Study of the conformations of stiff chain, rigid-rod and substituted rigid-rod polymers

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The conformational properties of a series of rigid-rod and stiff chain polymers have been investigated using semiempirical molecular orbital calculations. Poly(2,5-benzimidazole) (ABPBI), poly(2,5-benzoxazole) (ABPBO), poly(2,6-benzothiazole) (ABPBT), poly(p-phenylene benzobisimidazole) (PPBI), poly(p-phenylene benzobisoxazole) (PBO) and poly(p-phenylene benzobisthiazole) (PBZT) have been studied. For ABPBO and both cis and trans PBO, the results indicate that a coplanar arrangement of the heterocyclic and phenyl rings gives the lowest energy. For all the other polymers considered, non-coplanar conformations were found to have the lowest energies for isolated molecules. Molecular mechanics calculations were also used to investigate the conformational properties of cis-PBO and trans-PBZT having various substituents on the phenyl ring. Substituents considered included methyl, ethyl, t-butyl, hydroxyl, phenyl, and benzthiazole groups. The results show that most substituents have surprisingly little influence on the conformations of the molecules. Small substituents, as well as large, planar substituents, were uniform in their lack of inducing a specificity of conformation in the molecules. Bulky groups, especially t-butyl, and those introducing interactions of a more specific nature, such as coulombic or hydrogen-bonding, play a greater role in making specific conformations more energetically favourable. In most cases, the substituent causes a rotation of the backbone rings away from coplanarity, but once the steric interactions are relieved, there is considerable latitude for further rotation. In most cases, the conformational freedom is such that packing considerations could significantly influence the conformations of the materials in the solid state.

INTRODUCTION

Rigid-rod polymers have received much attention[1-16] because of their environmental resistance, thermal/oxidative stability and their unprecedented, high mechanical properties, resulting both from their inherent molecular modulus[16] and from their degree of molecular orientation, achieved by fibre-spinning from a liquid crystalline solution. Poly(p-phenylene benzobisthiazole), PBZT, and poly(p-phenylene benzobisoxazole), (PBO), have been studied[1-4] as alternative reinforcement fibres for aramid and carbon fibres. PBZT and PBO fibres have exceptional tensile properties, but have been found to have low compressive strengths[1,4,5] compared to state-of-the-art poly(acrylonitrile)-based carbon fibres[17]. Poly(p-phenylene benzobisimidazole), PPBI, would be expected to have comparable tensile properties, but the known affinity of the benzimidazole for moisture[18] has thus far limited its polymerization to a high molecular weight suitable for fibre spinning. The molecular geometries of the repeat units for these three polymers are shown in Figure 1.

Recently, these (and related) polymers have been found to display third order nonlinear optical properties[1,19-22].

Degenerate four wave mixing experiments indicate that PBZT films have an ultrafast response time in the sub-picosecond range. While their measured susceptibilities are not as large as those of other materials, their high damage thresholds, stability and excellent mechanical properties make them promising materials for nonlinear optical applications. In addition, the third order susceptibilities in biaxially oriented films are quite strongly orientation dependent[21]. This anisotropy may allow both mechanical and optical properties of a film to be optimized to suit a specific need, without having to sacrifice one property for another.

The molecular geometries (shown in Figure 1) of poly(2,5-benzimidazole) (ABPBI), poly(2,5-benzoxazole) (ABPBO), and poly(2,6-benzothiazole) (ABPBT) can be characterized as stiff, but not rigid and rod-like. The single bonds connecting successive rings are not colinear, so the molecules have neither the conformational flexibility associated with tetrahedral carbons in the backbone, nor must they be topologically straight as are the rigid rod materials. By virtue of their chemical similarity to PPBI, PBO and PBZT, the ABPBx (where x = I, O or T respectively) materials might be expected to be miscible with their rigid-rod counterparts, and in fact molecular composites have been prepared from the ABPBO/PBO and ABPBI/PBZT systems[23,24]. Such composites, having the rod-like molecules reinforcing the matrix at a molecular scale, may offer optimum properties, avoid
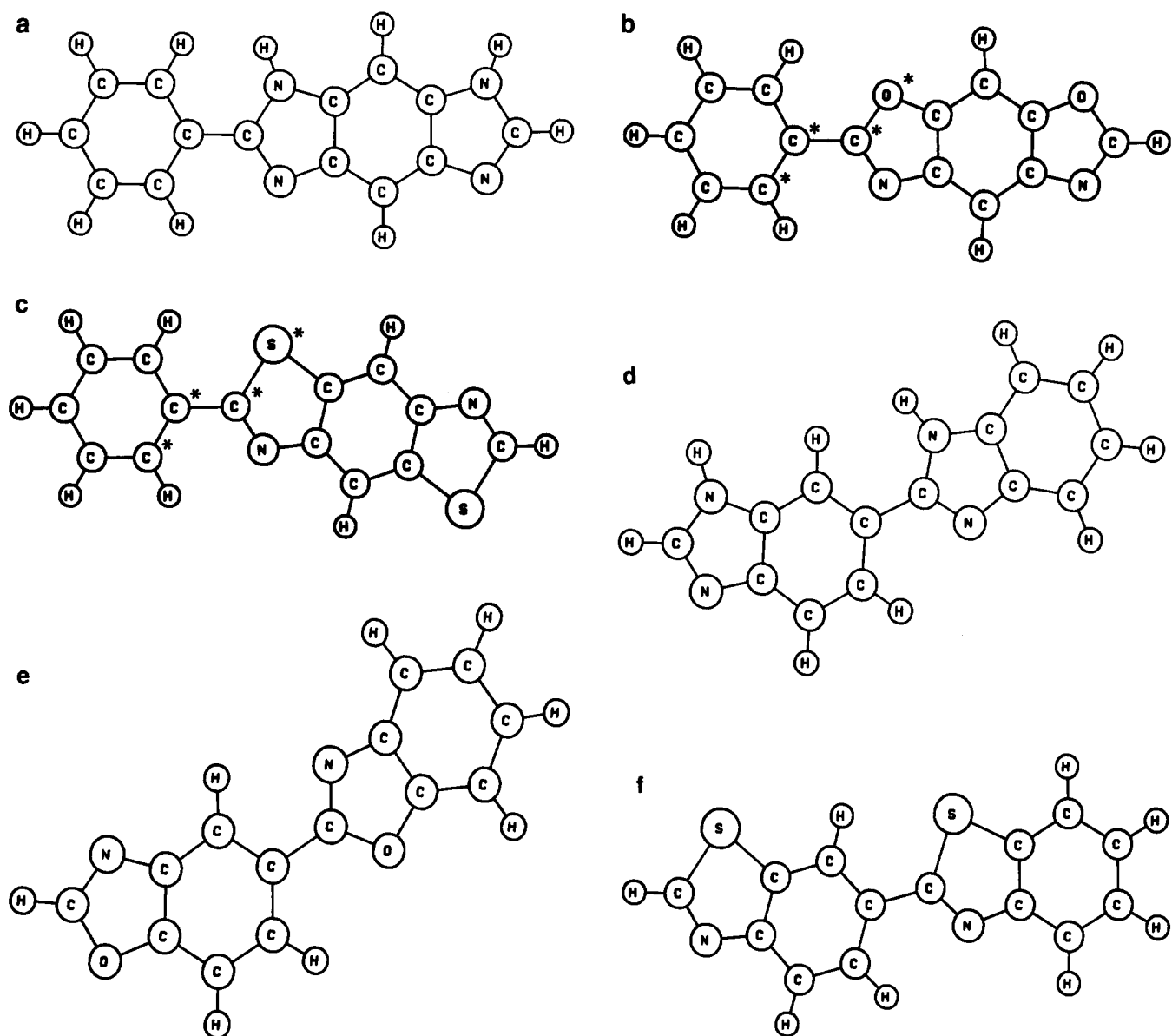
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a

b

c

d

e

f

Figure 1 Models used in the calculations for (a) *cis*-PPBI, (b) *cis*-PBO, (c) *trans*-PBZT, (d) ABPBI, (e) ABPBO and (f) ABPBT. In (b) and (c) the atoms denoted by * define the backbone rotation angle, shown in its *trans* (180°) position, used in subsequent energy contour maps

many of the interfacial problems that plague many composites, and be amenable to more flexible processing and forming techniques.

In an effort to improve their compressive properties, several new PBZT or PBO based polymers have been synthesized[25–29] which have substituents placed on the phenyl ring. By and large, the compressive strengths, while increasing somewhat, have proven to be rather insensitive to such chemical alterations[25–29]. As a step toward a computational study of the solid state form of these materials, it is first necessary to investigate the properties of individual molecules. This computational study was undertaken to determine whether correlations exist between the macroscopic compressive properties and the molecular conformational properties of these materials, and to establish a means whereby promising substituents might be examined prior to synthesis.

Semi-empirical molecular orbital calculations using the CNDO/2 (Complete Neglect of Differential Overlap) method[30] to examine the properties of PBO and PBZT have been reported previously[11,12]. The model used for

the calculations consisted of a single heterocyclic unit with phenyl groups attached to each end. The results for *cis* and *trans* PBO (*cis* and *trans* referring to the placement of the two oxygen atoms in the heterocyclic moiety) were similar with both having minima at 0° torsion angle and maxima at 90°. In *cis*-PBO the energy barrier to rotation was 1.6 kcal/mol, while that found for *trans*-PBO was about 2.2 kcal/mol. It is not clear why the *cis* or *trans* isomers should have different energies as a function of the phenyl group rotation, especially since it was noted that the interactions between phenyl groups were negligible. For *trans*-PBZT (*trans* referring to the placement of the two sulphur atoms in the heterocycle), the minimum energy torsion angle was 20°, and there were maxima at 0° (barrier = 0.5 kcal/mol) and at 90° (barrier = 6.0 kcal/mol). The magnitude of this latter energy barrier was attributed in part to a lack of geometrical optimization of the sulphur atoms.

Molecular mechanics calculations have also been reported[10,13] for unsubstituted PBZT and PBO. *Cis*-PBO was found to have the lowest energy when the

phenyl and heterocyclic rings were coplanar, in agreement with the CNDO results. *Trans*-PBZT was found to prefer a non-coplanar arrangement, the torsion angle being about 55° from coplanarity, in contrast to the CNDO result of 20°. The torsional potential parameter used was 4.6 kcal/mol, a value taken from studies on small molecules, and later suggested to have been too low[11]. The X-ray structure for a PBO model compound[14] shows an essentially coplanar ring arrangement (slight bowing was observed, but not rotation), while a model compound[14] for PBZT showed a torsion angle of 23°, arising from steric interaction between the *ortho*-hydrogen on the phenyl group and the sulphur of the heterocyclic ring. Thus the molecular mechanics calculations and experimental results were in qualitative, but not quantitative, agreement.

COMPUTATIONAL METHOD

Molecular orbital calculations

Semi-empirical molecular orbital calculations were carried out using the Modified Neglect of Diatomic Overlap (MNDO)[31] and Austin Method 1 (AM1)[32] programs in MOPAC version 3.11[33]. Because there is at present no AM1 parameterization for sulphur, the MNDO sulphur parameters were used for analysing ABPBT and PBZT by the AM1 method. For the ABPBx compounds, the computational models were dimers (as shown in *Figure 1*) constructed from fully optimized single monomers. For PPBI, PBO and PBZT, the computational models consisted of one heterocyclic ring and one phenylene ring (also as shown in *Figure 1*). Hydrogen atoms were used to cap the ends of each model. Within these computational models are represented all of the unique intramolecular structure and all of the important intramolecular interactions that would be found in the polymers. The figures of the model structures are made from the actual coordinates of the atoms, and thus reflect the geometry of the structures used.

Energies were calculated as a function of rotation angle about the single bond in the computational model compound, with full optimization carried out at high precision ('Precise' keyword) at each (fixed) rotation angle. Except for ABPBI and PPBI, initial calculations showed that there was no tendency for the individual rings to become non-planar, so the dihedral angles within the heterocyclic rings were not optimized. For ABPBI and PPBI, the sp³ nitrogen in the heterocyclic ring could introduce non-planarity, so the dihedral angles were also optimized for those materials. To generate the torsion angle vs. energy curves, it was only necessary (by virtue of the molecular symmetry) to consider torsion angles between 0° and 180° for the ABPBx materials, and between 0° and 90° for PBO, and PBZT. The range that must be considered for PPBI depends upon the geometry of the imide nitrogen and the placement of its attached hydrogen. If the nitrogen is non-planar and the hydrogen is out of the plane of the heterocycle, a range of 0° to 180° must be considered; otherwise, only the range of 0° to 90° is unique. Optimization of the geometry of PPBI showed the imide nitrogen to be nearly planar, with the hydrogen in the plane of the heterocycle. Thus, only the 0° to 90° range of torsion angles was considered. The extrema of the energy curves were determined by performing a full optimization which included the conformational rotation angle. Maxima were determined

using a nonlinear least-squares procedure in MOPAC. Force constants were then calculated to ensure that the resulting geometries did indeed represent the extrema.

Molecular mechanics

Molecular mechanics calculations were carried out on models of a single repeat unit of the rigid rod polymers as shown in *Figure 1*. Only the *cis* form of PBO and the *trans* form of PBZT were considered. Substituents were placed at the *ortho* position of the backbone phenyl ring. The construction of the molecular models and the energy calculations were made using Chem-X[34] molecular modelling software. With the exception of the parameter for torsion about the backbone single bond, the standard geometric and potential energy parameters embedded in the CHEM-X were used without modification.

RESULTS

Stiff chain polymers

The results of the AM1 and MNDO calculations for ABPBI, ABPBO and ABPBT are shown in *Figures 2–4*, wherein the heats of formation are plotted against the torsion angle. A 0° torsion angle corresponds to the *cis*oid conformations (as shown in *Figure 1*) having identical placement of the ring heteroatoms. In every case, the MNDO and AM1 methods give directly opposite results. X-ray diffraction data[35] indicate that in fact in the solid state, ABPBO and ABPBT adopt near planar conformations, roughly in agreement with the results of the AM1 method. Each MNDO curve, on the other hand, has maxima at 0° and 180° rotations and a minimum in the vicinity of 90°. The MNDO parameterization is known to overestimate internuclear repulsions. For materials such as those of interest here, a coplanar
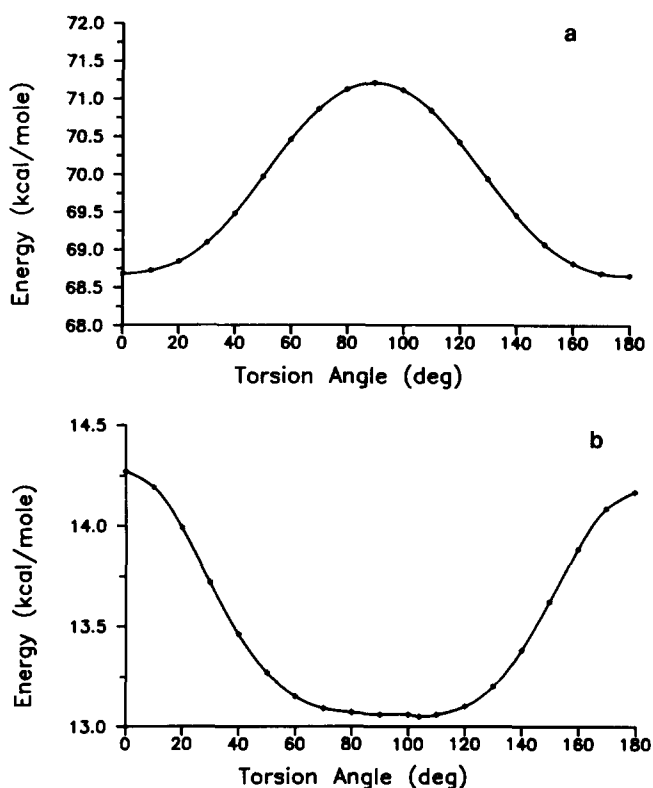

Figure 2   Energy *versus* torsion angle for ABPBO calculated using (a) the AM1 and (b) the MNDO methods
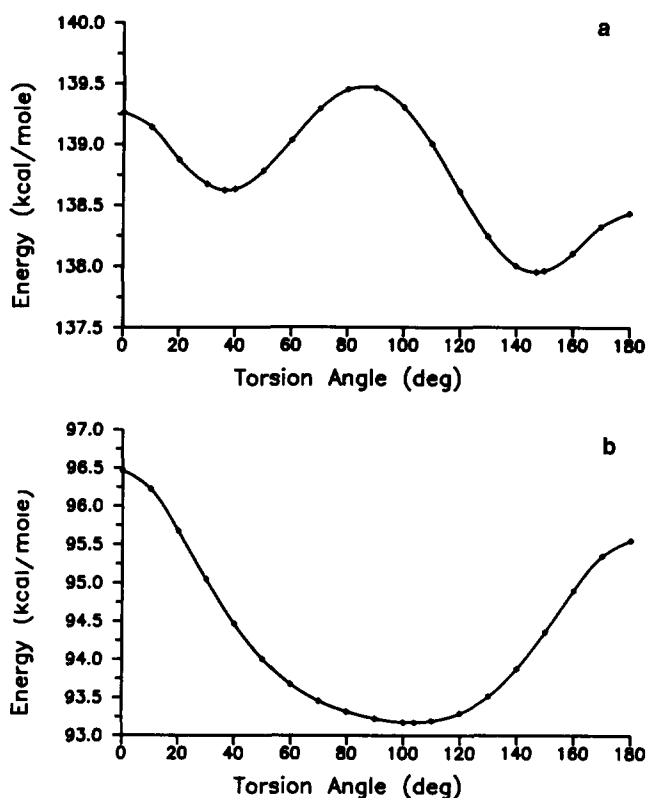
Figure 3 Energy *versus* torsion angle for ABPBI calculated using (a) the AM1 and (b) the MNDO methods
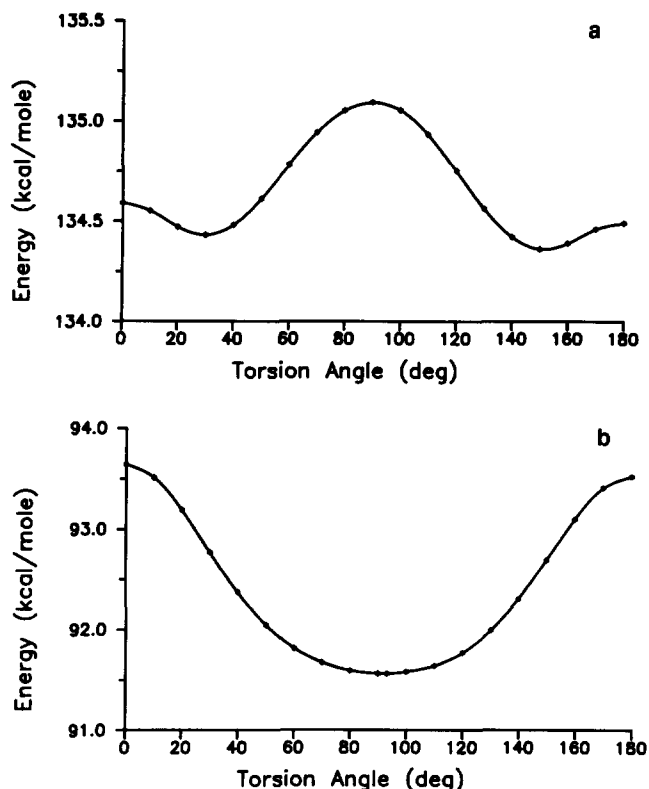
Figure 4 Energy *versus* torsion angle for ABPBT calculated using (a) the AM1 and (b) the MNDO methods

arrangement of the rings would be expected to allow extended conjugation, and might therefore be a low energy conformation. However, the MNDO repulsion terms dominate and force the molecule into conformations having the rings nearly perpendicular. To resolve the

discrepancy between MNDO and X-ray data, inter-molecular interactions might be invoked and said to shift the location of a conformational minimum some-what. However, they could hardly be expected to force the molecule into its highest energy conformation. Thus, it appears that for these kinds of molecules, the AM1 parameterization is more reasonable than that of MNDO.

For ABPBO, the AM1 results indicate that the coplanar conformations at 0° and 180° rotations have very similar energies and are most stable in agreement with the results of X-ray diffraction studies[33]. A confor-mation with the planes of the rings normal to one another has the highest energy, about 2.56 kcal/mol above the minima. The sp^3 oxygen is able to keep its tetrahedral geometry and still remain in the plane of the fused rings of the monomer.

ABPBI and ABPBT have their low energy confor-mations when the rings are 30° to 40° from coplanar. For ABPBI, this is due to interactions between the hydrogen attached to the sp^3 nitrogen in the five-member ring and the hydrogens that are in the *ortho* positions on the six member ring of the next repeat unit. The asym-metry of the minima (energy difference of 0.68 kcal/mol) is caused by the slight puckering of the five-member ring by the sp^3 nitrogen. The energy curve has three maxima, representing barriers to rotation, at 0°, 90° and 180°. The barriers at 0° and 90° are 0.64 and 0.84 kcal/mol, respectively, relative to the minimum at 36°. The barriers at 90° and 180° are 0.48 and 1.52 kcal/mol, respectively, relative to the minimum at 147°.

In ABPBT, the size of the sulphur atom itself is sufficient to give interference with the *ortho* hydrogens of the neighbouring repeat unit. The AM1 energy curve has barriers to rotation at 0°, 90° and 180°. The barriers at 0° and 90° are 0.16 and 0.66 kcal/mol, respectively, relative to the minimum at 30°. The barriers at 90° and 180° are 0.73 and 0.13 kcal/mol, respectively, relative to the minimum at 150°. The low energy barrier at 0° suggests that intermolecular interactions might easily force adjacent rings of this molecule into a coplanar arrangement, as is actually observed in X-ray data. Even the barrier at 90° is substantially lower than that calculated for ABPBI and ABPBO, suggesting further that at room temperature, the rings of the polymer could easily be in nearly free rotation.

Rigid-rod polymers

Figure 5 shows the results of AM1 calculations for PBO and PBZT. Both the *cis* and *trans* placements of the heteroatoms in the five-membered rings of the heterocyclic moiety were considered. The energy curves were virtually identical and therefore only the curves for the more technologically interesting configurations (*cis*-PBO and *trans*-PBZT) are shown. The curve for *cis*-PPBI is also shown in *Figure 5*.

Calculations were also carried out using the MNDO method. Not surprisingly, the results (not shown) differ from the AM1 results in much the same way as found for the stiff chain polymers. For each material, MNDO consistently predicts the lowest energy conformation to be that having the heterocyclic and phenylene rings mutually perpendicular, while the coplanar conformation (0° torsion angle) represents an energy maximum. Once again, these MNDO conformational results are directly contrary to X-ray data on PBZT[36] and on low molecular weight model compounds for PBZT and PBO[14].
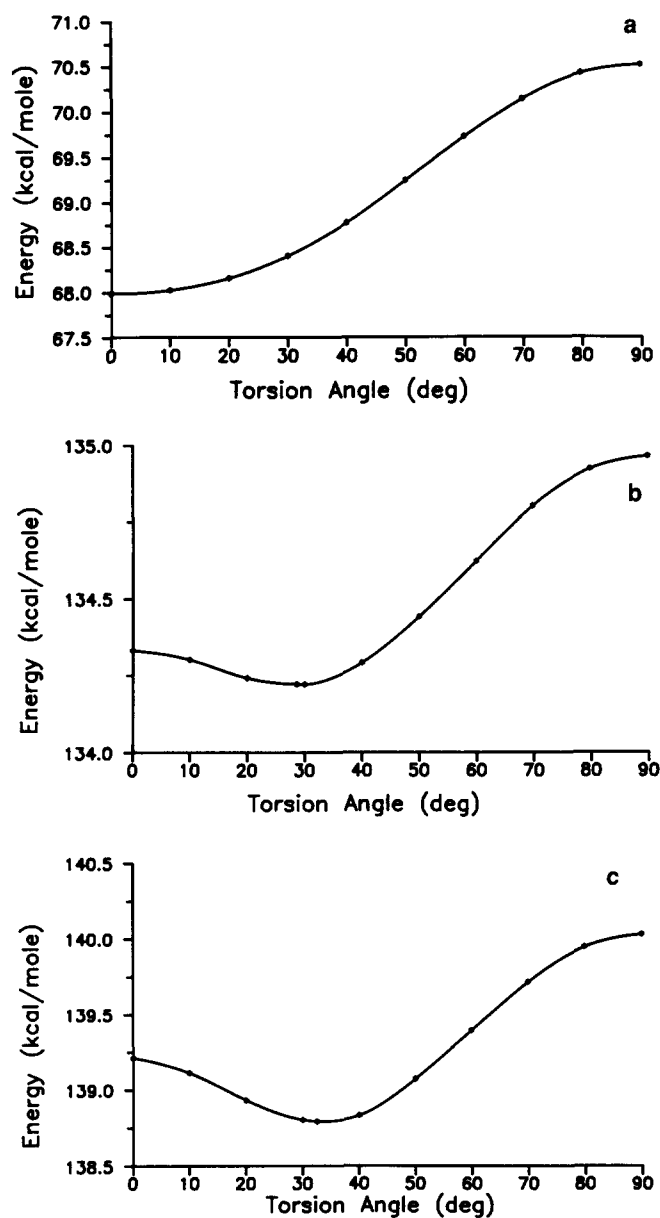
Figure 5   Energy *versus* torsion angle for (a) *cis*-PBO, (b) *trans*-PBZT, and (c) *cis*-PPBI, calculated using the AM1 method

Using AM1, the lowest energy conformation for PBO has the rings coplanar (torsion angle of 0°). The barrier to rotation about the single bond is 2.52 kcal/mol, the maximum occurring at a torsion angle of 90°. For PBZT, on the other hand, the minimum energy conformation is found at 29°. There is a small barrier (0.11 kcal/mol) at 0°, and a larger barrier (0.74 kcal/mol) at 90°. The position of the minimum is in excellent agreement with the torsion angle observed in a model compound for PBZT[14], and the very low energy at 0° is consistent with the observation of a coplanar arrangement of the rings in the polymer in the solid state where intermolecular forces might influence the conformation[36]. For *cis*-PPBI, the lowest energy is at a torsion angle of 32°. The rotational barriers at 0° and 90° are 0.42 and 1.23 kcal/mol, respectively.

The present results on PBO and PBZT are in agreement with recent AM1 calculations[37,38] using a slightly different model. Compared to earlier CNDO results for PBO[11,12] which gave a 1.6 kcal/mol difference in the energies at 0° and 90°, the value of 2.52 kcal/mol

by AM1 is substantially larger. More significantly, for PBZT the CNDO results estimated an energy difference of 6.0 kcal/mol between the maximum at 90° and at the minimum at 20°, a much larger energy difference than that found here for PBZT or even for PBO. The present results indicate just the opposite, with the barrier in PBZT being smaller than that in PBO by a factor of almost four. This discrepancy can be attributed to the acknowledged[11,12] lack of geometry optimization for the the earlier CNDO work.

Substituted PBO and PBZT

The torsional parameters used in the molecular mechanics study are critical parameters which can greatly influence the positions and relative depths of the energy minima. More than any of the other parameters, they most directly reflect the influence that electronic interactions between adjacent rings might play. In the present molecular mechanics calculations, the torsional parameters were chosen to give the best agreement between molecular mechanics and AM1 results for the position of the energy minimum, and the relative energies between that minimum and the energies at 0° and 90° torsions. For PBZT the best torsional parameter was 1.60 kcal/mol and for PBO, 2.56 kcal/mol. (Note: A torsion angle is defined by four atoms: an atom at each end of the bond about which rotation occurs, plus an atom attached to each of those, which serve to define the value of the torsion angle. For the single bond between rings, Chem-X computes the torsional energy eight times, once each as it is defined by the atoms at either end. Thus, the computational value input to the program was 1/8 of the barrier values given above.) For comparison with the AM1 data shown in *Figure 5*, the molecular mechanics energy curves for both PBZT and PBO are shown in *Figure 6*. The values of the torsion parameters are
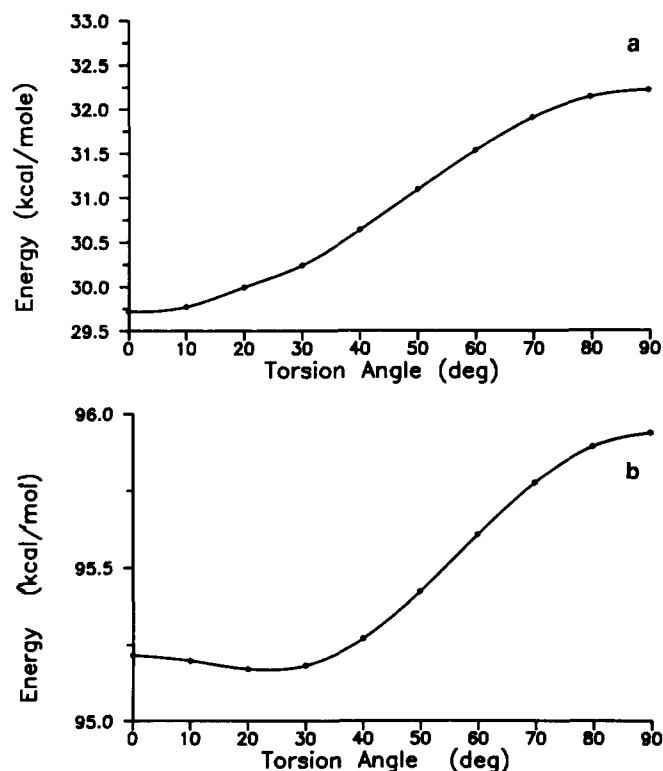

Figure 6   Energy *versus* torsion angle for (a) *cis*-PBO and (b) *trans*-PBZT calculated using molecular mechanics

significantly lower than those taken from small molecules[10]. The agreement with the X-ray structures[14] and the more fundamental AM1 calculations, however, justifies these selections.

Energy contour maps were calculated at 30° increments of the backbone single bond (joining the phenyl and heterocyclic rings) and of the bond joining the substituent to the phenyl ring. These rotation angles are labelled on the maps for a *trans* bond defined as having a value of 180°. The substituent replaced the hydrogen atom at the *ortho* position (not starred) of the backbone phenyl ring. The specific torsion angle that is plotted for the backbone rotation is defined by the atoms denoted by * in *Figure 1*. Thus, 0° and 180° rotations both make the backbone rings coplanar, but place the substituent in proximity to either the sulphur (180°) or nitrogen (0°) atoms in the heterocyclic ring in PBZT (oxygen and nitrogen in PBO). The substituent rotation angle which is plotted for each contour map, is shown in the accompanying molecular figures in the *trans* position as defined by the atoms denoted by *. The molecular figures accompanying the contour maps reflect the geometries of the models used. Bonds to atoms out of the plane of the rings are foreshortened.

The energy contours are drawn at 0.6 kcal/mol intervals (the value of kT at room temperature) relative to the minimum energy value on the map. Only the first five contour levels are shown. An 'x' is placed at the positions of the lowest energy conformation and of those conformations within 0.1 kcal/mol of the minimum. To the extent that the energy differences are accurately scaled (a function of the selected energy parameters), all torsion angles within the first contour would be expected to be populated at room temperature. Packing calculations have not yet been made, but it might be expected that intermolecular interactions could make torsions at a few contour levels accessible for those conformations which were able to pack most efficiently.

Rather than using the contouring capability within Chem-X, the contour maps shown here were made using the program SURFER[39]. Using the computed energy values, the program creates an interpolated grid to produce the contour maps. The interpolated grid has values at 15° intervals, with each grid value based on four adjacent grid points, weighted by the square of the inverse distance. The grid was also smoothed using cubic splines. The detailed shapes of the contours imply greater precision than is justified by the rather coarse level at which conformational energies were actually calculated. In particular, the waviness (with an apparent 30° periodicity) seen in some contours (most notably for a phenyl substituent on PBO), is an artifact of the gridding and contouring. In some cases, contour areas which probably should be interconnected are not. The maps should reflect the symmetry of the molecule, and do so reasonably well in most cases. Finally, note that in some cases the origins of the contour maps have been shifted so that low-energy regions are contiguous, in so far as possible.

Methyl, ethyl, hydroxyl, *t*-butyl, and benzothiazole substituents on PBZT and methyl, ethyl, hydroxyl, *t*-butyl, and phenyl substituents on PBO were investigated. For both PBZT and PBO, the presence of a methyl branch (*Figure 7*) has only a minor effect on the conformations of the molecules. If the rings are rotated out of coplanarity, there is little to distinguish one
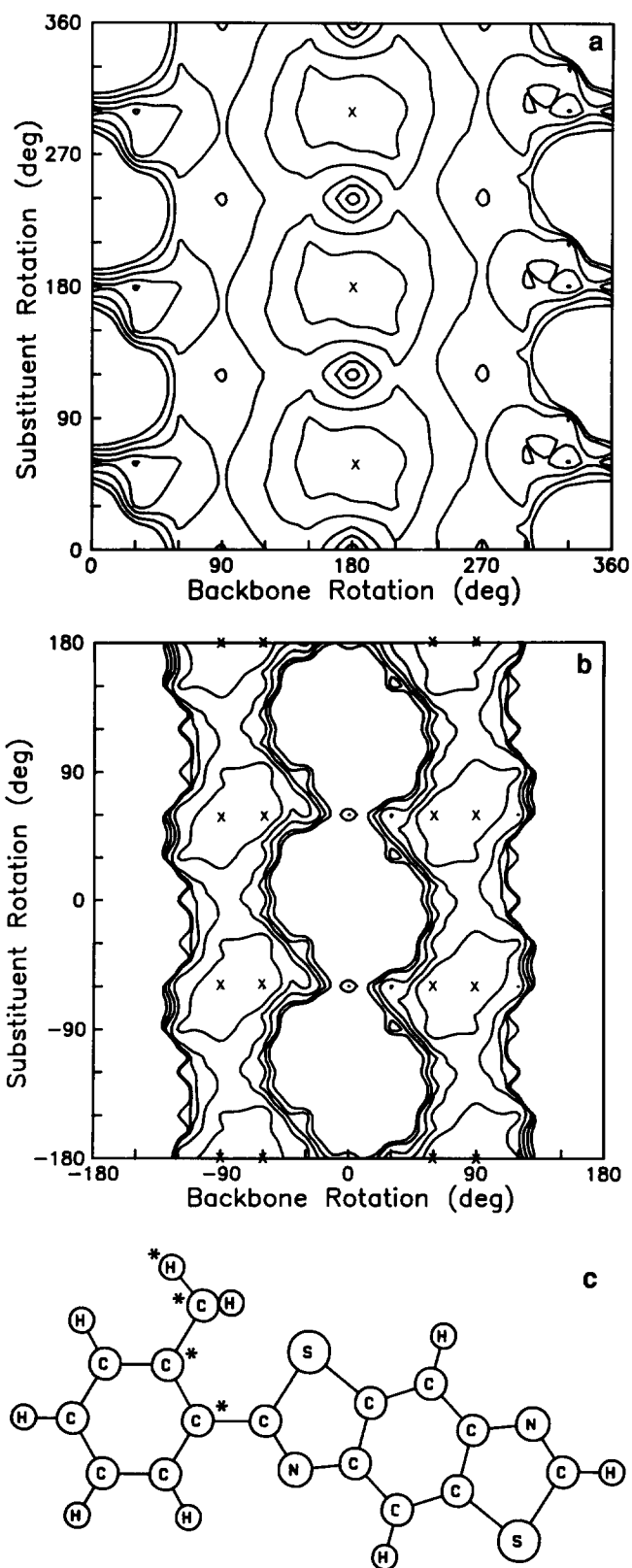

Figure 7 Energy contour maps for (a) methyl-PBO and (b) methyl-PBZT. The atoms indicated by * define the substituent rotation angle, shown in (c) the model for PBZT in its *trans* (= 180°) position

conformation from another. The low energy regions for PBZT are those in which the planes of the backbone rings are normal to one another, leaving the methyl group almost unhindered rotational freedom. For PBO, the lowest energies occur when two hydrogens of the methyl group straddle the oxygen side of the heterocyclic ring.
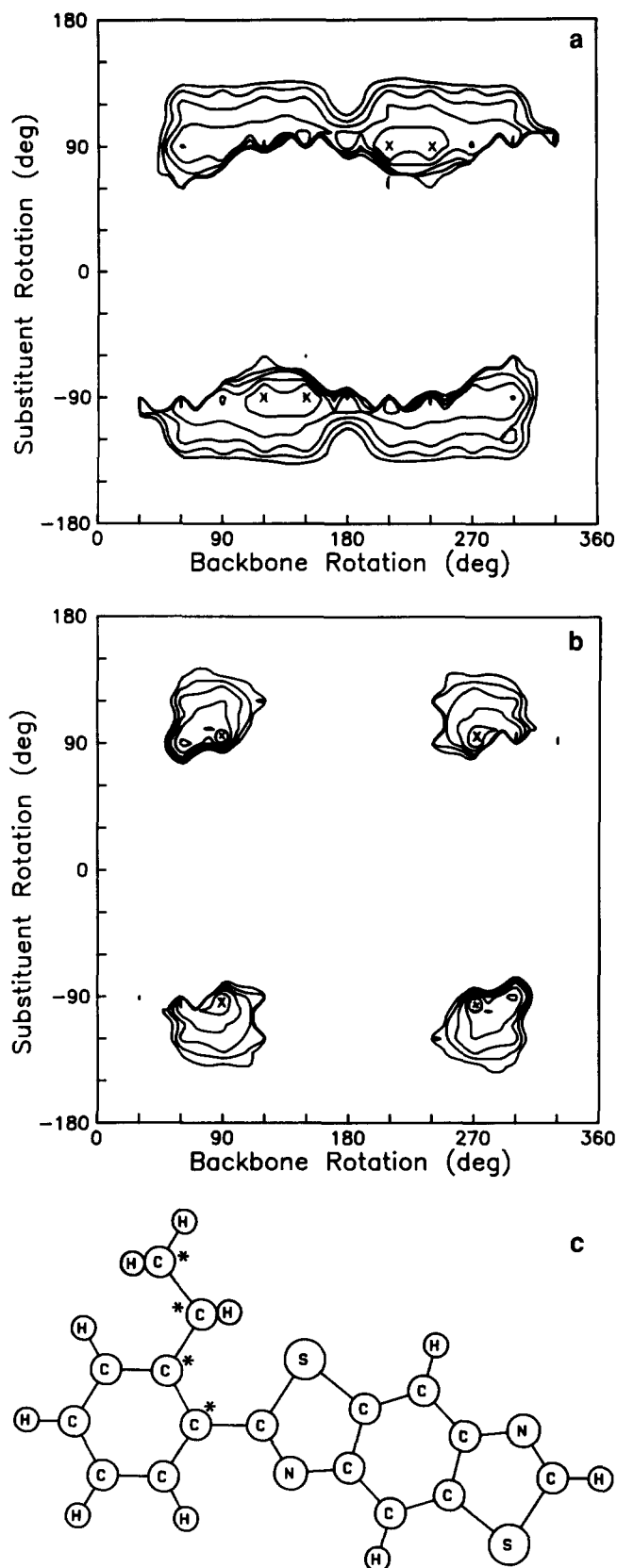
indicates a similar effect, but with the larger size of the sulphur atom constraining the backbone rotation to be within two 60° torsion ranges. Clearly the methylene hydrogens have substantial steric interaction with the sulphur for conformations outside these ranges, interactions that are not so severe in PBO with its oxygen atom. Of course, with an ethyl substituent, there is a third rotation to be considered, namely rotation about the C–C single bond in the ethyl group. Neither a three dimensional conformational search nor optimizing this rotation following a two dimensional conformational scan led to any lower energies.

A phenyl substituent on PBO (*Figure 9*) gives a map similar in character to that for an ethyl group, with the molecule retaining wide latitude for rotations about the backbone single bond. However, by virtue of the substituent's planarity, appropriate rotation of the substituent now allows the backbone phenyl and heterocyclic rings to be coplanar, rather than forcing those rings out of coplanarity.

Placing a *t*-butyl group on the backbone phenyl ring severely restricts PBZT to a single conformation (plus its symmetry related counterpart), with only a little more freedom allowed in PBO (*Figure 10*). In this calculation,

Figure 8 Energy contour maps for (a) ethyl-PBO and (b) ethyl-PBZT. The atoms indicated by * define the substituent rotation angle, shown in (c) the model for PBZT in its *trans* (= 180°) position

An ethyl substituent (*Figure 8*) is a little more confining in both polymers. For PBO, a rotation of the ethyl group so that it is normal to the plane of the phenyl ring is sufficient to allow almost free rotation about the backbone single bond. Comparing ethyl PBZT with ethyl PBO
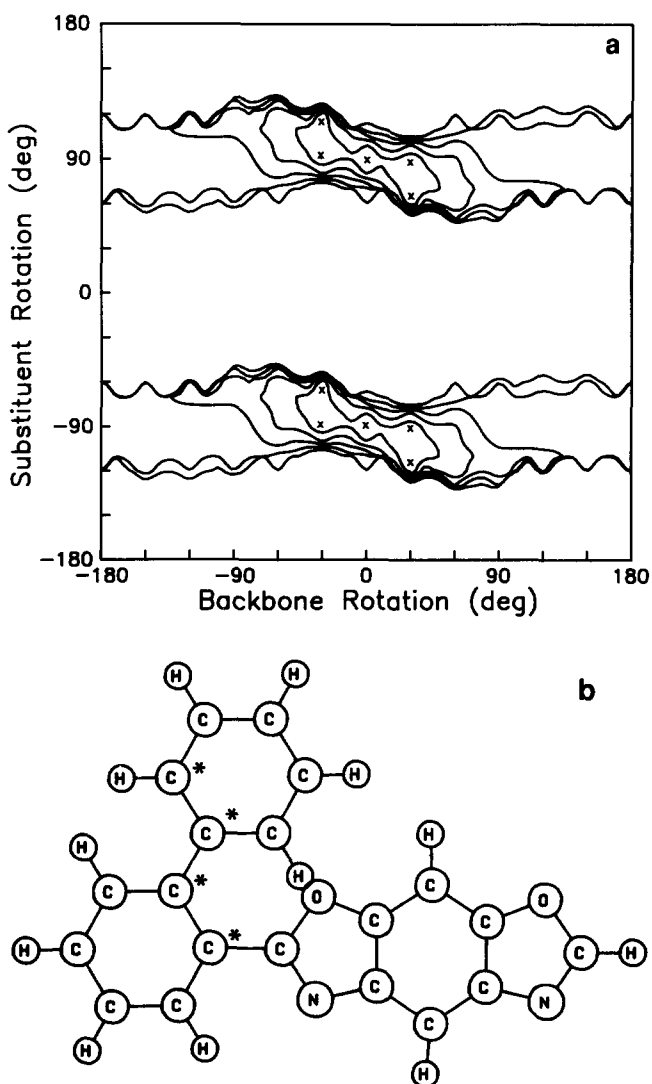
Figure 9 (a) Energy contour map for phenyl-PBO. The atoms indicated by * define the substituent rotation angle, shown in (b) the model in its *trans* (= 180°) position
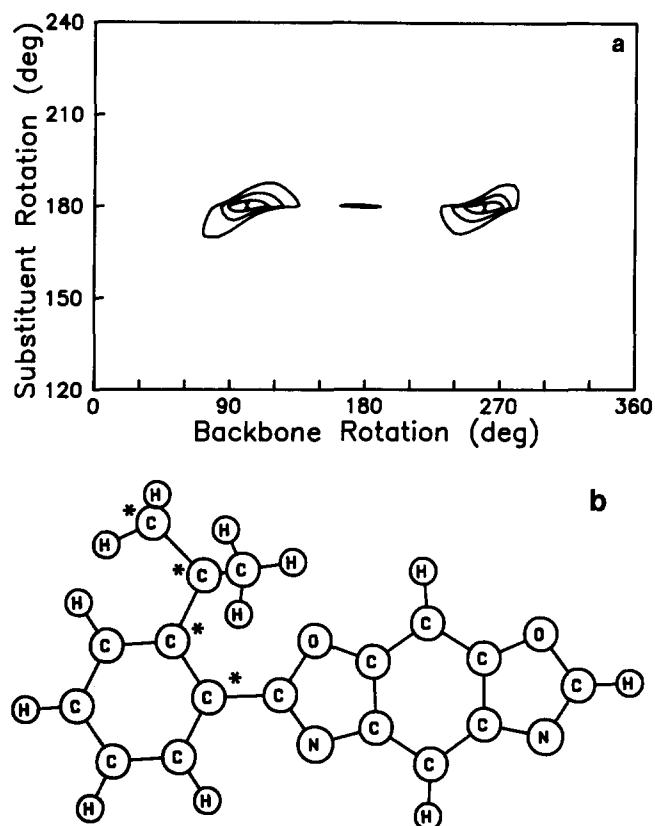
Figure 10 (a) Energy contour map for *t*-butyl-PBO. The atoms indicated by * define the substituent rotation angle, shown in (b) the model in its *trans* (=180°) position

the positions of the methyl groups on the tertiary carbon atom were minimized before the conformational scans were made. The low energy arrangements require the phenyl and heterocyclic rings to be normal to one another to accommodate the bulky side-group. Clearly the three dimensional character of the *t*-butyl group has a much more dramatic effect than would a large planar substituent.

A hydroxyl group gives a new character to the energy maps (*Figure 11*). For PBZT, the group is still not very restrictive, but the map does take on a diagonal nature. This indicates that the hydroxyl group has a preferred relationship to the heterocyclic ring, but that this relation can be maintained for most backbone torsion angles. The higher energy at the centre compared to the lower values in the upper-left and lower-right regions indicates the preferred interactions of the hydroxyl group with the sulphur atom of the heterocyclic ring. Hydroxy PBO shows this same diagonal character, but now with definite preference for backbone torsions which place the hydroxyl group at optimum distances to the ring oxygen atom. In large part, this is due to the stronger electrostatic interactions present in this fragment which were not significant for the hydrocarbon substituents. These interactions in hydroxyl PBO in fact make the nonbonded (negative energy) interactions larger than the (positive energy) contributions of bond length and angle distortions. Because of this new aspect to the energies, some caution should be used in comparing the results of this calculation with those for hydrocarbon substituents.

Although hydrogen bonding would be likely in the real material, the energy map in *Figure 11a* does not reflect the result of distinct hydrogen bonding, because there was no explicit account of hydrogen bonding in the

energetics calculations. Chem-X does have provision for evaluating hydrogen bonding by reducing the repulsive, non-bonded steric interaction that would normally be calculated for the atomic separation distances in a hydrogen bond[34]. However, the hydrogen bond thus treated is spherically symmetric, rather than having a
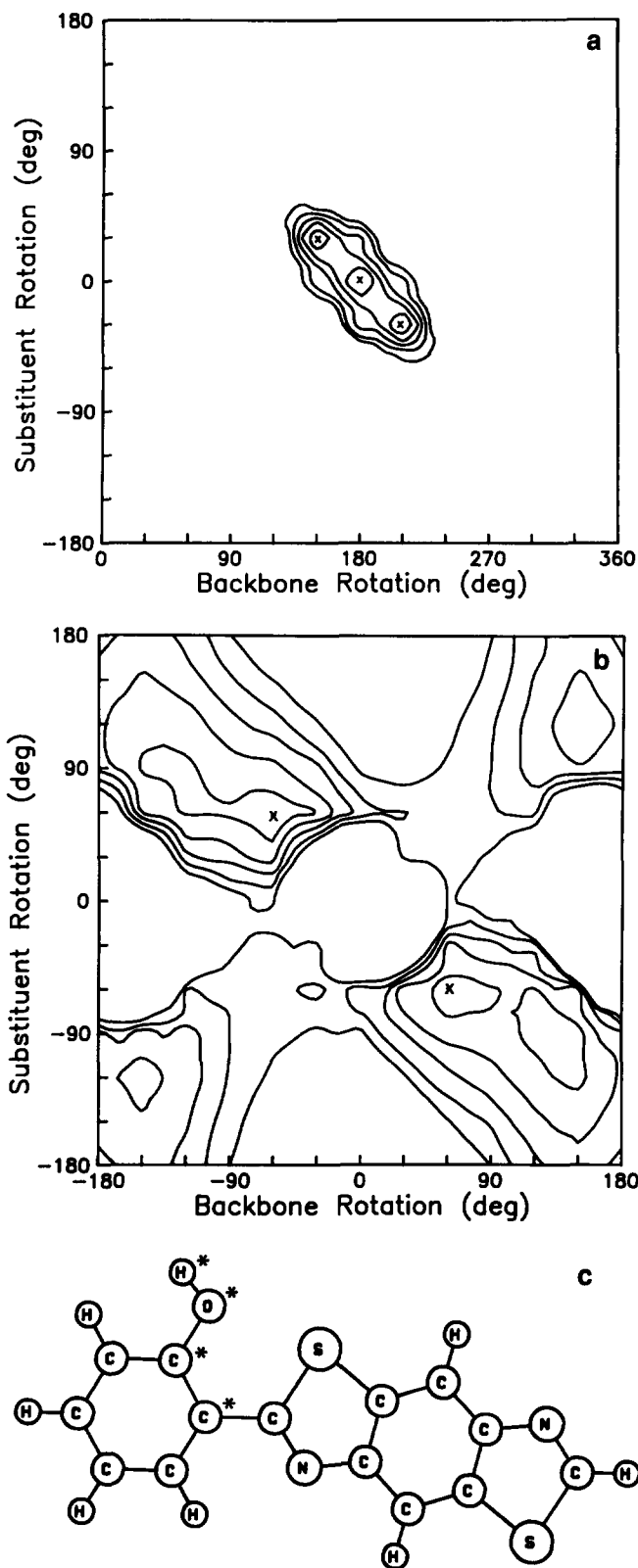
Figure 11 Energy contour maps, calculated without considering hydrogen bonding, for (a) hydroxyl-PBO and (b) hydroxyl-PBZT. The atoms indicated by * define the substituent rotation angle, shown in (c) the model for PBZT in its *trans* (=180°) position

strong directional character that might more accurately represent a real hydrogen bond. Deficiencies of the hydrogen bond function notwithstanding, energies were calculated for hydroxyl PBO and PBZT, taking hydrogen bonding into account in this manner. For PBZT, hydrogen bonds were introduced between the hydroxyl proton and both the sulphur and nitrogen atoms of the heterocycle. Similarly, for PBO, hydrogen bonds were formed with both the oxygen and nitrogen atoms of the heterocycle. The results, shown in *Figure 12*, show the expected enhanced favourability of a coplanar conformation for PBO with the hydroxyl substituent closest to the oxygen atom of the heterocycle. The map for PBZT not only shows a stronger diagonal nature, but also the preferred association of the hydroxyl substituent is now with the nitrogen atom of the heterocycle. The lowest energy conformation remains non-coplanar. This is contrary to the suggestion that hydrogen bonding causes di-hydroxy PBZT[28] to be planar. Experimental data also indicates that an analogous low-molecular weight model
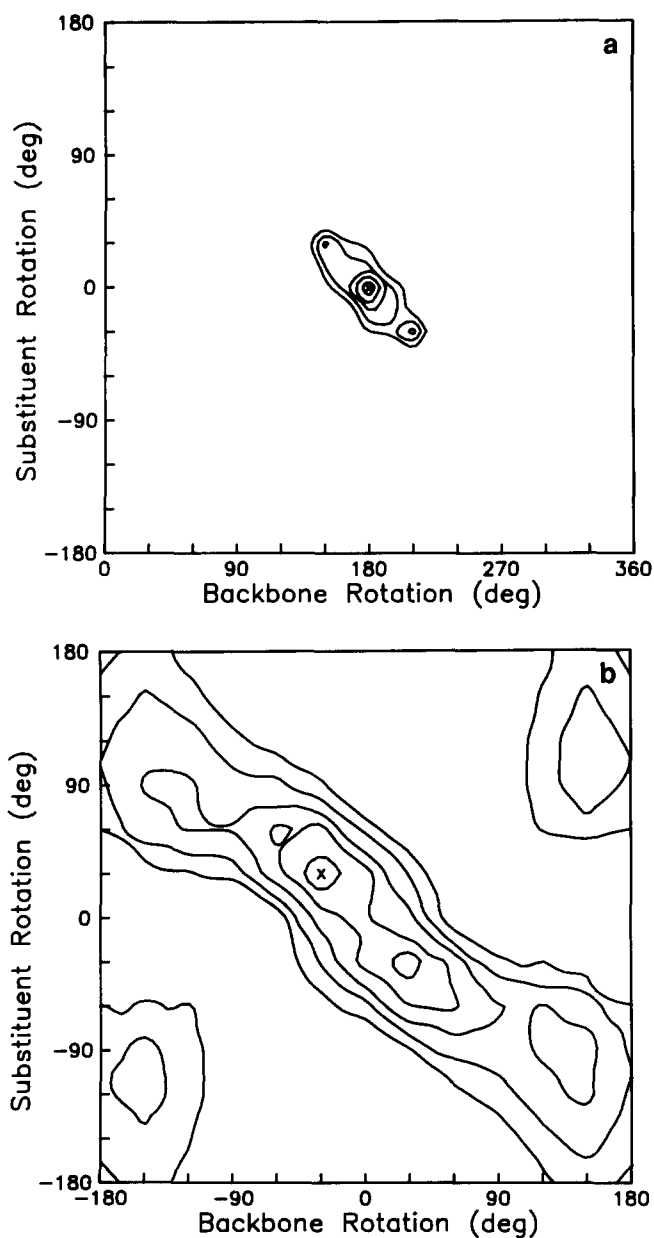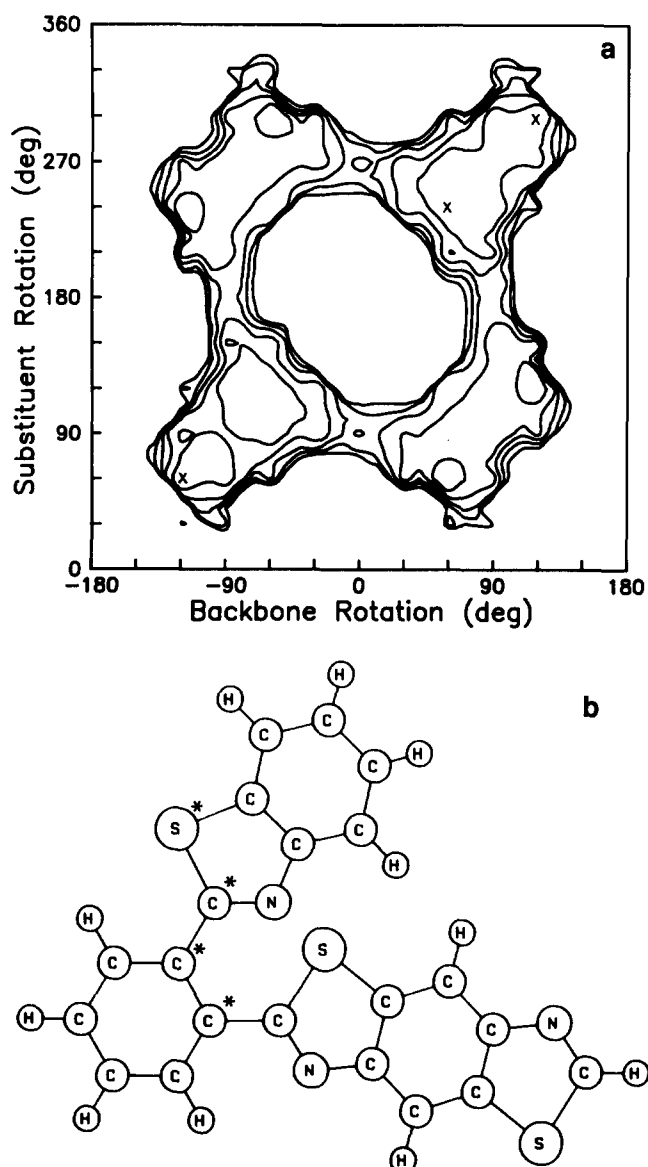

Figure 13 (a) Energy contour map for benzthiazole PBZT. The atoms indicated by * define the substituent rotation angle, shown in (b) the model in its *trans* (= 180°) position

Figure 12 Energy contour maps, calculated with hydrogen bonding, for (a) hydroxyl-PBO and (b) hydroxyl-PBZT

compound[40] does adopt a planar conformation, with a hydrogen bond existing between the hydroxyl substituent and the nitrogen of the heterocycle. The calculated non-planarity might be attributed to the cited shortcomings of the CHEM-X hydrogen bonding function and a more realistic hydrogen bonding function may give different results. Intermolecular packing energies might also force a coplanar conformation in the solid state.

PBZT having a benzothiazole substituent was analysed more extensively than were polymers having other substituents. This was prompted by previous work[25,41] on this polymer and by the uniqueness of the substituent, it being the only one (of those considered here) long enough for adjacent pendant groups to have the possibility of interfering with one another. The conformational energy map for a single repeat unit of the polymer, analogous to those shown previously for other substituents, is shown in *Figure 13*. The size of the substituent notwithstanding, the map offers broad, low energy regions in all four quadrants of the map, centred where the substituent and backbone heterocyclic rings are both perpendicular to the backbone phenyl ring. The two

regions having proximate sulphur atoms are slightly more restrictive and higher in energy.

The synthesis of the benzothiazole-PBZT polymers places the substituent groups randomly at the four available sites on the backbone phenyl group[25]. Of course, rotation of the phenyl group and the *trans* arrangement of the sulphur atoms in the benzobisthiazole moiety make these four sites pairwise equivalent. For the other substituents considered, the important interactions occur within a single repeat unit, and the occupation of the four sites is of no consequence. However, for a benzothiazole pendant, there is potential steric interference between side groups. The placement of two substituents *ortho* to the same backbone heterocyclic ring is distinctly different from one *ortho* and one *meta* placement. While the latter arrangement keeps the substituents well separated in all conformations, the former has the potential for significant interference. The results of calculations considering these possible arrangements will be presented elsewhere.

Inspection of the various contour maps show that there is clearly a range of conformational freedom among the various substituents considered. While most allow considerable latitude in the conformations of the rigid rod polymers, others such as *t*-butyl can be quite restrictive. To put this visual impression on a more quantitative basis, the conformational entropies for each substituted polymer were computed, along with those for the unsubstituted stiff chains and rigid rods. The overall partition function and the probabilities, P_i, for each conformation were computed. The conformational entropy, in entropy units, is then given simply by

$$S = -R \sum P_i \ln P_i.$$

For each polymer, the energies were taken relative to its lowest energy conformation. A temperature of 298 K was used in the computation.

For the unsubstituted polymers, the entropy was calculated using energies calculated by the AM1 method. To allow comparison between stiff and rigid chains, because their symmetries define different unique ranges of their torsion angles (180° and 90°, respectively), their entropies were calculated by extending the data over the full range of 0° to 350°, and using energies computed at 10° intervals. The results are listed in *Table 1*.

Overall, there is little variation in the conformational entropies calculated for the stiff and rigid chains. Four points can be made from the entropy values shown. First, consistent with the similarity of the energy curves, the entropies of *cis* and *trans* isomers of the three rigid rod materials are virtually identical. Second, there is little difference between corresponding stiff and rigid polymers: ABPBO vs. PBO or ABPBT vs. PBZT. Third, consistent with the lower barrier to rotation in PBZT compared to to PBO (or ABPBO vs. ABPBT), the entropy for the thiazoles is about 0.9 eu higher than that of the oxazoles. Fourth, the entropy for ABPBI is different from either *cis* or *trans* PPBI. As shown in *Figure 2*, ABPBI has asymmetric energy minima at 40° and 140°, reflecting the different interactions between hydrogenated and non-hydrogenated nitrogens in adjacent repeat units of the polymer. In PPBI, this asymmetry is effectively eliminated by the presence of the phenyl group. The barriers to rotation are also reduced. These factors result in a slightly larger entropy for PPBI than ABPBI.

One further point should be underscored. The term

conformational entropy is used advisedly, and in distinction from configurational entropy which is often estimated by application of the rotational isomeric state method. Our interest here is to compare the conformational properties of single repeat units of a series of polymers, rather than to assess the overall spatial arrangement and flexibility of the polymer chains. While the conformational entropies of corresponding rigid and stiff chain polymers (ABPBO vs. PBO for example) are quite similar (as shown in *Table 1*), their configurational entropies would be quite different.

For the substituted polymers, the energies from which the contour maps were prepared were used to compute the entropies (144 conformations: 30° intervals over the 0° to 330° range of two torsion angles). The results for all substituents examined for PBO and PBZT are presented in *Table 2*. So that the entropies for substituted and unsubstituted rods could be compared, the entropies reported in *Table 2* for the unsubstituted rigid rods were computed in an analogous manner: the appropriate energies (shown in *Figure 6*) were used to generate two-dimensional energy maps having energies at 30° intervals. Of course, the energy is constant parallel to the axis corresponding to the rotation of the substituent, in this case a single hydrogen atom.

Comparison of the entropies for *cis*-PBO and *trans*-PBZT as presented in *Tables 1* and *2* shows that the magnitudes of the entropies are dependent on the method of calculation, but that the differences in entropy for the two polymers are not. *Cis*-PBO is somewhat more restricted than *trans*-PBZT by either method of computation.

The entropies for the substituted polymers nicely reflect the visual impression conveyed by inspecting the energy

Table 1 Conformational entropies of stiff chain and rigid-rod polymers

Polymer	Conformational entropy (eu)
cis-PPBI	6.80
trans-PPBI	6.79
cis-PBO	6.03
cis-PBO	5.98 (MM[a])
trans-PBO	6.00
cis-PBZT	6.96
trans-PBZT	6.98
trans-PBZT	6.94 (MM[a])
ABPBI	6.53
ABPBO	6.02
ABPBT	6.98

[a] These values were computed from energies calculated using the molecular mechanics method

Table 2 Conformational entropies of substituted rigid-rod polymers

	Conformational entropy (eu)	
Substituent	PBO	PBZT
None	8.74	9.68
Methyl	8.56	8.08
Ethyl	6.55	5.08
t-Butyl	2.46	1.37
Phenyl	6.51	–
Benzthiazole	–	7.61
Hydroxyl		
(no hydrogen bonding)	2.88	7.77
(with hydrogen bonding)	1.11	6.73

contour maps. Consistent with the slightly more restrictive energy map for methyl-substituted PBZT compared to methyl-PBO, the entropy for methyl-PBZT is slightly lower. For each polymer, the entropy for the methyl-substituted rod is a bit lower than that of the unsubstituted rod, in keeping with the broad, energetically accessible regions of those energy maps.

It is also interesting to note that ethyl and phenyl PBO have comparable entropies, with the planarity of the phenyl ring apparently offsetting the potential impact of its larger size. For PBZT, an ethyl group is actually quite a bit more restrictive than the larger, but planar, benzthiazole group. Not surprisingly, the *t*-butyl substituent gives a drastically lower entropy for either PBZT or PBO. The conformational entropy of hydroxyl PBZT is comparable to that of the benzthiazole-substituted rod, and the inclusion of hydrogen bonding has relatively little effect. On the other hand, even without explicit consideration of hydrogen bonding, a hydroxyl group on PBO is almost as conformationally restrictive as a *t*-butyl group. Even though higher energy contours of hydroxyl-PBO are more expansive than those of *t*-butyl-PBZT, their energies are high enough that the molecule would only infrequently explore those conformations, and they thus contribute little to the conformational entropy. With the pseudo-hydrogen bonding included, the hydroxyl group decreases the conformational entropy of PBO by a factor of eight compared to the unsubstituted polymer.

Overall, whether judged by entropy or contour map, most substituents do not lock the molecules into specific conformations, but instead leave significant areas of the contour maps (and therefore, conformational space) energetically accessible. This might indicate that in the solid state, the polymers would be especially susceptible to packing forces, and could find a conformational arrangement suitable to almost any environment. On the other hand, more confined low energy regions might indicate that conformational energies could dictate the packing mode, and tend to give better defined solid state structures.

There is a further distinction to be made, even when just considering conformationally specific materials. If the preferred conformations have three dimensional character (with backbone rings and substituents giving the molecule a distinct cross-sectional shape modulated along the chain axis), the molecules might adopt specific arrangements to optimize their intermolecular interactions. However, if those strongly-preferred low energy conformations make the molecules ribbon-like (phenyl and heterocyclic rings coplanar), the intermolecular interactions may be just as ambiguous as for conformationally indifferent molecules. Thus, even though hydroxyl-PBO and *t*-butyl-PBO have similar conformational entropies, the fact that one is ribbonlike, while the other is distinctly three dimensional, may have a profound influence on the packing characteristics, and perhaps on the compressive properties, of the materials. By the same token, these considerations may explain why the substituted polymers synthesized to date do not have significantly different compressive properties, even though their conformational entropies may vary widely.

CONCLUSIONS

The conformational properties of a series of rigid-rod and stiff-chain polymers have been investigated using semi-empirical molecular orbital calculations. Poly(2,5-benzimidazole), poly(2,5-benzoxazole), poly(2,6-benzothiazole), poly(*p*-phenylene benzobisimidazole), poly-(*p*-phenylene benzobisoxazole) and poly(*p*-phenylene benzobisthiazole) have been studied using MNDO and AM1 molecular orbital methods. Both *cis* and *trans* configurations of the heterocyclic rings of PPBI, PBO, and PBZT were analysed.

It was found that the different molecular orbital computational methods gave dramatically different results, virtually predicting directly opposite variation of the energy *versus* conformation angle for all of the polymers studied. The AM1 results were in better agreement with available experimental data. For ABPBO and both *cis* and *trans* PBO, the AM1 results indicate that a coplanar arrangement of adjacent rings gives the lowest energy. For all the other polymers considered, non-coplanar conformations were found to have the lowest energies for isolated molecules.

Molecular mechanics calculations have been used to investigate the conformational properties of *cis*-PBO and *trans*-PBZT having various substituents on the phenyl ring. Substituents considered included methyl, ethyl, *t*-butyl, hydroxyl, phenyl, and benzothiazole groups. The torsional potential for rotation about the backbone single bond joining the phenyl and heterocyclic rings has a significant influence on the conformational energies. X-ray structure data and the results of the AM1 molecular orbital calculations were used to determine this parameter.

The results show that most substituents have surprisingly little influence on the conformations of the molecules. Small substituents, as well as large, planar substituents, were uniform in their lack of inducing a specificity of conformation in the molecules. Bulky groups, especially *t*-butyl, and those introducing interactions of a more specific nature, such as coulombic or hydrogen-bonding, play a greater role in making specific conformations more energetically favourable. In most cases, the substituent causes a rotation of the backbone rings away from coplanarity. Once the steric interactions are relieved, there is considerable latitude for further rotation. In most cases, the conformational freedom is such that packing considerations could significantly influence the conformations of the materials in the solid state.

REFERENCES

1   Ulrich, D. R. *Polymer* 1987, **28**, 533
2   Roche, E. J., Takahashi, T. and Thomas, E. L. *ACS Symp. Ser.* 1980, **141**, 303
3   Odell, J. A., Keller, A., Atkins, E. D. T. and Miles, M. J. *J. Mater. Sci.* 1981, **116**, 3309
4   Adams, W. W. and Eby, R. K. *MRS Bull.* 1987, **12**, 22
5   Allen, S. R., Filippov, A. G., Farris, R. J., Thomas, E. L., Wong, C.-P., Berry, G. C. and Chenevey, E. C. *Macromolecules* 1981, **14**, 1135
6   Wolfe, J. F. and Arnold, F. E. *Macromolecules* 1981, **14**, 909
7   Wolfe, J. F., Loo, B. H. and Arnold, F. E. *Macromolecules* 1981, **14**, 915

8   Choe, E. W. and Kim, S. N. *Macromolecules* 1981, **14**, 920
9   Cotts, D. B. and Berry, G. C. *Macromolecules* 1981, **14**, 930
10 Welsh, W. J., Bhaumik, D. and Mark, J. E. *Macromolecules* 1981, **14**, 947
11 Welsh, W. J., Bhaumik, D., Jaffee, H. H. and Mark, J. E. *Polym. Eng. Sci.* 1984, **24**, 218
12 Welsh, W. J. and Mark, J. E. *J. Mater. Sci.* 1983, **18**, 1119
13 Bhaumik, D., Welsh, W. J., Jaffe, H. H. and Mark, J. E. *Macromolecules* 1981, **14**, 951
14 Wellman, M. W., Adams, W. W., Wolff, R. A., Dudis, D. S., Wiff, D. R. and Fratini, A. V. *Macromolecules* 1981, **14**, 935
15 Chu, S.-G., Venkatraman, S., Berry, G. C. and Einaga, Y. *Macromolecules* 1981, **14**, 939
16 Wierschke, S. G. *Masters Thesis*, Wright State University, Ohio, 1988
17 Kumar, S. and Helminiak, T. E. *Mater. Res. Soc. Meeting Abstr.* Fall, 1988, p. 307
18 Hunsaker-Jubara, M. *Masters Thesis*, Wright State University, Ohio, 1982
19 Wolfe, J. F., Loo, B. H., Sanderson, R. A. and Bitler, S. P. in 'Nonlinear Optical Properties of Polymers', (Eds A. J. Heeger, J. Orenstein and D. R. Ulrich), *Mater. Res. Soc. Symp. Proc.* 1988, **109**, 291
20 Prasad, P. N. 'Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications', Society of Photo-Optical Instrumentation Engineers (SPIE), 1986, **682**, 120
21 Rao, D. N., Swiatkiewicz, J., Chopra, P., Ghoshal, S. K. and Prasad, P. N. *Appl. Phys. Lett.* 1986, **48**, 1187
22 Symposium J, *Mater. Res. Soc. Meeting Abstr.* Fall, 1988
23 Adams, W. W. and Helminiak, T. E. in 'Science of Ceramic Chemical Processing' (Eds L. L. Hench and D. L. Ulrich), Wiley, New York, 1986), p. 444
24 Wiff, D. R., Helminiak, T. E. and Hwang, W.-F. in 'High Modulus Polymers', (Eds A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, 1988, p. 225
25 Tsai, T. T. and Arnold, F. E. *ACS Polym. Prepr.* 1986, **27**, 221
26 Burkett, J. and Arnold, F. E. *ACS Polym. Prepr.* 1987, **28**, 278
27 Tsai, T. T. and Arnold, F. E. *ACS Polym. Prepr.* 1988, **29**, 324
28 Dang, T. D., Tan, L. S., Wei, K. H., Chuah, H. H. and Arnold, F. E. *ACS PMSE Prepr.* 1989, **60**, 424
29 Chuah, H. H., Tsai, T. T., Wei, K. H., Wang, S.-S. and Arnold, F. E. *ACS PMSE Prepr.* 1989, **60**, 517
30 Pople, J. A. and Beveridge, D. L. 'Approximate Molecular Orbital Theory', McGraw-Hill, New York (1970)
31 Dewar, M. J. S. and Theil, W. *J. Am. Chem. Soc.* 1977, **99**, 4899
32 Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, **107**, 3902
33 Stewart, J. J. P. *MOPAC*, QCPE Program #455
34 Chem-X Molecular Modeling Software, Users Documentation, Chemical Design, Ltd.
35 Fratini, A. V., Cross, E. M., O'Brien, J. F. and Adams, W. W. *J. Macromol. Sci. Phys.* 1985, **B24**, 159
36 Fratini, A. V., Resch, T., Lenhert, P. G. and Adams, W. W. *Mater. Res. Soc. Meeting Abstr.* Fall, 1988, p. 308
37 Mark, J. E. and Welsh, W. J. *Mater. Res. Soc. Meeting Abstr.* Fall, 1988, p. 312
38 Yang, Y. and Welsh, W. J. Submitted to *Macromolecules*
39 SURFER, Version 4, Golden Software, Inc., Golden, Colorado
40 Stenson, P. *Acta. Chem. Scand.* 1970, **24**, 3729
41 Deopura, B. *Systran Technical Report*, Contract #F33615-84-C-5116, 1986