Comparative Study on the Folded-Chain Structure in Polyethylene and Cycloparaffins. 2. Energy Calculation on the Surface Decoration of $(CH_2)_{36}$ and $C_{36}H_{74}$ with Polyethylene

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ABSTRACT: Potential energy was calculated to illuminate the optimum deposition site of polyethylene (PE) on the (001) surface of a monoclinic cycloparaffin, $(CH_2)_{36}$, and an orthorhombic normal paraffin, $C_{36}H_{74}$, in surface decoration with vaporized PE. Five spatial variables defining the orientation of a planar zigzag chain segment composed of nine CH_2 units were introduced into the calculation as parameters. The result of the energy calculation is in good agreement with the experimental result concerning the orientational relationship between the vapor-deposited PE and the $(CH_2)_{36}$ substrate: the molecular axis of deposited PE orients preferentially to the [010] direction of $(CH_2)_{36}$, namely, the "folding direction". The calculated result for the $C_{36}H_{74}$ substrate was consistent with the experimental fact that the molecular axis of PE tends to orient stably to ⟨110⟩ and second stably to [010] of $C_{36}H_{74}$. To find the stable contact plane of deposited PE on the substrates, an imaginary small crystal of orthorhombic PE comprising tens of chain segments was used in the calculation. The results of the calculation well explained the following: the contact plane of PE is (100) on $(CH_2)_{36}$ and (110) on $C_{36}H_{74}$. Lattice mismatching was also taken into consideration to discuss a possible contact plane.

1. Introduction

Thermal evaporation of polyethylene (PE) molecules under vacuum and subsequent crystallization on the alkali halide surface were introduced by Fischer.[1] The electron diffraction pattern reveals the preferential orientation of the vapor-deposited PE molecules in the ⟨110⟩ direction on the (001) face of NaCl.[2] This orientation is the same as in the case of epitaxial growth of PE on (001) of NaCl in a solution.[1] The epitaxial crystallization of PE on NaCl from a solution and that from its vapor phase have the common feature that the chain molecules orient preferentially along the rows of ions in the ⟨110⟩ direction of NaCl. Though crystallization mechanisms in epitaxial growth of PE on NaCl from a solution and from the vaporous state seem to be different, the chain molecules approaching the surface of the substrate may behave in the very similar manner irrespective of the circumstances. Mauritz et al. calculated the potential energies in terms of molecular interactions between a PE chain segment and an alkali halide substrate, and the calculation well explained the experimental results.[3]

Conformation and regularity of the chain folds in the PE single crystal lamella are of interest.[4] Wittmann et al. introduced a technique of thermal evaporation of PE to decorate the fold surface of PE lamellae.[5,6] The vapor-deposited PE molecules orient parallel to the (110) growth face in each (110) sector of PE lamellae. The preferential orientation is also reported by Georgiadis et al. from the epitaxial growth of nascent PE on the fold surface of a PE seed crystal in a solution.[7] In the previous papers,[8,9] we reported the experimental result that the vapor-deposited PE molecules orient in the folding direction on the (001) surface of monoclinic cycloparaffins ($(CH_2)_{36}$ and $(CH_2)_{60}$). This result strongly bears out the idea that the (110) fold is dominant in the (110) sector of the PE single crystal, which fact also suggests considerable regularity of the fold surface.

The surface decoration of orthorhombic normal paraffins with vaporized PE shows the characteristic feature that the vapor-deposited PE molecules orient most preferentially in the ⟨110⟩ directions and second preferentially in the [010] direction. This fact was reported for the first time by Wittmann et al. using the surface decoration of a $C_{36}H_{74}$ substrate with PE,[6] and it was also confirmed by us using the decoration of a longer normal paraffin ($C_{94}H_{190}$) substrate.[9] The contact plane of vapor-deposited PE is varied with the features of the substrate surface. The contact plane of PE on the monoclinic cycloparaffins and that on the orthorhombic normal paraffins are (100) and (110), respectively.[9]

The vaporized PE should deposit on the substrate surface so as to minimize the interfacial energy. This paper presents the results of energy calculation in terms of molecular interaction in order to interpret the manner of epitaxial crystallization of PE molecules on various substrates, such as $(CH_2)_{36}$ and $C_{36}H_{74}$, the structures of which were already analyzed. The adsorption energy is calculated according to the models of conceivable conformations in the epitaxial crystallization, and the results are discussed by comparing with experimental facts[9] of surface decoration.

2. Calculation

2.1. Geometry. The potential energy was calculated according to refs 3, 10, and 11, as described in the next section. Boistelle[12] reported by model calculation that the adsorption energy per CH_2 unit in planar zigzag chains longer than the chain of seven CH_2 units does not vary significantly on the (001) face of a monoclinic normal paraffin: short chains are bound more strongly, because they cover only a small area on the crystal surface, and therefore the fitting is better in certain adsorption sites. Our preliminary calculation was carried out under the limiting condition that two (ψ and θ) of five spatial variables mentioned below (see Figure 1) were fixed at the most plausible values: $\psi = 45°$ and $\theta = 90°$. Then the calculation showed that the adsorption energy per CH_2 on a cycloparaffin $(CH_2)_{36}$ substrate tends to level off at a certain value when the number of CH_2 units in a pla-

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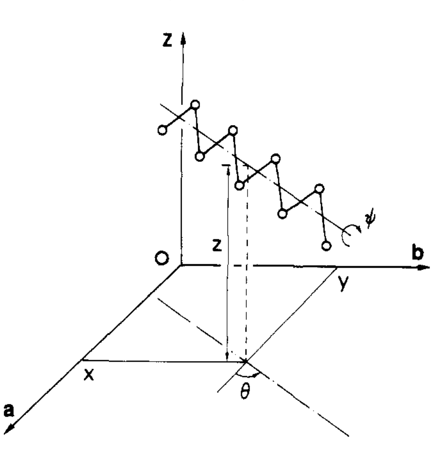

Figure 1. Schematic representation of a PE chain segment on the (001) surface of a substrate. The position and the orientation of the chain segment are defined with five spatial parameters (x,y,z,ψ,θ). Vectors **a** and **b** are the real lattice vectors of the substrate, and x- and y-axes are defined parallel to **a** and **b**, respectively. The z-axis is normal to the xy plane. Thus, (x,y,z) represents the center of the segment, where z is its height from the substrate surface. When the plane of the segment is parallel to the substrate surface, the rotation angle $\psi = 0°$. When the axis of the segment is parallel to **a**, the azimuthal angle $\theta = 0°$.

Table I
Bond Lengths and Bond Angles in a PE Chain Segment

bond length,[13] nm		bond angle, deg	
C–C	0.154	C–C–C	111.1
C–H	0.109	H–C–H	109.47

Table II
Unit Cell Dimensions of Materials Used in This Calculation

lattice const	PE[a]	$(CH_2)_{36}$[b]	$C_{36}H_{74}$[c]
a, nm	0.740	1.033	0.742
b, nm	0.493	0.824	0.496
c, nm	0.254	4.63	5.624
α, deg	90.0	90.0	90.0
β, deg	90.0	119.4	90.0
γ, deg	90.0	90.0	90.0

[a] Data by Bunn.[14] [b] Data[17] converted from the cell dimensions reported by Trzebiatowski et al.[15] [c] Data by Teare.[16]

nar zigzag chain exceeds five. Hence a linear chain with nine CH_2 units in the planar zigzag conformation was adopted as a model of the adsorbed molecule of PE. This chain comprising nine CH_2 units thus represents a PE chain segment. The coordination of atoms in the planar PE chain segment was calculated by using the data in Table I.[13] Table II shows the lattice constants of PE reported by Bunn,[14] including those of a cycloparaffin $(CH_2)_{36}$[15] and a normal paraffin $C_{36}H_{74}$,[16] which were used in this calculation as the substrates.

Figure 1 shows the geometry. Five spatial variables x, y, z, ψ, and θ are introduced in this calculation, and the chain axis of the planar zigzag chain segment is set parallel to the surface of the substrate. Here (x,y,z) denotes the position of the center of this chain segment. The variable z represents the height of the chain segment from the surface of the substrate, and the directions of x and y are defined parallel to [100] and [010] of the substrate, respectively. The rotation angle ψ of the chain segment about its own axis is defined so that $\psi = 0°$ corresponds to the case where the plane of the zigzag chain segment is parallel to the substrate surface. The angle θ is the azimuthal angle of the axis of the chain segment measured from the x-axis, namely, [100] of the substrate. The size of increments of five spatial variables used in this calculation is as follows: 5° for ψ and θ; 0.02 nm for Z; 4% of a and b for x and y, respectively (a and b are the lattice constants of the substrate). Half the above-mentioned increment for each variable is used when a detailed energy map is required.

Table III
Constants for Dispersive and Repulsive Energies[a]

interacting atomic pair	A_{ij}, kcal·nm^6/mol	B_{ij}, kcal·nm^{12}/mol
C···C	3.70×10^{-4}	2.86×10^{-7}
C···H	1.28×10^{-4}	3.80×10^{-8}
H···H	4.67×10^{-5}	4.46×10^{-9}

[a] Data from ref 17.

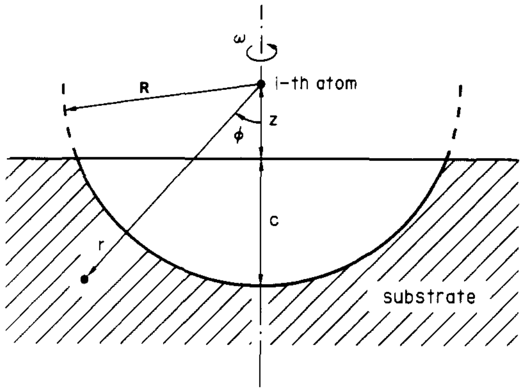

Figure 2. Two regions in the substrate divided to simplify the calculation. Atoms of the substrate in a hemisphere with radius R are treated discretely, and those in the rest of the region are treated as a continuum.

2.2. Molecular Energetics. The adsorption energy contributed by dispersion and repulsion forces was calculated by using the Lennard-Jones 6–12 potential equation:

$$u(r_{ij}) = -A_{ij}/r_{ij}^{\,6} + B_{ij}/r_{ij}^{\,12} \tag{1}$$

where r_{ij} is the distance between the ith atom in the CH_2 chain segment and the jth atom in the substrate. The constants A_{ij} and B_{ij} in eq 1 are listed in Table III and were cited from a paper by Scott and Scheraga.[17]

Mauritz et al. reported that dispersion and repulsion forces are more sensitive to orientation and greater in magnitude than the electrostatic forces in the energy calculation for epitaxial crystallization of PE even on NaCl, an ionic crystal. Accordingly, electrostatic forces are not included in this calculation.

The potential energy of atom–atom pairs was calculated within the distance $R = 1$ nm (Figure 2), because the potential energy of atomic pairs at a distance greater than 1 nm does not vary largely with the distance. The potential equation for $r_{ij} > R$ was expressed as a formula integrated from R to infinity, and in this case the atoms located discretely in the substrate were treated as uniformly distributed in a continuum. If n_k is the number density of the k-type atom in the substrate, the potential energy of the k-type atom outside of the hemisphere of radius R centered at the ith atom can be expressed as[3]

$$u_{ik}(z) = \int\int\int n_k u(r) r^2 \sin\phi \, dr \, d\phi \, d\omega \tag{2}$$

Substitution of eq 1 into eq 2 gives the following equation:[11]

$$u_{ik}(z) = \frac{\pi}{2R^3}\left[\frac{R-z}{R} + \frac{1}{3}\right] n_k A_{ik} + \frac{\pi}{5R^9}\left[\frac{R-z}{R} + \frac{1}{9}\right] n_k B_{ik} \tag{3}$$

where A_{ik} and B_{ik} are the constants of dispersion and

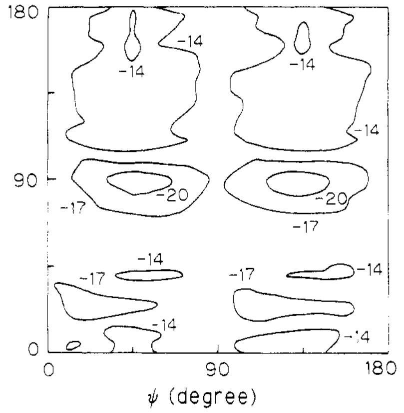

Figure 3. Energy contour map of a chain segment on the $(CH_2)_{36}$ substrate plotted as a function of (ψ,θ), in kcal/mol of nine CH_2s.

repulsion forces between the *i*th atom in the chain segment and the k-type atom in the substrate, respectively. Thus the adsorption energy U is described as

$$U(x,y,z,\psi,\theta) = \sum_{i}[\sum_{j} u(r_{ij}) + \sum_{k} u_{ik}(z)] \qquad (4)$$

3. Results and Discussion

3.1. Cycloparaffin Substrate. 3.1.1. Adsorption of One PE Chain Segment on the Substrate. The crystal structure of $(CH_2)_{36}$ analyzed by Trzebiatowski et al.[15] was used in this calculation. Their lattice constants were converted to the new ones for convenience as proposed in previous papers.[9,18] Consequently the [001] direction of the new unit cell is parallel to the molecular axis of the cycloparaffin. The position of carbon atoms in the new unit cell is obtained by multiplying the data reported by Trzebiatowski et al. with the transformation[18] matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$

On the basis of the coordinates of carbon atoms given by Trzebiatowski et al., the coordinates of hydrogen atoms were calculated with the following assumption: the distance of C–H is 0.109 nm and the plane of H–C–H in a methylene unit is perpendicular to the plane of C–C–C in the backbone (the angle H–C–H is 109.47°).

Potential contour maps showing the adsorption energy of the chain segment on the $(CH_2)_{36}$ substrate are plotted in kcal/mol of nine CH_2s in Figures 3–5. Figure 3 illustrates the potential contour map as a function of ψ and θ. To make this figure, the lowest value of potential energy was searched for all (x,y,z), with ψ and θ being fixed. Thus this lowest value is shown in the figure for given ψ and θ. The deep potential minima locate at $\psi = 45°$ and $\theta = 90°$ and at $\psi = 135°$ and $\theta = 90°$. These two minima are almost identical in shape and depth. The two minima at $\theta = 90°$ may cause the adsorbed molecule to take its preferential orientation. This result strongly supports the feature of surface decoration of the cycloparaffin lamellae that the vapor-deposited PE molecules orient parallel to the direction of the *b*-axis[8,9] of the cycloparaffin, $(CH_2)_{36}$, i.e., to the folding direction.

In order to see the influence of the variable z on the potential energy, Figures 4 and 5 were drawn. In both figures, the lowest value of potential energy was shown for a given set of variables, (z,ψ) or (z,θ). The potential contour map of Figure 4 is illustrated with respect to (z,ψ) when the axis of the chain segment is fixed in the [010] direction of $(CH_2)_{36}$, namely, $\theta = 90°$. This figure indicates the potential minima at $\psi = 45°$ and 135°. There is not significant difference in energy between these two minima. Next, the potential energy was calculated under the assumption of $\psi = 45°$ and illustrated in Figure 5 as a function of (z,θ). The potential minimum was obtained at $\theta = 90°$. Figures 4 and 5 also demonstrate that the potential energy is less affected by the unevenness of the substrate surface if the segment is far from the surface, while there appear some potential minima according to the surface topography of the substrate when $z < 0.3$ nm.

Figure 6 shows the potential map when the PE chain segment moves around on the xy plane, namely, on the ab plane of $(CH_2)_{36}$. It was assumed in the calculation

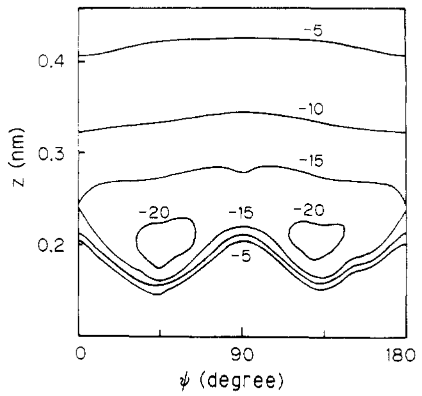

Figure 4. Energy contour map of a chain segment on the $(CH_2)_{36}$ substrate plotted as a function of (z,ψ), in kcal/mol of nine CH_2s, under the condition $\theta = 90°$.

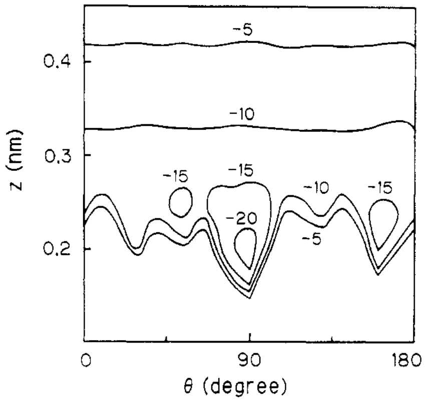

Figure 5. Energy contour map of a chain segment on the $(CH_2)_{36}$ substrate plotted as a function of (z,θ), in kcal/mol of nine CH_2s, under the condition $\psi = 45°$.

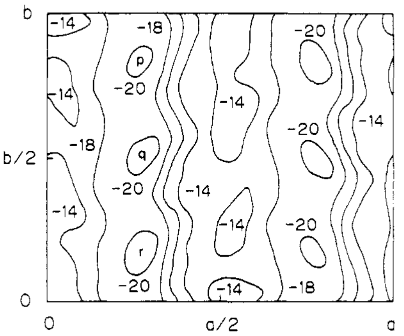

Figure 6. Energy contour map of a chain segment on the $(CH_2)_{36}$ substrate plotted as a function of (x,y), in kcal/mol of nine CH_2s. In this figure, a and b are the lattice constants of the substrate. In this calculation ψ and θ are fixed at 45° and 90°, respectively.

Table IV
The Number of Chain Segments in the Small Crystal of PE

contact plane of the small crystal of PE	no. of segments in a layer	no. of layers of segments	total no. of chain segments
(100)	5	3	15
(010)	4	4	16
(110)	6	3	18

that the chain segment aligned in the *b*-axis of $(CH_2)_{36}$, i.e., $\theta = 90°$, and ψ was fixed at 45°. The variable z was changed to find the lowest value at a position (x,y) with fixed ψ and θ. The value thus found is plotted for (x,y) in Figure 6. In this figure, a and b are the unit cell dimensions of $(CH_2)_{36}$. The center of four carbon atoms in a trans conformation, which make a fold in a $(CH_2)_{36}$ molecule, locates at the origin in the xy plane. Consequently five folds are set one by one at $(0,0)$, $(a,0)$, $(0,b)$, (a,b), and $(a/2,b/2)$ in the unit cell. Figure 6 demonstrates that an adsorbed chain segment parallel to the *b*-axis is the most stable when it locates near the center line of the neighboring two rows of chain folds in the [010] direction on the (001) face of $(CH_2)_{36}$. As a matter of course the sequence of potential minima marked with letters p, q, and r in Figure 6 reflects the fiber period of the planar zigzag chain of PE, i.e., the distance between the minima is 0.254 nm. The distance of an adsorbed chain segment from a row of folds, each of which consists of four carbon atoms in the trans conformation aligned parallel to the *b*-axis, is calculated to be about 0.45 nm. The distance is reasonable because it is very similar to the distance of the nearet two zigzag stems, for example, in the orthorhombic PE crystal.

3.1.2. Adsorption of a Small PE Crystal Comprising Methylene Chain Segments on the Substrate. The setting angle of PE, the angle between the zigzag plane of the chain and the *bc* plane, is reported to be in the range 42–48°.[19] Both the (100) and the (010) contact planes of PE are thus expected, because potential minima were observed at $\psi = 45°$ and 135° in Figure 3. To define the contact plane having the minimum adsorption energy, a set of chain segments that are arranged to make a three-dimensional lattice of orthorhombic PE[14] were used in the calculation. The number of chain segments used in the calculation is shown in Table IV. Each chain segment has nine CH_2 units, and the atoms within 1 nm in the z direction were used in the calculation because the atoms farther than 1 nm from the substrate surface give nearly the same value of potential energy regardless of orientation of the chain segment. The area of contact plane is set at about 3 nm^2.

Minimum potential energies are summarized in Table V for three conceivable types of contact plane, namely, (100), (010), and (110) of PE, when the axis of the chain segment is fixed parallel to [010] of $(CH_2)_{36}$. To compare the potential minima among three types of contact planes, the energy values should be normalized. Each energy value in Table V, therefore, was already divided by the area of the corresponding contact plane. The lowest potential energy is obtained for the (100) contact plane as shown in Table V. A higher potential energy was obtained for each type of contact plane when the axis of the chain segment oriented to other directions, such as [110] and [100] of $(CH_2)_{36}$. It is concluded that the adsorbed molecules are the most stable when the (100) plane of PE is in contact with the (001) surface of $(CH_2)_{36}$ and the molecular axis of PE is parallel to [010] of $(CH_2)_{36}$, namely, to the folding direction.

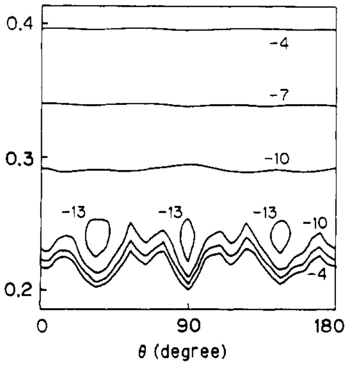

Figure 7. Energy contour map of a chain segment on the $C_{36}H_{74}$ substrate plotted as a function of (z,θ), in kcal/mol of nine CH_2s, under the condition $\psi = 14°$.

Table V
Adsorption Energy Minima of a Set of PE Chain Segments on the Cycloparaffin $(CH_2)_{36}$

contact plane of a set of PE chain segments[a]	adsorption energy minimum,[b] erg/cm^2
(100)	-85.7
(010)	-34.5
(110)	-67.6

[a] The molecular axis of PE chain segments directs to [010] of $(CH_2)_{36}$. [b] The energy minimum was searched for all (x,y,z). The value of energy was normalized with the area of a contact plane of a PE model crystal, which comprised tens of methylene chain segments.

Table VI
Adsorption Energy Minima (erg/cm^2) of a Set of PE Chain Segments on the Normal Paraffin $C_{36}H_{74}$[a]

contact plane of a set of PE chain segments	chain direction of a set of the segments	
	$[110]_{np}$[b]	$[010]_{np}$
(110)	-67.9	-62.6
(100)	-38.8	-46.7
(010)	-31.3	-45.4

[a] Calculation and normalization schemes are the same as in the case of $(CH_2)_{36}$ in Table V. [b] The subscript "np" means the orthorhombic normal paraffin, $C_{36}H_{74}$.

3.2. Normal Paraffin Substrate. The crystal structure of $C_{36}H_{74}$ was analyzed by Teare[16] and was used as an example of an orthorhombic normal paraffin. Calculation of the adsorption energy of a PE planar zigzag chain segment with nine CH_2 units on this normal paraffin substrate was done in the same manner as the case of the cycloparaffin substrate. Figure 7 shows the potential contour map as a function of (z,θ), when the (110) contact plane of PE is assumed, namely, $\psi = 14°$ or 76° for a setting angle of 48°. Potential minima are obtained at $\theta = 34°$, 90°, and 146° for $\psi = 14°$, corresponding to the directions [110], [010], and $[1\bar{1}0]$ of the normal paraffin, respectively. For example, when $\theta = 34°$, the position (x,y,z) of the center of the chain segment to give the energy minimum indicates that the chain segment locates near the center line between two neighboring rows of methyl groups in the [110] direction of normal paraffin. There is, however, no significant difference in depth among these three minima, when one chain segment is adsorbed on the substrate surface. When $\psi = 76°$, a similar conclusion was reached.

Table VI illustrates the relationship between the potential minimum and the orientation of an imaginary small crystal comprised of some chain segments that are arranged to make the three-dimensional lattice of orthorhombic PE. The normalization scheme in this case is identical

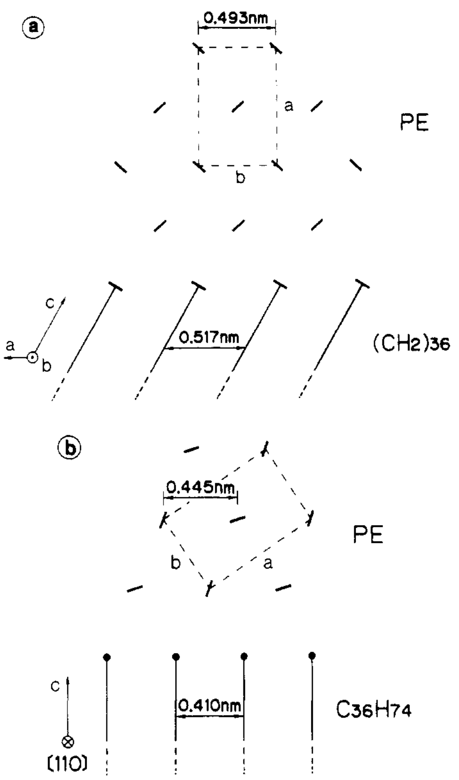

Figure 8. Schematic representation of the interface between deposited PE and the substrates. (a) Monoclinic cycloparaffin $(CH_2)_{36}$ substrate. PE chain segments are projected along their chain axis, and the $(CH_2)_{36}$ crystal is projected along the *b*-axis. (b) Orthorhombic normal paraffin $C_{36}H_{74}$ substrate. PE chain segments are projected along their chain axis, and the $C_{36}H_{74}$ crystal is projected along ⟨110⟩. [110] and [$\bar{1}$10] of $C_{36}H_{74}$ are identical in the figure. (\ or /) zigzag stem viewed along its chain axis; (·) methyl group.

with that for the cycloparaffin substrate. The lowest potential energy was obtained for the orientation where the chain segments direct to [110] or [1$\bar{1}$0] of the normal paraffin and the contact plane of PE is (110). The second lowest energy was obtained for the [010] orientation with the (110) contact plane of PE. These results well explain the orientation of vapor-deposited PE on the (001) face of orthorhombic normal paraffins in the surface decoration experiments. The difference in values of energy minimum among several orientations is, however, much smaller than that for $(CH_2)_{36}$ (compare Table VI with Table V). Boistelle[12] reported a result similar to ours: a planar zigzag methylene chain ($\psi = 0°$) on the (001) face of a monoclinic normal paraffin will orient to the [110] and [010] of the paraffin crystal, and the former direction is more favorable.

3.3. Crystallization Mechanisms of Vapor-Deposited PE in Surface Decoration. One or several PE molecules deposited primarily on the substrate surface will determine the orientation of overgrown crystals. The first molecule deposited on the surface may migrate to the stable position and then settle down there with a preferable angle ψ. Figure 8a is the schematic diagram showing the interface between the $(CH_2)_{36}$ substrate and deposited PE, which illustrates the case for the potential energy minimum for the (100) contact plane of PE (see Table V). This figure corresponds to the projection of a decorated $(CH_2)_{36}$ viewed along its *b*-axis and to the projection of deposited PE viewed along its chain axis. The four methylene units of a fold of $(CH_2)_{36}$ that are in a planar conformation are approximated to align normal to the plane of the figure. Figure 8a thus suggests that deposited PE may crystallize, incorporating the fold of the cycloparaffin $(CH_2)_{36}$. Figure 8b is the schematic diagram showing the interface between $C_{36}H_{74}$ and PE. This figure corresponds to the potential energy minimum for the (110) contact plane of PE, whose molecular axis is oriented in ⟨110⟩ of $C_{36}H_{74}$ (see Table VI).

Table VII
Degree of Mismatching for Various Orientations

contact plane of PE	repeating dist, nm		degree of mismatch, %
	PE[a]	$(CH_2)_{36}$[b]	
(100)	0.493	0.517	4.6
(010)	0.740	0.517	43.1
(110)	0.445	0.517	13.9
	PE[a]	$C_{36}H_{74}$[c]	
(100)	0.493	0.410	20.2
(010)	0.740	0.821[d]	9.8
(110)	0.445	0.410	8.5

[a] Distance between the stems of orthorhombic PE in the corresponding contact plane. [b] $a/2$ of $(CH_2)_{36}$. [c] Distance between the stems of $C_{36}H_{74}$ projected on the plane perpendicular to its [110] or [1$\bar{1}$0] direction. [d] Twice the primitive repeating distance.

What is the degree of lattice mismatching? The degree of mismatching is expressed as follows:

$$\text{degree of mismatching } (\%) = \frac{|a - a'|}{a} \times 100 \qquad (5)$$

where a and a' are a repeating distance in a substrate and that in deposited PE, respectively. Table VII shows the degree of mismatching between PE and $(CH_2)_{36}$ and that between PE and $C_{36}H_{74}$. The smallest degree of mismatching is obtained at (100) and (110) contact planes of PE among its possible contact planes for $(CH_2)_{36}$ and $C_{36}H_{74}$ substrates, respectively. The orientation of the chain axis of PE that gives the smallest degree of mismatching in Table VII is identical with the stable orientation predicted by energy calculations.

4. Concluding Remarks

When a PE chain segment is adsorbed on the (001) surface of a cycloparaffin $(CH_2)_{36}$, a deep valley of potential energy exists in the [010] direction of $(CH_2)_{36}$, which is parallel to the folding direction. Thus the chain segment orients stably in the folding direction of $(CH_2)_{36}$ owing to a large energy gain. This energy calculation result well explains the experimental fact for surface decoration of a $(CH_2)_{36}$ substrate with vapor-deposited PE. Moreover, it is predicted by the energy calculation that the chain segment directing parallel to the folding direction of $(CH_2)_{36}$ locates stably near the centerline of the neighboring two rows of folds on the (001) face of $(CH_2)_{36}$. The distance between the axis of the chain segment and the row of folds is about 0.45 nm, which is a relatively reasonable value compared with the distance of the nearest two stems in the orthorhombic PE crystal. The experimental result on surface decoration of the fold surface of a PE single-crystal lamella revealed that the molecules of vapor-deposited PE orient parallel to the (110) growth face in each (110) sector of the PE lamella.[6,9] The results for both $(CH_2)_{36}$ and PE substrates demonstrate the (110) fold in the PE lamella and considerable regularity of the fold, though the conformation of the fold in PE is different from that in $(CH_2)_{36}$.

The calculation of potential energies to predict the manner of adsorption of one chain segment on the substrate surface is unable to supply the detailed information about the orientation of a deposited PE crystal, except the infor-

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mation about the direction of the segment. Some models of imaginary small crystals comprising tens of chain segments that are set to make the three-dimensional lattice of orthorhombic PE were considered in the calculation. The (100) contact plane of PE whose chain axis orients in the [010] direction of $(CH_2)_{36}$ is the most probable. In the case of a normal paraffin ($C_{36}H_{74}$), the most stable orientation is obtained when a set of chain segments with the (110) contact plane orient in the $\langle 110 \rangle$ directions of $C_{36}H_{74}$ and the second most stable is the [010] orientation with a (110) contact plane. These stable contact planes are also predicted by lattice mismatching. The contact planes thus predicted are in good agreement with those observed in surface decoration of monoclinic cycloparaffins ($(CH_2)_{36}$ and $(CH_2)_{60}$) and orthorhombic normal paraffins ($C_{36}H_{74}$ and $C_{94}H_{190}$).[6,8,9]

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Registry No. PE, 9002-88-4; $(CH_2)_{36}$, 297-50-7; $C_{36}H_{74}$, 630-06-8.

High-Temperature Structures of Poly(*p*-hydroxybenzoic acid)[1]

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ABSTRACT: The structures of poly(*p*-hydroxybenzoic acid) (PHBA) at the two high-temperature phase transitions (ca. 340 and 430 °C) have been investigated by X-ray powder diffraction methods (X-ray tube focusing and synchrotron parallel beam), chain conformation/packing models, and dielectric measurements. The structure of PHBA between ca. 340 and 430 °C, derived from the X-ray patterns and available electron diffraction results, is satisfactorily accounted for by the following model: orthorhombic cell, a = 9.24 Å, b = 5.28 Å, and c = 12.50 Å, with two successive phenylene planes along the c-axis rotated 60° from each other in the unit cell; the phenyl groups in the a–b plane are oriented in an ordered herringbone-type packing in each phenyl layer with their planes 60° and 120° with respect to the a-axis; and each chain segment (of two monomer repeats) in the unit cell is positioned randomly in the a–b projection among the two different sites involving a twofold axis of reorientation through an angle π. The dielectric constants at high frequencies (100 kHz) indicate rapid chain mobility accompanying this high-temperature phase. This structure of PHBA therefore follows quite well the model of the smectic-E phase of small rodlike molecules. The second transition around 430 °C involves no change in the packing order along the chain axis or chain conformations but only the loss of long-range phenyl orientation order in the a–b plane, very much like the smectic-E to smectic-B transition of small rodlike molecules. The coherence length along the chain axis of PHBA crystals at room temperature is estimated to be ca. 2700 Å, according to the Sherrer formula, and this packing order along the chain axis is maintained throughout the two high-temperature transitions. Relevance of the smectic-type high-temperature structures of PHBA to the molecular order in aromatic copolyesters comprising majority HBA monomers is then discussed.

Introduction

The structures of the homopolymer poly(*p*-hydroxybenzoic acid) (PHBA), $-(C_6H_4-C(=O)O-)_x$, at high temperatures have been the subject of a considerable number of investigations,[5–11] owing to their close connection to the nature of molecular order in thermotropic copolyesters of commercial interest.[8,12–15] These copolyesters

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