Interchain Interactions in Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers

D. Bhaumik, W. J. Welsh, H. H. Jaffé, and J. E. Mark*

Department of Chemistry and Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221. *Received November 14, 1980*

ABSTRACT: Interaction energies between relatively rigid benzobisoxazole and benzobisthiazole polymers were calculated in an attempt to gain insight into the very high mechanical strength and unusual solvent resistance of these materials. The predicted details of the chain packing and the corresponding densities were found to be in good agreement with experimental results obtained on relevant model compounds in the crystalline state. The interaction energies are estimated to be very large, with van der Waals contributions being far more important than Coulombic ones. Additional calculations indicate that protonation of the chains should greatly decrease the intermolecular attractions, even at very high dielectric constant. This conclusion is consistent with the fact that only extraordinarily strong acids are solvents for these types of chain molecules.

Introduction

Para-catenated benzobisoxazole and benzobisthiazole polymers are relatively rigid chain molecules which can be used in fabricating materials having very high strength and unusual resistance to most common solvents.[1-16] One poly(benzobisoxazole) (PBO) of particular interest in this regard is shown in Figure 1; an alternate form, in which the O atoms are trans to one another is of comparable interest. The poly(benzobisthiazole) (PBT) related to the *trans*-PBO is shown in Figure 2. Although it and the alternate cis modification are both in this category, only the trans form has been extensively studied up to the present time.

One goal of foremost importance in this area is the elucidation of the unusual properties of these materials in molecular terms. Of obvious importance are intramolecular (conformational) effects,[15,16] particularly as they relate to the rigidity of the chains. Also of importance are intermolecular effects, and these are the focus of the present investigation. It deals with interchain interactions, both van der Waals and Coulombic, as estimated by standard methods based on semiempirical potential energy functions. The specific goals are elucidation of the nature of the chain packing and estimation of the corresponding densities, the magnitude of the total interaction energies, the relative importance of van der Waals and Coulombic contributions, and the extent to which the intermolecular interactions are modified by protonation of the chains, which occurs in the strongly acidic media used as solvents for these polymers.

Theory

The three polymers investigated were *cis*-PBO, *trans*-PBO, and *trans*-PBT. The bond lengths and bond angles characterizing their repeat units were obtained from the X-ray structural studies carried out on model compounds by Fratini and co-workers.[13,14] The values are typical of aromatic heterocyclic compounds.[17] In the case of the two PBO polymers the repeat units are planar, but the *trans*-PBT repeat unit has the *p*-phenylene group rotated by 23.2°.[13-16] Values of the atomic partial charges q were determined by the CNDO/2 (complete neglect of differential overlap) method.[18] In the case of the protonated chains, each repeat unit was given two protons, the number indicated by freezing-point depression measurements.[19] These protons were placed on the nitrogen atoms at a distance corresponding to the usual N—H bond length and at an orientation bisecting the C=N—C bond angle. This is shown diagrammatically in Figure 3. In some illustrative calculations, two additional protons were added to the two O or two S atoms in an analogous manner. In all cases, increasingly long sequences of repeat units were investigated until the charges calculated for the central repeat unit were seen to converge. Typical charge distributions thus obtained are given in Figures 1–3.

The total intermolecular interaction energy E was considered to be the sum of the steric or van der Waals energy E_{vdW} and the Coulombic energy E_C. The van der Waals interactions between a pair of atoms i and j separated by the distance d_{ij} were treated by using the Buckingham potential function[20]

$$E_{vdW} = \sum_{i<j}[a_{ij} \exp(-b_{ij}d_{ij}) - c_{ij}/d_{ij}^6] \quad (1)$$

with the parameters a, b, and c differing, of course, for different atom pairs. The parameter c characterizing the attractions was calculated from the effective number N_{eff} of electrons and atomic polarizabilities[21] α by application of the Slater–Kirkwood equation.[22] Values of b for a like atom pair were taken from Scott and Scheraga[23] while values for an unlike pair were given by $b_{ij} = (b_{ii}b_{jj})^{1/2}$. The corresponding values of the parameter a were then determined by minimizing eq 1 at $r_{min} = r_1 + r_2$, where r_1 and r_2 are the van der Waals radii, taken from crystal structure data.[24] Distinctions were made between aliphatic and aromatic carbon atoms, with the latter being assigned an increased thickness in directions nearly perpendicular to the aromatic ring,[25] as described elsewhere.[16] In addition, carbon atoms in N=C—O and N=C—S bond sequences were assigned the parameters found to be most suitable for carbon atoms of this type in peptide linkages, as suggested by Brant, Miller, and Flory.[26] A summary of the set of parameters employed is given in Table I.[15,16,27,28]

The Coulombic interaction energies were estimated from[20,29]

$$E_C = \sum_{i<j} 332.072 q_i q_j / \epsilon d_{ij} \quad (2)$$

where q_i and q_j are, respectively, the partial charges on atom i and atom j, separated by the distance d_{ij}. The dielectric constant ϵ of the medium was assigned a value of 3.0 (in cgs units) for the unprotonated, undiluted chains[20] and the range of values 10–100 in the case of the protonated chains in very strong acids.[19]

Because of the complexity of these systems, the calculations were of necessity very approximate, being based on only a pair of the chains of a given type in their planar or nonplanar conformations,[13,14] as mentioned above. The first chain was one repeat unit long, with the second being assigned a series of lengths in an attempt to make the interaction energies (per repeat unit) as realistic as possible without making the calculations impracticable. Four re-

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Table I
Parameters for the Buckingham Potential Functions

atom pair	N_{eff}[a]	$10^{24}\alpha$,[b] cm^3	r_{min},[c] Å	$10^{-3}a$[d]	b[d]	c[d]
C···C[e]	5.0	0.93	3.4	541.4	4.59	363.0
C···C[f]	5.0	1.23	3.7	1820	4.59	556.7
C···C[g]	5.0	1.30	3.4	895.6	4.59	600.5
N···N	6.0	1.15	3.1	393.2	4.59	547.3
O···O	7.0	0.59	3.0	135.8	4.59	217.2
S···S	14.8	3.04	3.6	906.3	3.90	3688
H···H	0.9	0.42	2.4	7.323	4.54	47.1

[a] Effective number of electrons. [b] Polarizability. [c] Sum of van der Waals radii. [d] Units are such as to give E in kcal/mol when d_{ij} is in Å. [e] Aliphatic carbon atoms. [f] Aromatic carbon atoms. [g] Carbon atoms in NCO peptide-type linkages.

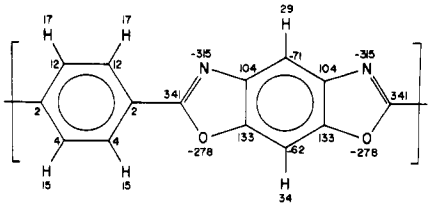

Figure 1. *cis*-PBO (unprotonated) repeat unit. In this and the following two figures, the charges shown were calculated by the CNDO/2 method and are in units of 10^{-3} of the electron charge.

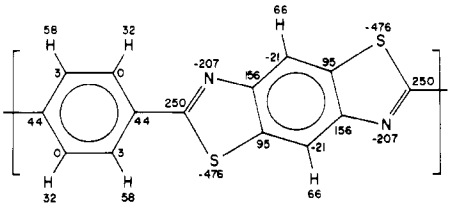

Figure 2. *trans*-PBT (unprotonated) repeat unit arbitrarily shown in the planar conformation; see legend to Figure 1.

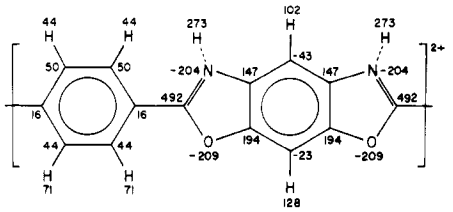

Figure 3. *cis*-PBO repeat unit with two protons. Two additional protons could possibly be added to the two (negatively charged) O atoms.

peat units were found to be appropriate in this regard. A Cartesian coordinate system was defined about the longer chain so that the x, y, and z coordinates lay along the length, width, and thickness, respectively, of the repeat units. (In the case of the nonplanar *trans*-PBT unit, the plane of the phenylene ring was taken to be the plane of the molecule.) In the initial series of calculations the chains were first placed in parallel arrangements, one above the other, and then one chain was rotated along its x, y, and z axes. The rotations invariably increased the energy,[15] and such arrangements were therefore not considered further. Thus, the calculations to determine minimum-energy arrangements were based primarily on two parallel chains shifted relative to one another along the x, y, and z axes. In the case of the density estimates, there are two specific sets of calculations which are relevant, one for a pair of chains above one another ($\Delta y = 0$) and the other for a pair alongside one another ($\Delta z = 0$).

Results and Discussion

The characteristics of the minimum-energy arrangements thus identified are summarized in Table II. For pairs of chains above one another the predictions are that

Table II
Interchain Spacings and Energies in Minimum-Energy Arrangements

	spacings, Å			energy, kcal/mol	
polymer	Δx	Δy	Δz	total	Coulombic
cis-PBO[a]	3.0	0.0	3.5	−22.44	0.07
cis-PBO[b]	2.0	6.2	0.0	−4.48	−0.02
trans-PBO[a]	3.0	0.0	3.5	−22.33	0.01
trans-PBO[b]	3.5	6.1	0.0	−6.81	−0.17
trans-PBT[a]	1.5	0.0	3.7	−29.44	0.57
trans-PBT[b]	1.0	6.1	0.0	−6.83	−0.23

[a] Chains above one another ⌊⌋ at a spacing of Δz.
[b] Chains alongside one another ⌊⌋ ⌊⌋ at a spacing of Δy. The shift parallel to the chain axes is Δx.

the chains are out of register by $\Delta x = 3.0$ Å in the case of the two PBO polymers (which would place a phenylene group of the upper chain over the bond bridging the two ring systems of the repeat unit of the lower chain) and by 1.5 Å in the case of the *trans*-PBT. These are rather approximate results, in part because of the large number of energy minima occurring as the chains are slid by one another.[15] The latter displacement is predicted to be smaller than the former because of the large size of a sulfur atom relative to oxygen and the much more irregular cross section of the nonplanar PBT molecule. These results are in at least qualitative agreement with the results of X-ray structural studies. The experimental values of these axial shifts were found to be approximately 4.5 Å in the case of model compounds for all three types of molecules.[13,14] The agreement between theoretical and experimental values of Δx could, of course, be considerably better for the polymeric chains, which have not yet been studied experimentally in this regard. In the case of the vertical spacings, the theoretical results are in excellent agreement with the experimental finding that $\Delta z \simeq 3.5$ Å for all three types of model compounds.[13,14] For the pairs of chains alongside one another, the spacing Δy is predicted to be approximately 6.1 Å. Although there are no experimental values of this quantity available for comparison, it is important for density estimates, which are to be discussed below.

The interaction energies are seen to be rather large, with contributions from only a few repeat units adding up to values approaching typical bond dissociation energies. This suggests that the failure mechanism in such materials might generally be bond breakage rather than bond slippage. The attractions are somewhat larger for the *trans*-PBT chain because S atoms give rise to larger van der Waals attractions than do O atoms because of their much higher polarizability (see Table I). Analogous differences are found in comparisons between poly(ethylene sulfide) (PES) and poly(ethylene oxide) (PEO).[28] The Coulombic

Table III
Densities of PBO and PBT Chains in the Crystalline State

polymer	densities, g/cm³ calcd	densities, g/cm³ exptl[a]
cis-PBO	1.46	1.38
trans-PBO	1.49	1.41
trans-PBT	1.55	1.44

[a] References 13 and 14.

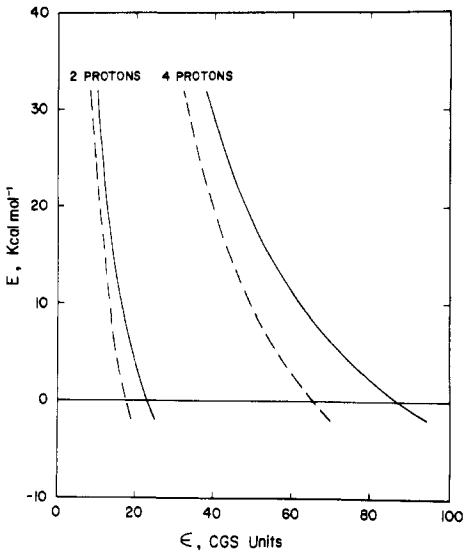

Figure 4. Total interaction energy per repeat unit shown as a function of degree of protonation and dielectric constant of the medium. The solid line refers to both *cis*- and *trans*-PBO and the broken line refers to *trans*-PBT.

contributions to the total interaction energy are seen to be very small, as was also observed in the case of PES and PEO.[28] This suggests that the dielectric constant of a potential solvent for these (unprotonated) polymers should be of no importance, and this is in agreement with experiment.[30]

The above information also permits estimation of the densities of the PBO and PBT polymers in the crystalline state. The two polymers were represented as having elliptical cross sections, with dimensions based on the results given in Table II and with six such ellipses closely packed around a central ellipse. The densities thus estimated are given in the second column of Table III. They are seen to be in good agreement with the experimentally obtained densities of the model compounds,[13,14] particularly in the way they vary with changes in the structure of the repeat unit. The results indicate that the higher density for the PBT polymer is due to the higher atomic weight of S relative to O rather than to more efficient chain packing.

The results of the calculations on the protonated chains are summarized in Figure 4. It is difficult to relate such results quantitatively to the polymer–solvent dissolution process, which is, of course, controlled by changes in *free* energy. They are nonetheless of considerable interest in that they indicate that protonation of the chains should greatly decrease the intermolecular attractions, even at the very high dielectric constants characteristic of strong, undiluted acids.[19] This conclusion is consistent with the fact that only extraordinarily strong acids are solvents for these types of polymers.[30]

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