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Flexibility of a New Thermoplastic Polyimide Studied with Molecular Simulations

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ABSTRACT: The flexibility of a new thermoplastic polyimide, PI-2, synthesized from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane (DMDA), is studied with atom-based molecular modeling. The BTDA part of PI-2 is often considered to be "rigid", because of the ring structures, while the DMDA part is believed to be flexible. By molecular dynamics simulations and conformational grid search, we discovered that there is in fact a substantial amount of flexibility within BTDA, the so-called rigid part of PI-2. Quantitative characterization of the flexibility of a PI-2 single chain is achieved by studying the persistence length and the characteristic ratio, using the transformation matrix and generator matrix formalisms. The upper value of the calculated persistence length is roughly two-thirds of the contour length of a repeat unit, depending on the choice of initial bond. The limiting characteristic ratio is calculated to be 6.43. The average persistence length obtained from the limiting characteristic ratio is ~12.7 Å. Both the persistence length and the limiting characteristic ratio indicate that the PI-2 chain is rather flexible.

Introduction

The development of high performance polymer composite consists of the search for strong fibers as well as advanced matrix materials so that the combined composite will have superior overall properties, such as high mechanical strength and thermal oxidative stability, so that the composite can work continuously at high temperatures for a long duration of time. The fiber component of a composite usually consists of a rodlike polymer, which contributes to the strong mechanical strength. The matrix component of the composite, in contrast, is usually made of a much more flexible material than the fiber. One major requirement for the matrix material is that it must have good adhesive properties with the fiber, so that mechanical stress can be transferred. Also required for the matrix material is its high continuous working temperature so that the composite can be used in the aviation industry. Recently, a class of new fibers and matrix materials have been developed.[1-3] One matrix materials that stands out is the thermoplastic semicrystaline polyimide of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane (DMDA), or PI-2, as conveniently named by its inventors.[3] This material has a high glass transition temperature (230 °C), whose difference from the melting temperature (325 °C) is less than most other materials in the same class.[3] The chemical structure of one repeating unit is depicted in Figure 1.

The BTDA part in a PI-2 repeat is usually considered rigid, based on the aromatic ring structures, while the DMDA part is believed to be flexible. The semiflexibility is one reason that makes PI-2 a candidate as a matrix material. In this study, we use a molecular modeling technique to assess the flexibility of this material. First, a molecular dynamics analysis will be performed in order to visualize the motions and flexibility of the chain. Then a conformational grid search will be carried out to scrutinize the energy barriers against the rotational motions of the critical bonds. Finally, we will calculate the persistence length of this material by analyzing the dynamics trajectory, using a transformation matrix formalism. It is the persistence length and characteristic ratio that can give some quantitative feeling about the stiffness of the chain.

Description of Method

The molecular simulations are performed using POLYGRAF with its DREIDING II force field.[4] The potential energy in the simulations contains the following terms,

$$E = E_{\text{stretching}} + E_{\text{bending}} + E_{\text{torsion}} + E_{\text{inversion}} + E_{\text{vdW}} \quad (1)$$

where $E_{\text{inversion}}$ is the improper-energy term for the out-of-plane interactions and E_{vdW} is the nonbonded van der Waals energy term. The Coulomb interactions due to electronic partial charges on the atoms have not been included, on the basis of the consideration that the long-range interactions will only have a minor effect on the conformations of the single chain. The only conjugations that are relevant to the chain rigidity are between the neighboring bonds, which are taken care of in the atomic force field.[4]

The molecular dynamics algorithm is based on the classic equations of motion, with the above mentioned empirical force field.[4] Initial velocities were assigned randomly to all atoms in the system, with due care that the average kinetic energy of the atoms corresponds to the temperature under study. The velocity and position of an atom at a new time step are determined by its position and velocity at the previous time step and the net force it feels from the rest of the system. An adiabatic process was used for the molecular dynamics.

For the molecular dynamics, we consider a PI-2 single chain with two chemical repeat units, terminated by a hydrogen atom on both ends. Since the long-range forces only have minor effects on the single chain statistics, the two-monomer segment, with a contour length of ~60 Å, should be considered as a reasonable approximation to a long chain, if only the statistics of the bonds away from the chain ends are considered. The virtual bonds near the center of the chain are used for the analysis, in order to suppress the end effect. The dynamics analysis is performed in a vacuum, at a temperature of 300 K. The length of the trajectory is 2.16 ns, with a time step of 0.5 fs. Because the polymer chain stays in one conformation

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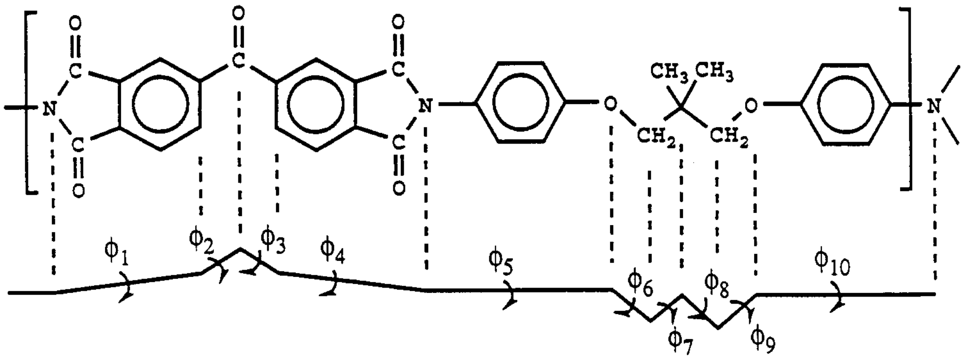

Figure 1. Chemical structure and virtual bond definitions of PI-2. Hydrogen atoms are not explicitly shown in the figure, but they were used in the calculation.

for many time steps before making a transition, it is not necessary to record every time step for analysis. A snapshot of the trajectory is taken only every 1 ps in the analysis.

Conformational grid searches were also conducted in order to study the potential energy barrier for rotational isomeric state transitions of certain bonds. For the conformational grid search, one repeat unit of PI-2 is considered, since we are only concerned with energies about particular bonds. We consider torsional rotations about one bond to see the energy barrier against such a rotation or two consecutive bonds in order to see if there are any correlations between these bonds such that a concerted motion of these bonds would be favored. During a conformational search, the conformations of the chain other than the concerned bonds are fixed.

When studying polymers with rigid moieties in the backbone, such as a phenyl ring, it is often convenient to define virtual bonds along the backbone, so that one can concentrate on the essential quantities relevant to the persistence length.[5,6] The chemical structure and virtual bond definitions of PI-2 are depicted in Figure 1. All substructures with a closed ring are rigid because of conjugation. The persistence length is mainly limited by the bond angle fluctuations and rotations about the virtual bonds. Rotations about the bonds that make larger angles with their neighbors are apparently more important. Otherwise the N–C_6H_4–O segment cannot be considered as one virtual bond.

Because the thermal fluctuations of the lengths of the virtual bonds are small, we can treat these lengths as constants represented by their average values. By using transformation matrices of the form

$$\mathbf{T}_i = \begin{pmatrix} -\cos\theta_i & \sin\theta_i & 0 \\ -\sin\theta_i\cos\phi_i & -\cos\theta_i\cos\phi_i & -\sin\phi_i \\ -\sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & \cos\phi_i \end{pmatrix} \qquad (2)$$

where θ_i is the angle between bonds $i + 1$ and i and ϕ_i is the torsional angle of bond i, with $\phi = 180°$ defined as *trans*, we can get a persistence length of the form[7]

$$a = \frac{1}{\langle l_i \rangle} \sum_{j=i}^{\infty} \mathbf{l}_i^{\mathrm{T}} \langle \mathbf{T}_i \mathbf{T}_{i+1} \cdots \mathbf{T}_{j-1} \rangle \mathbf{l}_j \qquad (3)$$

where

$$\mathbf{l}_i = \langle l_j \rangle \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad (4)$$

and $\mathbf{l}_i^{\mathrm{T}}$ is the transpose of $\mathbf{l}_i$.

For a polymer chain with independent virtual bonds, the average product of the transformation matrices in eq 3 can be equated to the product of the averaged transformation matrices, i.e.,

$$\langle \mathbf{T}_i \mathbf{T}_{i+1} \cdots \mathbf{T}_{j-1} \rangle = \langle \mathbf{T}_i \rangle \langle \mathbf{T}_{i+1} \rangle \cdots \langle \mathbf{T}_{j-1} \rangle \qquad (5)$$

Therefore the only task is to calculate the average properties of the individual bonds.

The fluctuations of the bond angles are independent of the torsional rotations, therefore the average concerning θ and ϕ can be done separately. From the structure of PI-2 (Figure 1), it is apparent that bonds 1 and 4, 2 and 3, 5 and 10, 6 and 9, and 7 and 8 are equivalent, as far as the bond length l_i or dihedral angle ϕ_i is concerned. For bond angles θ_i, θ_1 and θ_3, θ_4 and θ_{10}, θ_5 and θ_9, and θ_6 and θ_8 are equivalent. In equilibrium, corresponding properties of equivalent bonds should be the same. On the basis of this assumption, we average over the equivalent bonds for their equilibrium values in order to make more efficient use of the trajectory.

From symmetry, $\langle \sin \phi_i \rangle = 0$ for all bonds. The transformation matrices of all bonds will have a simplified form,

$$\langle \mathbf{T}_i \rangle = \begin{pmatrix} -\langle \cos\theta_i \rangle & \langle \sin\theta_i \rangle & 0 \\ -\langle \sin\theta_i \rangle \langle \cos\phi_i \rangle & -\langle \cos\theta_i \rangle \langle \cos\phi_i \rangle & 0 \\ 0 & 0 & \langle \cos\phi_i \rangle \end{pmatrix} \qquad (6)$$

For bonds 7 and 8, the rotational potentials are nearly 3-fold symmetric because of the presence of the dimethyl group. For bonds 5 and 10, the symmetry of the phenyl ring makes $\langle \cos \phi_5 \rangle = \langle \cos \phi_{10} \rangle = 0$. Therefore $\langle \cos \phi_i \rangle = 0$ for $i = 5, 7, 8$, and 10, and the transformation matrices for these bonds will be further simplified,

$$\langle \mathbf{T}_i \rangle = \begin{pmatrix} -\langle \cos\theta_i \rangle & \langle \sin\theta_i \rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (7)$$

Whether or not eqs 6 and 7 are pertinent for evaluation of the persistence length or characteristic ratio depends on whether or not the neighboring bonds are independent. If two neighboring bonds, e.g., m and $m + 1$, are interdependent, then the procedure in eq 5 cannot be undertaken. Instead,

$$\langle \mathbf{T}_i \mathbf{T}_{i+1} \cdots \mathbf{T}_m \mathbf{T}_{m+1} \cdots \mathbf{T}_{j-1} \rangle = \langle \mathbf{T}_i \rangle \langle \mathbf{T}_{i+1} \rangle \cdots \langle \mathbf{T}_m \mathbf{T}_{m+1} \rangle \cdots \langle \mathbf{T}_{j-1} \rangle \qquad (8)$$

will be the appropriate form, and one will need to evaluate $\langle \mathbf{T}_m \mathbf{T}_{m+1} \rangle$.

The persistence length, calculated according to eq 3, should in general depend on the choice of the initial bond, $\mathbf{l}_i$, when the bond lengths are different. For a rodlike polymer chain, the difference caused by the choice of the initial bond is negligible. In the case of a more flexible chain with different bond lengths, this difference is more pronounced. We therefore need to study the persistence length with each bond as the initial bond.

Another important quantity often used to characterize a polymer chain is the characteristic ratio, defined as[7]

$$C_n \equiv \frac{\langle r^2 \rangle_0}{\sum_{i=1}^{n} l_i^2} \tag{9}$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance of the unperturbed polymer chain. The characteristic ratio is usually given as the limiting value, C_∞, as, $n \to \infty$. This limiting value is independent of the initial bond.

The unperturbed average of r^2 can be computed as[8]

$$\langle r^2 \rangle_0 = \langle \mathbf{G}_1 \mathbf{G}_2 \cdots \mathbf{G}_{n-1} \mathbf{G}_n \rangle \tag{10}$$

where $\mathbf{G}_i$ are the generator matrices, with

$$\mathbf{G}_1 = (1 \quad 2\mathbf{l}_1^T \mathbf{T}_1 \quad l_1^2) \tag{11}$$

$$\mathbf{G}_i = \begin{pmatrix} 1 & 2\mathbf{l}_i^T \mathbf{T}_i & l_i^2 \\ 0 & \mathbf{T}_i & \mathbf{l}_i \\ 0 & 0 & 1 \end{pmatrix} \quad 1 < i < n \tag{12}$$

$$\mathbf{G}_n = \begin{pmatrix} l_n^2 \\ \mathbf{l}_n \\ 1 \end{pmatrix} \tag{13}$$

For averaging with independent bonds

$$\langle r^2 \rangle = \langle \mathbf{G}_1 \rangle \langle \mathbf{G}_2 \rangle \cdots \langle \mathbf{G}_{n-1} \rangle \langle \mathbf{G}_n \rangle \tag{14}$$

and all the $\langle \mathbf{G}_i \rangle$'s can be calculated by the knowledge of the $\langle \mathbf{T}_i \rangle$'s, assuming bond length fluctuations are independent of the angular fluctuations. In the example of a random flight chain, it is easy to prove that $C_\infty = 1$. In all other cases, $C_\infty > 1$. Usually, the greater the C_∞ is, the stiffer the chain will be. For a chain with a simple constitution (equal equilibrium statistics for each bond),[7]

$$a = \frac{\bar{l}}{2}(C_\infty + 1) \tag{15}$$

specifies the relationship between the persistence length, a, and the limiting characteristic ratio, C_∞, where $\bar{l}$ is either the bond length of a simple chain or the mean length of a bond unit of a complicated polymer chain. It was mentioned that the result of the persistence length usually depends on the choice of the initial bond for a complicated polymer chain. Using eq 15, one can estimate the average persistence length from the limiting characteristic ratio.

The calculations for the average bond lengths and the average transformation matrices are most easily done with the help of a molecular dynamics trajectory. A long molecular dynamics trajectory can provide equilibrium values of the above quantities at the temperature under study.

Different from a rodlike polymer, a thermoplastic matrix material usually contains some virtual bonds that are interdependent. The extent to which one can simplify the transformation matrices is reduced because the average of a product of two transformation matrices may no longer be assumed equal to the product of the averages of the two individual matrices (eq 5). One must now carry out the matrix multiplications at every time step for the correlated virtual bonds before taking the average. By a recursive relationship, the persistence length of a homopolymer chain is always solvable, although in this case more computation will be involved. For the characteristic ratio, one needs to calculate

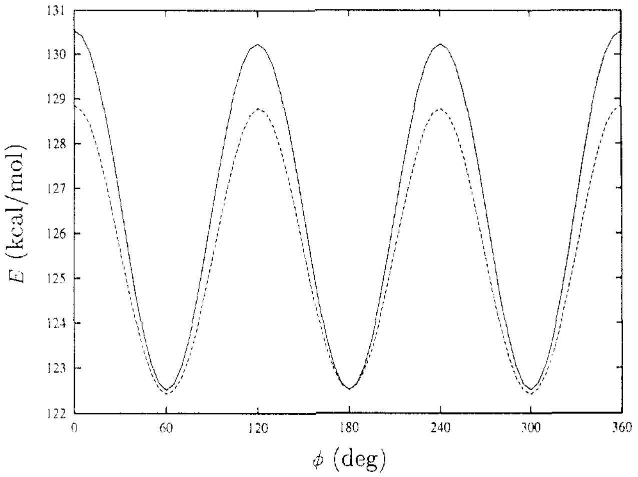

Figure 2. Potential energy as a function of ϕ_8: solid line, without minimizing the energy of the rest of the chain; dashed line, with the energy of the rest of the chain minimized.

$$\langle r^2 \rangle = \langle \mathbf{G}_1 \rangle \langle \mathbf{G}_2 \rangle \cdots \langle \mathbf{G}_{i-1} \mathbf{G}_i \rangle \cdots \langle \mathbf{G}_{n-1} \rangle \langle \mathbf{G}_n \rangle \tag{16}$$

if bonds $i - 1$ and i are interdependent, where

$$\langle \mathbf{G}_{i-1} \mathbf{G}_i \rangle = \begin{pmatrix} 1 & 2\langle \mathbf{l}_i \rangle^T \langle \mathbf{T}_i \rangle + 2\langle \mathbf{l}_{i-1} \rangle^T \langle \mathbf{T}_{i-1} \mathbf{T}_i \rangle & \langle l_i^2 \rangle + 2\langle \mathbf{l}_{i-1} \rangle^T \langle \mathbf{T}_{i-1} \rangle \langle \mathbf{l}_i \rangle + \langle l_{i-1}^2 \rangle \\ 0 & \langle \mathbf{T}_{i-1} \mathbf{T}_i \rangle & \langle \mathbf{T}_{i-1} \rangle \langle \mathbf{l}_i \rangle + \langle \mathbf{l}_{i-1} \rangle \\ 0 & 0 & 1 \end{pmatrix} \tag{17}$$

Results and Discussion

(i) Interdependency between Neighboring Bonds. In the repeat unit of PI-2, we found little interdependency between the neighboring pairs of bonds except between bonds 2 and 3. The virtual bonds in the DMDA part of the repeat unit are independent because of the relatively large spacings between the bonds. Although the DMDA part of PI-2 is flexible, no isomeric state transitions of bonds 7 and 8 were seen within the length of our trajectory. These bonds stayed near the *gauche* or *trans* conformations, respectively, where they had started. With a simple grid search of the rotational energy about bond 7 or bond 8, while keeping other chain parameters fixed, we found the energy barrier against a rotational isomeric state transition about the bond to be ~8 kcal/mol (Figure 2, solid line). If, however, we minimize the energy at each step during the grid search, then the barrier is reduced to ~6.4 kcal/mol (Figure 2, dashed line). This energy barrier is still too high for a transition to be seen within the 2-ns trajectory. In order to see isomeric state transitions of bond 7 or 8, a much longer trajectory would be needed. The near independency between bond 7 and bond 8 can be seen from Figure 3. From the upper left and lower right corners of Figure 3, we can see a slight disfavoring of the g^+g^- sequence due to the pentane effect. Because this effect is small, the independency between bond 7 and bond 8 is a good approximation. For the persistence length calculation, the symmetry of rotations about bonds 7 and 8 allows the assignment of zero values to the average sines and cosines of ϕ_7 and ϕ_8 without resorting to longer trajectories.

The BTDA part of PI-2 is often considered as "rigid". However, as we analyzed the history of the dihedral angles

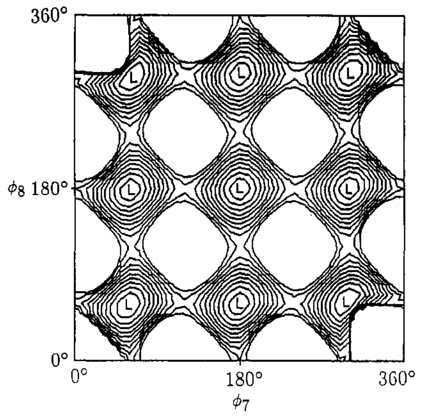

Figure 3. Potential energy contour map as a function of ϕ_7 and ϕ_8. Energy difference between contour lines: 1 kcal/mol.

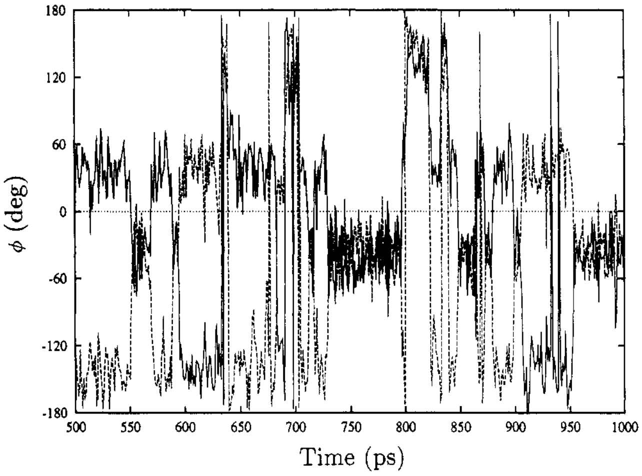

Figure 4. Dihedral angles of bond 2 (solid line) and bond 3 (dashed line) (500–1000 ps).

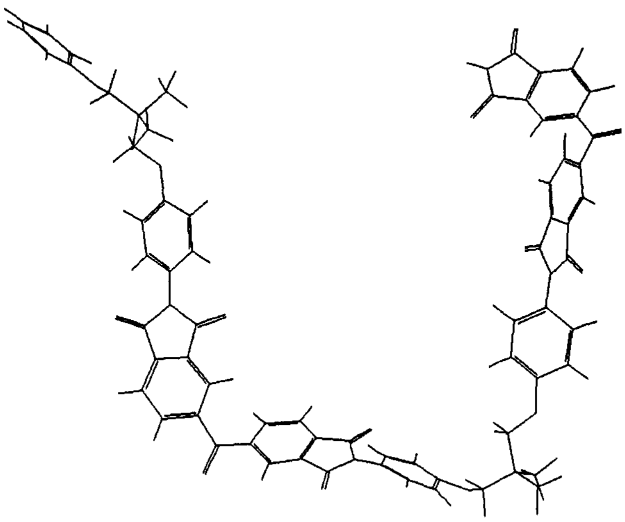

Figure 5. Snapshot of the molecule at 15 ps in the trajectory.

about virtual bonds 2 and 3, we found a great number of isomeric state transitions during the 2.2-ns trajectory, as can be seen in Figure 4, in which we plotted ϕ_2 and ϕ_3 between 0.5 and 1 ns. This finding is rather surprising, because if the BTDA part is truly rigid, then how could these transitions occur with such great frequencies, which would imply a substantial flexibility?

The flexibility of the "rigid" part can also be seen in the snapshot of the molecule at 15 ps, as shown in Figure 5. The bending of the chain near bonds 2 and 3 is nearly 90°. This type of conformation occurs in our trajectory quite often, making the chain seemingly rather flexible.

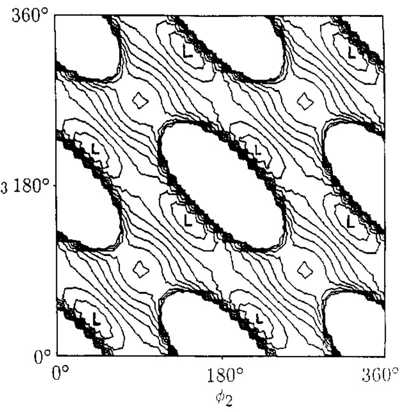

Figure 6. Potential energy contour map as a function of ϕ_2 and ϕ_3. Energy difference between contour lines: 1 kcal/mol.

If one looks at Figure 4 closely, one can see that the transitions of bond 2 and bond 3 occur simultaneously; i.e., there exists interdependency between bond 2 and bond 3. It is the interdependency that makes the transitions so much easier, by reducing the barrier height via a concerted motion of bond 2 and bond 3. The interdependency can be understood with the help of the potential energy contour map as a function of ϕ_2 and ϕ_3, shown in Figure 6. There are eight energy minima in this contour map, marked by "L". During the molecular dynamics trajectory, (ϕ_2, ϕ_3) take values close to the energy minima, and bonds 2 and 3 can make simultaneous transitions from one minimum to another. Suppose at one point in the trajectory (ϕ_2, ϕ_3) is at the minimum close to (140°,140°). The states it can make an immediate transition to are the minima close to (40°,220°) and (220°,40°), or even the minimum near (40°,40°), but not the minimum near (220°,220°) because of the huge energy barrier of the elliptic shape in the center of the figure. To make a transition to the minimum near (40°,40°), the rotation would need to overcome a small energy barrier of ~7 kcal/mol. Such a transition should occur quite frequently in a real process, whose time scale is much greater than the nanosecond. In the 2.2-ns trajectory, we do not see this transition, and the route of a transition is always along one of the antidiagonal "valleys", where the energy barrier is less than ~2.5 kcal/mol. This is exemplified by the coherent changes of ϕ_2 and ϕ_3, as shown in Figure 4.

There seem to exist two "channels", or low-energy valleys along the antidiagonal directions, for the transitions, and they do not communicate with each other on the time scale of the trajectory. (40°,40°), (140°,320°), (220°,220°), and (320°,140°) belong to one channel, and (40°,220°), (140°,140°), (220°,40°), and (320°,320°) belong to another. The division into two channels, or groups of minimum-energy states, is apparent if periodic tiling of the contour map is performed. The communication between the two channels is hindered by the ~7 kcal/mol energy barrier we mentioned above. Figure 7 is the joint probability distribution of ϕ_2 and ϕ_3 for the trajectory. Because the trajectory is not long enough for transitions from a state in one channel to a state in the other channel to occur, only states within one channel can be seen.

A major factor contributing to this type of potential energy contour map is the steric repulsion between the two marked hydrogen atoms in the rigid part of the structure (Figure 8). Therefore we expect to see similar behavior in potential energy contour maps of macromolecules with similar structures. A very similar contour map has indeed been reported by Hutnik *et al.*[9] in their study of the phenyl ring flip motions in the amorphous glassy polycarbonate of 4,4′-isopropylidenediphenol. The only

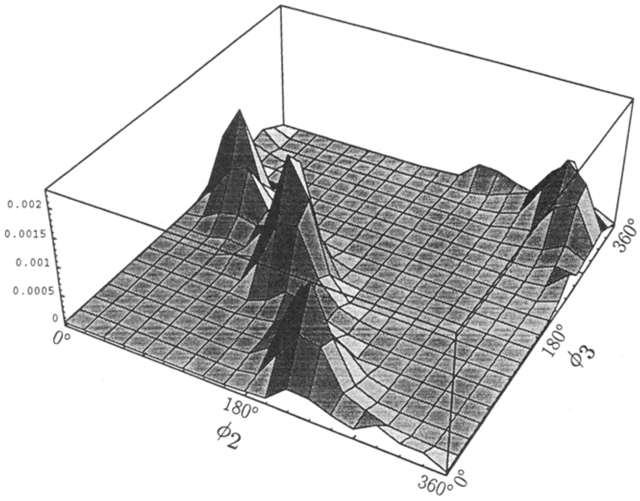

Figure 7. Joint probability distribution of ϕ_2 and ϕ_3 for the trajectory. Only states within one of the two channels can be seen because the trajectory is not long enough for transitions from a state in one channel to a state in the other channel to occur.

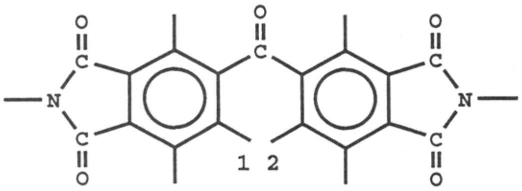

Figure 8. The "rigid" part of the PI-2 repeat unit showing steric repulsions between hydrogen atoms 1 and 2. Hydrogen atoms are explicitly shown.

Table I. Average Lengths of the Virtual Bonds (Å)

i	1, 4	2, 3	5, 10	6, 9	7, 8
$\langle l_i\rangle$	4.62	1.41	5.56	1.44	1.57

Table II. Average Sines and Cosines of the Bond Angles

i	1, 3	2	4, 10	5, 9	6, 8	7
$\langle \cos\theta_i\rangle$	−0.930	−0.561	−0.981	−0.673	−0.376	−0.334
$\langle \sin\theta_i\rangle$	0.364	0.827	0.184	0.737	0.925	0.941

Table III. Average Cosines of the Dihedral Angles

i	1, 4	2, 3	5, 10	6, 9	7, 8
$\langle \cos\phi_i\rangle$	0.837	0.000	0.000	−0.867	0.000

difference in the pertinent part of the structure is, instead of a carbonyl group to join the two aromatic imide groups, they have an isopropylidene group to join two phenyl rings. Fan *et al.*[10] in their study of an aromatic polysulfone system have also reported a similar-looking contour map. The pertinent part in their structure is identical to that of Hutnik *et al.*[9,10] Sundararajan in fact has conducted a study on the effect of substituting different atomic groups for the dimethyl group in the isopropylidene in polycarbonates.[11]

(ii) Persistence Length and Characteristic Ratio. As discussed earlier, the calculation of the persistence length depends on the choice of the initial bond. As an example, if we choose bond 0 (or bond 10, which is statistically equivalent to bond 0 because of the chemical periodicity) as the initial bond, the persistence vector will be

$$\begin{aligned}\mathbf{a}_0 = {} & \langle \mathbf{l}_0\rangle + \langle \mathbf{T}_0\rangle\langle \mathbf{l}_1\rangle + \cdots + \\ & \langle \mathbf{T}_0\rangle\langle \mathbf{T}_1\rangle\langle \mathbf{T}_2\mathbf{T}_3\rangle\langle \mathbf{T}_4\rangle\langle \mathbf{T}_5\rangle\langle \mathbf{T}_6\rangle\langle \mathbf{T}_7\rangle\langle \mathbf{T}_8\rangle\langle \mathbf{l}_9\rangle + \\ & \langle \mathbf{T}_0\rangle\cdots\langle \mathbf{T}_9\rangle(\langle \mathbf{l}_0\rangle + \langle \mathbf{T}_0\rangle\langle \mathbf{l}_1\rangle + \cdots + \\ & \langle \mathbf{T}_0\rangle\langle \mathbf{T}_1\rangle\langle \mathbf{T}_2\mathbf{T}_3\rangle\langle \mathbf{T}_4\rangle\langle \mathbf{T}_5\rangle\langle \mathbf{T}_6\rangle\langle \mathbf{T}_7\rangle\langle \mathbf{T}_8\rangle\langle \mathbf{l}_9\rangle) + \cdots \\ = {} & (\mathbf{E} + \mathbf{M}_0 + \mathrm{M}_0^2 + \cdots)\mathbf{L}_0 \qquad (18)\end{aligned}$$

where

$$\mathbf{M}_0 \equiv \langle \mathbf{T}_0\rangle\langle \mathbf{T}_1\rangle\langle \mathbf{T}_2\mathbf{T}_3\rangle\langle \mathbf{T}_4\rangle\langle \mathbf{T}_5\rangle\langle \mathbf{T}_6\rangle\langle \mathbf{T}_7\rangle\langle \mathbf{T}_8\rangle\langle \mathbf{T}_9\rangle \qquad (19)$$

and

$$\mathbf{L}_0 \equiv \langle \mathbf{l}_0\rangle + \langle \mathbf{T}_0\rangle\langle \mathbf{l}_1\rangle + \langle \mathbf{T}_0\rangle\langle \mathbf{T}_1\rangle\langle \mathbf{l}_2\rangle + \cdots + \langle \mathbf{T}_0\rangle\langle \mathbf{T}_1\rangle\cdots\langle \mathbf{T}_8\rangle\langle \mathbf{l}_9\rangle \qquad (20)$$

are defined as the effective transformation matrix and effective bond vector and **E** is the identity matrix. The subscripts "0" in $\mathbf{a}_0$, $\mathbf{M}_0$, and $\mathbf{L}_0$ denote starting the calculation from bond 0. The persistence length, a_0, is the first component of column vector $\mathbf{a}_0$. If we choose bond 1 as the initial bond, then we will have

$$\mathbf{a}_1 = (\mathbf{E} + \mathbf{M}_1 + \mathbf{M}_1^2 + \cdots)\mathbf{L}_1 \qquad (21)$$

and

$$\mathbf{M}_1 \equiv \langle \mathbf{T}_1\rangle\langle \mathbf{T}_2\mathbf{T}_3\rangle\langle \mathbf{T}_4\rangle\langle \mathbf{T}_5\rangle\langle \mathbf{T}_6\rangle\langle \mathbf{T}_7\rangle\langle \mathbf{T}_8\rangle\langle \mathbf{T}_9\rangle\langle \mathbf{T}_0\rangle \qquad (22)$$

and

$$\mathbf{L}_1 \equiv \langle \mathbf{l}_1\rangle + \langle \mathbf{T}_1\rangle\langle \mathbf{l}_2\rangle + \cdots + \langle \mathbf{T}_1\rangle\cdots\langle \mathbf{T}_9\rangle\langle \mathbf{l}_0\rangle \qquad (23)$$

The averaged quantities can be calculated from the molecular dynamics trajectory or assigned with zero values according to the symmetry of the structure. The symmetry in the contour map of ϕ_2 and ϕ_3 (Figure 6) makes $\langle \cos\phi_i\rangle = 0$ for $i = 2$ and 3. Therefore the simplified form of the transformation matrix in eq 7 applies to bonds 2 and 3 as well. The averages of the bond lengths are listed in Table I, and the sines and cosines of the bond angles and the cosines of the dihedral angles are listed in Tables II and III (the average sines of the dihedral angles being zero because of symmetry).

The fact that $\langle \cos\phi_2\rangle = \langle \cos\phi_3\rangle = \langle \sin\phi_2\rangle = \langle \sin\phi_3\rangle = 0$ by no means indicates that the average cross products between bonds 2 and 3 are zero. As a matter of fact, because bonds 2 and 3 are interdependent, the calculated cross products yield values of $\langle \cos\phi_2 \cos\phi_3\rangle = 0.044$, $\langle \cos\phi_2 \sin\phi_3\rangle = -0.457$, $\langle \sin\phi_2 \cos\phi_3\rangle = -0.451$, and $\langle \sin\phi_2 \sin\phi_3\rangle = 0.023$. In true equilibrium, $\langle \cos\phi_2 \sin\phi_3\rangle$ and $\langle \sin\phi_2 \cos\phi_3\rangle$ ought to be the same, and we take −0.454, the average of −0.457 and −0.451, as a better approximate of the equilibrium value of $\langle \cos\phi_2 \sin\phi_3\rangle$ and $\langle \sin\phi_2 \cos\phi_3\rangle$. These values, along with the average sines and cosines of individual bond angles and dihedral angles of bonds 2 and 3, serve to define $\langle \mathbf{T}_2\mathbf{T}_3\rangle$. We need not only to calculate the average transformation matrices for all individual bonds but also to calculate the average products of the transformation matrices associated with the correlated bonds.

The average product of the transformation matrices for bonds 2 and 3 calculated on the basis of the above discussion yields

$$\langle \mathbf{T}_2\mathbf{T}_3\rangle = \begin{pmatrix} 0.522 & 0.204 & 0 \\ 0 & 0 & 0.709 \\ 0.258 & -0.659 & 0.030 \end{pmatrix} \qquad (24)$$

The product of the average transformation matrices for

Table IV. Persistence Length (Å) Calculated with Different Initial Bond *i*

i	0	1	2	3	4	5	6	7	8	9
a_i	19.4	14.8	10.9	16.9	17.5	13.1	4.2	7.8	18.5	14.1

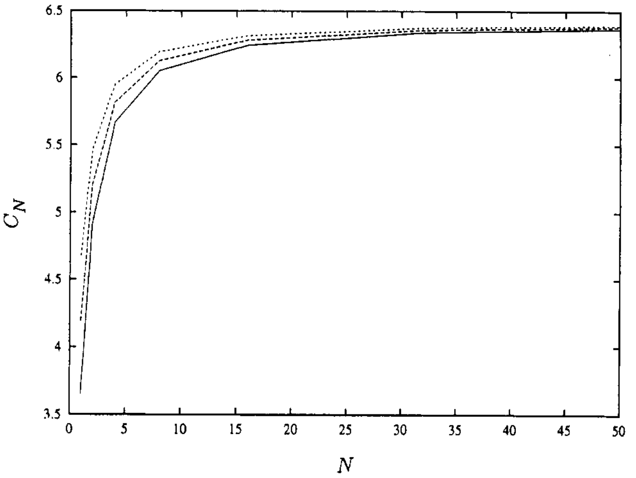

Figure 9. Characteristic ratios calculated as a function of the number of repeat units, N. Plotted for calculations with the repeat unit starting from bond 5 (solid line) bond 6 (long dashed line) and bond 8 (short dashed line). They converge to the same asymptotic value, 6.43.

bonds 2 and 3 is

$$\langle \mathbf{T}_2\mathbf{T}_3 \rangle = \begin{pmatrix} 0.522 & 0.204 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (25)$$

The calculated values of the persistence length with different initial bonds are listed in Table IV. The contour length of one repeat unit of PI-2 is ~29 Å. Therefore the largest calculated persistence length (~19 Å) is about two-thirds of this contour length. The small persistence length of ~4.2 Å when starting with bond 6 signifies the flexibility of the DMDA parts of PI-2.

The characteristic ratio is calculated according to eqs 9, 11, 12, 13, 16, and 17. If we define the repeat units by starting with bond 0, we then have an effective generator matrix of the form

$$\mathbf{G}_{0,\mathrm{eff}} = \langle \mathbf{G}_0 \rangle \langle \mathbf{G}_1 \rangle \langle \mathbf{G}_2\mathbf{G}_3 \rangle \langle \mathbf{G}_4 \rangle \langle \mathbf{G}_5 \rangle \langle \mathbf{G}_6 \rangle \langle \mathbf{G}_7 \rangle \langle \mathbf{G}_8 \rangle \langle \mathbf{G}_9 \rangle \quad (26)$$

We can then calculate the characteristic ratio, C_N, as a function of the number of repeat units, N, rather than the number of constituent bonds, n, of the polymer chain, i.e.,

$$C_{\mathrm{N}} = \frac{(\mathbf{G}_{0,\mathrm{eff}}^{N})_{1,5}}{N l_{\mathrm{rep}}^2} \quad (27)$$

where $(\mathbf{G}_{0,\mathrm{eff}}^{N})_{1,5}$ is the element of the first row, fifth column of the matrix product $(\mathbf{G}_{0,\mathrm{eff}}^{N})$ and l_{rep}^2 is the sum the squares of the lengths of the 10 virtual bonds (l_{rep}^2 = 117.65 Å^2). The limiting characteristic ratio is independent of the starting bond of the repeat unit, as can be seen in the example plots for repeat units starting with bonds 5, 6, and 8, respectively, in Figure 9.

Both the persistence length and the limiting characteristic ratio have been calculated on the basis that bond 2 and bond 3 are interdependent, with eq 24. We have also performed calculations assuming no interdependency between bonds 2 and 3, with eq 25. The results turned out to be essentially the same. If we assume free rotations about all virtual bonds, i.e., $\langle \cos \phi_i \rangle = 0$ as well as $\langle \sin \phi_i \rangle = 0$ for all i, then the limiting characteristic ratio is reduced to a value of 4.49.

The limiting characteristic ratio, 6.43, is comparable to that of polyethylene,[12] but notably larger than the calculated value of an amorphous polysulfone in the bulk[10] (2.11) and of a polycarbonate[11,13] (1.79). This is probably due to the longer stiff part made of an aromatic imide group and the phenyl ring next to it in the repeat unit of PI-2.

We can use eq 15 to evaluate the average persistence length of PI-2. Since the limiting characteristic ratio is calculated by the number of repeat units going to infinity, we can evaluate the mean length of a bond unit by the root mean square of the lengths of the 10 virtual bonds in a repeat unit, which is 3.43 Å. The persistence length evaluated using eq 15, with C_∞ = 6.43 and $\bar{l}$ = 3.43 Å, is 12.7 Å.

Conclusions

We have performed molecular simulations to study the flexibility of PI-2 and have found substantial flexibility in the so-called "rigid" part of PI-2. This flexibility is attributed to the concerted motions of the C–C bonds at the carbonyl group connecting the two aromatic imide groups in the repeat unit. The persistence length and limiting characteristic ratio have been studied with an interdependent bond model. Whenever possible, symmetry arguments have been used in order to achieve more accurate equilibrium values of the pertinent quantities. The upper estimate of the persistence length, ~19 Å, amounts to roughly two-thirds of the contour length of a repeat unit. The characteristic ratio, 6.43, is close to that of polyethylene. The average persistence length evaluated on the basis of the characteristic ratio is 12.7 Å. These quantitative characteristics also suggest that this polyimide is rather flexible.

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