Evaluation of the Persistence Length of the Rigid-Rod Polymers Poly(benzobisoxazole) and Poly(benzobisthiazole) Using Molecular Dynamics Simulations

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Received March 6, 1992; Revised Manuscript Received June 8, 1992

ABSTRACT: Rotational isomeric state theory provides a relatively simple formalism for the evaluation of the persistence vector, a, for a chain that can be represented by a repeating sequence of independent virtual bonds. The numerical problem can be reduced to the computation of the averages of the elements in the transformation matrices, $\langle T_i \rangle$. Here we apply this approach for the evaluation of the limiting length of a for poly(benzobisoxazole) and poly(benzobisthiazole) as the molecular weight becomes infinite. This length is denoted by a_∞. Some of the elements in $\langle T_i \rangle$ can be assigned by symmetry arguments, and the remaining nonzero elements are deduced from molecular dynamics trajectories. The values of a_∞ deduced by this approach are of a reasonable size for poly(benzobisoxazole). This study combines rotational isomeric state theory with long molecular dynamics simulations for small fragments in order to evaluate a_∞ for very stiff chains. The approach can be applied to other stiff polymers.

Introduction

The rigid-rod polymers of benzobisoxazole (PBO) and benzobisthiazole (PBT) have been of considerable interest because of their especially high tensile modulus and large persistence length. These polymers can therefore be used in their pure form or as an ingredient in polymer blends to make synthetic high-strength materials. A broad range of investigations have been carried out to study the conformational characteristics[1,2] and the electronic structure[3,4] of the isolated chain, the interchain interactions between two chains,[3,5] and the properties of these polymers in solutions.[6,7] With the development of computational techniques, molecular dynamics has become a very powerful tool in the study of atom-based models of polymeric materials. Although there has been much theoretical work aimed at studying rodlike polymers with semiempirical methods, attempts at using molecular dynamics simulations to quantitatively analyze the properties of rodlike polymers are relatively recent.[8]

The purpose of the present work is to demonstrate the applicability of the combination of the rotational isomeric state formalism, symmetry arguments, and pertinent averaged properties deduced from suitably long molecular dynamics trajectories for the computation of the persistence length of rodlike polymers and to explore the reasons why the persistence length of these polymers is large yet finite. The systems studied are the rodlike polymers PBO and PBT, but the methodology should be applicable to other types of rodlike polymers. A similar approach has been reported recently for the analysis of the conformations of poly(*p*-phenylene terephthalate) and poly(*p*-phenylene isophthalate).[9]

Theory

The persistence length of a simple long linear polymer chain is defined by[10,11]

$$a_\infty \equiv \sum_{j=i}^{\infty} \frac{\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle}{l_i} \tag{1}$$

where $\mathbf{l}_i$ is the vector representation of bond i (which is usually not close to either end of the chain), and l_i is the length of this bond. The averaging is over all conformations that the polymer chain can assume, with the probability distribution of each conformation determined by its statistical weight, i.e., by the energetics of that conformation and the Boltzmann factor.

For polymers with a complex structure, the definition and calculation of the persistence length are more difficult. In the types of polymer where there are rigid moieties in the backbone, one can extend the above formula by appropriately selecting a representative point in each rigid moiety and defining virtual bonds by linking these points in succession. The persistence length is then still well-defined in terms of these virtual bonds.

To facilitate the calculation of the scalar products in eq 1, it is necessary to express all bond vectors in the reference frame of bond i. A transformation matrix method has been established, with which a bond vector expressed in the reference frame of bond $i + 1$ can be transformed into the reference frame of bond i by[10,12]

$$\mathbf{l}_i = \mathbf{T}_i \mathbf{l}_{i+1} \tag{2}$$

The transformation matrix $\mathbf{T}_i$ has the form

$$\mathbf{T}_i = \begin{pmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{pmatrix} \tag{3}$$

where θ_i is the complement of the bond angle between bond $i + 1$ and bond i, and ϕ_i is the dihedral angle at bond i. The transformation matrix in eq 3 is written for the case where $\phi_i = 0$ for a trans placement at bond i, and the x axis for the coordinate system is collinear with bond i. By successively applying these transformation matrices, the jth bond vector can then be expressed in the reference frame of the ith bond ($j > i$) as

$$\mathbf{l}_j = \mathbf{T}_i \mathbf{T}_{i+1} \cdots \mathbf{T}_{j-1} \mathbf{l}_j^0 \tag{4}$$

where the vector $\mathbf{l}_j^0$ is expressed in its own reference frame, i.e.

$$\mathbf{l}_j^0 \equiv \begin{pmatrix} l_j \\ 0 \\ 0 \end{pmatrix} = l_j \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{5}$$
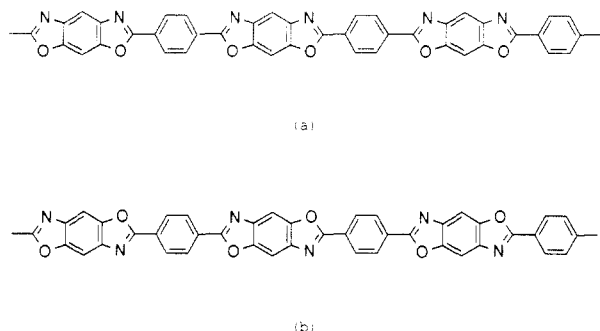
(a)

(b)

Figure 1. Three repeat units of (a) *cis*-PBO and (b) *trans*-PBO.

The persistence length is, from eqs 1 and 4

$$a_\infty = \frac{1}{l_i} \sum_{j=i}^{\infty} \langle \mathbf{l}_i^0 \cdot \mathbf{T}_i \mathbf{T}_{i+1} ... \mathbf{T}_{j-1} \mathbf{l}_j^0 \rangle \tag{6}$$

If $\mathbf{l}_i^0$ and $\mathbf{l}_j^0$ are constant vectors (in the approximation that we ignore the minor changes in their lengths resulting from vibrations) according to eq 5, the average matrix products in the above sum can be written as

$$\langle \mathbf{l}_i^0 \cdot \mathbf{T}_i \mathbf{T}_{i+1} ... \mathbf{T}_{j-1} \mathbf{l}_j^0 \rangle = \mathbf{l}_i^0 \cdot \langle \mathbf{T}_i \mathbf{T}_{i+1} ... \mathbf{T}_{j-1} \rangle \mathbf{l}_j^0 \tag{7}$$

Alternatively, one can introduce eq 7 by postulating that any fluctuations in the lengths of virtual bonds i and j are uncorrelated with the angles between successive virtual bonds and the rotations about virtual bonds. In this case the values of l_i and l_j implied by eq 5 are given by the averages for the lengths of each vector.

If all the virtual bonds are independent of each other, which is often an excellent appproximation for suitably defined virtual bonds in rodlike polymer chains constructed from rigid units connected by isolated rotatable bonds,[11,13] the average matrix product in eq 6 should be equal to the product of the average matrices, i.e.

$$\langle \mathbf{T}_i \mathbf{T}_{i+1} ... \mathbf{T}_{j-1} \rangle = \langle \mathbf{T}_i \rangle \langle \mathbf{T}_{i+1} \rangle ... \langle \mathbf{T}_{j-1} \rangle \tag{8}$$

In most polymers it is a useful first approximation to take the bond angles as independent of the dihedral angles in the conformations that have the largest statistical weights (and hence those conformations that dominate the values of the elements in the averaged transformation matrices). As a consequence, one can write

$$\langle \mathbf{T}_i \rangle = \begin{pmatrix} \langle \cos \theta_i \rangle & \langle \sin \theta_i \rangle & 0 \\ \langle \sin \theta_i \rangle \langle \cos \phi_i \rangle & -\langle \cos \theta_i \rangle \langle \cos \phi_i \rangle & \langle \sin \phi_i \rangle \\ \langle \sin \theta_i \rangle \langle \sin \phi_i \rangle & -\langle \cos \theta_i \rangle \langle \sin \phi_i \rangle & -\langle \cos \phi_i \rangle \end{pmatrix} \tag{9}$$

The solution to the persistence length will then solely depend on the average sine and cosine of the angles between successive virtual bonds (θ_i) and of the dihedral angles for rotation about virtual bonds (ϕ_i). Our task to solve for the persistence length should then be to concentrate on the evaluation of such averages. The covalent structure of certain rigid-rod polymers, including those considered here, may allow the use of symmetry arguments in the assignment of some of these averages. Molecular dynamics trajectories of suitable duration provide the data required for computation of the remaining averages of these trigonometric functions. The trajectory naturally takes account of the multidimensional character of the potential surface.

Model

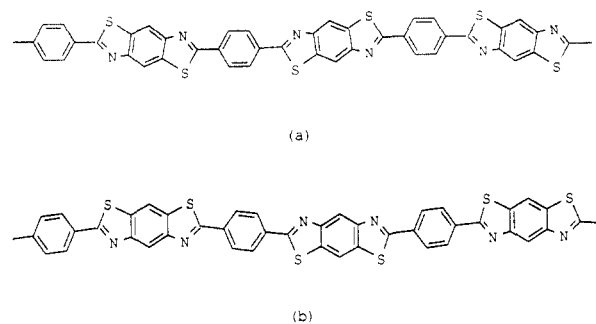The covalent structures of portions of PBO and PBT are depicted in Figures 1 and 2, respectively. The internal

(a)

(b)

Figure 2. Three repeat units of (a) *trans*-PBT and (b) *cis*-PBT.
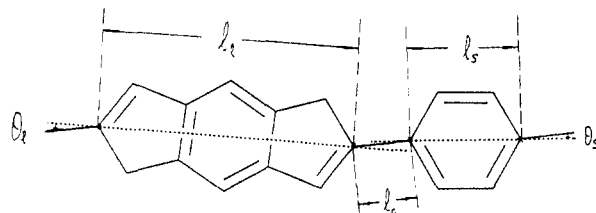

Figure 3. Definition of virtual bonds.

motions within the fused rings (bisoxazole and bisthiazole) and within the phenyl rings are much smaller than other internal motions that affect the persistence length. As a result, these rings can be considered as rigid moieties in the backbone because of the requirements for ring closure and the tendency for the aromatic π electrons in the rings to cause the out-of-plane potentials to be very large. We assign three types of virtual bonds, as illustrated in Figure 3. The indices used for these virtual bonds are l for the larger ring system, s for the smaller ring system, and c for the carbon–carbon bond. The motions that need to be analyzed are as follows: the fluctuations of the lengths of the virtual bonds (which are very small), the variations in the angles between successive virtual bonds, and the dihedral angles describing rotation about the virtual bonds. The interesting quantities are thus the lengths of the three different types of virtual bonds and the averages of the trigonometric functions that occur in the different types of transformation matrices.

In the systems we are studying here, increasing the cutoff range beyond three repeat units has a negligible impact on the result. Therefore, it is appropriate to say that the dominating interactions in the polymer chains are short-ranged. We therefore selected a segment with only three repeat units (six rings), terminated by a hydrogen atom on both ends, and analyzed the virtual bond lengths, bending angles, and dihedral angles from molecular dynamics trajectories and the symmetries in the structures. Because of the short-range nature of the interactions and the stiffness of the chain, such an analysis is a rather good approximation.

Molecular dynamics trajectories were computed for *cis*-PBO, *trans*-PBT, and *cis*-PBT, using the Dreiding force field[14] in POLYGRAF version 2.20 as provided by Molecular Simulations, Inc. All calculations are performed for a single chain in a vacuum, using a time step of 0.5 fs. Most of the calculations are done at a temperature of 300 K. These trajectories were computed for 1 ns. One other calculation, of length 0.3 ns, was carried out for a *cis*-PBO chain at 500 K. This calculation at 500 K was performed to investigate the temperature effect on the persistence length of a rodlike polymer chain.

It will become apparent in the presentation of the results that the values of a_∞ extracted from the calculations are extremely sensitive to the distortions in bond angles produced by thermal fluctuations. These distortions are

not always well represented in the force fields provided with commercial software packages. We confine our attention here to results obtained using POLYGRAF because the values of a_∞ extracted from the simulations performed with that package provide good agreement with experiment. Very much smaller values of a_∞ (not described here) can be obtained when the trajectories are computed with packages that overestimate the ease of the distortion of the bond angles in these polymers.

Results and Discussion

cis-**Poly(benzobisoxazole).** The first assumption in using a molecular dynamics trajectory to study the equilibrium statistics is that, within the duration of the dynamics trajectory, the system is in equilibrium. Therefore, the length of the trajectory is an important issue, as to how long a trajectory should be in order to achieve equilibrium. One criterion for equilibrium is to see if there are enough representations of each isomeric state. In our case, we ran a molecular dynamics trajectory of *cis*-PBO at 300 K for 1 ns, which for many purposes of molecular dynamics simulations should be considered adequately long. The average sine and cosine of the bond angles and dihedral angles were extracted with respect to these virtual bonds from the molecular dynamics trajectory.

According to the symmetry of the structure, the rotation of the phenyl ring by 180° should give an identical conformation. Therefore, one would expect to see equal populations of conformations in which the dihedral angle for rotation of the phenyl ring is ϕ and $\phi + 180°$, for any value of ϕ. If the values of ϕ correspond to stable rotational isomeric states, there should also be transitions between ϕ and $\phi + 180°$. Although the structure of the fused ring is not exactly symmetric, the same considerations apply to it in reasonable approximation because this asymmetry only affects interactions between two fused rings. Because the interactions are short-ranged, this asymmetric effect should be expected to be rather small, and again one would expect to see transitions at the fused-ring system between ϕ and $\phi + 180°$, with the two states at about equal populations.

The only motions seen of those dihedral angles in 1 ns at 300 K were fluctuations about stable states with $\phi = 0°$ or 180°, which were the two states of minimum energy. No rotational isomeric state transitions were observed from one state to the other. The molecule remained nearly coplanar throughout the trajectory.

The above finding led us to investigate the energy barrier for the transition between the two states separated by 180°. A simple unit with one phenyl ring and one fused ring was used. It was found that the energy maximum was midway between the two stable states, with an energy ~7 kcal mol⁻¹ higher than the energy at the minima. The probability for a transition to overcome such a barrier at 300 K in 1 ns is extremely small. To achieve equilibrium of the dihedral motions would require the computation of a forbiddingly long trajectory. The barrier might be as low as 2.3 kcal mol⁻¹, according to results obtained by the AM1 method in MOPAC,[1,4] but even with a barrier of that size the rate of transitions between stable rotational isomeric states might be too small to provide true equilibration of the dihedral angles in a trajectory of reasonable length.

Although there are almost no rotational isomeric state transitions of the dihedral angles in each polymer chain, the ensemble of polymer chains comprises a very good average of the fluctuations within each rotational isomeric state. It is that information which we require. An appeal

Table I
Lengths (Å) of the Virtual Bonds at 300 K

polymer	$\langle l_l \rangle$	$\langle l_s \rangle$	$\langle l_c \rangle$
cis-PBO	6.485	2.861	1.410
trans-PBO	6.484	2.861	1.410
cis-PBT	6.813	2.880	1.415
trans-PBT	6.835	2.879	1.415

Table II
Average Supplements of Angles (deg) between Virtual Bonds at 300 K

polymer	$\langle \theta_s \rangle$	$\langle \cos \theta_s \rangle$	$\langle \sin \theta_s \rangle$	$\langle \theta_l \rangle$	$\langle \cos \theta_l \rangle$	$\langle \sin \theta_l \rangle$
cis-PBO	4.56	0.9958	0.0794	5.10	0.9948	0.0888
trans-PBO	4.58	0.9957	0.0797	5.18	0.9945	0.0900
cis-PBT	4.39	0.9961	0.0765	14.88	0.9651	0.2564
trans-PBT	4.36	0.9962	0.0758	10.80	0.9808	0.1872

to the symmetry in the energetics can circumvent the need for a much longer trajectory.

Because the dihedral angles are symmetrically distributed about 0° and about 180°, it is straightforward to see that $\langle \sin \phi_i \rangle = 0$ in all of the $\langle T_i \rangle$. Furthermore, because for the phenyl rings the populations around 0° and around 180° must have a one-to-one correspondence in an infinitely long trajectory, $\langle \cos \phi \rangle = 0$ for the phenyl-ring virtual bonds.

It was mentioned before that the energetics associated with the fused-ring system are slightly asymmetric. We studied the energetics of a segment with three repeat units, with the nitrogen atoms in all three units lying on the same side (indexed by uuu for up–up–up), and with the nitrogen atoms in the central unit lying on the other side from the other two (indexed by udu for up–down–up). The minimum energies for these two conformations are

$$E_{uuu} = 172.17 \text{ kcal mol}^{-1}$$

$$E_{udu} = 172.14 \text{ kcal mol}^{-1}$$

The difference between the two states, 0.03 kcal mol⁻¹, is negligible. It is a good approximation to assume an equal distribution. Consequently, $\langle \cos \phi \rangle = 0$ can be used for the fused-ring systems also.

The average transformation matrices in eq 9 will then have a simple form given by

$$\langle T_i \rangle = \begin{pmatrix} \langle \cos \theta_i \rangle & \langle \sin \theta_i \rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (10)$$

Another consequence of this simplification is that there are now only two types of transformation matrices, because there are only two types of bond angles: the angle formed by the carbon–carbon bond and the virtual bond of the fused-ring system and the angle formed by the carbon–carbon bond and the virtual bond of the phenyl ring. We will from now on denote the first angle by θ_l and the latter by θ_s and the corresponding transformation matrices by T_l and T_s, respectively. We retain the three different bond lengths: l_l, for the big ring; l_s, for the phenyl ring; and l_c, for the carbon–carbon bond.

When the length scales are different for different virtual bonds, the persistence length may depend on the choice of the first bond. However, for a rodlike polymer chain, the difference caused by the choice of the first virtual bond should be very small relative to the persistence length itself. If we select a fused-ring system as supplying the first virtual bond, then, by substituting eq 10 into eq 6, we have

$$a_l = \langle l_l \rangle + \langle T_l \rangle \langle l_c \rangle + \langle T_l \rangle \langle T_s \rangle \langle l_s \rangle + \langle T_l \rangle \langle T_s \rangle \langle T_s \rangle$$
$$\langle l_c \rangle + \langle T_l \rangle \langle T_s \rangle \langle T_s \rangle \langle T_l \rangle \langle l_l \rangle + \ldots$$

$$a_l = \langle l_l \rangle (1 + \langle \cos \theta_s \rangle^2 \langle \cos \theta_l \rangle^2 + \langle \cos \theta_s \rangle^4 \langle \cos \theta_l \rangle^4 + \ldots) +$$
$$\langle l_c \rangle \langle \cos \theta_l \rangle (1 + \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle) (1 + \langle \cos \theta_s \rangle^2 \langle \cos \theta_l \rangle^2 +$$
$$\langle \cos \theta_s \rangle^4 \langle \cos \theta_l \rangle^4 + \ldots) + \langle l_s \rangle \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle (1 + \langle \cos \theta_s \rangle^2$$
$$\langle \cos \theta_l \rangle^2 + \langle \cos \theta_s \rangle^4 \langle \cos \theta_l \rangle^4 + \ldots) \quad (11)$$

This expression after simplification yields

$$a_l =$$
$$\frac{\langle l_l \rangle + \langle l_c \rangle \langle \cos \theta_l \rangle (1 + \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle) + \langle l_s \rangle \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle}{1 - \langle \cos \theta_s \rangle^2 \langle \cos \theta_l \rangle^2}$$

$$(12)$$

On the other hand, if we had selected a phenyl ring to be the starting bond, we would have had

$$a_s =$$
$$\frac{\langle l_s \rangle + \langle l_c \rangle \langle \cos \theta_s \rangle (1 + \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle) + \langle l_l \rangle \langle \cos \theta_s \rangle \langle \cos \theta_l \rangle}{1 - \langle \cos \theta_s \rangle^2 \langle \cos \theta_l \rangle^2}$$

$$(13)$$

In the case of a rodlike polymer, these two persistence lengths are expected to be almost the same.

Since we do not need to be concerned with achieving equilibrium of the dihedral rotations insofar as the transitions between rotational isomeric states is concerned, the dynamics trajectory does not need to be extremely long. The time period we used, i.e., 1 ns, is long enough for equilibration of the fluctuations of the bond lengths and bond angles. The results from our analysis of the molecular dynamics are summarized in Tables I and II. The persistence lengths a_l and a_s calculated from these results are 649 and 647 Å, respectively. The similar numerical values obtained for these two persistence lengths confirm our conjecture that, for rodlike polymers with different virtual bond lengths, the difference created by the choice of the first bond should be very small. This persistence length ~648 Å is in good agreement with an expected value somewhat greater than 500 Å,[15,16] as deduced from experimental data in solution.[6]

trans-Poly(benzobisthiazole). We studied the energetic symmetry of a segment with three repeat units, as we did with *cis*-PBO. The minimum energies for the two conformations uuu and udu are

$$E_{uuu} = 119.17 \text{ kcal mol}^{-1}$$

$$E_{udu} = 119.09 \text{ kcal mol}^{-1}$$

This slight difference rendered the two conformations almost symmetric in energy and allowed us to apply the same arguments we used to simplify the study of PBO when calculating the persistence length. The results for *trans*-PBT are listed in Tables I and II. The persistence lengths a_l and a_s calculated from these results are 273 and 272 Å, respectively. Again, these two numbers are almost identical. They signify a stiff polymer, but not quite as stiff as is found for *trans*-PBT in chlorosulfonic acid solutions. Light scattering measurements for the polymer in that solvent find a persistence length of 640 ± 90 Å,[17] which is larger by a factor of 2 than the values obtained here.

trans-Poly(benzobisoxazole) and *cis*-Poly(benzobisthiazole). The results in the previous sections find that the persistence length of *cis*-PBO is appreciably larger

Table III
Average Lengths (Å) and Supplements of Angles (deg) between Virtual Bonds for *cis*-PBO at 500 K

property	value	property	value
$\langle l_l \rangle$	6.479	$\langle \sin \theta_s \rangle$	0.0996
$\langle l_s \rangle$	2.859	$\langle \theta_l \rangle$	6.489
$\langle l_c \rangle$	1.411	$\langle \cos \theta_l \rangle$	0.9917
$\langle \theta_s \rangle$	5.727	$\langle \sin \theta_l \rangle$	0.1128
$\langle \cos \theta_s \rangle$	0.9934		

than that of *trans*-PBT. Conceivable causes are a difference between chains with trans and cis fused-ring systems or a difference between the chains with sulfur and oxygen atoms, and hence the related parameters in the force field. To understand the origin of the difference between the persistence lengths of *cis*-PBO and *trans*-PBT, it is interesting to conduct a parallel study of *trans*-PBO and *cis*-PBT. The same arguments about symmetry for *cis*-PBO and *trans*-PBT were applied, and the same methods were used for extraction of the persistence lengths from the trajectories. The results for *trans*-PBO and *cis*-PBT are listed in Tables I and II. The persistence lengths of *trans*-PBO and *cis*-PBT are ~621 and ~161 Å, respectively. Comparing these to the corresponding numbers for *cis*-PBO and *trans*-PBT, which are ~648 and ~273 Å, respectively, we conclude that the difference between *cis*-PBO and *trans*-PBT is caused by the difference between the bond characters due to the difference between sulfur and oxygen. Substitution of sulfur for oxygen produces a smaller value for $\langle \cos \theta_l \rangle$ and hence a smaller value for the persistence length.

Further insight into the origin of the differences in persistence lengths for PBO and PBT comes from examination of energy-minimized structures. In PBO energy minimization produces a structure in which successive virtual bonds are collinear. Collinear virtual bonds imply an infinite persistence length. Thus the thermally-induced fluctuations about the equilibrium angles are responsible for producing the finite persistence lengths of ~600 Å in PBO at 300 K. In contrast, successive virtual bonds are not collinear in the optimized structure for PBT. If thermal fluctuations in the bond angles are completely suppressed, finite persistence lengths of 455 and 216 Å, respectively, are obtained for *trans*-PBT and *cis*-PBT. Thus PBT without thermal fluctuations in the angles between virtual bonds has a smaller persistence length than PBO with thermal fluctuations at 300 K, due to the noncollinear virtual bonds in the optimized structures of the sulfur-containing polymers.

cis-PBO at 500 K. To examine the dependence of the persistence length on temperature, we computed a trajectory for *cis*-PBO for a length of 300 ps at 500 K. The persistence lengths calculated as a_l and a_s are 410 and 408 Å, respectively, which are markedly shorter than the persistence length of ~648 Å for the same molecule at 300 K. The results are summarized in Table III. The thermal fluctuations caused the supplements of the angles between virtual bonds at 500 K to become greater than those at 300 K. These larger fluctuations are the reasons why the persistence length has decreased substantially going from 300 to 500 K.

Ratio of a_n to Contour Length. Let a_n denote the length of the averaged end-to-end vector for a chain of finite degree of polymerization n. In this notation, the previous discussion has dealt exclusively with a_∞. The ratio r_n of a_n to the contour length must approach zero as $n \to \infty$. The rate at which this ratio approaches the limit can be estimated from the results presented here. According to eq 11, for $n > 0$

$$a_n = (l_1 + l_c \langle \cos \theta_1 \rangle (1 + \langle \cos \theta_s \rangle \langle \cos \theta_1 \rangle) +$$

$$l_s \langle \cos \theta_s \rangle \langle \cos \theta_1 \rangle) \left(\frac{1 - \alpha^n}{1 - \alpha} \right) \quad (14)$$

$$\alpha = \langle \cos \theta_s \rangle^2 \langle \cos \theta_1 \rangle^2 \quad (15)$$

The contour length is

$$L_n = n(l_1 + l_s + 2l_c) \quad (16)$$

and the ratio r_n is therefore

$$r_n \equiv \frac{a_n}{L_n} =$$

$$\left(\frac{(l_1 + l_c \langle \cos \theta_1 \rangle)(1 + \langle \cos \theta_s \rangle \langle \cos \theta_1 \rangle) + l_s \langle \cos \theta_s \rangle \langle \cos \theta_1 \rangle}{n(l_1 + l_s + 2l_c)} \right) \times$$

$$\left(\frac{1 - \alpha^n}{1 - \alpha} \right) \quad (17)$$

Figure 4 depicts the values of r_n, as a function of n, for the five systems described above. For *cis*-PBO this ratio falls to 0.5 when the molecular weight is about 20 000. The decrease in r_n with increasing n is faster for the systems with the smaller persistence lengths.

Conclusions

Classical rotational isomeric state theory has been combined with results obtained from molecular dynamics trajectories in order to investigate the persistence lengths of the rodlike polymers poly(benzobisoxazole) and poly-(benzobisthiazole). The results are of reasonable size for *cis*-PBO. The barriers to internal rotation are too high to permit significant rotational isomeric state transitions on the time scale of the simulations. The symmetry in the structures, however, has provided a way for us to simplify the transformation matrices so that we need not rely on the equilibration of the transitions between stable rotational isomeric states. Complete equilibration of the rotational isomeric states will not affect the assignments for $\langle \cos \phi \rangle$ and $\langle \sin \phi \rangle$. The molecular properties that play the greatest role in the determination of the sizes of the persistence lengths are the angles between successive virtual bonds at 0 K and the magnitudes of the fluctuations in these angles at higher temperatures. The angles at 0 K are important in determining whether the preferred conformations have collinear or noncollinear virtual bonds, with the former circumstance favoring larger persistence lengths, as in PBO. The fluctuations become larger when sulfur is substituted for oxygen, causing the sulfur-containing polymers to have smaller persistence lengths than those polymers that do not contain sulfur. The
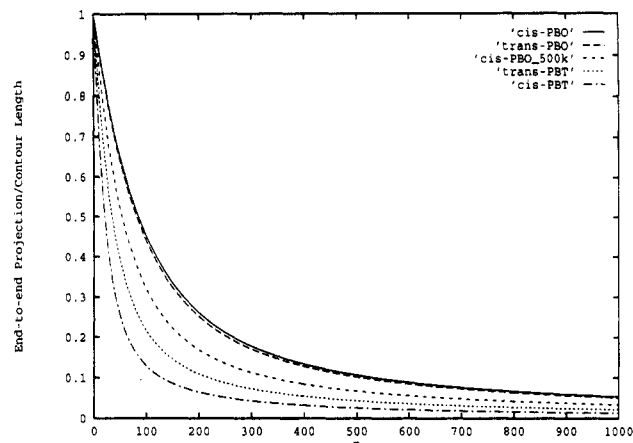

Figure 4. Values of r_n as a function of n for the five systems.

persistence length of *cis*-PBO decreases as temperature increases, primarily as a consequence of increases in the magnitude of these fluctuations.

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