



Thermal and optical properties of nano/micro single crystals and nanofibers obtained from semiconductive-dielectric poly(3-hexylthiophene) block copolymers

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ABSTRACT

Optical and thermal characteristics of single crystals and nanofibers prepared from poly(3-hexylthiophene) (P3HT)-based homopolymers and block copolymers were deeply studied in toluene, xylene, and anisole. The free exciton bandwidth of aggregates (W) decreased with increasing the ratio of A_{0-0}/A_{0-1} and, consequently, the conjugated length and the intrachain ordering enhanced. In these structures, the intrachain interactions were dominant interactions. The peaks of A_{0-0} , A_{0-1} and A_{0-2} appeared from longer wavelengths towards shorter ones in ultraviolet-visible (UV-Vis) spectra. The effective parameters on the aggregation type consisted of solvent quality, P3HT backbone length, and growth method. In the single crystals prepared from the longer conjugations, the P3HT₄₈₈₀₀ backbones acted as J-aggregate ($1.21 < A_{0-0}/A_{0-1} < 2.42$ and $-283 < W$ (meV) < -56). The P3HT₄₈₈₀₀ nanofibers grown from toluene and xylene were J-aggregate, but the ones grown from anisole were H-aggregate. The short and middle P3HT conjugated backbones acted as H-aggregate in both single crystals and nanofibers ($A_{0-0}/A_{0-1} < 1$). The crystallinity, as a fingerprint of highly ordered structures, was higher in J-aggregate structures compared to H-aggregate ones. The single crystals, due to having a highly ordered configuration, represented a higher red-shifted absorbance, melting enthalpy ($\Delta H_m = 35.85$ J/g), and crystallinity ($x_c = 97\%$) compared to the corresponding nanofibers ($\Delta H_m = 25.91$ J/g and $x_c = 70\%$). The crystallinity and chain ordering of homopolymer single crystals were also higher than those detected for the block copolymer ones.

1. Introduction

Due to their tunable properties and nano/microscale self-assembly, conjugated semiconducting polymers emerged as materials with wide applications consisting organic solar cells [1–6], field effect transistors [7–14], light emitting diodes [15,16], thin film transistors [17–20], optical and amperometric sensors [21], and chemical sensors [22–25]. The optoelectronic effects in the semicrystalline conjugated polymers depend on chain ordering and orientation [26,27]. Regioregular poly(3-alkylthiophene)s (P3AT) in particular poly(3-hexylthiophene) (P3HT), thanks to their favorable electronic and optical properties, good processability, and strong tendency to crystallization, are among the most widely studied conjugated polymers for organic electronics.

One-dimensional (1D) structures such as single crystalline nano/microwires [28–34], nanotubes [35–38], nanofibers [39–42], nanowire shish-kebab (NWSK) structures [43], micro/nano conductive-dielectric channels [44], needle-like lamellae [45], and sandwiched conductive-

dielectric-conductive structures [46,47] have attracted particular attentions due to their unique electronic characteristics. The nanofibers of polythiophene derivatives have also been prepared by various procedures like the template method [48], electro-spinning [49], non-template method [50], Langmuir-Blodgett method [51], dip-pen nanolithography [52], copolymerization [53], molecular combing [54], self-organization on a substrate during drying [55], and whisker method [56].

In order to correctly interpret the functional behavior of conjugated crystalline structures, it is necessary to unravel the relationship between the light absorption properties and nano/microstructures. The P3HT single crystals absorbed light at higher wavelengths compared to spin cast films, thus a remarkable 70 nm red shift occurred. The strong intrachain interactions along the fully planar chains reflected the large conjugation lengths and delocalized states [57]. The effect of various parameters such as solvent [39,58–61], sonication time [62], composition of P3HT fibers in solution [63], cooling rate

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[64], molecular weight [39,65,66], regioregularity [30], thermal annealing [3,67], and aging time [68] on the P3HT absorbance was investigated by different research groups.

Yuan et al. [69] showed that the microstructural difference of P3HT H-aggregates and J-aggregates might result in distinct thermal behaviors. Chan et al. [49] investigated the thermal properties of electro-spun fibers and cast films. The electro-spun fibers exhibited lower melting temperatures, suggesting that the smaller crystallites were developed within them. The differential scanning calorimetric (DSC) thermograms of P3HT/poly(stearyl acrylates) (PSA) nanofibers were also used to analyze the crystallinity change of P3HT after blending with PSA [70]. Based on DSC analyses, Dias and coworkers [38] reported a significant increase in polymer crystallinity in the carbon nanotube composites. The DSC analyses were also performed in order to investigate the effect of the copolymer on the crystallization properties of P3HT [71].

In the current work, the optical and thermal properties of P3HT-based homo and block copolymer single crystals and nanofibers were profoundly investigated using UV–vis and DSC analyses. The effects of P3HT backbone length, solvent quality, end coily blocks of polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(ethylene glycol) (PEG), and the growth methodology were unraveled in H-aggregate and J-aggregate structures.

2. Experimental

2.1. Synthesis

Regioregular (> 99%) P3HTs with different molecular weights ($M_n^{\text{P3HT}} = 7150, 21,000, \text{ and } 48,800 \text{ g/mol}$) and polydispersity indices (PDI) ranging from 1.21 to 1.25 were synthesized by Grignard metathesis polymerization [72]. FT-IR and ^1H NMR spectra of synthesized P3HT₇₀₀₀-Br with identifying peaks are reported in Fig. S1. Fig. S2 represents the cyclic voltammogram (CV) of the synthesized P3HT₄₈₈₀₀ homopolymer. The P3HT-*b*-PEG₇₅₀, P3HT-*b*-PMMA₄₉₇, and P3HT-*b*-PS₅₁₉ rod-coil block copolymers with PDIs of 1.28–1.35 were synthesized with Suzuki coupling [73] and atom transfer radical polymerization (ATRP) [74]. More details are reported in Supplementary information. All reactions are represented in Fig. S3. ^1H NMR spectra of synthesized P3HT₂₁₀₀₀-*b*-PEG₇₅₀ and P3HT₇₁₅₀-*b*-PS₅₁₉ block copolymers are illustrated in Fig. S4(a) and (b), respectively. Fig. S5 represents the size exclusion chromatography (SEC) traces of the synthesized homo and block copolymers.

2.2. Single crystal growth

The P3HT homopolymer (non-hairy) as well as P3HT-*b*-PS, P3HT-*b*-PMMA, and P3HT-*b*-PEG block copolymer (hairy) single crystals were grown from toluene (here the best solvent), xylene (intermediate solvent), and anisole (the poorest solvent) using the self-seeding method in dilute solutions (0.01 wt%). The solutions were dark orange for toluene, light orange for xylene, and colorless for anisole before heating. First, the thermal history of the samples was eliminated. To this end, all samples were heated for 30 min at 75 °C in toluene, at 85 °C in xylene, and at 95 °C in anisole. In this step, all dissolved samples were orange. Then, the vials were kept at 0 °C overnight to turn the orange color of samples to brownish violet. The seeding and crystallization steps were then performed for 3 min and 3 days, respectively, at respective seeding (T_s) and crystallization (T_c) temperatures. The single crystals were grown at $T_s = 30$ °C and $T_c = 20$ °C in toluene, at $T_s = 40$ °C and $T_c = 20$ °C in xylene, and also at $T_s = 50$ °C and $T_c = 20$ °C in anisole.

2.3. Nanofiber growth

In order to develop the nanofibers with the isothermal crystallization approach, the solutions (0.01 wt%) were homogenized for

30 min at 75 °C in toluene, at 85 °C in xylene, and at 95 °C in anisole. Upon turning to orange, the vials were transferred to the crystallization bath ($T_c = 10$ °C) and kept for 6 days. After 6 days, the brownish violet solutions reflected the growth of nanofibers.

2.4. Characterization

The grazing incidence wide angle X-ray scattering (GIWAXS) and grazing incidence small angle X-ray scattering (GISAXS) patterns were collected by a CMOS flat panel X-ray detector (C9728DK, 52.8 mm square) and a CCD detector (MAR165, 165 mm in diameter, 1024 by 1024 pixels resolution), respectively. The details of the instrumental configuration, operation, and data reduction procedures for the GISAXS and GIWAXS measurements are reported in the literature [75,76]. The layer spacings ($d_{(100)}$ or $d_{(020)}$) between the crystallographic planes were determined from $(100)_{\text{OOP}}$ and $(020)_{\text{IP}}$ Bragg peaks position for the edge-on P3HT single crystals and nanofibers with the alkyl chain perpendicular to the substrate [77]. Furthermore, the dimensions of P3HT nanofibers and single crystals ($D_{(100)}$ in thickness, $D_{(020)}$ in length, and $D_{(002)}$ in width) were monitored with AFM Nanoscope. Transmission electron microscopy (Philips CM10 TEM) equipped with selected area electron diffraction (SAED) was also used to detect the growth planes of the P3HT nanofibers and single crystals. The DSC measurement was performed on a TA Q20 calorimeter system under flowing nitrogen gas to determine the melting enthalpy (ΔH_m) and melting point (T_m) of single crystals and nanofibers at a heating rate of 10 °C/min. The UV–Vis absorption spectra were recorded by UV–Vis absorption spectrometer (Jasco spectrometer V-650) using the solutions of single crystals and nanofibers in various solvents.

3. Results and discussion

The single crystals and nanofibers grown from homo-P3HTs and rod-coil P3HT based block copolymers were called non-hairy and hairy structures, respectively. Fig. 1 illustrates AFM and TEM images of distinct single crystals and nanofibers grown in various conditions. Fig. 1(a) depicts AFM height image of P3HT₂₁₀₀₀-*b*-PEG hairy single crystals grown from toluene at $T_s = 30$ °C and $T_c = 20$ °C, and Fig. 1(b) shows AFM height image of homo-P3HT₂₁₀₀₀ non-hairy nanofibers grown from anisole at $T_c = 10$ °C. Fig. 1(c) represents TEM image of P3HT₄₈₈₀₀-*b*-PS hairy single crystal grown from xylene at $T_s = 40$ °C and $T_c = 20$ °C and Fig. 1(d) similarly depicts TEM image of P3HT₇₁₅₀-*b*-PMMA hairy nanofiber developed in anisole at $T_c = 10$ °C with the corresponding SAED patterns in the insets. The single crystals and nanofibers grown with a homogeneous cross section possessed (002) and (020) as growth fronts in their width and longitude, respectively. The P3HT crystalline structures extended their length in π - π stacking or (020) direction, their thickness in the hexyl side chains or (100) direction, and their width in the longitude of P3HT backbones or (002) direction. Surface morphologies of fibrillar crystals were also detected by scanning electron microscope (SEM). The SEM images of P3HT₇₁₅₀ single crystal grown from anisole at $T_s = 60$ °C and $T_c = 40$ °C and P3HT₄₈₈₀₀-*b*-PMMA single crystal grown from xylene at $T_s = 30$ °C and $T_c = 10$ °C are represented in Fig. 2(a) and (b), respectively.

Using GIWAXS measurements, the edge-on orientation with the main backbones parallel with and hexyl side chains perpendicular to the substrate and d -spacings ($d_{(100)}$ and $d_{(020)}$) were detected for grown single crystals and nanofibers. As shown in Fig. 3, (100) and (020) growth planes appeared in *out of plane* (OOP) and *in plane* (IP) axes of GIWAXS plots, respectively, indicating an edge-on orientation [75]. It was noteworthy that in 2D GIWAXS profiles of the single crystals, beside $(100)_{\text{OOP}}$ planes $(200)_{\text{OOP}}$ and $(300)_{\text{OOP}}$ were also detected. Appearance of these spots was the fingerprint of a higher ordering. In contrast, in GIWAXS patterns of nanofibers even in a better solvent, only $(100)_{\text{OOP}}$ planes were detected.

The regioregular conjugated polymers, especially P3ATs, usually

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