Electrical Signature of Ultrasound-Induced Anisotropic Self-Assembly of Poly(3-Hexylthiophene) (P3HT) during Channel Formation

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Abstract: We probed ultrasound irradiation-induced structural ordering of poly(3-hexylthiophene) (P3HT) chains during solidification of a sonicated P3HT solution by monitoring the temporal evolution of the electrical and spectroscopic signals. We observed a peak source-drain current in the test devices during the electrical channel formation, followed by a significant decrease, which has not been observed in the pristine P3HT solution as the solvent evaporates. Through P3HT concentration-dependent gated-sheet conductance and in-situ Raman spectroscopy measurements during channel formation, we found that the competition between aggregation of the disentangled P3HT chains in solution by sonication and the concentration-dependent chain interactions with solvent evaporation led to a distinct electrical signature in the channel formation of the sonicated P3HT film compared to that of the pristine P3HT. The finding provides insights into new opportunities through optimization between the thermodynamic and kinetic considerations in designing pre-deposition treatments for enhanced charge transport.

Keywords: P3HT; channel formation; sonication; molecular ordering; aggregation

1. Introduction

Enhancement of carrier mobility through molecular ordering has been an important issue in operating and optimizing flexible electronic devices that incorporate organic semiconductors [1–8]. Through various solution processing, particularly, researchers have tuned the crystallinity of the conjugated polymers based on retention of the solution phase in the solidified film phase [9–15]. Among various pre-deposition treatments including additive engineering, simple solution processing such as sonication-induced molecular ordering has attracted much attention due to dramatic mobility enhancement as well as its facile fabrication method [16–20].

It is very well-known that ultrasound irradiation induces increased P3HT chain interactions in solution state through molecular aggregation, where more enhanced π-π stacking is achieved, enabling tuning of molecular crystallinity [9,16]. Reichmanis et al. demonstrated ultrasound-induced disorder-order transition in P3HT solutions consistent with enhanced electronic transport in sonicated P3HT films [9,21,22]. Increase in the carrier mobility is explained by improved conjugation of the P3HT polymer chains, resulting from the anisotropic ordering of the molecules in ultrasound-irradiated solutions. The study also demonstrated tunable crystallinity through ultrasonic irradiation, allowing to control the extent of π-π stacking. Microscopic studies of the P3HT film morphology have revealed that molecular ordering can be tuned through competition between nucleation and growth mechanisms depending on the degree of supersaturation [21]. Extensive research themes have, however, focused on solidified films in articulating the structure-property relations in conjugated polymers, addressing the origin of the impact of solution treatment on the morphological change in the film state.
Several studies have been reported to understand electrical channel formation during solvent evaporation. Park et al. investigated the in-situ phase transition as a result of a change in the P3HT chain conformation during solvent evaporation using polarized Raman spectroscopy [16]. Angular-dependent Raman scattering peaks from P3HT thiophene rings point out that the crystalline phase appears in the formation of a P3HT conducting channel. The presence of an intermediate phase between isotropic and liquid crystalline phases was inferred from the fact that the vibrational frequency and the full width at half maximum (FWHM) of the C=C stretching mode during solvent evaporation decreased as solidification proceeds. Our previous work addresses the formation of the electrical conducting channel in poly(3-hexylthiophene) (P3HT) using in situ sheet conductance measurements, revealing the evolution of P3HT microstructure involving potential phase transitions between isotropic, liquid crystalline, and polycrystalline phases [10]. Fundamental and systematic studies of the in-situ electrical channel formation in which the conformation of the polymer chains are tuned through ultrasonic irradiation, however, have not been reported. As far as we know, comparison of the temporal evolution of the electrical current depending on the extent of nano-crystallites aggregation in forming a conducting channel has not been addressed. Given that electrical current is very sensitive to subtle structural change in solution, comparison between pristine and treated polymer solutions is complementary to in-situ microstructural analysis through conventional microscopic and spectroscopic methods.

Here, unlike structure-property correlation based on the ex-situ analytical methods, we focus more on the kinetic-oriented approach in which the final film morphology and crystallinity are tuned through ultrasonic irradiation, resulting in the evolution of the structural arrangement of molecules in the solvent during the solidification process. To elaborate on the mechanism through which electrical signature is specified by the extent of anisotropic molecular ordering in solution, we compared the temporal evolution of the electrical source-drain current during channel formation in the pristine and sonicated P3HT solution. Field-effect-modulated electrical properties were analyzed in correlation with the results from in-situ Raman spectroscopic measurements.

2. Materials and Methods

2.1. Fabrication of an Electrical Probe for In-Situ Channel Formation Investigation

We fabricated field-effect transistor (FET) devices by patterning the source and drain metal electrodes (Ti/Au) onto a SiO$_2$ gate dielectric (200 nm). Highly boron-doped silicon substrate (resistivity $\approx 0.005$ $\Omega \cdot$ cm) works as a gate electrode. We prepared pristine and sonicated P3HT solutions in chloroform (5 mg/mL). P3HT with a regioregularity of 92–94% was purchased from Sigma Aldrich.

To prepare a sonicated P3HT solution, we used a tabletop sonicator (~100 W) for ultrasonic irradiation. The P3HT solution was dipped in an ice-water bath for sonication, while the pristine P3HT solution was stirred with a magnetic bar without further treatment. To monitor the source-.drain current in the FET during solvent evaporation, we injected a drop of P3HT solution into the channel region of the FET device through a ceramic tube structured to confine droplets of a P3HT solution in the channel area, with a channel length of 20 $\mu$m and a width of 8 mm.

For in-situ electrical current measurements, the source and drain electrodes were biased with a small voltage (0.3 V) before the P3HT solution drop. The source-drain current was measured using a Keithley 2400 source meter. FET characterizations after solvent drying were carried out using an HP4145B semiconductor parameter analyzer. All the electrical measurements including in-situ current measurement and FET characterizations were carried out in a glove box. To measure P3HT chain conformational change, we used Raman (Kaiser Optical Systems, 785 nm laser source) spectroscopy, optical absorption, and photoluminescence (PL) measurements. To investigate the crystallinity of P3HT, out of plane grazing incidence X-ray diffraction (GIXD) data were collected. Tapping mode atomic force microscopy (AFM) images were obtained to compare the morphology of a P3HT film after sonication.
2.2. Calculation of FET Mobility and Four-Point Sheet Conductance Measurement

We calculated the FET mobility based on the assumption that, above the threshold voltage \( V_T \), the drain current, \( I_D \), increases linearly with carrier concentration, \( C_i(V_G - V_T) \), with the FET mobility being a proportional constant, as expressed in Equation (1),

\[
I_D = \frac{Z}{L} \mu C_i (V_G - V_T) V_D
\]  

(1)

where \( C_i \), \( Z \) and \( L \) are the areal capacitance, the width, and the channel length of the device, respectively. The FET mobility was calculated from the slope in the linear regime in which the drain current increases linearly with the gate voltage \( V_G \) in the \( I_D - V_G \) plot.

To rule out the P3HT/Au contact effect, we used gated four-contact geometry FET devices in which two voltage probes are placed between the source and drain electrodes to measure the potential in the P3HT channel. We measured the potential difference \( V_{diff} \) from the voltages at two probes spaced by \( d \) with the FET being in “on” state, in which a gate voltage above the threshold voltage is applied to induce mobile charge carriers in the channel. The sheet conductance \( (\sigma_{sq}) \) was estimated at a certain drain current from Equation (2):

\[
\sigma_{sq} = \frac{d}{W} \frac{I_D}{V_{diff}}
\]  

(2)

The four-contact field-effect mobility is calculated from the plot of the sheet conductance as a function of gate voltage, as shown in Equation (3):

\[
\mu = \frac{1}{C_i} \cdot \frac{d \sigma_{sq}}{dV_G}
\]  

(3)

3. Results and Discussion

The structural crystallinity of a solidified film after ultrasound irradiation of the P3HT solution was remarkably enhanced from the grazing incidence X-ray diffraction (GIXD) and photoluminescence (PL) measurements. The GIXD data of the spin-coated P3HT films with a distinct (100) diffraction peak in Figure 1a indicate, indeed, that \( \pi-\pi \) stack aggregation-induced molecular ordering is more prominent than that in the pristine P3HT, which is consistent with a lower PL intensity in the sonicated P3HT film, as seen Figure 1b [4]. Comparison of the PL intensity between the pristine and the sonicated P3HT films shows that a higher PL intensity was observed in the pristine P3HT, which is attributed to more enhanced interactions between the polymer chains in the sonicated P3HT [4]. The origin of the enhanced crystallinity in the sonicated P3HT film is consistent with the color change of the P3HT solution from bright orange to dark brown, as seen in the inset of Figure 1a, which is a feature of aggregation of P3HT polymer chains [1]. The structural difference will be discussed later.

The enhanced molecular ordering in the sonicated P3HT film led to a far larger hole mobility. Figure 2 compares the FET transfer characteristic curves of the pristine and sonicated P3HT FETs, from which the FET hole mobilities were extracted. The hole FET mobility increased from \( 2.2 \times 10^{-4} \) cm\(^2\)/Vs in the pristine P3HT to \( 3.2 \times 10^{-3} \) cm\(^2\)/Vs after ultrasonic irradiation. As reported in previous studies, indeed, sonicated P3HT films prepared by spin-coating show enhanced crystallinity, thereby enhanced carrier mobility [5,16]. For both P3HT FETs, we observed gate scan direction-dependent drain current hysteresis, which is typically observed in disordered materials such as organic semiconductors. With a high density of electronic traps, induced carriers in the electrical channel by the gate electric field are easily trapped or de-trapped depending on the polarity of the gate electric field.
We compared the temporal evolution of the source-drain current for the pristine and sonicated P3HT. As the solvent evaporates, the local concentration of the P3HT at the free surface remarkably increases, causing a higher electrical field. The enhanced molecular ordering in the sonicated P3HT film led to a far larger hole mobility. In the pristine P3HT, the FET hole mobilities were 2.2 × 10^{-4} cm^2/Vs, while after ultrasonic irradiation, the FET hole mobilities were 3.2 × 10^{-3} cm^2/Vs. The applied drain voltages were 8 V. For the pristine and sonicated P3HT films spin-coated from the P3HT solution (10 mg/mL, chloroform), the FET hole mobilities were 2.2 × 10^{-4} and 3.2 × 10^{-3} cm^2/Vs, respectively. The FET hole mobilities were extracted from the forward gate scan, which is scanned from the positive to the negative gate voltage.

To understand electrical channel formation depending on the aggregation-induced anisotropic ordering of the P3HT chains, thereby enhancing carrier mobility due to increased crystallinity, we monitored the magnitude of the drain current as a function of time during the solidification process. We compared the temporal evolution of the source-drain current for the pristine and sonicated P3HT with the in-situ probing structure, as shown in Figure 3a. On dropping a droplet of P3HT solution onto the test device, we observed a dramatic current increase in both devices due to percolation of the P3HT polymer chains in the solution state, as seen in Figure 3b,c. As the solvent evaporates, the local concentration of the P3HT at the free surface remarkably increases, causing a higher electrical conductivity near the free surface after the current onset [10,23–25]. This is consistent with our previous report in which the channel formation of the sonicated P3HT in different solvents was investigated [10].

Figure 1. (a) Grazing incidence X-ray diffraction (GIXD) data of the pristine and sonicated poly(3-hexylthiophene) (P3HT) films prepared by spin-coating of a P3HT solution (5 mg/mL, chloroform). The inset shows the image of the pristine (bright orange) and sonicated (dark brown) P3HT solutions. (b) Comparison of the photoluminescence (PL) intensity of the pristine and sonicated P3HT films. The spin-coated P3HT film thickness is estimated to be 90 nm.

Figure 2. Comparison of the transfer characteristic plots of the P3HT films prepared by spin-coating. The applied drain voltages were ~8 V. For the pristine and sonicated P3HT films spin-coated from the P3HT solution (10 mg/mL, chloroform), the FET hole mobilities were 2.2 × 10^{-4} and 3.2 × 10^{-3} cm^2/Vs, respectively. The FET hole mobilities were extracted from the forward gate scan, which is scanned from the positive to the negative gate voltage.
The magnitude of the drain current during solidification of the P3HT solution in the channel region is governed by the formation of the conducting pathways, the degree of ordering, and the carrier concentration [26–28]. The magnitude of the maximum current in the sonicated P3HT solution is more than an order of magnitude larger than that in the pristine P3HT solution, as seen in Figure 3d, which is attributed to enhanced π-π stacking of the polymer chains by the aggregation of the P3HT chains. The strong intermolecular interaction results in the formation of the ordered region with larger crystallites. The crystallite size in the sonicated P3HT film is, indeed, calculated to be 13 nm from the Debye–Scherrer method, while, for the pristine P3HT, the presence of the ordered region is not ensured from the GIXD data in Figure 1a. In other words, far higher drain current in the sonicated P3HT in comparison with that in the pristine P3HT clarifies that preferred P3HT chain alignment in the sonicated P3HT, resulting in enhanced molecular ordering, dominates over the formation of current path in determining the drain current.

Indeed, from the optical absorption data in Figure 4a,b, anisotropic orientation is more prominent in the sonicated P3HT. Two peaks at 570 and 610 nm in Figure 4a are identified with 0-1 and 0-0 vibrational peaks, respectively. The presence of the two peaks in the sonicated P3HT solution explains more prominent π-π stacking-induced aggregation due to enhanced P3HT interchain interactions [16]. After solidification, the ultrasonic irradiation process increases the planarity of the conjugated P3HT path in determining the drain current.

Figure 3. (a) A schematic diagram of the test structure for investigating the temporal evolution of the source (S)-drain (D) current. The ceramic tube confines a drop of P3HT solution (5 mg/mL) into the channel region during solidification. The inset shows an image of the experimental set-up. The channel length and the width of the device were 20 µm and 8 mm, respectively. Temporal evolution of the source-drain current in (b) pristine and (c) sonicated P3HT solution. The concentration of the P3HT solution in chloroform was 5 mg/mL. The drain voltage was fixed at 0.3 V, and the measurement was carried out in an argon-filled glove box. (d) Comparison of temporal change in the drain current (logarithmic scale).
nature of the polymer chains in solution state was retained after solidification, which is in accordance with a far higher current in the sonicated P3HT, as shown in Figure 3d.

![Image of Figure 4](image_url)

**Figure 4.** Comparison of optical absorbance between the pristine and the sonicated P3HT for (a) solution (5 mg/mL in CHCl₃) and (b) film states (90 nm).

More importantly, for the sonicated P3HT in Figure 3c, we reproducibly observed a significant current decrease after the current peak at 12 min following a dramatic increase in the current, while, for the pristine P3HT in Figure 3b, a less sharp current peak at 6 min is observed as the solvent evaporates with time. In our previous study, we found that the change in the source-drain current depends on the solvent–P3HT chain interactions as well as the boiling point of the solvent [10]. We hypothesize that the more anisotropic nature of the P3HT molecules in the sonicated P3HT solution, as demonstrated in the optical absorption feature in Figure 4, leads to a more significant decrease in the current after the peak current. The presence of the significant current peak results from a competition between vibration-induced aggregation of the disentangled P3HT chains (increasing the current) and immobilization of the chains during solidification, through which the concentration of P3HT solution is increased (decreasing the current). In other words, optimum P3HT concentration for the formation of the efficient electronic transport pathways exists during solvent evaporation in which P3HT solution concentration increases with time.

The disentangled P3HT chains in the sonicated P3HT solution is more sensitive to solvent evaporation than the pristine P3HT with entangled chains, leading to more orientational change than in the pristine P3HT, causing a sharp peak current in comparison with a less sharp peak current in the pristine P3HT, as seen in Figure 3b,c. As solvent drying proceeds with an increase in the P3HT concentration, the distance between P3HT chains become closer. The subsequent solvent evaporation varies the extent of anisotropic molecular self-assembly of the disentangled P3HT molecules. According to Park et al., sonicated P3HT back-bones interact in solution, leading to phase transition from the isotropic to the liquid crystalline phase [23]. From Raman spectroscopy data, C=C stretching peak frequency in the thiophene rings was varied during solvent evaporation, accounting for the fact that P3HT back-bones interact with each other. Angular-dependent Raman intensities indicate that the P3HT chains feature anisotropic ordering during solvent evaporation. For the sonicated P3HT solution, as the concentration increases with further evaporation, anisotropic ordering is suppressed with more entangled P3HT chains.

To demonstrate the proposed hypothesis, we carried out experiments in which FET mobilities were measured as a function of P3HT concentration in Figure 5. We observed that the mobility increased until a particular concentration followed by a decrease with a further increase in the concentration of the sonicated P3HT solution. The presence of a peak FET mobility was reproducibly observed in several experiments. This clearly indicates that an optimum distance between P3HT chains set by the
concentration of the P3HT solution exists in attaining the efficient electrical current path. In the case of the pristine P3HT, P3HT solution concentration-dependent FET mobilities were not observed.

![Graph](image)

**Figure 5.** Plot of P3HT four-point mobility as a function of P3HT concentration of sonicated P3HT solution. The inset shows a four-point geometry gated-device (L = 200 µm, W = 2800 µm d_y = 80 µm, and V_{diff} = V_1 - V_2).

In other words, for the pristine P3HT, change in the molecular orientation during solvent evaporation has a negligible effect on the source-drain current because the entangled P3HT chains are randomly oriented, forming the disordered region. The abrupt current increase until saturation in the pristine P3HT in Figure 3b is mainly, therefore, due to the increase in the P3HT chain density with solvent evaporation rather than the increase in molecular ordering, as demonstrated in a far lower drain current than that in the sonicated P3HT during channel formation, as observed in Figure 3d. The degree of ordering in the randomly oriented P3HT chains in the pristine P3HT solution state is not sensitive to further solvent evaporation, i.e., increase in the concentration, as supported by the little change in the drain current.

The change in the current after the peak current in the sonicated P3HT solution is associated with self-assembly of the polymer chains through a modified in-situ experiment. We tilted the substrate on which the source and drain contacts are patterned, as shown in the Supporting Information, Figure S1, to accelerate the elimination of the solvent in the channel region during the solidification process. For the sonicated P3HT, the current drop after the peak current was not significant, which is similar to that in the pristine P3HT. The absence of a dramatic current change indicates that abrupt immobilization of polymer chains by fast evaporation of solvent freezes the polymer chains, causing saturation of the current independent of pristine and sonicated P3HT. The result allows us to infer that the gradual current decrease after the peak current in the pristine P3HT is due to the isotropic nature of the polymer chains in the solvent in comparison with the sonicated P3HT solution. In other words, randomly oriented P3HT chains in the pristine solution are not significantly influenced by a fast solidification process in which the abrupt P3HT concentration increase, immobilizing the P3HT polymer chains.

In contrast, for the sonicated P3HT chains with anisotropic ordering in solution, the abrupt solvent depletion leads to a significant reduction in the mobility of the polymer chains, suppressing the self-assembly driven by the interactions between the polymer chains in solution. In the pristine P3HT, the effect of P3HT chain mobility on ordering with further evaporation is not significant because the P3HT chains are already entangled, resulting in randomly oriented polymer chains in the pristine P3HT, which are not sensitive to the change in the concentration of P3HT solution. To articulate the mechanism, however, further controlled experiments are required.

To provide insights into channel formation mechanism, the use of a high boiling point solvent such as 1,2,4-trichlorobenzene (TCB) benefits in probing polymer conformation in-situ during solvent
evaporation over the extended time. As seen in the Supporting Information, Figure S2, phase transition into the crystalline state is observed after an elapsed time following the current onset. The abrupt current onset in the initial stage results mainly from the formation of the conducting pathways, not by the phase transition from a non-crystalline to a crystalline phase. Comparing the magnitude of the current for both samples in Figure 3 with a lower boiling point solvent (CHCl$_3$), we observed a far larger current in the sonicated P3HT from the current onset, as seen in Figure 3d. This clearly explains that anisotropic self-assembly in the sonicated P3HT is retained during electrical channel formation, supporting that the source-drain current in the sonicated P3HT evolves with the change in the degree of anisotropic ordering in the P3HT solution. It is important to note that a possible current decrease due to doping in the Ar-filled glove box is excluded through comparison with that in air, in which the same trend was observed.

Retention of anisotropic phase in solution into the ordered film phase is often suppressed by many factors, such as molecular weight, the choice of solvent, polymer regioregularity, concentration, and interaction with substrate. As found in earlier experiments, indeed, the FET mobility in the sonicated P3HT is maximized at a narrow concentration range, evidencing that retention of a solution phase into a film phase involves many complicating factors. However, the far higher current observed during channel formation in the sonicated P3HT, whether in solution state or in film state, points out that aggregated P3HT clusters formed nano-crystallites both in the sonicated P3HT solution and solid film phase, dominating other factors in determining the film structure, and thereby the magnitude of the electrical current. Given that sonication-induced ordering effect is more effective to regioregular P3HT chains than regiorandom P3HT chains [9,22], ultrasonic irradiation is believed to act on facile formation of nano-crystallites by enhanced side-chain interactions between P3HT molecules.

To summarize, we found that enhanced anisotropic self-assembly of the P3HT chains in solution acquired by sonication leads to the distinctly different temporal evolution of the electrical current, which is distinguished from that of the entangled pristine P3HT chains. As the concentration increases with solvent evaporation, P3HT back-bone chains interact, forming an anisotropic crystalline phase. Importantly, an optimum concentration, at which an efficient charge transport path is achieved during the solidification process, differentiates temporal evolution of the current between the pristine and the sonicated P3HT. Our findings point out that the temporal evolution of the structural arrangement of polymer chains with anisotropic ordering reflects chain–chain interactions varied by concentration-dependent chain density in solution. A signature of anisotropic self-assembly is manifested through concentration-dependent molecular ordering, which can be probed and further applied in designing the pre-deposition treatment in solution state for enhanced charge transport in its film states.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/19/6886/s1, Figure S1: Drain current as a function of time during solvent evaporation, Figure S2: Structural evolution of P3HT during solidification.

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