Physico-chemical Characterization, Structuration and Morphology of Photo-active Heterojunction (P3HT-PCBM) used in Organic Photovoltaic Cells

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Abstract: In this paper, we propose a study on the physicochemical, morphological and structural characterization of the organic semiconductors (P3HT) (poly-3-hexylthiophene) and the (PC61BM) [(6,6) - phenyl - C61 - butyric acid methyl ester], as well as their structuration in lamellae of quasi-crystalline fibrils for the first one and in Nano-crystals for the second. These conformational transitions that the two macromolecules undergo allow their self-assembly in chlorobenzene into a photoactive donor-electron acceptor layer. By controlling the morphology of the layer, its film deposition on the electrodes and its orientation with respect to which, a donor charge transfers optimization (P3HT) is favoured to the PC61BM acceptor which aims to improve the efficiency of the organic photovoltaic cells.

1 INTRODUCTION

The study and characterization of the physicochemical properties of semiconducting materials based on conjugated polymers has been the subject of numerous studies, however, we are faced with a panoply of problems and difficulties posed by their use which are far to be solved and continue to receive increased attention and research (Destruel and Seguy, 2007), (Vanlaeke et al., 2006), (Baran et al., 2017).

The materials of choice on which we will focus this study, will be P3HT (poly (3-hexylthiophene)) as electron donor and PC61BM [(6,6) -phenyl-C61-butyric acid methyl ester) as electron acceptor (Berson et al., 2007). Which will be used to develop a one-dimensional network of organization, structure and shape thus optimizing the charge transfer by opting for the low oxidation potential of the donor, which results in the reduction of the width of the forbidden band. In addition, the presence of the $\sigma, \pi, \sigma$ bonds, which lead to the conjugation of the chain, and constitute traps for the electrons, which are essential to preserve the structuration and organization of the P3HT-PC61BM, network which is necessary for the transport of Frenkel excitons of small radius because of the low dielectric constant of the two materials (Björström et al., 2005), (Brabec et al., 2010), (Alet et al., 2006).

Therefore, the purification and obtaining of high molecular weight polymers and high regio-regularity is the key to the development of the ordered structure network and the electron-donor-acceptor interface. Different techniques for preparing, characterizing and depositing the active layer on the substrate and on the electrodes in order to obtain the volume heterojunction capable of collecting the photons and generating the excitons, which will dissociate into charge carriers. These processes will provide access to pure polymers, their molecular weight, their chemical, electrochemical, thermal, electrical and optical properties, and finally to their optimum size and shape ensuring their self-assembly in order volume heterojunction providing access to improved energy conversion efficiency of organic photovoltaic cells (Chen et al., 2011), (Dang, Hirsch and Wantz, 2011), (Rispens et al., 2003), (Peumans, Yakimov and Forrest, 2003).
2 SYNTHESIS AND CHARACTERIZATION OF THE ACTIVE LAYER

2.1 P3HT Donor Material

2.1.1 Synthesis and Spectroscopic Characterization

The synthesis is carried out starting from a starting material, which is 3bromo-4-methylthiophene-C11 in two stages starting from 4 g of the reagent, an alkylation followed by an aromatic nucleophilic substitution in the presence of Cu(I), then the brominated derivatives are purified by evaporation after isolation by chlorobenzene extraction of 3 hexyloxythiophene. For the polymerization, several processes are possible: Electrochemical polymerization, polymerization by chemical coupling of two aromatic rings catalyzed by complexes with transition metals, or opt for the polymerization by oxidizing chemical means the presence of (FeCl3, MoCl5, RuCl3) and then eliminates the mineral impurities methanol hot followed by training via a cyclohexane washing and finally proceeded to a purification by washing with soxhlet.

![Synthesis scheme and polymerization yields of P2 to P5.](image)

Figure 1: Synthesis scheme and polymerization yields of P2 to P5.

After extraction of the polymers with dichloromethane or with chloroform, the compound is isolated by filtration-centrifugation. And in order to control the regioregularity due to the presence of hexyl and hexyloxy chains which conditions the electrical and photovoltaic properties of the P3HT by, playing either on the temperature of the reaction or the steric hindrance, and it is found that the longer the polymer chain is, the higher its molecular weight, and the greater the degree of regioregularity which allows the polymeric chains of organize in ordered lamellar structure of fibrils, which are detected by UV absorption spectroscopy, and the resistance of fibril amalgams (lamellae) which is due to the interaction between the lateral alkyl chains is confirmed by 1H NMR spectroscopy, the aromatic protons close to the thiophene ring junctions are influenced by these and the aliphatic protons of CH3 and CH2 are influenced by the couplings, which makes it possible to observe the existence of long chains, thus of high molecular weight, and this gives them a high degree of regioregularity.

![Figure 2: Comparison of the proton NMR spectra in tetrachloroethane of poly (3-hexyloxy-4-methylthiophene) obtained by chemical coupling of Mc Cullough P3't type by oxidative coupling P3.](image)

2.1.2 Measurement of the Molar Mass of P3HT

Many techniques are existing for determination of molar mass of macromolecules in solution for example: viscosimetry, osmometry, polyacrylamid gel electrophoresis PAGE, static light scattering SLS, steric exclusion chromatography SEC, relaxation time visco-elastometry RTVE and ultracentrifugation...etc. The molar mass is obtained specially by measurements of the viscoelastic relaxation time expressed by the Zimm-Rouse relationship:

\[
\tau = \frac{M \eta_0 [\eta]}{R T} \frac{1}{\Lambda} \tag{1}
\]

\(M\): Molar mass of the molecule  
\(\Lambda\): Form factor.  
\(T\): Temperature.  
\(R\): Constant of perfect gases.  
\(\eta_0\): Viscosity of the pure solvent.  
\([\eta]\): Intrinsic viscosity of the solution of the polymer given by the formula of Staudinger:

\[
[\eta] = \frac{\eta}{\eta_0} = 1 + K.C.M^\alpha \tag{2}
\]

Where \(K\) and \(\alpha\) are constants and \(C\) is the concentration of the solution.
For de macromolecules on the long chain, we have the semi empirical relation:

\[ M = 1,45 \times 10^8 \tau^{3/5} \]  \hspace{1cm} (3)

The molar mass of P3HT in solution can also be measured by SEC molecular exclusion chromatography using the following formula:

\[ \ln \frac{1}{KM^a} = a \frac{V_e-V_0}{V_t-V_0} + b \]  \hspace{1cm} (4)

Or a and b are constants, K and a depend on the geometry of the studied polymer

\( V_e \): Volume of the elapsed buffer of the column before the exit of the polymer studied.

\( V_t \): Volume of the elapsed buffer of the column before the exit of the small molecules.

\( V_0 \): Volume of the elapsed buffer of the column before the release of very large molecules.

It is even possible to use static light scattering (SLS), gel electrophoresis, osmometry, translational diffusion, ultracentrifugation (sedimentation mass \( M_z \)), etc., to measure the molar masses on the number and on the weight of the polymer studied P3HT, which have the value:

\( M_n = 22620 \ \text{g/mol (by SEC and osmometry)} \)

\( M_w = 33910 \ \text{g/mol (by SLS and SEC)} \)

And an apparent molar mass of the macromolecule dependent on the molecular anisotropy \( \delta \) by equation:

\[ \delta = \sqrt{\frac{5}{4} \left( \frac{M_{app}}{M_w} - 1 \right)} \]  \hspace{1cm} (5)

The parameter \( \delta \) is obtained by used of flow birefringence

Table 1: Molecular masses and polydispersity index obtained by SEC in solution in polystyrene equivalent THF for the batch of P3HT from Aldrich and Rieke.

<table>
<thead>
<tr>
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<th>( M_n ) [g/mol Eq PS]</th>
<th>( M_w ) [g/mol Eq PS]</th>
<th>( I_p )</th>
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<td>P3HT</td>
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<tr>
<td>lot aldrich</td>
<td>22 620</td>
<td>33 910</td>
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<td>P3HT</td>
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<tr>
<td>lot Rieke</td>
<td>24 180</td>
<td>37 590</td>
<td>1.50</td>
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Figure 3: Chromatogram obtained for the different fractions of P3.

This chromatogram thus reveals the presence of three fractions obtained from the polymer P3 in addition to the complete p3 as a function of their elution time different can be distinguished and separated and by an optical method (spectrophotometry, differential refractometry, ...) can determine their abundance and also one can have information on the distributions of their molar masses.

2.2 Acceptor Material PCBM

Methyl [6,6]-phenyl-C61-butyrate PCBM is an electron-accepting organic semiconductor consisting of a C61 fullerene unit (a conventional C60 bearing a methylene -CH2- laterally) substituted with a phenyl group, C6H5 on one side as well as with a butyric acid ester -(CH2)3-COOH and methanol CH3OH, forming, on the other side, a methyl butyrate group -(CH2)3-COO-CH3.

It is extensively studied in the context of polymer 2,3 photovoltaic cells to form p-n junctions with polythiophenes such as P3HT. As regards its molecular weight, it is determined either by osmometry, viscosimetry, quantitative and qualitative chemical analyzes or by mass spectrometry \( M(\text{PCBM}) = 910.8804 \pm 0.0592 \ \text{g/mol.} \)

The PCBM is solubilized in chlorobenzene, which results in its crystallization into nanocrystals grouped together with different crystalline orientations. This crystallization depends on the nature of the solvent, in orthodichlorobenzene the polymer crystallizes in the monoclinic system, in contrast in chlorobenzene, it crystallizes in the triclinic system that promotes optimal electron transport. The covalent grafting of C60 fullerene with PCBM (necessary for more delocalization of electrons) is carried out by, immersing it in a
solution of C$_{60}$ dissolved in benzene or toluene with a concentration of 1 to 4 mmol/l. Then heating the mixture under reflux under a nitrogen atmosphere for 2 to 3 days. Then rinsing the samples obtained with the pure solvent in order to remove the physisorbed C$_{60}$ molecules. The deposition of the PCBM is carried out on the surface of a silica substrate in order to measure the thickness by ellipsometry, formed layers that can be calculated from the following formula:

$$d = \frac{M_1\lambda_2}{2(n_1\lambda_1)\Delta_2 - n_2\Delta_1}$$  \hspace{1cm} (6)

M: Number of oscillations.

$\lambda_1$ and$\lambda_2$: Wavelengths of the light passing through the solution and the substrate.

$n_1(\lambda_1)$ and$n_2(\lambda_2)$: indices of refractions of the two mediums as a function of $\lambda_1$ and$\lambda_2$.

The experimental measurement of the thickness results in the value $d = 44$ Å. This shows that the growth is carried out by 4 layers from bilayers.

Also the thickness can be measured by visible UV absorption spectrophotometry by applying the Beer-Lambert law:

$$A = a.d.\rho$$  \hspace{1cm} (7)

Where $A$ is the absorbance, $\alpha$ coefficient of absorption of the layer vis-à-vis the radiation, $\rho$ the density of the layer, $d$ the thickness of the studied layer.

The covalent grafting between PCBM and C60 fullerene leads to changes in the absorption and luminescence spectra of PCBMs that can be characterized by Fourier Transform Infrared Spectroscopy (FTIRS), so the evolution of the substrate layer can be followed by surface-excited Raman spectroscopy (SERS), this grafting is manifested by the appearance of the characteristic absorption bands in the infrared. For the visible UV spectrum, we observe the appearance of a single absorption band and this reveals a small amount of C60 presented on the layers of PCBM. The quantity of molecules on the surface remains constant as shown by ESCA (electron spectroscopy for chemical analysis) studies.

The stereochcmistry of PCBMs is studied in 2D ((1H) and (13) C) NMR solutions in Deuterated solvents (CDCl3, CD2Cl2) and the morphology of the layer is characterized by Atomic Force microscopy.

The mass percentages of C60 in the PCBM are determined by thermogravimetric analysis from the mass-temperature diagrams from which the different degradation temperatures of the compound can be derived. Concerning the P3HT crystallization exotherms, the fusion endotherms are obtained by the differential scanning calorimetry as well as the melting and crystallization temperatures of the P3HT: $T_{fus} = 232.4$°C and $T_c = 201.5$°C.

The thermal effects of crystallization and melting, the heating curves and those of the two materials were studied by microcalorimetry($\Delta H_{fus} = 20 J/g$ and $\Delta H_c = 20 J/g$) and the differential thermal analysis, as well as the crystallinity index of P3HT expressed by:

$$X_c = 100 \frac{\Delta H_{fus}}{\Delta H_0}$$  \hspace{1cm} (8)

Or

$\Delta H_{fus}$: The enthalpy of fusion.

$\Delta H_0$: The reference enthalpy.

### 3 CHARACTERIZATION AND ORGANIZATION OF THE ACTIVE LAYER P3HT-PCBM

#### 3.1 Organization of Polymer Chains P3HT

The solubilization of P3HT in chlorobenzene is dependent on the purity of the polymer, its high molecular weight which can reach 50000 g / mol, the stoichiometry, the chemical coupling conditions (catalyst type, quantity and concentration) the reaction conditions (1): absence of oxygen, good magnetic or mechanical stirring) and finally the solubility of the monomer and the polymers in the reaction solvent. And in order to lead to a strong fibrillar organization of the P3HT chains in the form of a network leading to a high value of current density, it is necessary that the interaction between the polymer chains is more intense than their interaction with the solvent. This aggregation of chains in fibrillar structure is governed by ($\pi$-stacking) and conditioned by the structure and the chemical nature of the polymer, the interchain interactions (hydrogen bonds, \( \pi \) interactions, dipolar interactions...), solute solvent interactions and finally the interactions of the substrate surface with the polymer chains. The solvent of choice used for structuring chains on fibrils is p-xylene.

$T_{ebu} = 138°C$; $\mu = 0.0$; $\varepsilon = 2.3$; $n_0^{20°C} = 1.458$ which completely dissolves P3HT. At a temperature of 80°C. For a concentration ranging from 0.5% (wt) to 3% (wt) for one hour, which leads to an organization of the chains or fibrils under low temperature $\nu_{cooling} = 20°C/h$ for 4 hours in the dark, the detection of these fibrils is carried out by
visible UV spectroscopy, we observe 3 absorption bands 525 nm; 555 nm; 610 nm at a concentration of 1% (wt) in p-xylene at a temperature of 80 °C, identical to those of a P3HT film deposited by spin coating on a glass substrate for 2 h to 48 h with \( \nu = 20 ^\circ \text{C.}/h. \)

This makes it possible to observe a good stack of chains, thus a structure identical to that obtained in the solid phase. An increase in the absorbance with the fibril structuring explained by induced dipole-induced dipole interactions, such as, for example, London dispersion between the two chains of interaction energy:

\[
U_L = -\frac{\tilde{\alpha}_1 \tilde{\alpha}_2 n e E_{ox}^D}{12\pi \varepsilon r^6} \quad (9)
\]

\( E_{ox}^D \): Donor oxidation potential (0.21 V) measured electrochemically (cyclic voltammetry) or by UV and XPS spectroscopy (X-RAY PHOTO ELECTRON SPECTROSCOPY)

\( \tilde{\alpha}_1 \) and \( \tilde{\alpha}_2 \): Anisotropic Polarisabilities of the two chains.

\( \varepsilon \): Dielectric constant of the solvent

\( r \): The sum of the two Van-der-Waals radii of the two chains

\( e \): Elementary charge

\( n \): Number of transferred electrons

Interactions between fibrils can occur and result in agglomeration of these which can be dispersed by agitation of the solution.

Studies of the shape of these fibrils show their lamellar organization in rod structure (measurement of diffusion constant, flow birefringence, sedimentation coefficient, electron microscopy, coefficient of friction, radius of gyration, ...) On the other hand, the transition from the disordered form to the ordered form induces a bathochromic effect which manifests a sol-gel transformation with an isobestic point of 450 nm, thus an increase in the regioregularity of the polymer, an optimization of structuration chains requires the control of the percentage of the fibrils in solution by means of centrifugation followed by filtration and deposition on the substrate by the dipping method or by the spin-coating method and according to the concentration used it is possible to obtain isolated fibrils, fibrillar networks or complete layers of morphology characterized by SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy): for the isolated fibrils found as dimensions: 0.5 μm(L)/5 μm; 5 nm(ε15 nm 30nm/(50nm)

Thus, the presence of the non-regioregular poly-3-alkylthiophene is observed, which leads to the conclusion that the texture of the spin-on film on the glass substrate coated with ITO (indium tin oxide) which represents the anode, is determined by the percentage of fibrils which is demonstrated by the AFM, the higher this percentage is, the higher the fibril surface concentration is important, this leads to a controlled structuring which improves further by heat treatment of P3HT (at 150 °C. for 5 min) which doubles crystalline domains and halves the disorder, as shown by XRD (X-ray diffraction) studies on films deposited on silicon substrates, lamellar organization of fibrils with inter-lamellar distance of 16.2 Å° and a coherence length \( l_c \) of 173 Å° are observed and this is due to the small thickness of the lamellae, also the stacking fluctuations are lower than those of the unannealed P3HT, so the heat treatment results in the increase of the regular order in the fibrils.
Finally, and to close with P3HT electrochemical studies by cyclic voltammetry and electrochemical impedance spectroscopy have shown that this fibrillar organization modifies the potential for oxidation-reduction of fibrilated P3HT as well as the HOMO and LUMO energy. By cyclic voltammetry at a scanning rate of 20 mV/s, two oxidation waves are observed for the unstructured P3HT, which means the presence of two forms: one structured with low oxidation potential and the other amorphous with high potential. As regards the fibrillated P3HT a single wave of oxidation observed therefore the presence of a single form.

There is a relationship between the energies of the HOMO and LUMO orbitals and the threshold redox potentials

\[ E_{\text{LUMO}} = -\left(4.8 + E_{\text{threshold}}^{\text{red}}\right) \]  
\[ E_{\text{threshold}}^{\text{red}} = -2.55 \text{V} \]  
\[ E_{\text{HOMO}} = -\left(4.8 + E_{\text{threshold}}^{\text{ox}}\right) \]  
\[ E_{\text{threshold}}^{\text{ox}} = 0.22 \text{V} \]  

These measures its calibrated compared to the ferrocene

\[ \Delta E_{\text{gap}} = e \left[ E_{\text{threshold}}^{\text{red}} - E_{\text{threshold}}^{\text{ox}} \right] \]  
\[ \Delta E_{\text{gap}} = -2.76 \text{ ev} \]

This three equations is very important because is represent relations between quantum chemical parameters \( E_{\text{LUMO}}, E_{\text{HOMO}} \) and electrochemical parameters \( E_{\text{threshold}}^{\text{red}} \) and \( E_{\text{threshold}}^{\text{ox}} \).
3.2 Organization of the Acceptor Donor Active Layer (P3HT-PCBM)

Donor and acceptor were mixed together after thermal annealing at 150 °C for 5 min with the use of the wrong solvent (chlorobenzene C = 10:10 mg/ml) resulting in self-assembly of P3HT and PCBM therefore the formation of a network of one dimensional objects by induced dipole interactions of the two polymers superior to the solvent-polymer polarization interactions, thus an active layer with donor-acceptor interfaces. The presence of PCBM does not disturb the structured P3HT organization but leads to the appearance of vibronic bands (515 nm, 551 nm, 603 nm) characterizing the formation of the active layer that modify the absorption spectrum of P3HT (hyperchromic effect).

The deposition of the layer on the ITO (Indium tin oxide) anode which covers the glass substrate is done by spin-coating at 2000 rpm for 2 min, the cleaning of the substrate of the impurities is carried out by ethanol under ultrasound. The aluminum cathode is deposited by evaporation in vacuo and the glass substrate is cleaned of the impurities is carried out by ethanol under ultrasound. The aluminum cathode is deposited by evaporation in vacuo and the glass substrate is cleaned of the impurities is carried out by ethanol under ultrasound. The aluminum cathode is deposited by evaporation in vacuo and the glass substrate is cleaned of the impurities is carried out by ethanol under ultrasound.

Finally, the controlled morphology of the active layer leads to the increase of the potential of the open circuit Voc:

$$V_{oc} = \frac{1}{e} (E_{HOMO}^{u} - 0.3) \quad \text{V} \quad \text{(11)}$$

or

$$E_{LUMO}^{u} = -4.3 \text{eV}$$

for the PCBM and $$V_{oc} = 0.6 \text{V}$$

4 CONCLUSIONS

The use of different physicochemical techniques and nanotechnology processes to characterize the electron donor and acceptor polymers allows the control at the nanometer scale of the morphology and the texture of the active layer. Optimal organization of the two materials P3HT and PC61BM, in the acceptor donor heterojunction, thus obtaining a privileged orientation of the molecular fibrils of P3HT and nano-crystals of PC60BM with respect to the electrodes, it is furthermore advantageous to macroscopically transfer the This is due to the stacking of the polymer chains and the weak coupling between them, which further optimizes inter-charge transfer at the expense of intrachain transfer, which can hardly lead to a macroscopic transfer of charge and thus to usable electric currents.

And this is of course considered as a step in advance of the molecular nanoelectronics that eclipses day by day and that relegates in the shadows conventional microelectronics derived from silicon and inorganic semiconductors.

REFERENCES


