

## Synthesis and infrared properties of ethylenedioxythiophene and octylthiophene based copolymers

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### RÉSUMÉ

Le contrôle des paramètres physico-chimiques des PATs et des conditions de dopage conduit à des matériaux quasi-métalliques. Nous nous sommes ici orientés vers des copolymères du PEDOT et des PATs pour augmenter le caractère métallique tout en conservant les propriétés de solubilité.

**Mots-Clés :** Polythiophène - Réflectance - Infrarouge - Métallique.

### ABSTRACT

The control of the structural parameters and doping conditions of PATs lead to quasi-metallic materials. We have developed the synthesis of copolymers and PAT to enhance the metallic properties with conservation of the solubility.

**Key-Words :** Polythiophene - Reflectance - Infrared - Metallic.

### INTRODUCTION

The metallic state of conducting polymers has been widely investigated for the past years since the discovery of high conducting and processable camphorsulfonic doped polyaniline in *m*-cresol [1]. Poly(3-alkylthiophenes) (PATs) are known to be a class of polymers with good solubility and processability properties [2] and were recently found to display some metallic behavior, but less pronounced than in polyaniline [3]. The poly(ethylenedioxythiophene) (PEDOT) is well known for its high conductivity [4] but also for its insolubility. So, Copolymers of PAT and PEDOT would lead to a new class of processable thiophene based materials with increased metallic properties.

The quasi metallic behavior can be associated with high reflectivity in the IR range[1,3]. We herein describe the infrared properties of two new original copolymers of octylthiophene (OT) and EDOT, i.e., P(EDOT-OT) and P(EDOT-OT-EDOT). Their properties are compared to results already obtained with regioregular (HT) and regiorandom (R) PATs.

## EXPERIMENTAL

The synthesis and characterization of regioregular (>98% head to tail) and regiorandom (70% head to tail) PAT were reported elsewhere [3]. P(EDOT-OT) and P(EDOT-OT-EDOT) were synthesized following figures 1 and 2 [5].

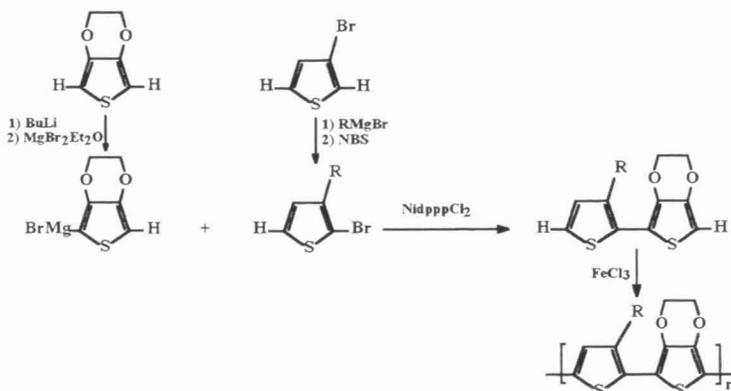


Figure 1 : General procedure for the preparation of the P(EDOT-OT)

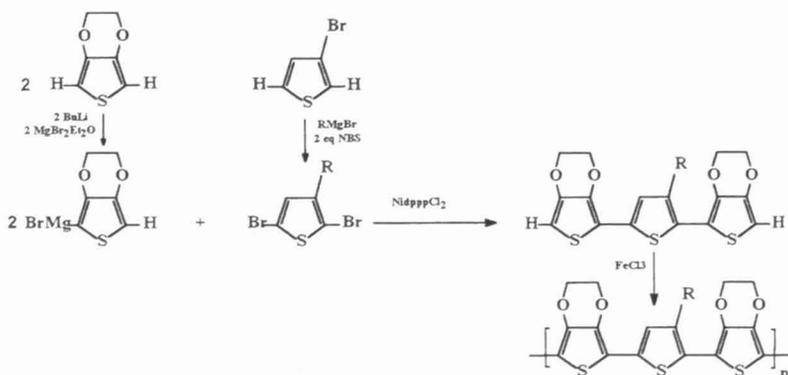


Figure 2 : General procedure for the preparation of the P(EDOT-OT-EDOT)

## RESULTS

In conjugated polymers, the extent of conjugation directly affects the energy of the  $\pi$ - $\pi^*$  transition. The effect of a micro structural irregularity is to create a sterically driven twist of the thiophene rings out of coplanarity with a decrease in conjugation. So, it is clear that HTPATs have a well-defined structure with no irregularity compared with RPATs (figure 3). Almost no change in the spectrum is observed when 50% of the octylthiophene moieties are replaced by EDOT. So P(EDOT-OT) and HTPOT must have the same conformation, indicating that no steric interaction between alkyl side chain and the EDOT bridge must occur. However, P(EDOT-OT-EDOT) spectrum is significantly redshifted. So, introduction of two EDOT moieties for one octylthiophene moiety induces a dramatic change in the conformation of the polymer. P(EDOT-OT-EDOT) can be considered as a small band gap polymer.

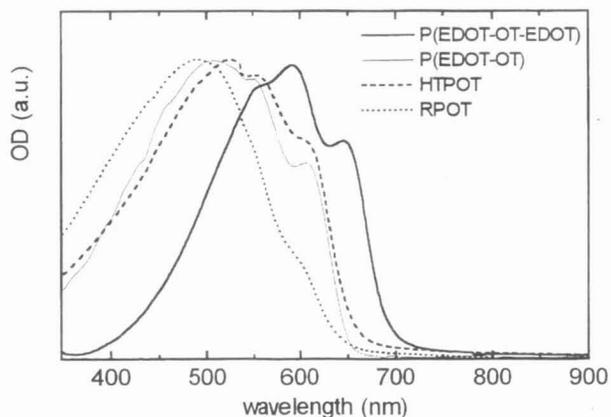


Figure 3 : UV-Vis spectra of polymer film cast from THF solutions

The visible-near IR spectra of nitrobenzene solution of  $\text{FeCl}_3$  doped (25%) polymers are shown in figure 4. As indicated by the two well defined bipolaron absorption bands at high energy, P(EDOT-OT) is characteristic of a localized doped system. Such feature suggests a disordered arrangement for the doped polymer chain. In the other hand, P(EDOT-OT-EDOT) is a more delocalized system than the regioregular poly(3-

dodecylthiophene) (HTPDDT) which is the more metallic system of the HTPATs [3]. Indeed, the first bipolaron band is significantly redshifted toward  $1 \mu\text{m}$  (versus  $0.85 \mu\text{m}$  for HTPDDT) and the second band appears without any maximum. This is characteristic of a quasi-metallic system. Figure 5 shows the reflectance spectra of films cast from nitrobenzene solutions. They are in good agreement with the vis-nir absorption properties. High metallic reflectance (70%) in the MIR range can then be obtained with P(EDOT-OT-EDOT). Such materials associate the processability properties of the PAT and the good conduction properties of the PEDOT.

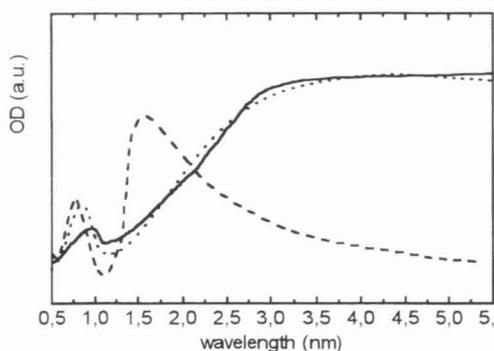


Figure 4 : Absorption spectra of a  $\text{FeCl}_3$  doped chloroform solution of (—) P(EDOT-OT-EDOT) (---) P(EDOT-OT) (.....) HTPDDT

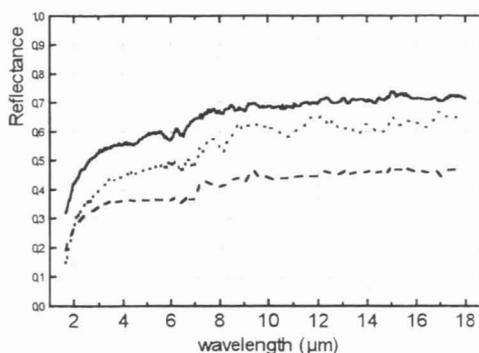


Figure 5 : IR reflectance of doped  $\text{FeCl}_3$  P3ATs film cast from nitrobenzene solutions of (—) P(EDOT-OT-EDOT) (---) P(EDOT-OT) (.....) HTPDDT

## CONCLUSION

We have developed a synthesis of EDOT and OT based copolymers. All these new conducting polymers are soluble and exhibit high reflectivity in the IR domain.

## REFERENCES

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