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A STUDY ON THE STRUCTURAL TRANSITION OF A SINGLE POLYMER CHAIN BY PARALLEL TEMPERING MOLECULAR DYNAMICS SIMULATION[*]

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Abstract The structural transition of a single polymer chain with chain length of 100, 200 and 300 beads was investigated by parallel tempering MD simulation. Our simulation results can capture the structural change from random coil to orientationally ordered structure with decreasing temperature. The clear transition was observed on the curves of radius of gyration and global orientational order parameter P as the function of temperature, which demonstrated structural formation of a single polymer chain. The linear relationships between three components of square radius of gyration R_{gx}^2, R_{gy}^2, R_{gz}^2 and global orientational order P can be obtained under the structurally transformational process. The slope of the linear relationship between x (or y-axis) component R_{gx}^2 (or R_{gy}^2) and P is negative, while that of R_{gz}^2 as the function of P is positive. The absolute value of slope is proportional to the chain length. Once the single polymer chain takes the random coil or ordered configuration, the linear relationship is invalid. The conformational change was also analyzed on microscopic scale. The polymer chain can be treated as the construction of rigid stems connecting by flexible loops. The deviation from exponentially decreased behavior of stem length distribution becomes prominent, indicating a stiffening of the chain arises leading to more and more segments ending up in the *trans* state with decreasing temperature. The stem length N_{tr} is about 21 bonds indicating the polymer chain is ordered with the specific fold length. So, the simulation results, which show the prototype of a liquid-crystalline polymer chain, are helpful to understand the crystallization process of crystalline polymers.

Keywords: A polymer chain; Structural transition; Parallel tempering molecular dynamics.

INTRODUCTION

Polymeric materials, which have so many freedom degrees, show various structural diversity and are extensively interested by industrialists and scientists. The structure formation of polymer chains, such as polymer crystallization has recently become the focus of attention in chemistry, physics, biology and material science. Many polymeric materials crystallize when cooled below their melting temperature and form the folded structures induced by van der Waals interaction. The varying degrees of crystallinity depend on the conditions under which the material was formed, the treatment history, as well as the chemical constitution. A lot of studies through experimental and theoretical efforts[1–5] have been focused mainly on the crystal nucleation and growth mechanism, where critical nuclei are formed from a metastable state during the first stages of crystallization, leading ultimately to the growth of crystal domains. Attention has also been given to the structure during the precrystallization characterized[3, 6, 7] as an unstable phase separation initiated by density and orientational

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fluctuations[8].

It's well-known that different conformations represent varying distances between the atoms or groups rotating about the bond, which determine the amount and type of interaction between adjacent atoms or groups. Therefore different conformations may represent different potential energies of the molecule. The rotational potential energy of a bond in a polymer generally exhibits several stable states: *trans* (t), *gauche* plus (g^+), and *gauche* minus (g^-) separated by barriers. The continuous *trans* states in the polymer chain show the rigidity of chain molecules. The parallel ordering of polymers is related to the increase of chain rigidity, which caused by an increase in the average length of rigid *trans* segments along the polymer backbone during the pretransition state occurring before crystallization. So, the transitions from state to state, *i.e.*, comformational changes, are an important relaxation mode of motion manifested in numerous physical properties.

Computer simulation is one of powerful ways to understand more detailed mechanism of the structure formation at atomistic level. Over the last decades, several computer simulation studies have been carried out in relation to the structural formation of polymer chain systems by molecular dynamics (MD) or Monte Carlo (MC) simulation in order to overcome experimental difficulties[9–18]. Despite the progress of computer power, the simulation of complex materials with all atomic details remains unfeasible for many relevant applications. There still remain many basic questions unanswered, such as the chain folded crystallization is intuitively acknowledged, but it is quite uncertain when and how the chain folds and why the thickness of the lamella is so uniform. On the other hand, the computer simulation results highly depend on what kind of system we use. Systems with a sufficiently high temperature pass over the potential, while it's not possible to achieve good sampling of systems that have a free-energy landscape with local minima at the low temperature. So, lots of efforts are kept spending to construct appropriate models retaining properties of the original chemistry and new simulation method, such as simulating annealing[19], J-walking[20] and parallel tempering (PT)[21–23], tries to solve these kinds of problems. The present paper reports the simulation results carried out by PTMD algorithms on a single polymer chain covering wide temperature range, especially in pretransition state to clarify the mechanisms of structure formation at molecular level. In particular, our concern is to investigate the orientational correlation of local *trans* segments and conformational transition.

SIMULATION MODEL AND METHOD

For many problems in polymer science, a detailed description of the chemical structure of the polymer is not necessary, and it suffices to focus on a coarse-grained model of a polymer chain that keeps only the essential features of the macromolecule, such as connectivity of the chain molecule, flexibility and non-bonded interaction (excluded volume).

The present computational model is a single chain described as a sequence of beads. The united beads interact via the bonded potentials (bond-stretching, bond-bending and torsional potentials) and the non-bonded potential (12-6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential[24]. The behavior of a single chain with N = 100, 200 and 300 beads has been studied by means of PTMD technique here.

We use four potential functions to construct the conformation of a model chain:

(i) The bond-stretching potential energies for every couple of adjacent beads connected by covalent bonds,

$$E_{\text{stretch}} = \sum_{i=2}^{N} \frac{1}{2} k_{\text{d}} (l_i - l_0)^2 \tag{1}$$

where the equilibrium bond length l_0 = 0.153 nm and l_i is the bond length between beads i-1 and i. The bond-stretching potential energy constant $k_\text{d} = 2.929 \times 10^5$ kJ/(nm^2 mol).

(ii) The bond-bending potential energies are defined for every triplet of adjacent beads,

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

where the equilibrium bond angle θ_0 = 1.231 rad and θ_i is the bond angle between three beads i–2, i–1 and i. The bond-bending potential energy constant k_θ = 418.4 kJ/(rad^2 mol).

(iii) The threefold torsional energies are defined for every quadruplet of adjacent beads,

$$E_{\text{torsion}} = \sum_{i=4}^{N} \frac{1}{2} k_\varphi (1 + \cos(3\varphi_i)) \tag{3}$$

where φ_i is the dihedral angle of two planes consisting of four consecutive beads i–3, i–2, i–1 and i along the backbone. The constant of torsional energy k_φ = 8.368 kJ/mol.

(iv) The van der Waals interaction is imposed on all pairs of the united atoms apart more than two bonds by the truncated 12-6 Lennard-Jones potential

$$E_{LJ} = \sum_{i=1}^{N} \sum_{j=1}^{N} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right] \quad (j - i \geq 3) \tag{4}$$

where r_{ij} is the distance between atoms i and j. The values of the van der Waals interaction parameters are ε = 0.8301 kJ/mol and σ = 0.3624 nm.

All the results will be presented in terms of reduced units. It follows that the reduced temperature, T^*, is equal to K_BT/ε, the reduced energy is E/ε, and the reduced time is $t\sqrt{\varepsilon / m\sigma^2}$. A single polymer is exposed to vacuum and other molecules such as solvent molecules are not considered. The MD simulations are performed from random configuration of the polymer chain at high temperature. And then the system is quenched to low temperature and simulations of 500 ns (1×10^7 time steps) are carried out under several temperatures from 1.5 to 0.3. The Nose-Hoover method is applied to keep the temperature of system constant[25, 26]. The integration time step and a relaxation constant are 2.5 fs and 0.025 ps respectively. The cutoff radius r_{cutoff} = 0.95 nm is used in our simulation. After equilibrating the polymer chain for 2.5 ns (50000 time steps), a polymer chain is treated as equilibrium state and taken count. The equilibrium geometries and parameters for the force field are the same as those described by Mayo, Olafson, and Goddard[11]. The time average is taken during the last 497.5 ns in each case. PTMD was executed under 10 temperatures, *i.e.*, 10 NVT canonical ensemble replicas in our simulation work.

The mass of chain is fixed to cancel overall chain translation. Here we also introduce the coordinate system with the three principal axes of inertia in order to analyze the anisotropic structure. 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. The radius of gyration tensor S characterizes the overall shape and orientation of a polymer chain. It is defined as

$$S = \begin{vmatrix} \overline{(x_i - x_0)^2} & \overline{(x_i - x_0)(y_i - y_0)} & \overline{(x_i - x_0)(z_i - z_0)} \\ \overline{(y_i - y_0)(x_i - x_0)} & \overline{(y_i - y_0)^2} & \overline{(y_i - y_0)(z_i - z_0)} \\ \overline{(z_i - z_0)(x_i - x_0)} & \overline{(z_i - z_0)(y_i - y_0)} & \overline{(z_i - z_0)^2} \end{vmatrix} \tag{5}$$

The diagonalization of the S matrix gives its principal values (eigenvalues) and their orientation (eigenvectors) in the Cartesian frame.

In the following sections, the detailed simulation results on the structure formation of a single polymer chain will be presented. The chain configuration and global orientational order in the process of structure formation have been analyzed by quenching at various temperatures.

RESULTS AND DISCUSSION

Radius of Gyration

We investigate a change in the single polymer chain dimensions during the structural formation process first.

The radius of gyration R_g is a basic measurement of the overall size of a chain molecule. To get insight in the average shape of a single chain molecule, the coordinate system with three principal axes of inertia of a single polymer chain is introduced. And the relation $R_g^2 = R_{gx}^2 + R_{gy}^2 + R_{gz}^2$ holds. Here, the radius of gyration, which shows the chain configurational information of a single polymer chain exposed to vacuum, is mainly discussed.

The temperature dependence of the radius of gyration with the chain length of 200 beads is shown in Fig. 1(a). The simulation results indicate the good coherence with the previous work[10]. At high temperatures $T^* > 1.0$, R_g decreases as the temperature decreases, which indicates the characteristic features of a random coil. In the medium temperature range $0.5 < T^* < 0.9$, R_g increases and the difference between R_{gz} and R_{gx} (or R_{gy}) become more and more evident as the temperature decreases, which indicates the polymer chain takes anisotropic configuration. When the temperature is lower than 0.5, the radius of gyration R_g reaches a plateau with almost constant value. It's clearly seen from the snapshots of the single chain equilibrium configuration under various temperatures (T^* = 0.5, 0.8, 1.2) in Fig. 1(a). Those configurations indicate that (i), at low temperatures, *trans* state is dominated, which makes the ordered structure with obvious anisotropy. (ii), at high temperatures, *gauche* states are located everywhere and a polymer chain takes a random coil. (iii) In the mid temperatures, a polymer chain is partly ordered and the *gauche* states are mainly located exclusively in the fold surfaces.

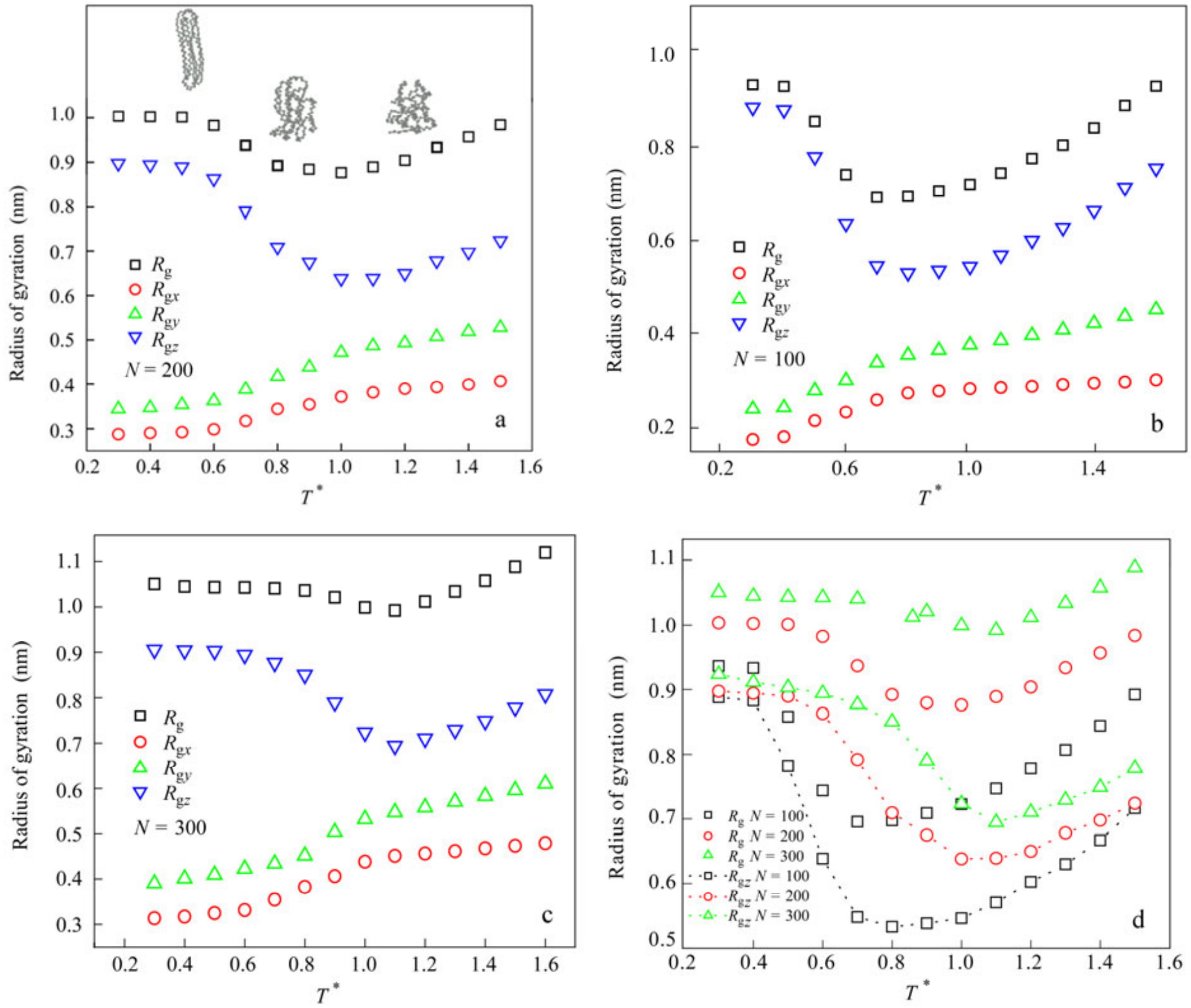

Fig. 1 The total and components of radius of gyration versus reduced temperature T^* with chain length of (a) $N = 200$, (b) N = 100, (c) $N = 300$ and (d) contrast results with $N = 100, 200, 300$

The calculations on the radius of gyration as the function of reduced temperature with the polymer chain length of 100 and 300 beads are shown in Figs. 1(b) and 1(c). The curves of radius of gyration R_g and the components of radius of gyration R_{gx}, R_{gy}, R_{gz} show the similar tendency as that in Fig. 1(a). The values of R_g (or R_{gz}), after the gradual decrease in the high temperature region, rapidly increase, and then reach to a constant with the temperature decreasing. While R_{gx} (or R_{gy}) keeps decrease with cooling the polymer chain. The difference between Figs. 1(a), 1(b) and 1(c) is the transition temperature. The critical temperature point indicating the structure transition is 1.0, 0.9, and 0.7 for the chain with length of 300, 200 and 100 beads, respectively. In the following discussion, we can find out that such conclusion is according to the structural transition with temperature shown by the global bond-orientational order parameter P in Fig. 2.

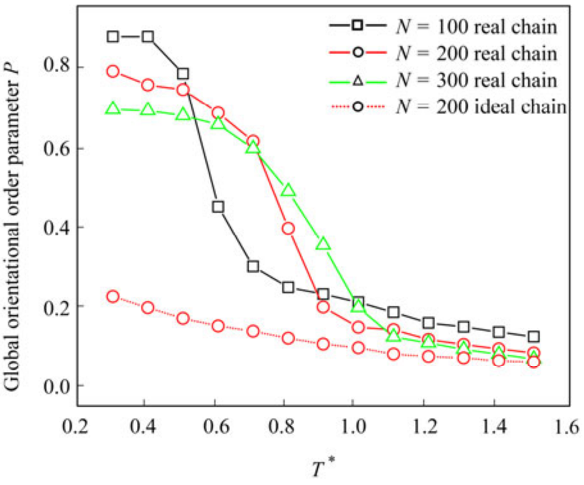

Fig. 2 The global orientational order parameter P versus reduced temperature T^*
The real chain is constructed by bond and non-bond potential energies; The ideal chain is constructed by bond interaction only without van der Waals interaction.

The size of a single polymer with the different chain lengths can be obtained from the data of radius of gyration. Figure 1(d) shows the radii of gyration as a function of the reduced temperature with chain length N = 100, 200 and 300, respectively. With the increase of chain length, the value of R_g increases, while the z-axis component R_{gz} is not changed much especially in the low temperature range than in the transition one. It means the folded length of single chain is independent on chain length and the increase of total radius of gyration R_g is mainly due to the increase of x- and y- components R_{gx} and R_{gz}. It's also clearly shown in Fig. 1(d) that the transition temperature increases with the chain length increasing.

Global Orientational Order Parameter

We also calculate the bond-orientational order parameter P defined by

$$P = \frac{1}{N-2} \sum_{i=3}^{N} \left(\frac{3\cos^2 \varphi_i - 1}{2} \right) \tag{6}$$

Here φ_i is the angle between the bond vector and the z-axis of the chain molecule coordinate system and N is the number of beads. The parameter P would takes a value of 1 for a polymer chain whose bonds are perfectly parallel, and that of 0 for randomly oriented. We have monitored the value of P for the whole chain. The temperature dependence of the global orientational order parameter P is plotted in Fig. 2.

Figure 2 shows the global orientational order parameter P of a real single polymer chain constructed by the four potential functions (1)–(4). It takes a value near 0 under high temperatures, which indicates the chain takes a random coil configuration. After the value of P gradually increases with temperature decrease in the range of

$T^* > 1.1$, it increases sharply with decreasing temperature leading to a large growth rate of the orientational order. After P reaching a plateau, it increases slowly with temperature decrease indicating the growth rate of the orientational order becomes small and the orientationally ordered structure is formed. Then the global conformational change of a single polymer chain ceases and only the local motion of united atoms with no global change takes place. The simulation results on polymer chain with different chain lengths show the same tendency, but the critical temperature that bonds starts to become parallel is $T^* = 1.0, 0.9, 0.7$ for chain length of 300, 200 and 100 beads, respectively. Meanwhile, the orientational order parameter P of polymer chain with different chain lengths reaches the plateau at the same temperature about $T^* = 0.5$. It means for a longer chain molecule, bonds start to become parallel at higher temperature, and the whole process to form ordered structure is in a larger temperature range as compared with short chains. Focus on the plateau, the short chain has the higher value of parameter P than the long polymer chain, which indicates the bonds are almost paralleled and the longer chain is partially paralleled under the same reduced temperature. The simulation results show that with decreasing temperature the bond-orientational order increases, in agreement with changes from a coiled state to a more ordered one, reminiscent of a single molecule crystal. In order to show the effect of the van der Waals interaction between the united atoms during the folding process, the parameter P of an ideal chain constructed by bond-interaction including bond-stretching, bond-bending and torsional potential energies and without van der Waals interaction, is plotted in Fig. 2. In this case, the value of P is increasing slowly with the decreasing temperature and the transition temperature is not found. The results indicate the van der Waals interaction plays the main role during the polymer folding process.

The temperature dependence of the parameter P, as well as the radius of gyration R_g, shows a clear transition from a random-coil structure to a bond-orientationally ordered structure. In the above discussion, we obtained the same structural transition temperature obtained by the radius of gyration and bond-orientational order parameter P as the function of temperature if the chain length is fixed. In order to study the transition of chain configuration and focus on its folding process, the relationships between the square components of radius of gyration R_{gx}^2, R_{gy}^2 or R_{gz}^2 and bond-orientational order parameter P are well discussed here.

The radius of gyration, which satisfied $R_g^2 = R_{gx}^2 + R_{gy}^2 + R_{gz}^2$, can be expressed in terms of order parameter P as $R_{gx}^2 = R_{gy}^2 = (1-P) \times R_g^2/3$ and $R_{gz}^2 = (1 + 2P) \times R_g^2/3$. Those two formulae are verified by simulation results on 3 components of radius of gyration as the function of bond-orientational order parameter P and the data are plotted in Fig. 3. We know the conformation of a freely-jointed-chain consisting of n bonds and with bond length l in nematic state is anisotropic and its radius of gyration components along the z- and x/y-axes are evaluated as follows

$$< R_{gx,}^2\ R_{gy}^2 >= \frac{nl^2(1-P)}{18} \tag{7}$$

$$< R_{gz}^2 >= \frac{1}{6} < (\sum_{i=1}^{n} l_{iz})^2 >= \frac{1}{6}(\sum_{i=1}^{n} < l_{iz}^2 > + \sum_{i=1}^{n} < l_{iz} \cdot l_{jz} >) = \frac{1}{6} n < l_{iz}^2 >= \frac{1}{6} nl^2 < \cos^2\theta >= \frac{nl^2(2P+1)}{18} \tag{8}$$

From Eqs. (7) and (8), the slope of linear relationship between R_{gx}^2 (or R_{gy}^2) and P is $-nl^2/18$, and the slope of R_{gz}^2 as the function of P is the positive value $2nl^2/18$. In Figs. 3(a), 3(b) or 3(c), the linear relationships between R_{gx}^2, R_{gy}^2 or R_{gz}^2 and P are also obtained in the middle range $0.2 < P < 0.6$, which indicates the polymer chain molecule under the folding process. When the chain takes ordered structure with $P > 0.6$, or random coil configuration $P < 0.2$, such linear relationship is not valid. Therefore, the linear fitting was applied under the scale $0.2 < P < 0.6$. In Fig. 3(a) or 3(b), it shows clearly that R_{gx}^2 or R_{gy}^2 has the negative slope as the function of bond-orientational order parameter P. Meanwhile, the positive slope of R_{gz}^2 as the function of P is obtained in

Fig. 3(c). The absolute value of slope increases with the chain length increasing. The slope of R_{gz}^2 as the function of P is 0.52, 1.10 and 1.24 for a polymer chain with 100, 200 and 300 beads respectively, and it is nearly proportional to the chain length. Comparing the Eq. (7) in the case of freely-jointed-chain, the slopes of R_{gx}^2 and R_{gy}^2 as the function of P in Figs. 3(a) and 3(b) are not same. The absolute value of slope along y-component is about 2 times larger than the one of x-component. Under the low value of P, the polymer chain will be expanded as the bond energy increasing. Under the high value of P, single polymer chain is folded and limited into small finite space, and then the radius of gyration will not change much as the low kinetic energy and the linear relationship is unconspicuous.

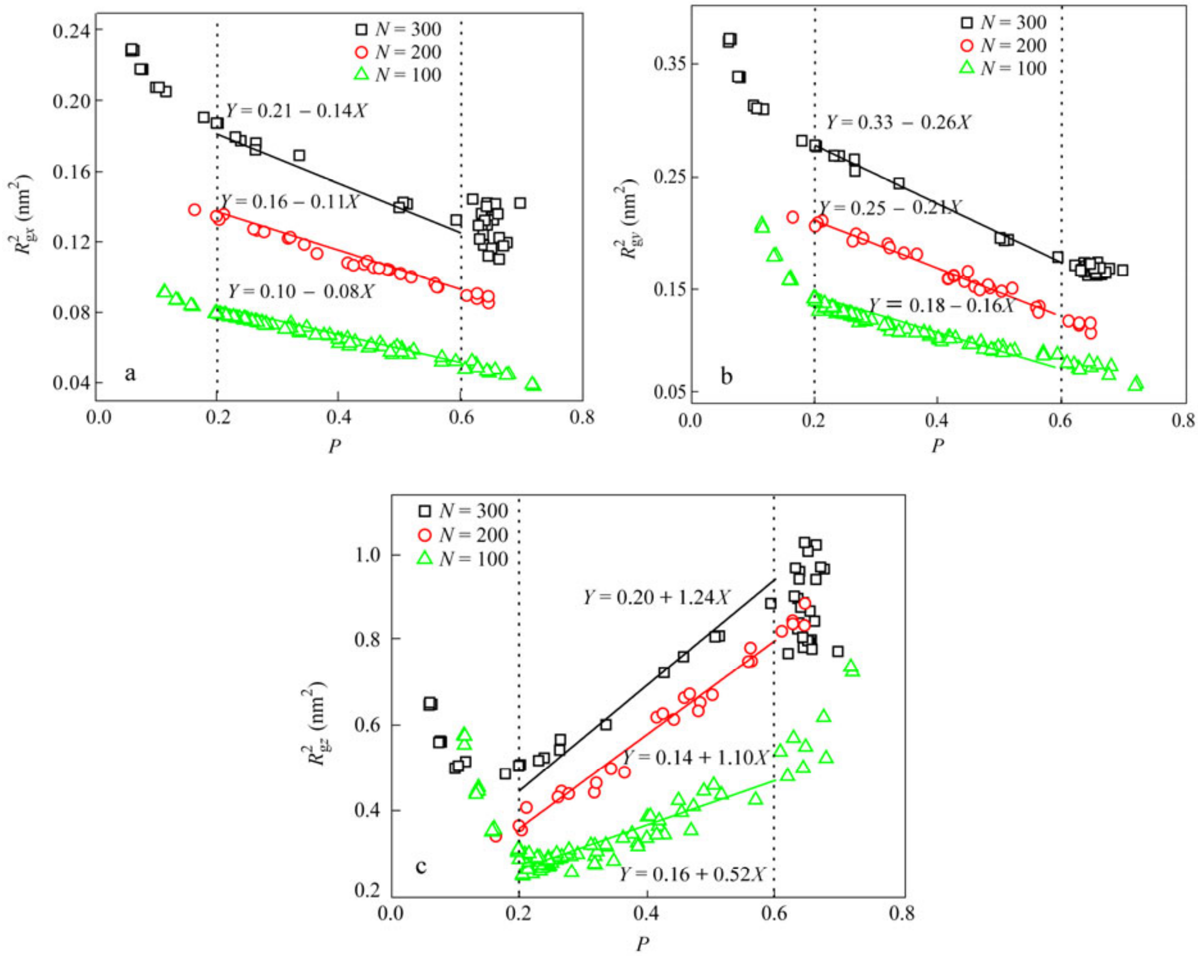

Fig. 3 The relationship between orientational order P and square component of radius of gyration along: (a) x-axis, (b) y-axis and (c) z-axis

Stem Length and Parallel Ordering Distribution

In this subsection, we investigate the conformational change of a single polymer chain by microscopic analysis. The bond of a single chain molecule takes the *trans* or *gauche* state, which is defined by dihedral angle $|\varphi| \le \pi/3$ or $|\varphi| > \pi/3$, respectively. Here, φ is the dihedral angle. We introduce the concept of a stem defined by more than 3 consecutive all-*trans* segments and study the stem length distribution at various temperatures. A single polymer chain is constructed by several stems with different stem length N_{tr}, *i.e.*, the number of consecutive *trans* bonds, and connected by loops. The distribution of stem length N_{tr} was analyzed as the function of temperature.

In the case of a chain without van der Waals interaction, the distribution of stem length can be calculated exactly from the torsion potential and decreases exponentially with the increase of the number of *trans* segment N_{tr}. In our work, the distribution of the stem size $P(N_{\mathrm{tr}})$ is normalized and the results are shown in Fig. 4. At high temperature the exponential decrease with the increase of stem size is observed, which shows the characteristic of the polymer chain without non-bond interaction. The reason is that each bond takes the *trans* or *gauche* state randomly with no spatial correlation under the high temperature. When the temperature keeps decreasing, the deviations from exponentially decreased behavior become more and more prominent. Highly non exponential behavior is observed when the temperature is low enough. For example, the linear-lg plot of stem length distribution $P(N_{\mathrm{tr}})$ is deviated slightly from exponential decrease at $T^* = 0.7$ in Fig. 4(a). And when $T^* < 0.7$, a peak is visible and becomes more and more obvious with the temperature decreasing. In other cases with chain length $N = 200$ and 300, the same tendencies can be obtained in Fig. 4(b) and 4(c). The difference between Figs. 4(a), 4(b) and 4(c) is that the critical temperature for deviation from the exponentially decreasing behavior is increasing with the polymer chain length, *i.e.*, $T^* = 0.9$ and $T^* = 1.0$ for a polymer chain with 200 and 300 beads. These results are exactly agreed with the conclusion obtained from the temperature dependence of radius of gyration in Fig. 1(d). It can be seen that stems with a specific length are preferentially formed. The peak of stem length N_{tr} is about 21 bonds. It indicates the polymer chain is folded with a specific length when the temperature is below its transition temperature. So the distribution of stem length exhibits an exponential decrease and then most of stems fixed to a specific length, indicating collective effects occurring in the molecule with decreasing temperature approaching the crystalline-like state.

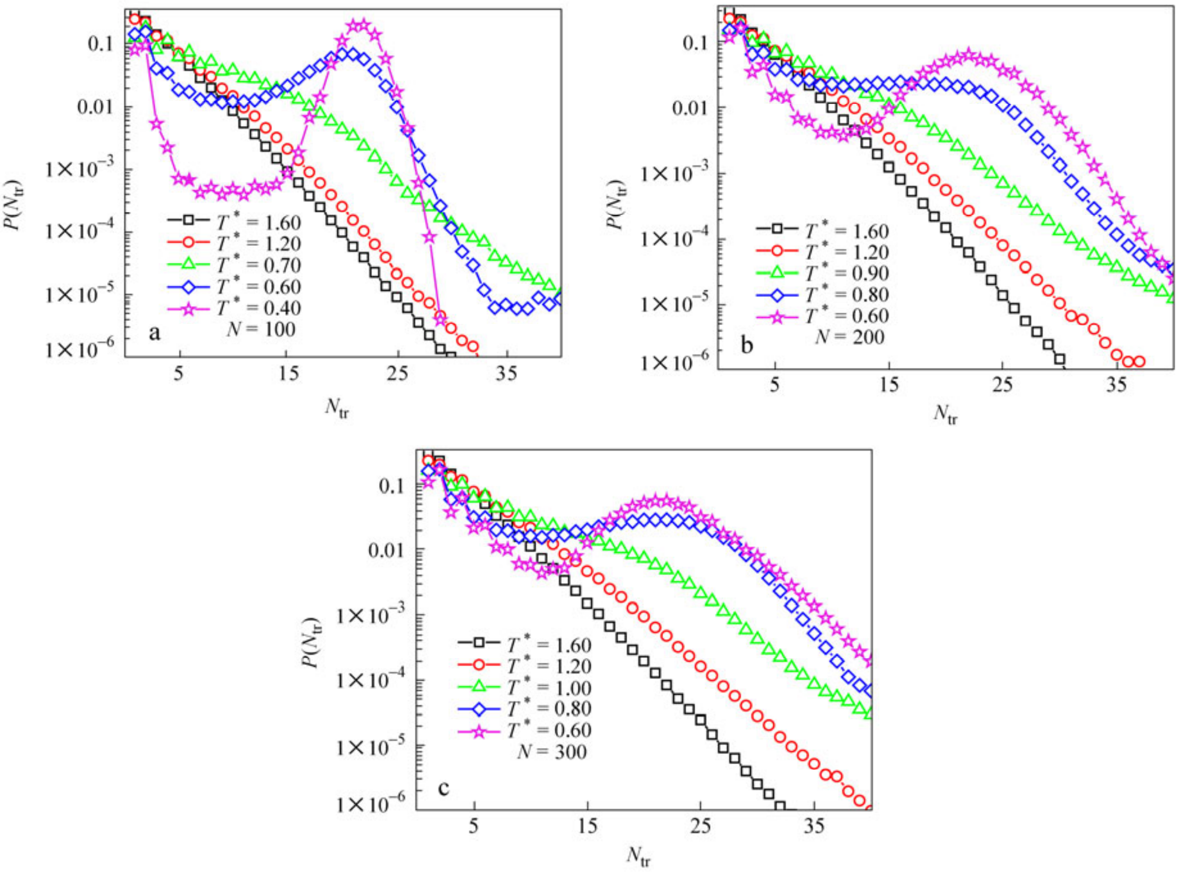

Fig. 4 Distribution of stem length under different temperatures in linear-lg plot with chain length (a) $N = 100$, (b) $N = 200$ and (c) $N = 300$ beads

In Fig. 5, the average size, *i.e.*, the number of segments over all stems or loops as parts of a polymer chain is calculated under certain temperature. In Fig, 5(a), the average length of stems is decreased with the increase of temperature and approached to the minimum value 3, which as the cutoff of stem definition. At high temperature, the average stem length does not change much with the different chain lengths. It demonstrates that the average stem length is independent on the chain length when the polymer chain takes a random coil configuration. The increase of stem length shows the structure transition from random coil to orientationally ordered structure with the decrease of temperature. Comparing chains of different lengths, the average value of stem length is increased rapidly in the case of longer polymer chain under the cooling process. In Fig, 5(b), the average length of loops is decreased at high temperature region and then increased during the cooling process. The minimum value is about 1.33 and located at $T^* = 1.0$, 0.9, 0.7 for polymer chains with $N = 300$, 200, 100 beads, which are the same as the structural transition temperature. It has also been concluded from radius of gyration and bond-orientational order parameter P as the function of temperature. The same result that the transition temperature increases with the chain length can be obtained from Fig. 5 by investigating the average stem and loop length. When the temperature is above the transition one, the polymer chain takes a random coil configuration and the total number of the unit including a stem and a loop is almost constant as the function of temperature. So the curves of the average stem and loop length show the inverse tendency with the temperature. When the temperature is below the critical one, a polymer chain takes a folded structure, including stems with fixed length and loops always located in the fold surfaces.

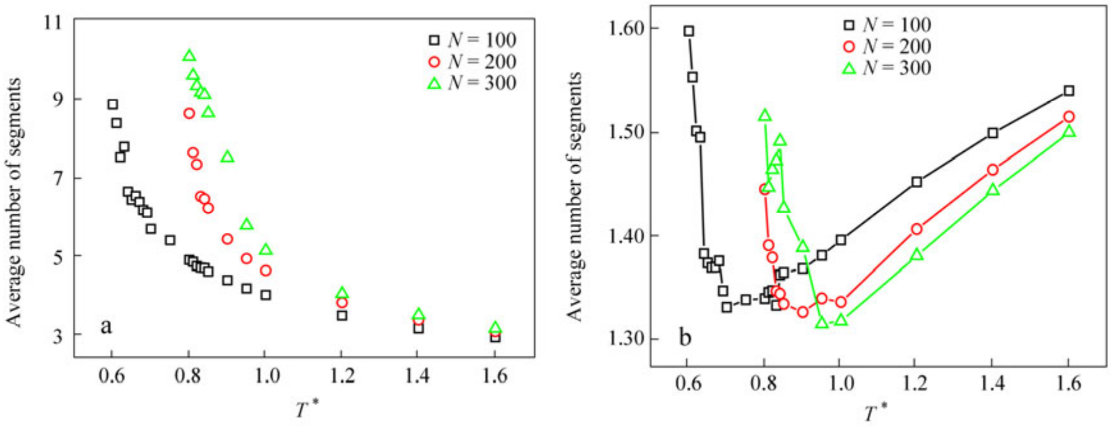

Fig. 5 (a) The average stem length with different chain length as the function of the reduced temperature; (b) The average loop length with different chain length as the function of the reduced temperature

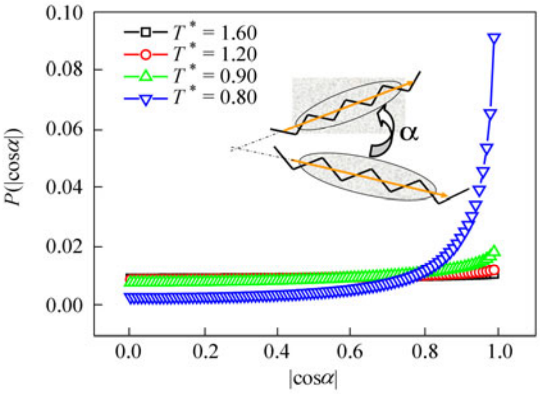

Fig. 6 Probability density distribution of the angle between 2 stems under different temperatures
A schematic definition of stems and angle α between 2 stems is given in the Figure.

Each stem has its own coordinate system. The angle α between 2 directions of the z-axis is an available parameter to examine the orientation between stems. The probability density distribution of angle α between two stems under different temperatures, as well as the stem length distribution, was calculated with the chain length $N = 200$. In Fig. 6, the value of abscissa represents the absolute value of cosine function of angle α between 2 stems and y-axis represents the normalized probability density distribution $P(|\cos\alpha|)$. It's clearly seen that at high temperatures, the probability density of angle distributions is quite the same, which shows the stems arrange randomly without particular orientation. With the decreasing temperature, the probability density distribution $P(|\cos\alpha|)$ shifts to large values close to 1, indicating the stems are tended to be parallel or anti-parallel, and the single polymer chain folds with global orientation as we mentioned before.

CONCLUSIONS

In this article, we have carried out PTMD simulation of a single polymer chain with 100, 200 and 300 beads under wide temperature range. The configurational transition was discussed in detail by investigating the global and local structural parameters such as radius of gyration, stem length distribution and orientational order. The current numerical results indicate:

(i) The curves of radius of gyration and its components as the function of temperature demonstrated the structural formation of a single polymer chain in vacuum. R_g decreases as the temperature decreases, which indicates the characteristic features of a random coil. The difference between R_{gz} and R_{gx} (or R_{gy}) becomes more and more clear with the temperature decrease, which indicates the polymer chain takes an anisotropic configuration.

(ii) The global orientational order increases gradually with temperature decrease in the high temperature region, then increases sharply with further decreasing temperature to a plateau indicating the formation of an orientationally ordered structure.

(iii) The single polymer chain starts to form ordered structure at temperatures depending on the chain length. The transition temperature $T^* = 1.0$, 0.9, 0.7 for a polymer chain with 300, 200, and 100 beads, respectively.

(iv) The temperature dependence of the radius of gyration, as well as the global orientational order parameter, shows the clear transition from random coil to ordered structure. During the transformational process, the typical linear relationship between the radius of gyration and global orientational order can be obtained. The absolute value of the slope is proportional to the chain length. When the single polymer chain takes the random coil or complete ordered configuration, the linear relationship is invalid.

(v) The structure formation process of a single polymer chain on the microscopic scale was analyzed. With decreasing temperature, the deviations from exponentially decreased behavior of stem length distribution become prominent. When the temperature is low enough, a peak is visible and always located at about $N_{tr} = 21$ bonds. It's independent of the chain length indicating a specific fold length for the ordered polymer chain. The average lengths of the stems and loops as the function of temperature imply a stiffening of the chain with decreasing temperature. The stiffening arises from the dihedral interaction potential and the van der Waals interactions leading to more and more segments ending up in the *trans* state, forming rigid rod stems separated by flexible spacers. Besides the stiffening of the polymer chain arises, stems, as a stiff part of a single polymer chain, become more and more paralleled or anti-paralleled with decreasing temperature.

In future work, we will make efforts to investigate the structure and molecular motion during cooling process of a single polymer chain in solution or polymer chains system to discover the solvent molecules or other chain interactions during the structure formation process.

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