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

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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,...) \cite{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) \cite{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 (dimethylsiloxane) (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 Polydimethylsiloxane (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.

![Spin coating method](image1.png)

![Drop casting method](image2.png)

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Substrate</th>
<th>solvent</th>
<th>Concentration (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7</td>
<td>PDMS (387 µm)</td>
<td>chlorobenzene</td>
<td>20</td>
</tr>
<tr>
<td>P3HT</td>
<td>PDMS (387 µm)</td>
<td>chlorobenzene</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 1.** Drop casting parameters

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Polymer</th>
<th>Solvent</th>
<th>Concentration (mg/ml)</th>
<th>Temperature</th>
<th>Spin speed (rpm)</th>
<th>Time (sec)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>P3HT</td>
<td>chlorobenzene</td>
<td>15</td>
<td>ambient</td>
<td>500</td>
<td>60</td>
<td>213 ± 19</td>
</tr>
<tr>
<td>Glass</td>
<td>PTB7</td>
<td>chlorobenzene</td>
<td>20</td>
<td>ambient</td>
<td>500</td>
<td>60</td>
<td>88 ± 7</td>
</tr>
</tbody>
</table>

**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 130µm). The incident angle of x-rays (beam size of 170*270 µm) 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 2Θ ranges in out-of-plane direction (from 1° to 8° and...
from 9° to 16°). 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).

![DiffAbs goniometer with stretching device](image1)

**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 (~100µm), and data were measured from 1.5 to 5 eV at incidence angle of 55°, 60°, 65° and 70°. For the sake of clarity, only results of 70° 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.

![Schematic view of the ellipsometry principle](image2)

**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 2Θ 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 2θ 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 2.76 nm 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°, and a shift of 0.026° 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°, and a shift of 0.023° for the (020) peak position.

To better understand, we plot the strain variations as a function of the stretching. Strain ($\varepsilon$) is defined as the change of the distance between plans ($d - d_0$) divided by the original (initial) distance ($d_0$) \[ (\varepsilon \%) = \left( \frac{d - d_0}{d_0} \right) \times 100 \]

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) π-π stacking peak c) PTB7 (100) peak d) PTB7 (020) π-π 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 in 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 Ψ and the Δ 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 \( \tan(\Psi) = \left| \frac{r_p}{r_s} \right| \) 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(Ψ) and cos (Δ) for: (a) P3HT thin film \([R^2 = 0.99; \text{RMSE} = 0.03]\), (b) PTB7 thin film \([R^2 = 0.99; \text{RMSE} = 0.0058]\), (c) PDMS substrate \([R^2 = 0; \text{RMSE} = 0.0007]\).
The optical indices $n$ and $k$ are connected to the dielectric function $\varepsilon$:

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

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

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Energy (eV)</th>
<th>Energy (eV)</th>
<th>Ref.</th>
<th>Amplitude (u.a)</th>
<th>Broadening (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian 1</td>
<td>2.23</td>
<td>2.20 [18]</td>
<td></td>
<td>2.26</td>
<td>0.3</td>
</tr>
<tr>
<td>Gaussian 2</td>
<td>2.46</td>
<td>2.38 [18]</td>
<td></td>
<td>2.09</td>
<td>0.45</td>
</tr>
<tr>
<td>Gaussian 3</td>
<td>2.95</td>
<td>3.01 [18]</td>
<td></td>
<td>1.07</td>
<td>0.99</td>
</tr>
<tr>
<td>Gaussian 4</td>
<td>1.65</td>
<td>2.06 [18]</td>
<td></td>
<td>0.19</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$\varepsilon = 2.71$

Thickness ellipso. (nm) 198

Thickness profilo. (nm) $213 \pm 19$

$R^2$ 0.99316

RMSE 0.03408

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

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Energy (eV)</th>
<th>Energy (eV)</th>
<th>Ref.</th>
<th>Amplitude (u.a)</th>
<th>Broadening (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian 1</td>
<td>2.43</td>
<td>2.58 [18]</td>
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<td>0.67</td>
<td>0.66</td>
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<tr>
<td>Gaussian 2</td>
<td>2.12</td>
<td>2.18 [18]</td>
<td></td>
<td>1.56</td>
<td>0.43</td>
</tr>
<tr>
<td>Gaussian 3</td>
<td>1.94</td>
<td>1.98 [18]</td>
<td></td>
<td>1.48</td>
<td>0.27</td>
</tr>
<tr>
<td>Gaussian 4</td>
<td>3.6</td>
<td>3.14 [18]</td>
<td></td>
<td>0.52</td>
<td>3.19</td>
</tr>
<tr>
<td>Gaussian 5</td>
<td>1.82</td>
<td>1.82 [18]</td>
<td></td>
<td>1.16</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$\varepsilon = 2.56$

Thickness ellipso. (nm) 62

Thickness profilo. (nm) $88.31 \pm 7$

$R^2$ 0.99881

RMSE 0.0058

**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 footprint 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.5c). 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
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Annex:

Fig. 8. Schematic presentation of the polymer chains

References

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