Dynamic Monte Carlo simulation of chain growth polymerization and its concentration effect

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Abstract  Free radical polymerization and living ion polymerization have been simulated via the dynamic Monte Carlo method with the bond-fluctuation model in this paper. The polymerization-related parameters such as conversion of monomers, degree of polymerization, average molecular weight and its distribution are obtained by statistics. The simulation outputs are consistent with the corresponding theoretical predictions. The scaling relationships of the coil size versus chain length are also confirmed at different volume fractions. Furthermore, the effect of diffusion on polymerization is revealed preliminarily in our simulation. Hence the simulation approach has been proven to be feasible to investigate polymerization reactions with the advantages that configuration and diffusion of polymer chains can be examined together with polymerization kinetics.

Keywords: living ion polymerization, free radical polymerization, concentration effect, configuration, Monte Carlo simulation.

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Polymerization kinetics and chain configuration are two of lasting hotspots in Polymer Science. As these problems are concerned, computer experiment affords a very useful method besides theoretical and experimental investigations. The conventional Monte Carlo method based on the number change of species is effective to study molecular weight and its distribution\(^{[1-4]}\). But chain configuration cannot be studied straightforwardly because spatial information has not been taken into consideration\(^{[5,6]}\). On the other hand, dynamic Monte Carlo (DMC) method is an ideal one by which the chain dynamics and configuration of a single chain or multiple chains can be investigated\(^{[7-11]}\). Although a lot of papers have been published to study either polymerization via the conventional Monte Carlo method or chain configuration and chain dynamics via DMC, there are few reports to combine them together. Jo et al. studied ester exchange reaction\(^{[9,10]}\) and super-graft polymerization\(^{[11]}\) via DMC based on a simple one-site lattice model and an off-lattice model respectively. But in the former case, the bond length and the bond angle were not allowed to have more than two choices based on their one-site model and may lead to the so-called “high frequency loss” of chain relaxation, whereas in the latter case the computing time should be quite long due to the off-lattice model.

The bond-fluctuation lattice model is between simple lattice and off-lattice models. It can have more chain configurations, because more bond lengths and bond angles are permitted compared with the one-site model. This method has been used successfully in in-
vestigation of glass-transition\cite{7}, and protein folding\cite{12-14}, etc. In this paper, chain growth polymerizations were investigated by the bond-fluctuation model combined with the DMC method. As our first paper to study chain growth polymerizations, the feasibility of the simulation method has been confirmed by reproducing the dynamical process of ion polymerization and that of radical polymerization. Chain configuration in polymerization and the effect of diffusion on polymerization were also investigated.

1 Model and simulation approach

Even on the fastest computer so far, it is still not available to examine the movements of all of structural elements for long polymeric chains. Since the chain behaviors on large spatial scale are independent of the details of chain models on small spatial scale, a cubic lattice model instead of an off-lattice model was used in our simulation.

The simulation was performed at the athermal state, and the bond-fluctuation cubic model was employed. An effective monomer, e.g., a Kuhn segment is represented by eight sites on the corner of a cubic lattice. The bond length between two effective monomers can fluctuate. The permitted set of bond vectors \( \{ b \} = \{ \Delta x, \Delta y, \Delta z \} \) should be the union of \( P(2,0,0), P(2,1,0), P(2,1,1), P(2,2,1), P(3,0,0) \) and \( P(3,1,0) \), so the bond length should be one of the following discrete values as \( 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10} \). According to such elementary movements, neither two beads occupy the same lattice site at the same time, nor two bonds cross in one trial motion. A jump is accepted only if both requirements of the bond length restriction are met.

In free-radical polymerization, the initiation efficiency was set to be unity. We assumed that no chain transfer occurred and the mode of termination was disproportionation. Reasonable probabilities for initiation, propagation and termination were inputted in our simulation. In ion polymerization, extremely fast initiation was assumed. The active centers were generated at the very beginning, and then propagated randomly without termination.

The periodic boundary condition was adopted in our simulation. The simulation system is composed of 64×64×64 lattices. At the initial state, monomers were distributed randomly. The volume fraction \( \phi \) is 0.5 unless otherwise indicated. There is only one reactive group in each monomer to ensure linear polymerization.

The species in the reaction system were marked in simulation. When the parameter \( k(i) \) is 0, 1 or 2, particle \( i \) is denoted as a monomer, an active center and a chain segment respectively. Monomers were distributed evenly. After being relaxed for 50000 Monte Carlo steps, an equilibrium initial state was recorded as the starting point of polymerization.

With radical polymerization as the demonstrated example, our simulation proceeds as follows:

(i) Initiation. If a bead selected randomly is a monomer, a random number is generated. The monomer is initiated only if the random number is less than or equivalent to the pre-set initiation probability. The associated \( k \) value is thus changed to "1".

(ii) Chain relaxation and reaction. At the stage of relaxation and reaction, a bead \( A \) is chosen at random first, and then a trial motion direction is set randomly. If the neighboring four sites along the chosen direction are empty, the random jump of this bead along this direction is accepted if the bond length restriction is also obeyed. Otherwise, the random jump is not accepted and the chain maintains its old configuration in this try. If the neighboring four sites are occupied by another bead called \( B \), the species of \( A \) and \( B \) are judged by their \( k \) values. If one of them is a radical and the other is a monomer, propagation will occur when a new generated random number is less than or equivalent to the propagation probability; termination occurs with a set probability if both beads are radicals; if the beads are monomer(s) and/or chain segment(s), no reaction will occur.

(iii) The above processes are repeated till the preset reaction period. The static and dynamic parameters are obtained via statistics at each specified simulation step.
The reaction time is in units of Monte Carlo step (mcs) which is defined as the number of tries among which all the beads are chosen once in average, and has been proven to be proportional to the physical time\cite{7,15}. The total reaction time was set between 20000 and 1500000 mcs, depending on polymerization requirements. Ensemble average was obtained from statistical average over independent runs. The results are shown in the form of mean value and standard deviation (err bar).

Macroscopic rate constants $k$ are closely related but not necessarily equivalent to microscopic rate constants (reaction probability $P$)\cite{15}: for the second order reaction, $k_{AB} = P_{AB} \cdot V$, while for the first order reaction, $k_{AB} = P_{AB}$. Here $V$ is the volume of the underlying reaction system. According to most of experiments, the ranges of three important rate constants in radical polymerization are: $k_i = 10^{-4} - 10^{-6} \text{ s}^{-1}$, $k_p = 10^2 - 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_t = 10^6 - 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for three mechanistic steps respectively. The relationships between $k_s$ and $P_s$ might be more complicated in our simulation due to the excluded volume effect etc. Hence, it is difficult to get a definite analytical formula. Our simulation adopted a set of reaction probabilities from 0 to 1 consulting the above relationships. In this paper, the parameters were set as $P_i = 5 \times 10^{-6}$, $P_p = 5 \times 10^{-3}$, $P_t = 1$.

2 Results and discussion

2.1 Simulation results of living ion polymerization

As shown in Fig. 1, the number average and the weight average molecular weights are approximately the same because of the simultaneous initiation and no termination in an ideal living ion polymerization. So the distribution index of molecular weight is close to 1.0, and the number average molecular weight is proportional to the conversion of monomers linearly. This illuminates the synchronized propagation of chains. Hence, our simulation method is feasible to study living ion polymerization and the results are in agreement with the theory.

One of the virtues of DMC compared with the conventional Monte Carlo simulation to study polymerization is that DMC can investigate chain configurations simultaneously. Time evolution of the mean-square coil size (Fig. 2) demonstrates that the static scaling law for chain size versus chain length is also obeyed in polymerization kinetic process. The slope of Fig. 2 gives value of $2\nu$. It is well known that the static exponent $\nu$ should be 0.5 for an ideal chain and 0.6 for a single self-avoiding chain at the athermal state in three dimensions\cite{16}. The exponent in polymerization (Fig. 2) is 1.03 for mean-square end-to-end distance $\langle H^2 \rangle$ and 1.02 for mean-square radius of gyration $\langle S^2 \rangle$ respectively. Considering that $\phi = 0.5$
indicates a concentrated solution similar to the Θ-state\cite{17,18}, the simulated static scaling exponents consist with theoretical predictions.

2.2 Simulation results of free-radical polymerization

The main part of this paper concerns the free-radical polymerization with gradual initiation, random propagation, and disproportionation termination between two active centers. The suitable reaction probabilities should lead to a quasi-steady state in order to make comparison with the present polymerization theory, and the resulting chains could not be very long in order to avoid finite size effect. In this paper, the number of radicals is 30—40 (Fig. 3). It is necessary to point out that the assumption of steady state in the classic theory of radical polymerization can be released in our simulation.

The degree of polymerization increases with time at the initial stage and reaches a relatively stable value at the later stage (Fig. 4). For a radical polymerization with disproportionation termination, the distribution index of molecular weight should be 2.0 on the assumption of equal activity together with the assumption of steady state. From Fig. 4, the simulation outputs coincide with the classic theory.

Typical distribution curves for number and weight distributions of molecular weight are shown in Fig. 5. Simulation results are represented by symbols. Each value of the point is gained by averaging over 200 points around the associated time. According to the famous Flory theory\cite{19}, the molecular weight distributions from an ideal radical polymerization are expressed as

\[
\frac{N_x}{N} = P^{x-1}(1-P),
\]  

(1)
where, \( N_x/N \) is the number fraction of \( x \)-mers, \( W_x/W \) is the weight fraction of \( x \)-mers. \( P \) is bonded probability, which can be calculated from \( P = 1 - 1/x \). The lines are calculation results according to eqs. (1) and (2). The simulation agrees with the theory quite well. So our simulation method is feasible to study radical polymerization.

2.3 Concentration effects of free-radical polymerization

In order to examine concentration effects, we adjusted the reaction parameters to make the chain length longer. The amount of initiators was halved and the propagation probability was increased to 0.02. Several bead concentrations of \( \phi = 0.625, 0.40, 0.25 \) and 0.125 were examined. The rate of polymerization is confirmed to increase with concentration (Fig. 6), which agrees with various experiments of radical polymerization.

Although such a conclusion can also be drawn from the conventional Monte Carlo simulation of polymerization, the DMC simulation is unique to examine straightforwardly chain configuration. The coil sizes in polymerization are shown in Fig. 7. The reaction time for each run was 200000 mcs, and the statistics was performed at the interval of 10000 mcs. For \( \phi = 0.625, 0.40, 0.25, 0.125 \), the numbers of independent runs were 50, 65, 100, 200 respectively. The horizontal ordinate \( \langle N-1 \rangle \) is the average chain length at the same time of different runs. Fig. 7 illustrates different coil sizes under similar molecular weight when the examined systems are with different concentrations. Coils in a denser system are smaller, which can be accounted for from the combination of excluded volume effect and shielding effect. Furthermore, the static scaling law of random coils results from all concentrations though the scaling exponents are different. \( \phi = 0.625 \) corresponds to a melt at \( \Theta \)-state, and thus the \( \nu \) value is the smallest. It is necessary to notice that \( \phi \) is the volume fraction considering all of chain segments.
and monomers. Since the conversion is less than one, volume fraction of chain segments must be less than $\phi$. Moreover, chains are flexible and the resulting chain lengths are short in simulation. So it should be careful to make comparison between simulated $\nu$ and the experimental exponent at the same $\phi$. But the basic behaviors obtained from our simulation still reproduced experimental observations. The decrease of scaling exponents with the increase of concentration in this paper is also consistent with the results of Monte Carlo simulation of flexible multiple chain systems without polymerization[20]. So our simulation of polymerization agrees with the scaling theory of de Gennes[18].

2.4 Effect of diffusion on the kinetics of free-radical polymerization

One of the special virtues of our simulation method is its convenience to study the effect of diffusion directly. The diffusion-controlled polymerization is rather complicated and important in Chemical Engineering. We introduced a diffusion probability, i.e. an accepted probability $P_D$ when two selected beads exchange their positions during relaxation. Decreasing $P_D$ leads to slowing down mobility of beads or equivalently increasing viscosity. The probabilities of three mechanistic reactions were set as $1 \times 10^{-6}$, $1 \times 10^{-3}$ and 0.1 here. The diffusion effects on radical polymerization are shown in Fig. 8.

The effects of $P_D$ on conversion and molecular weight are complex. When $P_D = 0.5$, the polymerization is, similar to the case of $P_D = 1$ from Fig. 8. When $P_D = 0.001$, the polymerization is much fastened. This reveals that the rate determining step is termination, which turns to be controlled by meeting of two active ends and thus by diffusion. When $P_D = 0.00001$, the over-large viscosity makes the reaction slow down reasonably. In this paper the effect of $P_D$ on kinetics of radical polymerization was just studied primarily. Nevertheless, our simulation demonstrates that the diffusion is a complicated factor to influence polymerization. Corresponding extensive researches are in progress.

3 Conclusions

In this paper, the chain growth polymerization has been simulated by dynamic Monte Carlo method with bond fluctuation algorithm of the eight-site lattice model. The molecular weight and its distribution were examined during polymerization. Meanwhile, time evolution of mean-square end-to-end distances and mean-square gyration radius were obtained, and the scaling law about the coil size has been confirmed. The simulation outputs under ideal conditions are consistent with the associated theoretical predictions, which confirms that the reaction model works and the simulation parameters are appropriate. The outputted reaction kinetics is reasonable as well as the concentration effect of the examined self-avoiding coils. Furthermore, we have revealed that this method is powerful to investigate diffusion-controlled polymerization, the details of which will be published in another paper.

Fig. 8. Time evolution of (a) number average degree of polymerization; (b) monomer conversion at different diffusion probabilities $P_D$. 
From the above discussion we draw the conclusions as follows: the method used in this paper is effective to study the chain growth polymerization, and can investigate polymerization kinetics and chain configuration simultaneously. The simulation approach used in this paper might be prospective in various applications, especially in examining kinetics of self-avoiding multiple chains and diffusion-controlled polymerization, which are rather difficult topics for the conventional Monte Carlo simulation of polymerization.

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