Examination of crystallinity in thin polymer films using GIWAXS

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Like many polymers the conductive polymer poly(3-octylthiophene-2,5-diyl) (P3OT) is counted among the semi-crystalline materials. This means P3OT includes regions in which the polymer chains order in a crystalline way. These regions are usually surrounded by amorphous regions without crystalline ordered structure. In conductive polymer devices crystallinity is of special interest since it has influence on its conductivity. The orientation of the crystalline phases can for instance lead to anisotropic conductivity [1].

Thin films consisting of P3OT were prepared by spin-coating from tetradytrofuran (THF) solution on pre-cleaned glass substrates. For exploration of the influence of thermal treatment, films were annealed at 130 °C for 15 minutes on a hot plate under vacuum conditions and quenched to room temperature.

To examine the crystallinity of the P3OT films grazing incidence wide angle x-ray scattering (GIWAXS) was used. For this reason an new experimental setup was constructed at the beamline BW4 at Hasylab. Placed at a distance of 123 mm behind the sample, the detector covers an angular region from 0° to 35°. This setup allows the detection of structures in the nm- and sub-nm-region.

The analysis of the scattering images is accomplished by sector integrals perpendicular (vertical) and parallel (horizontal) to the substrate surface. The integrals are compared with each other in two different ways.

Fig 1a shows the comparison of vertical and horizontal integrals of the same polymer film, like indicated by the pictograms. The top graphs (I) and (II) pertain to the annealed film, the bottom graphs (III) and (IV) to the unannealed film. All of the graphs displayed show scattering maxima caused by crystalline structures within the films. The (100), (200) and (300) maxima can be assigned to the same structural length named "a". The (100) is the main maximum of this structural length. (200) and (300) are higher order peaks. Consequently their values of \( q \) are twice \( (q_{(200)} = 5.1 \text{ nm}^{-1}) \) and three times \( (q_{(300)} = 7.7 \text{ nm}^{-1}) \) higher than \( q_{(100)} = 2.5 \text{ nm}^{-1} \) respectively. Via the formula \( a = \frac{2\pi h}{q} \), with the crystallographic indice \( h = 1 \) the value of \( a = 2.5 \text{ nm} \) can be calculated from the (100) peak . The (010) peak corresponds to a structure size \( b = 0.4 \text{ nm} \) oriented perpendicular to \( a \) [2] [3].

Although the structures \( a \) and \( b \) are perpendicular to each other within each crystalline region, the orientation of the different crystalline regions has an angular distribution. For the unannealed film the intensity of the (100) maximum is higher in vertical direction while the intensity of the (010) maximum is equal in horizontal and vertical direction. The corresponding comparison for the annealed film shows almost equal intensities for the (100) maximum in both directions. In vertical direction the intensity of the (010) maximum is higher than in horizontal direction.

The direct comparison of the annealed and unannealed films in vertical direction (Fig 1b, top), shows a shift towards higher values of \( q \) for the (100), (200), (300) and (010) maxima in the graphs of the annealed film. This corresponds to a 9 % shrinkage of the structures \( a \) and \( b \) in real space. For the annealed film the (100) maximum is less intense and broadened. In Fig 1c a region with a small slope can be found around the position of the (100) maximum of the unannealed film. The
intensity of the (010) maximum is enhanced in the annealed film with respect to the unannealed one.

The horizontal graphs (Fig 1b, bottom) show a shift of the maxima toward higher values of $q$ as well. In contrast to the vertical graph, the intensity of the (100) due to annealing and the intensity of the (010) maximum decreases.

In summary, the examined polymer films show crystalline features even without post production annealing. The relatively simple molecular structure of the P3OT monomer presumably promotes the formation of crystalline ordered regions in the film.

In the annealed film the scattering intensity caused by the structure $a$ is more strongly oriented in horizontal direction than it is for the unannealed film. Inversely the scattering intensity of the structure $b$ is oriented stronger in vertical direction. These observations lead to the conclusion that the predominant orientation of the crystalline regions changes due to the annealing.

The shrinkage of the crystalline structures can be explained by a structural optimization caused from reorientations of the side groups as well as by residual THF molecules leaving the polymer film during the annealing [4].

References