

MOLECULAR DYNAMICS SIMULATION OF THE RELAXATION OF A FULLY EXTENDED POLYETHYLENE CHAIN

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Abstract Molecular dynamics simulation of the relaxation at 300 K of a fully extended polyethylene chain of 800 CH₂ units has been carried out by following the changes in morphology, van der Waals energy, radius of gyration in the sense of mechanics and gyration radius in the sense of Flory, population of *trans*-conformation and orientation factor. The relaxation went through three stages: (1) relaxation from the morphology of a straight rod of 100 nm length to the morphology close to a random coil of gyration radius 5.9 nm in 110 ps; (2) collapse of the morphology of a coil to a highly compact globule close to a sphere of gyration radius 1.3 nm after 178 ps as the result of intersegmental van der Waals attractive interactions; (3) lateral ordering of the folded chain segments in the globule without appreciable changes in the chain dimension up to 1600 ps, the time limit of present simulation. Nearly complete relaxation of local segmental orientation was performed much faster than the relaxation of globule chain orientation even for a single chain of low degree of polymerization and at a temperature some 155°C above its *T_g*. The lateral ordering of the chain segments during the period 178 to 680 ps of the simulation time was found to obey the Avrami equation with an Avrami index of 1.44.

Keywords Molecular, Dynamics, Relaxation, Ordering, Polyethylene

INTRODUCTION

The theory or simulation of the behavior of a single chain with obvious simplicity of disregarding inter-chain interactions has its meaning in two respects. Early in the beginning of the development of polymer physics it was theoretically demonstrated^[1] that a single chain showed rubber elasticity. Later the dynamics of a Gaussian coil was first described mathematically from a single chain of connected Gaussian sub-chains known as the Rouse model^[2]. It is interesting to see that a theory of a single chain can show the salient features of the physical properties of polymer chains in condensed state. Recently it has been possible to study experimentally the behavior of a single-chain condensed state^[3], for example the single-chain glass and single-chain single crystal. A molecular dynamics (MD) simulation of a polyethylene coil approaching and residing on a carbon substrate surface showed crystalline nucleation of the coiled chain, i.e. folded chain, standing in peaks on the substrate surface^[4] in accordance with experimental findings. Therefore it really makes sense to do MD simulation of a single chain to extend our understanding of the behavior of polymer chains in the condensed state.

MD simulation of the relaxation of a fully extended polyethylene (PE) chain^[5] and poly(1,4-trans-butadiene) chain^[6] showed that the extended single chain will relax and collapse into folded chain globules due to inter-segmental attractive interactions. For PE of DP500 this process took

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around 200 ps at 300 K, and after 1000 ps ordered arrays of chain segments formed showing lamellar morphology of thickness 4.0–4.5 nm, with hexagonal close packing of the chain segments in all *trans*-conformations and with roughly equal numbers of adjacent versus nonadjacent reentries of the chain into the lamella^[5]. This is undoubtedly the initial stage of single chain crystallization. The lamellar crystallization of a single chain PE from a random coil was also demonstrated by MD simulation^[5].

In this paper MD simulation has been carried out starting from a fully extended PE chain examining the processes of local segmental relaxation and global chain relaxation to a coil and then the collapse of the coil to a globule and subsequent lateral ordering of the folded chain segments. The course of these processes was followed by changes in chain morphology, van der Waals energy, radius of gyration, population of *trans*-conformation and orientation factor.

OUTLINE OF METHODOLOGY

The starting geometry for the simulation is a fully extended single chain of polyethylene with 800 CH₂ units in all *trans*-conformations. Each methylene unit was treated as a united atom, i.e. as a sphere.

The simulation was performed by the PolygrafTM (version 3.2, Molecular Simulations Inc.) molecular modeling code. The time evolution of the chain conformations in 1600 ps with an integration time of 0.001 ps was simulated using the canonical (constant *T*) Nosé-Hoover molecular dynamics method^[7] which is consistent with real phase transitions which occur at constant temperature and involve a heat exchange with the surroundings. The simulation temperature was set at 300 K. A relaxation constant of 0.10 ps for the heat bath variable was used throughout. The system temperature fluctuations were always restricted to within 15 degrees of the mean value.

The atomic force field used here was the Dreiding II potential^[8] which includes quadratic functions for bond length and bond angle deviations from their equilibrium values and a cosine term with a barrier height of 2 kcal/mol for torsional potential. Both short and long range nonbonded interactions were modeled by Lennard-Jones 6-12 potential function, with a nonbonded cut-off distance of 0.9 nm. The total energy for the chain (E_{total}) is the sum of kinetic energy (E_K) and potential energy (E_P) which is expressed as a sum of valence, or bonded, interactions and nonbonded interactions. The valence interactions consist of diagonal terms (namely, bond stretching, dihedral angle torsion, and inversion), while the nonbonded interactions consist of van der Waals interactions (E_{vdw}).

The population of the *trans*-conformation was counted along the chain for each dihedral angle when it was within a range of 165°–195° (180±15°).

The shape of the chain was described by means of the gyration tensor^[9]. In general, when x_m , y_m , z_m are Cartesian components of the coordinates of the center of mass of an n -atom molecular system, the $n \times 3$ displacement matrix of each atom from the center of mass is expressed as:

$$X = \begin{bmatrix} x_1 - x_m & y_1 - y_m & z_1 - z_m \\ x_2 - x_m & y_2 - y_m & z_2 - z_m \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_n - x_m & y_n - y_m & z_n - z_m \end{bmatrix} \quad (1)$$

The radius of gyration tensor in the sense of mechanics is then obtained from an internal product:

$$R = \left(\frac{1}{n}\right) X^T X \quad (2)$$

The eigenvalues of the tensor give the principal components of R_a^2 in three mutually perpendicular directions ($\alpha = x, y, z$). R_a is one of the three radii of gyration of a prolate spheroid which is described by the tensor with the Z-axis corresponding to the long axis of the spheroid.

RESULTS AND DISCUSSION

Relaxation of A Fully Extended Chain

Applying the MD simulation method described above, we obtained the time evolution of the morphology of a single PE chain at 300 K from a fully extended rod to a collapsed coil, as the result of intersegmental attraction for a Gaussian coil in vacuum, and the subsequent lateral ordering of nearly parallel chain segments, which is the early stage of single-chain crystallization. The full course of the changes in shape of the PE chain is pictorially shown in Fig. 1.

It is interesting to observe the relaxation of a fully extended PE chain to a chain looped coil. Around 50 ps the global chain is still quite extended while the local segments have nearly random orientation. This demonstrates the state of a highly oriented global chain with component and an extensional component of deformation of amorphous polymers. For PE the glass transition temperature T_g is a matter of controversy because of its high crystallinity. If a value of 145 K is taken for amorphous PE^[13], MD shows that only 50 ps is needed for nearly complete relaxation of the local segmental orientation of a fully oriented single-chain at a temperature 155°C above T_g . Of course, for multi-chains in the condensed state the relaxation time may be several order of magnitude longer. For a quantitative presentation of the average orientation of chain segments we take the chain unit vector i of the i th C-atom of the chain as the vector connecting the $(i-1)$ C-atom to $(i+1)$ C-atom as sketched in Fig. 2. The orientation factor for i is taken as $1/2(3\cos^2\theta_i - 1)$

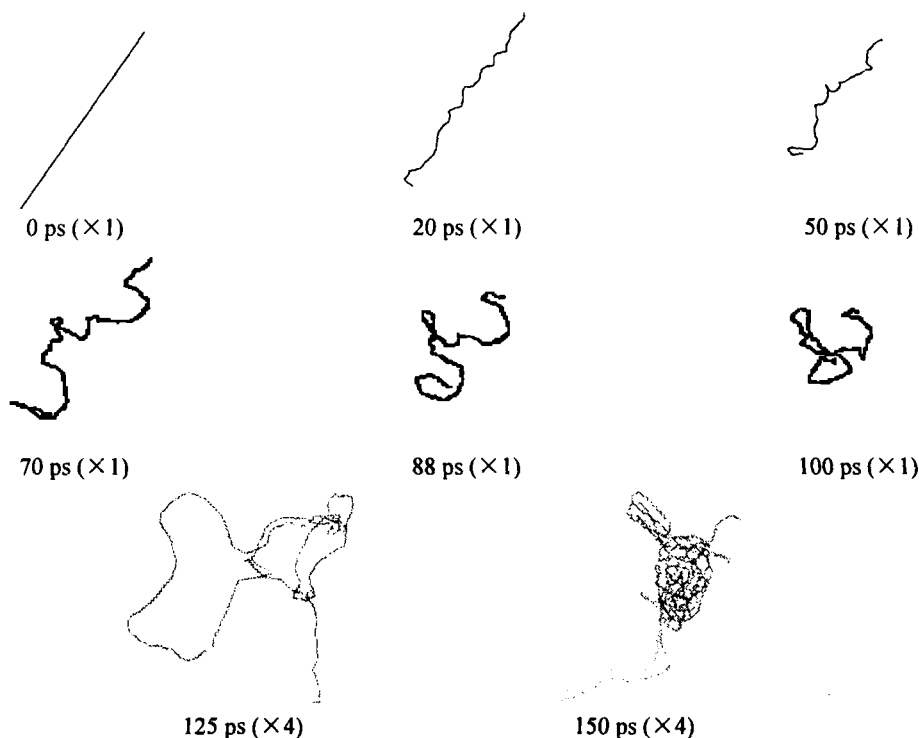


Fig. 1a

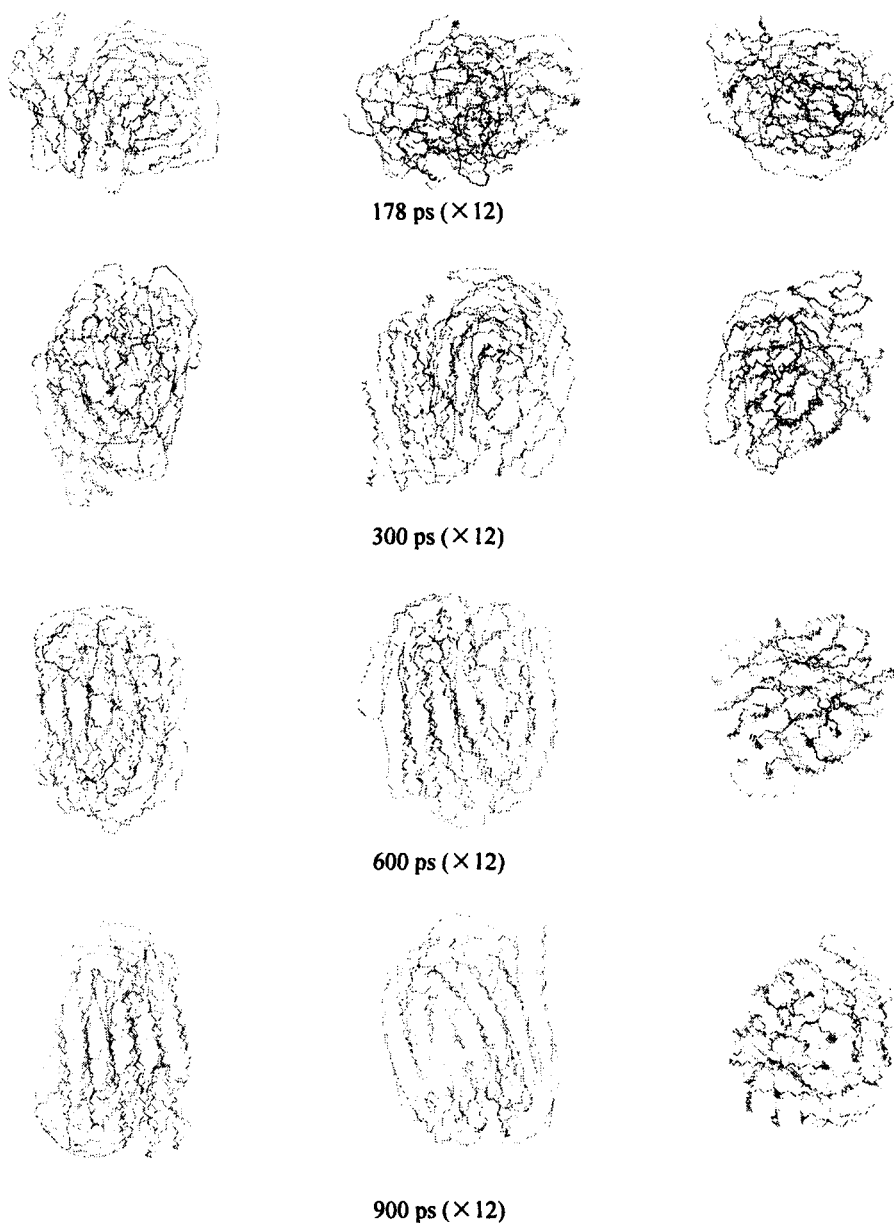
**Fig. 1b**

Fig. 1 Time evolution of change in the shape of a polyethylene chain with 800 CH₂ units at 300 K
a) Snapshots of the chain from 0 to 150 ps, b) Snapshots of the chain in three view-directions from 178 to 900 ps

along an arbitrary direction which makes an angle θ_i with i . Then the orientation factor of the chain segments can be defined as:

$$F_{\max} = 1/800 \sum (3 \cos^2 \theta_i - 1)/2 \quad (3)$$

with the arbitrary direction adjusted to maximize the value of F . As shown in Fig. 3, $F_{\max}$ drops to a minimum value of 0.04 at 59 ps, which means that the segmental orientation is nearly completely random. The drop of $F_{\max}$ follows the exponential decay with a relaxation time of 31 ps. After

60 ps the value of $F_{\max}$ starts to increase until 500 ps to reach a constant value close to 0.5. During this period some ordering process of the chain segments takes place.

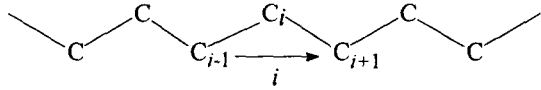


Fig. 2 Sketch showing of chain unit vector i and the C-atoms C_{i-1} , C_i , C_{i+1} of the polyethylene chain

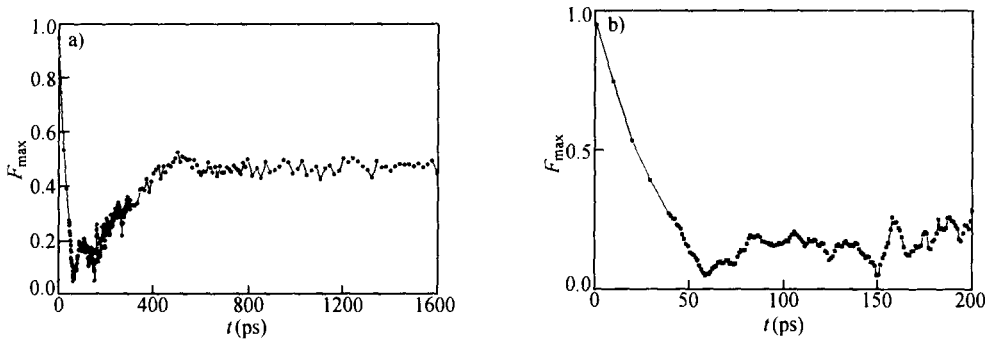


Fig. 3 Evolution of the maximum value of orientation function with simulation time

The change of the shape of the single chain can be represented by the values of three principal radii of gyration R_α , where $\alpha = x, y, z$, z being the long axis of the prolate spheroid of the single chain. The course of changes of the values of R_α is shown in Fig. 4. The morphology of the chain looped coil approaches a sphere after 178 ps. If the reverse process of the change of morphology from 178 to 0 ps is a process of global chain orientation of the spherical single-chain coil under uni-axial stretching, then it is clear that the relaxation process occurring from 0 to 178 ps is the

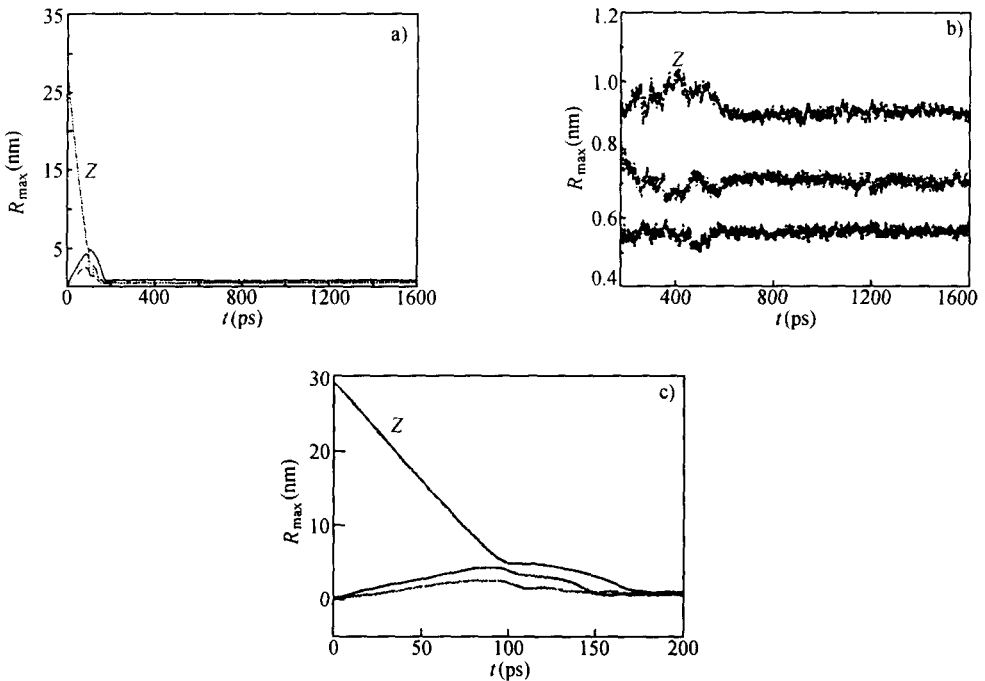


Fig. 4 The evolution of three radii of gyration in x, y, z directions
a) the overall process, b) from 178 ps to 1600 ps, c) from 0 ps to 200 ps

relaxation of the global chain orientation. It is interesting to observe that the change of R_z follows a linear decay with time in 0–100 ps, that is, the value of R_z drops in 71 ps to 37% of its initial value at 0 ps as compared to the drop of the value of segmental orientation factor to 37% of its initial value in 31 ps. The relaxation of global chain orientation is much slower than the relaxation of segmental orientations even at a temperature 155°C above its T_g and the molar mass of the chain is very low, 1.1×10^4 . The relaxation of segmental orientation requires conformational changes of a few consecutive C—C bonds, while the relaxation of global chain orientation may require long range cooperative conformational changes of the chain equivalent to that needed for the transition from glass to rubbery state. For a multi-chain polymer of moderate molecular mass at a temperature of 30°C above its T_g the relaxation time of global chain orientation may be several orders of magnitude slower than the relaxation of local segmental orientation. This is the origin of GOLR state.

The drop of the population of *trans*-conformers from unity at 0 ps occurs in two stages as shown in Fig. 5a. In the first stage it drops to a population of 0.7 in 1 ps and levels off at 88 ps, dropping to 0.5, a minimum, at 178 ps. Then it increases again to and levels off at a value of around 0.6 after 500 ps. Corresponding changes in the torsional energy due to the changes of conformation are shown in Fig. 5b.

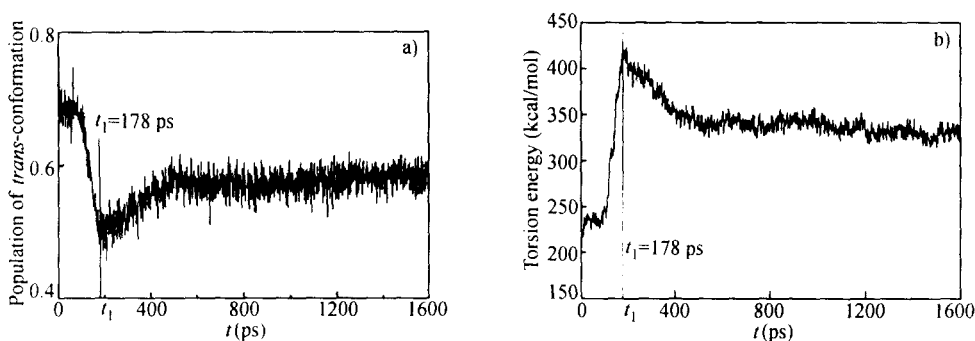


Fig. 5 Variation of the population of *trans* conformation and torsion energy with simulation time a) population of *trans* conformation ($180 \pm 15^\circ$), b) torsion energy of the Chain

From Coil to Globule

The second stage of population drop of *trans*-conformers starts at 88 ps which corresponds to the relaxation of the global chain orientation to a state having R_α values of 6.6, 4.2 and 2.5 nm in three directions from Fig. 4. It is already close to isotropy in the radii of gyration of the chain. This corresponds to a gyration radius of the chain in the sense of Flory (*vide infra*) of 8.2 nm. As the coil under simulation is in a vacuum, the action of van der Waals attraction between chain segments will lead to a more compact coil, the so-called collapsed coil or a globule of radii of gyration of 0.92, 0.80 and 0.55 nm after 178 ps. The transition from a single-chain coil to a globule is accompanied by no appreciable changes of segmental orientation but by a decrease of potential energy of around 2.1 kcal/mol of CH_2CH_2 unit due to intersegmental van der Waals attraction. Apparently this is a process of lateral cohesion of chain segments of roughly parallel alignment.

Lateral Ordering of the Folded Chain Segments in the Globule

As seen from Fig. 4 after 178 ps the globule dimension will no longer change appreciably even up to 1600 ps, the time limit of the present simulation. However, the potential energy continues to drop, and levels off after around 680 ps as shown in Fig. 6. This signifies that some lateral ordering of the chain segments is taking place due to intersegmental cohesion. The total energy evolved is 450 cal/mol per CH_2CH_2 unit. In fact a closer examination of Fig. 1 reveals pronounced chain

alignment of neighboring segments accompanied by significant increase of segmental orientation factor $F_{\max}$ as shown in Fig. 3 and some sort of hexagonal close packing of the stems of chain segments. This is also clearly shown in Fig. 3 of Ref. [5]. An evaluation of the degree of lateral ordering, $\theta(\tau)$, at time $\tau = t - t_1$, is as follows:

$$\theta(\tau) = (E_t - E_1)/(E_2 - E_1) \quad (4)$$

where E_t , E_1 and E_2 are energies at t , t_1 (178 ps) and t_2 (680 ps), showing that the lateral ordering process follows the Avrami equation as shown in Fig. 7 with an Avrami index $n = 1.44$. It is interesting to mention that the kinetics of formation of a nematic liquid crystalline phase of both small molecular mass compounds^[14] and lyotropic or thermotropic polymers^[15] also follows the Avrami equation with the index values close to unity, which signifies one dimensional growth. The morphology shown in Fig. 1 shows that the coil of single chain beyond 680 ps is not in the crystalline state yet. It perhaps takes a much longer time to show the crystallization process, which is beyond the reach of the computer time of this investigation. It is very interesting to point out here that the single extended chain relaxes into a coil before any ordering process or crystallization occurs. This is in accordance with the experimental finding that crystallization of amorphous oriented PET takes place after the relaxation of the global chain orientation^[16].

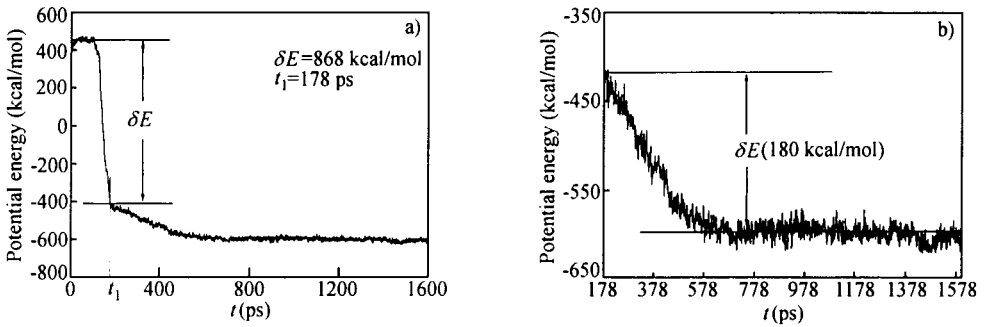


Fig 6 Variation of potential energy of polyethylene as a function of simulation time
a) The overall process, b) from 178 ps to 1600 ps

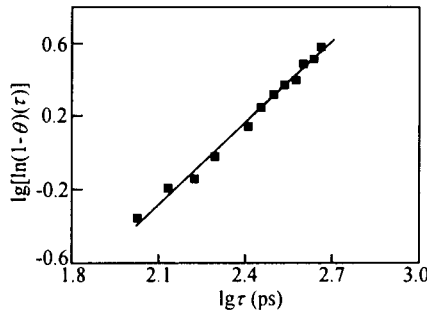


Fig. 7 Plot of $\lg\{-\ln[1-\theta(\tau)]\}$ against $\lg \tau$

Gyration Radius

The root-mean square distance of the chain elements from their center of mass, $S \equiv (\bar{S}^2)^{1/2}$, now widely known as gyration radius of the chain in the sense of Flory^[17], changes as a function of the time simulation as shown in Fig. 8. It is related to the radius of gyration in the sense of mechanics as follows, $S^2 = R_x^2 + R_y^2 + R_z^2$. The gyration radius of polyethylene chain, which represents the

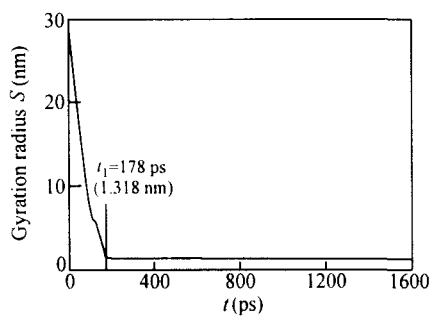


Fig. 8 Variation of the gyration radius of the polyethylene chain with simulation time

molecular size, decreases significantly with collapse of the chain. From a coil of $S = 5.9$ nm at 110 ps, the gyration radius shrunk to a globule of $S = 1.32$ nm at 178 ps, it then remained almost constant at $1.292^{+0.049}_{-0.033}$ nm, in the lateral ordering stage (from 178 ps up to 1600 ps), which is considerably smaller than the size for the same chain in the bulk state ($S \sim 4.5$ nm^[18]).

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