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Computer Modeling of {110} Adjacent Reentry of Polyethylene Molecules

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ABSTRACT: Conformations of adjacent reentry folds of polyethylene have been examined using molecular mechanics techniques. In addition to the lowest energy conformation ($g^-g^-g^+g^+tg^+$) described in previous studies, other conformations with similar energies but different spatial extents were identified. In particular, a fold conformation was found which was less than 1 kcal/mol higher in energy than the global minimum ($g^+g^+tg^+g^+tg^+$). The effects of different fold conformations on fold surface packing and the lamellar structure of polyethylene crystals were discussed. Fold energies for the five lowest conformations ranged from 4.5 to 6.2 kcal/mol. The small energy differences between the global minimum and the other conformations indicate that more than one fold type may be present in polyethylene crystals and should be considered in fold packing simulations.

Introduction

It is now close to 3 decades since the first reports of the structure of single crystals of polyethylene[1-3] and the suggestion that the chain exits and reenters the crystal through an adjacent reentry process. Folds are generally accepted as occurring predominantly in the {110} planes due to the growth process. It has also been assumed that the folds are as tight as possible and oriented approximately parallel to the {110} planes.

Few computational studies have addressed the geometries associated with polyethylene chain folds and have recently been reviewed.[4] The first attempt at generating a detailed molecular structure for the folds was reported by McMahon et al. using a simple model where only the carbon torsional angles varied.[5] Later, Corradini et al. predicted different fold structures with a more sophisticated model allowing for greater flexibility in the fold structure.[6] Their lowest energy fold geometry was found to be consistent[7] with infrared spectra of chain folds of polyethylene[8] and n-$C_{198}H_{398}$ molecules.[9]

Other studies have examined the packing of folds. Oyama et al. minimized the surface energy of packed folds with respect to the fold geometries.[10] They only varied the carbon torsional angles of the fold, however, and their lowest energy conformations were different from those of Corradini et al. Davé and Farmer determined the energetics of different packing habits and the associated changes in fold structure due to packing.[4] They used as initial structures the ones found by Corradini et al. and did not consider other possible conformation types in their calculations.

Most of the computational work has focused on the lowest energy conformation of the chain folds. McMahon et al. considered the possibility of other fold geometries,[5] but their methods were crude as compared to today's standards and did not yield the minimum structure of Corradini et al.[6] Currently, simulations of polymers explicitly include many atoms,[11-21] but many times they require information about the best geometries from which to start the calculations. With the advances of computer simulations, it is possible to reexamine the chain fold problem in a precise manner and investigate the population of possible folded chain structures. The importance of these folds can be evaluated and their geometries can then be used in further studies of fold packing similar to the one by Davé and Farmer.[4]

It is shown in this study that the fold geometry predicted by Corradini et al.[6] remains the lowest energy conformation possible. However, a second possible fold exists less than 1 kcal/mol higher in energy and hence is likely to occur in practice. This fold is slightly longer than the first and exhibits a geometry that is inclined to the {110} position rather than being parallel to it. The two types of folds are predicted to have different packing geometries in the folded surfaces and, if both are present, are expected to be segregated into sectors.

Methods and Model

The calculations were carried out using Version 2.2 of the POLYGRAF program.[22] Molecular mechanics energies were calculated using the default Dreiding force field[23] with the following exceptions in the nonbonded energy terms. We employed the exponential-6 expression (1) for van der Waals interactions because it yielded better agreement with experimental data than the default Lennard-Jones 6–12 potential in POLYGRAF (see below). In (1), A, B, and C are parameters

$$E_{\mathrm{vdw}}(i,j) = A\exp(-CR_{ij}) - \frac{B}{R_{ij}^{-6}} \qquad (1)$$

previously defined,[23] and R_{ij} is the distance between two atoms, i and j. Coulombic nonbonded terms were included using (2), where $\epsilon = 1$ and q_i and q_j are the partial charges on atoms i and j, respectively. This form of the Coulombic function differs from

$$E_{\mathrm{Coul}}(i,j) = \frac{(322.0637)q_iq_j}{\epsilon R_{ij}} \qquad (2)$$

the default in POLYGRAF where $\epsilon = R_{ij}$. Atomic charges were calculated using the method of Gasteiger and Marsili.[24] For polyethylene, q_H was defined to be 0.023 units and q_C was made equal to −0.023 times the number of C–H bonds at a given carbon atom.

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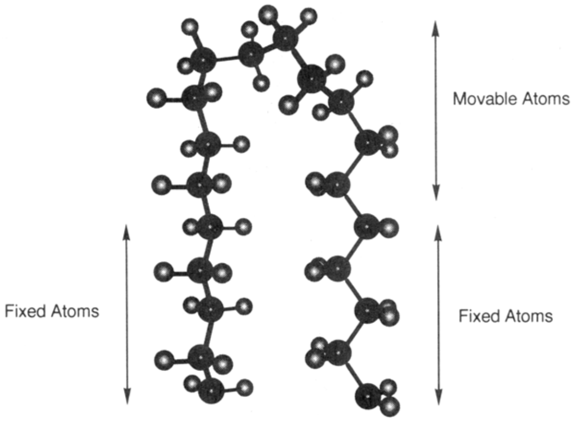


Figure 1. Polyethylene chain fold model.

Molecular geometries and polyethylene crystalline cells were optimized using the Fletcher–Powell method until the root mean square (rms) of the calculated forces was less than 0.002 kcal/mol·Å. Polyethylene crystalline cells were simulated using a periodic boundary method whereby the polyethylene chains were packed in a box which is repeated in three dimensions to simulate an infinite crystal (see, for example, ref 19). All atomic and cell lattice parameters could be optimized simultaneously and long-range electrostatic effects were included using the Ewald method.[25]

We adopted a model for a single fold in a polyethylene chain (Figure 1) similar to Corradini et al.[6] and Davé and Farmer.[4] The model consisted of two parts. The first part contained the middle 10 CH_2 units in a folded 20 CH_2 chain segment. The atoms in this portion of the fold were allowed to move during optimizations and molecular dynamics. The second part of the model consisted of the five CH_2 units at each end of the fold. These portions of the folded chain were held fixed during the simulations at the positions of two adjacent stems in a polyethylene crystal along the {110} plane. The stems were separated by 4.46 Å, corresponding to the room-temperature polyethylene unit cell parameters of $a = 7.400$ Å, $b = 4.930$ Å, and $c = 2.553$ Å and a setting angle of 47°.

We defined the fold energy in this model to be the energy difference between the *middle* 10 CH_2 segment of the fold model and an all-trans 10 CH_2 chain. This definition of the fold energy corresponds to the energy required to create the fold, independent of the fixed polyethylene stems. The same number of bond, angle, torsion, and nonbonded terms included for the 10 CH_2 all-trans chain were included in the energy expression for the middle segment of the fold.

A molecular dynamics/quenching scheme was employed to find the low-energy fold conformations. A series of molecular dynamics simulations of 60 ps were run at simulation temperatures in the range of 1000–2500 K. Every 0.5 ps, the current dynamics geometry was minimized and then saved for later examination. The lowest energy conformation from a given simulation was then used as input for the next 60-ps molecular dynamics run. Many fold conformations were generated in this process, but, after the third 60-ps run, no new conformations were produced that were within 4 kcal/mol of the lowest energy conformation.

Results and Discussion

Performance of the Force Field. The fold energies and geometries calculated using molecular mechanics will depend on the parameters in the force field. Before we began the fold model calculations, we tested the force field on three cases in order to assess how well conformational energies and nonbonded interactions were treated. The three cases were the polyethylene crystalline cell, *n*-butane, and *n*-pentane.[26] The standard Dreiding force field has already been tested on many molecules,[23] but not with the exponential–6 expression for van der Waals interactions. The Dreiding force field with the exponential–6 van der Waals expression is referred to as DE6 in the remainder of this paper.

Table 1. Comparison of Calculated and Experimental Unit Cell Parameters of Polyethylene

unit cell parameter	calcd (Å)	exptl (Å)[a]	% difference
a	7.160	7.121	0.6
b	4.935	4.851	1.7
c	2.553	2.548	0.2

[a] Reference 27.

The crystalline unit cell of polyethylene was optimized, allowing for the atomic coordinates and unit cell parameters to vary simultaneously. The results are compared with low-temperature (4 K) neutron scattering data in Table 1.[27] The calculated orthorhombic unit cell parameters are slightly larger than experiment, with the greatest percentage difference being for the *b* parameter of 2%. The optimized setting angle was 46°, larger than the experimental value of 41°, but in the range of 42–47° of other experiments.[28]

These polyethylene unit cell parameters are smaller than those calculated recently by Yang and Hsu[29] of $a = 7.21$ Å, $b = 5.15$ Å, $c = 2.58$ Å, and a setting angle of 41° using the Dreiding force field and the Gasteiger method for atomic charges. It was not stated whether they used the exponential–6 or the default Lennard-Jones 6–12 method for the van der Waals energy terms. If we used the Lennard-Jones 6–12 method, the optimized unit cell parameters increase to $a = 7.28$ Å, $b = 5.03$ Å, and $c = 2.58$ Å, approaching the values of Yang and Hsu but deviating more from experiment. These calculations indicate that the exponential–6 expression within Dreiding is better than the Lennard-Jones 6–12 expression for van der Waals interactions in polyethylene.

A large amount of research has been devoted to the conformational aspects of *n*-butane. Calculated values for the energy difference between the gauche and trans conformers range from 0.5 to 0.9 kcal/mol,[23,30–38] while experimental values range from 0.75 to 0.97 kcal/mol for species in the gas phase.[39–41] The DE6 force field calculated 0.76 kcal/mol for the relative energy of the gauche conformer, very close to the latest experimental value of 0.75 kcal/mol.[39] Previous calculations[23,31,34,36–38] for the two rotational barriers range from 3.3 to 4.0 kcal/mol for the gauche/trans barrier and from 4.7 to 6.3 kcal/mol for the gauche/gauche barrier. Of these, the values associated with the most sophisticated quantum mechanical calculations are 3.33 and 5.43 kcal/mol, respectively.[34] DE6 calculated 2.96 and 5.21 kcal/mol for the two barriers, respectively, consistent with the latter results. Spectroscopic values for the two barriers are 3.46 and 4.54 kcal/mol, respectively.[34,40] As with the quantum mechanical results, DE6 agrees better with the experimental gauche/trans barrier than with the gauche/gauche barrier.

For *n*-pentane, five conformers are present, g, g^+g^+, g^-g^-, g^+g^-, and all-trans, where $g^\pm$ represents a conformer with a gauche torsion of a positive or negative torsional angle. Of these structures, the g^+g^+ and g^-g^- conformers have the same energy. Recent ab initio calculations[31] yielded 0.76, 1.36, and 3.33 kcal/mol for the energies of the g, g^+g^+, and g^+g^- conformers, respectively, relative to the all-trans one. The MM3 force field predicted 0.86, 1.62, and 3.51 kcal/mol, respectively.[38] DE6 calculated the relative energies to be 0.75, 1.49, and 2.85 kcal/mol, respectively, similar to the ab initio results except for the g^+g^- conformer where the DE6 value is not as large.

Overall, the current force field agreed with previous calculations and experiments and was judged to be reasonable for this investigation.

Table 2. Comparison of Carbon Torsional Angles (deg) and Fold Energies for Different Polyethylene Chain Folds[a]

Corradini et al.[b]	Davé and Farmer[c]	fold A fold energy = 4.49 kcal/mol	fold B fold energy = 4.71 kcal/mol	fold C fold energy = 5.63 kcal/mol	fold D fold energy = 6.05 kcal/mol	fold E fold energy = 6.15 kcal/mol
		179.4 (t)	178.7 (t)	178.3 (t)	179.5 (t)	179.9 (t)
180.4 (t)		−178.2 (t)	−166.0 (t)	−172.5 (t)	−172.8 (t)	−166.2 (t)
171.3 (t)		177.7 (t)	169.5 (t)	162.4 (t)	177.7 (t)	167.0 (t)
174.4 (t)	182.9 (t)	177.1 (t)	73.8 (g$^+$)	65.9 (g$^+$)	175.2 (t)	178.4 (t)
−64.4 (g$^-$)	−62.1 (g$^-$)	−63.4 (g$^-$)	78.5 (g$^+$)	96.6 (g$^{+\prime}$)	−102.2 (g$^{-\prime}$)	−67.6 (g$^-$)
−58.4 (g$^-$)	−65.5 (g$^-$)	−63.5 (g$^-$)	−159.4 (t$'$)	−61.2 (g$^-$)	75.4 (g$^+$)	−56.8 (g$^-$)
91.6 (g$^{+\prime}$)	87.9 (g$^{+\prime}$)	92.4 (g$^{+\prime}$)	72.0 (g$^+$)	−62.0 (g$^-$)	−90.8 (g$^{-\prime}$)	100.7 (g$^{+\prime}$)
68.4 (g$^+$)	66.7 (g$^+$)	70.1 (g$^+$)	70.0 (g$^+$)	172.4 (t)	176.0 (t)	−152.0 (t$'$)
174.8 (t)	182.0 (t)	−178.7 (t)	−174.0 (t)	−167.0 (t)	−168.4 (t)	178.7 (t)
74.9 (g$^+$)	77.2 (g$^+$)	72.7 (g$^+$)	78.7 (g$^+$)	70.2 (g$^+$)	70.5 (g$^+$)	−60.9 (g$^-$)
176.7 (t)		171.4 (t)	−177.3 (t)	173.0 (t)	160.3 (t$'$)	168.4 (t)
184.5 (t)		−176.6 (t)	−175.8 (t)	180.0 (t)	−176.5 (t)	−175.1 (t)
		179.4 (t)	−179.6 (t)	179.6 (t)	178.7 (t)	−179.2 (t)

[a] g$^\pm$ signifies a *gauche* torsion and t signifies a *trans* torsion; g$'$ and t$'$ indicate torsions significantly deviated from the equilibrium values. [b] Reference 6. [c] Reference 4.

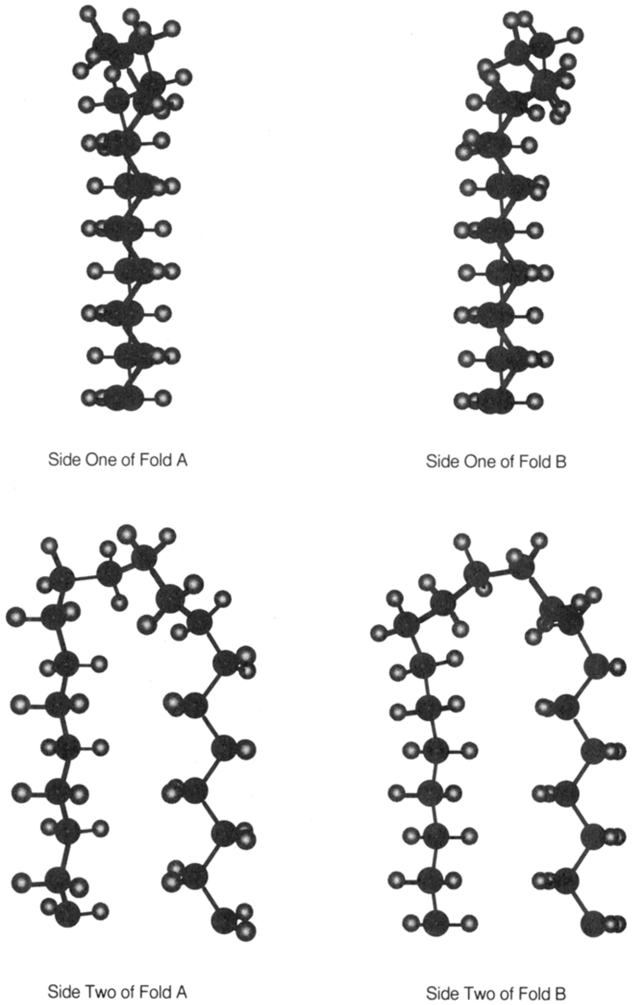
Chain-Folded Structures. From the conformational searches, many fold structures were generated. The torsional angles and fold energies of the five lowest ones are given in Table 2.

In agreement with previous computational[4,6,7] and experimental studies,[8,9] the lowest energy fold structure (fold A) had the sequence g$^-$g$^-$g$^+$g$^+$tg$^+$. On comparison with folds calculated by Corradini et al.[6] and Davé and Farmer,[4] the torsional angles were found to be very similar, with an average deviation of 4°. Each fold had the characteristic strained torsion at the g$^-$g$^+$ connection due to the so-called "pentane effect".[42] In all cases, the optimized dihedral angles were not at the ideal values of +60, −60, and +180° but rather fell in a range about these values.

The fold energy of fold A was calculated to be 4.49 kcal/mol, near the values of 4.0 kcal/mol of Corradini et al. and 5.61 kcal/mol of Davé and Farmer. The value of 4.49 kcal/mol also agreed well with Hoffman's q_{110} of 4.9 kcal/mol, which is defined as the average work associated with creating a chain fold in polyethylene.[43]

The conformations of the other low-energy folds are typified by features which would increase conformational energies, such as gauche torsions nearer to the stems (folds B and C) and strained torsional junctions (g$^-$g$^+$g$^-$ in fold D and strained t$'$g$^{+\prime}$ torsions in fold E).

Of these folds, fold B was calculated to be very close in energy (0.21 kcal/mol) to the minimum-energy fold, fold A. Both folds have the same number of gauche torsions, but in fold B they have only positive torsional angles. Fold B has the g$^+$g$^+$tg$^+$g$^+$ feature found in the minimum conformation of {200} folds[6] but with an additional gauche torsion further along the chain to form the {110} fold. As a result, the number of carbon atoms included in the fold sequence increased from seven to eight, causing fold B to be much wider than fold A (see Figure 2).


Side One of Fold A

Side One of Fold B

Side Two of Fold A

Side Two of Fold B

Figure 2. Structures of folds A and B.

Is it reasonable to accept the existence of another fold so close in energy to the minimum? As stated above, the calculated fold energies are dependent on the force field parameters and may be different using another force field. In order to compare the results from the DE6 force field, MM2 energies[44] were calculated for folds A and B. Fold energies computed at the DE6 optimized geometries were 5.52 and 6.14 kcal/mol, respectively, for folds A and B. Optimizing the geometries using MM2, the fold energies decreased to 5.17 and 5.86 kcal/mol, respectively. The fold energy difference between the two folds remained small using MM2 (0.69 kcal/mol for the optimized structures), but larger than with the DE6 force field. Therefore, fold B was not a spurious result of the DE6 force field. The variation in the relative energies between force fields may be ascribed to the lower gauche/trans torsional barrier in DE6 (2.98 kcal/mol in n-butane) as compared to MM2 (3.3 kcal/mol in n-butane).[38,44]

The small energy difference between folds A and B suggests that both may be present in a polyethylene crystal. Interconversion between the two folds can be achieved through a ring flip which resembles the half-chair transition state between the chair and twist-boat structures of cyclohexane. The DE6 energy of the interconversion was calculated to be 8.7 kcal/mol. For comparison, interconversion between the chair and twist-boat conformations of cyclohexane occurs readily at room temperature. The DE6 barrier in cyclohexane was calculated to be slightly higher at 9.2 kcal/mol, near the experimental activation of 10.8 kcal/mol.[45]

Temperature effects may change the relative energies of the folds. The computed fold energies were for adjacent stem separations associated with the room-temperature unit cell parameters. At lower temperatures, the stem separations will decrease, favoring the narrower fold A (see Figure 2) and decreasing the concentration of the higher energy folds. Such changes may have contributed to the observed differences in the infrared spectra associated with chain folds in polyethylene[8] and n-$C_{198}H_{398}$ molecules[9] at different temperatures.

Folds A and B may have different packing preferences due to their conformations. Davé and Farmer found that the fold conformation had little effect on the packing energy of folds in polyethylene.[4] They only considered folds similar to fold A, however. On comparison of the two folds, fold B is seen to take up a different spatial volume in the direction perpendicular to the {110} plane (see Figure 2), whereas most of fold *A* lies in the plane of the polyethylene stems. Thus, if the two conformations exist, it is likely that they will be in regions where only one type of fold is present and can accommodate better packing. An investigation of fold packing similar to Davé and Farmer's should be undertaken using other fold structures, especially the fold B one.

The possibility of chain folds of two different conformations, orientations, and volumes but slightly different energies may help to explain some recurrent problems in the physics of lamellar crystals. The mechanism of lamellar twisting has never been explained adequately, despite a number of valiant efforts. One explanation, by Keith and Padden,[46] postulated that different surface free energies in opposite fold surfaces would produce nonequivalent surface stresses leading to twisting. The second-most stable fold (fold B) reported here would be more stable in a convex surface than in a concave surface because of the extra volume it occupies. It is therefore suggested that twisting could be facilitated by the generation of B-type folds on one fold surface, which would produce the nonequivalent surface stresses in the Keith and Padden mechanism. Studies of the fold surfaces of single crystals of polyethylene using atomic force microscopy have been very difficult, and when seen, the folds tend to occur as patches.[47] It is possible that patches of folds A and B could occur randomly, perhaps with different populations, but currently reported studies have not yet attempted to determine the exact orientation of the folds in the surfaces. However, it remains possible that atomic force microscopy could provide the experimental evidence needed to test the predictions of the simulations reported here.

Conclusion

In this study of the folded chain region of polyethylene, fold geometries for adjacent reentry along the {110} direction were investigated. Conformational searches of a folded chain model indicate that the two lowest fold geometries are within 1 kcal/mol of each other and have the same number of gauche torsions but in different positions. These differences affect the spatial volume of each fold and may influence the lamellar structure of polyethylene in the folded chain region of the crystal. Additional fold structures, in particular the one found here to be close in energy to the global minimum, should be considered in future fold packing simulations.

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