Macromolecules **1981**, *14*, 1125–1126

(18) Bauer, D. R.; Brauman, J. I.; Pecora, R. *Macromolecules* **1975**, *8*, 443.
(19) Patterson, G. D.; Lindsey, C. P.; Alms, G. R. *Macromolecules* **1978**, *11*, 1242.
(20) Kramer, O.; Frederik, J. E. *Macromolecules* **1972**, *5*, 69.
(21) Nomura, H.; Miyahara, Y. *Polym. J.* **1976**, *8*, 30.
(22) Koda, S.; Nomura, H.; Miyahara, Y. *Macromolecules* **1978**, *11*, 604.
(23) Cerf, R. *Adv. Chem. Phys.* **1975**, *33*, 73.
(24) Cochran, M. A.; Dunbar, J.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 215.
(25) Dunbar, J. I.; North, A. M.; Pethrick, R. A.; Steinhauer, D. B. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 263.
(26) Nomura, H.; Kato, S.; Miyahara, Y. *Mem. Fac. Eng., Nagoya Univ.* **1975**, *27* (1), 72.
(27) Froelich, B.; Noël, C.; Monnerie, L. *Polymer* **1979**, *20*, 529.
(28) Valeur, B.; Jarry, J. P.; Geny, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 667. *Ibid.* **1975**, *13*, 2251. Valeur, B.; Jarry, J. P.; Monnerie, L. *Ibid.* **1975**, *13*, 675.
(29) Bullock, A. T.; Butterworth, J. H.; Cameron, G. G. *Eur. Polym. J.* **1971**, *7*, 445.
(30) Bullock, A. T.; Cameron, G. G.; Smith, P. M. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1202.
(31) Bullock, A. T.; Cameron, G. G.; Smith, P. M. *J. Phys. Chem.* **1973**, *77*, 1635.
(32) Bullock, A. T.; Cameron, G. G.; Reddy, N. K. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 727.
(33) Lang, M. C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 349.
(34) Yang, H. W. H.; Chien, J. C. W. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 63*, 263.
(35) Yang, H. W. H.; Chien, J. C. W. *Macromolecules* **1978**, *11*, 759.
(36) Ramasseul, R.; Rassat, A. *Bull. Soc. Chim. Fr.* **1970**, 4330.
(37) Friedrich, C.; Noël, C.; Ramasseul, R.; Rassat, A. *Polymer* **1980**, *21*, 232.
(38) Hodgman, C. D., Ed. "Handbook of Chemistry and Physics"; Chemical Rubber Publishing Co.; Cleveland, Ohio, 1957.
(39) Riddick, J. A.; Bunger, W. B. *Tech. Chem. (N.Y.)* **1970**, *2*.
(40) Grossi, P. J.; Marchetti, L.; Ramasseul, R.; Rassat, A. *J. Chim. Phys.* **1977**, *74*, 1167.
(41) Quantum Chemistry Program Exchange, Program No. 265.
(42) Freed, J. H.; Bruno, G. V.; Polnaszek, C. F. *J. Phys. Chem.* **1971**, *75*, 3385.
(43) Goldman, S. A.; Bruno, G. V.; Polnaszek, C. F.; Freed, J. H. *J. Chem. Phys.* **1972**, *56*, 716.
(44) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1095.
(45) Bach Van, Nguyen-Luong; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 52*, 283.
(46) Mashimo, S. *Macromolecules* **1976**, *9*, 91.
(47) Baysal, B.; Lowry, B. A.; Yu, H.; Stockmayer, W. H. In "Dielectric Properties of Polymers"; Karasz, F. E., Ed.; Plenum Press: New York, 1971; p 329.
(48) Kramers, H. A. *Physica* **1940**, *7*, 284.
(49) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(50) Bullock, A. T.; Cameron, G. G.; Smith, P. M. *Polymer* **1973**, *14*, 525.
(51) Matsuo, K.; Kuhlmann, K. F.; Yang, W. H.; Geny, F.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1347.
(52) Biddle, D.; Nordström, T. *Ark. Kemi* **1970**, *32*, 359.
(53) Lety, A. Thèse de Doctorat d'Etat, Paris, 1974.
(54) Tardiveau, N. Thèse de Docteur-Ingénieur, Paris, 1980.

Notes

Polarizabilities of Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers

D. BHAUMIK, H. H. JAFFÉ, and J. E. MARK*

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221.

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Introduction

The aromatic heterocyclic polymers considered in the present investigation are the *cis*-poly(benzobisoxazole) (PBO) shown in Figure 1, its trans modification, and the trans modification of the sulfur analogue, poly(benzobisthiazole) (*trans*-PBT). The electronic structures of these relatively rigid chain molecules are of considerable interest, for a variety of reasons. For example, charge distributions are relevant to both intramolecular[1,2] and intermolecular[1,3] energies of the chains, resonance stabilization is important with regard to conformational flexibility,[2] and energy band gap information is pertinent to electrical conductivity.[4] Also of considerable importance are polarizabilities, since they are needed for the interpretation of solution property studies such as flow birefringence measurements. Experimental studies of this type are carried out to obtain rheological time constants and orientation parameters relevant to the processing of these materials.[5] In this investigation, several theoretical approaches[6-9] are used to calculate repeat unit polarizabilities of the three polymers mentioned above.

Theory

The bond lengths and bond angles in the three repeat units were obtained from the X-ray structural studies conducted on model compounds by Fratini and co-workers.[10,11] The two PBO polymers have planar repeat units, but the *trans*-PBT repeat unit has the *p*-phenylene group rotated by 23.2°.[1,2,10,11] In this latter case, the plane of the phenylene ring was taken to be the plane of the molecule. For all three molecules, the plane of the molecule was in the xz plane, with the z axis coincident with the long molecular axis. The quantities of interest are the polarizability components α_{xx}, α_{yy}, and α_{zz}, their simple average $\bar{\alpha}$, and the anisotropic ratio defined by

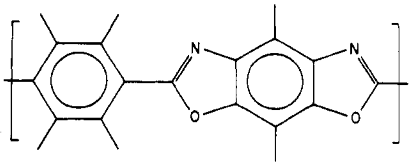

Figure 1. *cis*-PBO repeat unit.

$$\delta = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2} \right]^{1/2} \tag{1}$$

The first method employed for all of these quantities was the quantum mechanical method of Marchese and Jaffé,[6] in which second-order perturbation theory is combined with the CNDO/S CI formalism[7] (complete neglect of differential overlap, configuration interactions). The second was the empirical scheme of Miller and Savchik,[8] in which the average polarizability is obtained by summing atomic hybrid components τ_A

$$\bar{\alpha} = (N/4)[\sum_A \tau_A]^2 \tag{2}$$

in which N is the total number of electrons in the molecule. Pertinent values of τ_A for C, N, O, S, and H atoms are 1.428, 1.262, 1.290, 3.496, and 0.314 Å$^{3/2}$, respectively.[8] The

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Table I
Longitudinal and Transverse Bond Polarizabilities[a]

bond	b_l	b_t
C–C[b]	1.88	0.020
C–C[c]	2.25	0.48
C–N	1.59	0.89
C=N	2.46	0.91
C–O	1.34	0.75
C–S	3.93	2.20
C–H	0.79	0.58

[a] Reference 9; units are Å³ (10^{-24} cm³). [b] Aliphatic carbon atoms. [c] Aromatic carbon atoms.

third is the bond polarizability method of Denbigh,[9] in which both $\bar{\alpha}$ and the polarizability components are obtained by vectorial additions of longitudinal b_l and transverse b_t components of the polarizabilities of the bonds. The equations are

$$\alpha_{xx} = \sum_i (b_{li} \sin^2 \phi_i \cos^2 \theta_i + b_{ti} \sin^2 \theta_i + b_{ti} \cos^2 \phi_i \cos^2 \theta_i) \quad (3)$$

$$\alpha_{yy} = \sum_i (b_{li} \sin^2 \phi_i \sin^2 \theta_i + b_{ti} \cos^2 \theta_i + b_{ti} \cos^2 \phi_i \sin^2 \theta_i) \quad (4)$$

$$\alpha_{zz} = \sum_i (b_{li} \cos^2 \phi_i + b_{ti} \sin^2 \phi_i) \quad (5)$$

where ϕ_i is the angle between bond i and the z axis and θ_i is the angle between the x axis and the projection of bond i onto the xy plane.[9] The polarizabilities for C–C and C–H bonds are already available in the literature,[9] whereas for C–N, C=N, C–O, and C–S bonds, they were calculated from standard equations.[9] For single bonds not involving H these are $b_l = 0.600 + 0.098r^6$ (where the bond length r is in Å) and $b_t/b_l = 0.56$. For double bonds $b_l = 0.600 + 0.385r^6$ and $b_t/b_l = 0.37$. These values are summarized in Table I.

The quantum mechanical method[6] applied to the (H terminated) *cis*-PBO repeat unit gave $\alpha_{xx} = 4.69$, $\alpha_{yy} = 0.11$, and $\alpha_{zz} = 27.69$ and thus $\bar{\alpha} = 10.83$ Å³. This value of $\bar{\alpha}$ is almost the same as the experimental value of benzene,[6,12] whereas the structure of the repeat unit suggests it should be 2–3 times this value. Similar studies[13] of other, simpler molecules have also given serious underestimates of $\bar{\alpha}$, and this method was therefore not considered further.

The atomic additivity scheme[8] gives the value of $\bar{\alpha}$ listed in the second column of Table II; the separate components are unfortunately beyond the scope of this method. The bond additivity scheme[9] gave the values of $\bar{\alpha}$ listed in the following column, and these are seen to be in good agreement with those based on atomic additivities. The PBT chain is predicted to have a larger value of $\bar{\alpha}$ than the two PBO chains, since the C–S bond is much more polarizable than the C–O bond (as is shown by the data in Table I). The corresponding values of the polarizability components are given in the next three columns. They were used to calculate values of the anisotropic ratio δ; the results are given in the last column of the table and should be directly applicable to the interpretation of flow birefringence data.[5] The only relevant experimental value of δ is that obtained from light scattering measurements carried out on some solutions of *trans*-PBT in methanesulfonic acid.[5] Interpretation of these results in the very rough approximation that the chains have cylindrical symmetry gives $\delta = 0.5$.[5] It is gratifying that the experimental and theoretical results are in at least qualitative agreement, particularly since the experimental situation is almost certainly complicated by significant protonation of the PBT chains.

Table II
Calculated Average Polarizabilities, Polarizability Components, and Anisotropic Ratios for the Polymer Repeat Units[a]

polymer	atomic additivity value[b] of $\bar{\alpha}$	bond additivity method[c]				
		$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	δ
cis-PBO	25.0	26.9	31.0	15.8	33.7	0.30
trans-PBO	25.0	26.9	31.2	15.8	33.6	0.30
trans-PBT	30.0	34.2	37.5	23.3	41.7	0.23

[a] Units are Å³ (10^{-24} cm³). [b] Reference 8. [c] Reference 9.

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References and Notes

(1) Welsh, W. J.; Bhaumik, D.; Mark, J. E. Air Force Technical Report AFML-TR-78-3683. *J. Macromol. Sci., Phys.*, in press.
(2) Welsh, W. J.; Bhaumik, D.; Mark, J. E. *Macromolecules*, this issue.
(3) Bhaumik, D.; Welsh, W. J.; Jaffé, H. H.; Mark, J. E. *Macromolecules*, this issue.
(4) Bhaumik, D., work in progress.
(5) Berry, G. C.; Wong, C.-P.; Venkatraman, S.; Chu, S.-G. Air Force Technical Report AFML-TR-79-4115. Manuscript to be submitted to *Macromolecules*.
(6) Marchese, F. T.; Jaffé, H. H. *Theor. Chim. Acta* **1977**, *45*, 241.
(7) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.
(8) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206.
(9) Denbigh, K. G. *Trans. Faraday Soc.* **1940**, *36*, 936.
(10) Wellman, M. W.; Adams, W. W.; Wiff, D. R.; Fratini, A. V. Air Force Technical Report AFML-TR-79-4184, Part I. Private communications.
(11) Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Wiff, D. R.; Fratini, A. V. *Macromolecules*, this issue.
(12) Bridge, N. J.; Buckingham, A. D. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 334.
(13) Bhaumik, D.; Jaffé, H. H.; Mark, J. E. *J. Mol. Struct., THEOCHEM*, in press.

Density Difference Determinations of Ordinary and Freeze-Dried Polystyrenes in Bulk in the Analytical Ultracentrifuge

GENEVIÈVE POUYET, ANDRÉ KOHLER, and
JEAN DAYANTIS*

CNRS, Centre de Recherches sur les Macromolécules,
67083 Strasbourg Cedex, France. *Received June 9, 1980*

I. Introduction

The possibility that isolated chains of synthetic high polymers may undergo an abrupt change in molecular dimensions (collapse) when the solvent becomes poorer, as a result of either lowering the temperature or addition of nonsolvent, has long been considered.[1,2] Recently, several papers have appeared dealing with the theoretical[3–8] or experimental[9,10] aspects of the problem. On the other hand, it has long been known from electron microscopy experiments[11–14] that isolated macromolecules of glassy polymers in a vacuum are in a nearly spherical, compact form. Richardson[13] in particular has found that if the substrate was plain mica, agglomerates of macromolecules in compact form were obtained (Figure 1a). In fact

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