

# Structural, mechanical and optical properties of conjugated polymers on a stretchable substrate under mechanical load

M. Aliouat<sup>a,c</sup>, S. Escoubas<sup>a</sup>, L. Grodd<sup>b</sup>, S. Grigorian<sup>b</sup>, D. Duche<sup>a</sup>, M. C. Benoudia<sup>c</sup>, O. Thomas<sup>a</sup>

a. Aix-Marseille University, CNRS, IM2NP UMR 7334, Campus de St-Jérôme, 13397 Marseille, France

b. Institute of Physics, University of Siegen, Walter-Flex-Strasse 3, D-57068 Siegen, Germany

c. L3M ENSMM Annaba, Ex CEFOS Chaiba BP 233 RP Annaba, W129, Sidi Amar, Algeria

...

## Abstract:

*Grazing incidence X-ray diffraction (GIXRD) is used to study the structural properties of conjugated organic thin films (PTB7 and P3HT) on flexible substrates (thin PDMS), more precisely to measure the strain and crystallite size in the crystalline part of the polymer, under large stretching by using a specially designed stretching device. In parallel, spectroscopic ellipsometry is used to determine the optical properties and to extract the electronic transitions of PTB7 and P3HT in the UV-visible range. In our study, we correlate the structural and the optical properties of these polymers under large strain.*

**Keywords: structural and optical properties, strain, P3HT, PTB7, PDMS.**

## 1 Introduction:

The development of organic-based flexible electronics is a very important research area, which opens extremely promising opportunities for innovative and cheap devices (OLEDs, OFETs, OPV,...) [2,3,4,5,6]. Conjugated polymers play a role of increasing importance in the field of organic semiconductors. These conjugated polymers are conducting macromolecules with large number of repeating units and, in contrast to small molecules, are easy soluble in most of the common solvents. Therefore, the devices based on the conjugated polymers can be processed at low cost from solution or by printing technologies. Poly (3-hexylthiophene) (P3HT) is often used as a model system since it provides rather good electrical properties (i.e. field effect mobility). For photovoltaic applications, one promising copolymer with high power conversion efficiency is Polythienothiophene/benzodithiophene (PTB7) [1,15]. Moreover, the use of a flexible or even stretchable support opens many new applications in the fields of entertainment or health. There are indeed strong hopes that organic-based flexible electronics become widespread in the coming years. The autonomy of such devices will rely on their low consumption and the use of energy harvesting. In that respect organic solar cells are very promising. However, the relationship between optical properties and structural order in such

conjugated polymers is still little explored [4,6,7,17], and in particular the change of these properties under stress needs to be addressed.

We performed investigations of the structural properties of P3HT and PTB7 thin films drop casted on stretchable substrates of poly (diméthylsiloxane) (PDMS). The structural properties of the polymers have been investigated by in situ grazing incidence X-ray diffraction under applied tensile stress at DiffAbs beamline at SOLEIL (Saclay, Paris), by using a dedicated stretching setup. Modification of the structure has been monitored under stretching (up to 20%). In parallel we performed a variable angle spectroscopic ellipsometry study in order to extract the optical indices (n and k) of the materials, which are a footprint of the polymer microstructures.

## 2 Experimental setup:

### 2.1 Sample preparation:

For in situ X-ray diffraction under applied tensile uniaxial stress, stretchable samples are prepared by drop casting of P3HT and PTB7 solutions on Polydiméthylsiloxane (PDMS) stretchable substrates. The solvent and concentration of these solutions are summarized in **table 1**. For the ellipsometric measurements polymers were spin coated with a speed of 500rpm on a rigid glass substrate. The spin coating parameters are given in the **table 2**. The thicknesses of polymers thin layers spin coated on glass substrates were measured using a mechanical Bruker Dektak profilometer, and are reported in **table 2**.

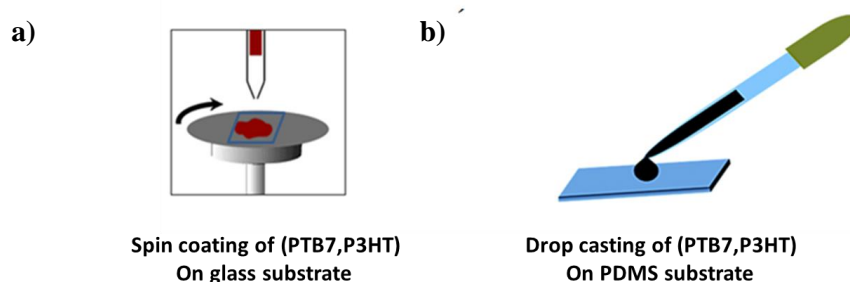


Fig. 1. a) Spin coating method, b) Drop casting method

Polymer	Substrate	solvent	Concentration (mg/ml)
PTB7	PDMS (387 $\mu\text{m}$ )	chlorobenzene	20
P3HT	PDMS (387 $\mu\text{m}$ )	chlorobenzene	15

Table 1. Drop casting parameters

substrate	polymer	Solvent	Concentration (mg/ml)	Temperature	Spin speed (rpm)	Time (sec)	Thickness (nm)
Glass	P3HT	chlorobenzene	15	ambient	500	60	213 $\pm$ 19
Glass	PTB7	chlorobenzene	20	ambient	500	60	88 $\pm$ 7

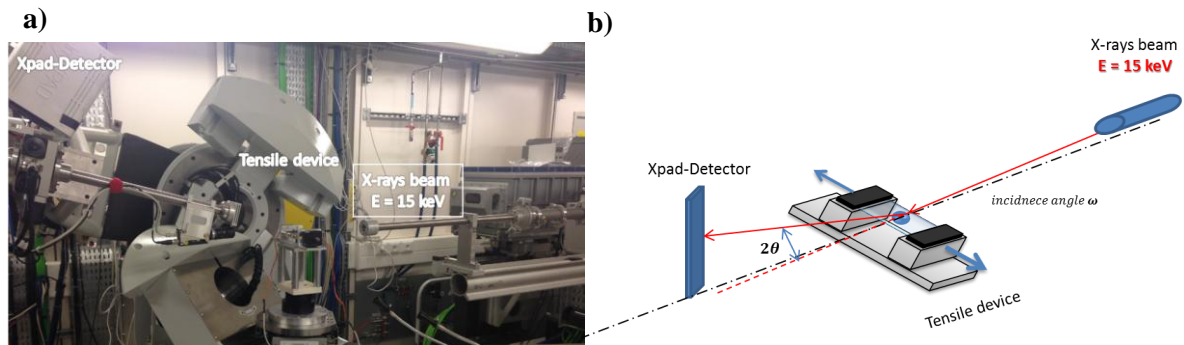
Table 2. Spin coating parameters

### 2.2 Grazing incidence X-ray diffraction:

Structural properties of thin film polymers are measured under grazing incidence x-ray diffraction at DiffAbs beamline (SOLEIL synchrotron at Saclay, France) using a wide area 2D XPAD detector (560\*840 pixels of 130 $\mu\text{m}$ ). The incident angle of x-rays (beam size of 170\*270  $\mu\text{m}$ ) is chosen at 0.1°-0.2° and the experiment is conducted at a fixed energy of 15 keV. The measurements are recorded from the XPAD detector at different 2 $\Theta$  ranges in out-of-plane direction (from 1° to 8° and

from  $9^\circ$  to  $16^\circ$ ). An integration of 2D intensity maps allows to plot and to fit the diffraction peaks with good statistics and accuracy.

The University of Siegen provided a specially designed stretching device with a controlled load (where uniaxial loading - up to 50% can be achieved).



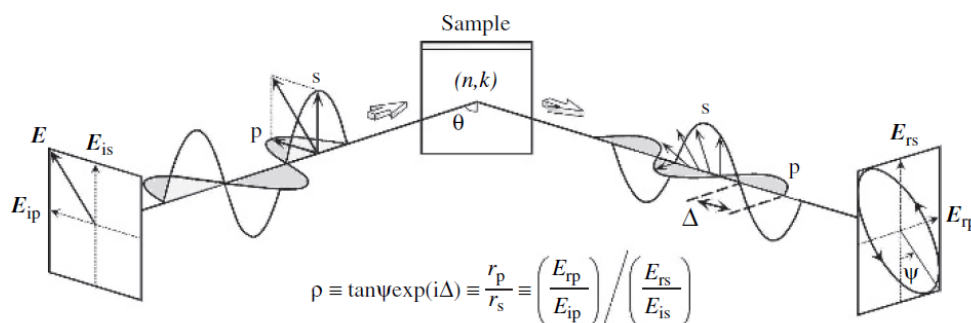
**Fig. 2.** a) DiffAbs goniometer with stretching device b) Real time grazing incidence X-Ray diffraction (GIXRD) setup schematic

### 2.3 Spectroscopic ellipsometry:

Spectroscopic ellipsometry is a powerful technique to investigate the electronic structure of semiconductor polymers. This technique is used to determine the optical properties and to extract the electronic transitions of thin films in the UV-Visible range.

We performed variable angle spectroscopic ellipsometry measurements (VASE) with a semi lab rotating compensator ellipsometer (RCE) using a micro spot which focuses the beam ( $\sim 100\mu\text{m}$ ), and data were measured from 1.5 to 5 eV at incidence angle of  $55^\circ$ ,  $60^\circ$ ,  $65^\circ$  and  $70^\circ$ . For the sake of clarity, only results of  $70^\circ$  are presented in the following. For data analysis the films are considered as homogeneous and isotropic. The SEA software [10] has been used to minimize the mean squared error (RMSE) between the measured and the fitted data through the Levenberg-Marquardt algorithm.

Our measurements are performed with thin films of PTB7 and P3HT spin coated on rigid glass substrates (**table 1**). The aim of these measurements is to extract the optical indices  $n$  and  $k$  of these materials.



**Fig. 3.** Schematic view of the ellipsometry principle

## 3. Results and discussion:

### 3.1 Grazing incidence X-ray diffraction:

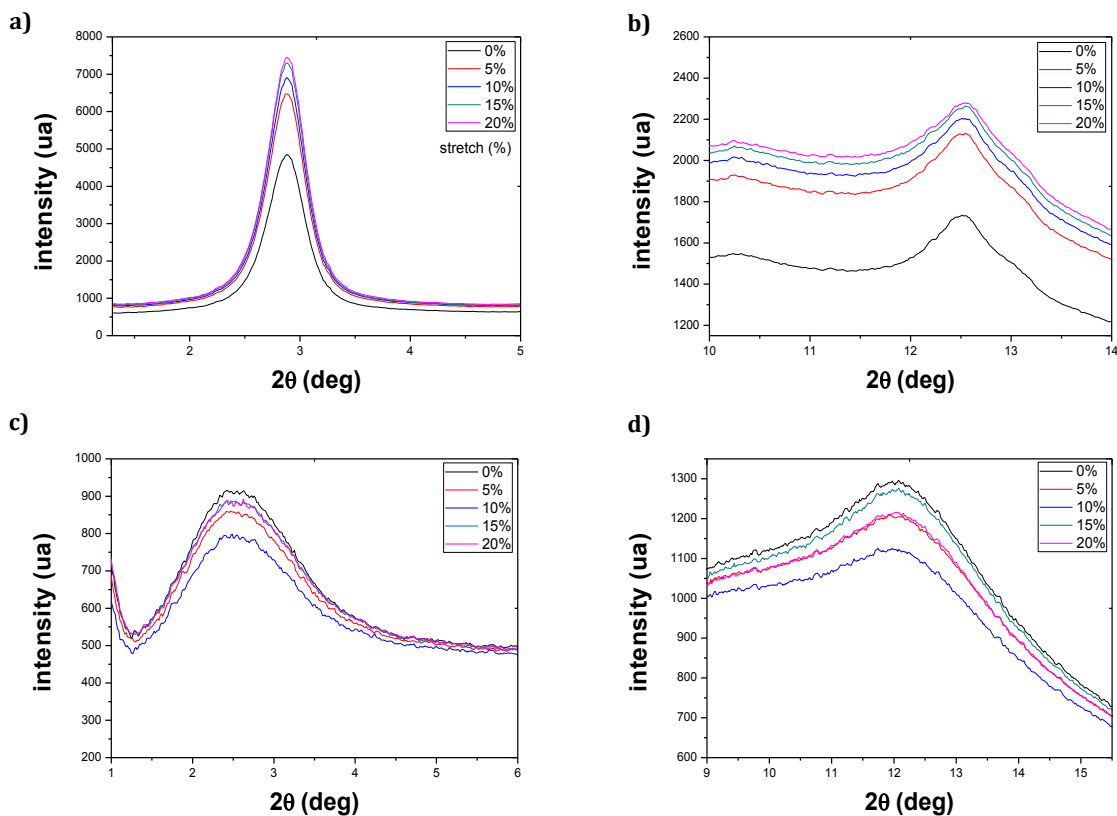
We employed grazing incidence x-ray diffraction to probe PTB7 and P3HT thin films in order to check the changing of distance between the polymer chains under stretching of 5%, 10%, 15% and 20%, we have stopped at 20% because the layer was delaminated. The x-ray diffraction intensities as a function of  $2\theta$  are obtained after azimuthal integration over the 2D detector area. The GIXRD

results on P3HT and PTB7 thin films are shown in **fig. 4**, we followed the (100) and (020) peaks [13,14,15] in the out-of plane direction for the two polymers (**fig8**).

P3HT shows better crystallinity and order than PTB7 with a FWHM of the scattering peaks three times smaller. Crystallites size are calculated via the Scherrer equation:  $\tau = \frac{K\lambda}{\beta \cos \theta}$ , where  $\lambda$  is the wavelength,  $\beta$  is the FWHM of scattering peak at  $2\theta$  Bragg angle, and  $K$  is the Scherrer's constant ( $K=0.93$ ) as derived in Scherrer's paper. We obtained crystallite size of 10.3 nm for P3HT (100) peak and 2.76nm for PTB7 (100) peak.

As shown in **fig. 4 (a, b)** shows for P3HT, at 0% of stretch we measure the (100) peak and (020) peak positions respectively at  $2\theta = 2.87^\circ$  and  $12.54^\circ$  corresponding to d-spacing of 1.65 nm and 0.38 nm (respectively). After a stretch of 20% we notice a very small shift of (100) peak position by  $0.003^\circ$ , and a shift of  $0.026^\circ$  for the (020) peak position.

Also **fig. 4 (c, d)** shows for unstretched PTB7 the (100) peak and (020) peak positions respectively at  $2\theta = 2.50^\circ$  and  $12.20^\circ$  corresponding to d-spacing of 1.89 nm and 0.39 nm (respectively). After a stretch of 20% we notice a small shift of (100) peak position by  $0.045^\circ$ , and a shift of  $0.023^\circ$  for the (020) peak position.

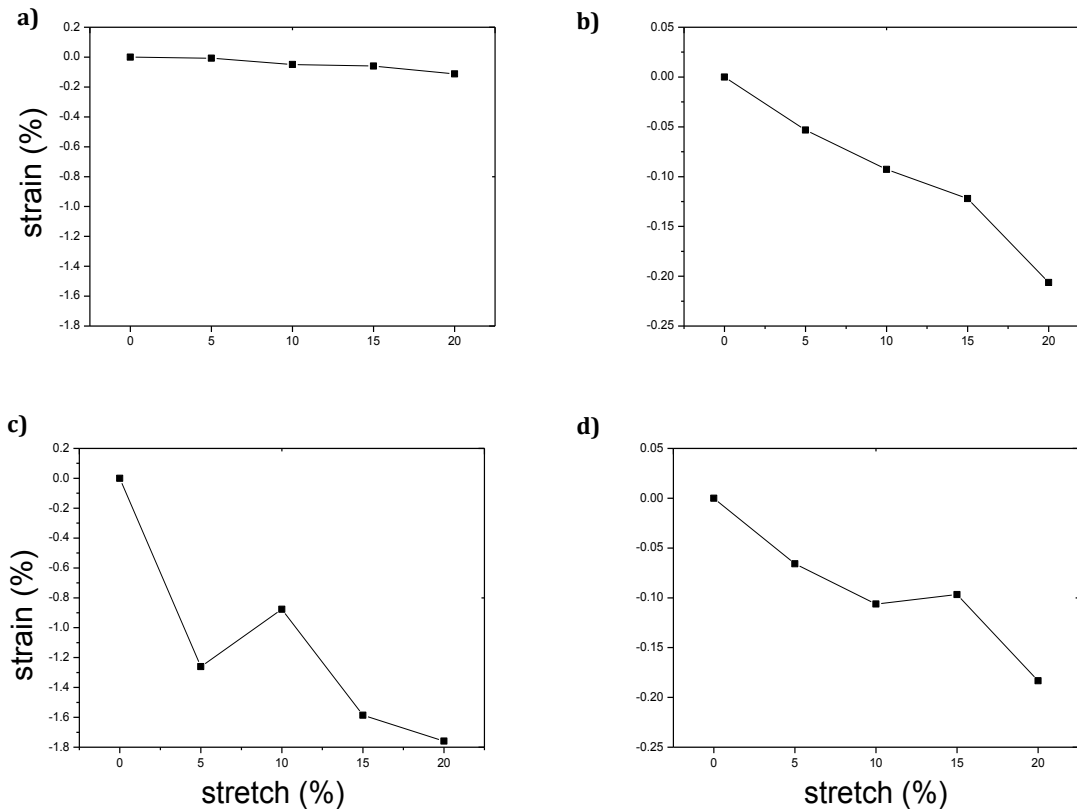


**fig. 4.**The GIXRD profiles for: **a)** P3HT (100) peak **b)** P3HT (020)  $\pi$ - $\pi$  stacking peak **c)** PTB7 (100) peak **d)** PTB7 (020)  $\pi$ - $\pi$  stacking peak, under stretching of 0%, 5%, 10%, 15%, and 20%

To better understand, we plot the strain variations as a function of the stretching. Strain ( $\epsilon$ ) is defined as the change of the distance between plans ( $d - d_0$ ) divided by the original (initial) distance ( $d_0$ ) [12]

$$(\epsilon \%) = (d - d_0) / d_0 \times 100$$

The strain of PTB7 and P3HT thin films corresponding of different peaks under 0%, 5%, 10%, 15%, and 20% of stretch are shown in **fig. 5**.



**fig. 5.** The strain profiles for: **a)** P3HT (100) peak **b)** P3HT (020)  $\pi$ - $\pi$  stacking peak **c)** PTB7 (100) peak **d)** PTB7 (020)  $\pi$ - $\pi$  stacking peak, under stretching of 0%, 5%, 10%, 15%, and 20%.

As shown, for the two polymer thin films and until 20% of stretching we notice a very small value of strain in the out-of plane direction. We might assume that the applied stretch is preferentially dissipated in the amorphous phase, which is a softer region, as it is also found by Chien Lu and Al [17]. Moreover, this low values might be due to cracking of the polymer [17] or even delamination of the thick drop-casted layer. We observed that the polymer drop casted layer was totally delaminated after 20 % stretch.

We plan to optimize PDMS surface preparation in order to deposit thinner and more homogeneous spin-coated layers.

## 3.2 Spectroscopic ellipsometry measurements:

Our first measurements were performed with spin coated polymers on rigid glass substrates in order to build their dispersion law models.

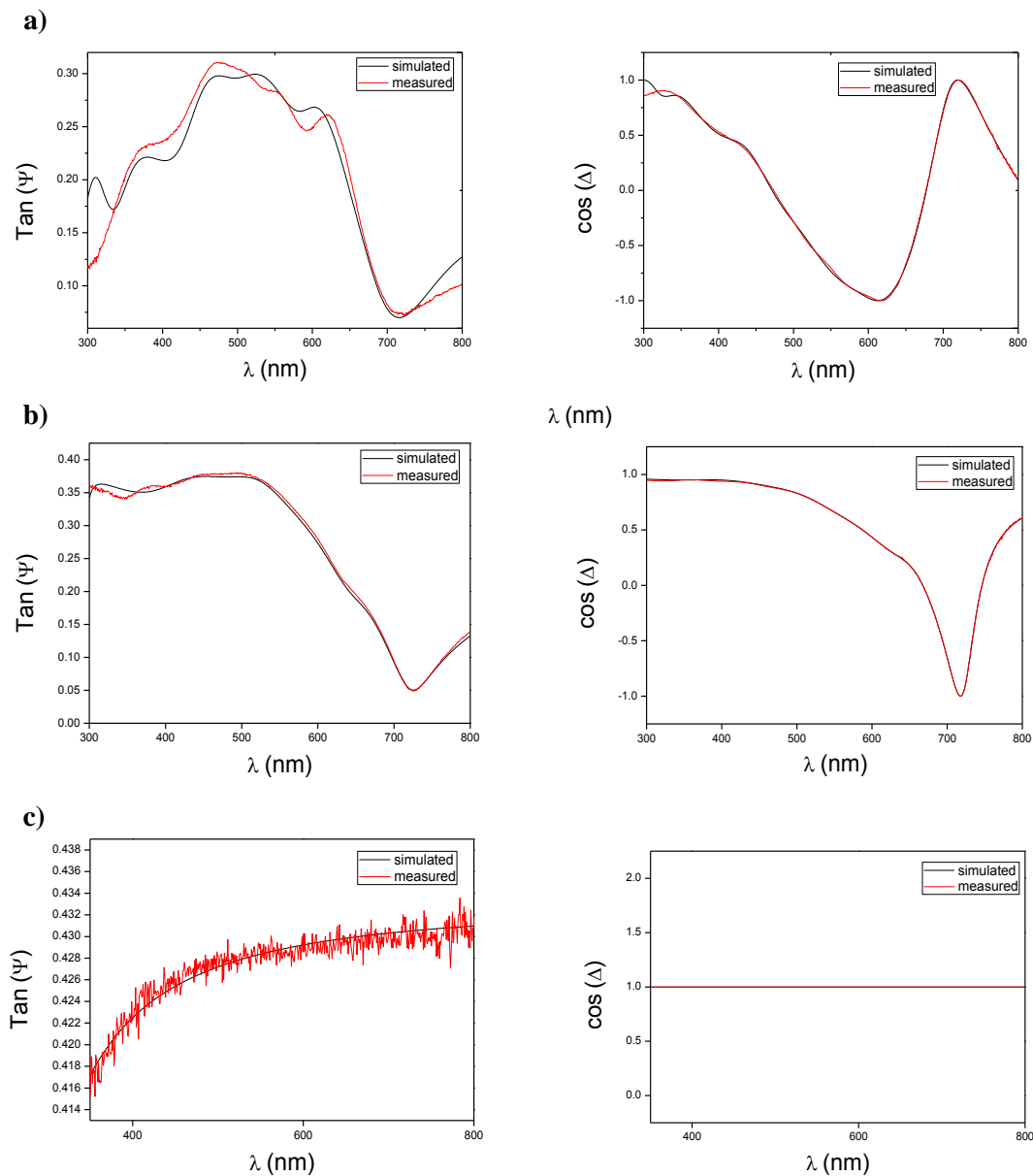
### 3.2.1 Spectroscopic ellipsometry data analysis:

We used the VASE to determine the dielectric functions of P3HT and PTB7 thin films. It consists in measuring of the polarization state change of beam light, by measuring the  $\Psi$  and the  $\Delta$  angles. These two angles are defined from the ratio of the Fresnel reflection coefficients  $r_p$  and  $r_s$  : [8,9]

$$\frac{r_p}{r_s} = \Psi e^{i\Delta}$$

Where  $\tan(\Psi) = \frac{|r_p|}{|r_s|}$  represents the relative amplitude attenuation and  $\Delta = \arg(r_p) - \arg(r_s)$  represents the change in the phase difference. In order to extract the dielectric  $\varepsilon(\lambda)$  constant of the polymers thin films, the measured  $\tan(\Psi)$  and  $\cos(\Delta)$  parameters were fitted by using optical

models. To take into account their wavelength dependence, the polymer dielectric functions have been fitted with Kramer Kroning consistent models composed of sum of Gaussians. Such models are adequate for the parameterization of polymer dielectric constants in the inter band region [8,9].



**Fig.6.** Simulated and calculated ellipsometric data  $Tan(\Psi)$  and  $cos(\Delta)$  for: (a) P3HT thin film [ $R^2 = 0.99$ ; RMSE = 0.03], (b) PTB7 thin film [ $R^2 = 0.99$ ; RMSE = 0.0058], (c) PDMS substrate [ $R^2 = 0$ ; RMSE = 0.0007].

Peaks	Energy (eV)	Energy (eV) Ref.	Amplitude (u.a)	Broadening (eV)
Gaussian 1	2,23	2.20 [18]	2,26	0,3
Gaussian 2	2,46	2.38 [18]	2,09	0,45
Gaussian 3	2,95	3.01 [18]	1,07	0,99
Gaussian 4	1,65	2.06 [18]	0,19	0,24
$\epsilon$			2,71	
Thickness ellipso.(nm)			198	
Thickness profilo. (nm)			213 ± 19	
R <sup>2</sup>			0,99316	
RMSE			0,03408	

Table 3: parameters of the Gaussian model used for P3HT thin film with obtained model

Peaks	Energy (eV)	Energy (eV) Ref.	Amplitude (u.a)	Broadening (eV)
Gaussian 1	2,43	2.58 [18]	0,67	0,66
Gaussian 2	2,12	2.18 [18]	1,56	0,43
Gaussian 3	1,94	1.98 [18]	1,48	0,27
Gaussian 4	3,6	3.14 [18]	0,52	3,19
Gaussian 5	1,82	1.82 [18]	1,16	0,14
$\epsilon$			2,56	
Thickness ellipso.(nm)			62	
Thickness profilo. (nm)			88.31 ± 7	
R <sup>2</sup>			0,99881	
RMSE			0,0058	

Table 4: parameters of the Gaussian model used for PTB7 thin film with obtained model

The optical indices n and k are connected to the dielectric function  $\epsilon$ :

$$\epsilon = (n + ik)^2 = (n^2 - k^2) + i2nk$$

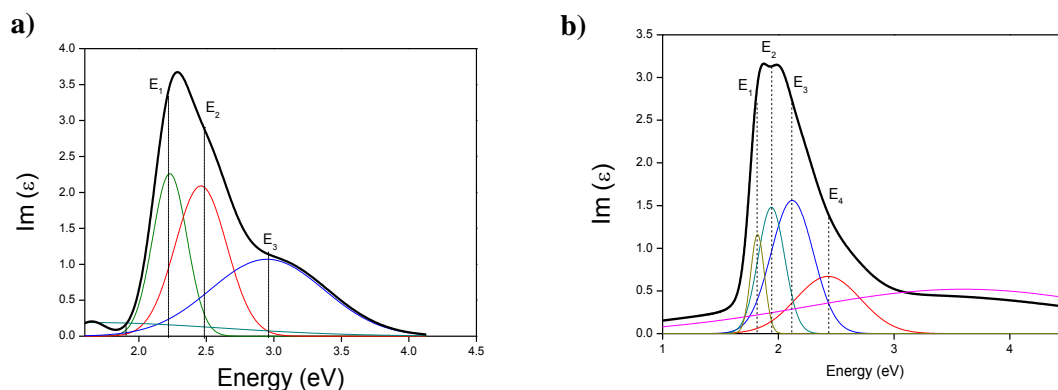


Fig.7. Imaginary part of the dielectric function for (a) P3HT (b) PTB7 thin films

The imaginary parts of the dielectric functions obtained by ellipsometry for P3HT and PTB7 are represented in **fig 7**. The Gaussian oscillators used to build their dispersion laws have been added on the spectra. The spectra shown in **fig 7** present vibronic peaks related to electronic transitions caused

by the optical absorptions of P3HT and PTB7 thin films. The centering energies of the Gaussian oscillators are presented in **tables 3.4**. These energies are a foot print of the crystalline structure of polymers thin films [16], they are in accordance with the literature [18] with a little shift which can be explained by the difference in the deposit method parameters.

The intensities of P3HT vibronic peaks are bigger than the PTB7 vibronic peaks (see tables 3,4 amplitudes); therefore we conclude that P3HT thin film shows better crystallinity than PTB7 thin film as it was observed in the XRD measurements.

For the PDMS substrate there is no vibronic peaks, which can be due to their amorphous structure, and also their transparency (**fig.5 c**). Further studies will include spin coated layers on PDMS substrate (in order to get thin and homogeneous layer for ellipsometric measurements) and VASE measurements on these samples under same stretching.

## Conclusions and perspectives:

The study of structural properties of conjugated polymers PTB7 and P3HT using GIXRD shows that P3HT thin film present more order and crystallinity than PTB7 thin film, and that was confirmed by measuring of the imaginary part dielectric function of these two polymers by using the ellipsometry technique. Under stretching, we followed the crystalline phase using the GIXRD measurements, and we showed overall decrease of the crystallinity. The strain in out-of plane direction is rather low and we might assume that the applied strain was mostly dissipated in the amorphous region or that the drop-casted layer is cracking or delaminated.

For further investigations, the ellipsometric and VASE measurements will be performed under same stretching to more understand the results obtained in the XRD measurements. In parallel, surface treatments and contact angle of solvents measurements are underway to improve of the deposits of layers on flexible substrates (PDMS), in particular spin-coating layers.

## Acknowledgements

We are grateful DiffAbs beamline scientists (SOLEIL synchrotron at Saclay, France) for assistance during the experiment and thankful for financial support from the DAAD-PROCOPE (project No. 57211900).



## Annex:

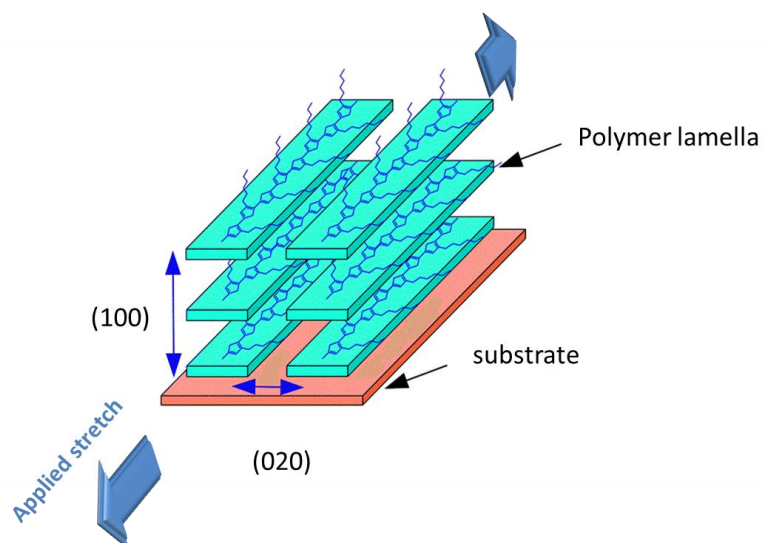


Fig.8. Schematic presentation of the polymer chains

## References

- [1] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, "Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure," *Nat. Photonics*, vol. 6, no. 9, pp. 593–597, Aug. 2012.
- [2] Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F. and Salleo, A., *Nat Mater*, 2013, 12, 1038-1044.
- [3] Heumueller, T.; Burke, T.M.; Mateker, W.R.; Sachs Quintana, I.T.; Vandewal, K.; Brabec, C.J.; McGehee, M.D. *Macromolecules Advanced Energy Materials*, 2015.
- [4] Joshi, S.; Grigorian, S.; Pietsch, U.; Pingel, P.; Zen, A.; Neher, D.; Scherf, U., *Macromolecules* 2008, 41, 6800.
- [5] Joshi, S.; Pingel, P.; Grigorian, S.; Panzner, T.; Pietsch, U.; Neher, D.; Forster M.; Scherf, U.; *Macromolecules* 2009, 42, 4651.
- [6] Grodd, L; Pietsch, U.; Grigorian, S., *Macromolecular Rapid Communications* 2012, 33, 20, 1765–1769.
- [7] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, *Nat. Photonics*, vol. 6, no. 9, pp. 593–597, 2012.
- [8] Fatima Bencheikh Aboura.; D. Duché.; J.J.Simon.; L.Escoubas ; *Chemical Physics* 450-451 (2015) 102-108
- [9] Fatima Bencheikh. ; David Duché. ; Carmen M. Ruiz, Jean-Jacques Simon.; and Ludovic Escoubas ; *J Phys. Chem C* 2015, 119, 24643-24648.
- [10] Software, Semilab Semiconductor Physics Laboratory Co., Ltd.
- [11] Natalie Banerji, Sarah Cowan, Eric Vauthey, and Alan J. Heeger, *Phys.Chem C* 15.19, 2011
- [12] David Roylance; *MECHANICAL PROPERTIES OF MATERIALS* ,2008
- [13] C. Gutt, L. Grodd, E. Mikayelyan et al, *J.Phys. Chem. Lett* 2014, 5, 2335
- [14] L. Grodd, U. Pietsch, S.G, *MRC* 2012, 33, 1765
- [15] Shuai Guo, Eva M. Herzig, Anna Naumann, Gregory Tainter, Jan Perlich, and Peter Müller-Buschbaum\*, *Phys. Chem. B* 2014, 118, 344-350
- [16] S. Grigorian, S. Escoubas, D. Ksenzov, D. Duche, M. Aliouat, J.-J. Simon, B. Bat-Erdene, S. Allard, U. Scherf, U. Pietsch, O. Thomas, *J.Phys. Chem.*, 2017
- [17] Chien Lu, Wen-Ya Lee, Xiaodan Gu, Jie Xu, Ho-Hsiu Chou, Hongping Yan, Yu-Cheng Chiu, Mingqian He, James R Matthews, Weijun Niu, Jeffery B.-H. Tok, Michael F. Toney, Wen-Chang Chen, and Zhenan Bao\*; *Adv. Electron. Mater.* 2017, 3, 1600311
- [18] Fatima BENCHEIKH, corrélation entre les propriétés optiques, la structure électronique et la morphologie des semi conducteurs organique  $\pi$ -conjugués, Aix Marseille Université