



Ultraviolet irradiation creates morphological order via conformational changes in polythiophene films



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ABSTRACT

Here, we developed a facile post-treatment method using ultraviolet irradiation that produced crystalline polymer nanofibrils in the solid film state. Ultraviolet irradiation over a few minutes effectively transformed the polymer chain conformational structure and promoted polymer chain extension and association in the film state. Brief ultraviolet irradiation of a thin film fabricated using a high boiling point solvent produced well-ordered molecular structures among the extended P3HT chains, whereas ultraviolet irradiation over longer times led to breaks in the chemical structures of the P3HT, resulting in shortened conjugation lengths. Conformational changes in the polymer main chain and resulting nanofibril morphologies induced by ultraviolet irradiation facilitated charge transport in organic transistors prepared using these films. The relationship between the molecular structural order and the electrical characteristics of the films was used to determine the optimum ultraviolet irradiation time.

1. Introduction

Organic field-effect transistors (OFETs) based on semiconducting polymers are of great interest due to their promising potential applications in flexible, large-area, transparent electronics [1–5]. Printing techniques in particular, including ink-jet printing [6], bar-coating [7], and dip-coating of semiconducting polymers [8], has enabled the rapid fabrication of sophisticated OFETs using low-cost solution processes. The primary requirement for solution-processed semiconducting polymer films is the attainment of an ordered molecular structure [9,10]. To achieve this goal, the chemical structure design and semiconducting polymer processing control must be optimized. Semiconducting conjugated polymers consist of a conjugated aromatic backbone and solubilizing alkyl side chains [11]. The interchain interactions among the conjugated polymers are predominantly π - π stacking structures among conjugated main chains and van der Waals forces among the alkyl side chain [12]. Crystalline building blocks that enhance π - π stacking among the conjugated backbones can increase electronic coupling and promote long-range charge carrier transport [13]. Polymer films processed using solution techniques often have a low crystallinity, which exhibits poor electrical characteristics due to charge carrier localization in small crystalline regions embedded within an amorphous matrix [14].

Poor electrical characteristics may be improved using a variety of approaches for enhancing the molecular ordering in semi-crystalline polymers, such as varying the solvent mixing [15–17], solvent solubility [18,19], solution aging time [20–22], film fabrication method [23–28], and post-treatments [29–33], including thermal and solvent vapor annealing [34–38]. Ultraviolet irradiation of conjugated polymer solutions was recently reported to induce formation of a crystalline phase in solution, demonstrating that ultraviolet irradiation disentangles polymer chains and facilitates the fabrication of ordered polymer thin films without post-treatments [39]. Self-assembled polymers in the solution state exhibit improved crystallinity and charge carrier transport compared to the comparatively amorphous as-cast polymer films; however, most solution crystallization processes are sensitive to experimental parameters, and careful attention and strict process conditions are required, unlike the various post-treatment processes. Process conditions, such as the mixing ratio of a poor solvent or the aging time, can increase the crystalline size to the point of incipient precipitation, leading to non-uniform films with structural defects [21]. Post-treatment steps tend to be simple and efficient for preparing large-area ordered uniform polymer films. High-temperature annealing, however, can deform and introduce mismatch among the organic layers. The time-consuming solvent vapor annealing approach is not universally applicable due to safety concerns [38].

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Herein, we present a systematic study of ultraviolet irradiation methods as a facile post-treatment for controlling the conformational structures of poly (3-hexylthiophene) (P3HT) chains. Post-treatment ultraviolet irradiation over only a few minutes may be much more convenient than growing crystals in solution or using other post-treatment methods. The polymer chain structural changes and the electrical characteristics of the P3HT films irradiated using ultraviolet light were characterized as a function of the irradiation time. Post-treatment over short times represents an effective alternative for the large-scale fabrication and high-throughput processing of highly crystalline polymer films due to the easy processing conditions compared to solution crystallization or other post-treatment methods.

2. Experimental section

2.1. Preparation of the P3HT films and OFETs

P3HT, with a M_w of 37 kDa (Rieke Metals, electronic grade, RR = 89–92%), was used as a semiconductor material and was dissolved in chlorobenzene (CB) to a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$. Chloroform (CF) and dichlorobenzene (DCB) were used to monitor the effect of residual solvent in the P3HT film. OFETs were fabricated on highly doped n-type Si wafers, which were used as the gate electrode and substrate. The surface of the Si wafer was a thermally grown 300 nm thick silicon oxide (SiO_2) layer used as a gate dielectric (capacitance = $10.8 \text{ nF}\cdot\text{cm}^{-2}$). Hexamethyldisilazane (HMDS) (Aldrich) was spin-coated onto the SiO_2 surface and used as an organic interlayer in the semiconductor-dielectric interface. P3HT CB solutions were spin-coated onto HMDS-treated silicon wafers at 1500 rpm for 60 s. After the spin-casting of the P3HT solution, P3HT films were promptly irradiated with ultraviolet light (254 nm) in a darkroom under ambient atmospheric conditions. P3HT films were irradiated with for various times (0–60 min) using a hand-held UV-lamp (VILBER, VL-4.LC) at room temperature. Ultraviolet-irradiated P3HT films were dried in a vacuum overnight to remove residual solvent from the films. Identical P3HT films were fabricated on transparent glass for use in UV-Vis absorption measurements. Source and drain electrodes were formed on the ultraviolet-irradiated P3HT films by evaporating gold through a shadow mask (channel length = $100 \mu\text{m}$ and channel width = $2000 \mu\text{m}$).

2.2. Characterization

The solid state UV-Vis absorption spectra were acquired using a Thermo Scientific, Genesys 10S spectrometer. The polymer chain structural transition was analyzed using Raman spectrometry (LabRAM, HR-800) and Fourier transform infrared (FT-IR) spectrometry (Perkin Elmer, Spectrum Two). The surface morphologies of the P3HT films spin-coated onto silicon substrates were characterized using an atomic force microscope (AFM) (Bruker, Multimode 8) operated in the tapping mode. The electrical characteristics of the OFETs were measured using a semiconductor analyzer (Keithley 4200-SCS) in a vacuum at a room temperature.

3. Results and discussion

The effects of the ultraviolet irradiation on the structural changes in the P3HT thin films were investigated as a function of the irradiation time. Fig. 1 shows the UV-Vis absorption spectra of the P3HT films spin-cast using a CB solution, for short and long irradiation times. Rapid evaporation of the solvent molecules during the spin-casting process led to kinetically unfavorable conditions within the crystalline aggregates of the conjugated polymer. The spectra of the as-prepared P3HT thin films displayed a peak at $\lambda = 525 \text{ nm}$ with an intrachain $\pi\text{-}\pi^*$ transition (0–2), and weak energy features at 555 and 605 nm corresponding the second transition (0–1) and first transition (0-0), respectively [40].

As the ultraviolet irradiation time increased to 7 min, the intensities of the (0–1) and (0-0) transitions gradually increased. This change was attributed to an increase in the conjugation length due to an increase in the number of ordered aggregates involved in $\pi\text{-}\pi$ stacking interchain interactions (Fig. 1a) [41]. Once the spinning process was finished, a large amount of residual CB solvent remained in the P3HT film due to its high boiling point. Ultraviolet irradiation transformed the P3HT molecular structures in wet films, which promoted P3HT planarization and improved association during the solidification process. In the case of a film cast from a CF solution, the effects of the ultraviolet irradiation were minimal due to CF's low boiling point, as shown in Fig. S1. A P3HT film cast from CB and DCB and vacuum-dried displayed nearly no changes in the UV-vis spectrum (Fig. S2). Removing residual solvent molecules from the P3HT film prevented mobilization and association of the polymer chains [42]. During the ultraviolet post-treatment process, the quantity of residual solvent in the as-prepared films was key to mobilizing the polymer chains and rearranging the molecular structures during solidification. Increasing the ultraviolet irradiation time above 10 min reduced the intensities of both the (0–1) and (0-0) transitions (Fig. 1b), indicating that long ultraviolet irradiation times deteriorated the molecular order in the resultant P3HT films [43]. Care must be taken not to extend the ultraviolet irradiation time to the point at which the molecular order decreases. The interchain coupling energy, W was calculated from the ratio of the intensities of the (0-0) and (0–1) transitions [42]. The calculated W values are plotted as a function of the ultraviolet irradiation time under various solvent conditions in the inset of Fig. 1a. P3HT films cast from CB and DCB showed lower W values than those prepared using CF solution, and the lowest W value, 74.72 meV, or 57.72 meV, were obtained after ultraviolet irradiation for 7 min. A low W value indicates that the conjugation lengths are longer, which corresponds to a higher crystalline order in the films.

The ultraviolet irradiation effect could be understood, in part, in terms of the structural changes that accompanied p-doping in the P3HT main chains. Variations in the conformations of the p-doped P3HT chains with the ultraviolet irradiation time were investigated using Raman spectroscopy (Fig. 2). The band between 1400 and 1500 cm^{-1} corresponded to the $C_\alpha = C_\beta$ stretching vibration in regioregular P3HT: two bands were evident at 1445 and 1421 cm^{-1} , and these bands were assigned to the benzoid and quinoid stretching bands, respectively [44]. The benzoid and quinoid vibrations are observed in the pristine film, and the quinoid-to-benzoid peak area ratio was 0.205. The quinoid-to-benzoid peak area ratio increased to 0.452 after ultraviolet irradiation over 7 min, indicating that the conformational structure of the P3HT main chains partially changed from a benzoid to a quinoid structure under ultraviolet irradiation [45,46]. The quinoid-to-benzoid peak area ratio was 0.419 after 20 min irradiation, and the peak area ratio did not increase further above a 7 min ultraviolet irradiation time.

Fig. 3 shows a schematic diagram of the mechanism underlying the ultraviolet-induced P3HT chain transformation. The benzoid structure favored the random-coil conformation due to the presence of a single rotatable main chain, whereas the quinoid structure favored a linear or extended-coil conformation due to the double-bond character of the P3HT inter-ring bond. The resulting partial quinoid geometry in the P3HT chains exhibited a higher degree of coplanarity, which improved the neighboring $\pi\text{-}\pi$ interactions. The association strength among linear P3HT chains is expected to be stronger than the association strength among random-coil P3HT chains.

The degradation of the polymer chains during long ultraviolet irradiation times was characterized by measuring the infrared vibrational spectra of the P3HT thin films (Fig. 4). Ultraviolet irradiation in the presence of oxygen and water molecules led to polymer chain degradation, resulting in rapid and noticeable changes in the FT-IR spectrum. Fig. 4 shows typical FT-IR absorption spectra featuring the thiophene rings and the aromatic C-H region of the P3HT thin film. Upon ultraviolet irradiation, the FT-IR absorption bands associated with various functional groups in P3HT rapidly decreased. Signals

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