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Aligned rrP3HT film: Structural order and transport properties☆

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Abstract

Aligned regioregular poly(3 hexyl thiophene), rrP3HT, thin films have been fabricated by a rubbing technique. Structural studies indicate orthorhombic crystalline domains (CDs) with *c*-axis aligned principally along the rubbing direction. The backbones of the macromolecules are stacked along the *b*-axis, forming a plane of parallel backbones with π-electron overlap and with side chains between the planes (along the *a*-axis). There is no π-overlap between these planes due to the long side chains along the *a*-axis. The optical and electronic properties are correlated with the anisotropic structure. Both for light polarized parallel and for light polarized perpendicular to the chain direction, the onset of photocurrent coincides with the onset of absorption. The larger photoconductivity observed with light polarized along the *c*-axis suggests the films are of sufficiently high quality to reveal the intrinsic anisotropy of the electronic structure.

Keywords: Polythiophene and derivatives; Scanning transmission electron microscopy; X-ray diffraction; Polycrystalline thin films; Optical absorption spectroscopy

1. Introduction

The electronic structure of semiconducting polymers continues to be an active area of study. Important issues include the role of interchain overlap of the π-electron wavefunctions and the magnitude of the exciton binding energy [1–4]. The electronic structure of a semiconducting (conjugated) polymer is directly related to the molecular structure, the orientation of the macromolecular chains, and the packing of the macromolecular chains within the crystal structure. Films cast from solution have a complex microstructure comprising microcrystalline domains, CDs, imbedded in an amorphous matrix. Alignment can improve the orientation of both the CDs and the amorphous chains. Previously, the improvement of optical and electronic properties of polythiophene (PT) films has been demonstrated by stretch alignment [5] and by rubbing treatment of liquid crystalline PT derivatives [6]. With aligned films one can utilize polarized opto-electronic measurements to separate the intrachain from interchain contributions to the electronic structure.

Although the microstructure of the rrP3HT films has been extensively studied [7–13], a correlated study of the crystallographic structure and interchain packing (which determine the details of the Brillouin zone and thereby the band structure) with the opto-electronic properties, has not to our knowledge, been reported.

With polarized optical and electronic measurements as the goal, we fabricated aligned rrP3HT films by "rubbing", determined the microstructure/crystal structure, and measured the optical absorption and steady-state photoconductivity with light polarized along the principal crystallographic axes.

2. Experimental

The rrP3HT, was purchased from Aldrich and used without further purification. The solution (1%, w/v) in chlorobenzene was cast onto a hydrophobic substrates and rubbed during drying at ∼95 °C. Alignment was achieved by rubbing the polymer film with the smooth edge of a quartz slide. The microstructure was studied by polarized optical microscopy (Nikon, Japan),

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transmission electron microscopy (TEM) (using a JEM-1230 operated at 80 kV), and by X-ray diffraction (using a Philips X'pert diffractometer operated at 40 kV and 50 mA with $\lambda = 0.154$ nm). For determination of the unit cell of the CDs, dip-cast films were also prepared from 0.2% (w/v) chloroform solution and studied. The polarized absorbance was measured on a Perkin-Elmer Lambda 20 UV–vis Spectrometer. For photoconductivity measurements, gold electrodes were deposited onto the film with 15 μm separation. Steady-state photocurrent spectra (normalized to constant incident photon flux) were measured using the conventional light modulation technique with a lock-in amplifier. The light incident on the sample was dispersed by a monochromator and focused on the sample at the gap between the electrodes. Photoconductivity data were obtained with light polarized parallel and perpendicular with respect to the rubbing direction axis. In both cases, the 400 V/cm external electric field was parallel to the rubbing axis direction.

3. Results and discussion

3.1. Microstructure of the dip rrP3HT film

Fig. 1 is a TEM micrograph of a dip-cast film, showing the film morphology of the rrP3HT film (dark regions are more highly exposed, i.e. less and/or no material there). The granular domains indicate that the film is not uniform on the microscopic scale. Formation of the granular domains is an intrinsic feature of rrP3HT, the chains of which tend to fold and crystallize [9]. The diffraction pattern of the same film is shown in the inset. The regular spots arise from a relatively large (~10 nm) single crystal domain, CD, with the proper orientation with respect to the e-beam. The narrow rings are from randomly oriented CDs. The continuous background originates from amorphous regions of the film. This means that the CDs are embedded in an amorphous matrix. The degree of crystallinity is estimated to be greater than 30%, depending on sample preparation and treatment. The spots indicate CDs with orthorhombic symmetry with cell parameters $b = 0.75 \pm 0.01$ nm and $c = 0.49 \pm 0.01$ nm. Using X-ray diffraction (shown in Fig. 2) we obtain the cell parameter $a = 1.62 \pm 0.01$ nm, as indicated in Fig. 2 on strong diffraction peak at $2\theta = 5.4°$. In the sketch shown in the inset of Fig. 2, the half of the unit cell of CD along the *b*-direction is indicated by the dashed lines (for clarity, only half of the unit cell is sketched). It is seen that the polymer chain backbones are oriented along *c*-axis and the chains are face-to-face stacked with π-overlap along the *b*-axis. The hexyl side chains are directed along the *a*-axis and separate the planes of molecular backbones. The crystallographic *a*-, *b*- and *c*-axes are shown in inset at right down corner.

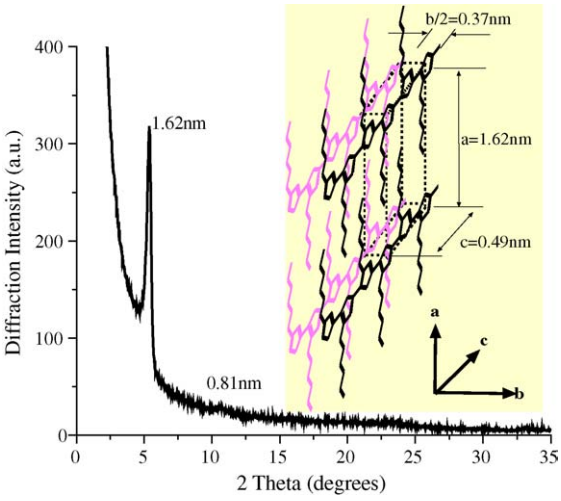

Fig. 2. X-ray diffraction spectrum of the rrP3HT films, the sketch in the inset shows half of the unit cell of the CD along the *b*-direction indicated by the dashed lines.

3.2. Microstructure of the aligned film

Knowing the crystal structure and *a*, *b* and *c* lattice parameters, we conclude that in the oriented films, the *b*- and *c*-axes of most of CDs are oriented, respectively, perpendicular and parallel to rubbing direction, as shown in Fig. 3. Fig. 3 shows the birefringence of the rubbed rrP3HT film, observed under crossed polarizers (optical microscope). The bright granular contrast

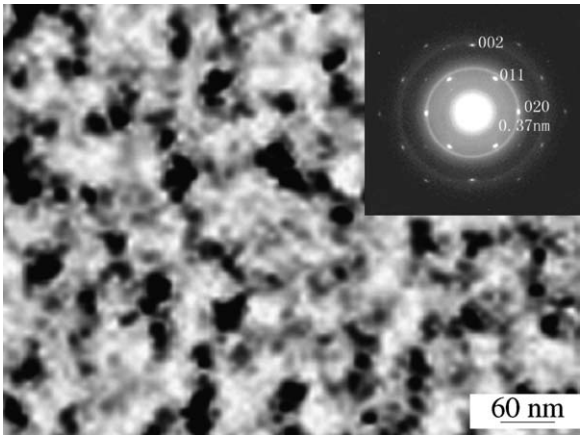

Fig. 1. TEM micrograph, showing the morphology of the dip-cast film. The inset shows the electron diffraction pattern of the film.

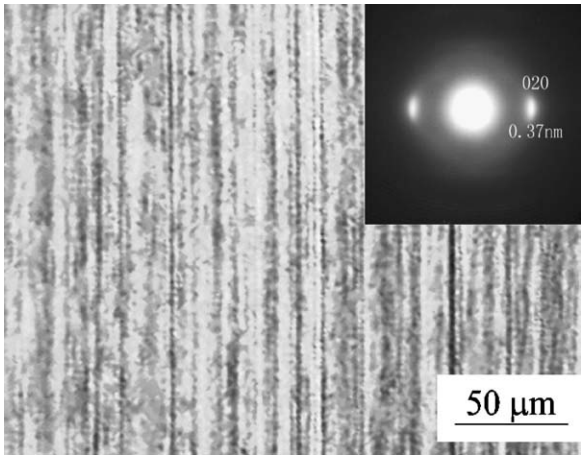

Fig. 3. Crossed polarized optical micrograph. The inset is a TEM diffraction pattern of the aligned film.

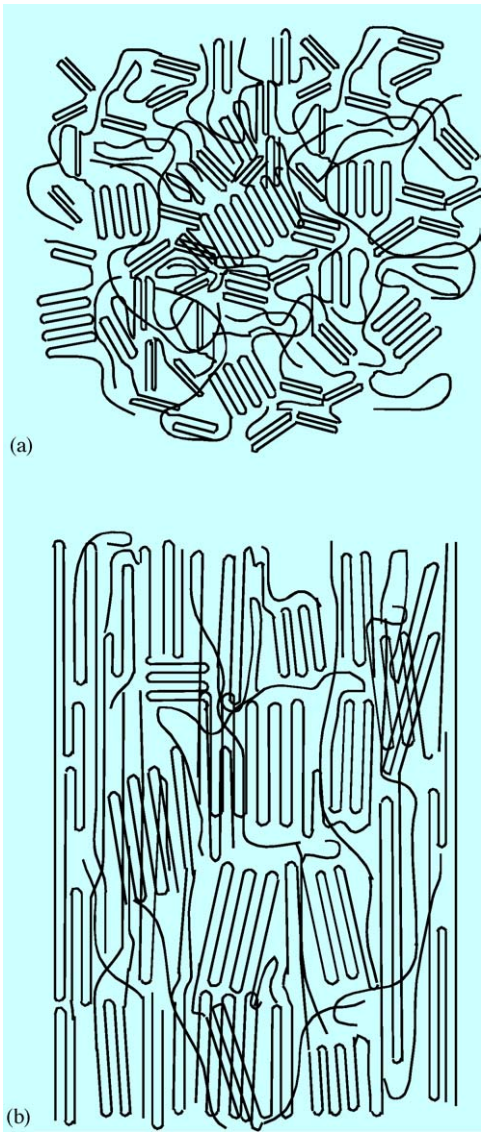

Fig. 4. The schematic drawings of the microstructure of the non-oriented (a) and oriented (b) films, resulted from Figs. 1 and 3, respectively. The macromolecular backbones are sketched by black lines, the side chains are omitted for clarity.

means that most CDs are aligned along the rubbing direction (vertical direction in Fig. 3). By using the TEM diffraction pattern, shown in the inset of Fig. 3 we can determine the orientation of the *b*- and *c*-axes of CDs that are perpendicular and parallel to the rubbing direction, respectively. That is, the chains in CDs are stacked along the *b*-axis (the reflections of 0 2 0 that are similar to the 0 2 0 spots observed in Fig. 1 for the dip-cast film are indicated in inset of Fig. 3), and directed along the *c*-axis.

More clear illustration of the aligned CDs in the oriented film can be seen in the schematic drawings of Fig. 4, which compares the microstructure with that of the non-aligned film. In non-aligned film, the CDs are oriented randomly in an amorphous matrix (Fig. 4a), while in aligned films the CDs are mostly oriented with *c*-axis along and *b*-axis perpendicular to the rubbing direction (in Fig. 4b, the rubbing direction is vertical).

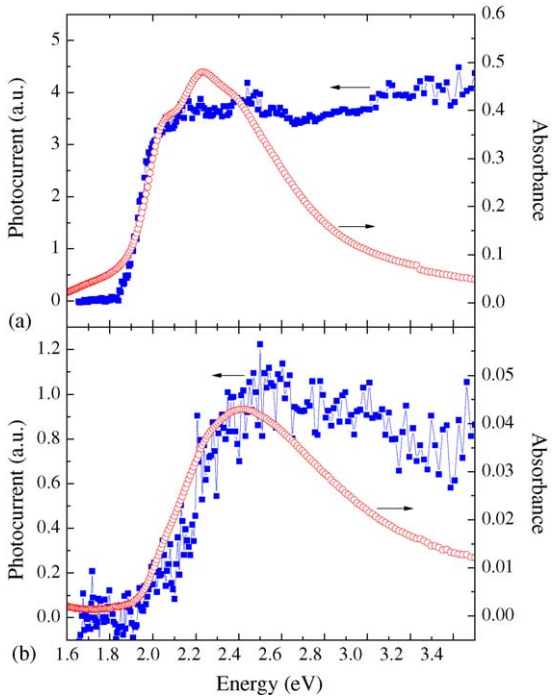

Fig. 5. The absorption spectra (circles) and photoconductivity (squares) obtained with polarized illumination: (a) along the chain direction (the *c*-axis) and (b) perpendicular to the chain direction (the *b*-axis).

3.3. Optical absorption and photoconductivity

Fig. 5 shows optical absorption and photoconductivity spectra measured with the illumination polarized parallel (a) and perpendicular (b) to the rub direction, i.e. along *c*- and *b*-axes, respectively. There is significant anisotropy in the optical absorption; the dichroism is around 10. Note that the onsets of absorption and photoconductivity coincide (the photoconductivity data are normalized to the maximum of the first peak of the absorption in both cases). The low energy peak (2.05 eV) observed with light polarized along *c*-axis is reminiscent of the field-induced exciton line observed in PPV [4]. As in PPV, this peak is not observed for light polarized along *b*-axis. If that is the correct interpretation, the 2.05 eV photocurrent would arise from dissociation of excitons by defects and impurities. Measurements in high electric fields are underway to check this interpretation.

Alternatively, the anisotropy in the absorption and photocurrent might simply be the result of the anisotropic band structure, since the crystallographic anisotropy is evident in aligned film, as discussed above. The Brillouin zone in two dimensions for an orthorhombic single crystal (see Fig. 1) is illustrated in Fig. 6a, marked out simply by {0 0 2}, {0 2 0} and {0 1 1} planes (Fig. 6b) of a rrP3HT crystal at $k_z = 2\pi/c$, at $k_y = 2\pi/b$, and at $k_z = \pi/c$, $k_y = \pi/b$ in *k*-space, respectively [14,15]. In addition, in the principal crystal *c*- and *b*-axes directions, there is good overlap of the π-electron wavefunctions.

Actually the backbone planes ((*c*, *b*) planes) form two dimensional π-electron transport planes. This is consistent with Ref. [12]. The identical photoconductivity and absorption spectra imply that the exciton binding energy is not resolved (<0.1 eV).

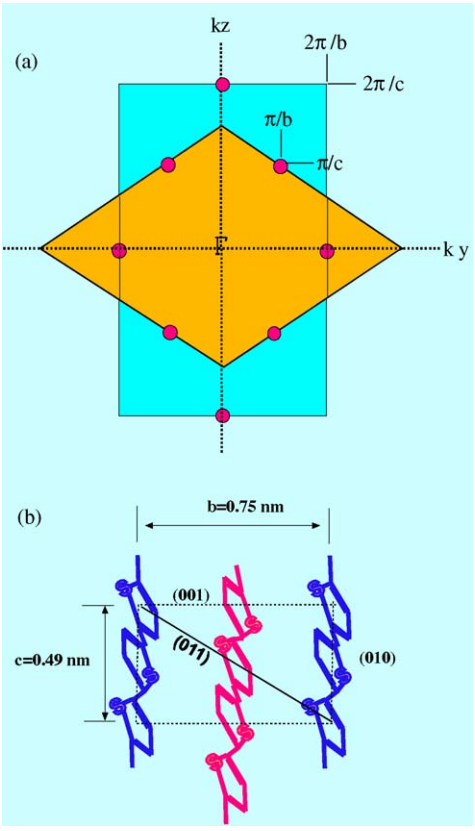

Fig. 6. (a) Sketch of the first and second Brillouin zones in two dimensions of a rrP3HT crystal and (b) the sketch of the {0 0 2}, {0 2 0} and {0 1 1} crystal planes in real space.

4. Conclusions

The aligned rrP3HT films are comprised of crystalline domains within an amorphous matrix. The crystal structure is orthorhombic with $a = 0.74 \pm 0.01$ nm, $c = 0.51 \pm 0.01$ nm and $b = 1.64 \pm 0.01$ nm. The rrP3HT chains are parallel to the c-axis with near neighbor chains stacked with good π-overlap along the b-axis. The optical and electronic properties are correlated with the anisotropic structure. In both cases (light polarized parallel and perpendicular to the chain direction), the onset of photocurrent coincides with the onset of absorption. The larger photoconductivity observed with light polarized along c suggests the films are of sufficiently high quality to reveal the intrinsic anisotropy of the electronic structure.

Acknowledgments

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