Notes

Molecular Dynamics Simulations of Folding in Cyclic Alkanes

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Cyclics of polymers or oligomers have been a subject of interest for a number of years.[1,2] The small cyclics form the components of molecular architectures such as catenanes and rotaxanes.[3,4] Collapse of the rings to form nematic order has been observed in the case of cyclic polyethers.[5] The crystal structure and morphology of cyclic alkanes have been considered models for understanding the crystallization of polyethylene by chain folding. The tight folds at both ends of the folded cyclic alkanes are thought to represent the fold conformation of polyethylene with adjacent reentry of the chain stems. To this end, several structural and thermal studies on cyclic alkanes of various sizes have been reported.[6−13]

Studies on polymer chain collapse using Monte Carlo[14,15] and molecular dynamics[16−19] (MD) methods have been reported recently. In our first MD studies[16] on polyethylene (PE) chains, varying in length from 500 to 2000 CH_2 units, we reported that the polymer chains collapsed in the form of a chain-folded lamella. Our subsequent MD simulations of PE as a function of chain length[18] showed that the chain must be at least about 150 CH_2 units long for stable folding to occur. This was in agreement with the conclusions from the experimental work on linear long chain paraffins.[11,20]

In our first MD study, although the lamellar formation occurred during the collapse of the PE chain, the resulting lamellar dimension of 40−50 Å from the simulations was significantly smaller than the experimental value of ≥ 100 Å, as were the calculated radii of gyration (R_g) of the collapsed chains. The small lamellar dimension, obtained in the simulations with single chains, was traced[18] to a low torsional barrier of 2 kcal/mol for the C−C bonds in the Dreiding (Polygraf) force field[21] that we used.

In molecular conformational studies, it is common practice to use a torsional barrier of 3 kcal/mol for rotations around the C−C bonds, similar to the barrier in the case of *n*-butane. It is through the torsional rotations that conformational transitions of chain segments occur. However, during solution crystallization, the frictional force due to the solvent medium and due to the intermolecular interactions must be overcome for the conformational transitions to occur. This is the basis of the discussion of Allegra and Ganazzoli[22] on the role of torsional barriers on the relaxation and dynamics of polymer chains. On the basis of the concept of the role of internal viscosity of long chains on their viscoelasticity, Allegra[23] predicted a barrier of 6 kcal/mol between the trans and gauche states of polyethylene, when *a pair of bonds* is involved in a conformational transition. Following this thought, in our subsequent work[18] on the simulations with single chains, we increased the torsional barrier around the C−C bonds to values ranging from 3 to 6 kcal/mol. This strategy of increasing the torsional barrier led to good agreement between the lamellar dimensions and the radii of gyration obtained from the simulations with isolated chains and the experimental results. The effect of the increased torsional barrier was significant in the case of long chains with 1000 or 2000 CH_2 units. This is in accord with the expectation that the longer chains would experience a higher frictional resistance than the shorter ones.

In this paper, we discuss the results of MD simulations of cyclic alkanes. The differences between the conformation at the folds obtained with simulations using the united atom approximation and the explicit hydrogens are mentioned. The effect of the torsional barrier used in the simulations on the folding behavior of the larger cyclics is also discussed. The fold lengths of the cyclics are compared with the long spacings (L_{LAM}) derived from longitudinal acoustic mode (LAM) frequencies.[11]

Simulations were performed with cyclics varying in size from 20 to 200 CH_2 units. The initial conformation of each of the cyclic alkanes was that of an *n*-fold rotationally symmetric cyclic. For example, for generating a symmetric cyclic with 100 CH_2 units, the difference in the bond angles at alternate CH_2 units was set at 7.2° (360°/50), i.e., 109.5 and 116.7°. Alternation of successive bond angles in this manner leads to ring closure. The simulations were carried out using the Polygraf (versions 3.0, 3.1, and 3.2, from Molecular Simulations Inc.) molecular modeling code, with Dreiding II potential[21] and simulation parameters as described before.[16,18] The CH_2 groups were treated with the united atom approximation. As described above, values ranging from 2 to 6 kcal/mol were used for the torsional barrier. The rest of the parameters of the Dreiding II force field were not modified.

One feature that distinguishes the cyclic alkanes from their linear counterparts is that whereas a chain length of at least 150 CH_2 units is required for chain folding to occur in the latter, cyclics with as few as 20 units fold, with an interstem distance of ~4 Å. The calculated stem lengths for cyclics with 24, 36, 60, and 72 CH_2 units were 13.6, 20.4, 35.0, and 44 Å, respectively. These distances are roughly half that of the *c* dimensions (31, 46.3, 77.3, and 92.6 Å, respectively) in the crystal structures of the molecules, as shown in Figure 1. This is to be expected since in these crystal structures, two molecular lengths comprise the *c* dimension of the unit cell. Allowing for the van der Waals separation of the folds of two end-on molecules, the length of each molecule would be less than half of the *c* dimension. The fold length of 44 Å calculated for $(CH_2)_{72}$ is also in agreement with the long spacing values of 42.8 Å derived from small angle X-ray scattering measurements and 47.3 Å from the LAM frequencies.[11] A comparison of the calculated fold lengths of the various cyclics, the crystal structure *c* dimensions,

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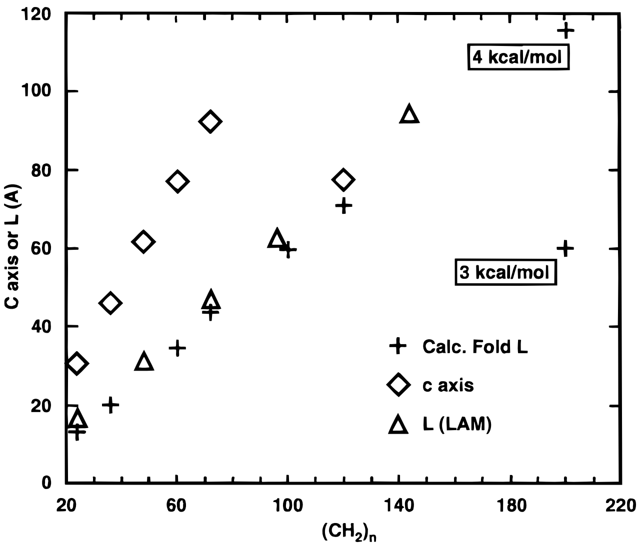

Figure 1. Calculated fold lengths of cyclic alkanes of various sizes shown, along with the crystallographic *c* dimensions.[8] The long spacings (L_{LAM}) calculated from the experimental results of Lee and Wegner[11] are also plotted. The results of the simulations correspond to a torsional barrier of 3 kcal/mol for cyclics with up to 100 units, and both 3 and 4 kcal/mol in the case of cyclic $(CH_2)_{200}$.

and the long spacings derived from LAM frequencies is shown in Figure 1.

The fold conformation for $(CH_2)_{36}$ in the crystal structure[7] consists of a ggtgg conformational sequence of the bonds. When the united atom approximation was used in the simulations of the cyclics mentioned above, the conformations of the bonds at the fold were always in a sequence of g and/or g^- states. Since a fold is initiated with a transition from the trans to a nonstaggered or a gauche conformation, these states resulted when the united atom approximation was used. However, simulations with explicit hydrogens led to ggtgg conformation at the fold, similar to the crystallographic conformation. This illustrates the importance of including explicit hydrogens in the simulations, if one is interested in the details of the conformations at the folds.

The effect of the torsional barrier used in the simulations begins to influence the fold length with cyclics of 100 or more CH_2 units. With a 2 kcal/mol torsional barrier, for the cyclic alkane with 100 CH_2 units, multiple stem folding occurred within 50 ps, and the lamellar dimension was only about 15−18 Å. Such a formation of multiple stems, with a small lamellar dimension, occurred in the simulations of linear alkanes as well with more than 150 CH_2 units, when a low torsional barrier was used.[16] As discussed previously,[16] with a barrier of 2 kcal/mol, profuse occurrence of gauche and nonstaggered conformations leads to multiple stem folding and a small lamellar dimension. In the crystal structures of $(CH_2)_{72}$ and $(CH_2)_{120}$, the *c* dimensions ("chain axis") are 92.6 and 77.7 Å, respectively, with four molecules in the unit cell in the former and one molecule in the case of $(CH_2)_{120}$. Allowing for the projected overlap of the adjacent molecules and the nonbonded distance between the folds of end-on adjacent molecules, an end-to-end folded dimension of at least 50 Å is expected in the case of the cyclic $(CH_2)_{100}$. The long spacing L_{LAM} obtained[11] for $(CH_2)_{96}$ is 62.9 Å.

With a torsional barrier of 3 kcal/mol, the cyclic $(CH_2)_{100}$ folded into two stems within 10 ps and further folding did not occur during the rest of the simulation (up to 1000 ps). Thus, with a small increase in the barrier, the multiple stem formation was precluded. The fold length was 60 Å, which is to be expected on the basis of the crystal structure *c* dimension for cyclic $(CH_2)_{120}$. This is also similar to the long periods of 60 and 62.9 Å obtained for $(CH_2)_{96}$ from SAXS and LAM measurements.[11] Increasing the barrier to 4 or 6 kcal/mol still led to the two-stem folding, although the time taken to fold increased.

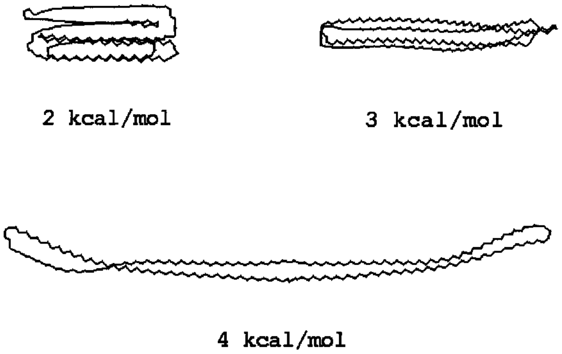

Figure 2. Folded conformations of $(CH_2)_{200}$ obtained from the simulations using torsional barriers of 2, 3, and 4 kcal/mol. With a barrier of 6 kcal/mol, folding did not occur up to 1000 ps of dynamics.

With cyclic $(CH_2)_{120}$, the molecule folded into two stems with a fold length of 71 Å, when a barrier of 3 kcal/mol was used. With an increase of the barrier to 4 kcal/mol, it took nearly 650 ps for the cyclic to fold during the MD simulation. With a barrier of 6 kcal/mol, no folding occurred during the 1000 ps of simulation.

Let us now consider the case of an even larger cyclic alkane, with 200 CH_2 units. The value used for the torsional barrier affects the results of the simulations with single molecules significantly in these cases. When the torsional barrier was excluded from the force field, the cyclic alkane with 200 units folded into a globule of diameter ~20 Å. No lamellar organization occurred.

Figure 2 shows the folded structures obtained for $(CH_2)_{200}$, with barriers of 2, 3, and 4 kcal/mol. With a barrier of 2 kcal/mol, multiple stem folding occurs, with a small lamellar dimension of 27−29 Å. Increasing the barrier to 3 kcal/mol led to irregular folding initially, which then diffusively rearranged to a four-stem folded structure, with a lamellar dimension of 60 Å. The entire rearrangement process was completed in about 150 ps of dynamics. When the barrier was increased to 4 kcal/mol, the folding was completed only after about 750 ps. The cyclic folds into two stems, with a fold length of 115 Å. With a further increase in the barrier height to 6 kcal/mol, the cyclic did not fold within the 1000 ps duration of dynamics.

The fold length of the cyclic $(CH_2)_{200}$ increases almost linearly from 29 to 115 Å with the barrier height between 2 and 4 kcal/mol. Although with a 4 kcal/mol barrier the two-stem folding is obtained, the folding process was retarded significantly with the barrier height of 6 kcal/mol. This points to the possibility that the kinetics of chain-folded crystallization might be understood in terms of the barrier to conformational transitions imposed by solvents of various types and the temperature.

The time taken for the folding increases with the value used for the torsional barrier. With 2, 3, and 4 kcal/mol, folding occurred after 50, 150, and 750 ps, respectively. The fact that, with a barrier of 6 kcal/mol, the cyclic did not fold during 1000 ps of dynamics is due to the lack of conformational transition of any of the bonds to a gauche state. We do not believe that it is simply due to not having a long enough simulation. We used a temperature of 300 K for the simulations. The combined effect of the temperature and the barrier height has not been investigated here.

The calculated fold lengths for $(CH_2)_{200}$ using both the 3 and 4 kcal/mol barrier are shown in Figure 1. The crystal structure of this molecule is not available in the literature. The fold length of 115 Å for the two-stem folding with $(CH_2)_{200}$ is in line with the long spacing of 91 and 94.8 Å derived for $(CH_2)_{144}$ from SAXS and LAM data, respectively.[11] Lee and Wegner[11] concluded that cyclics with up to 288 CH_2 units do not show additional folding. Using the value of 21 cm^{-1} for the measured first-order longitudinal acoustic mode (LAM) frequency (as given in Table 2 of ref 11), the long spacing for $(CH_2)_{288}$ is 180.5 Å, which indicates a two-stem folding. On the basis of these results, a multistem folding in $(CH_2)_{200}$ can be ruled out and the fold length obtained from the simulations using a torsional barrier of minimum of 4 kcal/mol is in accord with experimental observations.

The results of the MD simulations presented here show that the fold lengths in the collapsed state of the large cyclics depend on the value used for the torsional barrier in the simulations. Whereas in the case of linear alkanes we were able to compare[18] both the lamellar dimensions and the radii of gyration from the simulations with the experimental results, the latter are not available in the literature for the cyclic alkanes. While the barrier height does not play a significant role in the case of small cyclics, those with 60 or more CH_2 units require an appropriate barrier in the calculations to reproduce the experimental results. The influence of the torsional barrier was found to be similar in the case of both linear and cyclic alkanes. For a molecule, both cyclic and linear, with up to 150 CH_2 units, a barrier of 3 kcal/mol leads to fold lengths similar to the experimental results. For both types of molecules, with 200 or more CH_2 units, a higher barrier is required in these simulations. During the multiple stem folding in the case of linear alkanes, it was found that one of the chain ends initiates the diffusive rearrangement process.[18] In the case of the cyclics, one of the folded ends performs a similar function. The details of these lamellar reorganizations are not discussed here in the interest of brevity.

The values of barrier heights which we chose, from 2 to 6 kcal/mol, were rather arbitrary, and the purpose was simply to reduce the populations of the gauche and nonstaggered conformations, so as to achieve fold dimensions in the range of the experimental results. The barrier height also influences the time required for folding i.e., conformational transitions, to occur. The present results are in agreement with the predition of a barrier of 6 kcal/mol, by Allegra,[23] between the trans and gauche states of polyethylene, when *a pair of bonds* is involved in the conformational rearrangement. An accurate determination of the barrier height relevant to the various cases would require comparison with the experimental results derived from using solvents of different viscosities, temperatures, and other crystallization conditions, leading to different lamellar dimensions. Such experimental studies are abundant in the literature with respect to linear alkanes and polyethylene. The results of our studies in this direction will be published in due course. The effect of the torsional barrier discussed here could perhaps be simulated equally well by scaling the van der Waals potential.[24] However, we felt that changing the torsional barrier is a simpler approach to follow when using commercial modeling codes of the type used here.

With the united atom approximation, the conformations of the bonds at the fold resulting from the simulations differ from the crystallographic conclusions. The latter are reproduced when explicit hydrogens are used. However, irrespective of how the hydrogen atoms are treated, the torsional barrier has an effect on the fold length in the simulations of the large cyclics as well as the linear chains.

References and Notes

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