

Conformation Structure of Conjugated Polymer P3HT in Solution

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I. INTRODUCTION

Conjugated conductive polymer materials are of significant interest due to optical and electrical properties of semiconductors combined with moldability and easy processing of polymers. The P3HT (Figure 1) is a polymer of this family which is widely used in photovoltaic devices, where there is a strong interest in solar cell applications [1].

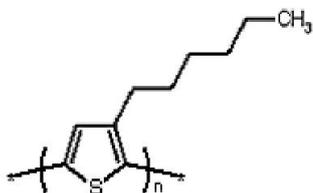


FIG. 1: Structural formula of P3HT.

This work is intended to simulate P3HT thin films utilized as active layer of organic solar cells, employing methods to calculate the electronic structure. So, we must first understand which is the preferential conformation in the solvent (precursor of film) so that we can predict its structure after processing the film. This preliminary analysis is discussed.

II. RESULTS AND DISCUSSION

The conformational structure of the polymer is extremely important in order to obtain a more realistic model of the same. For the simulation of P3HT, we use Molecular Dynamics to obtain random structures which are employed as the inputs for Restricted Hartree-Fock (RHF) PM6 [2] semiempirical calculations implemented in MOPAC2009 [3] to get the most stable configurations. The solvent (chloroform) was simulated by the COSMO method [4].

We investigated two types of regioregularity: Head-to-Tail-to-Head-to-Tail (HT-HT) and Head-to-Head-to-Tail-to-Tail (HH-TT). We also studied the monomer, dimer and tetramer in order to understand the interactions between the alkyl chains of all monomers, and the inter-monomer geometric

conformation, to build the most probably structure of the polymer.

We find that the alkyl chains prefer on a ladder conformation. The inter-monomers dihedral angle should be approximately 107° for Head-to-Tail, 150° for Head-to-Head and 86° for Tail-to-Tail regioregularities.

Knowing the behavior of the alkyl chain and inter-monomer dihedral angle, we built larger structures (6, 8 and 10 repeat units). Figure 2 shows the most stable structures for the decamers HH-TT and HT-HT.

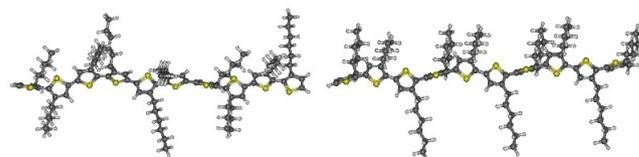


FIG. 2: Obtained structures for the decamers HH-TT and HT-HT respectively.

To have an idea of the reliability of the model, we simulated the absorption spectrum with the ZINDO/S [5] semiempirical method in conjunction with the CIS method. By extrapolation to infinity, we found a maximum theoretical peak of 421 nm for the HH-TT and 394 nm for the HT-HT regioregularities, getting differences of about 6% and 11% from the experimental data (446 nm [6])(see Figure 3).

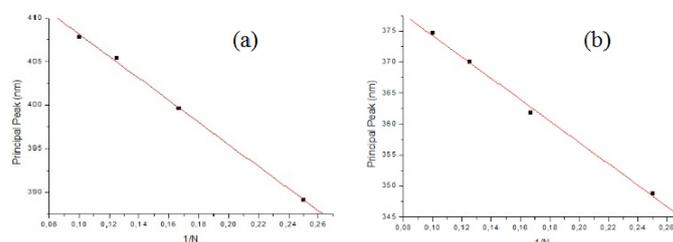


FIG. 3: Linear fit for the principal peak for the regioregularity: (a) HH-TT and (b) HT-HT.

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III. CONCLUSIONS

By observing the results of the calculations, we predict that the P3HT solution is not planar and it is observed that the C₆H₁₃ chain form a ladder, in interactions with other monomers. Up to now, comparisons with experimental data favor the HH-TT regioregularity. From the model found for the solution, we will do further studies, simulating P3HT thin

films.

IV. ACKNOWLEDGMENTS

I thank Augusto Batagin Neto by helping in calculating the absorption spectrum, Grid-UNESP, CNPq, and Unicamp for financial support.

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