Persistence Length of the "Rodlike" Molecule Poly(*p*-phenylene-*trans*-benzobisthiazole) Revisited Again

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Four issues are pertinent with regard to Roitman and McAdon's comment[1] (RM) on our paper about the persistence lengths of poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBT) obtained from molecular dynamics simulations in vacuum.[2]

First, there is a question about the experimental value of the persistence length of *cis*-PBO. Earlier published works[3-5] seem to indicate this value to be ~500 Å. In the work done by RM *et al.*, as cited in their comment,[1] the persistence length of PBO was claimed to be 190–300 Å.[1] We do not judge which result is more conclusive and will leave this controversy to the experimentalists.

Second, in the paper of Welsh and Mark[6] cited by RM[1] in support of their rather short persistence length of PBO, we did not find evidence that PBO has a "kidney-bean" shaped distortion in the heterostructure, as was suggested by RM,[1] that is pertinent to our calculation without protonation. Furthermore, the research reported in this paper[6] was done with the CNDO/2 method, not with the AM1 method as Roitman and McAdon suggested.[1]

Third, RM suggested that the segment with a phenyl ring and the two C–C bonds next to it can be considered as one virtual bond, thereby reducing the number of virtual bonds in a repeat unit from four in our model to two. This assumption would be valid and sensible only if the bond angle fluctuations about the phenyl rings are negligible compared to the fluctuations about the heterostructures. In our simulations, we found the thermal fluctuations of the angles between virtual bonds C–C and the phenyl ring to be as large as the thermal fluctuations of the angles between virtual bonds C–C and the heterostructure[2] (*e.g.*, 4.6° and 5.1°, respectively, for *cis*-PBO at 300 K). This similar magnitude of fluctuations can be understood in terms of the strong conjugations in the heterostructures as well as in the phenyl rings. Therefore, it was not felt suitable to take the simplification as has been done by RM.

Let us explain why Roitman and McAdon's suggestion would not apply to our simulations, using a simple example.

Consider a freely rotating chain with n identical bonds of unit length and identical bond angles of 180° − θ. Suppose that this is a stiff chain as is in our case, such that $\cos\theta = 1 - \delta$, where δ is much less than 1. If one chooses the natural bonds along the backbone, similar to what we have done, then one will get a persistence length a, with a value

$$a = \frac{1}{1 - \cos\theta} \approx \frac{1}{\delta} \tag{1}$$

Alternatively, one can choose to connect every second joint along the backbone to form $n/2$ new virtual bonds, which resembles the treatment of RM. The persistence length calculated with the latter scheme would be

$$a' = \frac{1 + \cos\theta}{1 - \langle\cos\Theta\rangle} \tag{2}$$

where $1 + \cos\theta$ is the length of the new virtual bonds and Θ is the supplement angle between two neighboring virtual bonds. The angular brackets stand for the statistical average. Because $\delta \ll 1$, we may write

$$a' \approx \frac{2}{1 - \langle\cos\Theta\rangle} \tag{3}$$

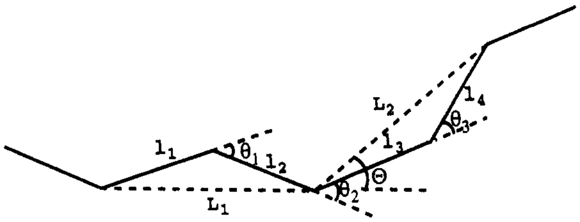

Figure 1. Model of freely rotating bonds with different definitions of virtual bonds.

To solve for $\langle\cos\Theta\rangle$, let us consider Figure 1.

In Figure 1, $\mathbf{l}_i$ (i = 1–4) are the natural virtual bond vectors, pointing from left to right along the backbone, $\mathbf{L}_1$ and $\mathbf{L}_2$ are the virtual bond vectors of the second scheme mentioned above, and θ_i (i = 1–3) and Θ are the angles formed by the virtual bonds. It is easy to see that

$$\cos\Theta = \frac{\mathbf{L}_1\cdot\mathbf{L}_2}{|\mathbf{L}_1|\cdot|\mathbf{L}_2|} = \frac{(\mathbf{l}_1 + \mathbf{l}_2)\cdot(\mathbf{l}_3 + \mathbf{l}_4)}{|\mathbf{l}_1 + \mathbf{l}_2|\cdot|\mathbf{l}_3 + \mathbf{l}_4|} \tag{4}$$

Assuming $\cos\theta_i = 1 - \delta_i$ ($\delta_i \ll 1$) for i = 1–3, for a freely rotating model,

$$\langle\mathbf{l}_1\cdot\mathbf{l}_3\rangle = \cos\theta_1\cos\theta_2 \approx 1 - \delta_1 - \delta_2 \tag{5}$$

$$\langle\mathbf{l}_1\cdot\mathbf{l}_4\rangle = \cos\theta_1\cos\theta_2\cos\theta_3 \approx 1 - \delta_1 - \delta_2 - \delta_3 \tag{6}$$

$$\langle\mathbf{l}_2\cdot\mathbf{l}_3\rangle = \cos\theta_2 \approx 1 - \delta_2 \tag{7}$$

$$\langle\mathbf{l}_2\cdot\mathbf{l}_4\rangle = \cos\theta_2\cos\theta_3 \approx 1 - \delta_2 - \delta_3 \tag{8}$$

and

$$|\mathbf{l}_1 + \mathbf{l}_2| = [(\mathbf{l}_1 + \mathbf{l}_2)\cdot(\mathbf{l}_1 + \mathbf{l}_2)]^{1/2} = (2 + 2\cos\theta_1)^{1/2} \approx 2(1 - \delta_1/4) \tag{9}$$

$$|\mathbf{l}_3 + \mathbf{l}_4| \approx 2(1 - \delta_3/4) \tag{10}$$

Therefore

$$\cos\Theta = \frac{\mathbf{l}_1\cdot\mathbf{l}_3 + \mathbf{l}_1\cdot\mathbf{l}_4 + \mathbf{l}_2\cdot\mathbf{l}_3 + \mathbf{l}_2\cdot\mathbf{l}_3}{|\mathbf{l}_1 + \mathbf{l}_2|\cdot|\mathbf{l}_3 + \mathbf{l}_4|} \approx \frac{4 - 2\delta_1 - 4\delta_2 - 2\delta_3}{4(1 - \delta_1/4)(1 - \delta_3/4)} \approx 1 - \delta_2 - \frac{\delta_1 + \delta_3}{4} \tag{11}$$

In the ideal model we presented above, all δ_i have the same value, δ, therefore,

$$\langle\cos\Theta\rangle \approx 1 - \frac{3}{2}\delta \tag{12}$$

The persistence length would then be

$$a' = \frac{2}{1 - \langle\cos\Theta\rangle} \approx \frac{4}{3\delta} = \frac{4}{3}a \tag{13}$$

We thereby conclude that the simple approach equivalent to what was taken by RM would overestimate the persistence length by $^1/_3$ in this simple model. Since the thermal fluctuations in the two angles about the phenyl rings are comparable to those about the heterostructures, the simple approach taken by RM should not be valid.

Finally, one suggestion we did find very valuable in RM's comment is the "crankshaft" type of motion in PBT.[1] In our treatment of PBT, we neglected the fact that the potential surface about the virtual bond formed by the heterostructure is actually nonsymmetric, which should

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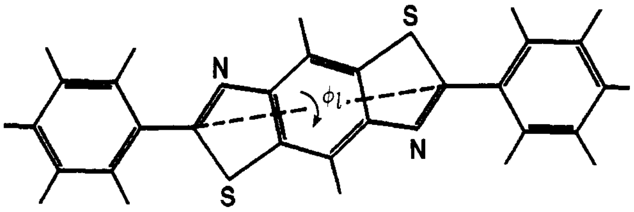
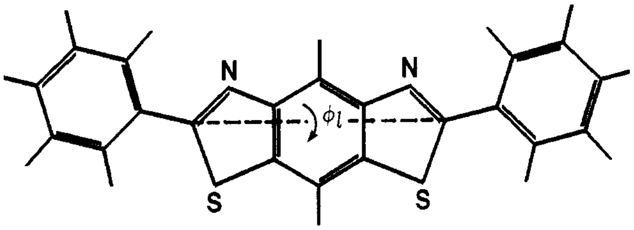


trans-PBT



cis-PBT

Figure 2. The *trans* and *cis* natures of the virtual bonds formed by the heterostructures in *trans*-PBT and *cis*-PBT.

have invalidated the use of the simplified approach that was valid for PBO (transformation matrices with only two nonzero elements) in the case of PBT.

If we do take into account of the fact that the dihedral angle about the virtual bond formed by the heterostructure is nearly always *trans* in *trans*-PBT and *cis* in *cis*-PBT (dashed lines in Figure 2) and use the equilibrium values from the molecular dynamics trajectories, then we should have a more accurate prediction of the persistence lengths of PBT.

With this approach, the average transformation matrices associated with the C–C bonds and the phenyl ring still have only two elements because of symmetry, while the average transformation matrices for the virtual bonds formed by the heterostructures will have a less simplified form

$$\langle \mathbf{T}_i \rangle = \begin{pmatrix} \langle \cos \theta_i \rangle & \langle \sin \theta_i \rangle & 0 \\ \langle \sin \theta_i \rangle \langle \cos \phi_i \rangle & -\langle \cos \theta_i \rangle \langle \cos \phi_i \rangle & 0 \\ 0 & 0 & -\langle \cos \phi_i \rangle \end{pmatrix} \quad (14)$$

with $\phi = 0°$ defined for *trans*. The matrix elements involving $\langle \sin \phi_i \rangle$ are zero because the symmetric torsion potential requires that $\langle \sin \phi_i \rangle = 0$, while the elements involving $\langle \cos \phi_i \rangle$ now become nonzero. The persistence length will then be

$$a_l = \langle \mathbf{l}_l \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{l}_c \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{l}_s \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{l}_c \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_l \rangle \langle \mathbf{l}_l \rangle + \ldots = (\mathbf{E} + \mathbf{M} + \mathbf{M}^2 + \mathbf{M}^3 + \ldots)\mathbf{L} \quad (15)$$

if we start the calculation from a heterostructure. In the above equation, **E** is the identity matrix, and **M** and **L** are the effective transformation matrix and effective bond vector, with

$$\mathbf{M} = \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_l \rangle \quad (16)$$

and

$$\mathbf{L} = \langle \mathbf{l}_l \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{l}_c \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{l}_s \rangle + \langle \mathbf{T}_l \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{T}_s \rangle \langle \mathbf{l}_c \rangle \quad (17)$$

respectively. Note that there are four virtual bonds in a repeat unit.

The $\langle \cos \phi_i \rangle$ at the virtual bond formed by the heterostructure are 0.6632 for *trans*-PBT and –0.8762 for *cis*-PBT at 300 K. With these values and the $\langle \cos \theta_i \rangle$ that was known previously,[2] using the above equations, the persistence length can be calculated to yield 515–554 Å for *trans*-PBT, depending on the choice of the initial bond. For *cis*-PBT, the persistence length is notably smaller, namely, 88–100 Å. The large difference between the persistence lengths of the two types of structures of PBT is caused by the extension and contraction due to the intrinsic *trans* and *cis* natures in the heterostructures. In the case of PBO, because the virtual bonds are almost collinear, the difference caused by *trans* and *cis* is consequently much smaller compared to the case of PBT. The newly achieved result for *trans*-PBT is in good agreement with experiment (640 ± 90 Å).[7]

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References and Notes

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