

## Low Spin-Casting Solution Temperatures Enhance the Molecular Ordering in Polythiophene Films

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High-crystallinity poly(3-hexylthiophene) (P3HT) thin films were prepared by aging the precursor solutions, prepared using a good solvent, chloroform, at low temperatures prior to spin-casting. Lower solution temperatures significantly improved the molecular ordering in the spin-cast P3HT films and, therefore, the electrical properties of field-effect transistors prepared using these films. Solution cooling enhanced the electrical properties by shifting the P3HT configuration equilibrium away from random coils and toward more ordered aggregates. At room temperature, the P3HT molecules were completely solvated in chloroform and adopted a random coil conformation. Upon cooling, however, the chloroform poorly solvated the P3HT molecules, favoring the formation of ordered P3HT aggregates, which then yielded more highly crystalline molecular ordering in the P3HT thin films produced from the solution.

**Key Words :** Molecular ordering, Polythiophene, Organic field-effect transistors, Solubility, P3HT

### Introduction

Emerging optoelectronic applications rely on the development of easy and low-cost solution-based thin film deposition techniques for producing polythiophene thin films.<sup>1-9</sup> Structural defects in the semiconductor layer of organic field effect transistor (FET) as a result of poor organization among the polythiophene molecules can present a major challenge to obtaining high-performance devices based on these thin films.<sup>10</sup> Charge carrier transport through a material is limited by the need to hop between molecules in disordered regions with weak intermolecular electronic coupling. An effective and rational approach to overcoming this drawback has been to prepare ordered polythiophene aggregates in which  $\pi$ - $\pi$  stacking planes are oriented parallel to a dielectric substrate.<sup>11,12</sup> Thin film fabrication methods, such as spin-coating, which are used to fabricate large-scale homogeneous films, typically produce amorphous-like films with less ordered structures. Rapid solvent evaporation during film formation can kinetically disrupt the growth of well-ordered structures.<sup>13</sup>

Aside from the use of post-treatment processing steps, such as thermal<sup>14-17</sup> or solvent annealing,<sup>18-21</sup> a key strategy for enhancing the molecular ordering of polythiophene films for use in high-performance electrical devices is to use high boiling point solvents or marginal solvents with bad solubility.<sup>22-25</sup> Relatively few studies have examined the advantages of controlling the solubility of polythiophene in good volatile solvents in which the molecular ordering of the polythiophene molecules may be readily enhanced by cooling the solution below 0 °C.<sup>26,27</sup>

Here, we studied the temperature-dependent solubility of poly(3-hexylthiophene) (P3HT), a representative polythiophene, in an effort to control the molecular ordering in thin films fabricated *via* spin-coating under rapid solvent evaporation conditions. The assembly of chains in solution translates to various levels of order in a film prepared simply by cooling the solution or aging the solution at low temperatures using a good solvent, such as chloroform. FETs with good performance characteristics may be readily fabricated by optimizing the polymer molecular assembly in solution. Our focus in this study was to identify the relationship between molecular order in solutions containing P3HT and the field-effect mobilities of the resulting FETs. This goal was achieved by preparing ordered precursors through cooling P3HT solutions in a good solvent, chloroform.

### Experimental

**Preparation of Polymer Thin Films and Devices.** P3HT obtained from Rieke Metals, Inc. (regioregularity ~90%, molecular weight,  $M_w$  = 20-30 kDa) was used as received without further purification. Field-effect transistors with a top-contact geometry were fabricated using doped *n*-type Si wafers as the gate electrodes and a 300 nm thick thermally grown silicon dioxide (SiO<sub>2</sub>) layer as the gate dielectric. Octadecyltrichlorosilane (Gelest) was used as an organic interlayer between the active material and the dielectric layer and was self-assembled on the SiO<sub>2</sub> surface *via* a dipping method. The P3HT (Rieke Metals Inc.) solution in chloroform (5.0 mg/mL) was stirred at room temperature (RT) overnight to permit complete dissolution of the P3HT. A

temperature-controlled bath was cooled to 0 °C and allowed to stand for 30 min to ensure thermal equilibrium. The P3HT solution in vial was then placed in a temperature-controlled bath and aging process is timed. The P3HT solution was left to self-assemble and characterized at regular time intervals. A simple spin-casting method was used to fabricate P3HT thin films with thicknesses of 25–31 nm. The source–drain electrodes (channel length 100 μm, channel width 1000 μm) were prepared by inkjet printing a water-based ink containing the conducting polymer, poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (Bytron P) onto the P3HT film.

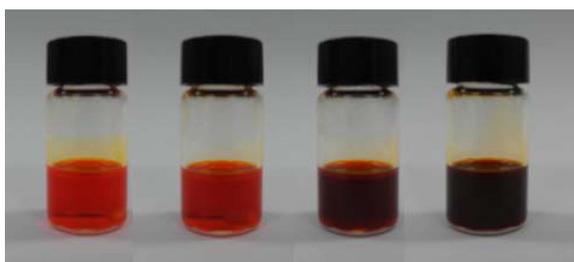
**Characterization of the P3HT Thin Films and Devices.** Grazing incidence X-ray diffraction (GIXRD) experiments were carried out at the 3D and 8D beamlines (wavelength approx. 1.54 Å) at the Pohang Accelerator Laboratory. The electrical characteristics of the FETs were measured in the accumulation mode using Keithley 4200 and 236 source/measure units at room temperature and under ambient conditions.

## Results and Discussion

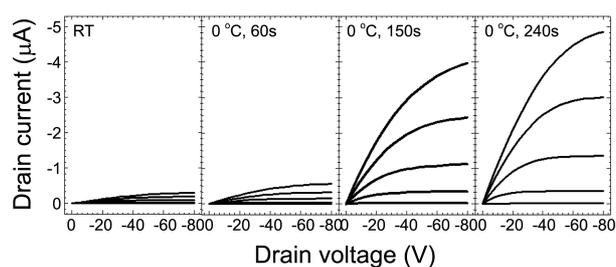
The P3HT used in this study was found to have solubility exceeding 30 mg/mL in chloroform at room temperature. A 5 mg/mL P3HT solution in chloroform was stirred at room temperature overnight to permit complete dissolution of P3HT. The P3HT solution was then cooled to 0 °C. The color changes displayed by the P3HT solution were examined with the aging time, as shown in Figure 1.

At 0 °C, chloroform was not a good solvent for P3HT; therefore, the color of the P3HT solution changed from orange to dark brown during the aging period (see the color change observed between 60 and 150 seconds in Figure 1). This observation suggested that the P3HT molecules began to crystallize and form ordered aggregates in the solution.<sup>28</sup> This state minimizes the unfavorable contacts between the poorly soluble P3HT and the chloroform, and maximizes the favorable  $\pi$ - $\pi$  stacking interactions in the solution. Interestingly, P3HT solutions containing ordered precursors could be prepared, even in chloroform (a good solvent for P3HT) by decreasing the solution temperature.

The impact of the aging time on the electrical characteristics and the field-effect charge carrier transport properties was examined by fabricating and evaluating thin film



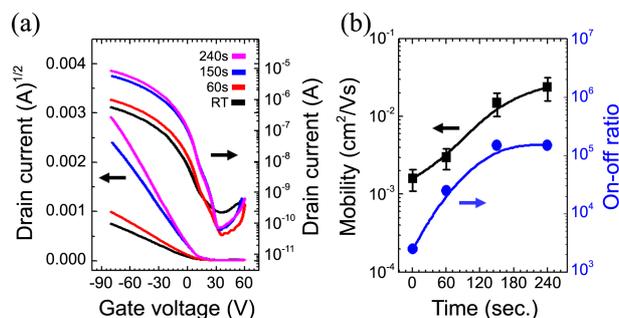
**Figure 1.** Photographs of P3HT solutions aged for various periods of time: 0 s (RT), 60 s, 150 s, and 240 s at 0 °C.



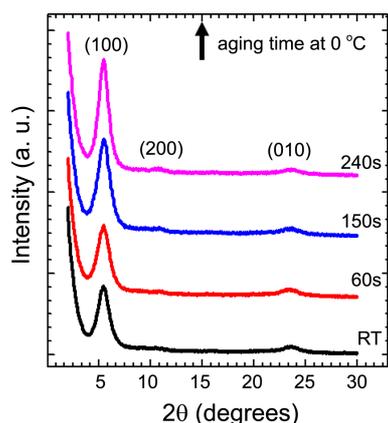
**Figure 2.** Current–voltage characteristics of the P3HT FETs (Channel length: 100 μm, channel width: 1000 μm) prepared from P3HT solutions with various aging times (0 s at RT, 60 s at 0 °C, 150 s at 0 °C, and 240 s at 0 °C). The drain voltage was swept from 0 V to –80 V at a fixed gate voltage of 0, –20, –40, –60, and –80 V.

transistors with top contacts. A simple spin-coating method was used to fabricate P3HT thin films with thicknesses of 25–31 nm using a P3HT solution at 0 °C aged over different intervals of time. Typical drain current vs. drain voltage plots at five different gate voltages, as a function of the aging time, are shown in Figure 2. A clear progression to higher currents was observed as the precursor solution was allowed to stand up to 240 sec prior to film deposition. The saturation current reached a value of only 0.16 μA at  $V_G = -80$  V for FETs prepared from the solution stored at RT; however, devices prepared from solutions aged over 240 sec yielded a current of 4.7 μA at  $V_G = -80$  V. The device performances were determined by measuring the transfer characteristics (Figure 3). The average field-effect mobility of each transistor prepared from solutions aged for a given period of time was calculated in the saturation regime ( $V_D = -80$  V) by plotting the square root of the drain current versus gate voltage.<sup>29</sup>

The average field-effect mobility of the P3HT FET prepared from a solution aged for 150 sec ( $1.5 \times 10^{-2}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) at 0 °C was about one order of magnitude greater than the mobility obtained from a P3HT FET fabricated from an as-prepared solution ( $1.6 \times 10^{-3}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) stored at RT. A maximum mobility of  $2.4 \times 10^{-2}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was obtained for an FET prepared from a solution aged over 240 sec at 0 °C. The field-effect mobilities of FETs prepared with P3HT thin films formed by spin-coating were low mainly due to the



**Figure 3.** (a) Plot of drain current versus gate voltage for a fixed drain voltage of –80 V: linear (left axis) and log (right axis) scales. (b) Summary of the device characteristics obtained from the P3HT FETs.

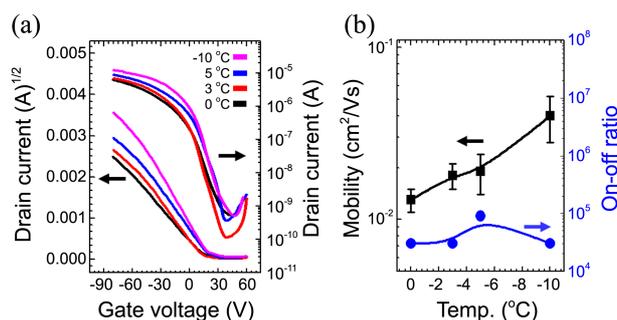


**Figure 4.** Out-of-plane GIXRD patterns as a function of the scattering angle  $2\theta$  for P3HT thin films on  $\text{SiO}_2/\text{Si}$  substrates prepared from  $2.5 \text{ mg mL}^{-1}$  precursor solutions. The aging time at  $0^\circ\text{C}$  increased in the direction of the arrow.

poor crystallinity of the film resulting from the rapid solvent evaporation during spin-coating and the preferential assumption of random coil conformations by the P3HT molecules in a good solvent. The remarkable increase in the field-effect mobility resulted from the enhanced molecular ordering of the P3HT chains in solution, as shown in Figure 1. However P3HT at higher aging time than 240 sec form gels, the viscosities of which increase strongly. This property makes it difficult to fabricate uniform film by spin-coating.

The changes in the crystalline structures of the P3HT layers as a result of solution aging were probed by synchrotron GIXRD measurements. Figure 4 shows the out-of-plane X-ray diffraction patterns of the P3HT films after a variety of aging times. The first Bragg peak (100) in the as-prepared film, which corresponded to a lamellar layer structure ( $16.0 \text{ \AA}$ ),<sup>30</sup> was weak. As the P3HT solution aging time increased, the (100) reflection became stronger. This structure was beneficial for facilitating lateral charge carrier transport because the  $\pi$ - $\pi$  stacking was maximized along the parallel direction. Considering that thin films prepared from these precursor solutions were found to be the same thickness (25–31 nm, as measured by ellipsometry), the enhanced peak intensity was directly correlated with the formation of ordered aggregates in the aged P3HT solution. As the P3HT solution aging time increased, P3HT thin film showed a higher root-mean-square surface roughness; this is attributed to the larger ordered aggregates formed from an aged solution at low temperature (data not shown).

The electrical properties of the P3HT thin film FETs prepared using solutions aged at different temperatures (0,  $-3$ ,  $-5$ , and  $-10^\circ\text{C}$ ) were measured. Devices fabricated from solutions aged at  $-10^\circ\text{C}$  for 120 s yielded a higher saturation current of  $7 \text{ \mu A}$  at  $V_G = -80 \text{ V}$ . The average field-effect mobility of the P3HT FET fabricated from the aged solution ( $4.0 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) at  $-10^\circ\text{C}$  for 120 sec was a factor of three greater than that of a P3HT FET fabricated from a solution aged at  $0^\circ\text{C}$  ( $1.3 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ). It was difficult, however, to prepare uniform thin films after long aging



**Figure 5.** (a) Plot of drain current versus gate voltage for a fixed drain voltage of  $-80 \text{ V}$ : linear (left axis) and log (right axis) scales. The aging time was fixed at 120 s and the aging temperature was varied ( $0^\circ\text{C}$ ,  $-3^\circ\text{C}$ ,  $-5^\circ\text{C}$ , and  $-10^\circ\text{C}$ ). (b) Summary of the device characteristics obtained from the P3HT FETs.

times or at temperatures below  $-10^\circ\text{C}$  due to the gelation of the solution. Note that the viscosity of the solution increased as the solubility of the solution decreased.

P3HT is highly soluble in chloroform at RT, and this solubility is strongly dependent on temperature due to the thermochromic properties of polythiophene.<sup>31,32</sup> The solubility of P3HT, as determined from the observed color changes, could be modulated by varying the aging time at  $0^\circ\text{C}$  or by decreasing the solution temperature. Conformational changes in P3HT, from random coils to ordered aggregates, occurred in P3HT chloroform solutions cooled to very low temperatures.<sup>33</sup> As the P3HT solution aging time increased at temperatures below  $0^\circ\text{C}$ , or as the temperature of the P3HT solution decreased, the thin films formed with more ordered structures, and the electrical characteristics of the resulting FETs also improved. The molecular ordering of the P3HT thin films could be varied by changing the solution or the substrate temperature, the aging time, or the solvent choice. Our study demonstrated that the electrical properties of P3HT FETs can be greatly enhanced by decreasing the solution temperature. This method is simpler than common post-treatment methods, such as thermal or solvent annealing.

## Conclusion

Here, we examined the development of P3HT structure as a function of the chloroform solution aging time at  $0^\circ\text{C}$ , or as a result of cooling the precursor solution. Chloroform was a good solvent at room temperature, but the solvation of the P3HT molecules changed with the temperature. The field-effect mobilities of P3HT films may be enhanced by manipulating the solubility of P3HT in solution.  $\pi$ - $\pi$  stacking among the P3HT chains in thin films could be enhanced by aging the precursor solution at  $0^\circ\text{C}$  or by reducing the temperature of the solution. Importantly, no post-treatment was required in the method developed here. Our study shows that the formation of low-crystallinity P3HT thin films may be avoided by optimizing the temperature-dependent self-organization of P3HT structures in a good solvent, which subsequently form highly crystalline structures during

spin-casting. Such films produced FETs with good electrical properties. This method for enhancing the molecular ordering in solution is straightforward and requires no additional post-treatment steps prior to device fabrication.

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