

# CONFORMATION AND CHAIN PACKING STRUCTURES OF POLY(*p*-PHENYLENE BENZOBISTHIAZOLE) BY MOLECULAR SIMULATION\*

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## ABSTRACT

The conformation, the chain packing stabilization and the unit cell modeling of poly(*p*-phenylene benzobisthiazole) have been investigated by using molecular simulation technique in the present work. A coupling behaviour of  $\sigma$ -bond rotations at either side of the phenylene ring or the heterocyclic ring was found surely to exceed a length of the repeat unit of the polymer chain. For a single chain model, the stable torsion angle of the repeat resulted at 14°. In the crystalline cell minimization, the dihedral angle along the polymer chain could even be stabilized in various values. It therefore indicates that the intermolecular interaction does play a considerable role for this polymer forming the conformation. According to cohesive energies calculated for these unit cell models, the torsion angle in the most stable crystalline cell is 0°. When the chains packing together, there exist so many energy stable wells along the chain axis 0.35–0.36nm apart from neighbouring chains. Most of the unit cells have quite closed cohesive energies. These factors thus cause the difficulty of forming an unique perfect crystalline structure of the polymer. The present study suggested a number of reasonable unit cells, and the most stable crystalline structure for this polymer that is monoclinic, non-primitive unit cell.

## INTRODUCTION

With the properties of high-modulus, high-strength and excellent thermal stability, the wholly aromatic, heterocyclic rigid-rod polymer, poly(*p*-phenylene

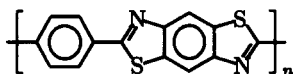
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benzobisthiazole) (PBZT), has been extensively studied<sup>[1-5]</sup>. The studies revealed that rigid chains of the polymer are likely to align to a very high extent but exist with irregularly axial shift of the chains along chain axis. Even though many efforts were carried out on making a more ordered structure for the rigid chains, there has been no suitable crystals of PBZT so far obtained for a perfect structural observation of X-ray diffraction or Electron diffraction. As a result, a stable conformational structure of PBZT repeat still remains unknown. It is obviously a fundamental subject to be understood. Here the conformation is about the phenylene ring turning around the chain axis and having different dihedral angles from the plane of itself to the plane of heterocyclic ring in the repeat. In the situation of lack of experimental data which reveal the crystalline structure of the rigid polymer, molecular mechanics<sup>[3]</sup> and quantum mechanics<sup>[5,8]</sup> were used to study the conformation, and gave rise to different dihedral angles. Most of the calculations support that the two different rings are not coplanar. It thus conflicts with the evidence that the  $\pi$  conjugation along the rigid chain was getting enhanced during annealing at high temperature<sup>[2]</sup>.



In general, a molecule prefers a conformation that is substantially based on both the intramolecular interaction and the intermolecular interaction. In most cases the intramolecular interaction predominates the conformation of a molecule. Therefore, a lot of theoretical methods treat molecular model being along in a vacuum. In some cases, the intermolecular interaction is promoted to be more important than the intramolecular interaction in determination of a molecular conformation, such as polyethylene terephthalate in the crystalline state. Nowadays, data-base of molecular structures is cumulated from X-ray diffraction of crystalline samples. It has been somehow adopted as sources of knowing stable conformation of molecules. Strictly speaking, the conformation preferred for an individual molecule sometimes is not a stable structure for the molecule in crystal. In other words, a stable conformation in crystal discovered by using X-ray diffraction is not guaranteed good for the same molecule individually. To obtain a better understanding of the conformation of PBZT, the polymer in the individual state and in the crystalline state have all to be taken into account in our molecular simulation.

Molecular simulation or molecular modeling are recently fast emerging in the materials science. Applications of this technique showed a remarkable efficiency in research and design of polymeric materials. It provides much suitable molecular

force field, convenient interface, and a package of various means such as molecular mechanics, molecular dynamics, Monte Carlo and quantum mechanics for users. It is obviously a powerful tool to solve problems of polymeric materials at molecular level.

For PBZT the difficulty of crystal formation blocks the door of gaining insight into molecular structure. One day, a new way may be found for making a perfect crystal of the polymer. However, a reason for the difficulty in or the mechanism of forming very ordered crystals from PBZT chains is now not exposed. In the present study, the stable conformation for an individual chain or/and for chains in crystalline state, possibilities of the chains packing in crystal, and various possible crystalline cells were examined by molecular simulation technique.

## METHOD

Molecular models were built for PBZT model compounds,  $\Phi$ -H,  $\Phi$ -H- $\Phi$  and H- $\Phi$ -H (where  $\Phi$  = phenylene ring, H= heterocyclic ring) as shown in Fig.1, and for the repeat of PBZT. The computer program utilized is a material simulation package, CERIU and POLYGRAF, provided by Molecular Simulation, Inc. The force field used in molecular mechanics calculation is Dreiding II<sup>[6]</sup>. The periodic boundary condition is used for reaching long-range interactions. A newly developed semi-empirical quantum mechanics method, PM3<sup>[7]</sup>, was adopted in analysis of intramolecular interaction of the polymer and determining the atomic partial charges for molecular mechanics calculation.

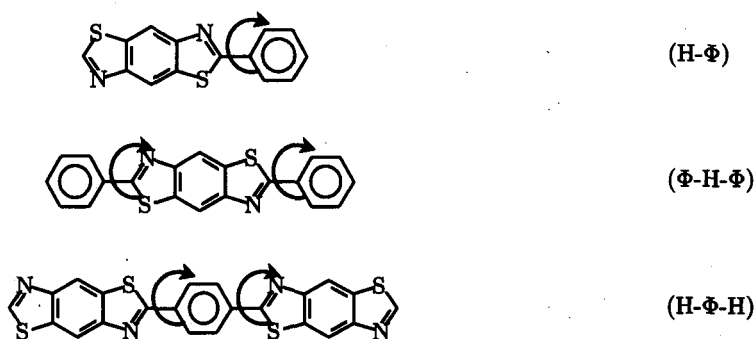


Fig.1. Molecular models of model compounds for PBZT

## RESULTS AND DISCUSSION

The calculations in the present study are classified for different models, such as the model compounds, the single chain polymer, two chain packings, and crystalline

cells. Discussions are as follows: the conformation of PBZT repeat, the stable packings of PBZT chains, and the unit cell modeling of PBZT crystals.

### *Conformation of PBZT repeat*

The conformation of the stiff chain drew much attention in the past sixteen years. Molecular mechanics<sup>[3]</sup>, semi-empirical molecular orbital calculations, such as CNDO/2, MNDO, AM1<sup>[5,8]</sup>, were carried out for the subject. The minimum energy torsion angle of the bond between the phenylene ring and the heterocyclic ring was obtained to be 20° from CNDO/2<sup>[5]</sup> and 29° from AM1<sup>[8]</sup>. These values are very close to 23° which is experimentally measured from a model compound<sup>[4]</sup> for the dihedral angle.

In the present work, a stable torsion angle 20° was obtained by using PM3 for the model  $\Phi$ -H. For the model  $\Phi$ -H- $\Phi$ , two stable torsion angles calculated under the key word "PRECISE" are 20° and 16°. For the model H- $\Phi$ -H, they are 20° and 10°. These results, firstly, showed an unsymmetry feature of the potential well for the torsion angle around 20°. Two unequal torsion angles obtained for the two central symmetric model compounds are somehow surprising. Since they have the same decrease of torsion angles, it indicates that the potential curve at the side down to 0° arises more slowly than the energy increases at the side up to 90°. It therefore supports the early studies about two different barriers at either side of the well. The barrier at 0° is markedly small, 0.5 kcal/mol<sup>[5]</sup> or 0.11 kcal/mol<sup>[8]</sup> in comparison with the main barrier at 90°, 6.0 kcal/mol<sup>[5]</sup> or 0.75 kcal/mol<sup>[8]</sup>. On drawing in picture for this potential well, it looks like an energy *basin* centred at 0° broadening to about  $\pm 20^\circ$ . The other point suggested in above calculation is that the two torsion angles turning out different for the models,  $\Phi$ -H- $\Phi$  and H- $\Phi$ -H, reflects a coupling behavior between two torsions at either side of  $\Phi$  or H through non-bonded potential terms. This coupling behavior is surely beyond the repeat unit of PBZT, thus indicating the models of small molecules are not good enough to solve the conformation problem for this polymer.

We made the polymer chain model with a repeat unit using the periodic boundary condition along a dimension of polymer chain axis. When this model was calculated under PM3 potential, the dihedral angle was stabilized at 29° which indeed reflects the coupling feature between the repeats but is even higher than those obtained from small molecular models. This model was also calculated by using Dreiding II force field. Energy of the single infinite chain was optimized in a full-relaxation process of molecular mechanics. The calculation thus resulted in 14° for stable torsion angle of the repeat. This is different from the stable torsion angle from the run for the small

molecular model  $\Phi$ -H where the dihedral angle was stabilized at  $0^\circ$  under the same force field. As were obtained, the torsion angle increased from  $0^\circ$  in small molecular model to  $14^\circ$  in the single chain model. The increase reflects again that the coupling feature works between the repeats.

As we discussed above, intermolecular interaction may sometimes become important for mastering molecular conformation. To investigate this effect, a number of crystalline cell models were sketched in terms of the reasonable factors as will be stated below in the section "the unit cell modeling of PBZT crystals". Result from these models, the dihedral angle studied was obtained to be  $0^\circ$  in some cases, to be  $18^\circ$  in some cases and to be  $28.6^\circ$  in the other cases. In these minimized crystalline cells, the dihedral angle could even be stabilized in different values, thus indicating the intermolecular interaction does play a considerable role in the case of PBZT as estimated by Welsh et al.<sup>[3]</sup>. According to cohesive energies calculated for these models the torsion angle in the most stable crystalline cell is  $0^\circ$ .

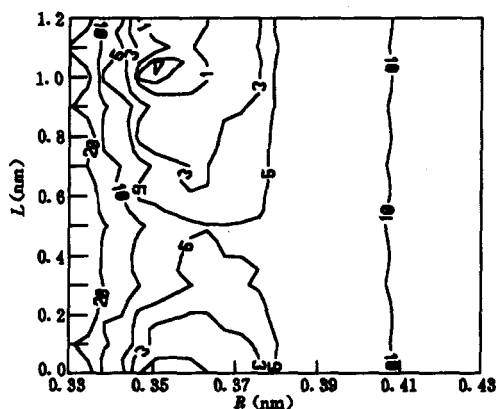


Fig. 2. Energy contour map of the interchain interaction of two parallel PBZT chains, Model A in which the torsion angle between the phenylene ring and the heterocyclic ring is  $20^\circ$ . The numbers along with the contour lines are in kcal. The contour levels from the minimum to the maximum are 0, 0.3, 0.5, 1, 3, 5, 10

### *Stable packing of PBZT chains*

Interchain interaction of PBZT has been studied here with a model of two infinite chains, which is different from the model in the early study<sup>[9]</sup>. The adopting of this kind of model is to avoid interaction effect of the chain ends. We designed two of the model in the simulation. Difference between the two is on the torsion angle. In Model A, the torsion angle is  $20^\circ$ , and it is  $0^\circ$  in Model B. The interaction behaviors of the two chains calculated from the two models are substantially different. As shown in Fig.2, the low energy contours which are under 1.0 kcal/mol are located

around the shifts  $L$  between chains 0.0–0.2 nm while the chains are 0.35–0.36 nm apart. It must be noticed that the length of the repeat unit of PBZT is  $\sim 1.22$  nm. The interaction minimum is at the point of the 0.16 nm or 1.06 nm along  $L$  as shift between chains and the 0.35 nm along  $R$  as chains apart.

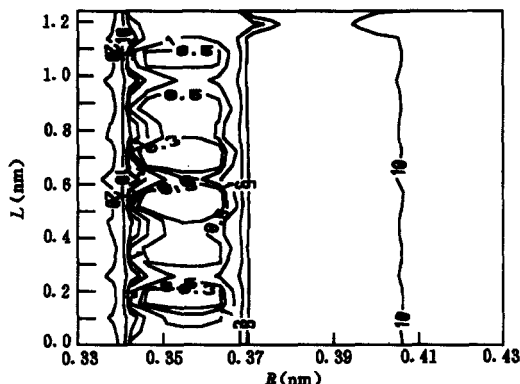


Fig. 3. Energy contour map of the interchain interaction of two parallel PBZT chains, Model B, in which the torsion angle between the phenylene ring and the heterocyclic ring is  $0^\circ$ . The numbers along with the contour lines are in kcal. The contour levels from the minimum to the maximum are 0, 0.3, 0.5, 1, 3, 5, 10

The different feature of Model B is shown in Fig.3. A lot of low energy wells are located side by side as the two chains are 0.35–0.36 nm apart. In the view of the low energy contours under 1.0 kcal/mol, it looks like a channel towards the 0.35–0.36 nm in the abscissa and along the ordinate from 0.1 to 1.1 nm. The energy contours under 0.5 kcal/mol make another channel along the ordinate from 0.3 to 0.9 nm towards the same range in the abscissa. In turn, three wells are made of the energy contours under 0.3 kcal/mol. Their shifts along the ordinate are around 0.18, 0.56 and 0.7 nm.

As studied above, both the intrachain and the interchain interaction made the chain packing difficult. In order to illustrate this point much more clear, we can go through an examination as follows. If the PBZT chains are fixed as Model A with a  $20^\circ$  torsion angle, and the starting position is that they shift from each other as far as 0.56 nm, they will slide along themselves down to the end position where their relative shift is 0.16 nm. This move can make an energy decay of  $\sim 5$  kcal/mol. However, we have known that in the conformational interaction there is an energy basin centered at  $0^\circ$  broadening to about  $\pm 20^\circ$  for the torsion angle. The obstacle in the basin to be overcome for the torsion travelling down through is under 0.5 kcal/mol. In reality, the two chains are able to undergo another path to reduce the packing energy. In the path, no shift occurs to the chains but the torsion angle turns to  $0^\circ$ . It is also a  $\sim 5$  kcal/mol energy decay as shown in the above two

model's calculations. With this suggestion, it is quite possible for the low energy channel to detain some chains and to impede the chain sliding. As a result, there exist so many energy stable positions that are much more than those revealed in the two models. The existence of these stable positions causes the difficulty of forming an unique perfect crystalline structure of PBZT.

#### *Unit cell modeling of PBZT crystals*

Having the knowledge of the chain conformation and the packing features of PBZT chains as mentioned above, we can further carry out unit cell modeling of PBZT crystals. Factors were taken into account in modeling are 1) conformation of the  $\sigma$ -bond between the phenylene ring and the heterocyclic ring, 2) orientations of two chain-planes or dihedral angle between neighboring chain-planes, 3) numbers of the chains in a unit cell, and 4) site of the chains in the unit cell. In this modeling, the initial conformation where a torsion angle has  $14^\circ$  is used. Two kinds of orientations of neighboring chain-planes were adopted: the parallel orientation of two chains and the perpendicular orientation of two chains. Two sorts, one chain in a unit cell and two chains in a unit cell, were considered. Consequently, we built up 12 unit cell models. Adding a model as well as that in literatures, totally 13 unit cell models were taken to initiate total energy minimization without any constraints.

Model X is a unit cell with one chain, and other models are the unit cells with two chains. Model VI, VII, IX, XI and XII are two chains parallel to each other. Those set as perpendicular to each other are two chains in Model I, II, III, IV, V, VIII and XIII. Before minimization the dihedral angle along PBZT chain for all models is the same value,  $14^\circ$ , but became various dihedral angles when the minimization met convergence. Most of them, 8 models, have a  $0^\circ$  torsion angle. They are Model I, II, III, IV, V, VIII, XI and XII. For remainders, Model VI and X have a  $29^\circ$  torsion angle. Model VII and XIII have a torsion angle of  $\sim 19^\circ$ . For the last one, Model IX, the torsion angle is  $10^\circ$ . In view of the dihedral angle between neighboring chains for all models, change in the angle did not occur to those models having two chains parallel to each other. The angle became different from initial settings for those models having the dihedral angle between two chains perpendicular. Most of them, finally, have the value around  $46^\circ$  for the angle.

Cohesive energies of all models can be calculated by comparing the energy of isolated single chain and the energy of each unit cell model. As well known, it is a criterion to judge the most stable crystalline structure among the models. The larger the cohesive energy, the more stable forms the aggregation. The order of stability of the crystalline structures is as follows: Model II, III, V ( $41.3 \text{ kcal/mol}$ ), Model VI,

X (39.8 kcal/mol), Model IV (39.1 kcal/mol), Model VII (38.2 kcal/mol), Model I (38.1 kcal/mol), Model IX (37.3 kcal/mol), Model XIII (36.9 kcal/mol), Model VIII (36.6 kcal/mol), Model XI, XII (36.3 kcal/mol). For the most stable structures, Model II, III, V started from different initial parameters eventually converged to the same crystalline cell. At the start point, difference between Model II and Model III is one of the two chains in the cell just being turned  $180^\circ$ . Model V adopted the initial parameters,  $a = 0.710$  nm,  $b = 0.665$  nm,  $c = 1.235$  nm,  $\gamma = 63^\circ$  [7], different from Model III that begins with a longer  $b$  than  $a$  in cell. At convergence, Model II and V become the same cell parameters in which  $a$  and  $b$  is just opposite values to Model III. Another parameter  $\alpha$  in Model III is as well as  $\beta$  in Model II and V. Therefore they are the same crystalline structure. This unit cell is shown in Fig.4A and close to that proposed by Roche et al.[7].

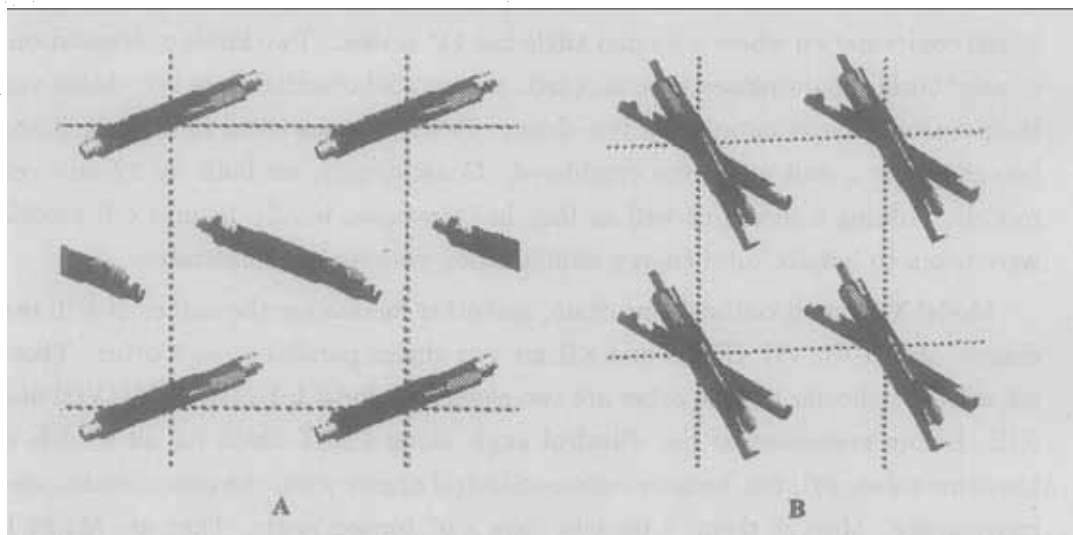


Fig.4. Simulated unit cell. A: Model III,  $E_{\text{cohes.}} = 41.30$  (kcal/mol); B: Model X,  $E_{\text{cohes.}} = 39.81$  (kcal/mol)

When one chain in unit cell, such as Model X, PBZT chain stabilized at a conformation where the dihedral angle between the phenylene ring and the heterocyclic ring is  $29^\circ$  (Fig.4B). Data of the sub-energy terms indicate that this conformation decreases a large amount of van der Waals energy (about 2.5 kcal/mol). Model VI has the same conformation but two chains in unit cell. Odell et al. felt a concern about the non-planar conformation that might reduce density of the unit cell [2]. Results from the present simulation (Table 1) show that the density of unit cell of Model X or Model VI possesses the same value to that of Model II that has a co-planar conformation. The density, therefore, does not matter with the amount of degree of the dihedral angle between two kinds of rings along PBZT chain.

**Table 1** Simulated cell parameters, densities, internal rotations, angles between ring-planes and cohesive energies for each unit cell model of PBZT

|                          | I      | II    | III   | IV    | V     | VI    |
|--------------------------|--------|-------|-------|-------|-------|-------|
| A                        | 6.97   | 7.24  | 5.90  | 5.73  | 7.24  | 6.36  |
| B                        | 11.07  | 5.90  | 7.24  | 7.54  | 5.90  | 7.24  |
| C                        | 12.51  | 12.50 | 12.50 | 12.51 | 12.50 | 12.45 |
| $\alpha$                 | 36.61  | 90.02 | 79.12 | 89.47 | 90.01 | 67.53 |
| $\beta$                  | 116.10 | 78.99 | 90.09 | 88.85 | 78.97 | 92.86 |
| $\gamma$                 | 110.38 | 90.00 | 90.03 | 90.03 | 90.01 | 97.28 |
| $\rho(\text{g/cc})$      | 1.64   | 1.68  | 1.69  | 1.64  | 1.69  | 1.68  |
| $\Phi_{\text{dihedral}}$ | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  | 28.63 |
| $\phi_{\text{plane}}$    | 34.37  | 46.36 | 46.28 | 52.45 | 46.22 | 0.00  |
| $E_{\text{cohes.}}$      | 38.14  | 41.29 | 41.30 | 39.10 | 41.30 | 39.85 |

|                          | VII   | VIII   | IX     | X      | XI    | XII    | XIII   |
|--------------------------|-------|--------|--------|--------|-------|--------|--------|
| A                        | 6.58  | 6.88   | 7.67   | 6.63   | 5.31  | 15.30  | 7.04   |
| B                        | 6.64  | 7.61   | 8.88   | 6.76   | 8.25  | 7.89   | 13.32  |
| C                        | 12.48 | 12.53  | 12.51  | 12.45  | 12.51 | 12.52  | 12.48  |
| $\alpha$                 | 89.24 | 87.84  | 46.53  | 46.11  | 86.80 | 32.43  | 49.81  |
| $\beta$                  | 89.17 | 122.23 | 117.36 | 139.11 | 93.46 | 133.96 | 135.44 |
| $\gamma$                 | 99.89 | 91.11  | 114.52 | 123.23 | 87.49 | 136.38 | 136.10 |
| $\rho(\text{g/cc})$      | 1.65  | 1.60   | 1.63   | 1.68   | 1.62  | 1.62   | 1.61   |
| $\Phi_{\text{dihedral}}$ | 19.80 | 0.00   | 9.50   | 28.70  | 0.00  | 0.00   | 18.70  |
| $\phi_{\text{plane}}$    | 0.00  | 53.62  | 0.00   | 0.00   | 0.00  | 0.00   | 79.00  |
| $E_{\text{cohes.}}$      | 38.24 | 36.59  | 37.26  | 39.81  | 36.25 | 36.29  | 36.85  |

## CONCLUSION

In the present work, the conformation, the chain packing stabilization and the unit cell modeling of PBZT have been investigated by using molecular simulation technique. The two torsion angles calculated different for the models,  $\Phi$ -H- $\Phi$  and H- $\Phi$ -H, reflects a coupling behavior between two torsions at either side of  $\Phi$  or H through non-bonded potential terms. Since this coupling behavior surely exceeds a length of the repeat unit of PBZT, the models of small molecules are not good enough to study the conformation for this polymer. For the polymer chain model, the stable torsion angle of the repeat resulted in  $14^\circ$ . In the crystalline cell minimization, the dihedral angle along the polymer chain could even be stabilized in various values. It therefore indicates that the intermolecular interaction does play a considerable role

in the case of PBZT as estimated by Welsh et al.<sup>[3]</sup>. According to cohesive energies calculated for these models the torsion angle in the most stable crystalline cell is 0°. It coincides with the evidence that the degree of conjugation of PBZT chains increased during annealing at high temperature<sup>[2]</sup>.

When PBZT chains packing together, there exist so many energy stable wells along the chain axis  $\sim 0.35$  nm apart from neighboring chains. In the unit cell modeling, the dihedral angle along PBZT chain can vary in different unit cells. Most of the unit cells have quite closed cohesive energies. These factors thus cause the difficulty of forming a unique perfect crystalline structure of PBZT. The diffraction data up-to-now obtained show a serious longitudinal chain shift along chain axis. Results here indicate that the chains or even a chain may have different conformations along with, may go through various ranges where the chain packing approach different unit cells. The present study suggested a number of reasonable unit cells for PBZT, and the most stable crystalline structure which is monoclinic, non-primitive unit cell.

#### Keywords:

Poly(p-phenylene benzobisthiazole); Molecular mechanics; Crystalline structure; Cohesive energy

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