebiatowski et al.[11] [c] The data were obtained from the analysis of electron diffraction patterns. The length c was, however, tentatively assumed from the 001 reflections in the electron diffraction pattern of "edge-on" crystals grown epitaxially on the (001) face of NaCl.[18] [d] mono, monoclinic, ortho, orthorhombic. [e] The number of molecules in the unit cell.

It is informative to compare the fold structure in PE with that in a model compound composed of methylene units, if the crystal structure of the compound is fully analyzed. Recently the methods to synthesize pure long-chain normal paraffins and cycloparaffins were established.[5,6] Lee et al.,[5] Leung et al.,[7] and Organ et al.[8] studied the morphologies of low molecular weight PE fractions or normal paraffins, which are folded once or several times, and then reported that the morphologies were influenced by their contour length. In particular, Organ et al. reported that the crystals containing once-folded chains are often lozenge shaped with {110} folds.[8] Cycloparaffins have been regarded as model compounds with regular sharp folds. In the case of triclinic[9] and monoclinic[10,11] cycloparaffins, the conformation of the fold is proposed to be -(ggtgg)-. There exist some differences between PE and these cycloparaffins in the distance of the nearest stems and in the setting angle of planar zigzag stems in their unit cell. On the basis of the electron diffraction experiment, Lieser et al. discussed in detail the crystalline modifications and molecular packing of various cycloparaffins depending on their chain perimeters;[12] cycloparaffins ($(CH_2)_n$, $n \geq 144$) crystallize in an orthorhombic crystal system.[12,13] The lattice constants of the subcell of the cycloparaffins are supposed to be very similar to those of orthorhombic PE. Thus the differences and similarities in the manner of chain folding between PE and cycloparaffins are very interesting to study.

In studying the structure of the fold, electron microscopy is one of the most efficient techniques. It is, however, almost impossible at present to observe directly the chain fold with an electron microscope. Some indirect methods have been introduced into the study of the fold structure in PE crystals. One of the indirect methods is to observe peculiar morphological patterns on the fold surface of the decorated materials. This method includes decoration with metals,[14] epitaxial growth of nascent PE,[15] and polymer decoration.[3,16] Bassett et al. evaporated gold on the surface of solution-grown PE single crystals that had different crystallization histories.[14] They reported preferential nucleation of gold at crystal edges and surface steps. The stripes (spacing about 20 nm) revealed by gold particles are distributed nearly parallel to the (310) plane in each (110) sector and to (100) in {100} sectors. These stripes originate from the pleats made in the course of sedimentation of the crystal platelets on the support film for transmission electron microscopy. The stripes emphasized with gold particles indicate the surface topography due to collapse, and the direction of the stripes has no direct relation with the folding. These facts demonstrate that the surface of collapsed lamella has a number of steps. Georgiadis et al. observed the epitaxial growth of nascent PE on the fold surface of a PE single crystal used as a seed crystal.[15] The overgrown rodlike crystallites orient with their long axis perpendicular to the {110} growth faces of the seed crystal. Although Georgiadis et al. could not take electron diffraction patterns, they assumed that molecular chains were oriented parallel to the substrate surface and normal to the rod axis in a manner analogous to solution-grown PE crystals. In the surface decoration with vaporized PE on the fold surface of a PE single crystal, Wittmann et al. also confirmed that the deposited molecules align parallel to the {110} growth faces.[3]

We recently reported a preliminary result in the surface decoration of monoclinic cycloparaffins, $(CH_2)_{36}$ and $(CH_2)_{60}$, with vaporized PE: the PE molecules orient parallel to the folding direction of the cycloparaffins, which undoubtedly have regular sharp folds.[17] In this paper, the orientational features of vapor-deposited PE on the surface of several substrates, e.g., single crystals of PE, a normal paraffin, and cycloparaffins, are described in detail. In particular, the chain folding of a PE single crystal is discussed in comparison with that of a cycloparaffin $(CH_2)_{120}$, which crystallizes in an orthorhombic form[18] in the nature of the long chain.

2. Experimental Section

2.1. Synthesis of Cycloparaffins. Cycloparaffins, $(CH_2)_{12n}$ (n = 3, 4, ..., 10) were synthesized via the metathesis reaction in a hexane solution.[6,19] Commercial cyclododecene was used after being purified by distillation over sodium. As a catalyst, WCl_6 and $EtAlCl_2$ (1:5 mol ratio) were used and the mole ratio of the monomer to tungsten was 1000. After polymerization at room temperature for 30 min, the polymerized material was precipitated in methanol. Oligomers were separated crudely from polymers by using a Soxhlet extractor with acetone as the solvent. The oligomers still having double bonds were fractionated by GPC. A monodisperse material was subsequently hydrogenated by reaction with an excess of (p-toluenesulfonyl) hydrazine in a xylene solution.

2.2. Preparation of Single Crystals. Single crystals of $(CH_2)_{36}$ were directly grown from a xylene solution by evaporating the solvent on the carbon support film deposited on a copper specimen grid. $(CH_2)_{60}$ single crystals were grown in a xylene solution by slow cooling. $(CH_2)_{120}$ single crystals were grown isothermally from a 0.001 wt % xylene solution at 55 °C. PE (MW = 13 600; NBS Reference Material #1482) single crystals were grown from a 0.001 wt % xylene solution at 80 °C by using the self-seeding technique.[21]

2.3. Decoration of Crystal Surfaces with Vaporized PE. A specimen to be decorated was prepared by drying the crystal suspension on the carbon support film deposited on a copper specimen grid. Commercially produced PE (Sholex 6050) was evaporated onto the specimen under vacuum (10^{-3} Pa) from a quartz crucible coiled with a tungsten wire. To suppress the influence of radiant heat, the specimen is about 10 cm from the electrical heat source. Damage to specimens due to radiant heat, especially in the case of $(CH_2)_{36}$ with a low melting point, was not detected. The specimens thus prepared were shadowed subsequently with Pt-Pd to enhance the contrast for morphological observation. To estimate lattice spacings, aluminum was

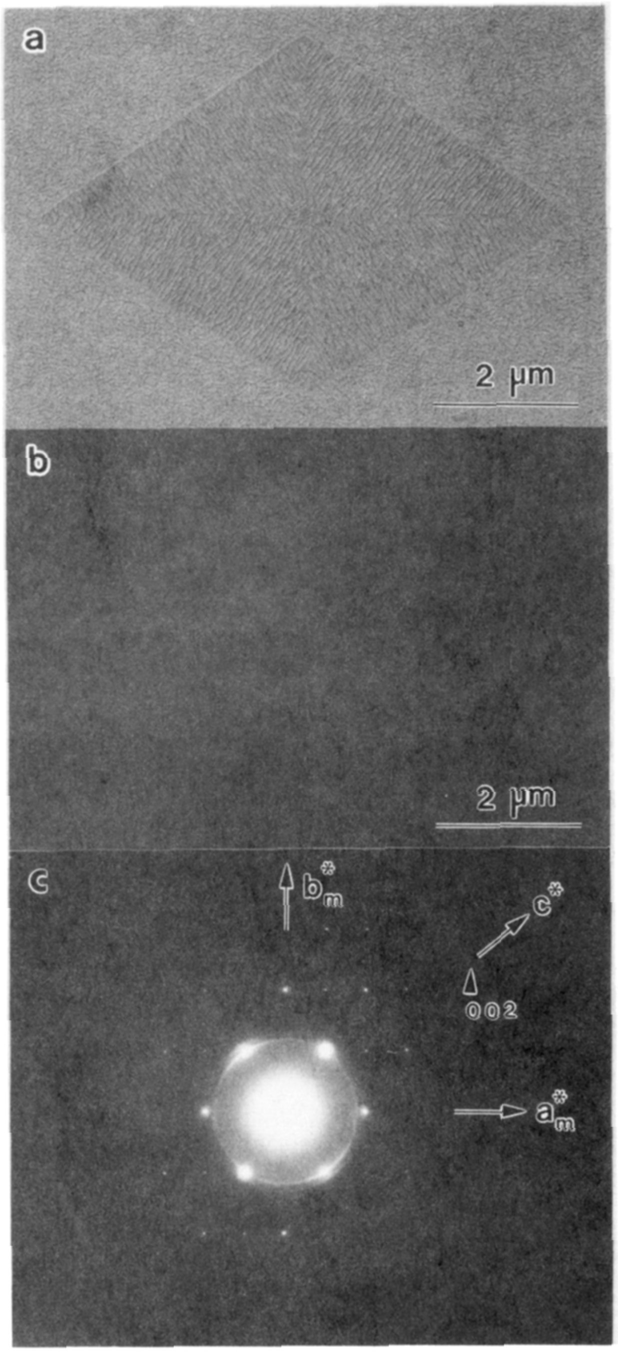

Figure 1. (a) PE single-crystal lamella decorated with vaporized PE. (b) Dark-field image of a decorated PE lamella using the 002 reflection in (c). The bright diagonal sectors demonstrate that the vapor-deposited PE molecules orient parallel to the (110) growth face of the mother crystal. (c) Selected-area electron diffraction pattern from the lower right sector in the crystal of (a). Spotlike reflections show the *hk*0 net pattern from the PE mother crystal. Arc-shaped reflections originate from the vapor-deposited PE.

evaporated on the specimen as a reference. Transmission electron microscopy was performed by using a JEOL JEM-200CS operated at 200 kV.

3. Results

3.1. Molecular Conformation of Monoclinic Cycloparaffins. The crystal structure of $(CH_2)_{36}$ was analyzed by Trzebiatowski et al.[11] In the unit cell of $(CH_2)_{36}$ the molecular axis is parallel to the $[\bar{1}01]$ direction in the crystal system defined by them. The averaged subcell of $(CH_2)_{36}$ is supposed to be similar to the unit cell of monoclnic PE, though the stems are skewed in the crystal. In our previous paper,[20] new lattice constants were proposed on the basis of the data reported by Trzebiatowski et al. The *c*-axis in the new unit cell is defined to be parallel to the molecular axis. The new lattice constants of $(CH_2)_{36}$ are listed in Table I. Other monoclinic cycloparaffins are assumed to have a similar crystal structure to that of $(CH_2)_{36}$. Their unit cells, thus, were converted to the new cells as described above. The results are listed in Table I. This table clearly demonstrates that the dimensions *a*, *b*, and β of different cycloparaffins are almost identical. On the other hand the table also shows that only the length *c* has a linear relationship with the number of carbon atoms in the molecule.[21] These facts indicate that each of the monoclinic cycloparaffins in Table I has a similar molecular structure in the crystal. For example in the crystal of $(CH_2)_{36}$ the molecule is composed of two slightly twisted trans-zigzag stems linked with two methylene units at both ends. The molecular plane defined by the two stems of $(CH_2)_{36}$ is nearly parallel to the (200) plane in the crystal, so that the fold plane is defined as (200). The "folding direction" of molecules is thus in the direction of the *b*-axis. This situation is probably the same for other monoclinic cycloparaffins. In the following part of this paper, newly defined unit cells in Table I are used to indicate the crystallographic planes and directions in the crystals.

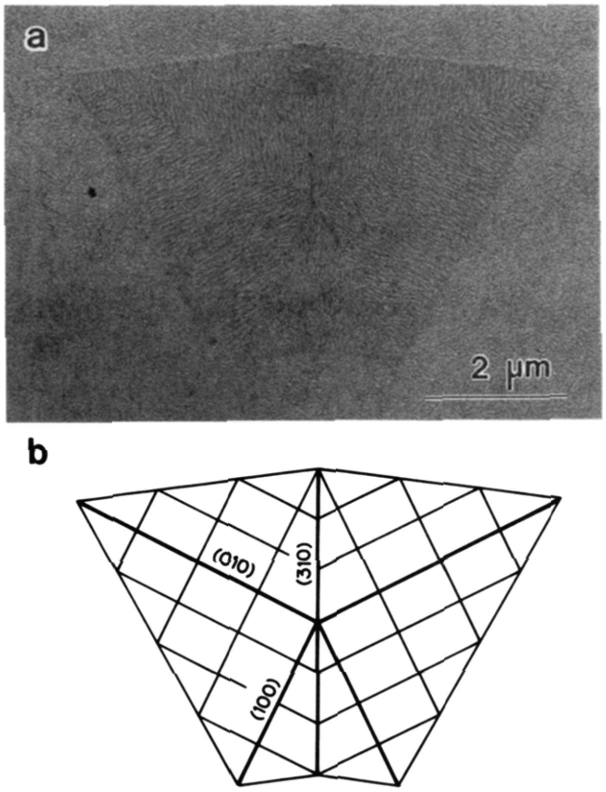

Figure 2. (a) (310) twin crystal of PE decorated with vaporized PE. (b) Schematic representation of the twin boundary and sector boundaries of the crystal in (a).

3.2. Surface Decoration with Vaporized PE. 3.2.1. PE and Normal Paraffin Single Crystals as Substrates. Decoration on the surface of PE and normal paraffin single crystals with PE from its vapor phase was used for the first time by Wittmann et al.[16] Similar results to theirs were obtained by us, e.g., as shown in Figure 1. The selected-area electron diffraction pattern of Figure 1c originated from the lower right sector of the

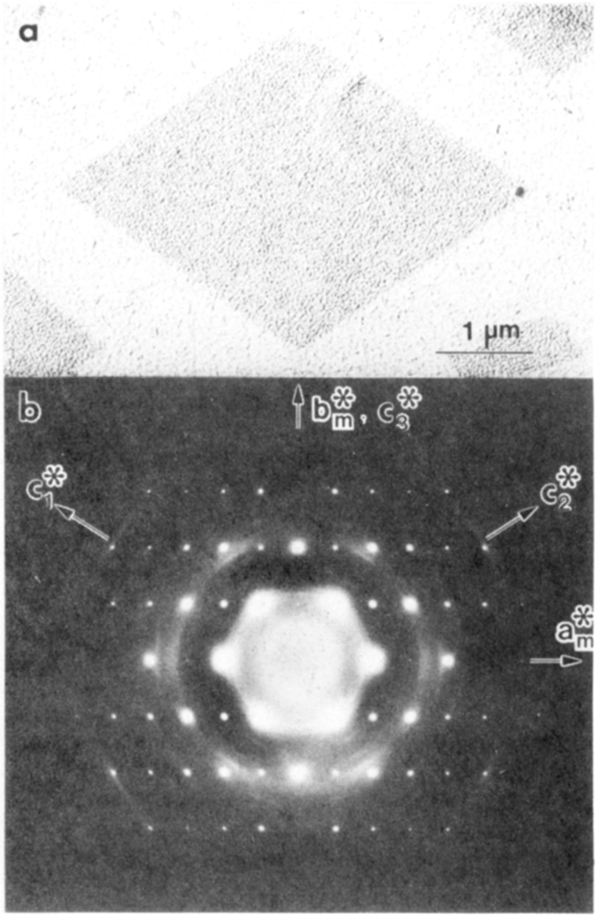

Figure 3. (a) Orthorhombic normal paraffin, $C_{94}H_{190}$, decorated with vaporized PE. (b) Selected-area electron diffraction pattern from the crystal in (a). Spotlike reflections show the *hk*0 net pattern from the $C_{94}H_{190}$ lamella. The arc-shaped reflections reveal that the molecular axis of vapor-deposited PE orients to ⟨110⟩ and [010] of $C_{94}H_{190}$ and that the contact plane is (110) of PE. This is the same as surface decoration of $C_{36}H_{74}$.[3]

lozenge-shaped PE crystal decorated with PE in Figure 1a. The spotlike reflections represent the *hk*0 pattern of the mother crystal, namely, a PE single crystal lamella. The rodlike crystals in two opposite sectors can be seen in the dark-field image (Figure 1b) by using the 002 reflection that appeared in Figure 1c. This fact indicates that the molecules of vapor-deposited PE in the opposite sectors orient nearly parallel to the [110] folding direction. Figure 2a shows a decorated twin crystal of PE. The rodlike crystals are grown normal to each prism face even on the twin crystal and clearly reveal the sector boundaries and the twin boundary. As schematically shown in Figure 2b every prism face of the twin crystal is identified as (110), and the crystal has the (310) twin boundary.[21,22]

Figure 3a shows a decorated single crystal of a normal paraffin ($C_{94}H_{190}$). Seemingly, the rodlike crystals are grown randomly over the whole surface of the crystal. The electron diffraction pattern (Figure 3b), however, shows that the molecules of vapor-deposited PE orient parallel to the ⟨110⟩ directions and rather weakly to the [010] direction of the $C_{94}H_{190}$ substrate, as also shown by Wittmann et al. for $C_{36}H_{74}$.[3] Energy calculation indicates that the molecules of deposited PE orient most preferably in the ⟨110⟩ directions and next preferably in the [010] direction of orthorhombic normal paraffin.[25] In Figure 3b, the arc-shaped reflections such as 210, 310, 211, 311 and 002 from deposited PE are recognized for both the ⟨110⟩ and [010] orientations. A procedure to determine the contact plane of PE on the (001) surface of $C_{94}H_{190}$ is the following: (1) find a plane passing through the origin and the vicinity of the reciprocal lattice points corresponding to the observed reflections, (2) find a reciprocal lattice point with lower indices in the vicinity of the normal at the origin of the plane. In this way, it is concluded that the (110) plane of vapor-deposited PE is in contact with the mother crystal, i.e., the (110) contact plane. This was already proposed by Wittmann et al. using a normal paraffin $C_{36}H_{74}$ substrate.[3] The reflections such as 210, 310, 211, 311, etc. are observed together with the 002 reflection only if the crystal is slightly tilted around its *c*-axis. The main causes for this orientational distribution are considered as follows: (1) the distribution in orientation of the rodlike crystallites themselves; (2) the undulation of the surface of a mother crystal. The first cause is more probable, because all the reflections mentioned above were observed when rodlike PE crystals were epitaxially grown on the (001) cleavage face of NaCl from a solution[21] or from the vapor phase.[23,24]

3.2.2. Monoclinic Cycloparaffin Substrates. Parts a and b of Figure 4 show the morphology of the $(CH_2)_{36}$ single crystal decorated with vaporized PE and the corresponding electron diffraction pattern, respectively. The subscript "m" means reflections originated from the mother crystal. The reflections of $\bar{2}04_m$ and 020_m indicate that the basal plane of the mother crystal is (001).[20] Rodlike PE crystals are grown with their long axis parallel to the *a*-axis of the mother crystal. The molecules in the rodlike crystal orient parallel to the *b*-axis of $(CH_2)_{36}$, since the *b**-axis of $(CH_2)_{36}$ and the *c**-axis of PE are in the same direction (Figure 4b). In other words vapor-deposited PE molecules orient in the folding direction on the fold surface of $(CH_2)_{36}$. The reflections of 020, 011, and 002 indicate that the contact plane of rodlike PE crystals is (100). The orientational relationship in surface decoration of $(CH_2)_{36}$ is schematically shown in Figure 5.

Crystal structures of $(CH_2)_{60}$ and $(CH_2)_{36}$ seem to be very similar to each other except for the length of their trans zigzag stems. A decorated single crystal of $(CH_2)_{60}$ and the corresponding electron diffraction pattern are shown in parts a and b of Figure 6, respectively, which demonstrate the same tendency as in the case of $(CH_2)_{36}$. The vapor-deposited PE molecules orient parallel to the *b*-axis of $(CH_2)_{60}$, the direction of which has been deduced as the folding direction, as in the case of $(CH_2)_{36}$.

In a paper of this series, energy calculation has indicated that one chain segment comprising some CH_2 units orients in the folding direction of $(CH_2)_{36}$ and locates stably near the center line between the neighboring two rows of folds when the chain segment is adsorbed on the fold surface of the monoclinic cycloparaffin.[25] This calculated result explains well the experimental results of surface decoration of monoclinic cycloparaffins with vaporized PE.

3.2.3. Orthorhombic Cycloparaffin Substrate. Modifications of the crystal system in cycloparaffins has been reported, depending upon the number of methylene units in a molecule: cycloparaffins having sufficiently long chains crystallize in an orthorhombic form,[12,13] while shorter cycloparaffins primarily crystallize in a monoclinic or triclinic form.[9-12] The subcell dimensions of $(CH_2)_{120}$ are nearly the same as the unit cell dimensions of orthorhombic PE (see Table I).[18] It was recently confirmed from the small- and wide-angle

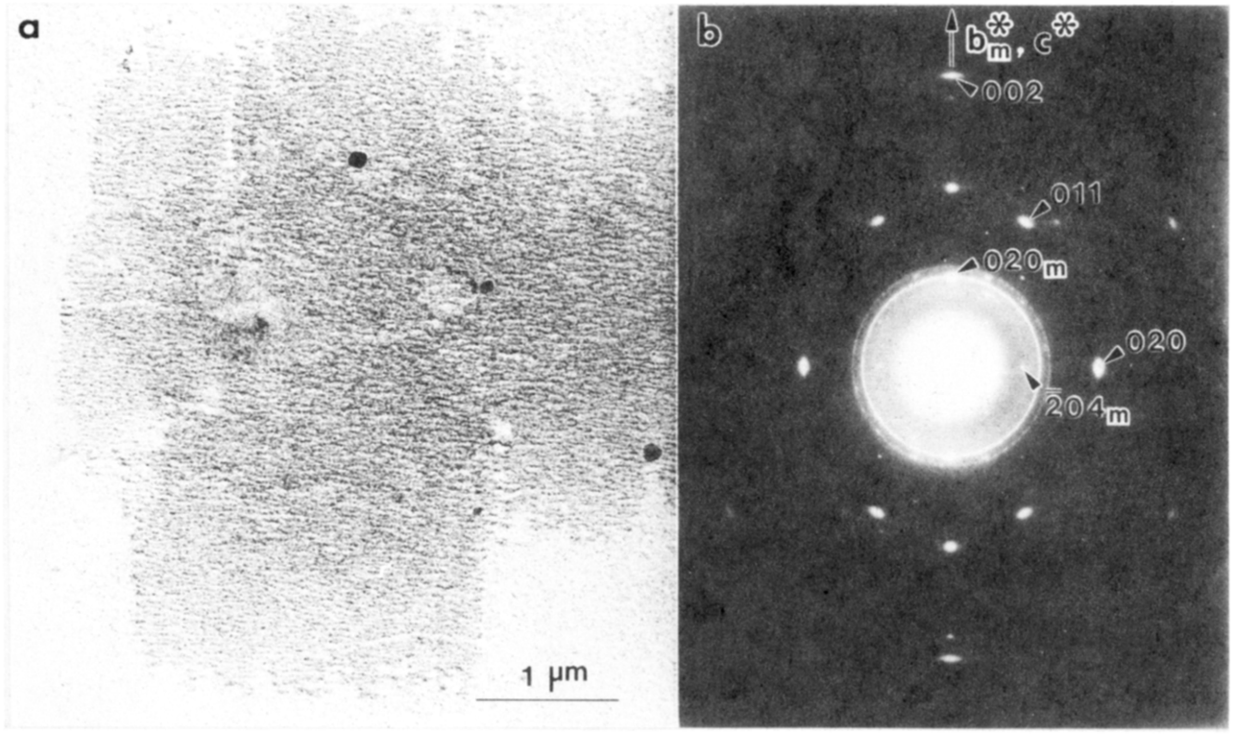

Figure 4. (a) Monoclinic cycloparaffin ($(CH_2)_{36}$) lamella decorated with vaporized PE. The rodlike crystals are grown parallel to [100] of $(CH_2)_{36}$. (b) Selected-area electron diffraction pattern from the crystal in (a). Reflections with the subscript "m" originate from the mother crystal ($(CH_2)_{36}$). Note that the b^*-axis of $(CH_2)_{36}$ and the c^*-axis of PE are in the same direction, i.e., the molecules of vapor-deposited PE orient parallel to the folding direction of $(CH_2)_{36}$.

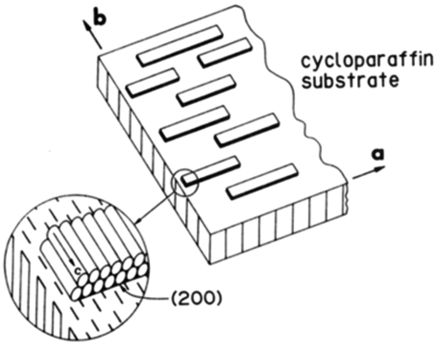

Figure 5. Schematic representation of the structure of rodlike crystals of PE on a monoclinic cycloparaffin lamella. The rodlike crystals orient parallel to [100] of cycloparaffin. The molecular orientation in the rodlike crystal is shown in the enlarged circle: the molecules of PE deposit parallel to the folding direction (b-axis) of cycloparaffin.

X-ray diffraction experiments of the sedimented single crystal mat of $(CH_2)_{120}$ that $(CH_2)_{120}$ crystallizes in the orthorhombic form. Figure 7a shows the lozenge-shaped single crystal of $(CH_2)_{120}$ decorated with PE. Rodlike PE crystals are grown in each sector with their long axis perpendicular to the (110) growth face of the mother crystal. The electron diffraction pattern is shown in Figure 7b, which originated from the lower left sector of the mother crystal in Figure 7a. The spotlike reflections show the *hk*0 net pattern of the $(CH_2)_{120}$ single crystal. This *hk*0 electron diffraction pattern of the $(CH_2)_{120}$ lamella is very similar to that of PE. Thus the *ab* projection of the planar zigzag stems of $(CH_2)_{120}$ may belong to the two-dimensional space group of *pgg* like orthorhombic PE. Both upper and lower ends of the nearest two stems forming a molecule must be linked with a few methylene units. Consideration of the directional relationship reveals that the molecular axis of vapor-deposited PE orients parallel to the [110] direction of $(CH_2)_{120}$. From the assumption that the vapor-deposited PE tends to orient in the folding direction, it is concluded that the (110) fold is dominant in the $(CH_2)_{120}$ single crystal. Figure 8 schematically illustrates an example showing the orientational relationship between vapor-deposited PE molecules and the folding direction on the (001) surface of $(CH_2)_{120}$.

4. Discussion

4.1. Orientation Distribution of the Molecular Axis of Vapor-Deposited PE. The 002 reflection (in Figures 4b and 6b) of PE overgrown on the (001) surface of monoclinic cycloparaffin lamellae is not arc-shaped, while the arc-shaped 002 reflection is characteristic of surface decoration of PE and $(CH_2)_{120}$ lamellae (Figures 1b and 7b). The arc-shaped reflection of 002 in Figure 1b demonstrates the distribution in orientation of the chain axis of vapor-deposited PE on the PE sedimented lamella. The distribution is attributed to the defects in the fold surface. The defects may include the pleats formed during sedimentation of the lamella on a support film.

The 002 arc-shaped reflection of the deposited PE is also observed in the case of surface decoration of the $(CH_2)_{120}$ lamella (Figure 7b). This cycloparaffin has regular sharp folds as long as the purity of the sample is very high. Unfortunately, the purity of the sample used in this study is estimated at about 90%, the impurities of which are mainly $(CH_2)_{108}$ and $(CH_2)_{132}$. Thus one of causes of the surface defects of $(CH_2)_{120}$ is the polydispersity. Another cause is the collapse of the $(CH_2)_{120}$ crystal lamellae during sedimentation, as is the case with the PE lamellae.

4.2. Contact Plane of Vapor-Deposited PE. The topography of the crystal surface in PE, normal paraffins, and cycloparaffins leads the vapor-deposited PE to a certain preferable orientation. The contact plane of deposited PE on the single crystal of the orthorhombic normal paraffin was (110), and that on the monoclinic

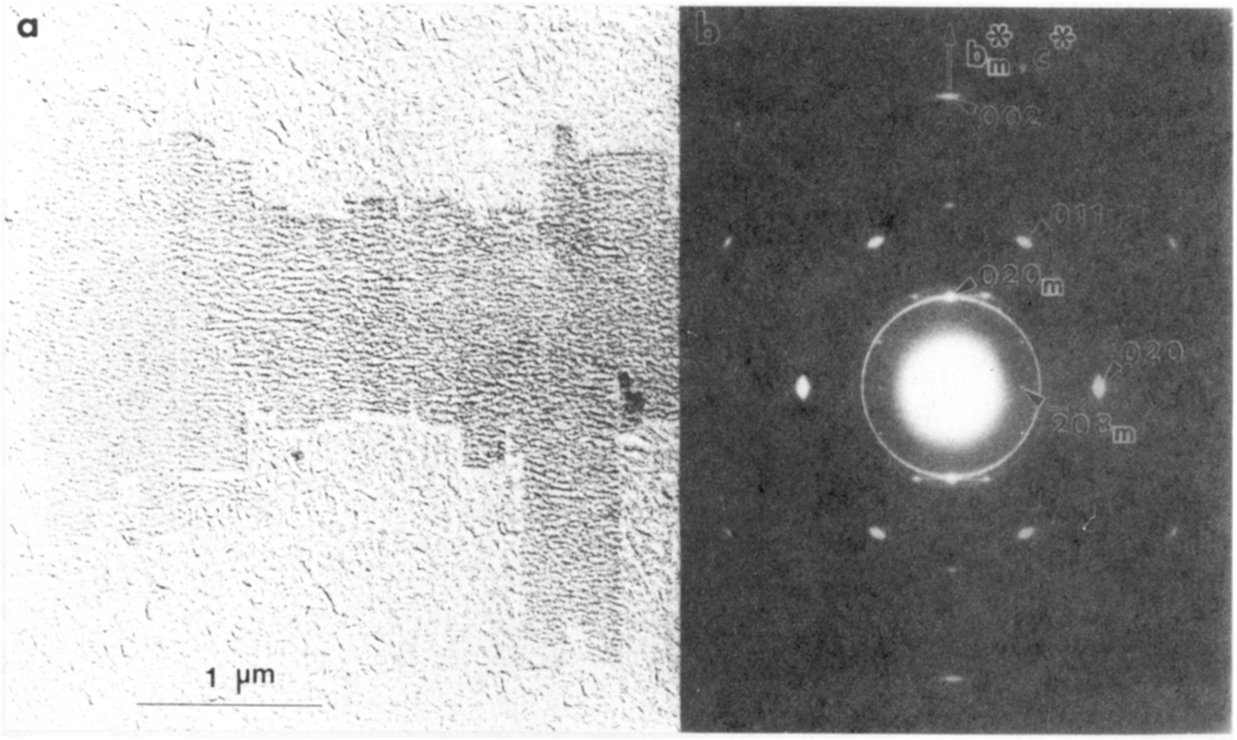

Figure 6. (a) Monoclinic cycloparaffin ($(CH_2)_{60}$) lamella decorated with vaporized PE. (b) Selected-area electron diffraction pattern from the crystal in (a). The orientational relationship is the same as the case of $(CH_2)_{36}$. The subscript "m" means $(CH_2)_{60}$ as a mother crystal.

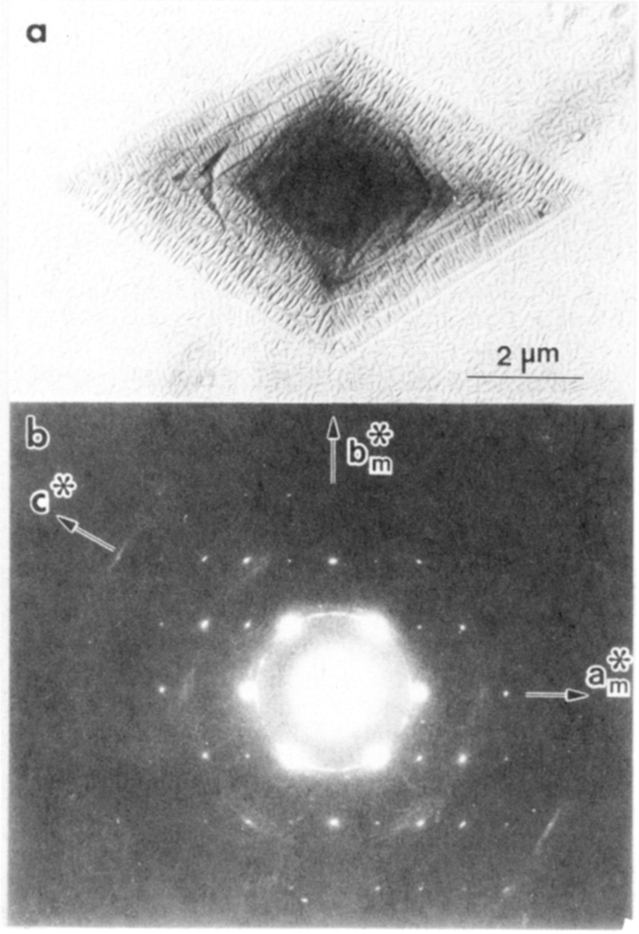

Figure 7. (a) Orthorhombic cycloparaffin ($(CH_2)_{120}$) lamella decorated with vaporized PE. The rodlike crystals are grown perpendicular to the growth face of the lozenge-shaped $(CH_2)_{120}$ lamellar crystal. (b) Selected-area electron diffraction pattern from the lower left sector in the crystal of (a). This pattern is very similar to that of the decorated PE single-crystal lamella (see Figure 1).

cycloparaffin was (100). The surface topography of normal paraffin $C_{36}H_{74}$ and cycloparaffin $(CH_2)_{36}$ substrate is already known, because their crystal structures were fully analyzed.[26,11] Adsorption energy of a set of methylene chain segments arranged to make the orthorhombic PE lattice was calculated when the segments were adsorbed on the (001) surface of these two substrates, and the degree of lattice mismatching was also examined.[25] These results explain well the experimentally observed chain orientation and contact plane in surface decoration of these substrates.

Single-crystal lamellae of PE have a characteristic three-dimensional shape of a hollow pyramid in a suspension.[27] The direction of the molecular chain axis is the same throughout the pyramid. The crystals are collapsed and flattened during sedimentation on a support film for transmission electron microscopical observation[27] as briefly mentioned in section 4.1. The striation owing to (310) slipping planes is usually recognized in the sedimented crystal. The gold decoration of the sedimented crystal also shows the stripes resulted from pleats generated by collapse.[14] Thus the surface of the sedimented lamellar crystal is not a smooth flat plane, though the *hk*0 net pattern in electron diffraction from the lamella usually suggests the basal plane of the lamella is (001). The pleats of the lamella surface may produce a contact plane oblique to the support film. From surface decoration of the PE single crystal, Wittmann et al. reported the following:[3] the contact plane is nearly parallel to (210), since the 110 arc-shaped reflection of vapor-deposited PE is superposed on the 110 spot from the mother crystal. We cannot affirm that the contact plane of the vapor-deposited rodlike PE crystal is (210), because arc-shaped reflections such as 110, 210, 200, and 310 were observed simultaneously with 002.

The $(CH_2)_{120}$ lamella decorated with vaporized PE shows nearly the same electron diffraction pattern as the decorated PE lamella. The contrast originating from (310) slipping planes can be observed in the lamellar crystal

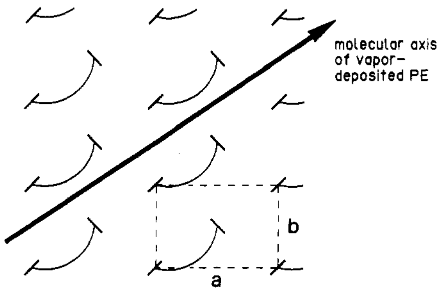

Figure 8. Schematic representation of plausible orientation of the vapor-deposited PE molecules on the $(CH_2)_{120}$ fold surface.

of $(CH_2)_{120}$. This is a piece of evidence that the original shape of a $(CH_2)_{120}$ lamellar crystal may be hollow pyramidal. This fact also indicates that the sedimented lamella of $(CH_2)_{120}$ has the discontinuous basal surface even though the $(CH_2)_{120}$ single crystal has perfectly regular sharp folds. The arc-shaped reflections of 110, 210, 310, 002, etc. from the vapor-deposited PE bring no definite contact plane, as is the case of the surface decoration of the PE lamella.

5. Conclusions

The surface decoration of monoclinic cycloparaffins well evidenced that the vapor-deposited PE molecules orient in the "folding direction" of the cycloparaffins, which direction is uniquely defined according to their crystal structure. It is supposed that the PE molecules deposited on a PE single crystal also orient in its folding direction. We thus concluded that the (110) fold is dominant in each (110) sector of a PE single crystal. Analogously it is also concluded that an orthorhombic cycloparaffin, $(CH_2)_{120}$, has a (110) fold in its single crystal, which shows a morphology very similar to the lozenge-shaped single crystal of PE.

The electron diffraction pattern of a decorated PE single-crystal lamella indicates that the vapor-deposited PE molecules have some distribution in their chain direction, and the contact plane of deposited PE was unable to be defined. This distribution seems to be attributed to the defects in the fold surface, which have existed in the lamella since its birth. The surface irregularity may include discontinuity generated during sedimentation onto a support film.

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References and Notes

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Registry No. PE, 9002-88-4; $(CH_2)_{24}$, 297-03-0; $(CH_2)_{36}$, 297-50-7; $(CH_2)_{48}$, 36355-90-5; $(CH_2)_{60}$, 36441-99-3; $(CH_2)_{72}$, 63217-76-5; $(CH_2)_{120}$, 63217-82-3; $C_{94}H_{190}$, 1574-32-9.