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CONFORMATIONAL ANALYSIS AND CONDUCTIVITY VIA DOPANT INTERCALATION MODEL FOR PPS AND PPO (POLYPHENYLENE SULFIDE AND OXIDE)

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Semi-empirical potential energy functions in conjunction with quantum mechanical methods were used to characterize the intrachain interactions and conformational aspects of the processable polymers PPS and PPO. The purpose of this study was to elucidate the structural aspects of the dopant-polymer interaction and mechanism of electrical conduction subsequent to doping of these materials. These polymers, upon doping, can reach high levels of conductivity in spite of the fact that the crystalline conformation of the chains is non-planar and little conjugation along the chains is expected due to the presence of the chalcogenide atom. Chain flexibility and rearrangement upon doping will be discussed. Calculations have indicated that the rotations about C-X (X=O,S) bonds and stretching of the ∠ C-X-C angle can facilitate the intercalation of a dopant moiety in a manner that conduction can occur via an interchain mechanism. A dopant intercalation model will be presented and its consequences on conductivity anisotropy will be discussed.

INTRODUCTION

The preparation of Poly(Phenylene Sulfide) (PPS) was first described as early as 1897 by Grenvesse.[1] Since then, numerous investigations have been carried out on PPS. This is primarily due to the resistence to chemicals of this industrial resin and also because of its excellent mechani-

cal and thermal properties.[2,3] Recent interests in PPS have been mainly due to its interesting electrical properties. PPS is the only processable polymeric system that has been rendered conducting upon doping with different oxidizing dopants.[4-6]

As opposed to all other known doped conducting polymer systems, the morphology of PPS can be manipulated very easily using standard polymer processing techniques. In contrast to this, the microstructure of polyacetylene (PA), the most studied conducting polymer system to date, can be influenced primarily at the synthesis stage. This has important consequences upon the mechanism of conduction. The effect of structural variation on conduction for both these systems has been investigated in our laboratory.[7]

The lack of processibility of PA stems from its rigid chain structure which principally exists in three chain conformations viz. trans-transoid, cis-transoid and trans-cisoid.[8] Although slightly off-planar geometries have been speculated upon, the overwhelming theoretical, as well as experimental evidence, supports a planar conformation. This forms the basis for some of the conduction mechanism models proposed for PA and also explains the very high degree of crystallinity that can be reached in some samples. The work in our laboratory[7] has shown that higher crystallinity of the samples leads to higher levels of conductivity.

PPS has been found to be highly crystalline. However, unlike PA, PPS can be easily oriented upon stretching. Although some controversy regarding the crystal structure of PA still exists (difficult to obtain oriented PA for reasons mentioned before), the crystal structure of PPS has been elucidated by Boon et al[9] using highly oriented films and pellets. In the crystalline arrangement, the PPS chains pass through the centre and corners of an orthorhombic unit cell. They have also shown that the planes of the successive phenyl rings alternate at $\pm 45^{o}$ to the (100) crystal plane. In this regard, the crystal structure of PPS is very similar to that of Poly(Phenylene oxide) (PPO).[10]

In view of the orthogonal arrangement of successive phenylene groups, and the presence of a chalcogen in the backbone, a significant overlap in the orbitals is not expected.[11] Besides, the polymer chain in bulk PPS is not expected to have an extended chain fibrilar morphology because of enthalpic considerations.[12] Also, the conducting anisotropy in the "chain" and orthogonal to the chain direction has been found to be approximately 2:1, which is quite different from the 7:1 ratio found for PA

and which is expected for a quasi one dimensional conductor. Further, doping of biaxially stretched films of PPS has led to anisotropic optical and electrical properties consistent with the chain orientation of the starting polymer. It is thus expected that the disruption in crystallinity (as seen in the x-ray patterns of the doped samples) does not seriously distort the parallel orientation of the PPS chains.

An intercalation model has been proposed[11] for some of the conducting polymer systems, including PA.[11] However, as mentioned before, the polymer chain in these systems are rigid and adopt a planar conformation. Intercalation has been postulated to occur in these systems in the form of a dopant layer displacing two adjacent crystallographic planes.[13] However, such a situation will seem unlikely for the nonplanar PPS chains. To get an understanding of this and its other seemingly uncorrelated properties, we have carried out the conformational analysis of a segment of PPS and PPO. The present study employs semi-empirical potential energy functions to investigate intrachain interactions in PPS and PPO, specifically as they relate to the mode of intercalation of the dopant species. Another question of particular interest is whether or not the intrachain features alone can explain the two orders of magnitude difference in conductivity of PPS and PPO[14] upon doping, and also the problem of structural changes which can occur in the process of doping.

THEORY

Valence Geometry

The starting geometry for both PPS and PPO was assumed to conform to the crystal structure. Thus, the starting bond lengths and bond angles were taken as follows: for PPS, C-S = 1.755 $\angle$C-S-C = 110°; for PPO, C-O = 1.42 $\angle$C-O-C = 124°. The partial charges were calculated using the CNDO/2[15] method. The calculations were carried out on sequences having increasing numbers of repeat units until constant values are obtained for the central unit in the sequence. The partial charges were found to differ only slightly between crystal conformation and upon excursions up to 30° around each C-S bond. In any event, slight conformation dependence of partial charges is adequately accounted for in the process of defining the torsional function for rotations about the C-X bonds. Thus, the

partial charges in these calculations were taken as shown in Fig. 1.

Potential Energy Functions

Non-bonded interatomic interactions were represented by a 6-12 dispersive repulsive and coulomb type electrostatic interactions. A fixed dielectric constant of 4 was employed in all calculations. The torsional potential for rotations about the C-S and C-O bonds were established by comparing the CNDO/2 energies and the non-bonded molecular mechanics energies for different conformer states.

Conformational Analysis

Fixed valence geometry molecular mechanics calculations were done on a dimer of PPS and PPO. Rotations about the ϕ,ψ bonds were carried out at 5^{o} intervals to scan the entire range of rotations from 0^{o}-360^{o}. Molecular mechanics segment of the CHEMLAB[16] software system, in conjunction with the torsional potential functions, was used for this purpose. Subsequently, the conformational energy of the PPS and PPO dimers were calculated as a function of the C-S-C and C-O-C angles for the crystal conformation as well as the intrachain energy minimum.

RESULTS AND DISCUSSION

The torsional function for the C-S and C-O bond rotations are shown in Fig. 2. Clearly, a preference for the adjacent phenyl rings to be orthogonal to each other, is evidenced. The energy minima occurs at 45^{o} for the C-S bond rotations, while for the C-O bond, it is around 50^{o}. However, the amplitude of the torsional barrier is very small except when conformations very close to a planar structure are realized.

The isoenergy contour maps in Figs. 2 and 3 for PPS and PPO incorporate the respective torsional functions and the overall minima are represented by x's. As expected, the total intrachain energy minimum corresponds closely to the crystal conformation. The small deviation from crystal conformation can be easily justified on the grounds that crystalline packing will produce slight deviations from intrachain energy minimum. This is especially true if the stabilization energy gained in packing, more than offsets the loss in energy as a result of the excursion away from

the intrachain minima. The energy minima in the map are characterized by very deep wells separated by large sterically hindered regions (shown by flat plateaus). The bottoms of the wells themselves are fairly shallow and this provides extreme rotational flexibility about the crystal conformation and rotations up to ± 25° can be performed about the C-S or C-O bond starting at that conformation.

These conformational characteristics answer many of the important questions pertaining to the structure of these two polymers. The "shallow bottoms" around the energy minima provide the necessary flexibility for processing (melt, solution) and also explain the fact that the chains can be highly oriented upon stretching.[11] The large plateau covering most of the map, on the other hand, explains the rigidity, toughness, high melting point, and the fact that the films don't lose the orientation even as the crystallinity is lost upon doping.

These conformational features also explain the relative difficulty in doping highly crystalline PPS. The orthogonal arrangement of successive phenyl rings does not provide any room for the dopant moiety to intercalate. However, in the amorphous and semicrystalline regions the flexibility of the phenyl ring facilitates the dopant species to intercalate into the interstices. This, on the other hand, leads to a chain conformation where the successive phenyl rings adopt a quasi-planar arrangement. In this conformation, the aromatic hydrogens (4) and (6) (Fig. 1) are physically close enough to be chemically extracted by the dopant moiety. This leads to the formation of thiophene rings and other chemical modifications in heavily doped PPS as observed by Shacklette et al[6] and by Rubner and coworkers.[17] This arrangement of polymer chains with the dopant species in the interstices (at heavy doping, there is a 1:1 ratio of the dopant species and the phenyl groups) leads to a possibility of conduction via an interchain mechanism where the electrons of the phenyl rings of adjacent chains can interact via the dopant species. This can account for the small conductivity anistropy of 2:1 observed for doped PPS, which is quite different from the 7:1 ratio found for PA and expected for a quasi one dimensional conductor.

However, in spite of the structural similarities of PPS and PPO (which explains their similar thermal and mechanical properties) there is a 2 orders of magnitude difference in the levels of conductivity reached upon doping of these two polymers. Although intrachain energy calculations alone cannot provide the complete answer to

this question, two conclusions are evident: Intrachain electron delocalization via the sulfur atom is better facilitated as compared to the intervening oxygen atom. Secondly, two adjacent PPO chains can pack closer to each other compared to PPS (as evidenced in the crystal structure as well) due to smaller van der Walls radius of oxygen. Thus, intercalation of the dopant moiety in PPO is more difficult than it is in the case of PPS. A third feature that emerges from calculations shown in Table I is that due to the higher polarizability of the sulfur atom, the ∠ C-S-C angle is much more easily deformed compared to the ∠C-O-C angle. This further assists the PPS chains in accommodating the dopant species.

CONCLUSION

In conclusion, intrachain conformational analysis on a segment of PPS and PPO has helped answer many of the pertinent questions relating to their structure property relationship. A model for the intercalation of the dopant species into the interstices is proposed. Unlike PA, this predominantly occurs in the amorphous regions and is facilitated by the flexibility of the phenyl rings. The intercalation process itself forces the adjacent phenyl rings to adopt a quasi-planar arrangement which can subsequently lead to formation of thiophene bridges.

A smaller value of the polarizability of the oxygen atom (as compared to sulfur), its smaller van der Walls radius, and the lesser flexibility of the ∠C-O-C bond angle are some of the reasons for the lower levels of conuctivity reached for PPO.

A complete packing analyses, in conjunction with the electronic structure calculations will be necessary to get a quantitative answer to the electronic behavior of these systems. These and other experimental investigations are underway at present in our laboratory.

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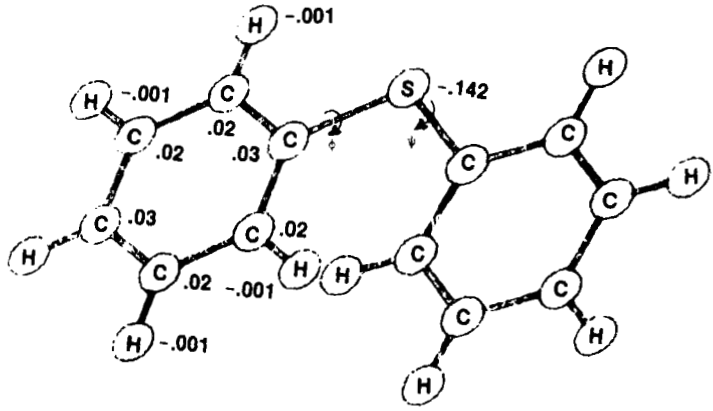

FIGURE 1 Partial charges and valence geometry of a truncated segment of PPS

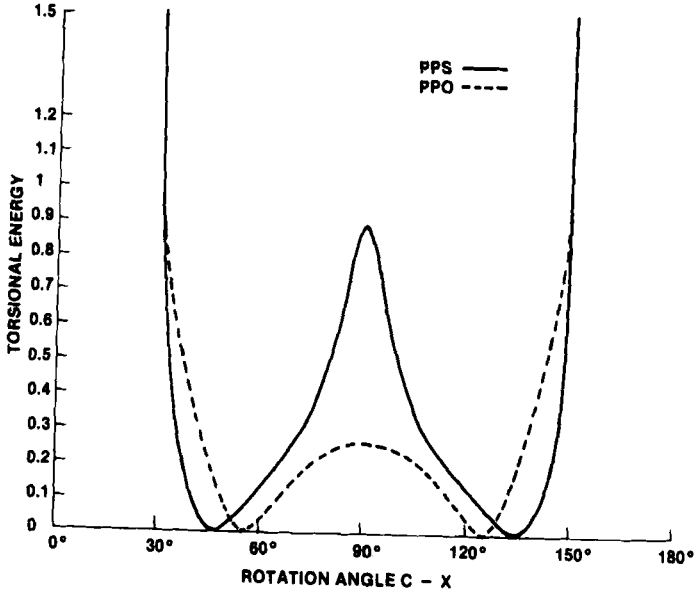

FIGURE 2 Torsional potential energy for rotations about the C-X bond (X=S,O) in PPS and PPO. Energies are in KCals

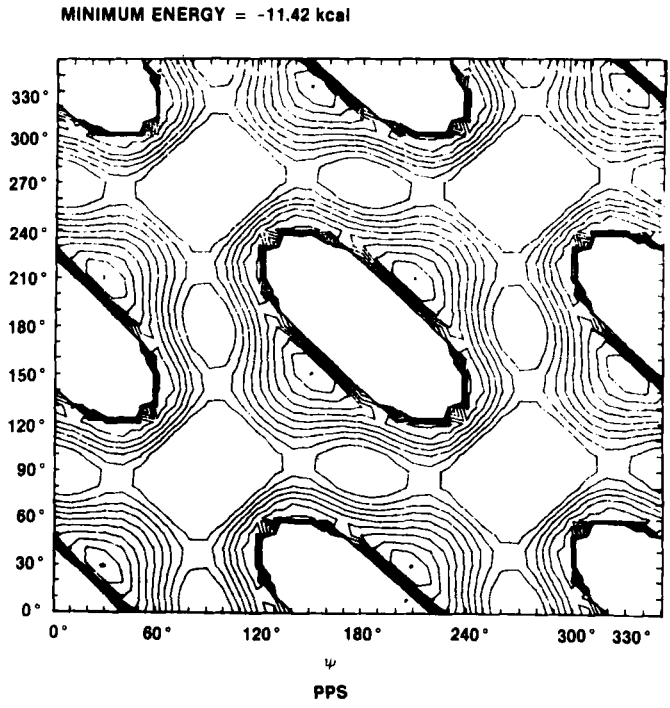

FIGURE 3 Conformational energy contour maps of a dimer of PPS. Minima are represented by dots. The rotations are performed about C-S bonds shown in Figure 1.

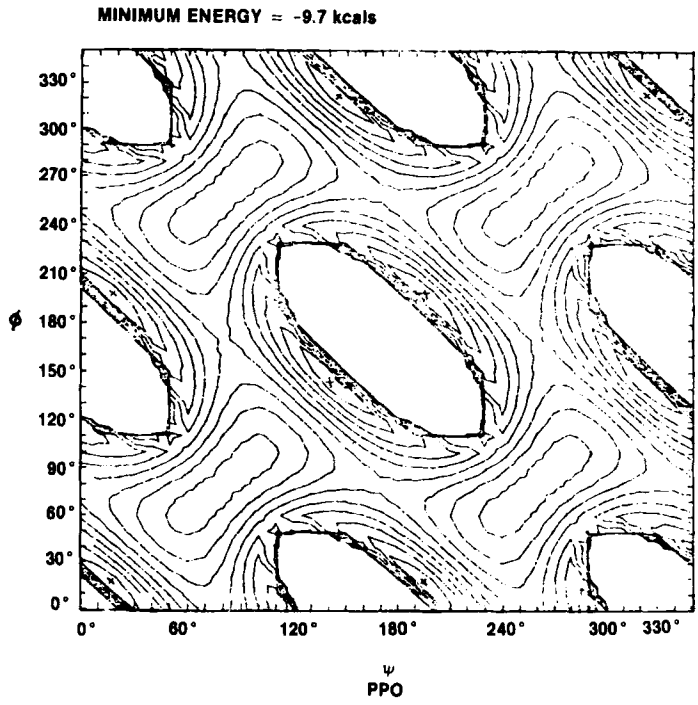

FIGURE 4 Conformational energy contour maps of a dimer of PPO. Minima are represented by x's. The rotations are performed about C-O bonds shown in Figure 1.

< CSC ANGLE (°)	STABILIZATION ENERGY kcal/mole
102	0.945
106	0.160
108	0.0
110	0.132
112	0.501
114	0.664
116	1.239

TABLE I Deformation energy for stretching of ∠ C-S-C angle