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Modeling of helix reversal defects in polytetrafluoroethylene
I. Force field development and molecular mechanics calculations

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

A force field suitable for modeling fluoropolymers and oligomers in the solid state has been derived from MOPAC semiempirical molecular orbital calculations on perfluorohexadecane. A conformational energy profile was generated using the PM3 Hamiltonian, and then valence parameters of a molecular mechanics (MM) energy expression, including a six-term cosine dihedral potential, were adjusted with a nonlinear least squares fitting algorithm to reproduce the profile. Minimum energy helical conformations of 48/22 and 13/6 were obtained when the geometries of $C_{60}F_{122}$ molecules in isolation and in a crystalline cluster, respectively, were optimized using the refined force field. The X-ray diffraction pattern calculated from the crystalline cluster indicated an equatorial d-spacing of 4.9685 Å. These intra and intermolecular structural characteristics for the cluster are in agreement with experimental X-ray diffraction data. Energy penalties of helix reversal defects in isolated chains and in a crystalline environment were also investigated.

Keywords: Fluoropolymers; Force field; Molecular mechanics

1. Introduction

Molecular simulation of the thermal behavior of fluoropolymers has proven to be difficult due to a lack of force field parameters which adequately describe their structures and packing over a wide range of temperatures. Restrictions on intra- and intermolecular degrees of freedom were imposed in previous studies to maintain certain structural characteristics while others were investigated [1–3]. While this method produces minimum energy structures and packing arrangements consistent with experimental data, it is inadequate for the study of the thermally generated conformational defects in fluoropolymers known as helix reversals. Conformational freedom is required for defect formation and migration. Further, they are subject to intermolecular influences. Therefore, to study helix reversals in polytetrafluoroethylene (PTFE) with molecular dynamics simulations, a force field is needed which reproduces known chain structures and intermolecular distances in fluoropolymers when all degrees of freedom are allowed.

To improve upon existing force field parameters, an intramolcular term describing the complex dihedral potential surface of fluoropolymers was needed in order to maintain van der Waals parameters at values which adequately describe the intermolecular interactions found in fluoropolymer crystals. A six term cosine dihedral potential of the form

$$E_\tau = \sum |V_n| - V_n{}^* \cos(n\tau), \qquad n = 1, 2, \ldots, 6 \quad \tau = \text{torsion angle} \tag{1}$$

was chosen for this purpose. In initial force field refinement attempts, it was found that a three-term cosine function (found in many commercial modeling packages) was not sufficient to describe the complex conformational profile of linear fluorocarbons. The three additional terms provide this flexibility. Results of the force field refinement and molecular mechanics (MM) calculations on chain packing and conformational defects are presented in this work.

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Table 1
Force field parameters

Van der Waals parameters for 6–9 potential

Interaction	ϵ (kcal/mol)	$r_{\min}$ (Å)
F–F	0.0211	3.538
C–C	0.0844	3.884
F–C[a]	0.0422	3.711

Valence force field parameters for harmonic bond stretching and angle bending terms (Stretch constants in kcal/mol/Å^2. Bend constants in kcal/mol/rad^2.)

Interaction	Force constant	Equilibrium value
C–C stretch	722.46	1.54 Å
F–C stretch	892.60	1.34 Å
C–C–C bend	110.30	108.5°
F–C–C bend	152.98	111.2°
F–C–F bend	256.80	104.8°

Coefficients for six-term dihedral potential (units are kcal/mol)

$V1 = -0.4005$
$V2 = -0.9980$
$V3 = -2.3612$
$V4 = -1.6149$
$V5 = -1.1447$
$V6 = -1.0025$

Partial atomic charges

F	−0.09
C	+0.18

[a] Calculated from $\epsilon_{ij} = (\epsilon_{ii} \times \epsilon_{jj})^{1/2}$ and $r_{ij} = 1/2(r_{ii} + r_{jj})$.

2. Methods

2.1. Force field development

A conformational energy profile for backbone torsions was generated for a model molecule, perfluorohexadecane (PFHD), using MOPAC v. 5.0 semiempirical MO calculations with the PM3 Hamiltonian. Compared to AM1, it was found that the PM3 parameterization provides barrier heights in better agreement with those suggested by extrapolation of ab initio results on small perfluorocarbons [4]. Other studies have also indicated that the PM3 Hamiltonian results in a better description of fluoropolymer conformations and energy barriers than AM1 or MNDO[5]. Increments of 5.0° for the backbone dihedrals were used to generate the profile over the range from 180 (*trans*) to 30°. In the vicinity of the minimum, 0.1° steps were used. All backbone torsions were incremented simultaneously and held fixed at each value (with the SYMMETRY function available in MOPAC), while the remaining geometric variables were optimized. Conformational energies were then calculated as the differences between the heat of formation (HOF) at each backbone torsion angle and the HOF at the minimum energy conformation.

Eq. (1) was added to a MM energy expression containing quadratic bond stretching and angle bending terms, a 9–6 van der Waals interaction term, and a distance dependent dielectric term ($\epsilon = \epsilon' r$, where $\epsilon' = 1.0$). Only C–C–C–C backbone torsion angles were treated explicitly. This energy expression was fit to the MOPAC PM3 conformational energy calculations with a non-linear least squares fitting algorithm. The bond stretching and angle bending parameters were allowed to vary within experimentally suggested limits [6], while the van der Waals parameters for carbon and fluorine were held fixed at values known to give excellent agreement with the crystallographic data on polyvinylidene fluoride (PVF_2) in MM calculations [7]. Atomic charges derived from the semiempirical MO calculations at the minimum energy conformation were used in the calculation of electrostatic energy. The *trans* barrier and minimum energy conformation were given additional weighting during the fitting so that these important data points would be duly reproduced. The resulting parameter set is shown in Table 1.

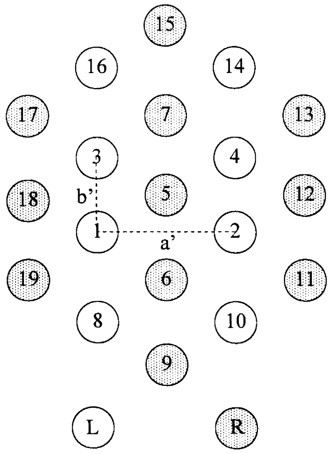

Fig. 1. Schematic diagram of the 19 chain cluster and important crystallographic directions.

2.2. Molecular mechanics calculations

2.2.1. Conformational analysis of isolated chain

The refined valence and van der Waals parameters were added to the CFF91 force field available in Biosym *Discover*®. As this force field does not offer a dihedral term of the same functional form as Eq. (1), in-house programs to calculate torsional energy and gradient contributions were written and interfaced with *Discover*®. A conformational energy profile for PFHD was then calculated by setting and holding all backbone torsions to the same value at each point and allowing the remaining geometry to optimize. In addition, the force field was tested for applicability to PTFE in an amorphous or melt phase where individual gauche bonds play important roles in the properties and dynamics of the material. A potential energy profile for rotation about

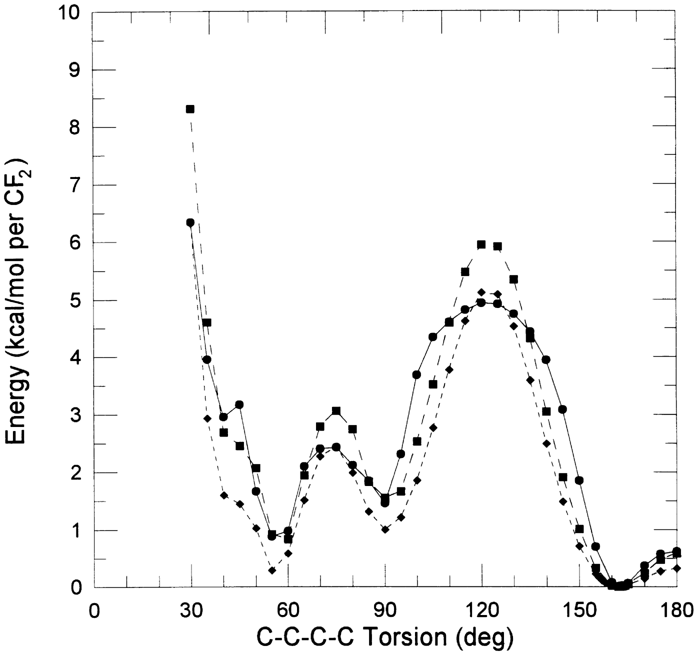

Fig. 2. Total conformational energy surfaces for pefluorohexadecane: (●) MOPAC PM3 calculations; (■) curve resulting from fit of MM expression to PM3 data; (◆) profile from MM calculations with the refined force field.

the C8–C9 bond in PFHD (in the direction that reverses the handedness of this dihedral) was calculated and compared with the corresponding conformational energy profile obtained from MOPAC v 5.0 PM3 semiempirical molecular orbital calculations.

2.2.2. Packing calculations

Packing energy calculations with rigid and flexible helices were performed with the refined force field. $C_{60}F_{122}$ molecules (left and right handed) minimized in isolation (having a 48/22 conformation) with the force field were used to build a nineteen chain crystalline array in a Phase II packing arrangement. This cluster is shown schematically in Fig. 1. For the rigid chain packing calculations, an assembly of seven chains (such as chains 1–7 of the nineteen chain cluster shown in Fig. 1) was used. Grid search methods were used to minimize the energy of the crystal with respect to the projected unit cell vectors a' and b', and setting angles. The setting angles were searched in increments of 7.5°, the ‘‘notch’’ angle for a 48/22 helix. The angle between a' and b', γ', was held fixed at 90° in these calculations.

For the flexible helix calculations, the entire array of 19 chains (Fig. 1) was used. This system was allowed to minimize all inter- and intramolecular degrees of freedom under the influence of the refined force field. All computation was handled with Biosym *Discover*® and the aforementioned in-house software. No restraints on the outer ring chains were in effect during this minimization.

2.2.3. Simulated X-ray diffraction patterns

The calculation of diffraction patterns from the cluster is a convenient method for summarizing structural characteristics. It also provides a link between the model/simulation data and experimental data. The Diffraction module available in the *Cerius*^{2} (version 3.0) molecular modeling package was used to calculate fiber diffraction patterns from the static, minimized nineteen chain cluster. The X-ray wavelength considered was 1.54178 Å corresponding to CuK$_\alpha$ radiation. Reciprocal space coordinates (Q) were scanned in 0.1 Å^{-1} increments (2θ increments of 1.580°) between $Q = 0.0$ and $Q = 6.0$. Therefore, the 6.0 Å^{-1} by 6.0 Å^{-1} ‘‘film’’ was sampled at 3600 points. Q, the magnitude of the scattering vector, is defined as

$$Q = (4\pi \sin \theta)/\lambda. \qquad (2)$$

Cylindrical averaging was applied to the scattering along with a model size correction to reduce the size of the peak at the origin of reciprocal space. The correction subtracts the cylindrically averaged scattering from a cylinder of uniform scattering density [8]. The length and radius of the correction cylinder were optimized by the *Cerius*^{2} software based on the dimensions of the nineteen chain cluster.

2.2.4. Defect energies

Helix reversals might be imagined to occur individually or in pairs. In pairs, they would introduce, say, a left-handed section in otherwise right-handed molecules. This section is referred to here as a ‘‘helix reversal band’’. The energy costs of helix reversal structures were calculated for an isolated chain and in the 19-chain cluster. For an isolated molecule, a single helix reversal and helix reversal bands consisting of one to ten dihedrals were built into the molecule by simply changing the sign (e.g. from + 162.5 to

Table 2
Minimum energy geometry for PFHD from MOPAC PM3 and MM calculations

Parameter	MOPAC PM3	This Work
C–C	1.60 Å	1.56 Å
F–C	1.35 Å	1.34 Å
C–C–C	110.0°	110.5°
F–C–C	110.4°	110.0°
F–C–F	104.5°	104.1°
C–C–C–C	162.5°	161.9°
trans barrier	0.62 kcal/mol/CF_2	0.32 kcal/mol/CF_2

−162.5°) of torsion angles in the center of the chain. The molecule was subsequently fully and freely relaxed (minimized). A helix reversal band consists of two single helix reversals and any intervening dihedrals that have the opposite hand of the host chain. Therefore the number of individual helix reversals in these calculations was always two, no matter the size of the reversal band. The sequences …LL_R_LL… and …LL_RRR_LL7… demonstrate this (the underscore character designates the position of the reversal). A single helix reversal in a chain gives the sequence …LLL_RRR…

To evaluate the energy penalty of a reversal band in a crystalline environment, a defect consisting of three dihedrals of reversed hand was built into the center chain (chain 5) of the 19 chain model. In the calculations on isolated chains, it was observed that bowing of the chain occurred upon introduction of the reversal band defects. To keep the axis of the center chain parallel to those of the other molecules in the cluster, intermediate *trans* torsions (180°) were introduced. The sequence …RR*t*LLL*t*RR… demonstrates this situation. The cluster was then freely minimized.

3. Results and discussion

3.1. Force field refinement

The dihedral potential energy profile resulting from the MOPAC PM3 calculations is shown in Fig. 2 (solid line). The minimum energy backbone torsion angle is 162.5°. Table 1 gives the refined force field parameters after fitting the MM energy expression to the torsion profile. The conformational profile obtained by calculating energies of MOPAC PM3 geometries using the refined force field is also shown in Fig. 2 (dashed line), along with the curve obtained from MM minimization of PFHD (dotted line). The force field successfully approximates the complex dihedral behavior of fluoropolymers, even reproducing the split gauche minima suggested by high level ab initio calculations on short perfluoroalkanes [9]. Optimization of PFHD with the refined force field does not reproduce the PM3 geometries exactly because the equilibrium values used in the valence terms were not held fixed at PM3 values, but were allowed to vary within narrow limits during the refinement. The minimum energy geometries of PFHD from MM with the refined force field and from the MOPAC PM3 calculations are given in Table 2. The *trans* barrier given by the MM calculations is 0.3 kcal/mol per CF2 lower than that from the PM3 calculations, but is nevertheless adequate for molecular dynamics simulations.

The MOPAC PM3 and MM potential profiles for rotation

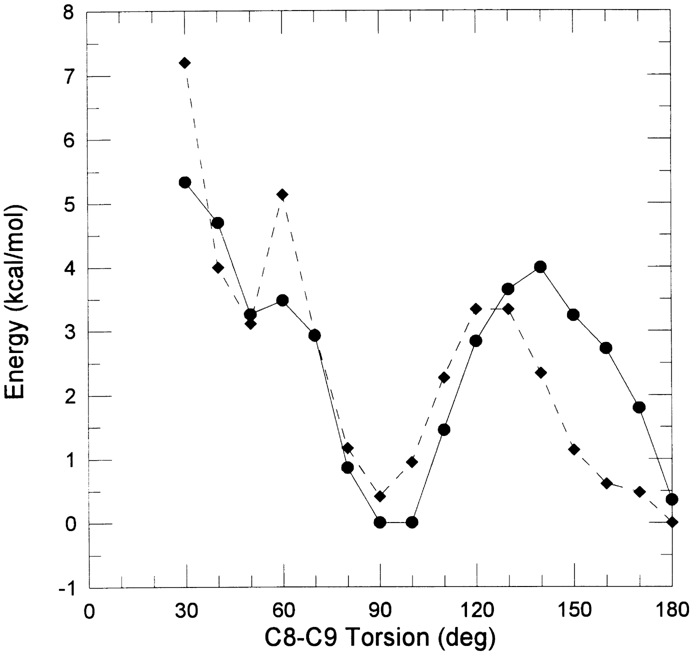

Fig. 3. Conformational energy surfaces for rotation about a single bond (C8–C9) in PFHD. (●) MOPAC PM3 calculations. (◆) MM calculations using the force field listed in Table 1.

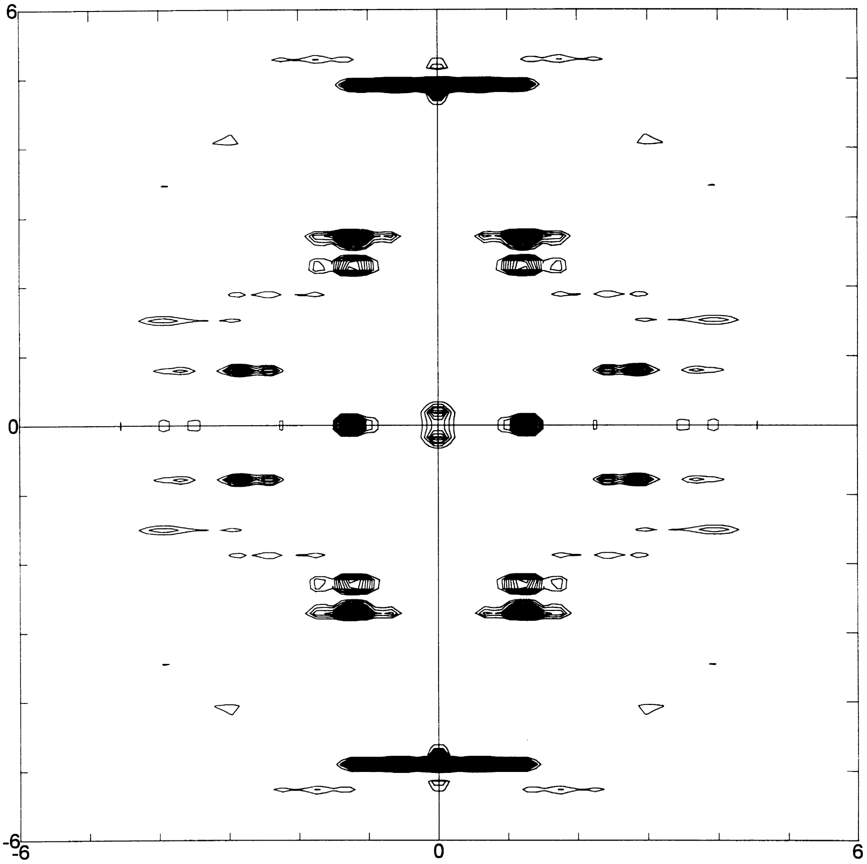

Fig. 4. Calculated fiber diffraction pattern of the nineteen chain cluster after minimization.

about a single bond (C8–C9) in PFHD are shown in Fig. 3. Note that these data were not used in the fitting procedure and therefore suggest that transferability of the force field parameters to non-crystalline fluoropolymer structures should be good. The force field reproduces the general characteristics of this potential profile, and therefore could be used with some confidence in modeling and simulation investigations of PTFE chain folding behavior and in the melt

3.2. Molecular mechanics calculations

3.2.1. Conformational analysis of isolated chains

The minimum energy geometry for PFHD obtained with MM calculations was reported in the previous section in conjunction with the results of the force field refinement. In addition, the geometries of left- and right-handed $C_{60}F_{122}$ molecules in isolation were optimized. The resulting minimum energy helical conformation was 48/22 (2.1818). This helix is more tightly coiled than the 54/25 (2.1600) helix reported for phase II PTFE [10].

Table 3
Energies of reversal bands as a function of size in isolated $C_{60}F_{122}$ molecules. Values are relative to a defect free chain

Number dihedrals	ΔE (kcal/mol)
2	1.4
3	1.7
4	1.5
5	1.7
6	1.6
11	1.5

3.2.2. Packing calculations

Rigid chain packing calculations with seven molecules (chains 1–7, Fig. 1), each having a 48/22 helical conformation, yielded intermolecular distances of 9.58 Å and 5.54 Å in the a' and b' directions, respectively. Minimization of the entire 19 chain cluster in which all degrees of freedom were allowed yielded parameters of $a' = 9.41$ Å and b' 5.72 Å. Fig. 4 shows the calculated diffraction pattern of the minimized cluster. The numbers on the axes are in scattering vector units [see Eq. (2)]. Based on the pattern, the helical conformation of the chains is nearly 13/6 (2.1667), and the d-spacing of the most intense equatorial reflection is 4.9685 Å. Both of these numbers are in good agreement with the experimental values for phase II (2.1600 helical conformation and d-spacing of 4.866 Å) [10,11].

3.2.3. Defect energies

The energy of an isolated $C_{60}F_{122}$ molecule containing a single helix reversal (…LLL_RRR…) is 0.87 kcal/mol higher than that of a defect free chain. Recent calculations (using a less-refined force field) yielded a value of 1.55 kcal/mol for the energy penalty of a reversal in an isolated PTFE chain [12]. For helix reversal bands in isolated molecules, Table 3 shows the defect energy as a function of the size (number of dihedrals between reversals) of the band. The energy oscillates, possibly due to an even/odd effect, but the values are approximately twice that of a single helix reversal. Near-*trans* torsions did not form at the reversal interface(s) upon minimization of these isolated chains, which contained either a single helix reversal or a band defect. As a result, the linearity of the molecular axis was lost (chain was bent or kinked) at the site of the reversal. Therefore the energy of the defect (either a single reversal or band) is localized to the immediate region containing the defects *for isolated chains*. It is also noteworthy that a chain starting with a band defect consisting of only one torsion (…LLLRLLL…) was not stable. The reversals were eliminated by the energy minimization procedure.

The three dihedral defect in the nineteen chain cluster minimized to a two dihedral reversal band with a final energy penalty was 3.3 kcal/mol (This includes contributions from near-*trans* bonds. Discussed later.) Assuming additive contributions, the portion of the defect energy attributable to intermolecular effects is ∽ 1.7 kcal/mol. In addition, splitting the defect energy evenly between the two helix reversals defining the band gives a formation energy of ∽ 1.7 kcal/mol for a single helix reversal. This is in fair agreement with the value of 1.25 kcal/mol estimated previously from infrared absorption intensities [13]. As with the isolated chains, the distortion caused by the defect is fairly local to the defect. As noted previously, the presence of a reversal band without near-*trans* torsions caused isolated chains to bow. To prevent large lattice strains and maintain registry with the surrounding crystal, near-*trans* torsions are therefore needed on either side to interface the helix reversal band into the chain. Therefore, four dihedrals are affected in this particular case (two reversed and two near-*trans*). Inspection of dihedral angle sequences of chains 1–4 in the region of the band defect on chain 5 revealed that there were no severe perturbations of geometry on these surrounding chains.

4. Conclusions

A set of force field parameters which adequately describe the intra- and intermolecular interactions of fluoropolymers in the solid state has been developed from experimental data and semiempirical MO calculations. When used in MM calculations on isolated model molecules and for crystalline clusters, the force field generates helical conformations and intermolecular distances which are in agreement with X-ray diffraction data on PTFE in Phase II. Calculations of defect energies in isolated helices and crystalline clusters were within ranges previously reported. The success of the force field in reproducing the static properties of fluoropolymers suggests that molecular dynamics simulations of PTFE in the solid state should be quite fruitful in investigating the dynamic properties of helix reversal defects in fluoropolymers. This is the subject of a companion paper in this series.

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