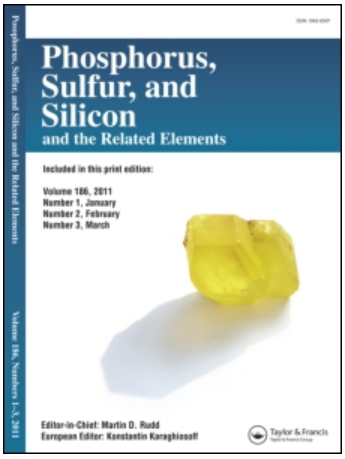

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Characterization and Electrochemical Polymerization of Oligomethylthiophenes

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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL POLYMERIZATION OF OLIGOMETHYLTHIOPHENES

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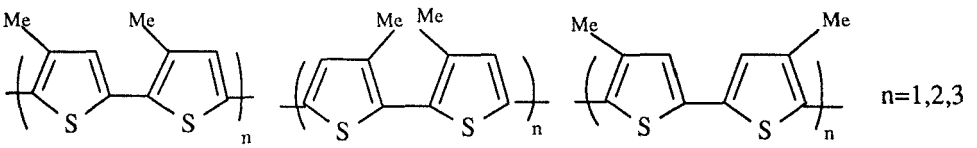
Abstract. Regiospecifically methyl substituted α-conjugated thiophene oligomers have been synthesized and their structural and conformational properties investigated by ^{13}C NMR, X-ray and force field MMP2 calculations. The use of these molecules as 'monomers' for electropolymerization affords poly(3-methylthiophenes) showing spectroelectrochemical properties which depend on the size and the substitution pattern of the starting oligomer.

Semiconducting α-conjugated polythiophenes have attracted increasing interest in recent years because of their unique electrical, electrochemical and optical properties[1]. Due to their chemical stability, a variety of applications in the field of molecular electronics, electrochromic devices, sensors, etc.. have been proposed for these materials. Recently, it has been found that α-conjugated thiophene oligomers may have better semiconducting properties than polythiophene itself[2].

The presence of substituents β to sulfur allows polythiophenes to become soluble in organic solvents or in water[3], opening the way to a better control of their chemical and physical properties for specific technological applications.

The relationship between the structure and the conformation of substituted polythiophenes and their electric and optical properties is a matter of great current interest. To explore this relationship in the case of poly(3-methylthiophenes) we have synthesized, characterized and electrochemically polymerized a series of α-conjugated methylsubstituted bi-, quater- and sexi- thiophene oligomers with *head-to-head*, *head-to-tail* or *tail-to-tail* junctions between adjacent rings (see next page). The synthetic strategy for the preparation of oligomethylthiophenes was based on a combination of metalation/cross coupling reactions for the creation of carbon-carbon bonds starting from commerical 3-methylthiophene[4-9].



head-to-tail *head-to-head* *tail-to-tail*

On the basis of ^{13}C NMR and UV spectroscopies and MMP2 calculations it was found that in solution and in the gas phase the molecular skeleton of these compounds is not planar and that it is conformationally very mobile. On the contrary, X-ray data indicate that in the solid state a fully coplanar arrangement can be attained, even in the presence of strong steric interactions such as those of a head-to-head junction, although at the cost of severe deformations of bond lengths and bond angles.

The electropolymerization of isomeric dimethyl bithiophenes and tetramethyl quaterthiophenes allows the preparation of poly(3-methylthiophenes) with very different optical properties. The polymer optical properties are, in fact, modulated by the size and the regiospecificity of substitution of the starting oligomers and can be interpreted on the basis of the conformational properties of the starting systems[10,11].

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