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

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The extraordinary tensile properties[1] of poly(*p*-phenylene-*cis*-benzobisoxazole) (*cis*-PBO) and poly(*p*-phenylene-*trans*-benzobisthiazole) (*trans*-PBT) have been attributed to the high stiffness and collinearity of their molecular backbones. In a recent paper[2] Zhang and Mattice (ZM) considered rotational isomeric state (RIS) models to analyze the persistence length, Q, of *cis*-PBO and *trans*-PBT. They used a three virtual bond model as reproduced in Figure 1 (Figure 3 in their paper) where l_l, l_c, and l_s, are the bonds representing the large heterocycle ring, the C–C bond between the two rings, and the phenylene ring, respectively. The angles θ_l and θ_s are the complement angles between l_l, l_c, and l_s, l_c, respectively. The geometries were computed with the Dreiding force field (DFF) method. These authors incorporated thermal angle bond fluctuations in their calculations and showed that these have an important effect on the persistence lengths at 300 K. Their results are $Q \sim 62$ nm for *trans*-PBO, $Q \sim 65$ nm for *cis*-PBO, $Q \sim 27.3$ nm for *trans*-PBT, and $Q \sim 16.1$ nm for *cis*-PBT. According to these results, therefore, *trans*-PBT is expected to be considerably *more flexible* than *cis*-PBO.

ZM noted that the light scattering (LS) persistence length of *trans*-PBT,[3] $Q = 64 \pm 9$ nm, is considerably higher than their computed value. Recent LS and intrinsic viscosity (IV) studies[4] of *cis*-PBO, on the other hand, indicate that this polymer may be considerably more flexible in a methanesulfonic acid (MSA) solution ($Q \sim$ 20–30 nm). There is additional evidence, furthermore, suggesting that *trans*-PBT is stiffer than *cis*-PBO: the isotopic-to-nematic transition of *trans*-PBT in MSA is observed[5] at $c \sim 2.6$–2.9%, but it appears at[4,8,9] $c \sim 5$–6% for *cis*-PBO (sample IV > 10 dL/g); the *lower* viscosity of *trans*-PBT in the nematic phase suggests[5] that it is probably less entangled than *cis*-PBO. While it has been proposed that the apparent flexibility shown by *cis*-PBO in solution might be caused by rod aggregation,[6] there is general experimental agreement[3-9] that *trans*-PBT is considerably stiffer than the ZM estimate.

There are probably two contributing factors to the discrepancies between the ZM calculations and experiments. First, ZM approximated the RIS transformation matrices with an effective "freely rotating" (in the ϕ angles) bond model[10] (eq 10 in their paper). This approximation would be valid if the rings were symmetric around the chain axes, but it does not account for the *trans* and *cis* configurational constraints imposed by heterocycle asymmetries. The second factor involves the accuracy of the molecular shapes and the role of geometrical changes induced by backbone protonation.

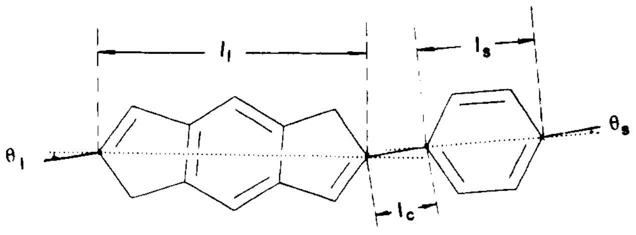


Figure 1. Virtual bonds used by Zhang and Mattice.

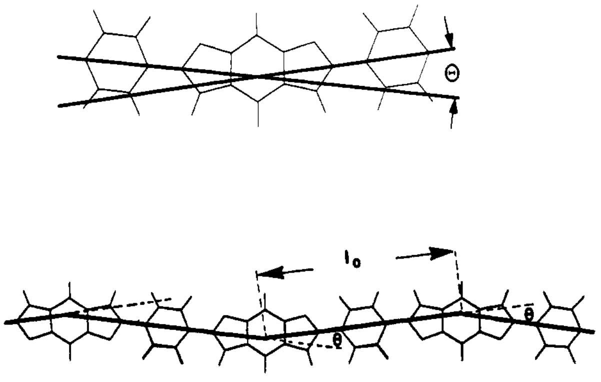
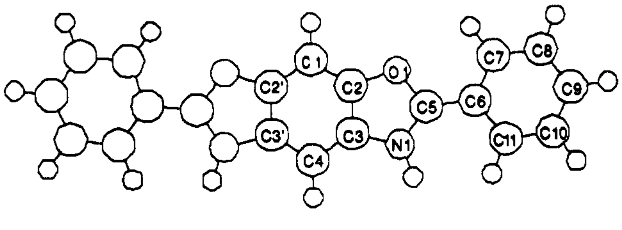


Figure 2. Top: Geometry of the diprotonated *cis*-PBO model compound obtained from *ab initio* HF/3-21G* molecular orbital calculations. All the bonds are shown, including the H atoms. Θ = 14.7° is the angle between the lines defined by the equatorial carbon atoms of the phenylenes (C6-C9 and C6′-C9′ in Table I). Bottom: Single virtual bond model for *cis*-PBO in solution; the angle is $\Theta \sim 12$–15° at 0 K, corresponding to $Q \approx 34$–55 nm.

Table I. HF/3-21G* Coordinates of the *cis*-PBO Model Compound[a]

	neutral		diprotonated	
	X (Å)	Y (Å)	X (Å)	Y (Å)
C1	0.0000	1.4576	0.000	1.4576
C2	1.1428	0.6943	1.1364	0.6912
C3	1.1620	−0.7024	1.1539	−0.6946
C4	0.0000	−1.4415	0.0000	−1.4508
O1	2.4602	1.1112	2.4630	1.1199
N1	2.5106	−1.1157	2.5190	−1.0433
C5	3.2215	−0.0561	3.2748	0.0515
C6	4.6670	0.0843	4.6833	0.1974
C7	5.2505	1.3419	5.2195	1.4921
C8	6.6275	1.4553	6.5848	1.6595
C9	7.4161	0.3180	7.4163	0.5489
C10	6.8302	−0.9380	6.8897	−0.7708
C11	5.4558	−1.0579	5.5303	−0.9216
H9	8.4841	0.4084	8.4791	0.6832

[a] The coordinates of the other atoms are $X'_i = -X_i$ and $Y'_i = Y_i$.



For the case of *cis*-PBO the discrepancy may be accounted, for the most part, by the 0 K geometry of the DFF. This method predicts a nearly perfect linear backbone for *cis*-PBO. Molecular orbital calculations such as the semiempirical Austin Method 1 (AM1) computations of Welsh and Yang,[11] however, show considerable differences between C-O-C bonds and C-N-C bonds on the *cis*-PBO heterocycle. Their results are consistent with a "kidney-bean" shape distortion as illustrated in Figure 2 (with Θ defined as the angle between the C-C bonds linking the heterocycle with the phenylenes on each side). The unprotonated AM1 structure corresponds to Θ = 15.1°. *Ab initio* molecular orbital calculations[12] (HF/3-21G*) also suggest a nonsymmetric shape,[13] Θ = 9.7°, and the

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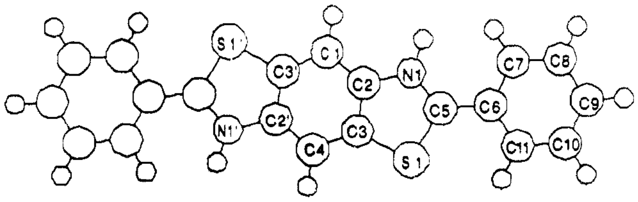
Table II. HF/3-21G* Coordinates of a *trans*-PBT Model Compound[a]

	neutral		diprotonated	
	X (Å)	Y (Å)	X (Å)	Y (Å)
C1	0.2695	1.3941	0.22108	1.44079
C2	1.2930	0.4657	1.2600	0.5131
C3	1.0201	−0.9134	1.0569	−0.8653
C4	−0.2695	−1.3941	−0.2108	−1.4079
S1	2.5205	−1.7995	2.5848	−1.7132
N1	2.6517	0.7758	2.6280	0.81294
C5	3.3967	−0.2637	3.4548	−0.2222
C6	4.8643	−0.2037	4.8911	−0.1377
C7	5.4743	1.0457	5.5393	1.1056
C8	6.8503	1.1451	6.9119	1.1702
C9	7.6306	0.0000	7.66043	0.00000
C10	7.0284	−0.2454	7.0331	−1.2374
C11	5.6497	−1.3478	5.6599	−1.3091
H9	8.6995	0.0786	8.7301	0.0539

[a] The coordinates of the other atoms are $X'_i = -X_i$ and $Y'_i = Y_i$.



nonlinearity is larger for the diprotonated case, $\Theta = 14.7°$ (AM1 is not very sensitive to protonation). These results (Table I) are in agreement with the work of Shaffer and Wiershke,[14] although these authors considered smaller compounds, and did not discuss protonation effects.

If the *cis*-PBO chain is represented, for simplicity, by an equivalent freely rotating chain with only one single virtual bond[10] (Figure 2, bottom) with $l_0 \approx 1.21$ nm and $\Theta = 14.7–15.1°$, one can use the expression

$$Q \approx (1/2) l_0 \frac{[1 + \langle \cos \Theta \rangle]}{[1 - \langle \cos \Theta \rangle]} \tag{1}$$

to estimate $Q \approx 34–37$ nm for the protonated *cis*-PBO *without* thermal fluctuations. This simplified model assumes that $\theta_s \approx 0°$ (perfectly symmetric phenylene) and that the rotation of the C-C bond between the phenylene and the heterocycle has symmetric potential around $\phi = 0°$ and 180°. Note: There is a relatively small phenylene distortion ($\theta_s \approx 1.4°$) caused by the bulky protonated N-atom (relative to the O-atom). Without this distortion, the value of Θ is reduced to $\sim 12°$, and $Q \approx 55$ nm. A rigorous treatment of Q, however, should include the effects of *two* neighboring heterocycles in up-up and up-down positions relative to each other.

We made no attempt to calculate thermal bond bending from the *ab initio* (or AM1) computations: We assumed, instead, that the *gradients* of the Dreiding fields are reasonably accurate. An effective bond bending, δ, was estimated by defining a statistically equivalent single bond chain (eq 1) with[15,16]

$$\langle \cos \Theta \rangle = \cos \Theta \exp(-\delta^2/2) \tag{2}$$

The bending $\delta \approx 11.04°$ was obtained from eqs 1 and 2, assuming the small DFF value $\Theta \approx 1.18$ and ZM's $Q \approx 65$ nm.

Assuming this bending, the value $Q \approx 22.5–23.3$ nm is obtained with these equations for the **nonsymmetric** geometries ($\Theta = 14.7–15.1°$), and $Q \approx 30$ nm with $\Theta = 12°$. These Q's are in excellent agreement with experiments.

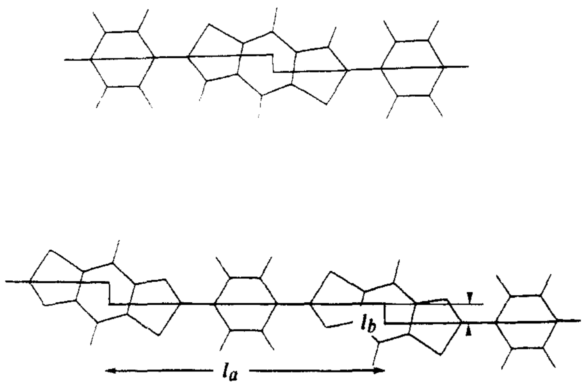


Figure 3. Top: Geometry of the diprotonated *trans*-PBT model compound obtained from *ab initio* HF/3-21G* molecular orbital calculations. The phenylene rings are parallel to each other due to the symmetry of the heterocycle, but they are displaced by l_b = 0.08 nm relative to each other. Bottom: Crankshaft bond model for the *trans* structures. The persistence length for this model is practically infinity at 0 K.

The diprotonated *trans*-PBT model compound is shown in Figure 3 (top). In this case, the phenylenes are perfectly parallel to each other (at 0 K) as a result of the *trans* symmetry of the heterocycle (Table II). The effect of diprotonation on the HF/3-21G* geometry of *trans*-PBT is quite different from the *cis*-PBO case. Here, diprotonation leads to a *more collinear* chain configuration. The angle θ_s, in particular, is reduced from $\theta_s \approx 1.9°$ to only $\theta_s \approx 0.5°$; *i.e.*, the phenylenes become almost perfectly collinear. The displacement between the phenylenes also becomes smaller ($l_b \approx 0.11$ nm neutral, $l_b \approx 0.09$ nm diprotonated).

For estimating Q of *trans*-PBT (and *trans*-PBO), it is useful to consider the virtual bond model shown in Figure 3 (bottom). The phenylenes are collinear with the C-C bonds connecting them with the heterocycles and are *practically parallel* to each other (assuming no thermal fluctuation). This model then involves a *nonrandom* bond l_a along the equatorial C atoms of the phenylene rings and a short bond l_b with random orientation in the plane perpendicular to l_a (this bond, l_b, represents the asymmetry of the *trans* heterocycles caused by the differences in bond lengths and angles between N and S in *trans*-PBT or N and O in *trans*-PBO).

Table III. Summary of the Persistence Lengths for PBO and PBT

	Q (nm) for *cis*-PBO		Q (nm) *trans*-PBT	
	0 K	300 K	0 K	300 K
exptl		20–30		55–80
this work[a] (diprotonated)	34–55, $\Theta \sim 12–15°$	22–30	>6000, $\Theta \sim 0°$	67.4
Zhang–Mattice (Dreiding)	$\sim$5800, $\Theta \sim 1.18°$	65	NA	27.3
Farmer et al. (SYBYL)	900,[b] $\Theta \sim 3°$	32.5	300,[b] $\Theta \sim 5.17°$	21.5

[a] The 300 K bond bendings (δ in eq 2) were estimated from the Zhang–Mattice bond fluctuation potentials. [b] Farmer et al. used slightly different expressions, but their persistence lengths and the corresponding values for Θ are in agreement with our expressions.

For n repeat units the mean-square end-to-end distance is

$$\langle r^2 \rangle = (nl_a)^2 + nl_b^2 \tag{3}$$

In the absence of thermal bond bending, this model suggests that the *trans* structures are virtually rodlike:

$$\lim_{n\to\infty} \frac{\langle r^2 \rangle}{nl_a^2} \to \infty \tag{4}$$

Assuming the same bond angle fluctuation as before, $\delta \approx 11.04°$, eqs 1 and 2 estimate $Q \approx 67.4$ nm for *trans*-PBT at room temperature (the virtual bond is $l_0 = 1.25$ nm, and $\Theta = 0°$), in excellent agreement with the experimental results (Table III). This interpretation suggests, furthermore, that the persistence length of *trans*-PBO in solution should be very close to that of *trans*-PBT.

The simple models described in this publication show the essential features differentiating the *cis vs trans* symmetry constraints of these polymers and illustrate the dramatic effects on Q caused by subtle geometric changes, such as those induced by protonation. The reason for the high flexibility of *trans*-PBT estimated by ZM was most likely caused by their neglect of nonsymmetric constraints in the heterocycles. The crankshaft model illustrated in Figure 3, on the other hand, is in excellent agreement with experiments. This agreement also suggests that the bond bending effects of ZM are probably very realistic. The results are summarized in Table III.

A new computational study of the flexibility of these chains has been published by Farmer and co-workers[17] (FCDA). These authors obtained $Q = 32.5$ nm for *cis*-PBO and $Q = 21.5$ nm for *trans*-PBT. As in the study of ZM, their 0 K *cis*-PBO is nearly collinear (see Table III), and protonation effects were not considered. The force fields used by FCDA (SYBYL) are considerably softer than ZM's, and consequently their backbone bendings are dominated by large out-of-plane heterocycle deformations. The FCDA predictions for Q are close to the experimental *cis*-PBO value, but there is no such agreement for *trans*-PBT. The work of FCDA illustrates that, in addition to the symmetry constraints, Q is extremely sensitive to the choices of potential gradients. We wonder, however, if it is appropriate to neglect protonation since spectroscopic studies[18] suggest that there is enhancement of conjugation (and backbone planarity) for these chains in strong acid solutions.

References and Notes

(1) Eby, W. W., McLemore, D. E., Adams, W. W., Eds. *The Materials Science and Engineering of Rigid Rod Polymers*; Symposium Proceedings; Materials Research Society: Pittsburgh, PA, 1989; Vol. 134.

(2) Zhang, R.; Mattice, W. L. *Macromolecules* **1992**, *25*, 4937.

(3) Crosby, C. R.; Ford, N. C.; Karasz, F. E.; Langley, K. H. *J. Chem. Phys.* **1981**, *75*, 4298.

(4) Roitman, D. B.; Wessling, R. A.; McAlister, J. Submitted to *Macromolecules*.

(5) Ventrakaman, S.; Berry, G. C.; Einaga, Y. *J. Polym. Sci., Polym. Phys.* **1985**, *23*, 1275.

(6) Berry, G. C.; Metzger Cotts, P.; Chu, S. G. *Polym. J.* **1981**, *13*, 47.

(7) Choe, W. E.; Kim, S. N. *Macromolecules* **1981**, *14*, 920.

(8) Roitman, D. B.; Janek, R.; McAlister, J.; Rochefort, S. Unpublished data.

(9) Lee, C. C.; Chu, S. G.; Berry, G. C. *J. Polym. Sci., Polym. Phys.* **1983**, *21*, 1573.

(10) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: Evanston, IL, 1971; Chapter 2.

(11) Welsh, W. J.; Yang, Y. *Comput. Polym. Sci.* **1991**, *1*, 139.

(12) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Polple, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; Chapter 4.

(13) Roitman, D. B.; McAlister, J.; McAdon, M.; Martin, E.; Wessling, R. A. Submitted to *J. Polym. Sci.*

(14) Shaffer, A. A.; Wierschke, S. G. *J. Comput. Chem.* **1993**, *14*, 75.

(15) Mansfield, M. L. *Macromolecules* **1983**, *16*, 1863.

(16) Cook, R. *Macromolecules* **1987**, *20*, 1961.

(17) Farmer, B. L.; Chapman, B. R.; Dudis, D. S.; Adams, W. W. R. *Polymer* **1993**, *34*, 1588.

(18) Shen, D. Y.; Venkatesh, D. J.; Burchell, D. J.; Shu, P. H. C.; Hsu, S. L. *J. Polym. Sci., Polym. Phys.* **1982**, *20*, 509.