# Molecular Structure Calculations in Two Classes of Conducting Polymers

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ABSTRACT: We have shown that structural aspects such as planarity of the polymeric backbone may play an important role in reaching high levels of conductivity upon doping. Most polymers for which high conductivities are reported have planar equilibrium conformations while some others have grossly nonplanar backbones. This has led to the belief that planarity of the polymer backbone may not be an important criterion in forming conducting complexes. On the other hand, a continuous overlap of backbone atomic orbitals is considered necessary to reach high conductivity after doping. In order to better understand the structure–conductivity relationship in two classes of polymers (type I: polyacetylene and analogues; type II: poly(phenylene sulfide) and homologues), we have carried out conformational analysis on segments of polymers using molecular mechanics and quantum chemical methods. The results indicate that high conductivities upon doping are reached when adoption of a quasi-planar structure for the polymer backbone is energetically feasible. These calculations on polyacetylene and polyacetylene–poly(methylacetylene) (PA–PMA) copolymers also explain many of the experimental features obtained in these systems and indicate that electronic structure calculations should go hand in hand with molecular structure studies to account for the electrical behavior of these systems.

## Introduction

Since the early discovery of conducting forms of $(CH)_x$[1], many structurally diverse polymers have been doped to high levels of conductivity.[2] Many of these polymers, like $(CH)_x$, have planar backbones as preferred conformations. They also have a continuous system of overlapping $\pi$ and p orbitals along the polymer backbone. Many other conducting polymers, however, have been identified whose preferred conformer states are grossly nonplanar.[2] In poly(phenylene sulfide) (PPS), for example, the neighboring phenyl rings are inclined at ±45° with respect to the planar-zigzag chain of the sulfur atoms. This and other examples have led to the belief that planarity of the polymer may not be an important criterion in forming conducting complexes.[3] On the other hand, the orbital overlap along the backbone has been considered to be the most important criterion for high conductivity.[4] Apart from some theoretical investigations, the main experimental evidence for this comes from the fact that if backbone overlap is interrupted (for example, by replacing the sulfur atom in PPS by a $-CH_2-$ moiety), there is a precipitous drop in conductivity after doping.[5] Substitution of the $-CH_2-$ moiety for sulfur, however, also involves drastic distortion of the chain structure and packing.

In the present paper, we report the results of a structural investigation of PPS and other conducting polymers, including copolymers of polyacetylene. These results seem to indicate that high levels of conductivity upon doping are reached when adoption of a quasi-planar extended-chain structure for the polymer backbone is energetically feasible. The observation that thiophene bridges are formed when PPS is doped with $AsF_5$[6] indicates that PPS first adopts a quasi-planar structure prior to chemical modification.

Our results indicate that the replacement of the backbone sulfur atom by the $-CH_2-$ moiety leads to severe distortions of the chain backbone. We believe that, although a loss in orbital overlap and a structural distortion may go hand in hand, one cannot be emphasized at the other's cost. Lastly, the extensive calculations on polyacetylene and polyacetylene–poly(methylacetylene) (PA–PMA) copolymers support the importance of planarity in this class of polymers and explain many of the experimental results obtained in these systems.

## Theory

In order to investigate the structural flexibility of the two classes of polymers (type I: PA and copolymers of PA; type II: chalcogen-containing aromatic polymers such as PPS), we performed conformational analysis of segments of the polymers. The starting geometries were constructed by using a combination of crystal data and standard valence geometries. A combination of molecular mechanics and quantum chemical methods such as CNDO/2 and MNDO was used to calculate the torsional barrier about the backbone bonds and ionization potentials for different chain geometries. Subsequently, these methods were used to scan the conformational energy spectrum as a function of backbone bond rotation. The molecular mechanics and quantum chemical calculations were carried out with the chemical modeling laboratory CHEMLAB.[7] Hopfinger's 6–12 dispersive repulsive potential energy functions were used along with a coulomb-type electrostatic term to represent the nonbonded interatomic interactions.[8] Energy calculations were performed at interval scans of a 5° rotation about the polymer backbone single bond.

## Results and Discussion

The torsional energy barrier for backbone bond rotations for a segment of PPS and for the same segment with the sulfur atoms replaced by a $-CH_2-$ moiety is shown in Figure 1. The rotational flexibility of the phenyl groups in PPS (Figure 2a) as opposed to poly(methylene-1,4-phenylene), PMP (Figure 2b), is evident. Unlike for PPS, it will be energetically prohibitive for PMP to adopt a quasi-planar structure. Thus, just as PPS and PMP are drastically different in their electronic features, they are also very much dissimilar in their structural features. Therefore, it is conceivable that the inability of PMP to obtain a quasi-planar structure may be an important factor for its not obtaining high levels of conductivity upon doping. The conformational energy contour map for PPS is shown in Figure 3. The interchain energy minima are represented by dots. Due to the shallow region around the minima, it will be possible for the phenyl rings to "flatten" to a certain extent. After "flattening", hydrogen abstraction occurs, to lead to the formation of thiophene bridges. In fact, only after chemical modification of PPS occurs does it reach high levels of conductivity ($>1\ \Omega^{-1}\ cm^{-1}$). It is important to realize (as these calculations illustrate) that one needs not have a quasi-planar structure before doping. It is important, however, for the quasi-planar structure to be energetically obtainable. This is the case for PPS but not for PMP. For poly(phenylene selenide) (PPSe) on the other hand, a better orbital is expected along the backbone, conceivably leading to higher

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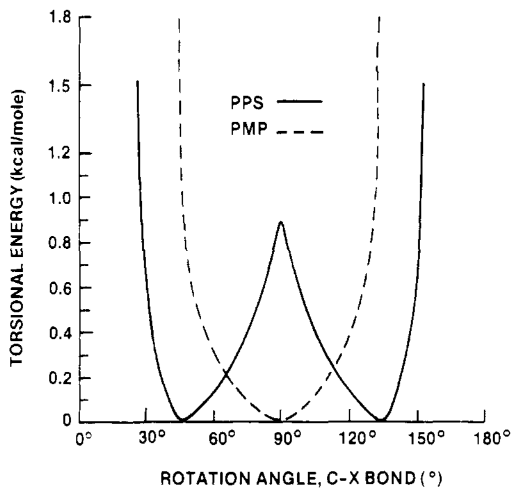


**Figure 1.** Torsional energy barrier for backbone bond rotations vs. rotation angle of C–X bond. X = –S– (PPS) and $-CH_2-$ (PMP).

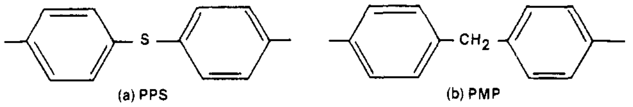


**Figure 2.** (a) Poly(*p*-phenylene sulfide) (PPS); (b) poly(methylene-1,4-phenylene) (PMP).

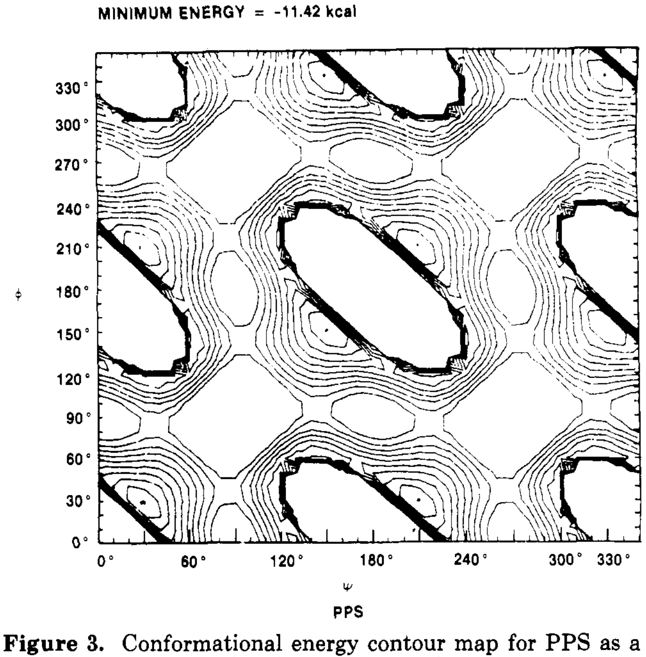
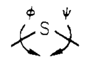
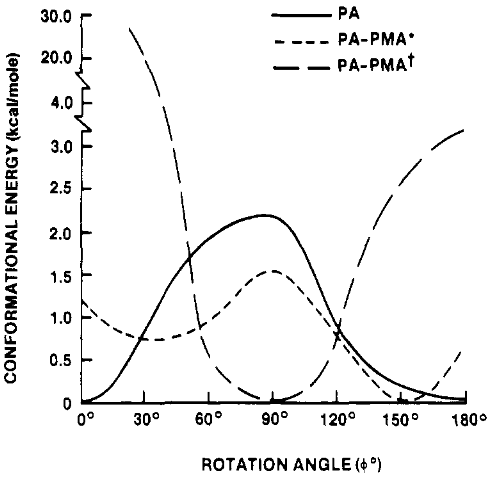


**Figure 3.** Conformational energy contour map for PPS as a function of backbone bond rotation $\phi$ and $\psi$. Dots represent intrachain energy minima.



levels of conductivity after doping. Calculations that are presently being performed on PPSe, however, indicate a lesser degree of flexibility of the phenyl rings. This will add to the difficulty in adopting a quasi-planar structure. The difficulty in adopting a quasi-planar structure leads to a hindrance of the effective "coherence length" (the effective coherence length may be regarded as the length that charge carriers may travel without being scattered or trapped). Therefore, the expected improvement in orbital overlap may not materialize.

Results of calculations of conformational energy vs. C–C backbone bond rotations for PA and PA–PMA copolymers are shown in Figure 4. Characteristically, PA has the intrachain energy minima at the cis and trans position of the backbone bond. The results for the copolymer PA–PMA and the homopolymer PMA have very interesting features. When a methylacetylene (MA) unit has acetylene units adjacent to it on either side (Figure 5a), the conformational features are similar to that of PA (Figure 4). However, for two adjacent MA units (Figure 5b), the barriers are prohibitive against bond rotations to obtain a quasi-planar structure. Obviously, for the case of poly(methylacetylene), the frequency of the dyads of MA units is ≃100%. These results have a striking correlation with the experimental findings of Chien et al.,[9] showing the relationship between conductivity (after doping with $AsF_5$ and $I_2$) and the fraction of methylacetylene in the PA–PMA copolymer. Up to 30% MA content in the copolymer, PA–PMA copolymers have similar levels of conductivity after doping as PA itself. At this MA content, assuming random distribution, few MA groups will have another MA group as their nearest neighbors. As a result, as suggested by the conformational features of Figure 4, the effective coherence length will remain largely unaffected. Beyond the 30% content of methylacetylene in PA–PMA copolymers, the probability of two or more adjacent MA groups increases very rapidly (Figure 5b). As a result, the effective coherence length will decrease, as indicated by the features of the conformational energy curve of Figure 4, and the conductivity begins to fall dramatically. Similar arguments may be made concerning the results of Deits et al.[10] on copolymers of polyacetylene and poly(phenylacetylene) (PA–PPA) and of Deits et al.[11] on analogues of PA.



*Up to 30% MA Content in Copolymer PA-PMA.

†Beyond 30% Content in Copolymer PA-PMA.

**Figure 4.** Conformational energy vs. C–C backbone bond rotation for PA and PA–PMA copolymers.

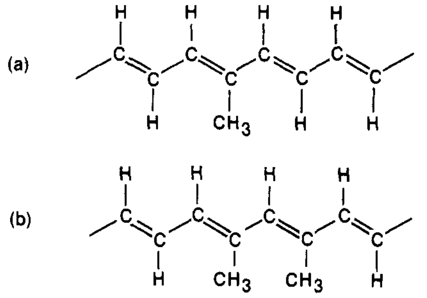


**Figure 5.** (a) Methylacetylene unit with actylene units adjacent to it on either side in PA–PMA. (b) Two adjacent methylacetylene units in PA–PMA.

Results of calculations of ionization potentials for PA and PA–PMA copolymers are shown in Table I. The

Table I
Results of Ionization Potential Calculations

| rotation angle $\phi$, deg | ionization potential, eV | | |
|---|---|---|---|
| | PA | PA–PMA[a] | PA–PMA[b] |
| 0 | 4.7 | 4.7 | 4.7 |
| 30 | 4.8 | 4.8 | 4.8 |
| 60 | 5.0 | 5.0 | 5.0 |
| 90 | 5.4 | 5.3 | 5.3 |
| 120 | 5.0 | 5.0 | 5.0 |
| 150 | 4.8 | 4.8 | 4.8 |
| 180 | 4.7 | 4.7 | 4.7 |

[a] Up to 30% MA content in copolymer PA–PMA.
[b] Beyond 30% content in copolymer PA–PMA.

calculations were optimized for the side-group rotations. As can be seen, the ionization potential for PA–PMA copolymers does not appreciably vary with backbone bond rotation and methylacetylene content. This is an expected result as was corroborated experimentally by Deits and co-workers[10,11] and Chien and co-workers.[9] We feel, however, that as explained above, the actual chain arrangement plays an important role in the carrier transport. An extended coherence length, either inter- or intrachain, is a structural requirement for carrier transport and, thus, high conductivity after doping.

In conclusion, there is a strong correlation between structural features and conductivity in the general class of conducting polymers. In fact, the minimum-energy conformation for all conducting polymers (reported to date) is a $2_1$ helix. While most of these structures are planar, such polymers as poly(phenylene sulfide) and poly(*p*-phenylene) have a nonplanar equilibrium geometry. Our calculations suggest that even in the case of grossly nonplanar PPS, a quasi-planar structure is energetically accessible. Calculations presently being carried out also indicate there is not a significant loss in packing energy in going from a nonplanar to a quasi-planar structure.[12] As shown by Brédas et al. and Duke et al.,[4] even with the grossly nonplanar conformation in PPS there is substantial orbital overlap along the backbone. In order to fully understand the relationship of structure and conductivity, the $\pi$ bandwidth of these systems will have to be explored as a function of the conformer states that will be accessible as a result of doping.

The adoption of a quasi-planar structure may lead to an improved interchain packing and thus an extended interchain coherence length and better interchain orbital overlap. This is a strong possibility in the case of PPS, where maximum conductivity levels are reached for one dopant moiety per phenyl ring and conductivity anisotropy is very small.[13]

On the other hand, the correlation of possible chain arrangements with conductivity in the case of PA–PMA copolymers is much more dramatic and clearly establishes the importance of planarity and extended-chain geometry in this class of polymers. Lastly, it is important to realize that one need not have a quasi-planar structure before doping. It is important, however, for the quasi-planar extended-chain structure to be energetically obtainable.

**Added Note**: Since the submission of the manuscript, Diaz et al. (Diaz, A. F.; Castillo, J.; Kanazawa, K. K.; Logan, J. A.; Salmon, M.; Fajardo, O. *J. Electroanal. Chem.* **1982**, *133*, 233) have observed a precipitous drop in conductivity in going from the unsubstituted polypyrrole system to the poly(*N*-alkylpyrrole) system. They speculate that the loss of conductivity is a result of a loss of planarity of the polymer backbone.

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