

A MONTE CARLO STUDY OF THE GLASS TRANSITION OF POLYMETHYLENE*

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Abstract By this Monte Carlo simulation we studied the glass transition of polymethylene using the modified bond-fluctuation model combined with considering the rotational-isomeric state model. The configurational properties in the polymethylene (PM) melts, such as the mean length, the mean energy per bond and the mean square radius of gyration were monitored. We found that the chains cannot be in the equilibrium states after a very long time when the temperature of the dense PM chains decreases to 120 K. As the melt vitrifies, these quantities gradually become independent of temperature in a narrow range. The glass transition temperature T_g depends upon the chain length of PM chains, and extrapolation to $(CH_2)_\infty$ gives $T_g^\infty = 212$ K. The dynamics in the PM melts was also studied. It was found that the diffusion coefficients can be described by the Vogel-Fulcher law and the Vogel-Fulcher temperature T_0 is 124 K. This method may be used to investigate the glass transition of other real polymer chains.

Keywords Monte Carlo simulation, Glass transition, Polymethylene

INTRODUCTION

The glass transition of polymer chains is an important phenomenon in polymer physics. Although a lot of experimental and theoretical work has been done in order to explain the physical nature of the glass transition^[1], the theoretical description of this transition is still regarded as an unsolved problem^[2]. The glass transition is observed from a rather pronounced discontinuity of the thermal expansion coefficient, or of the specific heat at constant pressure, and by the 'Kauzmann' paradox^[3]. Now it is speculated that there is an underlying thermodynamic glass transition of second order that is blurred by the finite experimental observation time^[4]. In the theories the glass transition is related to the vanishing of a percolation path for the 'free volume' around a molecule or of the configurational entropy. Although it is possible to understand the empirical Vogel-Fulcher law^[5, 6] within the framework of these thermodynamic theories, they cannot account for the detailed dynamical aspects of the glass transition. Besides the experimental glass transition temperature, two other characteristic temperatures have been introduced, one lies below and the other above the glass transition temperature (T_g). The one below T_g is the Vogel-Fulcher temperature T_0 stemming from the empirical Vogel-Fulcher equation by which one may rather accurately fit the strong increase of the viscosity over more than ten orders of magnitude in the interval viscosity poise. The Vogel-Fulcher temperature is the temperature, at which the viscosity becomes infinitely large, and

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has thus been looked upon as the transition temperature of the experimentally unreachable underlying thermodynamics liquid-glass phase transition^[7]. Contrary to that, the second temperature lies in the experimentally well accessible region. It is the critical temperature T_c of the mode coupling approach to the glass transition. Which of the three temperatures is actually the most relevant to glass transition is still an open question.

This simulation, as a third method between experiment and analytical theory, may provide valuable information. The bond-fluctuation model, originally proposed by Carmesin and Kremer^[8], is known to reproduce the expected static and dynamic behavior of a dense melt in both two^[9] and three dimensions^[10]. It has been successfully applied to very diverse theoretical problems of polymer science, such as interdiffusion^[11], the unmixing transition of symmetric and asymmetric binary polymer mixtures^[12], reptation dynamics^[13], adsorption on surfaces^[14–16], wetting phenomena^[17], the glass transition of two-dimensional polymer melts^[18] and three-dimensional polymer melts^[19–21]. Recently, a modified bond-fluctuation model was developed to study the statics and dynamics of polymethylene (PM)^[22] with consideration of the rotational-isomeric state (RIS) model^[23, 24], and the static results are in good agreement with the theoretical results. In this study, the glass transition of PM chain was investigated using the modified bond-fluctuation model. The essential features of the modified bond-fluctuation model and also the simulation parameters were reviewed before the discussion of our simulation results.

SIMULATION METHOD^[22]

In the past Monte Carlo simulation of glass transition in polymer melts, the bond-fluctuation model^[18] was adopted with the introduction of the Hamiltonian^[18–21] only:

$$H(b) = \begin{cases} 0 & \text{if } b \in (3,0,0) \\ \varepsilon & \text{otherwise} \end{cases} \quad (1)$$

where b is the bond vector between the monomers n and $n+1$. The effect of this Hamiltonian is that a bond in the ground state blocks four lattice sites which are no longer accessible for other monomers due to the self-avoidance condition. In fact, for the real chain, the minimum energy of the Kuhn bond is not zero, and the energy difference between the ground state and the activated state is not the same. For example, the possible energy of the polymethylene Kuhn bond consisting of four carbon-carbon bonds is from 1000 cal/mol to 10000 cal/mol. In the meantime, it is unreasonable that the basic bond length is 2, $\sqrt{5}$, $\sqrt{6}$, 3, $\sqrt{10}$ for real polymer chains. Since our simulation is performed using the lattice model and not the off-lattice model, the tetrahedral lattice model is adopted. For a real linear PM chain, it is known that $\angle CCC = 112^\circ$ and each bond rotamer is assumed to be in one of the three conformations: *trans* conformation (t) which has the lowest energy and two *gauche* conformations (g^+ and g^-) situated at rotations $\varphi_\pm = 120^\circ$ from the *trans* conformation. The tetrahedral lattice model can give a reasonable approximation to the rotational state of the carbon-carbon backbone bond. It takes $\angle CCC = 109.5^\circ$ and $\varphi_\pm = 120^\circ$. The method of computer simulation for diamond lattice chains on a tetrahedral lattice was first described by Smith *et al.*^[25, 26], and we gave a more direct relation between the conformational and orientation of bonds^[27]. In this paper, the interaction between the carbon atoms was taken only as the second order interaction, which is the rotational-isomeric state (RIS) model^[23, 24]. The interactions between chains are ignored in the melt systems^[19, 20]. A Kuhnian bond in our bond-fluctuation model includes four carbon-carbon backbone bonds. In theory, a Kuhnian bond may include five C—C bonds or six C—C bonds or even more. Through calculation, we found that the number of C—C bonds in a Kuhnian bond has no effect on the dynamic and configurational properties. In a long unperturbed chain, a Kuhnian bond (segments between the i th carbon atom and the $(i+4)$ th carbon) includes 243 (3^5) possible configurations, and the Kuhnian bond lengths

include 243 possible values. Through calculation, we found that in all the 243 possible Kuhnian bond vectors, only 54 bond vectors are distinct, and the possible Kuhnian bond lengths (or the allowed distances between two Kuhnian monomers) are $\sqrt{2}$, 2, $\sqrt{6}$, $\sqrt{8}$ (where the carbon-carbon bond length is $\sqrt{3}/2$)^[22]. Each of the 54 Kuhnian vectors may have different energies, and for the same Kuhnian bond vector there also are many possible energy values. The possible energy is calculated through comparing the Kuhnian bond vector and rotational state of carbon-carbon backbone bond. Here, the following statistical weight matrix^[23, 24] of the PM chain is adopted

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (2)$$

where

$$\begin{cases} \sigma = \exp(-E_{\sigma}/kT) \\ \omega = \exp(-E_{\omega}/kT) \end{cases} \quad (3)$$

In this paper, $E_{\sigma} = 2090$ J/mol, and $E_{\omega} = 8360$ J/mol. Each carbon-carbon bond is assumed to be one of the three conformations (t , g^+ and g^-), and we calculate the possible energy for the Kuhnian bond including four carbon-carbon bonds. The possible energy for the Kuhnian bond was given in another paper^[22]. Through calculation, we found that there are several possible energy values for the same Kuhnian bond vector^[22]. The reason may be that the g^+ conformation and the g^- conformation have the same symmetry about the *trans* conformation. To move the chain, a monomer is selected at random. Then it tries to jump at random a distance of $\sqrt{2}$ into one of the 12 possible lattice directions, which is different from the distance of unity in the bond-fluctuation bond^[8]. If it tries to jump at random the distance of unity into one of the six possible lattice directions, it is found that the new bond never belongs to the Kuhnian bonds because the length of the new bonds is never equal to $\sqrt{2}$, or 2, or $\sqrt{6}$, or $\sqrt{8}$. The 12 possible lattice directions are (1, -1, 0), (1, 1, 0), (-1, 1, 0), (-1, -1, 0), (0, 1, 1), (0, 1, -1), (0, -1, -1), (0, -1, 1), (1, 0, 1), (1, 0, -1), (-1, 0, 1), and (-1, 0, -1) in a Cartesian coordinate system. In fact, the configuration in the case that the Kuhnian monomer moves one step in our simulation model may be the same as the configuration in the case that the Kuhnian monomer moves two steps in the bond-fluctuation model. For example, the vector (1, 1, 0) may be regarded as the vector (1, 0, 0) adding the vector (0, 1, 0) in a Cartesian coordinate system. Here the Metropolis method^[28] should be considered. If ΔE is the energy change on generating a new configuration, then for $\Delta E < 0$, the new configuration is accepted. If $\Delta E > 0$, the new configuration is accepted with a probability of $\exp(-\Delta E/kT)$ and rejected with a probability of $1 - \exp(-\Delta E/kT)$. In our calculation, the density $\phi = 0.53$ ^[19], and a box length $L = 13$. A single simulation was carried out as follows. After creation, the chains were relaxed at least for 1.0×10^6 Monte Carlo steps (MCS). 1 MCS corresponds one attempted jump per monomer. After equilibrium was obtained, the measurements were performed at intervals of 30,000 or 60,000 MCS for 3.0×10^6 MCS. In order to improve the statistics further, 100 independent configurations of this system were run.

RESULTS AND DISCUSSION

Mean Energy Per Bond

The mean energy per bond is defined as the average of the bond energy over all bonds, polymers and configurations, i.e.

$$E_b = (1/PCN) \sum_{n=1}^N \sum_{p=1}^P \sum_{c=1}^C \langle E(b_{npc}) \rangle \quad (4)$$

where N is the number of bonds per chain, P is the number of chains in box ($13 \times 13 \times 13$) and C is the number of independent configurations. Here $N = 10$, $P = 116$ and $C = 100$ in our simulation. The mean energy per bond is measured in units of J/mol. Figure 1 shows a plot of E_b against temperature T (K). In the high-temperature region ($T > 300$ K), the statistical properties are not investigated here. If the temperature is reduced, the bonds go into the lower energy states, and the mean energy per bond slowly decreases. If the temperature is reduced further, more and more bonds go into the ground state until the curves level off in a narrow temperature range around $T = 135$ K. However, if the temperature is close to $T = 120$ K, the system is not yet in the equilibrium state after the system is relaxed for 2.0×10^6 MCS. Within the region, this may be the Vogel-Fulcher temperature T_0 , which lies below T_g . The mean energy per bond is almost constant in the region $T \approx 130$ K–140 K, and glass transition may have occurred.

Specific Heat

If the temperature dependence of the mean energy per bond is known, the specific heat per bond, C_b , can be defined. As long as the system is in equilibrium, C_b can be calculated by the temperature derivative of E_b

$$C_b = dE_b/dT \approx \Delta E_b/\Delta T (\Delta T \rightarrow 0) \quad (5)$$

The results are given in Fig. 2. In the region of $T > 150$ K, the specific heat increases with the temperature. In the low-temperature region, the specific heat increases insignificantly with the temperature. Around $T = 140$ K, a discontinuity of specific heat occurs. In the region of $T < 130$ K, as the equilibrium state is never reached, the specific heat cannot be obtained. We think the discontinuity of the specific heat may correspond to the glass transition, and the glass transition temperature is $T_g = 140$ K for $N = 10$.

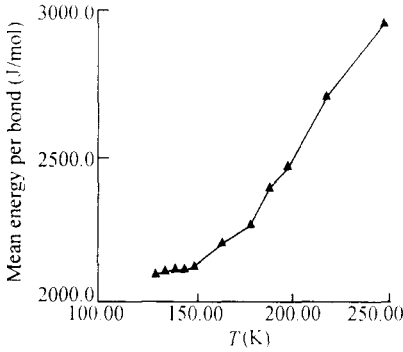


Fig. 1 Plot of the mean energy per bond E_b versus temperature T for $N = 10$

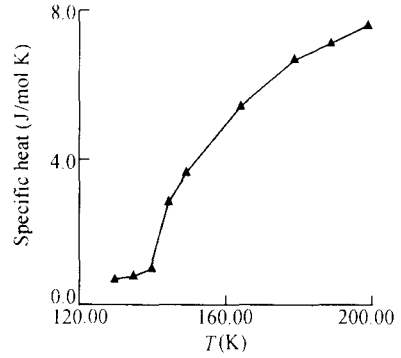


Fig. 2 Plot of the specific heat C_b versus temperature T for $N = 10$

Chain Dimensions

In order to obtain the quantities discussed in the previous sections it is also worthwhile looking at a quantity like the mean square bond length $\langle b^2 \rangle$, which directly measures the stretching on the length scale of a bond vector. The temperature dependence of $\langle b^2 \rangle$ is shown in Fig. 3. In the region of $T = 150$ K–250 K, the mean square bond length increases slowly. The reason for this may be the decrease of the mean energy per bond E_b . However, in the temperature region studied, E_b decreases about 26% in comparison to only a 4% increase of $\langle b^2 \rangle$. If a bond reaches its ground state the lattices are no longer available for other monomers. This loss of volume has to be

compensated by a corresponding shrinking of other bonds in order to make the density remain the same. However, the compensation can only take place if the melt has enough time to overcome the energy barriers at the respective temperatures. The increase of $\langle b^2 \rangle$ continues until the temperature reaches $T = 140$ K.

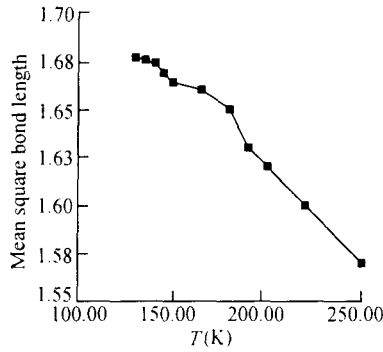


Fig. 3 Mean square bond length $\langle b^2 \rangle$ versus temperature T for $N = 10$

Here we also calculate the mean square radius of gyration $\langle S^2 \rangle$ and the mean square end-to-end distance $\langle R^2 \rangle$, which are defined by,

$$\langle S^2 \rangle = (1/NPC) \sum_{n=1}^N \sum_{p=1}^P \sum_{c=1}^C \langle r_{npc} - r_{pc} \rangle_{pc}^2 \quad (6)$$

$$\langle R^2 \rangle = (1/PC) \sum_{p=1}^P \sum_{c=1}^C \langle R_{pc}^2 \rangle \quad (7)$$

where r_{npc} is the vector to monomer n in polymer p of configuration c , r_{pc} is the vector to the centre of mass and R_{pc} is the end-to-end distance for the respective polymer. The results are shown in Figs. 4 and 5. Similar to the temperature dependence of the mean bond length, the values of $\langle S^2 \rangle$ and $\langle R^2 \rangle$ increase with decreasing temperature. However, these quantities become independent of temperature in a narrow temperature range around $T = 135$ K.

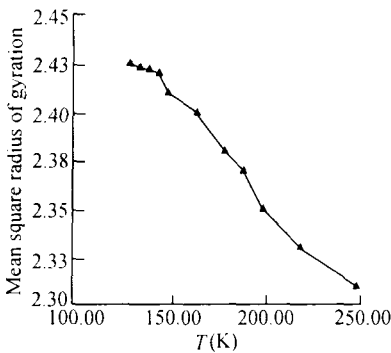


Fig. 4 Mean square radius of gyration $\langle S^2 \rangle$ versus temperature T for $N = 10$

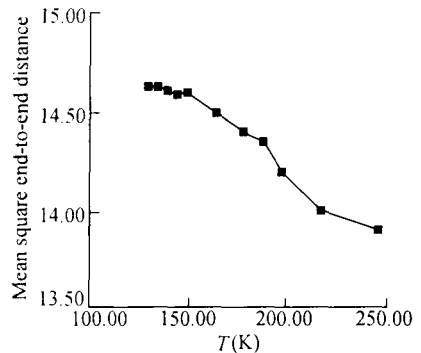


Fig. 5 Mean square end-to-end distance $\langle R^2 \rangle$ versus temperature T for $N=10$

Dynamics

In order to study the dynamics of the chains we calculate the mean-square displacement $g(t)$ of the center of mass:

$$g(t) = \langle (r_{\text{cm}}(t) - r_{\text{cm}}(0))^2 \rangle \tag{8}$$

where $r_{\text{cm}}(t)$ is the position of the center of mass at time t in polymer p . $\langle \rangle$ represents the average over all bond N , polymer P and configuration C . In the region above the glass transition temperature, the Rouse model is fitted for description of dynamics of polymers. We found that the values of $g(t)/t$ are constant in the large time limit. The temperature dependence of diffusion coefficient, calculated by $D_T = g(t)/(6t)$ in the limit $t \rightarrow \infty$, are given in Fig 6. D_T remains roughly constant for temperature above $T = 220$ K, and starts to decrease slowly for $T < 220$ K. Around $T \sim 140$ K, D_T decreases drastically as the temperature decreases. The diffusion coefficient D_T may be expressed by the Vogel-Fulcher law^[51]:

$$D_T = D_\infty \exp(-C/(T-T_0)) \tag{9}$$

In Fig. 7, we obtain the parameter $T_0 = 124$ K and $C = 46.5$ K.

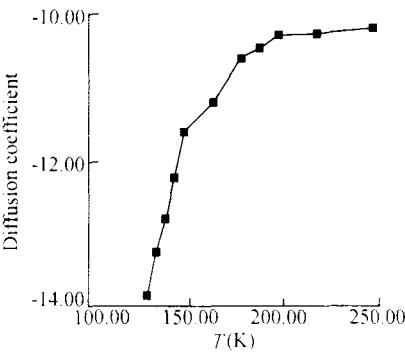


Fig. 6 Plot of the diffusion coefficient $\ln D_T$ versus temperature T for $N=10$

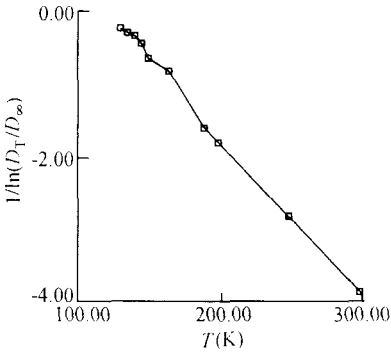


Fig. 7 $1/\ln(D_T/D_\infty)$ versus temperature T for $N=10$

The dependence of the glass transition temperature on chain length was determined, and the results are presented in Fig 8, which shows a plot of T_g , obtained from the corresponding specific heat data (see Fig. 2) versus $1/N$. A linear relation between T_g and the inverse chain length was obtained, i.e.

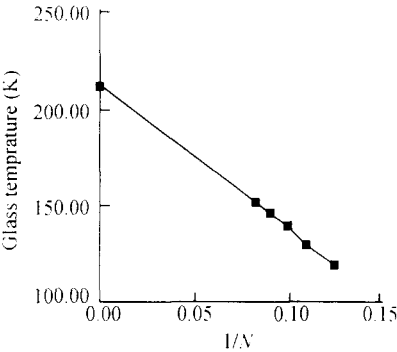


Fig. 8 Glass temperature T_g versus $1/N$

$$T_g(N) = T_g^\infty - A/N \tag{10}$$

The fit with Eq. (10) provides the following values for the two parameters appearing in the equation: $T_g^\infty = 212$ K, and $A = 715$. These values therefore show that the glass transition temperature of an infinitely long chain T_g^∞ does not depend upon the circumstance. However, we have to bear in mind that the fit values of the extrapolation Eq. (10) would presumably change if

much longer chains have been simulated. This is particularly the case if we take into account the fact that Eq. (10) is an asymptotic expansion, which is only valid for very large polymers. One cannot unambiguously conclude from these results that T_g^∞ is 212K in the limit $N \rightarrow \infty$ ^[19]. As our model may simulate the real dense polymer chains, and may be reasonable by making some supposition, this simulation may also be performed for the other real polymer melts. This work is in progress.

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