

# Structure formation of a single polymer chain. I. Growth of *trans* domains

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Molecular dynamics simulations are carried out to study structure formation of a single polymer chain with 500 CH<sub>2</sub> groups. Our simulations show that the orientationally ordered structure is formed at a low temperature both by gradual stepwise cooling and by quenching from a random configuration at a higher temperature. The growth of the global orientational order proceeds *in a gradual manner* in the case of gradual stepwise cooling, whereas it proceeds *in a stepwise manner* in the case of quenching. The latter feature endorses the previously proposed hypothetical grand view of self-organization [e.g., see T. Sato, *Phys. Plasmas* **3**, 2135 (1996)]: when a system is driven far from equilibrium, it will evolve to a more stable state in a stepwise fashion irrespective of its fundamental interaction forces. From the microscopic analysis of the structure formation process, we find the following characteristic features: (i) In the case of gradual stepwise cooling, the global orientational order grows gradually through the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain. (ii) In the case of quenching, the growth of the orientational order is either due to the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain or to the elongation of the *trans* segments in the largest *trans* domain. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356440]

## I. INTRODUCTION

Structure formation or self-organization of chain molecules, such as *n*-alkanes, polyethylene chains, and lipid molecules, has recently become the focus of attention in physics, chemistry, biology, and materials science. The crystal structure of the rotator phase of *n*-alkanes has been extensively studied by several experimental techniques including x-ray diffraction,<sup>1–4</sup> infrared and Raman spectroscopy,<sup>5,6</sup> neutron scattering,<sup>7,8</sup> and nuclear magnetic resonance.<sup>9</sup> The primary nucleation in the crystallization induction period of polyethylene<sup>10–12</sup> and poly(ethylene terephthalate)<sup>13–18</sup> has been investigated by various time-resolved measurements. The morphologies of the self-assembled aggregates formed by the association of lipid molecules in solution, such as spherical micelles, cylindrical micelles, and lipid bilayers, have been experimentally studied.<sup>19–21</sup> Although numerous experimental investigations have thus been made on the structure formation of chain molecules, little is known about the detailed mechanisms of the structure formation of chain molecules *at the molecular level*.

Computer simulation is one of the powerful tools for investigating the mechanisms of the structure formation process at the molecular level. Over the last decade, several molecular dynamics (MD) simulations have been performed on structure formation of an isolated crystalline polymer chain in order to examine the primary nucleation process.<sup>22–26</sup> Kavassalis *et al.* carried out MD simulations of the folding process of a polyethylene chain from an all-*trans* conformation and rotational isomeric state conformation below the equilibrium melting temperature.<sup>22,23</sup> Fujiwara and

Sato studied the formation process of the orientationally ordered structure of a single polymer chain from a random configuration by gradual stepwise cooling.<sup>24</sup> The relaxation of a fully extended polyethylene chain was investigated by Liao and Jin.<sup>25</sup> They found that the relaxation proceeds in three stages when a chain has more than 1200 methylene groups. Iwata and Sato performed MD simulations on the melting and crystallization processes of a single polymer chain and analyzed chain movement in the crystallization process.<sup>26</sup> Computer simulation has also been done on the coil-globule transition<sup>27–31</sup> and the relaxation<sup>32,33</sup> of an isolated single polymer chain. Atomistic MD simulations of atactic poly(vinyl chloride) have been performed in order to study the collapse of amorphous polymer chains.<sup>27</sup> The thermodynamics of an isolated single homopolymer chain has been investigated using a lattice Monte Carlo (MC) simulation<sup>28</sup> and an off-lattice MC simulation.<sup>29–31</sup> The relaxation modes and rates of a single polymer chain have been studied by MC simulations<sup>32</sup> and MD simulations.<sup>33</sup>

The purpose of this paper is to clarify the mechanisms of structure formation of polymer chains *at the molecular level*. In particular, our concern is to investigate the structure formation process of a single polymer chain by cooling. To this end, we carry out the MD simulations of a single polymer chain and analyze the formation process of the orientationally ordered structure during gradual stepwise cooling and quenching.

In our previous paper<sup>24</sup> we investigated the global orientational order and the conformational defects of a single polymer chain during gradual stepwise cooling. It was found from our previous simulations that the orientationally ordered structure was formed from a random configuration by a gradual stepwise cooling and the global orientational order

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TABLE I. Potential energy parameters used in our simulation.<sup>a</sup>

Parameter	Value	Unit
$d_0$	0.153	nm
$\theta_0$	1.2310	rad
$k_d$	70 000	kcal/nm <sup>2</sup> mol
$k_\theta$	100	kcal/rad <sup>2</sup> mol
$k_\phi$	2.0	kcal/mol
$\epsilon$	0.1984	kcal/mol
$\sigma$	0.362 39	nm

<sup>a</sup>See Ref. 34.

grew below  $T=550$  K. In this series of papers, we first discuss the growth process of *trans* domains which physically mean bunches of local orientationally ordered *trans* segments. In the subsequent paper, we will investigate structure and molecular motion during the structure formation process. This paper is organized as follows. In Sec. II we give a detailed description of our simulation model and method. Our simulation results by gradual stepwise cooling are presented in Sec. III and those by quenching in Sec. IV. A summary and discussion are given in Sec. V.

## II. MODEL AND METHOD

The present computational model is the same as that used in the previous work on the structure formation of a single polymer chain.<sup>24</sup> The model polymer chain consists of a sequence of methylene (CH<sub>2</sub>) groups, which are treated as united atoms. The mass of each methylene group is 14 g/mol. The united atoms interact via bonded potentials (bond stretching, bond bending, and torsional potentials) and a non-bonded potential (12-6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential:<sup>34</sup> (i) the bond-stretching potential

$$V_{\text{stretch}}(d) = \frac{1}{2}k_d(d - d_0)^2, \quad (1)$$

where  $d_0$  is the equilibrium bond length and  $d$  is the actual bond length, (ii) the bond-bending potential

$$V_{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2, \quad (2)$$

where  $\theta_0$  is the equilibrium bond angle and  $\theta$  is the bond angle between three adjacent atoms; (iii) the torsional potential

$$V_{\text{torsion}}(\phi) = \frac{1}{2}k_\phi[1 - \cos(3\phi)], \quad (3)$$

where  $\phi$  is the dihedral angle formed by four consecutive atoms, and (iv) the 12-6 Lennard-Jones potential between atoms separated by more than two bonds

$$V_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (4)$$

where  $r$  is the distance between atoms. 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 Verlet algorithm<sup>35</sup> and we apply the Nosé–Hoover method in order to keep the temperature of the system constant.<sup>36–38</sup> The integration time step and the relaxation constant for the heat bath variable are 1.0 fs and 0.1 ps, respectively. The cutoff distance for the 12-6 Lennard-Jones

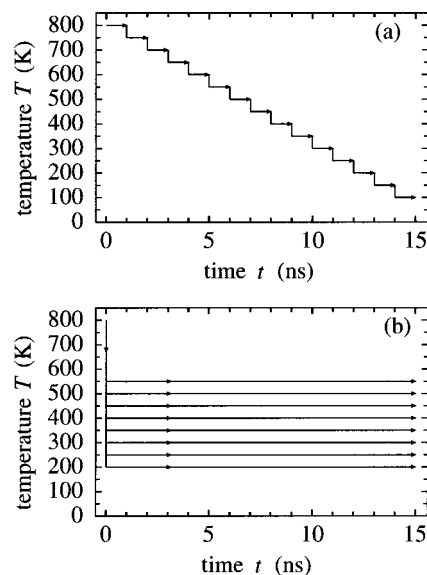


FIG. 1. Schematic explanation of the cooling process: (a) gradual stepwise cooling and (b) quenching.

potential is  $10.5 \text{ \AA}$ . A single polymer chain with 500 methylene groups is exposed to vacuum and other molecules such as solvent molecules are not considered. The total linear momentum and angular momentum are set to zero in order to cancel overall translation and rotation of a polymer chain. The MD simulations are carried out as follows. At first, we provide a random configuration of a single polymer chain with 500 united atoms at high temperature ( $T=800$  K). The system is then cooled to lower temperature by the following cooling manners: (i) Gradual stepwise cooling. The system is cooled stepwise to  $T=100$  K with the rate of 50 K/1 ns and a simulation of 1 ns ( $1 \times 10^6$  time steps) is carried out at each temperature [Fig. 1(a)]. (ii) Quenching. The system is quenched to a lower temperature and simulations of 15 ns ( $1.5 \times 10^7$  time steps) are carried out for several quenching temperatures ( $T=200, 250, \dots, 550$  K) [Fig. 1(b)].

In the following sections, we describe, in detail, our simulation results by gradual stepwise cooling (Sec. III) and by quenching (Sec. IV).

## III. STRUCTURE FORMATION BY GRADUAL STEPWISE COOLING

### A. Formation process of global orientational order

In this subsection, we analyze the chain configuration and the global orientational order in the process of structure formation by gradual stepwise cooling.

#### 1. Chain configuration

Snapshots of the final chain configuration at various temperatures ( $T=800, 500, 400,$  and  $100$  K) are shown in Fig. 2. Here we introduce the coordinate system with three principal axes of inertia of a single polymer chain. 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 figure, top and bottom snapshots are, respectively, viewed along the  $z$  axis (top view) and along the

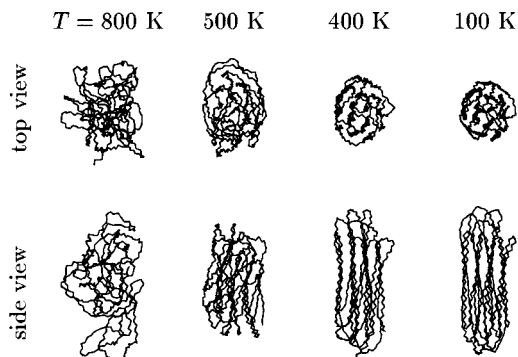


FIG. 2. Snapshots of the final chain configuration of a single polymer chain at each temperature:  $T = 800, 500, 400,$  and  $100$  K (from left to right) in the case of gradual stepwise cooling. Top and bottom snapshots are, respectively, viewed along the  $z$  axis (top view) and along the direction perpendicular to the  $z$  axis (side view), where the  $z$  axis is defined as the principal axis with the smallest moment of inertia.

direction perpendicular to the  $z$  axis (side view). Figure 2 indicates the following features: (i) At high temperature ( $T = 800$  K), *gauche* states are excited everywhere and a polymer chain takes a random configuration. (ii) At lower temperature ( $T \leq 400$  K), the orientationally ordered structure is formed by gradual stepwise cooling and the global change of the chain conformation is not recognized. (iii) In the orientationally ordered structure, the *gauche* excitations are located exclusively in the fold surfaces.

## 2. Global orientational order parameter

In order to investigate the growth process of the global orientational order, we calculate the global orientational order parameter  $P_2$ , which is defined by

$$P_2 = \left\langle \frac{3 \cos^2 \psi - 1}{2} \right\rangle_{\text{bond}}, \quad (5)$$

where  $\psi$  is the angle between two chord vectors and  $\langle \dots \rangle_{\text{bond}}$  denotes the average over all pairs of chord vectors. The chord vector is defined as the vector formed by connecting centers of two adjacent bonds along the polymer chain. The parameter  $P_2$  takes a value of 1.0 when all chord vectors are parallel and that of 0.0 when chord vectors are randomly oriented. The temperature dependence of the global orientational order parameter  $P_2$  is plotted in Fig. 3. The time average is taken during the last 0.8 ns for each temperature. The following features are found from this figure: (i) At high temperature above  $T = 550$  K, the parameter  $P_2$  takes a value near zero, which shows that there exists no global orientational order in this temperature region. (ii) At temperature lower than  $T = 550$  K,  $P_2$  gradually increases as the temperature decreases, which indicates that the global orientational order starts to grow below  $T = 550$  K. (iii) At temperature lower than  $T = 350$  K, the growth rate of the orientational order becomes small. The reason for this is that, in this temperature region, the global conformational change of the polymer chain ceases and only the local motion of united atoms with no global change takes place.

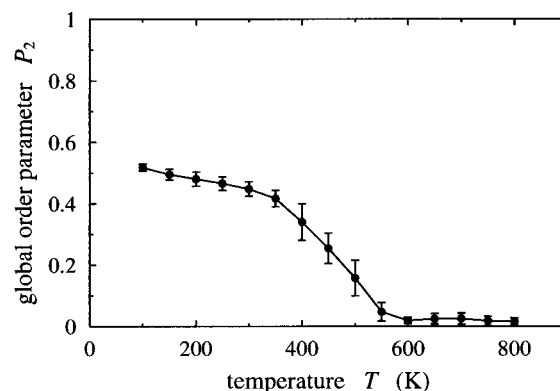


FIG. 3. The global orientational order parameter  $P_2$  vs temperature  $T$  in the case of gradual stepwise cooling. Time average is taken during the last 0.8 ns.

## B. Microscopic analysis of the structure formation process

In this subsection, we first examine the conformational change and then analyze the parallel ordering process in order to investigate, at the molecular level, the structure formation process by gradual stepwise cooling.

### 1. Conformational change

In order to investigate the conformational change, we examine the stretching of chain molecules. We define the *trans* state and the *gauche* state by  $|\phi| \leq \pi/3$  and  $|\phi| > \pi/3$ , respectively, where  $\phi$  is the dihedral angle. We calculate the distribution of the size of the *trans* segments, i.e., the number of consecutive *trans* bonds  $n_{\text{tr}}$ . The distribution of the size of the *trans* segments  $P(n_{\text{tr}})$  is normalized as

$$\sum_{n_{\text{tr}}=1}^{N-3} P(n_{\text{tr}}) = 1, \quad (6)$$

where  $N$  is the number of atoms in a polymer chain ( $N = 500$  in this work). The distribution  $P(n_{\text{tr}})$  is shown in Fig. 4 at various temperatures. The time average is taken during the last 50 ps for each temperature. At  $T = 800$  K,  $P(n_{\text{tr}})$  decreases exponentially with the increase of the size  $n_{\text{tr}}$  [inset of Fig. 4(a)]. The reason for this exponential decrease is that, at high temperature, each bond takes the *trans* state or the *gauche* state randomly; that is, there is no spatial correlation between the *trans* state and the *gauche* state. At  $T = 500$  K, the fraction of the small *trans* segments with  $n_{\text{tr}} < 10$  decreases while that of the large *trans* segments with  $n_{\text{tr}} > 10$  increases [Fig. 4(b)]. As shown in Figs. 4(c) and 4(d), a flat region appears between  $n_{\text{tr}} = 10$  and  $n_{\text{tr}} = 20$  at  $T = 450$  K and extends to  $n_{\text{tr}} = 25$  at  $T = 400$  K. When the temperature is reduced to  $T = 350$  K, the flat region disappears and another peak becomes visible around  $n_{\text{tr}} = 24$ , which results in a bimodal distribution [Fig. 4(e)]. At  $T = 100$  K, we can see two peaks around  $n_{\text{tr}} = 2$  and  $n_{\text{tr}} = 25$ , which are completely separated. This suggests that the orientationally ordered structure consists of two parts: fold surface and stem region. A peak around  $n_{\text{tr}} = 2$  corresponds to the *trans* segments in the fold surfaces and another peak around  $n_{\text{tr}} = 25$  corresponds to those in the stem region.

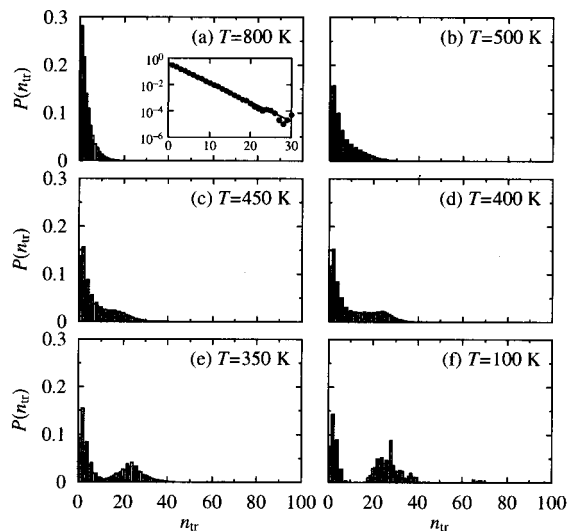


FIG. 4. The distribution of the size of the *trans* segments  $P(n_{tr})$  averaged during the last 50 ps: (a) at  $T=800$  K, (b) at  $T=500$  K, (c) at  $T=450$  K, (d) at  $T=400$  K, (e) at  $T=350$  K, and (f) at  $T=100$  K in the case of gradual stepwise cooling. The inset of (a) is plotted in a linear-log scale.

In Fig. 5 we show, the average size of the *trans* segments,  $\bar{n}_{tr}$ , which is defined by

$$\bar{n}_{tr} = \sum_{n_{tr}=1}^{N-3} n_{tr} P(n_{tr}) \quad (7)$$

and satisfies  $1 \leq \bar{n}_{tr} \leq N-3 (=497)$ , as a function of the inverse temperature. The time average is taken during the last 0.8 ns for each temperature. The average size of the *trans* segments  $\bar{n}_{tr}$  corresponds to the persistence length, which should satisfy the following relation at high temperature:<sup>39</sup>

$$\bar{n}_{tr} \propto \exp\left(\frac{\Delta\varepsilon}{k_B T}\right), \quad (8)$$

where  $\Delta\varepsilon$  is the torsional energy difference between the *trans* and the *gauche* conformations and  $k_B$  is the Boltzmann

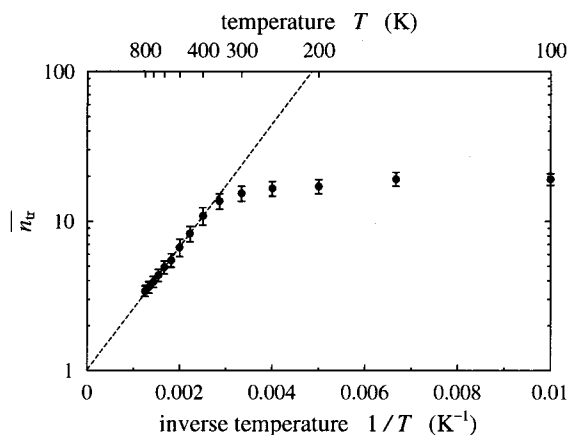


FIG. 5. The average size of the *trans* segments  $\bar{n}_{tr}$  vs inverse temperature  $1/T$  in the case of gradual stepwise cooling. Time average is taken during the last 0.8 ns. The dashed line represents the line fitted by Eq. (8) with  $\Delta\varepsilon/k_B \approx 1.88$  (kcal/mol).

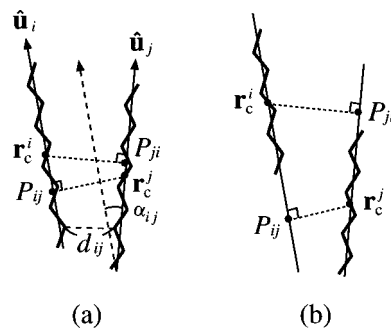


FIG. 6. (a) Schematic illustration for the definition of a “*trans* domain.”  $d_{ij}$  is the shortest distance between the  $i$ th *trans* segment and the  $j$ th *trans* segment,  $P_{ij}$  is the foot of a perpendicular drawn from the center of mass of the  $j$ th *trans* segment to the  $i$ th *trans* segment, and  $\alpha_{ij}$  is the angle between the principal axis with the smallest moment of inertia of the  $i$ th *trans* segment and that of the  $j$ th *trans* segment. (b) An example of two *trans* segments that do not belong to the same *trans* domain under the second condition.

constant. As can be seen from Fig. 5, the data at high temperature ( $T \geq 400$  K) are well fitted by Eq. (8) and the fitting parameter  $\Delta\varepsilon/k_B$  is estimated as  $\Delta\varepsilon/k_B \approx 1.88$  (kcal/mol). At low temperature of  $T < 400$  K, on the other hand, the average size  $\bar{n}_{tr}$  is almost constant because of the formation of the orientationally ordered structure.

## 2. Parallel ordering

We investigate, in this subsection, the parallel ordering process. In order to measure the extent of the local orientational order, we need to introduce the concept of a “*trans* domain,” which will physically mean a bunch of local orientationally ordered *trans* segments which is formed through parallel ordering. The *trans* domain is an expansion of a “domain” defined in the context of short chain–molecule systems.<sup>40–44</sup> Our precise definition of a *trans* domain is as follows. Two *trans* segments,  $i$  and  $j$ , belong to the same *trans* domain if the following three conditions are satisfied:

- (i)  $\min_{k,l} |\mathbf{r}_k^i - \mathbf{r}_l^j| < r_0$ ,
- (ii)  $\min_k (\hat{\mathbf{u}}_i \cdot \mathbf{r}_k^i) < \hat{\mathbf{u}}_i \cdot \mathbf{r}_c^j < \max_k (\hat{\mathbf{u}}_i \cdot \mathbf{r}_k^i)$   
or  
 $\min_k (\hat{\mathbf{u}}_j \cdot \mathbf{r}_k^j) < \hat{\mathbf{u}}_j \cdot \mathbf{r}_c^i < \max_k (\hat{\mathbf{u}}_j \cdot \mathbf{r}_k^j)$ ,
- (iii)  $\alpha_{ij} < \alpha_0$ ,

where  $\mathbf{r}_k^i$  is the position vector of the  $k$ th atom in the  $i$ th *trans* segment,  $\hat{\mathbf{u}}_i$  is the unit vector directed along the principal axis with the smallest moment of inertia of the  $i$ th *trans* segment,  $\mathbf{r}_c^j$  is the position vector of the center of mass of the  $j$ th *trans* segment, and  $\alpha_{ij}$ , which satisfies  $0 \leq \alpha_{ij} \leq \pi/2$ , is the angle between the principal axis with the smallest moment of inertia of the  $i$ th *trans* segment and that of the  $j$ th *trans* segment. The first condition means that the shortest distance,  $d_{ij}$  between two *trans* segments is relatively short [Fig. 6(a)]. The second condition indicates that the foot of a perpendicular drawn from the center of mass of the  $j$ th *trans* segment to the  $i$ th *trans* segment  $P_{ij}$  stands on the  $i$ th *trans*

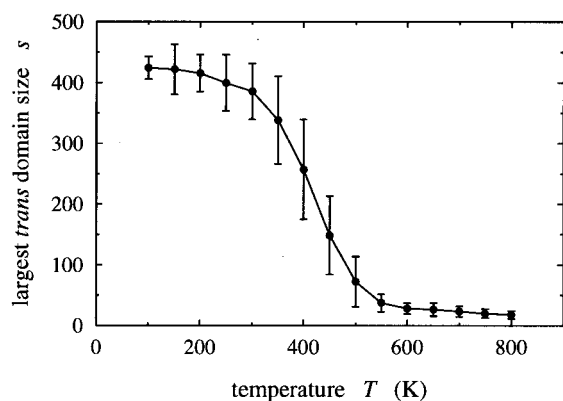


FIG. 7. The largest *trans* domain size  $s$  vs temperature  $T$  in the case of gradual stepwise cooling. Time average is taken during the last 0.8 ns.

segment, or vice versa [Fig. 6(a)]. Under this condition, two *trans* segments shown in Fig. 6(b) do not belong to the same *trans* domain. The last condition shows that the directions of two *trans* segments are almost parallel. In our calculations, we set  $r_0 = 1.5\sigma$  and  $\alpha_0 = 10^\circ$ . We show, in Fig. 7, the temperature dependence of the largest *trans* domain size  $s$ . The time average is taken during the last 0.8 ns for each temperature. At  $T \geq 550$  K, only small *trans* domains whose sizes are smaller than 50 can be observed. At  $T < 550$  K, the largest *trans* domain size  $s$  gradually increases with the decrease of temperature. At  $T < 350$  K,  $s$  reaches about 400. This result, together with the result in Sec. III A 2, leads to the conclusion that both the global orientational order and the local orientational order grow in a gradual manner in the case of gradual stepwise cooling.

We then calculate the number of *trans* segments in the largest *trans* domain,  $n_{(1)}$ , and the average *trans* segment size in the largest *trans* domain,  $\bar{n}_{tr}^{(1)}$ , in order to investigate the growth process of *trans* domains in detail. Note that the relation  $s = \bar{n}_{tr}^{(1)} \times n_{(1)}$  holds. The time evolution of  $P_2$ ,  $s$ ,  $n^{(1)}$ , and  $\bar{n}_{tr}^{(1)}$  at  $T = 400$  K is plotted using the segmental average with  $\Delta t = 5$  ps in Fig. 8. From this figure, we find the

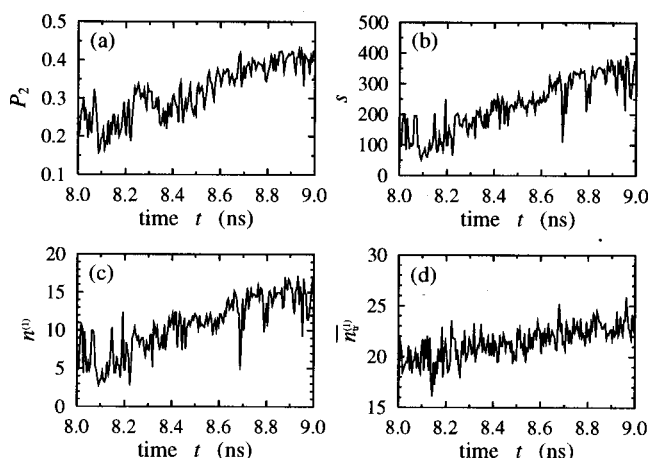


FIG. 8. The time evolution of: (a)  $P_2$ , (b)  $s$ , (c)  $n^{(1)}$ , and (d)  $\bar{n}_{tr}^{(1)}$  at  $T = 400$  K in the case of gradual stepwise cooling. Segmental average is taken with  $\Delta t = 5$  ps.

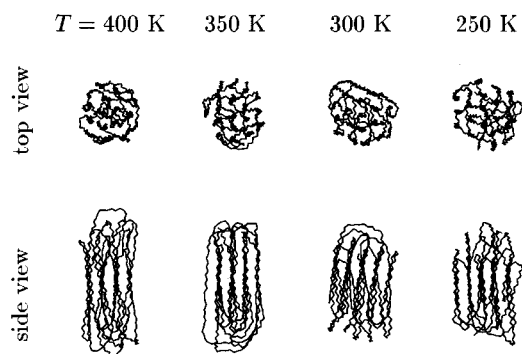


FIG. 9. Snapshots of the final chain configuration of a single polymer chain at each temperature:  $T = 400, 350, 300,$  and  $250$  K (from left to right) in the case of quenching. Top and bottom snapshots are, respectively, viewed along the  $z$  axis (top view) and along the direction perpendicular to the  $z$  axis (side view).

following features: (i) At  $T = 400$  K, both the global orientational order and the local orientational order grow in a gradual manner [Figs. 8(a) and 8(b)]. (ii) The number of *trans* segments in the largest *trans* domain  $n_{(1)}$  increases more markedly than the average *trans* segment size in the largest *trans* domain  $\bar{n}_{tr}^{(1)}$  [Figs. 8(c) and 8(d)]. This fact indicates that the growth of the orientational order is mainly due to the increase of  $n_{(1)}$ ; that is, the orientational order grows through the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain.

## IV. STRUCTURE FORMATION BY QUENCHING

### A. Formation process of global orientational order

In this subsection, we analyze the chain configuration and the global orientational order in the process of structure formation by quenching.

#### 1. Chain configuration

Snapshots of the final chain configuration at various low temperatures ( $T = 400, 350, 300,$  and  $250$  K) are shown in Fig. 9. This figure shows the following features: (i) The stem length becomes shorter as the temperature decreases. (ii) The *gauche* excitations are located chiefly in the fold surfaces as in the case of gradual stepwise cooling.

#### 2. Global orientational order parameter

We then calculate the global orientational order parameter  $P_2$  defined by Eq. (5). The temperature dependence of the global orientational order parameter  $P_2$  is shown in Fig. 10 in the case of quenching. The time average is taken during the last 10 ns for each temperature. This figure tells us the following features: (i) At high temperature above  $T = 500$  K, the parameter  $P_2$  takes a value below 0.2, which means that the global orientation is almost random in this temperature region. (ii) At temperature lower than  $T = 500$  K,  $P_2$  increases with the decrease of temperature as in the case of gradual stepwise cooling (Sec. III A 2). (iii) At temperature lower than  $T = 400$  K,  $P_2$  decreases gradually as

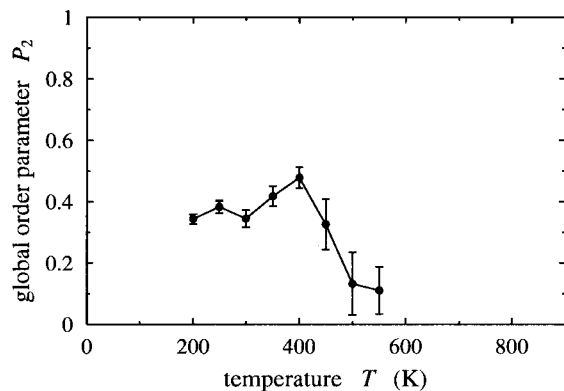


FIG. 10. The global orientational order parameter  $P_2$  vs temperature  $T$  in the case of quenching. Time average is taken during the last 10 ns.

the temperature decreases, which is in marked contrast to the temperature dependence of  $P_2$  in the case of gradual stepwise cooling (Sec. III A 2). This temperature dependence is probably caused by the fact that the polymer chain is easily trapped in the metastable state at lower temperature.

We show, in Fig. 11, the time dependence of the global orientational order parameter  $P_2$  for various temperatures using the segmental average with  $\Delta t = 20$  ps in the case of quenching. At  $T = 500$  K, we can see the clear transition between the orientationally ordered state ( $P_2 > 0.2$ ) and the randomly oriented state ( $P_2 < 0.1$ ) [Fig. 11(a)]. The similar transition can be also observed at  $T = 450$  K [Fig. 11(b)]. At  $T = 400$  K, the parameter  $P_2$  gradually increases up to  $t \approx 2.3$  ns and is almost constant afterward [Fig. 11(c)]. When the temperature is  $T = 350$  K,  $P_2$  takes a value smaller than 0.2 up to  $t \approx 2.5$  ns. The parameter  $P_2$  increases sharply at  $t \approx 2.5$  ns and reaches about 0.4 at  $t \approx 3.5$  ns [Fig. 11(d)]. Similar stepwise growth of the global orientational order can

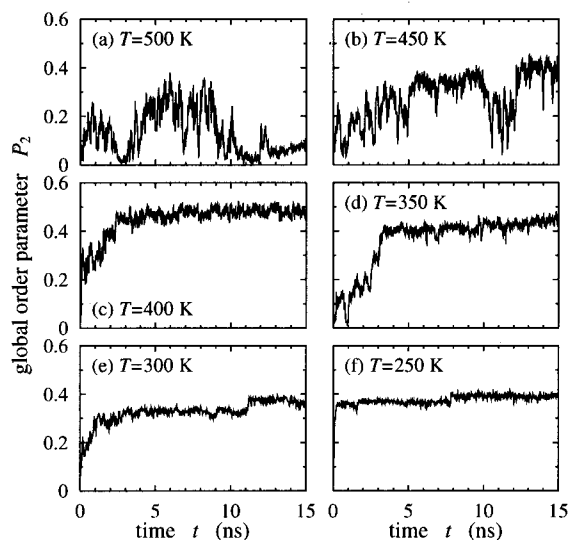


FIG. 11. The global orientational order parameter  $P_2$  vs time  $t$ : (a) at  $T = 500$  K, (b) at  $T = 450$  K, (c) at  $T = 400$  K, (d) at  $T = 350$  K, (e) at  $T = 300$  K, and (f) at  $T = 250$  K in the case of quenching. Segmental average is taken with  $\Delta t = 20$  ps.

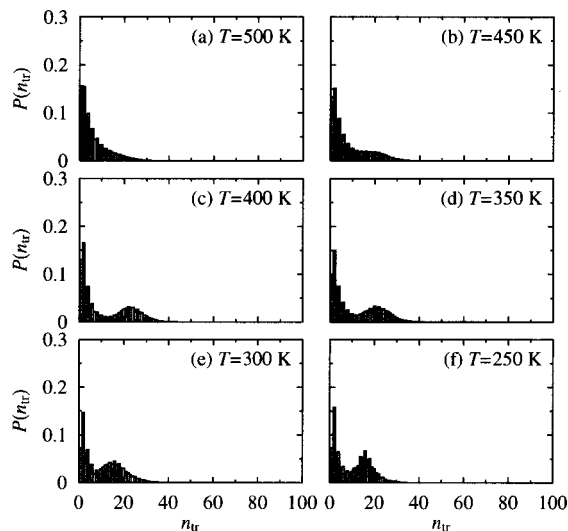


FIG. 12. The distribution of the size of the *trans* segments  $P(n_{tr})$  averaged during the last 1 ns: (a) at  $T = 500$  K, (b) at  $T = 450$  K, (c) at  $T = 400$  K, (d) at  $T = 350$  K, (e) at  $T = 300$  K, and (f) at  $T = 250$  K in the case of quenching.

also be seen at  $t \approx 11$  ns for  $T = 300$  K and at  $t \approx 7.8$  ns for  $T = 250$  K [Figs. 11(e) and 11(f)]. This fact indicates that the global orientational order grows in a stepwise manner at lower temperature in the case of quenching, which exhibits a striking contrast to the growth manner of the global orientational order in the case of gradual stepwise cooling (Sec. III A 2). As we shall see later (Sec. IV B 2), the main cause of the stepwise increase of  $P_2$  at  $T = 300$  K differs from that at  $T = 250$  K.

## B. Microscopic analysis of the structure formation process

In this subsection, we first examine the conformational change and then analyze the parallel ordering process at the molecular level during structure formation by quenching.

### 1. Conformational change

The distribution of the size of the *trans* segments  $P(n_{tr})$  is shown in Fig. 12 at various temperatures. The time average is taken during the last 1 ns for each temperature. At  $T = 500$  K,  $P(n_{tr})$  decreases monotonically with the increase of the size  $n_{tr}$  [Fig. 12(a)]. At  $T = 450$  K, a flat region appears between  $n_{tr} = 10$  and  $n_{tr} = 20$  [Fig. 12(b)]. At  $T \leq 400$  K, the distribution becomes bimodal [Figs. 12(c)–12(f)]. It is found from Figs. 12(c)–12(f) that the second peak position around  $n_{tr} = 20$  becomes smaller as the temperature is reduced. This fact means that, as observed above (Sec. IV A 1), the stem length becomes shorter as the temperature decreases because the second peak corresponds to the *trans* segments in the stem region.

The average size of the *trans* segments  $\bar{n}_{tr}$  is plotted in Fig. 13. The time average is taken during the last 10 ns for each temperature. It is found from this figure that the data at  $T \geq 400$  K are well fitted by Eq. (8) with the fitting parameter  $\Delta \varepsilon/k_B \approx 1.88$  (kcal/mol). On the other hand, the average size  $\bar{n}_{tr}$  is almost constant at  $T < 400$  K. These features are also seen in the case of gradual stepwise cooling (Sec. III B 1).

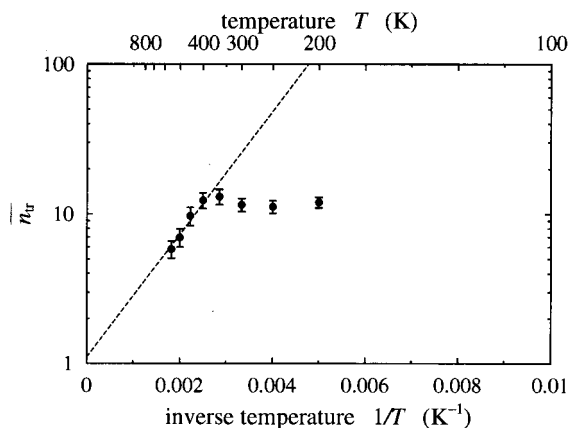


FIG. 13. The average size of the *trans* segments  $\overline{n_{tr}}$  vs inverse temperature  $1/T$  in the case of quenching. Time average is taken during the last 10 ns. The dashed line represents the line fitted by Eq. (8) with  $\Delta\epsilon/k_B \approx 1.88$  (kcal/mol).

## 2. Parallel ordering

In this subsection, we study the parallel ordering process. We show, in Fig. 14, the time evolution of the largest *trans* domain size  $s$  at various temperatures using the segmental average with  $\Delta t = 20$  ps. At  $T \geq 450$  K [Figs. 14(a) and 14(b)], the largest *trans* domain size  $s$  fluctuates greatly in accordance with the temporal behavior of the global orientational order parameter  $P_2$  [Figs. 11(a) and 11(b)]. When the temperature is  $T = 400$  K,  $s$  gradually increases with the elapse of time, reaches about 370 at  $t \approx 2.3$  ns, and fluctuates between 300 and 400 afterward [Fig. 14(c)]. At  $T = 350$  K [Fig. 14(d)], only small *trans* domains whose sizes are smaller than 100 can be seen up to  $t \approx 2.5$  ns. The largest *trans* domain  $s$  sharply increases at  $t \approx 2.5$  ns and reaches about 350 at  $t \approx 3.5$  ns. The similar stepwise growth of the largest *trans* domain size can also be observed at  $t \approx 11$  ns for  $T = 300$  K [Fig. 14(e)]. At  $T = 250$  K, a clear change in the

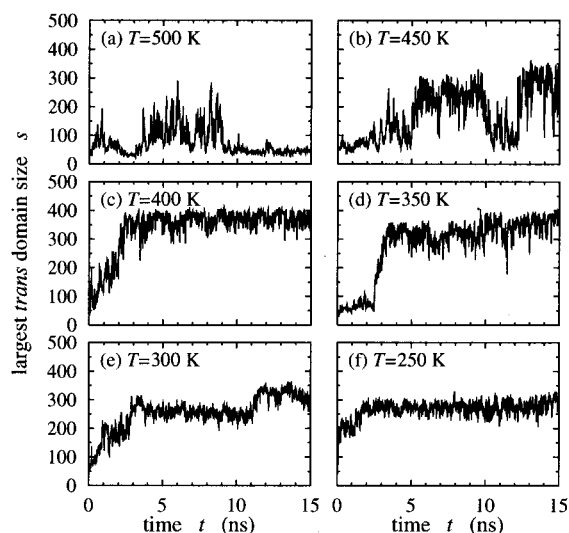


FIG. 14. The largest *trans* domain size  $s$  vs time  $t$ : (a) at  $T = 500$  K, (b) at  $T = 450$  K, (c) at  $T = 400$  K, (d) at  $T = 350$  K, (e) at  $T = 300$  K, and (f) at  $T = 250$  K in the case of quenching. Segmental average is taken with  $\Delta t = 20$  ps.

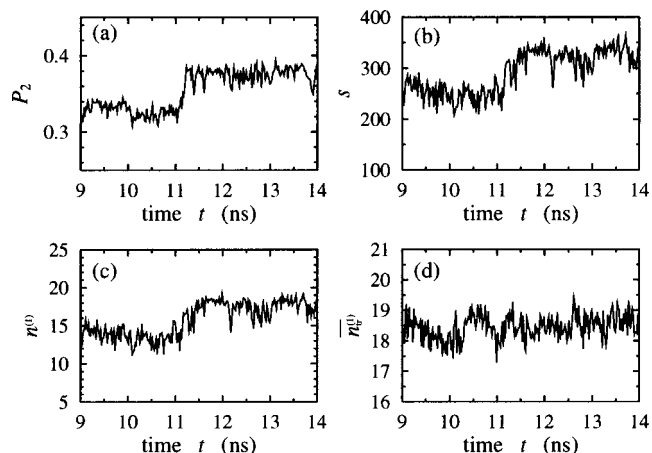


FIG. 15. The time evolution of (a)  $P_2$ , (b)  $s$ , (c)  $n^{(1)}$ , and (d)  $\overline{n_{tr}^{(1)}}$  at  $T = 300$  K in the case of quenching. Segmental average is taken with  $\Delta t = 20$  ps.

largest *trans* domain size cannot be recognized at  $t \approx 7.8$  ns [Fig. 14(f)] while the stepwise growth of the global orientational order can be observed at  $t \approx 7.8$  ns [Fig. 11(f)].

We show the time evolution of  $P_2$ ,  $s$ ,  $n^{(1)}$ , and  $\overline{n_{tr}^{(1)}}$  at  $T = 300$  K and  $T = 250$  K using the segmental average with  $\Delta t = 20$  ps in Figs. 15 and 16, respectively. Figure 15 tells us that, at  $T = 300$  K, both the global orientational order and the local orientational order grow in a stepwise fashion at  $t \approx 11$  ns [Figs. 15(a) and 15(b)]. It is found from Fig. 15 that the growth of the orientational order is due to the increase of  $n_{(1)}$  as in the case of gradual stepwise cooling (Fig. 8). It is ascertained that the stepwise growth of the orientational order at  $T = 350$  K is also due to the stepwise increase of  $n_{(1)}$ . From Fig. 16, we find the following features at  $T = 250$  K: (i) The global orientational order parameter  $P_2$  increases sharply at  $t \approx 7.8$  ns [Fig. 16(a)]. On the other hand, a marked change in the largest *trans* domain size  $s$  cannot be observed at  $t \approx 7.8$  ns [Fig. 16(a)]. (ii) The growth of the global orientational order is due to the increase of the average *trans*

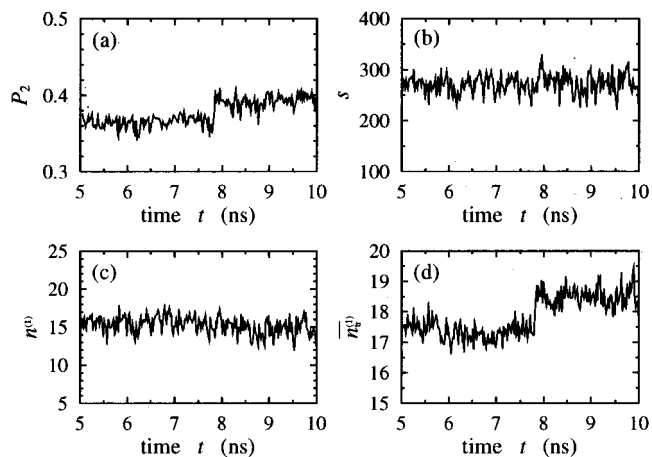


FIG. 16. The time evolution of (a)  $P_2$ , (b)  $s$ , (c)  $n^{(1)}$ , and (d)  $\overline{n_{tr}^{(1)}}$  at  $T = 250$  K in the case of quenching. Segmental average is taken with  $\Delta t = 20$  ps.

segment size in the largest *trans* domain,  $\overline{n_{tr}^{(1)}}$ . This means that, at  $T=250$  K, the growth of the orientational order is not caused by the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain but by the elongation of the *trans* segments in the largest *trans* domain.

## V. SUMMARY AND DISCUSSION

In this paper, we have carried out MD simulation of a single polymer chain with 500 methylene groups. By investigating the growth process of the global orientational order and making a microscopic analysis of the structure formation process, the following results have been obtained:

(i) The orientationally ordered structure is formed at a low temperature by gradual stepwise cooling or by quenching from a random configuration at a higher temperature.

(ii) The global orientational order grows *in a gradual manner* in the case of gradual stepwise cooling, whereas it grows *in a stepwise manner* in the case of quenching.

(iii) In the case of gradual stepwise cooling, the global orientational order starts to grow at  $T=550$  K and the orientationally ordered structure is formed at  $T=400$  K. At  $T=400$  K, the global orientational order grows gradually through the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain.

(iv) In the case of quenching, the orientationally ordered structure is formed at  $T \leq 400$  K. At  $T \leq 400$  K, the global orientational order grows in a stepwise fashion in contrast to the case of gradual stepwise cooling. The growth of the orientational order is mainly due to the incorporation of small *trans* domains and the surrounding *trans* segments into the largest *trans* domain at  $T=350$  and  $T=300$  K, whereas it is caused by the elongation of the *trans* segments in the largest *trans* domain at  $T=250$  K.

The result that the global orientational order grows in a stepwise fashion in the case of quenching can be interpreted in the following way. In the case of quenching, the system tends to be trapped in a metastable state, which corresponds to less orientationally ordered structure and stays in the metastable state for some duration. Once the system finds a path to another metastable state, it makes a sudden transition from the original metastable state to another metastable state through the path.

Here we discuss structure formation of a single polymer chain from the energetic point of view. Let us imagine a polymer chain in the all-*trans* conformation. When the polymer chain folds, the Lennard-Jones potential energy  $E_{LJ}$  decreases, whereas the bonded potential energy  $E_b$  increases. For the folded orientationally ordered structure to be formed, the total potential energy  $E_{tot}$  should be smaller than that of the all-*trans* conformation. In Fig. 17, we show potential energies,  $E_b$ ,  $E_{LJ}$ , and  $E_{tot}$ , as a function of temperature in the case of gradual stepwise cooling. Time average is taken during the last 0.8 ns. It is found from Fig. 17(a) that both the bonded potential energy and the Lennard-Jones potential energy decrease as the temperature decreases. Figure 17(b) tells us that the total potential energy becomes smaller than that of the all-*trans* conformation [a broken line in Fig.

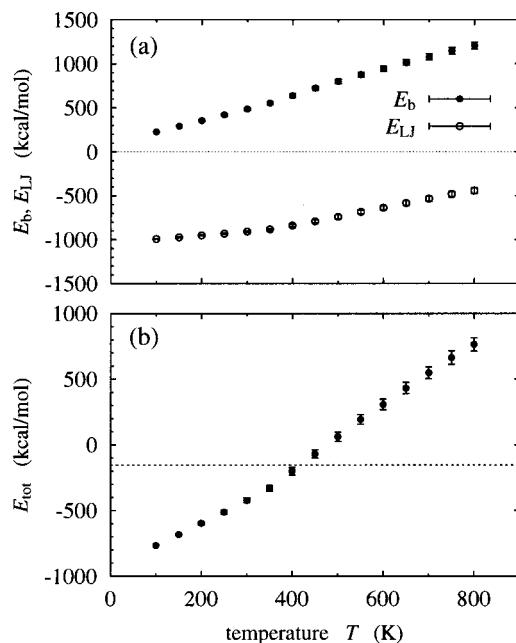


FIG. 17. The temperature dependence of: (a) the bonded potential energy  $E_b$  and the Lennard-Jones potential energy  $E_{LJ}$  and (b) the total potential energy  $E_{tot}$  in the case of gradual stepwise cooling. Time average is taken during the last 0.8 ns. A broken line represents the total potential energy of the all-*trans* conformation.

17(b)] below about 400 K. This suggests that the transition into the orientationally ordered structure takes place around  $T=400$  K, which is consistent with the above third result (iii).

Incidentally, a hypothetical grand view of self-organization is proposed by one of the authors (T.S.) on the basis of extensive computer simulations on plasmas.<sup>45–48</sup> According to this grand view, when a system is driven far from equilibrium, it will evolve to a more stable state *in a stepwise fashion*, irrespective of the types of particle interactions. Our simulation result that the orientational order grows *in a stepwise fashion* in the case of quenching lends support to this hypothetical grand view of self-organization.

In a subsequent paper, we will study structure and molecular motion during the structure formation process. For future work, we will carry out MD simulation of a single polymer chain in solution in order to investigate the effect of solvent molecules on the structure formation of a single polymer chain.

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