Molecular Dynamics Simulation of the Collapse of Poly(1,4-*trans*-butadiene) to a Globule and to a Thin Film

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ABSTRACT: The formation and the structure of a polymer thin film have been studied by molecular dynamics simulations. A poly(1,4-*trans*-butadiene) chain with a degree of polymerization of 180 and terminated by methyl groups was initially constructed so that all dihedral angles at the skeletal bonds are in the *trans* state. The model film, exposed to vacuum on both sides, was formed by a transition of the fully extended chain to a coil at a temperature of 300 K, with the use of periodic boundary conditions in two dimensions. A collapse transition of the extended chain to a globule was also simulated as a comparison. Simulations have been performed for a duration of 1500 ps. The conformations of the chains in the film and in the globule were examined. The collapse process of the chains can be divided into two regions for the transition to both the coil and the globule. In the first region the chain size shows a dramatic drop, while in the second region it decreases slowly with fluctuations. The density near its center of mass is close to the bulk density of amorphous poly(1,4-*trans*-butadiene). The coil that is the parent chain for the film exhibits a very loose structure, and its density at the center of mass is close to zero. The radius of gyration for the coil from the simulation is very close to the estimated value from rotational isomeric state theory. The local density of the film follows a sigmoidal profile at the free surfaces. The maximum thickness of the polymer/vacuum interface is about 10 Å, as judged by the density profile. The backbone bonds exhibit a tendency for parallel orientation in the vicinity of the free surfaces. The *trans* conformation is favored in the equilibrium distribution of the dihedral angles at the CH_2–CH_2 bonds within the film.

I. Introduction

The properties of polymers at surfaces are important in many applications, which manipulate the wetting, friction, and wear characteristics of a surface. Obtaining detailed microscopic level information on the surface conformation and mobility of polymer chains could greatly aid in the improvement of existing polymer materials and the development of new ones. In the last 2 decades, considerable effort has been devoted to the examination of the surface properties of polymers. Some of them have used computer simulation as a useful tool for exploring local structure and properties at the surfaces.[1-6] The first work in simulating the free surface of dense polymer systems was presented by Madden,[1] using a lattice Monte Carlo simulation method which employed a combination of reptative and pseudokinetic "movements". The film which forms exhibits three distinct layers, with two interfacial regions sandwiching a central region. The polymer in the central region is shown to have characteristics of the bulk melt. The densities of beads and ends decrease monotonically across the melt/vacuum interface. Analysis of the conformations of the polymer in the neighborhood of the interfaces shows the chains to be asymmetrically flattened at both surfaces. Monte Carlo simulations were also applied to study the polymer melts between solid surfaces.[2-4]

Molecular mechanics and molecular dynamics simulations were performed by Mansfield and Theodorou[5,6] to study the surface structural features and interfacial thermodynamic properties. Their work rested mainly on the following assumptions: A glass is envisioned as locally consisting of solidlike microstates, each "locked" in the vicinity of a local minimum of total potential energy in configuration space. Estimates of thermodynamic properties were obtained by arithmetically averaging the properties of individual microstates. They assumed that their method of generating liquidlike initial-guess configurations and subsequently relaxing them by energy minimization or molecular dynamics simulation yields a sufficiently accurate representation of a real glass formed by slowly cooling a melt. They found the density profile is sigmoidal in a 10-Å-thick region at the polymer/vacuum interface. Backbone bonds in the interfacial region exhibit a tendency to orient parallel to the surface. Enhancements in the mean-square displacement of atoms, and in the torsion angle fluctuations within a conformational state, are observed near the free surface. Their work is the first to look at the free surface of an amorphous polymer in atomistic detail using molecular dynamics simulation.

Several approaches to the modeling of dense polymers,[7-10] proposed in recent years, can be adapted to the modeling of a polymer film. Theodorou and Suter[7] generated the initial structure by using a modified Markov process, based on rotational isomeric state (RIS) theory and incorporating long-range interactions. This structure was then relaxed by potential energy minimization. The method was extended to simulate polymer surfaces by placing "soft walls" at the upper and lower faces of the unit cell.[5] Brown and Clarke[9] generated the chain with an acceptance criterion very similar to the Monte Carlo method. The structure was heated up to 500 K to relax for 500 ps, followed by a subsequent period of relaxation on the order of 1 ns at the desired temperature. This method is very computationally intensive. Relaxation at higher temperature, like 1000 K,[10] can reduce the central processing unit (CPU) time significantly. The common feature in the above methods is a two-step strategy: (1) generating an initial structure as realistic as possible and (2) relaxing the initial structure by energy minimization or molecular dynamics simulation. As we know, thermal motion consists mainly of localized segmental fluctuations within the potential energy wells in the dense structure. The reliability of the results obtained in the simulations mainly depends on the performance of the initial-guess structure and the following relaxation process.

Unlike previous works, here we develop a new approach to build a polymer film by molecular dynamics simulations. We started from a fully extended chain, the simplest state

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for a linear chain molecule. This structure is intrinsically unstable for the long chain, and any distortion of some of the skeletal bonds away from the extended conformation leads to a lower energy due to the nonbonded interactions. The approach has been designed so as to allow the extended polymer chain to form a dense film during the simulation. In other words, we need not generate the initial-guess structure. The equilibrium conformation of the chain is formed by itself as the simulation proceeds. The procedure is facilitated by the relatively low barriers to rotational isomeric state transitions in poly(1,4–*trans*-butadiene). The objectives of this paper are to study the collapse transition of an extended chain to a coil or to a globule, the conformation and the structure of the globule and the film, and the polymer/vacuum interface properties. The simulations also provide some information about the behavior of the polymer in the bulk.

II. The Model

The molecular dynamics simulations which were performed by classical mechanisms and involved integration of Newton's equations of motion for all the atoms in the system, were carried out by using version 21.3 of CHARMm[11] as provided by Polygen Corp., Waltham, MA.[12] For constant temperature–pressure simulations for periodic systems in CHARMm, the method described in the paper by Berendsen *et al.*[13] is used. The potential energy of the system, E, was calculated as

$$E = E_{\mathrm{stretch}} + E_{\mathrm{bend}} + E_{\mathrm{dihe}} + E_{\mathrm{improper}} + E_{\mathrm{vdW}} \qquad (1)$$

where the terms on the right-hand side represent the contribution from bond stretching, bond angle bending, torsion potentials, improper dihedral angle contributions, and van der Waals interactions. The electrostatic contribution was not taken into account in our simulations. Some geometrical parameters were changed from the values supplied with CHARMm to those proposed by De Rosa *et al.*[14] These changes are 100° → 109.47° for $\mathrm{CH_2{-}CH_2{-}CH}$, 120° → 125° for $\mathrm{CH_2{-}CH{=}CH}$, and 120° → 117.5° for $\mathrm{H{-}C({=}CH){-}CH_2}$ and $\mathrm{H{-}C({-}CH_2){=}CH}$, as described by Dodge and Mattice.[15]

The poly(1,4-*trans*-butadiene) chain with a degree of polymerization of 180 and terminated by methyl groups was constructed. The molecular weight of the chain is 9738. The chain was initially formulated so that all dihedral angles at the skeletal bonds are in the *trans* state. The long axis of the polymer chains is parallel with the Z-axis of the coordinate system at the beginning. A typical strategy used in the simulations is as follows: (1) The potential energy of the *all-trans* structure was minimized using a conjugate gradient method. (2) The temperature of the system was increased from 0 to 300 K in 5 ps, and the system was equilibrated for 15 ps. (3) The simulations were then performed at a constant temperature and a constant volume with a duration of 1500 ps. A time step of 0.001 ps was used. During the simulation of the film formation, periodic boundary conditions were implemented in all three directions, with a unit cell of dimensions $L_x = L_y = 20.0$ Å and $L_z = 1000$ Å. The size in the Z direction was chosen so large that it could be considered as infinite. The periodic boundary conditions permit treating the cell as part of a system that is macroscopic in two directions. We also performed a simulation in which the fully extended chain collapses into a globule in vacuum, and no periodic boundary condition is needed. All the individual hydrogen atoms were included in the calculation of the potential energy during the simulations. The coordinates of all atoms in the system were monitored at intervals of 1 ps for subsequent analysis. The equilibrium properties reported for the system are the average over the last 1000 ps of the simulations, and they are not ensemble average.

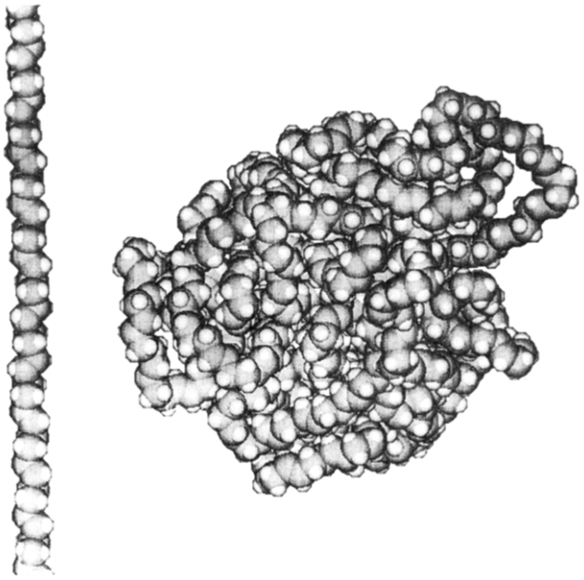

Figure 1. Views of the globule structure (right) formed with a fully extended poly(1,4-*trans*-butadiene) chain (left) after a molecular dynamics simulation of 1500 ps at 300 K in vacuum. Both structures are at the same magnification. Only about 6% of the fully extended chain is depicted.

Figure 2. Two views of the coil conformation of the parent chain in a film formed with a poly(1,4-*trans*-butadiene) chain of 180 repeat units after a molecular dynamics simulation of 1500 ps at 300 K. Left: XY projection (X horizontal, Y vertical). Right: YZ projection (Z, horizontal, Y vertical).

III. Results and Discussion

There are three types of bonds in the backbone of poly(1,4-*trans*-butadiene). The initial conformation of the chain was built with all dihedral angles at the backbone bonds in the *trans* state and its initial chain length is about 900 Å. After energy minimization, the $\mathrm{CH{=}CH}$ and $\mathrm{CH_2{-}CH_2}$ bonds remain in the *trans* states while the $\mathrm{CH{-}CH_2}$ bonds change to *anticlinal*$^{\pm}$ (or *skew*$^{\pm}$) states, and the chain length is reduced to about 890 Å. Applying the molecular dynamics prescription described above, the poly(1,4-*trans*-butadiene) chain contracts rapidly. Without the periodic boundary condition, the chain will collapse to form a globule, which is not spherical but is dense at the center of mass (Figure 1). With the periodic boundary conditions, the chain will begin to interact with its images at a certain time during the simulation and then form a film with its images. The parent chain adopted a loose conformation, which should be isotropic in the X and Y directions but not in the Z direction (Figure 2).

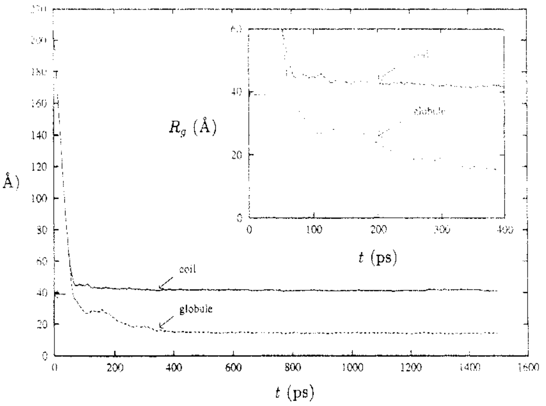

Figure 3. Variation of the radius of gyration with time for the coil in the film (solid line) and the globule (dashed line) during the molecular dynamics simulations at 300 K. The inset is a magnification of the data from 0 to 400 ps. The short arrows on the vertical axes denote the unperturbed root-mean-square radius of gyration estimated from rotational isomeric state theory.

Therefore, the collapse process of the isolated chain in vacuum undergoes a transition of the extended chain to a globule, while the collapse process of the chain with the periodic boundary conditions is a transition of the extended chain to a coil. Next, we will discuss the conformational properties of the coil (or the parent chain in the film) and the structure of the film. The conformational properties of the coil are compared with the conformation of the chain which forms the globule.

A. Properties of the Coil. The conformational characteristics of a coil can be analyzed (1) at the level of individual bonds and (2) at the level of the whole chain. The latter includes quantities like the radius of gyration, the end-to-end distance, etc. Because only one coil was generated in this study, it would be hard to place confidence in the analysis of the end-to-end distance. However, the value for the radius of gyration may be roughly used to characterize the size of the coil. In our simulation, the difference between the transition of the extended chain to a coil or to a globule is whether there is intermolecular interaction or not. The comparison of results for the coil and the globule permits an assessment of the effect of intermolecular interaction on the conformation of the chain.

Radius of Gyration. A plot of the radius of gyration as a function of time of the simulation is shown in Figure 3. The conformations of the chains when time is zero are not the *all-trans* conformations because the chains have experienced energy minimization, heating, and equilibration processes. After that, the collapse process of the chain can be divided into two regions. In the first region the radius of gyration shows a dramatic decrease for both the globule and the coil. The variation of the radius of gyration is almost linear with time. This result is similar to that of Kavassalis and Sundararajan[16] which shows a significant reduction in the radius of gyration in the first 200 ps of dynamics of an initially extended polyethylene. In the second region, the radius of gyration decreases slowly with small fluctuations. The former may be considered a process of collapse to the globular state, and the latter, a process of local equilibration.

It is interesting to note that the time of transition from one region to the other is nearly the same for both systems. As we know, the transition of an extended chain to globule only has intramolecular interaction, but the transition to a coil has both intramolecular and intermolecular interaction. The simulation results suggest that the intermolecular interaction can be ignored in the first region. In other words, before the parent chain has interaction with its images during the simulation, the collapse process entered the second region. The relaxation time for poly(1,4-*trans*-butadiene) is faster than that for polyethylene, presumably because the activation energy for rotational isomeric state transitions is smaller at $CH-CH_2$ than at CH_2-CH_2. In our simulation the transition from one region to the other is less than 100 ps (even including the time for heating and equilibrium), while the simulation of collapse for a polyethylene chain with 750 CH_2 units showed the transition point is at more than 100 ps.[16]

There is a difference between the dimensions of the two systems after the first region of collapse. For the transition to the coil, the size of the chain drops to a value which is very close to its equilibrium dimension, where the radius of gyration is about 41 Å. In the second region, the radius of gyration of the coil decreases very slowly and finally approaches a limiting value with small fluctuations. For the transition of the globule, the radius of gyration of the chain is less than the equilibrium dimension of the coil after the sharp decrease in the first region. The chain contracts rapidly in the initial 100 ps, followed by a slight expansion between 100 and 160 ps, and then followed by a stronger collapse. Kavassalis and Sundararajan[16] also observed a slight expansion after the initial collapse of polyethylene. The origin of the slight expansion is not understood.

In the study of Kavassalis and Sundararajan,[16] the calculated value of the radius of gyration from the simulation of the single chain falls below that for the real system of solution-grown crystals. This result is because the simulation of an isolated chain did not consider the intermolecular interaction of multiple chains. They also calculated the radius of gyration from a simulation containing four chains, in which the dimensions are nearly double those seen in the simulation of a single chain. Thus, the effect of multiple chains is to increase the radius of gyration. In our case, the radius of gyration from the simulation of the coil is nearly 3 times larger than that of the globule. The intermolecular interaction of the parent chain with its images in the film has a higher effect on the radius of gyration than in the case of the four chain system of polyethylene and is closer to the situation in the bulk.

Rotational isomeric state schemes for the statistical treatment of the poly(1,4-*trans*-butadiene) chain were formulated by Mark[17] and by Abe and Flory.[18] The analysis by Mark gave the characteristic ratio $C_\infty = (\langle r^2\rangle_0/\sum_{i=1}^{n} l_i^2)_{n\to\infty} = 5.8$ for poly(1,4-*trans*-butadiene) and is in satisfactory accord with results of experiments. The radius of gyration estimated from the characteristic ratio is 39 Å for the poly(1,4-*trans*-butadiene) chain with 180 repeat units by the following equation:

$$\langle R_g^2\rangle_0 = \frac{C_\infty}{6}[x(l_1^{\,2} + 2l_2^{\,2} + l_3^{\,2}) - l_1^{\,2}] \qquad (2)$$

where $x = 180$ is the degree of polymerization of the chain, $l_1 = 1.54$ Å is the length for the CH_2-CH_2 bond, $l_2 = 1.51$ Å is the length for the $CH-CH_2$ bond, and $l_3 = 1.35$ Å is the length for the $CH{=}CH$ bond. The radius of gyration from the simulation of the parent chain in the film is about 41 Å, which is very close to the estimated value for RIS theory.

Density Profile. The local density of a chain was calculated by using a polar coordinate system where the origin is at the center of mass of the chain. The local density profiles, accumulated using 1-Å-thick bins along the radial direction, were averaged separately at intervals

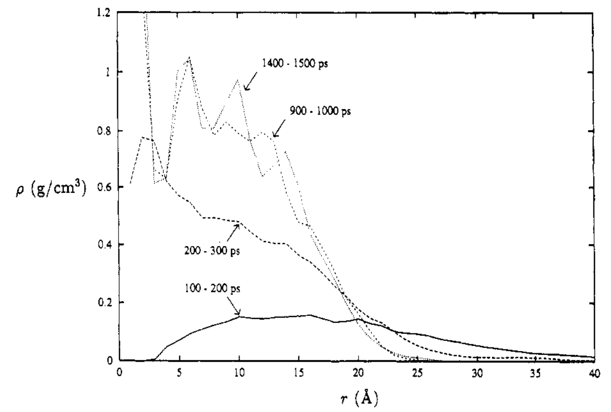

Figure 4. Local density profiles of the globule as a function of distance along the radial direction during the simulation: 100–200 ps (solid line); 200–300 ps (long-dashed line); 900–1000 ps (short-dashed line); 1400–1500 ps (dotted line).

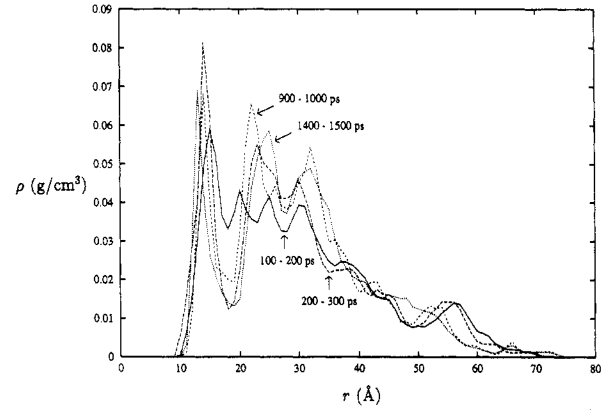

Figure 5. Local density profiles of the coil in the film as a function of distance along the radial direction during the simulation: 100–200 ps (solid line); 200–300 ps (long-dashed line); 900–1000 ps (short-dashed line); 1400–1500 ps (dotted line).

of 100 ps to examine the formation of a globule or a coil. Let us begin with the transition of the extended chain to a globule. Figure 4 shows how the local density profiles vary with time. Initially, the chain is fully extended, and the atoms are dispersed in a large range of the radial direction. The local density is low at every point. As the collapse process proceeds, the chain contracts toward the center of mass. The local density near the center of mass increases. When equilibrium is reached, the local density near the center of mass is close to 0.89 g/cm^3, the bulk density of poly(1,4-*trans*-butadiene) in the amorphous state.[19] The final globule is not spherical. Some of the atoms in the globule may extend as far as 25 Å from the center of mass, although the radius of gyration is only 14 Å.

The situation for the transition to the coil is different. When the collapse of the chain happens, the atoms are not strongly attracted to the center of mass (Figure 5). As we pointed out before, the radius of gyration for the coil is triple that for the globule. If estimated from the value of the radius of gyration, the average local density inside the coil would be $^1/_{27}$ of the density for the interior of the globule. As can be seen from the final density profile, the local density is so low that even the maximum of the local density is less than $^1/_{10}$ of the bulk density. Figure 5 shows that the segment density decays as r increases from the center of mass. The statistical error becomes large as r decreases because of the average over a small volume. The density at the center of mass is zero in Figure 5, because the center of mass for our system is located in part of the system (Figure 2) that is not occupied by any segment from the parent chain.

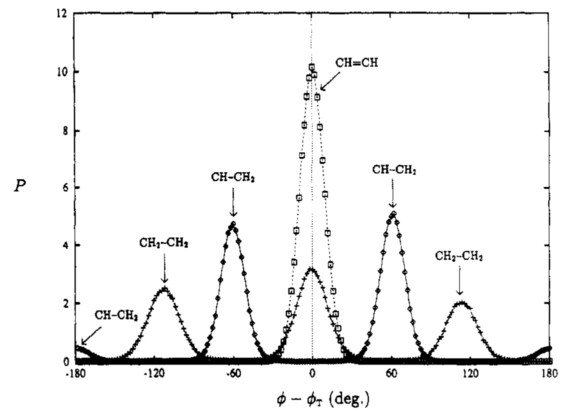

Figure 6. Distribution of the dihedral angles for the CH_2–CH_2 bonds (+), the CH–CH_2 bonds (♦), and the CH=CH bonds (□) in the globule at equilibrium.

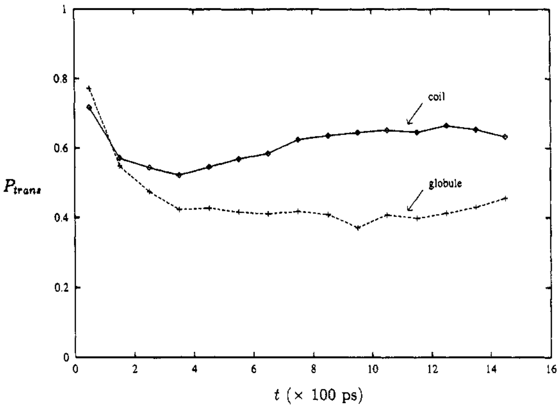

Figure 7. Population of the *trans* state at the CH_2–CH_2 bonds as a function of time in the coil (♦) and in the globule (+).

Dihedral Angles. The *trans* conformation is the only stable rotational isomer for the CH=CH bonds (Figure 6). During the simulations, the rotation about the CH–CH_2 bonds provides access to three rotational isomeric states denoted by *cis* and *anticlinical*$^\pm$. The CH–CH_2 bonds have a very strong preference for *anticlinal* states, and the probability for the *cis* placement is about 5% (Figure 6), which is consistent with the previous simulation.[19,20] The probability profiles observed for all three bonds are close to the expectation based on the symmetry of the torsion potential energy function.

We will focus our attention on the population at the CH_2–CH_2 bonds. The population of the *trans* state as a function of time in the coil and in the globule is depicted in Figure 7. For a 1500 ps trajectory, the rotation angles at the CH_2–CH_2 bonds were averaged separately at intervals of 100 ps. Initially, all dihedral angles at the CH_2–CH_2 bonds are in the *trans* state, even after energy minimization. As the molecular dynamics simulation proceeds, the population of the *trans* state decreases to about 50% in the initial 300 ps for the transition of the extended chain to the coil. There follows an increase in the population of the *trans* states, because in the formation of the film the segments of the chain prefer orientations parallel to the surface.

For the collapse to a globule, the population of the *trans* states decreases to about 40% in the initial 400 ps and fluctuates about this value. Unlike the formation of the film, there is no increase in the population of the *trans* state after the initial drop. Figure 8 shows the radial distribution of the *trans* state at the CH_2–CH_2 bonds in the globule. Within 15 Å of the center of mass, a value

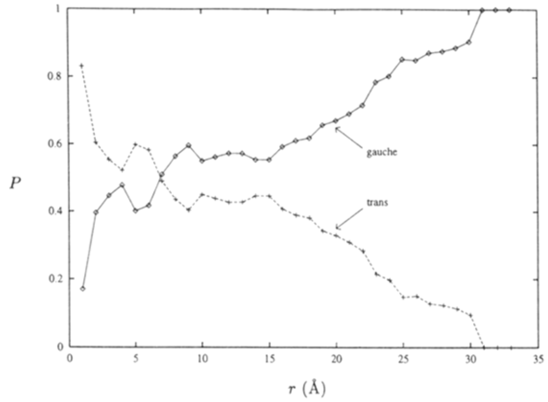

Figure 8. Radial distribution of the *trans* (+) and the *gauche* (♦) conformations at the CH_2–CH_2 bonds for the globule.

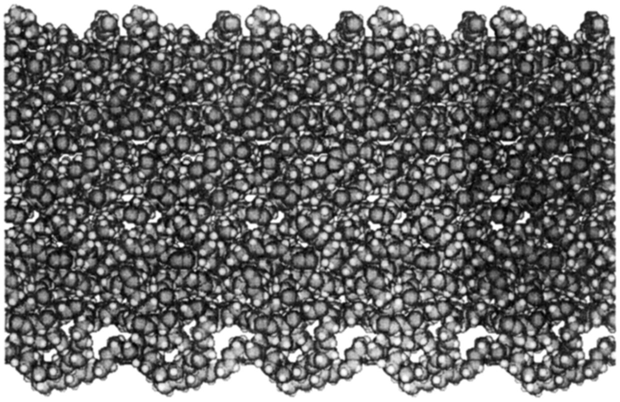

Figure 9. Five adjacent *XZ* projections (*X* horizontal, *Z* vertical) of the same model structure with the same single parent chain. The *XZ* projection appears porous because the unit cell is thin in the *Y* direction.

close to the radius of gyration, the population of the *trans* state is nearly constant, although there is some fluctuation near the center of mass where the number of samples is small. The segments of the chain at the surface of the globule should fold back to its inside, so the *gauche* population increases (and the *trans* population falls) at large radial distances.

B. Properties of the Film. Molecular dynamics simulation provides detailed information of the film formation and the equilibrium structure. Five adjacent XZ projections of the same model structure with the same single parent chain at 300 K are shown in Figure 9. The periodic length in the *X* and *Y* directions is 20 Å, and the thickness of the film in the *Z* direction is about 50 Å. The *Z* dependence of structural characteristics was examined at a local level. The film was partitioned into equal bins by drawing planes normal to the *Z* axis, and the contents of each bin was analyzed. Since the two faces of the film are macroscopically symmetric, our results represent averages over halves of the film. Position $Z = 0$ corresponds to the film midplane, and vacuum lies at large *Z* values.

Density Profiles. The local density profiles, accumulated using 1-Å-thick bins along the *Z* axis, are displayed in Figure 10. The data were averaged separately at intervals of 100 ps. The local density follows a sigmoidal profile at the free surfaces. One way of characterizing interfacial thickness is through the distance over which the mass density falls from its bulk value to zero. With this definition, we found the thickness of a polymer/vacuum interface is about 10 Å. The middle region of the film (around $Z = 0$) is indisitinguishable from the center region of the globule in terms of density.

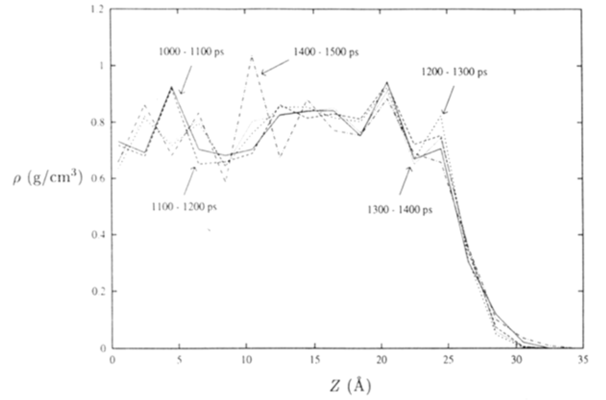

Figure 10. Local density profiles of the film as a function of distance from the film midplane during the simulation: 1000–1100 ps (solid line); 1100–1200 ps (long-dashed line); 1200–1300 ps (short-dashed line); 1300–1400 ps (dotted line); 1400–1500 ps (dot-dashed line). Vacuum is located at the extreme right.

Bond Orientation. To characterize bond orientation, we define an order parameter, averaged over all bonds whose midpoint lies within a given bin and over every 100 ps:

$$S_B = 1/2[3\langle \cos^2 \theta \rangle - 1] \tag{3}$$

where θ is the angle between the *Z* axis and the bond under examination, and $\langle\ \rangle$ is indicative of averaging within the bin. S_B equals 0, 1, and $-^1/_2$ for bonds with perfectly random, perpendicular, and parallel orientations relative to the surface plane, respectively.

In the study of Mansfield and Theodorou,[5] the atactic polypropylene chains in the film grew in a bond-by-bond fashion within the unit cell. In order to prevent chains from exiting the film and wandering into the surrounding vacuum, soft walls were placed at the upper and lower faces of the unit cell. Their results showed that all bonds are randomly oriented in the bulk, and there is a weak tendency for parallel orientation in the vicinity of the free surface. The order parameter for C–C displayed a minimum, about −0.13, a few angstroms away from the extreme edge of the film. This result suggested a tendency for chain segments to run parallel to the surface in the film constructed under their conditions. In our study, the situation more closely resembles a film formed by an extended chain depositing itself onto a surface. In other words, the film is formed in a layer-by-layer fashion from the midplane. Therefore, each layer has some characteristics of the surface layer. The results, shown in Figure 11, indicate that backbone bonds exhibit a tendency for parallel orientation over most of the range of *Z*. The average value of S_B is close to the minimum of S_B obtained by Mansfield and Theodorou.[5] It is remarkable that bond orientation effects are not short-ranged. If the simulation was performed long enough, the bonds in the center region of the film should approach a more random orientation, with S_B close to zero. In the bins closest to the vacuum phases, where the polymer is highly attenuated, S_B for C–C has less negative values, which means the backbone bonds are a little more randomly oriented than in the vicinity of the free surfaces.

Dihedral Angles Distribution. The RIS analysis showed that the statistical weight of each *gauche* state is equal approximately to that of the *trans* state at the CH_2–CH_2 bonds.[17] An atomistic model of amorphous poly(1,4-*trans*-butadiene) was obtained at bulk density by molecular dynamics simulation.[17] The calculation of

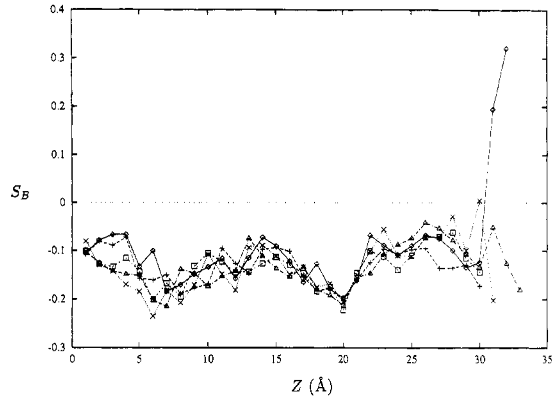

Figure 11. Local order parameter for C–C bonds as a function of distance from the film midplane during the simulation: 1000–1100 ps (◇); 1100–1200 ps (+); 1200–1300 ps (□); 1300–1400 ps (×); 1400–1500 ps (△).

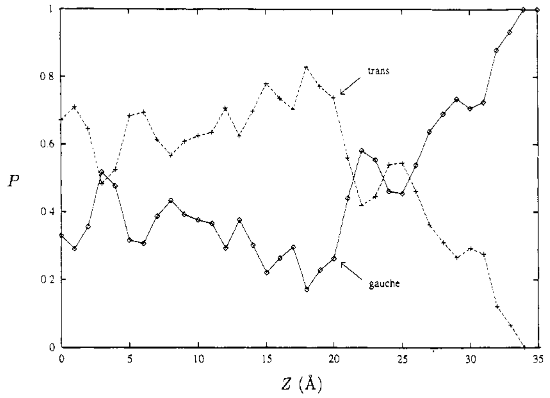

Figure 12. Distribution of the *trans* (+) and the *gauche* (◇) conformation at the CH_2–CH_2 bonds for the film as a function of position in the Z direction at 300 K.

conformational statistics revealed that it retains the properties predicted by the RIS theory. All three states, *trans* and *gauche*$^{\pm}$, seem to be equally populated. A single chain collapsing into a globule or a coil in film may cause the conformational preferences of the chain to depart from what they are in the bulk. To assess this effect, we undertook a study of the distribution of the dihedral angles as a function of the position of the bond midpoints. Within each 1-Å-thick bin, the dihedral angles were grouped into three rotational states. The distribution of the dihedral angles at the CH_2–CH_2 bonds for the film at 300 K is shown in Figure 12. The *trans* state is most favored in the middle region, but a significant conformational perturbation occurs in the surface region. The relative frequency of the *trans* state decreases, and a corresponding enhancement in the *gauche* state is observed at the surfaces. The *gauche* states allow a chain to quickly turn back from the vacuum into the energetically more favorable bulk.

The equilibrium distribution of the dihedral angles at the CH_2–CH_2 bonds for the film and the globule at 300 K is shown in Figure 13. The *trans* state is more favored in the film than in the globule. There are two reasons for the differences in these distributions. As we mentioned above, the chain in the vicinity of the free surface prefers the parallel orientation with the surface, and the *trans* state is favorable for this parallel orientation. Another favor is that for the globule there is a larger surface area at which the *gauche* state is needed for the chain to turn back from the vacuum into bulk.

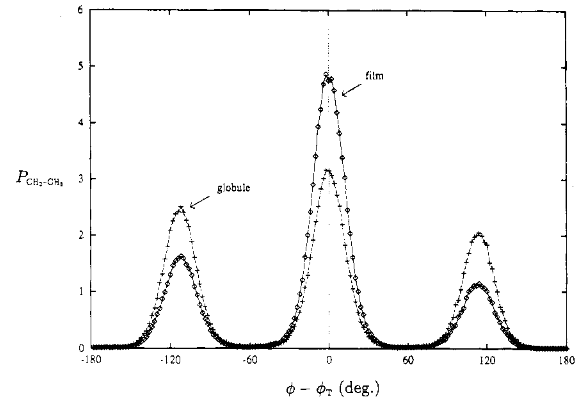

Figure 13. Distribution of the dihedral angles for the CH_2–CH_2 bond after a molecular dynamics simulation of 1500 ps at 300 K in film (◇) and in globule (+), where ϕ_T is the dihedral angle for a *trans* placement.

IV. Conclusion

Atom-based molecular dynamics simulations were performed on a polymer thin film and a single chain globule. The film is formed by a transition of a fully extended chain to a coil using periodic boundary conditions in the X and Y directions. A collapse transition of the extended chain to a globule was also simulated as a comparison. The conformational properties of the coil and the structure of the film were examined. The collapse process of the chains can be divided into two regions for the transition to both the coil and the globule. In the first region the chain size shows a dramatic drop, while in the second region it decreases slowly with fluctuations. The density in its center of mass is close to the bulk density of amorphous poly(1,4-*trans*-butadiene). The coil that is the parent chain for the film exhibits a very loose structure, and its density at the center of mass is close to zero. The radius of gyration for the coil from the simulation is very close to the estimated value from RIS theory.

Local structural features of the film were analyzed at the level of atoms. The local density of the film follows a sigmoidal profile at the free surfaces. The maximum thickness of a polymer/vacuum interface is about 10 Å, as judged by the density profile. The backbone bonds exhibit a tendency for parallel orientation in the vicinity of the free surfaces. The *trans* conformation is favored in the equilibrium distribution of the dihedral angles at the CH_2–CH_2 bonds within the film.

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