

Molecular dynamics simulations of structural formation of a single polymer chain: Bond-orientational order and conformational defects

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The structural formation of a single polymer chain with 500 CH₂ groups is studied by the molecular dynamics simulations. Our simulations show that the bond-orientationally ordered structure at low temperatures is formed from a random-coil structure at high temperatures by a gradual stepwise cooling. From the radii of gyration and the bond-orientational order parameters, it is found that the anisotropy of a polymer chain also grows during the growth of the bond-orientational order. In the bond-orientationally ordered structure at low temperatures, 16 stems form a structure with deformed hexagonal symmetry and the stems in the outer layer have a tilted configuration. Furthermore, the *gauche* states are localized in the fold surface and the conformational states in the fold surface change more readily than those in the orientationally-ordered region. © 1997 American Institute of Physics. [S0021-9606(97)50126-7]

I. INTRODUCTION

Computer simulation of the structural formation of polymer chain systems has recently become the focus of attention in physics, chemistry and material science. Intensive studies of various model polymer systems, such as *n*-alkanes¹⁻⁸ and polyethylene chains,⁹⁻¹⁵ have been made in order to understand the dynamics of the ordered or partially ordered polymer chain systems.

Polymer chains show diverse static and dynamical structures since they have many internal degrees of freedom, for example the rotational freedom about each C-C bond in the polyethylene molecule. Owing to their structural diversity, polymeric materials have various mechanical and thermodynamical properties. It is well known that solution-grown single crystals of polyethylene are usually very thin lamellae whose width and thickness are respectively several tens of μm and 10–20 nm, and consist of folded chains. Polyethylene chains are perpendicular to the fold surface.¹⁸⁻²⁰ Macroscopic properties of polyethylene single crystals have been studied by various experimental techniques: the molecular weight and the radius of gyration of the polymer chain can be obtained by the neutron scattering experiment and the lamellar thickness can be estimated by small angle x-ray scattering, electron spectroscopy and Raman scattering.²⁰ On the other hand, it seems very difficult to observe the structural formation process of polymer chains, such as the crystal growth process, *at the molecular level* by the present experimental techniques. Computer simulation is one of the strongest tools for investigating the mechanisms of the structural formation at the molecular level.

Over the last decade, several studies have been done in relation to the structural formation of polymer chain systems. Esselink *et al.* carried out molecular dynamics (MD) simulations of nucleation and melting of *n*-alkanes in order to determine the crystallization and melting temperatures and compute the crystallization rate of a nucleus.⁵ Yamamoto *et al.* performed Monte Carlo (MC) simulations of the struc-

ture and the molecular mobility at free surfaces and the crystal/melt interfaces of an *n*-alkane crystal on the basis of the rigid-chain assumption.^{6,7} They also studied the dynamics of the conformational defects by MD simulations of a polyethylene chain confined in cylindrical potentials.¹³ Noid *et al.* performed MD simulations on the motion of the conformational defects in a polyethylene-like crystal.⁹⁻¹² Kavassalis *et al.* carried out MD simulations of the folding process of a polyethylene chain below the equilibrium melting temperature.^{14,15} Hikosaka *et al.* pointed out several important aspects of polymer crystallization: the existence of and the role played by a *metastable phase* and the high chain mobility associated with this phase.^{16,17}

The purpose of this paper is to clarify the mechanisms of the structural formation of polymer chains at the molecular level. In particular, our concern is to investigate the bond-orientational order and the conformational defects of polymer chains. With a view to investigating the process of the structural formation of polymer chains, we carry out the MD simulations of a single polymer chain and analyze the formation process of the orientationally ordered structure during cooling. Only few studies have so far been made at the transition process from the random-coil structure to the bond-orientationally ordered structure. Although Kavassalis *et al.* performed MD simulations of the structural formation of a polyethylene chain with the initial rotational isomeric state distribution, the bond-orientational order and the conformational defects were not analyzed.¹⁴

In this study the effect of the interchain interaction is neglected. In order to take the effect of the interchain interaction into account, the MD simulations of many polymer chains will be carried out in the near future.

This paper is organized as follows. In Sec. II we describe in detail our simulation model and method. Our results obtained by MD simulations are presented in Sec. III. In Sec. IV a summary and a discussion are given.

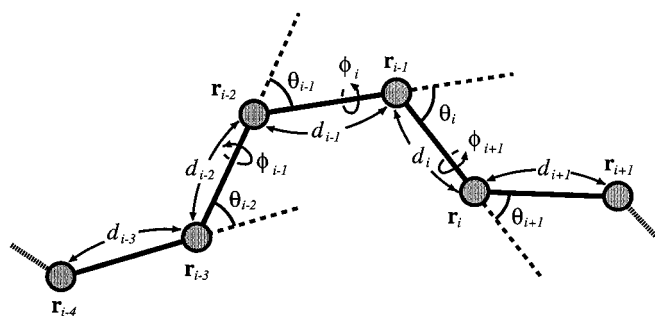


FIG. 1. A model polyethylene chain. Each CH_2 group is treated as a spherical united atom. The bond length d_i is calculated as $d_i = |\mathbf{d}_i|$, where $\mathbf{d}_i \equiv \mathbf{r}_i - \mathbf{r}_{i-1}$ is the bond vector between atoms $i-1$ and i , and \mathbf{r}_i denotes the position vector of atom i . The bond angle θ_i is the angle between three adjacent atoms $i-2$, $i-1$ and i , and the dihedral angle ϕ_i is the angle between the plane formed by \mathbf{d}_{i-2} and \mathbf{d}_{i-1} and that formed by \mathbf{d}_{i-1} and \mathbf{d}_i . The *trans* conformation corresponds to $\phi = 0$.

II. MODEL AND METHOD

Following Refs. 14 and 15, the model polyethylene consists of a linear chain of n CH_2 groups, which are treated as united atoms (Fig. 1). The mass m of each CH_2 group is 14 g/mol. The united atoms interact via the bonded potentials (bond-stretching, bond-bending and torsional potentials) and the non-bonded potential. The atomic force field used here is the DREIDING potential.²¹ The total potential energy E_{tot} consists of four parts: (i) the bond-stretching energies for C-C bonds,

$$E_{\text{stretch}} = \sum_{i=2}^n \frac{1}{2} k_d (d_i - d_0)^2, \quad (1)$$

where d_0 is the equilibrium bond length and d_i is the bond length between atoms $i-1$ and i , (ii) the bond-bending energies,

$$E_{\text{bend}} = \sum_{i=3}^n \frac{1}{2} k_\theta (\theta_i - \theta_0)^2, \quad (2)$$

where θ_0 is the equilibrium bond angle and θ_i is the bond angle between three adjacent atoms $i-2$, $i-1$ and i , (iii) the torsional energies,

$$E_{\text{torsion}} = \sum_{i=4}^n \frac{1}{2} v_\phi \{1 - \cos(3\phi_i)\}, \quad (3)$$

where ϕ_i is the dihedral angle formed by four consecutive atoms $i-3$, $i-2$, $i-1$ and i , and (iv) the 12-6 Lennard-Jones potential between non-bonded atoms separated by more than two bonds,

$$E_{\text{LJ}} = \sum_{i=1}^n \sum_{\substack{j=1 \\ (j-i \geq 3)}}^n 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (4)$$

where r_{ij} is the distance between atoms i and j . The values of all the potential parameters are listed in Table I.

The equations of motion for all atoms are solved numerically using the velocity version of the Verlet algorithm.²² We

TABLE I. Potential energy parameters used in our simulation.^a

parameter	value	unit
d_0	0.153	nm
θ_0	1.2310	rad
k_d	70000	kcal/nm ² · mol
k_θ	100	kcal/rad ² · mol
k_ϕ	2.0	kcal/mol
ϵ	0.1984	kcal/mol
σ	0.36239	nm

^aReference 21.

apply the Nosé-Hoover method in order to keep the temperature of the system constant.^{23–25} The integration time step is 0.001 ps and a relaxation constant for the heat bath variable is 0.1 ps. The cutoff distance for the Lennard-Jones potential is 10.5 Å. The total momentum and the total angular momentum are taken to be zero in order to cancel overall translation and rotation of the chain.

The MD simulations are performed by the following procedure. First, a polymer chain with $n=500$ united atoms is placed in the *all-trans* conformation with no total momentum and no total angular momentum. Secondly, we obtain random configuration of the polymer chain at high temperature ($T=800$ K) by the MD run of 1000 ps. Thirdly, it is cooled stepwise to $T=100$ K with the rate of 50 K/1000 ps (Fig. 2). Note that the equilibrium melting temperature of polyethylene is $T_m^\circ = 414$ K, for reference.

In the following section, we study the bond-orientational order and the distribution of the dihedral angles at various temperatures in detail.

III. RESULTS

A. Chain conformations

In order to see the formation process of the orientationally ordered structure, we show, in Fig. 3, the snapshots of the chain conformation at time $t=1000$ ps for various temperatures ($T=800, 500, 400$ and 100 K) obtained by our MD simulations. In this figure, the ellipsoids, whose axes are determined as three principal axes of inertia, are depicted to roughly show the shape of a polymer chain. From Fig. 3(a), it is found that, at high temperature ($T=800$ K), *gauche*

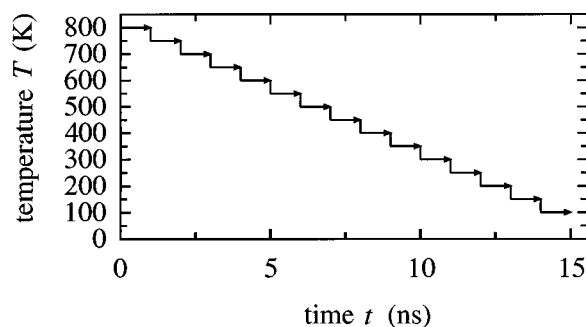


FIG. 2. Schematic explanation of the cooling process. The cooling rate is 50 K/ns.

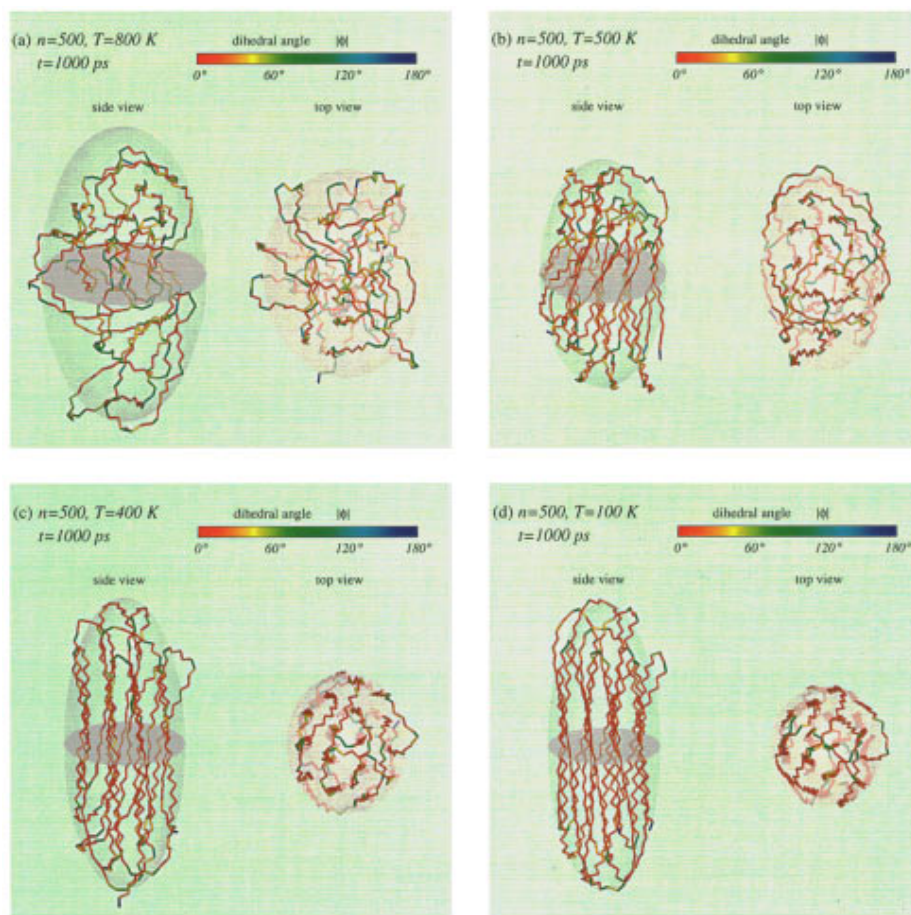


FIG. 3. The chain conformation of a polyethylene chain at 1000 ps (a) for $T=800$ K, (b) for $T=500$ K, (c) for $T=400$ K and (d) for $T=100$ K (Left: side view, Right: top view). Color denotes the absolute value of the dihedral angle around each bond and the ellipsoid roughly shows the shape of a polyethylene chain. The end bonds are colored with blue.

states (deep green to light blue) are excited everywhere and a polymer chain forms a *random-coil structure*. Figures 3(b)–3(d) indicate that the orientationally ordered structure is formed at low temperatures by a stepwise cooling. It is also found that the chain configuration becomes more anisotropic as the temperature decreases. From Figs. 3(c) and 3(d), we find the following features concerning the obtained orientationally ordered structure: (i) the *gauche* excitations are located only in the fold surfaces, (ii) most bonds in the adjacently re-entered fold are in the *gauche* state and (iii) in the non-adjacently re-entered fold, there are several *trans* bonds as well as *gauche* bonds.

In the following subsections, we analyze the radius of gyration, the bond-orientational order and the conformational defects in the process of the structural formation.

B. Radius of gyration

In Sec. III A, it was shown that the orientationally ordered structure at low temperatures is anisotropic. Here we introduce the coordinate system with three principal axes of inertia in order to analyze the anisotropic structure (Fig. 4). In this coordinate system, the origin is located at the center-of-mass position, the x -axis is the principal axis with the

largest moment of inertia and the z -axis is that with the smallest moment of inertia. In this subsection, we investigate a change in the chain dimensions in the structural formation process.

The chain dimensions can be characterized by its radii of gyration parallel to individual axes defined as

$$R_{gx}^2 = \frac{1}{n} \sum_{i=1}^n \langle (x_i - x_c)^2 \rangle, \quad (5a)$$

$$R_{gy}^2 = \frac{1}{n} \sum_{i=1}^n \langle (y_i - y_c)^2 \rangle, \quad (5b)$$

$$R_{gz}^2 = \frac{1}{n} \sum_{i=1}^n \langle (z_i - z_c)^2 \rangle, \quad (5c)$$

where $\mathbf{r}_i = (x_i, y_i, z_i)$ is the position vector of the i -th atom, $\mathbf{r}_c = (x_c, y_c, z_c)$ is the position vector of the center of mass and $\langle \dots \rangle$ denotes the ensemble average. The usual radius of gyration R_g is defined by

$$R_g^2 = \frac{1}{n} \sum_{i=1}^n \langle (\mathbf{r}_i - \mathbf{r}_c)^2 \rangle, \quad (6)$$

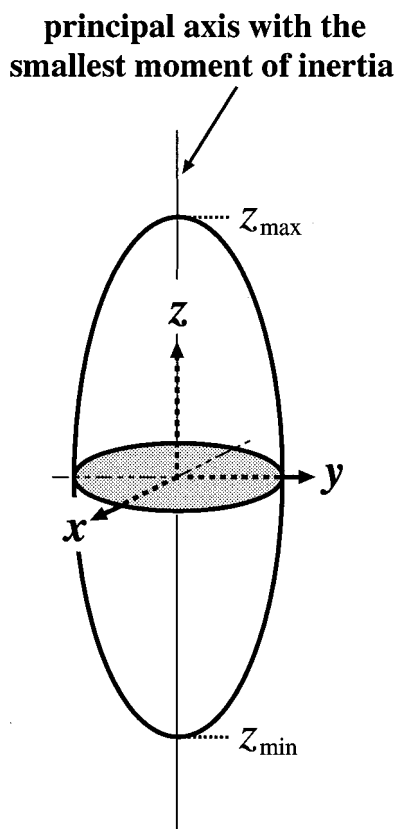


FIG. 4. Explanation of the coordinate system with three principal axes of inertia. The origin of the coordinates is the center of mass. The main axis (z -axis) is determined as the principal axis with the smallest moment of inertia and the x -axis is the principal axis with the largest moment of inertia.

and the relation $R_g^2 = R_{gx}^2 + R_{gy}^2 + R_{gz}^2$ holds.

In Fig. 5, we show the temperature dependence of the radii of gyration. The time average is taken between 0.2 and 1.0 ns for each temperature. From the temperature dependence of R_g , we find the following features: (i) At high temperatures ($T > 550$ K), R_g decreases as the temperature decreases. This temperature dependence is one of the characteristic features of a random coil. (ii) On the other hand, in

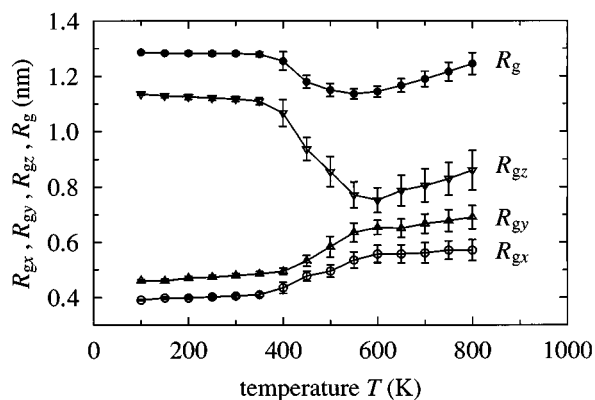


FIG. 5. The radii of gyration R_{gx} , R_{gy} , R_{gz} , R_g versus temperature T . Time average is taken between 0.2 and 1.0 ns.

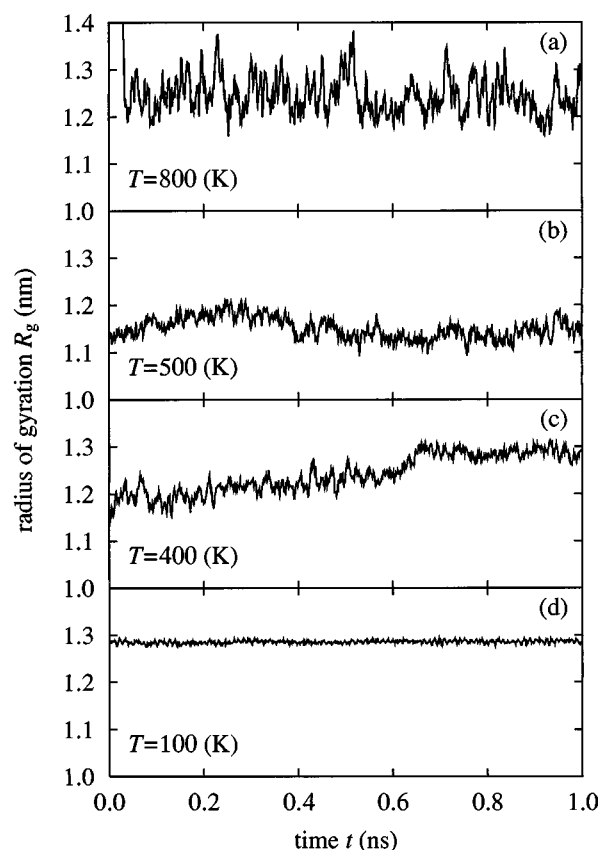


FIG. 6. The radius of gyration R_g versus time t (a) at $T=800$ K, (b) at $T=500$ K, (c) at $T=400$ K and (d) at $T=100$ K.

the temperature region below $T=550$ K, R_g increases as the temperature decreases. As is clearly seen from the temperature dependence of R_{gx} , R_{gy} and R_{gz} , the reason for this temperature dependence is that the shape of the polymer chain becomes more anisotropic as the temperature is reduced. From Fig. 5, the ratio R_{gz}/R_{gx} is found to be $R_{gz}/R_{gx} \approx 1.5$ at $T=800$ K while $R_{gz}/R_{gx} \approx 2.9$ at $T=100$ K. It is ascertained by investigating the orientational order parameter in Sec. III C. that the orientationally ordered structure is formed in this very temperature region. (iii) When the temperature is lower than $T=400$ K, R_g is almost constant and the global change of the chain conformation is not recognized.

The radii of gyration R_g are plotted in Fig. 6 as a function of time for various temperatures. At $T=800$ K [Fig. 6(a)] and $T=100$ K [Fig. 6(d)], R_g only fluctuates around each mean value and no remarkable change is found. It is seen from Fig. 6(b) that, in the case of $T=500$ K, after the gradual increase of R_g within the first 0.3 ns, R_g slowly decreases and returns to a value corresponding to R_g at $t=0$ ns. At $T=400$ K [Fig. 6(c)], R_g gradually increases up to 0.6 ns and sharply increases between 0.6 and 0.7 ns. It is expected that the abrupt structural change might occur in this time interval. After the sharp increase, R_g has a constant value of about 1.29 nm, which almost corresponds to the value of R_g at lower temperatures.

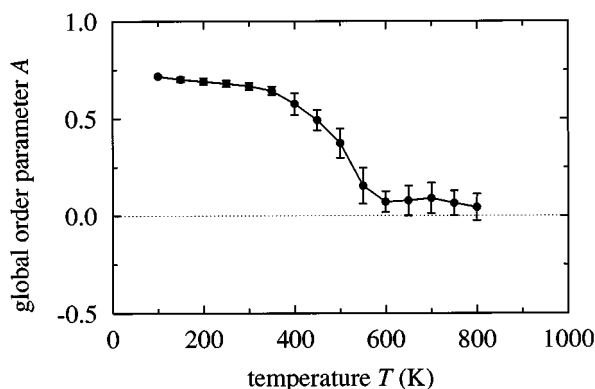


FIG. 7. The global bond-orientational order parameter A versus temperature T . Time average is taken between 0.2 and 1.0 ns.

C. Bond-orientational order

In this subsection, we study the bond-orientational order of a polymer chain. To begin with, we calculate the *global* bond-orientational order parameter A , which is defined by

$$A = \frac{1}{n-2} \sum_{i=3}^n \left\langle \frac{3 \cos^2 \psi_i - 1}{2} \right\rangle, \quad (7)$$

where ψ_i is the angle between the sub-bond vector \mathbf{b}_i and the z -axis, and $\mathbf{b}_i = (\mathbf{d}_i + \mathbf{d}_{i-1})/2 = (\mathbf{r}_i - \mathbf{r}_{i-2})/2$ is the vector formed by connecting centers of two adjacent bonds i and $i-1$. The parameter A would assume a value of 1.0, 0.0 or -0.5 , respectively, for a polymer chain whose sub-bonds are perfectly parallel, random or perpendicular to the z -axis. The parameter A is one of the simplest measures of the global bond-orientational order of a polymer chain. The global bond-orientational order parameter A versus temperature T is plotted in Fig. 7. At high temperatures above $T=550$ K, the parameter A assumes a value near zero, which shows that there is no global bond-orientational order in this temperature region. At lower temperatures than $T=550$ K, A increases as the temperature decreases, which indicates that the global bond-orientational order grows below $T=550$ K. The growth rate of the bond-orientational order below $T=400$ K is smaller than that above $T=400$ K, that is, the orientationally ordered structure is formed around $T=400$ K. The temperature dependence of A shows a clear transition from a random-coil structure to a bond-orientationally ordered structure. We also see the clear transition in the temperature dependence of R_g (Fig. 5). It is a very fundamental and important problem whether the transition of a single polymer chain from a random-coil structure to a bond-orientationally ordered structure is an equilibrium phase transition or not. We must investigate more carefully in order to solve this problem.

We show the time dependence of the global bond-orientational order parameter A for various temperatures in Fig. 8. At $T=800$ K, the parameter A fluctuates around zero. When the temperature is $T=500$ K, the parameter A has a nearly-constant value of 0.45 up to $t=0.4$ ns, sharply drops to 0.35 at $t=0.4$ ns and is almost constant afterwards. This

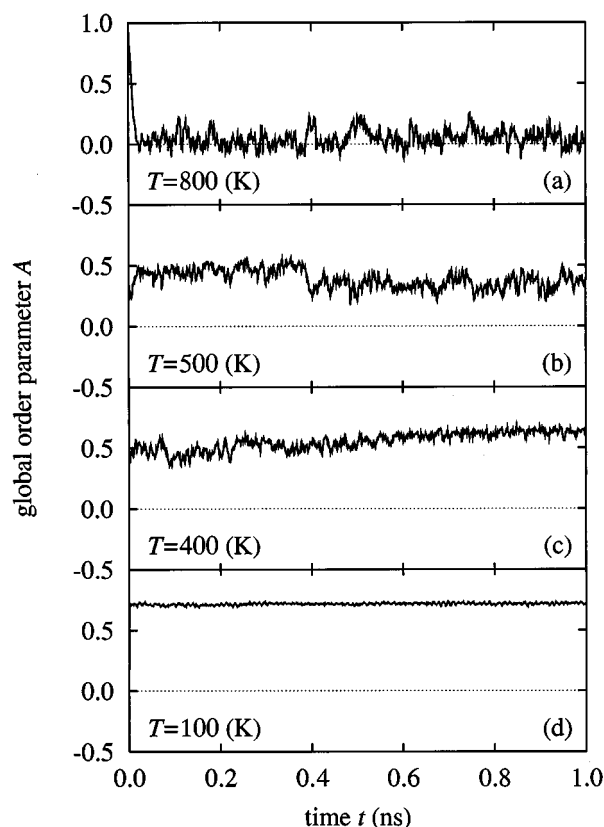


FIG. 8. The global bond-orientational order parameter A versus time t for (a) $T=800$ K, (b) $T=500$ K, (c) $T=400$ K and (d) $T=100$ K.

time dependence of A indicates that the relatively ordered state up to $t=0.4$ ns is unstable. It can be seen from Table II that the total potential energy E_{tot} averaged before $t=0.4$ ns is smaller than that averaged after $t=0.4$ ns, that is, the state up to $t=0.4$ ns is *energetically* more stable than that after $t=0.4$ ns. Therefore, the instability of the relatively ordered state up to $t=0.4$ ns should be caused by the *conformational entropy* of a polymer chain. The fact that the conformational entropy after $t=0.4$ ns is larger than that before $t=0.4$ ns is suggested by the following rough discussion on the fraction of the *trans* states ($|\phi| < \pi/3$), P_{trans} , of a polymer chain (Table II). From Table II, it is found that the fraction P_{trans} after $t=0.4$ is smaller than that before $t=0.4$ ns. Roughly speaking, the decrease of the fraction of the *trans* states means the increase of the available states, which indi-

TABLE II. Average potential energies and the fraction of the *trans* states ($|\phi| < \pi/3$) P_{trans} at $T=500$ K before $t=0.4$ ns and after $t=0.4$ ns.

	average before $t=0.4$ ns	average after $t=0.4$ ns
E_{stretch}	255.9 ± 16.2 (kcal/mol)	243.6 ± 14.1 (kcal/mol)
E_{bend}	245.8 ± 15.3 (kcal/mol)	252.9 ± 16.1 (kcal/mol)
E_{torsion}	295.7 ± 14.3 (kcal/mol)	306.9 ± 13.4 (kcal/mol)
E_{LJ}	-754.5 ± 20.6 (kcal/mol)	-734.0 ± 19.8 (kcal/mol)
E_{tot}	42.9 ± 36.7 (kcal/mol)	69.4 ± 32.1 (kcal/mol)
P_{trans}	0.849 ± 0.016	0.832 ± 0.015

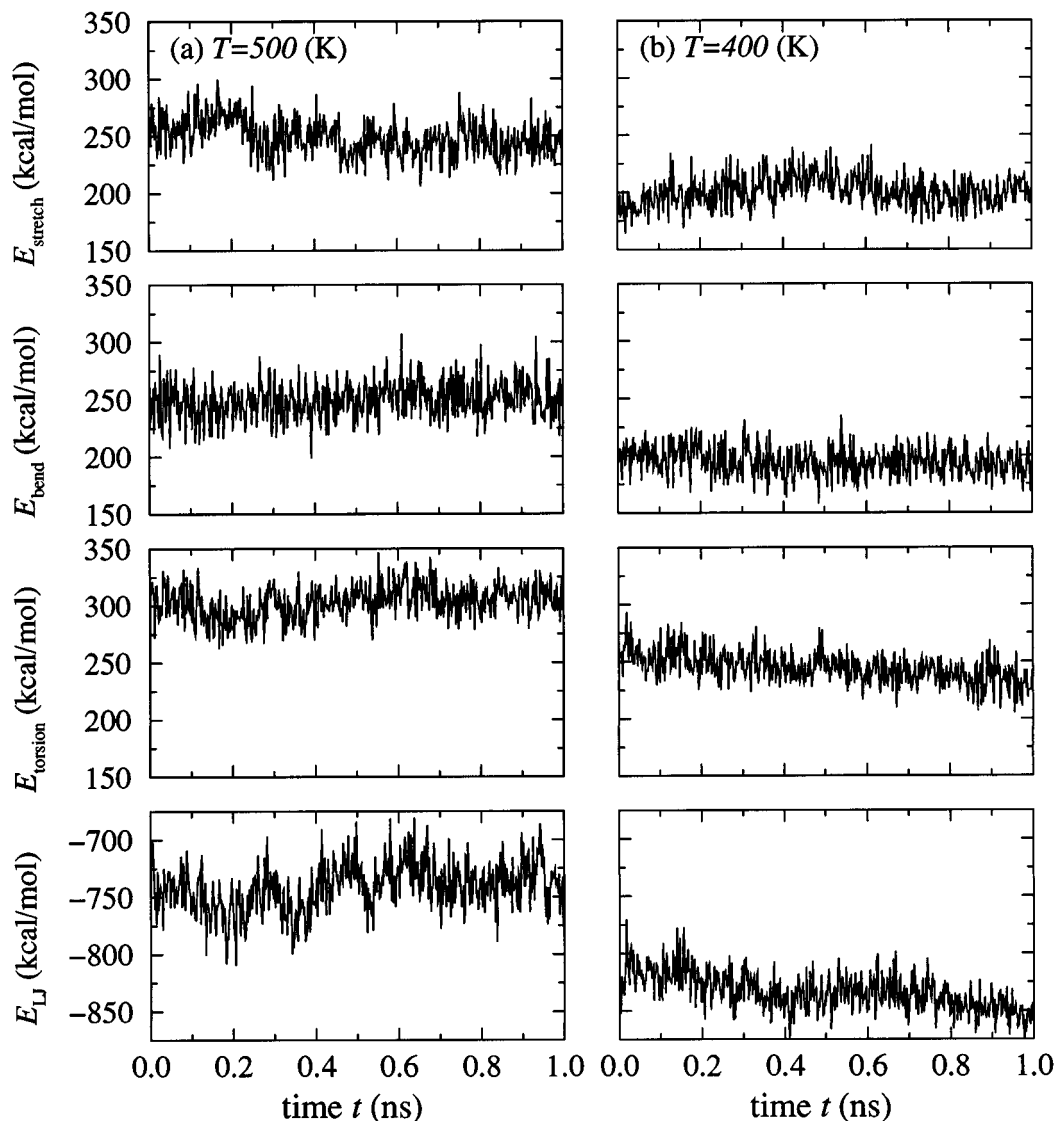


FIG. 9. The bond-stretching energy E_{stretch} , the bond-bending energy E_{bend} , the torsional energy E_{torsion} and the Lennard-Jones energy E_{LJ} versus time t (a) at $T=500$ K and (b) at $T=400$ K.

cates the increase of the conformational entropy. At $T=400$ K, A gradually increases with time. Although the radius of gyration R_g abruptly rises between $t=0.6$ and $t=0.7$ ns (Fig. 6), the abrupt change in A is not found. It is worth noting that the way of change in E_{stretch} is opposite to that in E_{LJ} , that is, E_{stretch} increases when E_{LJ} decreases, and vice versa [Fig. 9(b)]. From Fig. 9(b), it is found that E_{bend} is constant and E_{torsion} gradually decreases in the formation process of the orientationally ordered structure. At $T=100$ K, there is no change in the parameter A .

In order to investigate the *local* bond-orientational order, we next calculate the bond-orientational order parameter $S_B(z)$ which is defined by

$$S_B(z) = \left\langle \left\langle \frac{3\cos^2(\psi(z)) - 1}{2} \right\rangle_{\text{bond}} \right\rangle, \quad (8)$$

where $\psi(z)$ is the angle between the sub-bond vector \mathbf{b} in a

slab $[z, z+dz]$ and the z -axis, and $\langle \cdots \rangle_{\text{bond}}$ denotes the average over the sub-bonds in a slab between z and $z+dz$. The parameter $S_B(z)$ would assume a value of 1.0, 0.0 or -0.5 , respectively, for sub-bonds in a slab $[z, z+dz]$ perfectly parallel, random or perpendicular to the z -axis. We set $dz=0.5\sigma$ in our calculations of $S_B(z)$.

We show the bond-orientational order parameter $S_B(z)$ at $t=0.2, 0.4, 0.6, 0.8$ and 1.0 ns for various temperatures in Fig. 10. This figure shows the following features: (i) At high temperature $T=800$ K, [Fig. 10(a)], $S_B(z)$ is almost zero independent of z , which indicates that a polymer chain forms a random-coil structure. (ii) In the case of $T=500$ K [Fig. 10(b)], a relatively orientationally ordered structure is found to appear at $t=0.2$ ns. The structure, however, breaks down after $t=0.4$ ns. We have already discussed the cause of this breakdown in the earlier part of this subsection. (iii) At $T=400$ K [Fig. 10(c)], it is clear that the more

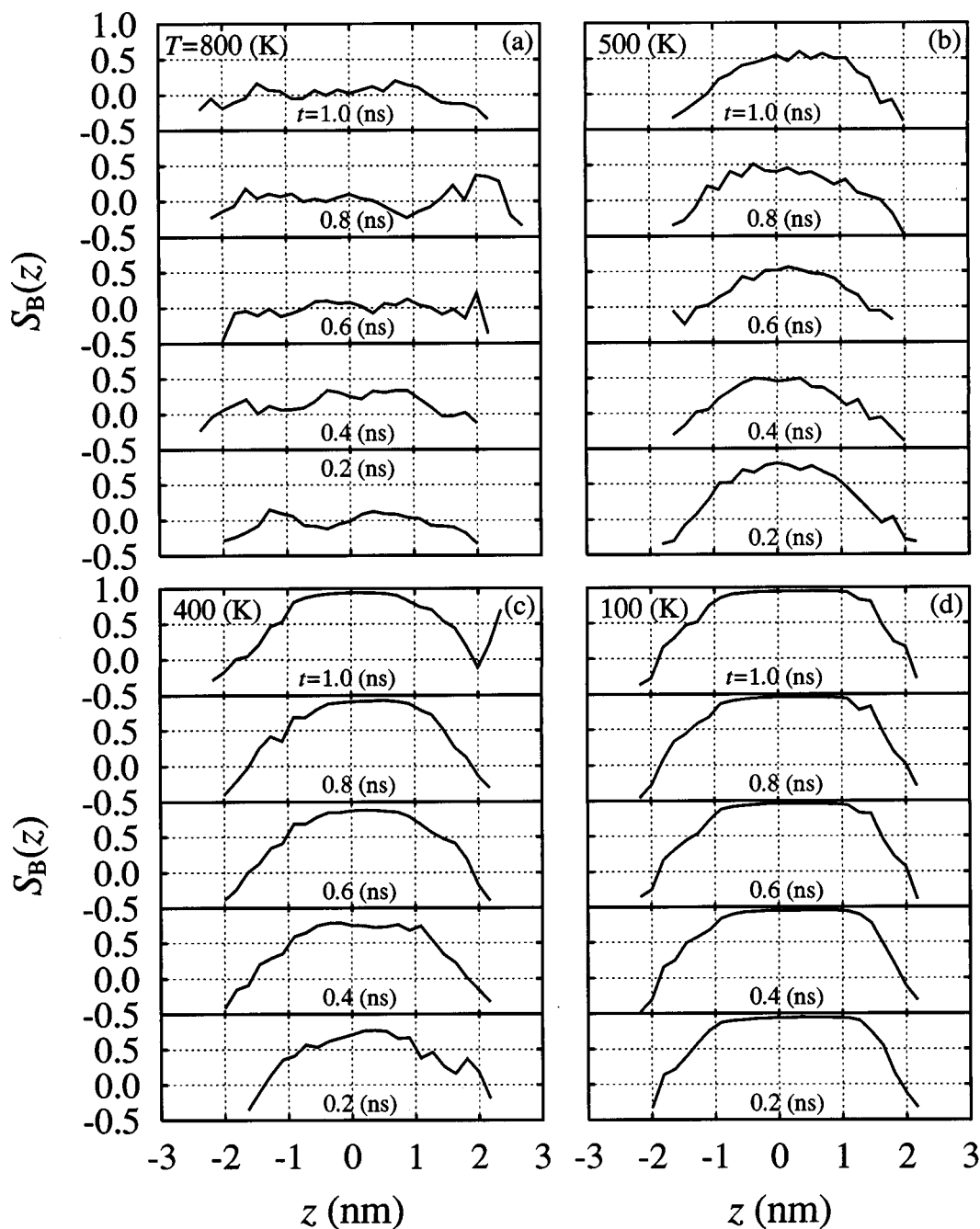


FIG. 10. The bond-orientational order parameter $S_B(z)$ versus z at $t=0.2, 0.4, 0.6, 0.8$ and 1.0 ns for (a) $T=800$ K, (b) $T=500$ K, (c) $T=400$ K and (d) $T=100$ K.

orientationally ordered structure is formed with the elapse of time. (iv) At $T=100$ K [Fig. 10(d)], the orientationally ordered structure is formed and there is a flat part between $z=-0.9$ and $z=1.2$ nm. The bond-orientational order parameter $S_B(z)$ in this flat region reaches 0.9, which indicates that the sub-bonds in this region are almost parallel to the z -axis.

Finally, we analyze the orientationally ordered structure of a polymer chain obtained by our MD simulations in detail. It is very useful to introduce the concept of “stem” in order to characterize the orientationally ordered structure. We define a *stem* as a series of atoms whose z -coordinates are

located in the region ($z_{\min}^s < z < z_{\max}^s$) where $S_B(z)$ is larger than 0.9 (Fig. 11). A snapshot of stems at $t=1.0$ ns for $T=100$ K is displayed in Fig. 12. In this case, z_{\min}^s and z_{\max}^s are set to be $z_{\min}^s = -0.7$ nm and $z_{\max}^s = 1.1$ nm, respectively. As clearly seen from this figure, 16 stems, each of which contains 14 or 15 atoms, form a bond-orientationally ordered structure with deformed hexagonal symmetry. The mean distance between stems is 0.416 nm, which corresponds to the minimum of the Lennard-Jones potential $R_0=0.40677$ nm. The length of stems ($z_{\max}^s - z_{\min}^s$) is about 1.8 nm and the thickness of the fold surface along the

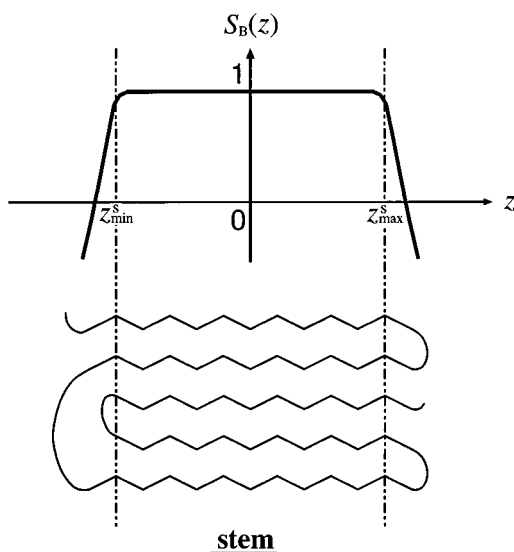


FIG. 11. Schematic explanation of stems. Each stem is defined as a series of atoms whose z -components are located between z_{\min}^s and z_{\max}^s .

z -axis is around 1.0 nm; accordingly, the lamellar thickness in our simulations is about 3.8 nm. This value is several times as small as that of the lamellar thickness of solution-grown single crystals of polyethylene (10–20 nm). We expect that the lamellar thickness becomes large when the interchain interaction is taken into account. This was suggested in Ref. 14 in the case of four-chain system. It is found from

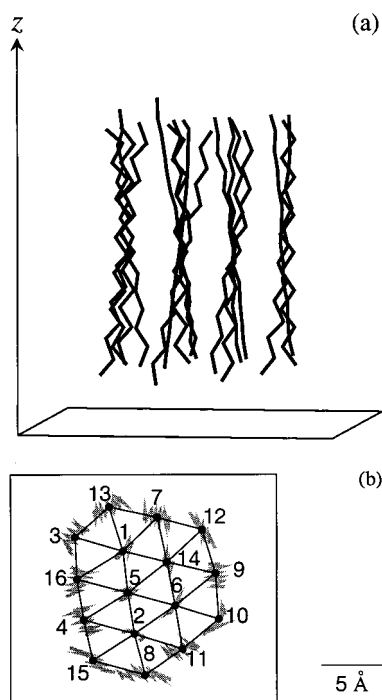


FIG. 12. The configuration of stems at $t = 1.0$ ns for $T = 100$ K; (a) side view and (b) top view. Numbers beside stems in (b) denote the connection of stems along the chain. Filled circles represent the central positions of individual stems.

Fig. 12(b) that the stems in the outer layer of the folded structure have a tilted configuration. As indicated by numbers beside stems in Fig. 12(b), which denote the connection of stems along the chain, the number of folds with nonadjacent re-entry is about three times as many as that with adjacent re-entry. The ratio of the nonadjacently re-entered folds to the adjacently re-entered folds may depend on the initial configuration and the cooling history.

D. Conformational defects

In the previous subsection, we studied the formation process of the bond-orientationally ordered structure. In this subsection, we investigate the conformational defects in the bond-orientationally ordered structure. In Fig. 13, we show the histogram of the dihedral angles $P(\phi)$ at $z = 0, 1.0$ and 1.5 nm at several times for $T = 800, 500, 400$ and 100 K. Note that the position at $z = 1.5$ nm corresponds to the inside of the fold surface at $T = 100$ K (Fig. 10). From Fig. 13(a), it is found that, at $T = 800$ K, there is no marked change in the shape of the histogram for any z and the distribution of ϕ is broad. At temperatures $T = 500, 400$ and 100 K [Fig. 13(b)–13(d)], the shape of the histogram depends on z . At $z = 0$ nm, almost all the conformations are *trans* around $\phi = 0$, especially for $T = 400$ and 100 K. On the other hand, the *gauche* states ($|\phi| > \pi/3$) are excited at $z = 1.0$ and 1.5 nm for $T = 500$ and 400 K and at $z = 1.5$ nm for $T = 100$ K. It is clearly seen from this figure that, even at low temperature ($T = 100$ K), the distribution $P(\phi)$ changes its shape with time at $z = 1.5$ nm. This fact suggests that the conformational motion is easy to occur at the fold surface even at low temperatures.

We show the three-dimensional plot of the distribution $P(\phi)$ at $t = 1.0$ ns for several temperatures in Fig. 14 in order to illustrate the dependence of $P(\phi)$ on z clearly. At $T = 800$ K, the distribution $P(\phi)$ does not depend on z very well. At low temperatures, on the other hand, $P(\phi)$ depends on z and the *gauche* states are located only in the fold surface.

IV. SUMMARY AND DISCUSSION

In this article, we have studied the formation process of the bond-orientationally ordered structure of a single polymer chain with 500 CH_2 groups during the gradual stepwise cooling by MD simulations. The bond-orientational order starts to grow at $T = 550$ K and the orientationally ordered structure is formed at $T = 400$ K. The new results obtained in our simulations are as follows:

- (i) The bond-orientationally ordered structure was formed from a random-coil structure by a gradual stepwise cooling.
- (ii) The anisotropy as well as the bond-orientational order of a polymer chain grew below $T = 550$ K.
- (iii) In the formation process of the bond-orientationally ordered structure at $T = 400$ K, the way of change in the bond-stretching energy E_{stretch} was opposite to that in the Lennard-Jones energy E_{LJ} .
- (iv) In the bond-orientationally ordered structure obtained

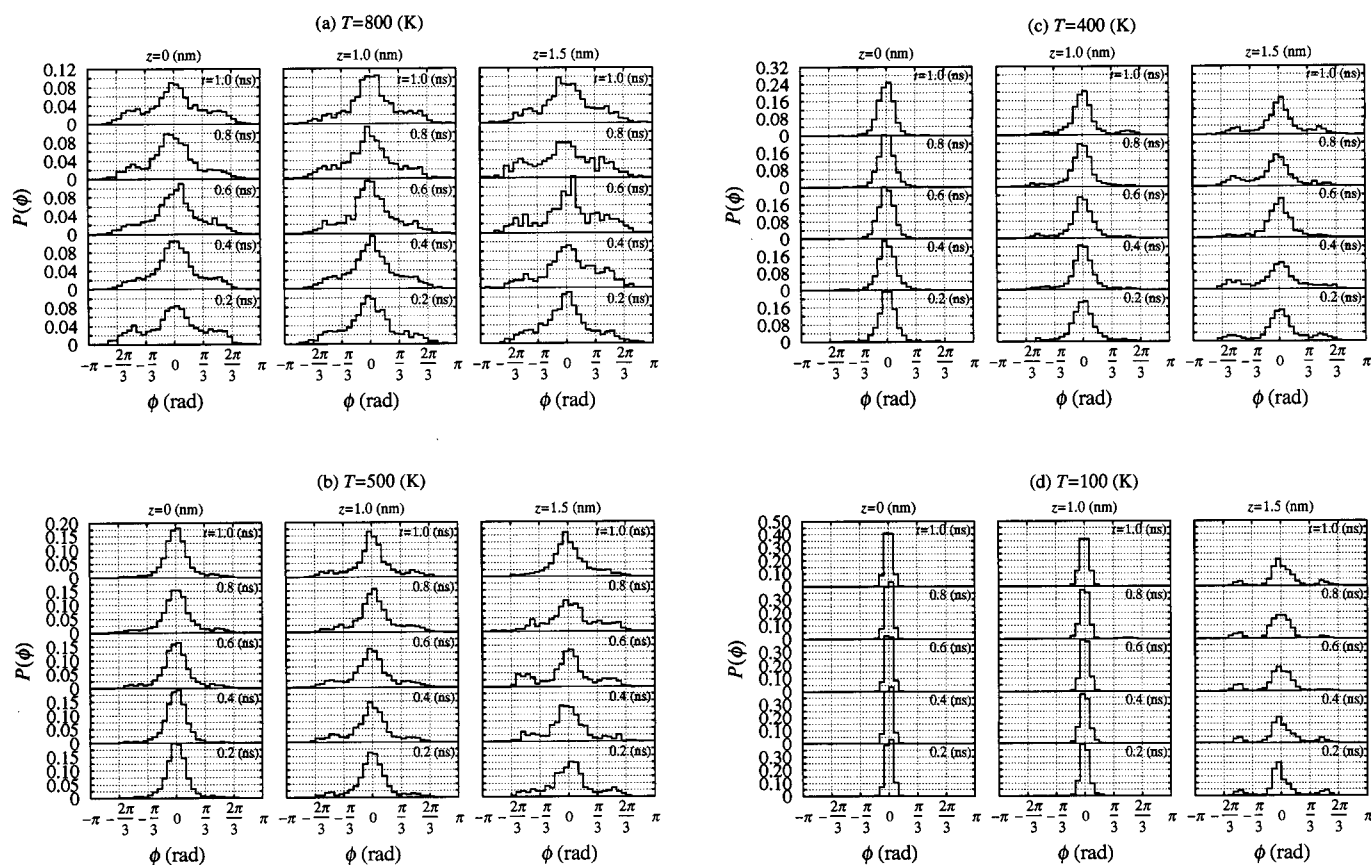


FIG. 13. Distribution of the dihedral angle $P(\phi)$ at times $t=0.2, 0.4, 0.6, 0.8$ and 1.0 ns at $z=0, 1.0$ and 1.5 nm for (a) $T=800$ K, (b) $T=500$ K, (c) $T=400$ K and (d) $T=100$ K. In the low temperatures ($T=400$ and 100 K), $z=1.0$ nm corresponds to z_{\max}^s and the position at $z=1.5$ nm is inside the fold surface.

by our simulations at $T=100$ K, there were 16 stems, each of which involved 14 or 15 atoms. These stems formed a structure with deformed hexagonal symmetry and the stems in the outer layer had a tilted configuration.

- (v) In the bond-orientationally ordered structure at low temperatures, the *gauche* states were located exclusively in the fold surface and the conformational motion was easy to occur at the fold surface.

The third result, (iii), is not necessarily an evident result. Within the context of the presented data we cannot deduce the physical explanation of the opposite tendency of E_{stretch} and E_{LJ} . In order to elucidate this opposite tendency, an elaborate molecular motion analysis must be done, which is left for the future work.

The fourth observation, (iv), can be interpreted by the following simple argument. The energy loss due to the tilt of stems in the outer layer is considered to be small since the outer layer is a free surface. Therefore, the entanglement in the fold surface can be alleviated by the tilt of stems in the outer layer with the minimal energy loss.

In our simulations, the obtained lamella is very thin and the fold structure is very disordered made up of long loops. We cannot say for certain from our analysis whether it should be interpreted as intrinsic structure of the lamella or

an artifact due to rapid cooling, but we think that the lamellar thickness and the fold structure can depend on the cooling rate.

Here we comment on the effect of the length of a polymer chain on the structural formation. In our simulations, we treated a relatively short polymer chain with 500 CH_2 groups. Whether the global bond-orientationally ordered structure is formed from a random-coil structure within a simulation time (at most a few tens of nanoseconds) or not may depend on the length of a polymer chain. In the case of a very long polymer chain, it is expected that the aggregate of locally-ordered regions, such as a fringed micelle, is formed.

In this study, we concentrated on the analyses of the bond-orientational order and the conformational defects. In order to understand the mechanisms of the formation process of the bond-orientationally ordered structure clearly, we need analyze the molecular mobility and the conformational motion in this formation process. We will report the results of these analyses in the subsequent paper. Moreover, we will carry out the MD simulations of a many-chain system in order to take the effect of the interchain interaction into account in future. Furthermore, we plan to investigate the manner in which polymer chains are incorporated into the crystal surface from the point of view of *self-organization*.

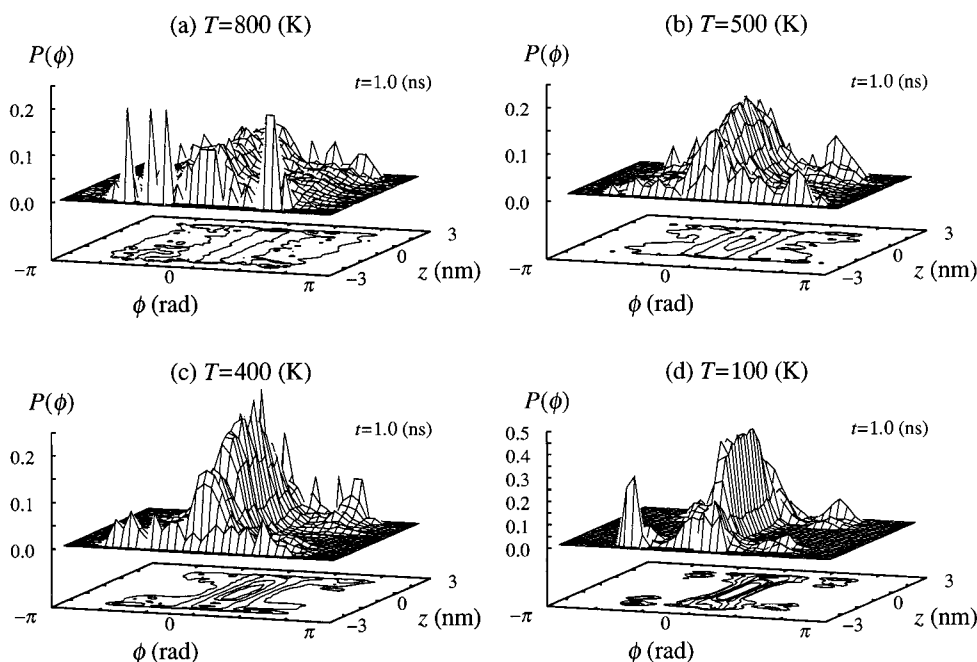


FIG. 14. Three-dimensional plot of the distribution $P(\phi)$ as a function of ϕ and z at $t=1.0$ ns for (a) $T=800$ K, (b) $T=500$ K, (c) $T=400$ K and (d) $T=100$ K.

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