

## Molecular Dynamics Simulation of Structural Formation of Short Polymer Chains

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Molecular dynamics simulations are carried out to study the structural formation of 100 short polymer chains, each of which consists of 20 CH<sub>2</sub> groups. Our simulations show that the orientationally ordered structure at low temperature is formed from a random structure at high temperature by a sudden cooling. The essentially extended chains form a monolayer structure with a hexagonal packing. From detailed analyses of the local and global orientational order, it is found that the formation of the global orientational order as well as the growth of the local ordered regions proceeds stepwise. [S0031-9007(97)05205-8]

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The crystal structure of the rotator phase of *n*-alkanes, which are typical of short polymer chains with simple chemical structure, has been extensively studied by experiments [1–9], theoretical analyses [10,11], and computer simulations [12–18]. Several experimental techniques including x-ray diffraction [1–4], infrared and Raman spectroscopy [5,6], neutron scattering [7,8], and NMR [9] have been used to reveal interesting features of the molecular packing, intramolecular defects, and molecular motions in the rotator phase of *n*-alkanes. The crystal structures of the rotator phase of odd-numbered *n*-alkanes from C<sub>11</sub>H<sub>24</sub> to C<sub>25</sub>H<sub>52</sub> have been carefully investigated by Doucet *et al.* [1–3] and Ungar [4]. With increasing temperature, shorter *n*-alkanes up to C<sub>21</sub>H<sub>44</sub> transform from an ordered, orthorhombic structure to a disordered, face-centered-orthorhombic (FCO), rotator phase (referred to as *R*<sub>I</sub> or FCO phase) with orthorhombic subcell. Longer *n*-alkanes (C<sub>23</sub>H<sub>48</sub> and C<sub>25</sub>H<sub>52</sub>) show another rotator phase (referred to as *R*<sub>II</sub> or hexagonal phase) with hexagonal subcell above the *R*<sub>I</sub> phase. In the *R*<sub>I</sub> phase, the ratio of the lattice constants *a*/*b* varies rapidly with temperature from the ordinary orthorhombic value of about 1.5 to the hexagonal value  $\sqrt{3}$ .

Structures and molecular motions in the rotator phases of *n*-alkanes have been studied by Monte Carlo simulations [12–14] and molecular dynamics (MD) simulations [15–17]. In the *R*<sub>I</sub> phase, each chain has four possible orientations. By contrast, in the *R*<sub>II</sub> phase, each chain has six equivalent orientations and the molecules make sporadic large rotations to the different directions. The longitudinal motion of the molecules is very active and independent of the rotational motion. Esselink *et al.* carried out MD simulations of nucleation and melting of bulk *n*-alkane systems in order to determine the crystallization and melting temperatures [18]. They introduced a new method to identify crystalline regions and computed the crystallization rate of a nucleus.

The purpose of this Letter is to clarify the dynamical processes of the structural formation of short polymer chains at the molecular level. With a view to investigating

the transition process of short polymer chains from a random structure to the orientationally ordered structure, we perform the MD simulations of 100 short polymer chains and analyze the growth process of the local orientationally ordered regions (clusters). We believe that our simulation results can provide an essential clue to understand the molecular motion in the metastable hexagonal phase whose importance in crystal growth has been recently pointed out [19].

The present computational model is the same as that used in the previous work on the structural formation of a single long polymer chain [20]. The model polymer chain consists of a sequence of CH<sub>2</sub> groups, which are treated as united atoms. In reality, the hydrogen atoms must be explicitly considered [17]. Since we are concerned with the dynamical formation process of the orientationally ordered structure in this study, we adopt the united atom approximation. The united atoms interact via the bonded potentials (bond-stretching, bond-bending, and torsional potentials) and the nonbonded potential (12-6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential [21]. The numerical integrations of the equations of motion are performed using the velocity version of the Verlet algorithm [22]. We apply the Nosé-Hoover method in order to keep the temperature of the system constant [22]. The integration time step and the relaxation constant for the heat bath variable are 0.001 and 0.1 ps, respectively. The cutoff distance for the Lennard-Jones potential is 10.5 Å. The polymer chains are exposed to vacuum and there is no box to confine them. The total momentum and the total angular momentum are taken to be zero in order to cancel overall translation and rotation of chains. The MD simulations are carried out by the following procedure. At first, we provide a randomly distributed configuration of 100 short polymer chains, each of which consists of 20 CH<sub>2</sub> groups, at high temperature (*T* = 700 K). Note that there are no preferred directions in the system. It is then quenched to low temperatures (*T* = 300, 320, . . . , 460 K).

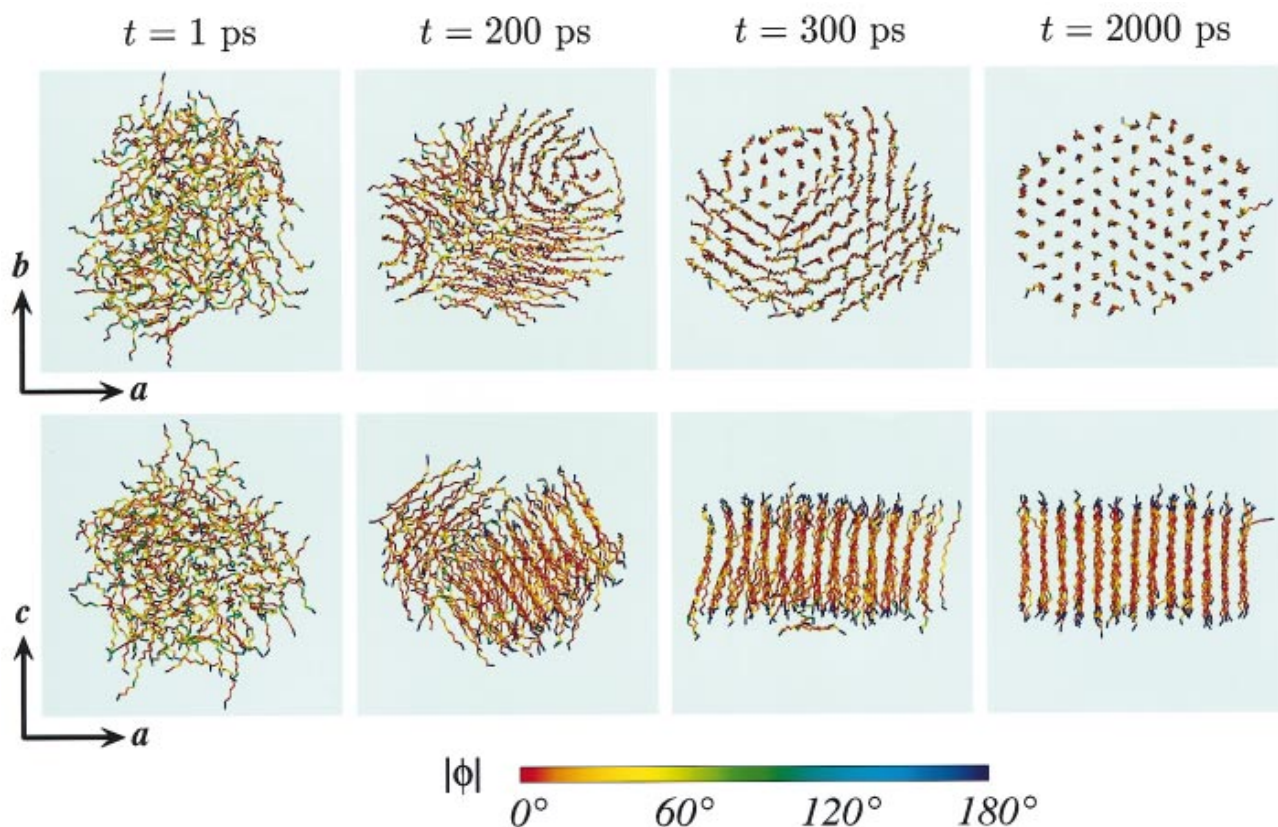


FIG. 1(color). The chain configurations of 100 short polymer chains for  $T = 400$  K at various times:  $t = 1, 200, 300,$  and  $2000$  ps (from left to right). Top and bottom figures are viewed, respectively, along the  $c$  axis and the  $b$  axis. Color denotes the absolute value of the dihedral angle around each bond and the end bonds are colored with blue.

We show, in Fig. 1, the chain configurations at various times ( $t = 1, 200, 300,$  and  $2000$  ps) obtained by our MD simulations at  $T = 400$  K. The  $a, b,$  and  $c$  axes in this figure correspond, respectively, to the crystalline  $a, b,$  and  $c$  axes in the orthorhombic system. The unit vector parallel to the  $c$  axis is defined as the eigenvector corresponding to the largest eigenvalue of an orientational order parameter tensor  $Q$  which is constructed by

$$Q_{\alpha\beta} = \langle \langle \hat{u}_{m\alpha} \hat{u}_{m\beta} \rangle_{\text{inner}} \rangle - \frac{1}{3} \delta_{\alpha\beta}, \quad (1)$$

where  $\alpha, \beta = x, y, z,$   $\hat{u}_m$  is a unit vector directed along the principal axis with the smallest moment of inertia of the  $m$ th chain, and  $\langle \dots \rangle$  and  $\langle \dots \rangle_{\text{inner}}$  denote the time average and the average over the inner 37 chains after the ordered structure is already formed (between 1500 and 2000 ps) (Fig. 2), respectively. The  $a$  and  $b$  axes are determined from the individual average central positions of the inner chains between 1500 and 2000 ps. The lattice constants  $a$  and  $b$  are calculated as  $a = 0.750$  nm and  $b = 0.433$  nm, respectively. Since the ratio  $a/b$  is equal to  $1.733 \approx \sqrt{3}$ , polymer chains are found to be packed hexagonally (Fig. 2). From Fig. 1, we find the following features: (i) In the early time ( $t = 1$  ps), *gauche* states (deep green to light blue) are excited in various places

and the configuration of the polymer chains is *random*. (ii) With the elapse of time, the local orientationally ordered regions (clusters) grow in several positions ( $t = 200$  ps) and at last they coalesce into a large cluster ( $t = 300$  ps). (iii) At  $t = 2000$  ps, a highly ordered structure is formed and almost all the bonds are in the *trans* state.

In order to investigate the *local* orientational order, we introduce the concept of “cluster” according to Ref. [18]. The definition of cluster is as follows. Two polymer chains belong to the same cluster if the following two conditions are satisfied: (i)  $|\mathbf{r}_c^i - \mathbf{r}_c^j| < r_0$  and (ii)  $\alpha_{ij} < \alpha_0$ , where  $\mathbf{r}_c^i$  is the position vector of the center of mass of the  $i$ th chain,  $\alpha_{ij}$  is the angle between the principal axis with the smallest moment of inertia of the  $i$ th chain and that of the  $j$ th chain and satisfies  $0 \leq \alpha_{ij} \leq \pi/2$ . In our calculations, we set  $r_0 = 1.5\sigma$  ( $\sigma = 0.36239$  nm) and  $\alpha_0 = 10^\circ$ . We show, in Fig. 3, the number of polymer chains in the largest cluster as a function of time. At  $T = 400$  K, from Fig. 3(a), only small clusters whose sizes are smaller than 10 can be seen up to  $t = 120$  ps. The size of the largest cluster  $s$  starts to increase at  $t = 120$  ps and reaches about 30 at  $t = 150$  ps. Between 150 and 210 ps,  $s$  only fluctuates around a mean value. The size  $s$  increases rapidly at  $t = 210$  ps and becomes

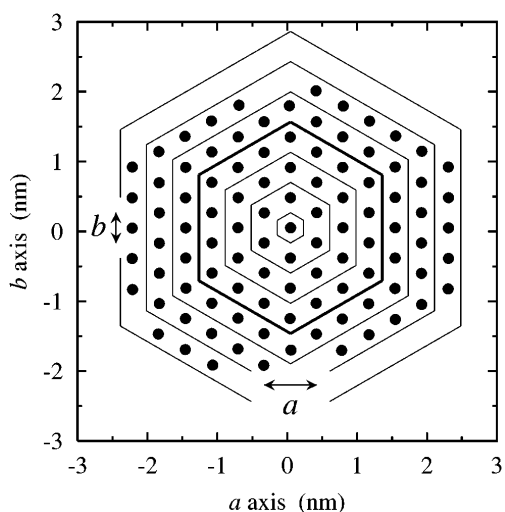


FIG. 2. The center-of-mass positions of individual polymer chains for  $T = 400$  K viewed along the  $c$  axis averaged between 1500 and 2000 ps. The lattice constants  $a$  and  $b$  are, respectively,  $a = 0.750$  nm and  $b = 0.433$  nm. Hexagons are depicted in order to show a hexagonal packing of the polymer chains. “Inner chains” are defined as the central 37 chains within a thick hexagon.

over 50. At  $t = 240$  ps,  $s$  also increases sharply and reaches about 90. Thus it is concluded that the growth of the clusters proceeds *stepwise*. This stepwise behavior can be seen more remarkably at  $T = 440$  K [Fig. 3(b)]. At  $T = 440$  K, there are two marked increases in the largest cluster size  $s$  at  $t = 130$  ps and  $t = 240$  ps.

In order to investigate the growth process of the *global* bond-orientational order, we calculate the global bond-orientational order parameter  $S$ , which is defined by

$$S = \frac{1}{N(n-2)} \sum_{m=1}^N \sum_{i=3}^n \frac{3 \cos^2 \psi_i^m - 1}{2}, \quad (2)$$

where  $N$  and  $n$  are, respectively, the number of polymer chains and the number of  $\text{CH}_2$  groups per polymer chain ( $N = 100$ ,  $n = 20$ ) and  $\psi_i^m$  is the angle between the subbond vector of the  $m$ th chain  $\mathbf{b}_i^m$  and the  $c$  axis. The subbond vector  $\mathbf{b}_i^m = (\mathbf{r}_i^m - \mathbf{r}_{i-2}^m)/2$  is the vector formed by connecting centers of two adjacent bonds  $i$  and  $i - 1$  of the  $m$ th chain and  $\mathbf{r}_i^m$  represents the position vector of the  $i$ th atom of the  $m$ th chain. The parameter  $S$  would take a value of 1.0, 0.0, or  $-0.5$ , respectively, for polymer chains whose subbonds are perfectly parallel, random, or perpendicular to the  $c$  axis. We show the time dependence of  $S$  in Fig. 4. At  $T = 400$  K [Fig. 4(a)], the parameter  $S$  takes a value near zero up to  $t \approx 120$  ps, which shows that there is no global bond-orientational order in this time region. The value of  $S$  starts to increase at  $t \approx 120$  ps and the increase continues until  $t \approx 300$  ps. While it is not so clear in Fig. 4(a) that the growth of the bond-orientational order also proceeds stepwise, we can clearly see the stepwise behavior in

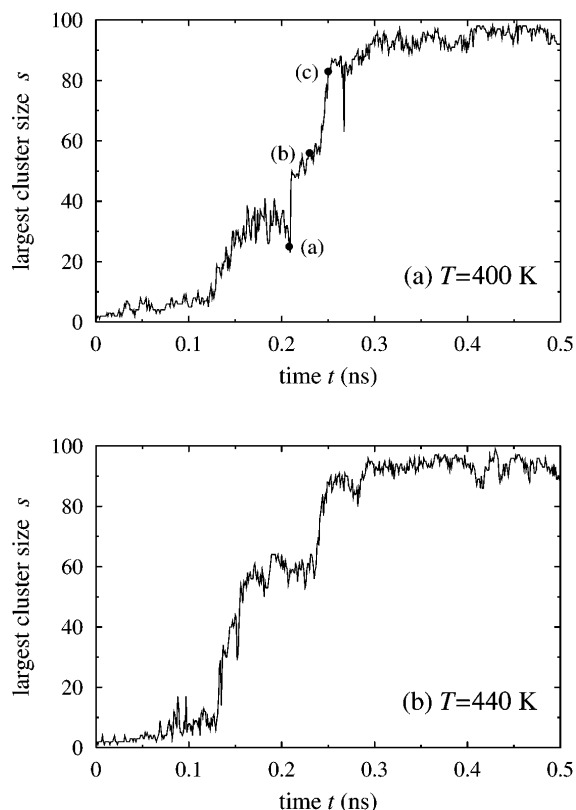


FIG. 3. The size of the largest cluster  $s$  versus time  $t$  (a) at  $T = 400$  K and (b) at  $T = 440$  K. Filled circles (a), (b), and (c) in part (a) correspond to  $t = 208$ , 230, and 250 ps, respectively (see Fig. 5 below).

Fig. 4(b) at  $T = 440$  K. At  $T = 440$  K, there are two sharp increases in the parameter  $S$  at  $t \approx 130$  ps and  $t \approx 240$  ps as seen in the largest cluster size  $s$  [Fig. 3(b)].

Finally we study the coalescence of clusters. We show clusters at  $t = 208$ , 230, and 250 ps for  $T = 400$  K in Fig. 5. It is found from this figure that two large clusters (red and blue) at  $t = 208$  ps coalesce into a cluster (red) at  $t = 230$  ps and three clusters (red, blue, and yellow) at  $t = 230$  ps coalesce into an overall cluster (red) at  $t = 250$  ps. During coalescence, the surrounding small clusters (gray) are also incorporated into a large cluster.

In summary, by carrying out MD simulations of 100 short polymer chains and analyzing the growth process of clusters, we have obtained the following new results: (1) The orientationally ordered structure at low temperature is formed from a random structure at high temperature by cooling. The essentially extended chains form an orientationally ordered structure with a hexagonal packing. (2) The local orientationally ordered clusters grow in a *stepwise* fashion. (3) The formation of the global orientational order also proceeds *stepwise* in connection with the growth of clusters.

We have also carried out the MD simulations of the systems with  $(n, N) = (20, 80)$  and  $(20, 120)$  at

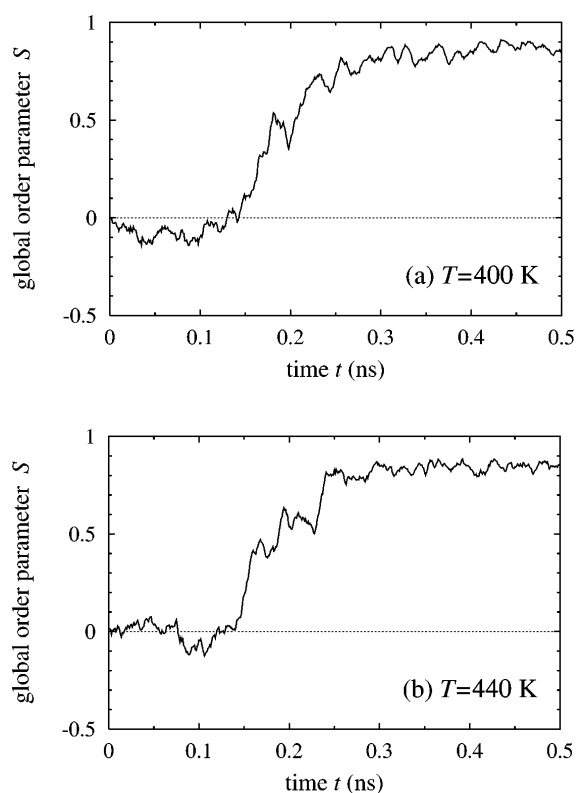


FIG. 4. The global bond-orientational order parameter  $S$  versus time  $t$  (a) at  $T = 400$  K and (b) at  $T = 440$  K.

$T = 400$  K. Our simulation results all indicate that the steps exist in the process of the structural formation.

In this study, we dealt with the short polymer chains in order to ignore the effects of the entanglement. As a result, the obtained structure was a monolayer structure in which the essentially extended chains aggregated two

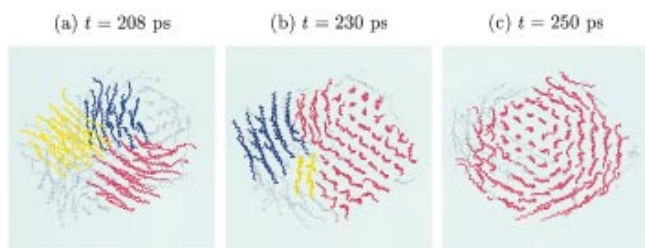


FIG. 5(color). Coalescence of clusters: (a)  $t = 208$  ps, (b)  $t = 230$  ps, and (c)  $t = 250$  ps, which are indicated by filled circles in Fig. 3(a). The largest, the second largest, and the third largest clusters are, respectively, denoted by red, blue, and yellow colors. Gray denotes small clusters whose sizes are smaller than 5.

dimensionally. We will carry out MD simulations of long polymer chains in order to investigate the effect of the entanglement on the structural formation.

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