

High Molecular Weight Conjugated Polymer Thin Films with Enhanced Molecular Ordering, Obtained *via* a Dipping Method

Yeong Don Park

Department of Energy and Chemical Engineering, Incheon National University, Incheon 406-772, Korea

E-mail: ydpark@incheon.ac.kr

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The fabrication of polymer field-effect transistors with good electrical properties requires the minimization of molecular defects caused by low molecular weight (MW) fractions of a conjugated polymer. Here we report that the electrical properties of a narrow bandgap conjugated polymer could be dramatically improved as a result of dipping a thin film into a poor solvent. The dipping time in hexanes was controlled to efficiently eliminate the low molecular weight fractions and concomitantly improve the molecular ordering of the conjugated polymer. The correlation between the structural order and the electrical properties was used to optimize the dipping time and investigate the effects of the low MW fraction on the electrical properties of the resulting thin film.

Key Words : Molecular weight, Dipping, Narrow bandgap polymer, OFET

Introduction

Conjugated polymers can display excellent optoelectrical properties and are useful as soft active components in organic-based electronic devices, such as field-effect transistors (FETs),¹⁻⁶ light-emitting diodes,⁷ and photovoltaic cells.^{8,9} Polymeric semiconductors can be easily processed using low-cost solution-based thin film deposition techniques, such as spin-coating, ink-jet printing, dip-coating, and screen-printing, to yield films that are flexible, large in area, and lightweight.¹⁰⁻¹³ The device performance depends on the conjugated polymer molecular weight distribution, and structural defects in the films due to poor self-assembly *via* weak van der Waals interactions can cause variations in the device performance, particularly when fabricated using solution processes.¹⁴

Previous studies focusing on the effects of the conjugated polymer MW have shown that the MW can tune the charge transport properties over several orders of magnitude.^{15,16} Previous studies found that the mobility increased with the MW, suggesting that the high MW polymers formed an interconnected network that provided a high mobility, whereas the low MW polymers formed isolated microstructures that did not efficiently conduct charge carriers. The mobility-MW relationship resulted mainly from the backbone conformation, suggesting that the low MW conjugated polymers assumed a twisted and disordered backbone conformation that reduced the effective conjugation length for charge hopping.¹⁷ The electronic properties of conjugated polymer films may potentially be improved by identifying a straightforward procedure for optimizing the semiconducting polymer MW distribution.^{18,19}

Here, we used a simple physical method for eliminating the low MW polymer in a spin-coated polymer thin film by immersing the film in a poor solvent for a few minutes. This

method was systematically examined in an effort to improve the charge carrier transport properties in the films. The thin films displayed an enhanced intermolecular ordering that yielded high-performance FETs.

Experimental

Synthesis. Poly[2,6-(4,4-bis-(2-dodecyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT), a class of narrow band gap conjugated polymers under consideration for their use in polymer solar cells due to their good electrical characteristics, was synthesized as previously reported, as summarized in Figure 1(a).^{20,21} Once the polymerization had gone to completion, the reaction was quenched with methanol and the product was purified *via* Soxhlet extraction successively with hexanes, THF, and acetone. The number average MW, M_n , was 29 kDa and the polydispersity index was 2.4, as measured by gel permeation chromatography against a polystyrene standard. The MW of the hexanes-soluble extract from the PCPDT-BT film was estimated by comparison to a 10 kDa standard that had been prepared by adjusting the stoichiometry of the reactants.

Device Fabrication. Transistors having a bottom-gate, top-contact geometry were fabricated using highly doped Si wafers with a 150 nm thermal oxide gate dielectric layer (SiO₂, capacitance = 20 nF cm⁻²). These wafers were cleaned in a piranha solution (7:3 mixture of H₂SO₄ and H₂O₂) for 30 min, rinsed with deionized water, and dried under a nitrogen stream. Hexamethyldisilazane (HMDS) was spin-coated onto the SiO₂ substrate to form an organic interlayer material that reduced interface charge trapping. The PCPDT-BT thin films were spin-coated from a 5 mg/mL solution in chlorobenzene on HMDS-treated SiO₂ substrates. The resulting films were subsequently dipped into three different poor solvents: meth-

ylene chloride, hexanes, and acetone. Gold source and drain electrodes (channel length: 50, width: 1000 μm) were thermally evaporated through shadow masks.

Characterization of the PCPDT-BT Solution and Thin-film. The solubility of PCPDT-BT in various solvents was determined by UV-vis absorption spectroscopy applied to saturated solutions at room temperature. The solubility of the polymer was found to be: 10.5 ± 0.4 mg/mL in chlorobenzene, 0.46 ± 0.01 mg/mL in methylene chloride, 0.095 ± 0.003 mg/mL in hexanes, and almost insoluble in acetone.

The UV absorption spectra of the low MW fractions dissolved in hexanes were investigated by dipping 40 films that had been spin-coated onto a wafer (2×2 μm) into a hexanes solution for a few minutes. After the dipping process, the hexanes solution was dried and the low MW fraction had dissolved in chlorobenzene. One of the films was redissolved in chlorobenzene for UV-vis analysis, after the hexanes dipping step. The solid and solution state UV-vis absorption spectra were recorded on a Beckman Coulter DU 800 series spectrophotometer. The absolute MW of the samples was measured by matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (Bruker REFLEX III). All MALDI-TOF spectra were recorded in the linear mode with an accelerating potential of 20 kV. Dithranol was employed as a matrix without adding any salt, and a standard kit (calibration mixture 2: Applied Biosystems) was used for the calibration. Grazing-incidence X-ray diffraction (GIXD) measurements were performed at the 3D and 8D beamline (wavelength approx. 1.54 \AA) at the Pohang Accelerator Laboratory (PAL) in Korea. The film thickness values were determined using an ellipsometer (M-2000V, J.A. Woollam Co., Inc.). The electrical characteristics of the OFETs were measured in the accumulation mode using Keithley 4200 source/measure units at room temperature and under ambient conditions.

Results and Discussion

Figure 1(b)-(d) shows the dipping time-dependent UV-vis absorption spectra of the PCPDT-BT films obtained from three different solvents. The UV-vis absorbance band intensity of the PCPDT-BT thin films after dipping in hexanes decreased over time by 7-10%, suggesting a decrease in the film thickness (Figure 1(c)). The film thickness was measured using ellipsometry techniques, which revealed that the thickness of the as-prepared film was 26.3 ± 0.1 nm. Films dipped into hexanes were found to be approximately 25.3-24.4 nm thick, depending on the dipping time (Figure 1(e)). Dipping in methylene chloride resulted in a greater loss in thickness, as evidenced by the 12-19% reduction in the absorbance band intensity, whereas the intensity after dipping in acetone did not change significantly. These results revealed that the small MW fractions of the PCPDT-BT thin films could be selectively eliminated by dipping in the appropriate solvent.

The UV-vis absorption spectra of PCPDT-BT having a 10 kDa or 29 kDa MW were examined in chlorobenzene, as

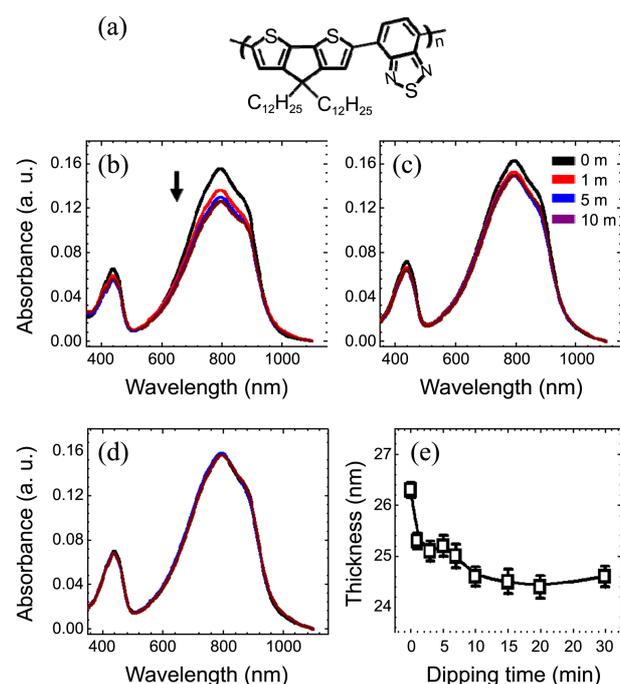


Figure 1. (a) Chemical structure of the PCPDT-BT monomer. UV-vis absorption spectra of the PCPDT-BT thin films prepared with various dipping times in (b) methylene chloride, (c) hexanes, (d) acetone. The dipping time increased in the direction of the arrow. (e) The PCPDT-BT thin film thickness as a function of the dipping time in hexanes.

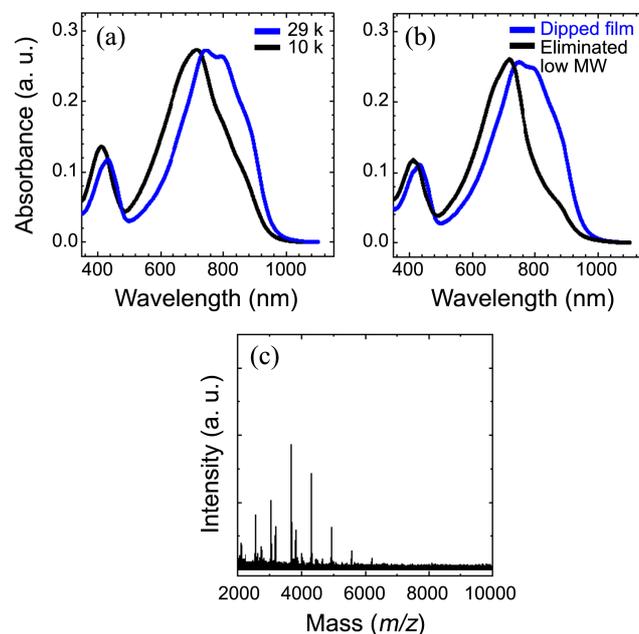


Figure 2. UV-vis absorption spectra in the solution state for PCPDT-BT samples prepared to have a MW of (a) 10 kDa or 29 kDa; (b) UV-vis absorption spectra of the low MW fraction dissolved in hexanes and the film dipped in hexanes. (c) MALDI-TOF spectra of the low MW fraction obtained from the PCPDT-BT film after dipping in hexanes.

shown in Figure 2. The PCPDT-BT having a MW of 10 kDa exhibited a significant (~ 30 nm) blue shift in the absorption band due to the distortion of the backbone. The spectra

broadened, exhibiting a well-resolved vibrational structure for the high MW. These results suggested that the absorption spectra of PCPDT-BT depended significantly on the MW. Next, the 40 thin films were dipped into hexanes to obtain sufficient quantities for analysis. The UV-vis absorption spectra of the fraction soluble in hexanes were measured in chlorobenzene. The λ_{max} corresponding to the fraction soluble in hexanes was blue-shifted by approximately 30 nm with respect to the λ_{max} of the solution UV spectrum of the dipped film (Figure 2(b)). The spectrum was similar to what one would expect for a sample having M_n approximately 10 kDa. This result indicated that only the low MW fraction of the PCPDT-BT was preferentially removed from the as-prepared films by dipping into hexanes.

The MW of the hexanes-soluble fraction obtained from the PCPDT-BT film was characterized by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS), as shown in Figure 2(c). MALDI-TOF provides direct evidence that the low MW fraction below 3.3 kDa had been eliminated by dipping into hexanes. As reported in the literature, the MW determined by MALDI-TOF was a few times smaller than that determined by GPC because the conjugated polymers assumed a rod-conformation in solution, unlike the coil-like PS.²² Attempts to determine the MW of the dissolved fraction in hexanes using GPC techniques were unsuccessful because the quantity of the low MW fraction dissolved in hexanes is insufficient for analysis. Atomic force microscopy (AFM) showed that the films were not damaged by dipping in hexanes, and no porous structures were present that could be assisted by molecular rearrangements (data not shown).

The dipping time-dependent changes in the electrical characteristics of the PCPDT-BT films were examined by measuring the field-effect charge transport properties in fabricated thin film transistors. Transistors having a bottom-gate, top-contact geometry were fabricated. All devices exhibited good behaviors in terms of the transistor properties. The output characteristics showed a strong increase in the drain current as the gate voltage increased, reaching a well-defined plateau at high drain voltages. The device performances were assessed by examining the transfer characteristics, as shown in Figure 3. The removal of the low MW fraction

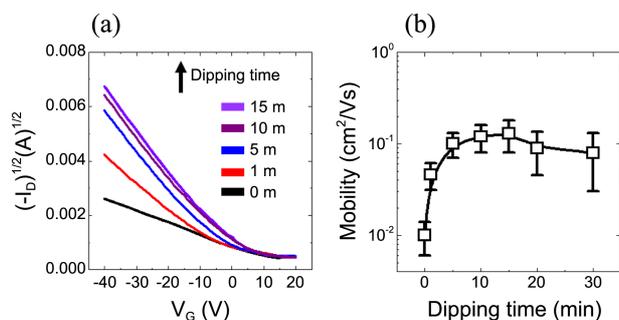


Figure 3. (a) Transfer characteristics of the PCPDT-BT FETs (for dipping times of 0, 1, 5, 10, and 15 minutes). (b) Field-effect mobilities obtained in the saturation regime of the PCPDT-BT FETs for various dipping times.

resulted in a strong increase in the drain current, mainly due to a large increase in the charge carrier mobility. The average field-effect mobility of each transistor was calculated in the saturation regime ($V_D = -40$ V) by plotting the square root of the drain current versus the gate voltage and fitting the data.²³ Figure 3(b) summarizes the average field-effect mobilities of the PCPDT-BT devices. The best average field-effect mobility among the FETs was achieved for a PCPDT-BT film dipped into hexanes for 15 minutes ($0.13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). This mobility was approximately 10-fold greater than that of the FET fabricated from the as-prepared film ($0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The enhanced mobility was related to the removal of the low MW polymer fraction from the as-prepared film and the concomitant enhanced molecular ordering of the PCPDT-BT chains, as discussed in detail below.

However the FETs dipped in hexanes for more than 15 minutes slightly showed lower field-effect mobilities and a larger deviation than the values obtained from a 15 minute dipping time. As dipping time increases, hexanes penetrate into interface between polymer film and SiO_2 gate dielectrics, which results in interfering intimate contact of the dielectric/polymer interface. We also tried to test the bottom-contact transistors. Solvent molecules affect the interface between polymer film and Au electrodes, therefore overall the bottom-contact transistors showed bad performance compared to top contact-transistors.

The structural changes in the PCPDT-BT thin films as a function of the dipping time and the relationship between the crystalline nanostructure and the electrical properties were examined by measuring the UV-vis absorption spectra and GIXD measurements. First, the influence of the dipping time on the extent of p-orbital overlap in PCPDT-BT films was investigated using UV-vis absorption spectroscopy (Figure 4). The dipping process induced a red shift in the absorption maximum (λ_{max}) from 794 to 797 nm, and the intensity of the shoulder at ~ 876 nm increased. Both features are as-

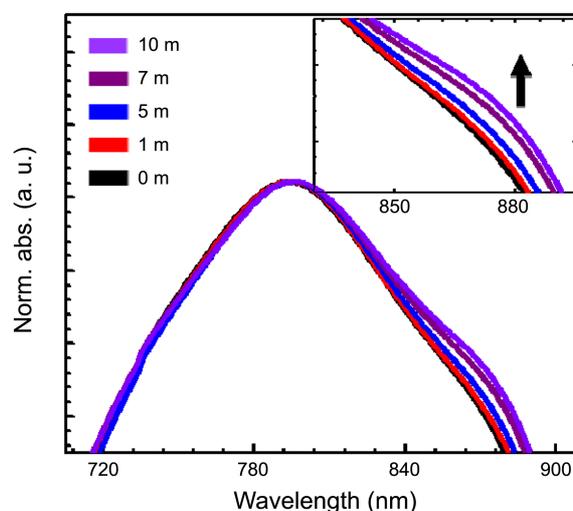


Figure 4. Magnified normalized maximum of the UV-vis absorption bands of the PCPDT-BT thin films for various dipping times in hexanes. The dipping time increased in the direction of the arrow.

sociated with increased molecular ordering in the conjugated polymer thin films,²⁴ which indicated an increase in the conjugation length of the dipped PCPDT-BT film having a higher crystalline order. These results were consistent with a higher degree of main chain planarization and interchain ordering in the PCPDT-BT film after dipping process.²⁵

The solvent-assisted characteristics of the PCPDT-BT molecules were explored by performing the same experiments in methylene chloride and acetone (in place of hexanes). No significant structural or performance differences were observed from these dipped films, except that crystallization was somewhat more rapid and the surface roughness of the film after dipping in methylene chloride was higher than the roughness obtained after dipping in hexanes and acetone. Thus, we deduced that the p-orbital overlap in PCPDT-BT films was enhanced by the solvent-assisted self-organization effects; however, solvents that were better solubility for PCPDT-BT than methylene chloride damaged the films during the dipping process by introducing porous structures.

Figure 5 shows the out-of-plane X-ray diffraction patterns of the PCPDT-BT films as a function of the dipping time. The diffraction patterns consisted solely of a (100) diffraction peak, regardless of the time point. No other diffraction peaks were observed in the X-ray diffraction pattern except for the (100) reflection, indicating that the PCPDT-BT molecules were preferentially oriented edge-on relative to the substrate. Only a weak peak at $2\theta = 4.25^\circ$ was observed in the as-prepared pristine films (20.6 \AA),²⁶ indicating the absence of well-oriented crystals immediately after spin-coating.²⁷ The intensity of the (100) peak increased with the dipping time. At short times, *i.e.*, 1-10 minutes, the (100) reflection was enhanced. After 10 minutes, the (100) reflection was saturated, corresponding to the trend in the mobilities, as observed in the FET measurements.

Because the solvent rapidly evaporated after spin-coating, it was difficult for the PCPDT-BT molecules to crystallize, leading to a low-crystallinity film prior to the post-treatment.²⁸ During dipping into a poor solvent, the PCPDT-BT film became permeated with the solvent, and the PCPDT-BT molecules in disordered regions became mobile. The mobile PCPDT-BT molecules then facilitated the formation of an

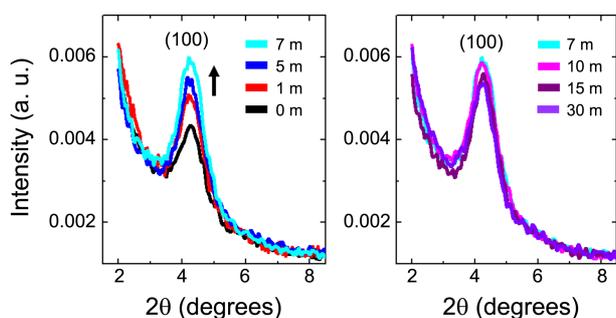


Figure 5. Out-of-plane grazing incidence angle X-ray diffraction intensities as a function of the scattering angle 2θ for PCPDT-BT thin films prepared on SiO_2/Si substrates upon dipping. The dipping time increased in the direction of the arrow.

energetically stable structure. This result could be attributed to the molecular rearrangement that occurred after solvent absorption onto the PCPDT-BT film, suggesting that the PCPDT-BT molecules bound through weak interactions in the solid state.

Conclusion

In conclusion, dipping a PCPDT-BT film into a poor solvent is a simple and efficient method for eliminating the low MW fraction from a polymer thin film to improve the molecular ordering in the film state. Controlling the dipping time in hexanes efficiently eliminated the low MW fraction and concomitantly produced an ordered enhanced thin film with an edge-on structure, resulting in a higher charge carrier mobility. This effective method is simple and of practical importance for the preparation of conjugated polymer-based devices.

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