

AN INVESTIGATION ON FOLD STRUCTURE IN POLYETHYLENE LAMELLA WITH DIAMOND LATTICE MODEL*

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Abstract Based on perfect rotational isomeric state model of polyethylene chain without any torsional stretch or chain twisting, the separation distance between a zig-zag segment and its re-entry ones in lamella has been investigated. The intervals were defined by a pair of quantum numbers (k_x, k_y) according to the formula:

$$D = \frac{0.153}{\sqrt{3}} \sqrt{8k_x^2 + 16k_y^2} \quad (\text{nm})$$

k_x and k_y are integers just as the lattice coordinates on the respective b - and a - axes of the crystal lattices for polyethylene. The crystal lattices of polyethylene can be accessible by the re-entry stems, whether it is adjacent fold or not. Conformations, until 14-bond fold, of the fold part were investigated. The sequence TTGTTG'G'TTGTTG possesses the lowest average conformation energy per bond for (110) fold, and TGTG'G'TTG' for (020) fold, TTTGGTGGTTGTG' etc. for (200) fold.

Keywords Fold conformation; Crystal; Polyethylene lamella

INTRODUCTION

Keller^[1], based on the studies of the properties of single crystals in 1957, concluded that the polymer molecules in the crystals folded back upon themselves. Since then, the fold structure has been a subject of interest and many researchers^[2~9] have appreciated the regular chains fold, although some rebuttal evidences^[10~13] are also available. The main approach to predicting the conformation of a fold was, on the basis of the rotational isomeric approximation, to assign different torsion (internal rotations) and bond angles within the folded segment of the long chain and then to minimize the energy of the fold. The conformation giving the lowest energy for the fold was considered the most plausible.

The rotational isomeric state chains of polyethylene can be approximately represented by a path on a diamond lattice^[6,9] and diamond lattice chain can be

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generated by restricted walk on a body-centered cubic lattice^[14]. The purpose of this work is to investigate the possible separation distance between a stem and its re-entry stems by the perfect rotational isomeric state model of molecule chains on diamond lattices.

THEORY

We assign a Cartesian coordinate system on a body-centered cubic lattice with the origin locating on a vertex of the cube and the three edges of the cube as the directions of the coordinate axes, as shown in Fig. 1. In this system chains generate along semi-diagonal of the cubes and there are actually eight different bond vectors involved, which are identified with the walk from body center to eight corners. According to previous denotation^[14], they are vectors 1, 2, 3, 4, 5, 6, 7 and 8, respectively. The length of each side of the cube is taken equal to 2 and the length of the semi-diagonal, $\sqrt{3}$, is that of the bond vectors. In this case, every bond vector projects on the coordinate axes as 1 or -1 . The eight possible vectors may be given as follows:

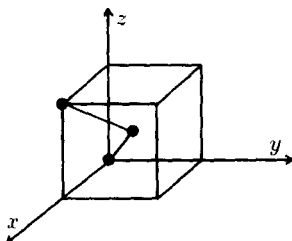


Fig. 1 A unit cell of body-centered cubic.
Bond is along the semi-diagonal

1 $(-1, -1, -1)$	2 $(1, 1, 1)$
3 $(1, -1, 1)$	4 $(-1, 1, -1)$
5 $(-1, 1, 1)$	6 $(1, -1, -1)$
7 $(1, 1, -1)$	8 $(-1, -1, 1)$

We suppose a molecule chain possesses an original zig-zag segment A, and it folds back upon itself after a folding with n

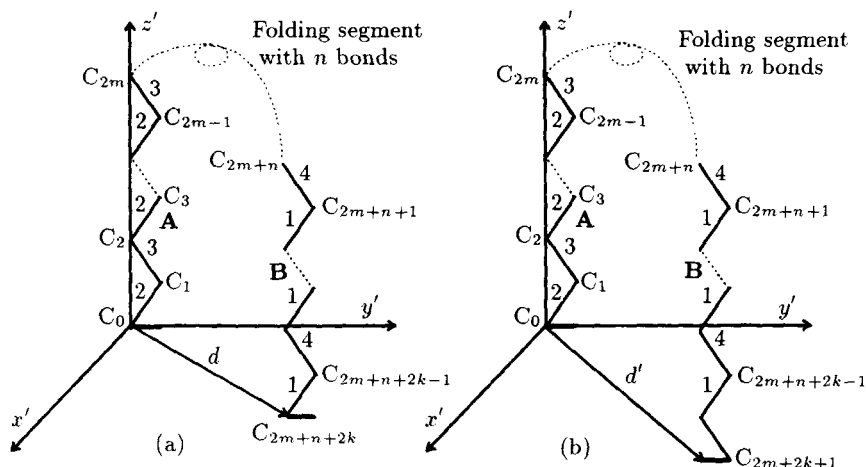


Fig. 2 A zig-zag segment and its re-entry stems linked by the fold segment with n bond

bonds, as shown in Fig. 2. The segments A and B are the stems in crystal. This investigation will focus on the possible intervals between two stems according to the rotational isomeric state model of the chain. It can be arbitrarily suppose that the segment A consists of $2m$ bonds which are alternately vectors 2 and 3, and the carbon C_0 is located at the origin of coordinates. Accordingly, the zig-zag segment B consists of alternating bonds 4 and 1. According to the relationship of the projects of the eight bond vectors, the coordinates of the first $2m$ carbon atoms are

$$\begin{array}{ccc}
 & x & y & z \\
 C_0 & (0 & 0 & 0) \\
 C_1 & (1 & 1 & 1) \\
 C_2 & (2 & 0 & 2) \\
 \vdots & & & \\
 C_{2m} & (2m & 0 & 2m)
 \end{array}$$

Based on the arbitrary supposition that the last bond is vector 3 in segment A and the first one is vector 4 in segment B, n is an even due to the regulation^[14] that even bond vectors follow odd ones and vice versa. Let $n_1, n_2, n_3, n_4, n_5, n_6, n_7$ and n_8 denote the numbers of bond vectors 1, 2, 3, 4, 5, 6, 7 and 8 contained in fold-segment with n bonds, respectively. Obviously,

$$n = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 \quad (1)$$

and

$$n_1 + n_3 + n_5 + n_7 = n_2 + n_4 + n_6 + n_8 \quad (2)$$

The coordinates of the $(2m + n)$ -th carbon are

$$\begin{cases}
 x_{2m+n} = -n_1 + n_2 + n_3 - n_4 - n_5 + n_6 + n_7 - n_8 + 2m \\
 y_{2m+n} = -n_1 + n_2 - n_3 + n_4 + n_5 - n_6 + n_7 - n_8 \\
 z_{2m+n} = -n_1 + n_2 + n_3 - n_4 + n_5 - n_6 - n_7 + n_8 + 2m
 \end{cases} \quad (3)$$

and

$$\begin{array}{ccc}
 & x & y & z \\
 C_{2m+n+1} & (x_{2m+n} - 1 & y_{2m+n} + 1 & z_{2m+n} - 1) \\
 C_{2m+n+2} & (x_{2m+n} - 2 & y_{2m+n} & z_{2m+n} - 2) \\
 \vdots & & & \\
 C_{2m+n+2k} & (x_{2m+n} - 2k & y_{2m+n} & z_{2m+n} - 2k) \\
 C_{2m+n+2k+1} & (x_{2m+n} - 2k - 1 & y_{2m+n} + 1 & z_{2m+n} - 2k - 1)
 \end{array}$$

To study the intervals between the two stems more directly, let coordinate system xyz take a rotation around y axis by 45° to form a new coordinate system $x'y'z'$

as shown in Fig. 2. The coordinates (x, y, z) and (x', y', z') in the two systems are related by the following equation:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \sqrt{2}/2 & 0 & -\sqrt{2}/2 \\ 0 & 1 & 0 \\ \sqrt{2}/2 & 0 & \sqrt{2}/2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (4)$$

Then the coordinates of carbons in the new system are

$$\begin{array}{ccc} & x' & y' & z' \\ C_0 & (0 & 0 & 0) \\ C_1 & (0 & 1 & \sqrt{2}) \\ C_2 & (0 & 0 & 2\sqrt{2}) \\ \vdots & & & \\ C_{2m} & (0 & 0 & 2m\sqrt{2}) \end{array}$$

and

$$\begin{cases} x'_{2m+n} = \sqrt{2}(-n_5 + n_6 + n_7 - n_8) \\ y'_{2m+n} = -n_1 + n_2 - n_3 + n_4 + n_5 - n_6 + n_7 - n_8 \\ z'_{2m+n} = \sqrt{2}(-n_1 + n_2 + n_3 - n_4 + 2m) \end{cases} \quad (5)$$

$$\begin{cases} x'_{2m+n+2k} = x'_{2m+n} \\ y'_{2m+n+2k} = y'_{2m+n} \\ z'_{2m+n+2k} = z'_{2m+n} - 2\sqrt{2}k \end{cases} \quad (6)$$

$$\begin{cases} x'_{2m+n+2k+1} = x'_{2m+n} \\ y'_{2m+n+2k+1} = y'_{2m+n} + 1 \\ z'_{2m+n+2k+1} = z'_{2m+n} - \sqrt{2}(2k + 1) \end{cases} \quad (7)$$

The planes of stems are parallel to the $y'z'$ plane in the new coordinate system, as shown in Fig. 2.

Model (a)

When $z'_{2m+n+2k} = 0$, i.e. the $(2m + n + 2k)$ -th carbon locates in the plane $x'y'$, the distance, d , between the $(2m + n + 2k)$ -th carbon atom and the origin point is that of the two stems, as shown in Fig. 2(a). In that case

$$-n_1 + n_2 + n_3 - n_4 = 2(k - m) \quad (8)$$

$$\begin{cases} x'_{2m+n+2k} = \sqrt{2}(-n_5 + n_6 + n_7 - n_8) \\ y'_{2m+n+2k} = -n_1 + n_2 - n_3 + n_4 + n_5 - n_6 + n_7 - n_8 \end{cases} \quad (9)$$

By substituting Eq. (2) and (8) into Eq. (9), it gives

$$\begin{cases} x'_{2m+n+2k} = 2\sqrt{2}k_x \\ y'_{2m+n+2k} = 4k_y \end{cases} \quad (10)$$

where

$$\begin{cases} k_x \equiv k - m - n_3 + n_4 - n_5 + n_6 \\ k_y \equiv k - m - n_3 + n_4 \end{cases} \quad (11)$$

k_x and k_y are integers since $k, m, n_1, n_2, \dots$ are integers. Finally

$$d^2 = 8k_x^2 + 16k_y^2 \quad (12)$$

Model (b)

Another possible situation may be $z'_{2m+n+2k+1} = 0$. It gives

$$-n_1 + n_2 + n_3 - n_4 = 2(k - m) + 1 \quad (13)$$

$$\begin{cases} x'_{2m+n+2k+1} = \sqrt{2}(-n_5 + n_6 + n_7 - n_8) \\ y'_{2m+n+2k+1} = 4(k - m - n_3 + n_4) + 3 \end{cases} \quad (14)$$

By substituting Eqs. (2) and (13) into Eq. (14) gives

$$\begin{cases} x'_{2m+n+2k+1} = \sqrt{2}(2k_x + 1) \\ y'_{2m+n+2k+1} = 2(2k_y + 1) + 1 \end{cases} \quad (15)$$

In this case, the distance, d' , between the two stems is (see Fig. 2(b))

$$d'^2 = (x'_{2m+n+2k+1})^2 + (y'_{2m+n+2k+1} - 1)^2 = 2(2k'_x + 1)^2 + 4(2k'_y + 1)^2 \quad (16)$$

RESULTS AND DISCUSSION

The model (b) may result in non-orthorhombic system, so we mainly discuss the model (a) here. If the conformations in the fold segment are confined to perfect rotational isomeric state on diamond lattices, the possible intervals between a zig-zag segment and its re-entry zig-zag segments have been defined by Eq. (12). Fig. 3 is the projections of stems in the first quadrant of plane $x'y'$, and Table 1 gives the possible intervals by the formula

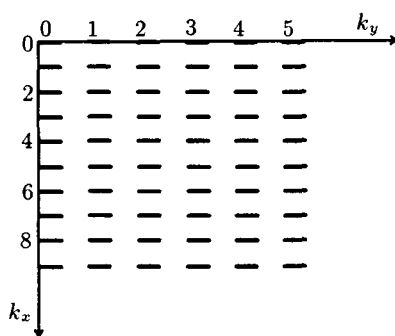


Fig. 3 Projection of the original stem and possible re-entry stems on $x'y'$ plane

$$D = d \times \frac{0.153}{\sqrt{3}} \quad (\text{nm}) \quad (17)$$

where C—C bond length is taken to be 0.153 nm.

Fig. 3 shows that the zig-zag planes of the original stem and any probable re-entry stems of PE are parallel to each other on the diamond lattices structure. A comparison between Table 1 and the parameters of orthorhombic lattice for PE ($a = 0.74\text{ nm}$ and $b = 0.493\text{ nm}$) indicates that the projection figure approximately resembles the unit cell lattices of PE crystals except for the setting angle of the C—C plane. Every lattice of crystal unit cell is accessible by the re-entry stems with even $(k_x + k_y)$, whether it is adjacent fold or not. k_x and k_y are integers representing the lattice coordinates on the respective b - and a - axes of the crystal lattices of PE. The re-entry with $k_x = 1$ and $k_y = 1$ represents the conventional adjacent (110) folds^[6,9], and the one with $k_x = 2$ and $k_y = 0$ is that of (200) folds, etc. Chang and Hu^[15,16] have suggested the pair s -chain crystalline growth philosophy. In their model, each of the pair chains folds alternatively along (100) and (010) planes. These can be realized by the re-entry with $k_y = 0$ and $k_x = 0$, alternatively.

Table 1 Separation distance between a stem and its re-entry stem for PE chain on diamond lattices (nm)

$k_x \backslash k_y$	0	1	2	3	4	5	6	7	8	9	10
0	0.000	0.353	0.707	1.060	1.413	1.767	2.120	2.473	2.827	3.180	3.533
1	0.250	0.433	0.750	1.089	1.435	1.784	2.135	2.486	2.838	3.190	3.542
2	0.500	0.612	0.865	1.172	1.499	1.836	2.178	2.523	2.871	3.219	3.569
3	0.750	0.829	1.030	1.298	1.600	1.919	2.249	2.585	2.924	3.267	3.612
4	0.999	1.060	1.224	1.457	1.731	2.030	2.344	2.668	2.998	3.333	3.672
5	1.249	1.298	1.435	1.638	1.886	2.164	2.461	2.771	3.090	3.417	3.748
6	1.499	1.540	1.657	1.836	2.060	2.317	2.596	2.892	3.200	3.516	3.838
7	1.749	1.784	1.886	2.045	2.249	2.486	2.748	3.029	3.324	3.629	3.943
8	1.999	2.030	2.120	2.262	2.448	2.668	2.914	3.180	3.462	3.756	4.060
9	2.249	2.276	2.357	2.486	2.656	2.860	3.090	3.343	3.612	3.895	4.188
10	2.498	2.523	2.596	2.714	2.871	3.060	3.277	3.516	3.773	4.044	4.327

Since the planes of a stem and its re-entry stem are paralell, the diamond lattice chain can not explain the setting angle. However, in a real crystal, the stems of any chain molecule are constrained by the surrounding stems. The setting angle may result from the interaction of stems.

CONFORMATION OF THE FOLD PART

Using the model introduced above, we can check up the conformation in the fold part conveniently.

(110) *fold*

The shortest fold for (110) is 8-bond fold. There are only a group of conformation in the fold. It is

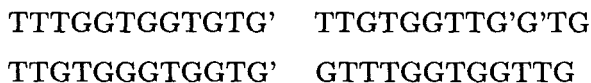


and its symmetric forms



Here and hereafter every group of conformation means four or two conformations symmetric to each other.

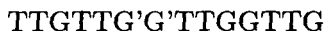
There is no 10-bond fold for (110) fold. The 12-bond fold contains 4 groups of conformations:



and there are 12 groups of conformations in 14-bond fold:



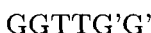
If only the usual short-range rotational isomeric state energies of polyethylene are accounted, the more gauches it contains, the higher the conformation energy of a sequence is. According to Abe et al.^[17] the conformation energy for the shortest 8-bond fold is $6E_\sigma$, by assigning the trans conformation a energy of zero and E_σ being the energy at the gauche minimum. Of the four groups of conformation in 12-bond fold, there are 3 groups which possess the energy $6E_\sigma$. However, the average conformation energy per bond of 12-bond fold is less than that of 8-bond fold. Accordingly, the average conformation energy per bond of the 14-bond fold



is the lowest among the fold forms mentioned above. It may be the most plausible conformation for (110) fold.

(200) *fold*

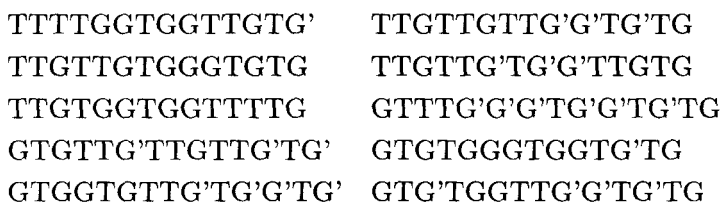
The shortest fold for (200) is 6-bond fold:



There is no 8-bond and 12-bond fold for (200). The 10-bond fold has only a group of conformation



and there are 10 groups of conformation in 14-bond fold:



Of the 10 groups of conformation, 5 groups possesses the energy $6E_\sigma$ and have the lowest average conformation energy per bond for (200) fold.

(020) *fold*

The shortest fold for (020) is 10-bond fold, which contains 3 groups of conformations:



12-bond fold contains 2 groups of conformation:



There are 16 groups of conformation in 14-bond fold



The sequence $\text{TGTTG}'\text{G}'\text{TTTG}'$ possesses the lowest average conformation energy among the conformations mentioned above for (020) fold.

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