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MORPHOLOGY AND CRYSTALLOGRAPHIC STRUCTURE OF
POLYTHIOPHENE AND DERIVATIVES

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F. GARNIER *

Abstract The structural regularity is one of the key parameters controlling the electrical properties of organic conducting polymers. In the case of five membered heterocycles as thiophene, we have analysed the effects on morphology and on crystallization of 3,4 mono and disubstitution, which should force a regular coupling of thiophene units in the 2,5 positions. The unsubstituted polythiophene is fully amorphous and shows a compact morphology. In contrast, poly 3 methylthiophene is fibrillar, with fiber diameter of 200 Å (undoped state) to 800 Å (doped state). When doped with CF_3SO_3 , doping levels up to 50 % are obtained, associated with a partial crystallization. The X ray and electron diffraction data show a hexagonal lattice ($a=9.7\text{\AA}$, $c=12.2\text{\AA}$), consistent with a coil structure. Similar results have been obtained with poly 3,4 dimethylthiophene. However large steric interactions between methyl groups lead to the distorsion of the polymer chain.

INTRODUCTION

Organic conducting polymers form a new class of interesting metallic-like compounds, and the improvement of their conductivity and stability represents a very attractive goal. Among the needed criteria¹, two parameters seem to play a critical role : i- the doping level, and ii- the regularity of the chain structure.

In this respect, whereas polyacetylene and polypara-phenylene can be reversibly doped to about 6% and 20% respectively^{2,3}, the electrochemically synthesized poly-

pyrrole⁴ and polythiophene⁵ appeared very promising, owing to their larger doping level of 25 to 50%. These two last polymers however are completely amorphous. Furthermore, the metallic behaviour of these polymers has been shown by BAUGHMAN et al⁶ to strongly depend on the stereoregularity of the chain structure.

Five membered heterocycles (pyrrole, thiophene, furan) polymerize by an $\alpha\alpha'$ coupling, leading to a highly conjugated chain. Among the structural defects which can affect the configuration, the most probable one concerns an $\alpha\beta'$ coupling. In order to enhance the polymer regularity, we have synthesized several thiophene monomers, mono or disubstituted in the β position. We report here the influence of this substitution on the morphology and on the crystallization for the corresponding polymers.

EXPERIMENTAL

The grafting of the polymers on Au or Pt electrode involves the oxidation of the monomer $5 \cdot 10^{-1} \text{ M}$ in $\text{CH}_3\text{CN} - \text{N}(\text{Bu})_4\text{CF}_3\text{SO}_3$ $5 \cdot 10^{-1} \text{ M}$ ⁵. The thickness of the doped conducting film is adjusted by the electrolysis time. The elemental microanalysis were performed on thick deposits scratched off from the electrode. The X ray measurements were obtained on a Philips PW 1130 with a Norelco goniometer and a Co anticathode ($K\alpha$ line at 1.78865 \AA). Transmission electron microscopy and electron diffraction data involved a Jeol 120 CX apparatus. The polymer was put in suspension in an alcoholic medium, and the solution was evaporated on an amorphous carbon grid.

RESULTS AND DISCUSSION

The doping level for all the studied polymers lies in the range 25 - 30%, except for poly 3 methylthiophene, PMeT, where levels up to 50% have been obtained. This polymer exhibits under transmission electron microscopy, TEM, a fibrillar structure with apparently randomly oriented fibrils of about 250 Å diameter (fig. 1a). When doped to about 25%, the fibril diameter increases up to about 800 Å, but some undoped fibrils still remain (fig. 1b). This result shows that the doping process is unhomogeneous and that the doping level, as determined by microanalysis, must be considered as stastical.

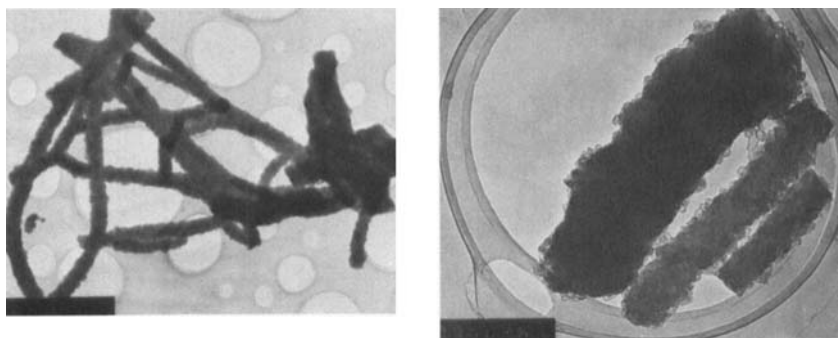


Fig.1 : TEM picture of poly 3 methylthiophene PMeT.

a : undoped state ; fibril diameter 200 Å.

b : doped fibrils ($d \sim 800$ Å) together with undoped ones.

Polythiophene, PT, appears fully amorphous under TEM as well as under X ray. In contrast, some microcrystallites are observed along the fibers of PMeT doped to 30% with CF_3SO_3^- (fig. 2). When doped to 50%, TEM pictures clearly display reticulations (fig. 3), and the electron diffraction patterns associated to these areas reveal a six

fold symmetry (fig. 4). X ray measurements performed on PMeT doped

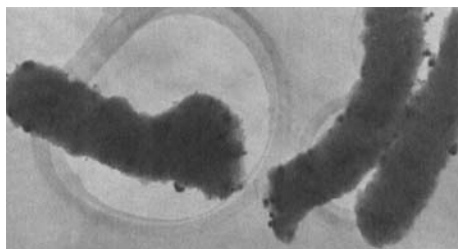


Fig. 2 : TEM picture of PMeT-SO₃CF₃⁻ 30% fibrillar structure with crystallites.

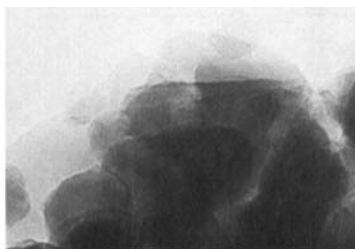


Fig. 3 : TEM picture of crystallized areas of PMeT doped with 50% SO₃CF₃⁻ ion reticulation planes.

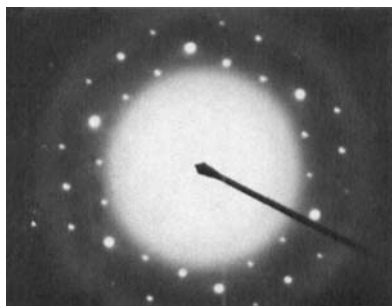


Fig. 4 : Electron diffraction patterns of crystallized areas of PMeT. 50% doped SO₃CF₃⁻.

to 30 and 50% give two peaks located at $2\theta = 17^\circ$ and $2\theta = 29.8^\circ$. The peak intensity increases with the doping level, but it must be pointed out that the signals are weak, corresponding to a low percentage of crystallinity, of about 5%.

The six fold symmetry defined by electron diffraction can be related either to a cubic or to a hexagonal structure. The indexation of the reticular distances, performed on a computer, do not at all fit with a cubic structure. On the other hand, the indexation with a hexagonal structure led to a good agreement with the X ray diffraction and the electron diffraction data (Table 1). These results show that :

- the characteristic distances for the hexagonal lattice are $a = 9.7 \text{ \AA}$ and $c = 12.2 \text{ \AA}$
- the most intense X ray diffraction peaks are related to the $[002]$ and $[202]$ planes, and the intense electron diffraction spots to the $[110]$, $[300]$ and $[330]$ planes.
- the two main sets of atomic planes visualized on fig.3 correspond to $[002]$ separated by 6.1 \AA (experimental 6.2 \AA) and $[212]$ separated by 2.77 \AA (experimental 2.8 \AA), the zone axis pattern being $[120]$. The measured angle between these two planes agrees fairly well with the calculated one from the proposed cell, 68° on the micrograph and 63° for the calculated value.
- the diffraction patterns shown on fig.4 correspond to the $[001]$ zone axis, with the $[110]$ and the $[\bar{1}20]$ on the first ring.

Two extreme models for the polymer chain can be derived from an ideal ordering of the thiophene units, whether all s-trans, or all s-cis. An alternated s-trans sequence would lead to a planar structure for the polymeric chain, whereas the rotating s-cis sequence would lead to a coil structure. The diameter of the coil can be calculated on the basis of the angle between the two exocyclic \angle bonds in the thiophene molecule, 147.6° ⁷. Each thiophene unit being rotated with an angle of 32.4° , one loop of the coil would involve 11 thiophene units. This coil should thus have an outer diameter of about 20 \AA , agreeing with the 19.4 \AA experimental value. In this coil model, the dopant anions should be intercalated between the thiophene molecular planes of two superposed loops, the inner hole of the coil, of about 12 \AA diameter, remaining empty. A theoretical coil pitch value can be estimated, using the experimental diameter of CF_3SO_3^- , 2.15 \AA ⁸

and the distance of closest approach between acceptor and donor molecule, $1.8 - 3.2 \text{ \AA}$ ⁹. The calculated value is $7.1 \pm 1.3 \text{ \AA}$. The two loops in the hexagonal lattice will correspond to a distance of $14.2 \pm 2.6 \text{ \AA}$, in good agreement with the experimental c parameter, 12.2 \AA .

This coil structure hypothesis has received a further confirmation from UV-Visible spectra analysis¹⁰. PMeT presents, as PT, a band maximum at 480 nm, corresponding to the expected value for conjugated polythiophenes¹¹. On the other hand, poly 3,4 dimethylthiophene and poly 3,4 diethylthiophene show an absorption maximum lying respectively at 330 and at 280 nm. This important loss of conjugation must be related to a large twist between adjacent thiophene units along the $\alpha\alpha'$ bond. Only the s -cis sequence agrees with such a high steric hindrance between adjacent thiophene units.

CONCLUSION

The substitution by methyl group of the carbon atoms in polythiophene lead to more regular and for the first time to a partial crystallization of the polymers. The X ray and electronic diffraction data agree fairly well with a coil structure hypothesis in which the dopant intercalation determines the pitch. Steric interactions however appear in 3,4 disubstituted polythiophenes which break the π delocalization along the polymeric chains. The geometry and the electronic characteristics of the dopant play also an important role for the charge delocalization in the polymers.