

Molecular weight effect on surface and bulk structure of poly(3-hexylthiophene) thin films



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ABSTRACT

Recently, the synthesis of P3HT with high head-to-tail regioregularity and the control of the molecular weight have been achieved. Herein, we evaluated the structure in thin films of various molecular weight P3HT (from $M_w = 13$ k to 828 k) prepared under diverse conditions through X-ray diffraction measurements. Higher molecular weight P3HT had the increase of “Face-on” structure in the thin films. From the structure of thin films prepared under other conditions, the main attribution was the speeds of sedimentation and inhabitation of the crystallization. Moreover, at the surface, the P3HT thin films with high molecular weight ($M_w = 828$ k) emerged “Edge-on”-rich structure. With the larger distance from thin film surface, the structure gradually changed from “Edge-on” to “Face-on”. These fundamental results would lead the suggestion in fabrication and performance of organic electronic devices.

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1. Introduction

For several decade years, organic electronic devices have attracted much attentions in the view point of advantages on their flexibility, lightness and low-cost fabrication compared to inorganic material-based devices [1–4]. Especially, poly(3-hexylthiophene) (P3HT) shows a high hole carrier mobility and is applied as hole transport layers of various organic devices such as photovoltaic cells, fields-effect transistors, light-emitting diodes, thermoelectric transducers, memories and so on [5–8]. The low steric hindrance of the five-membered thiophene rings of P3HT leads the higher planarity of the main chain originated from π - π stacking and higher expansion of the conjugation system possesses relative to phenyl-based conjugated polymers. Therefore, the self-assembly of P3HT produces high crystallinity and high carrier mobility [9,10].

The carrier mobility of P3HT receives drastic effects on morphology and crystallite orientation in solid states. In particular, P3HT crystallites show anisotropic carrier mobility [9,11–14]. In the direction along the P3HT main chains, the crystallite shows the highest mobility. On the other hand, the mobility in the direction to π - π stacking of P3HT shows higher relative to that parallel to the side chains (Fig. 1). Therefore, the control of crystallite orientation is

a key factor for the electronic performance of various organic devices [9,11–14]. The crystallinity and crystallite orientation have been considered to be variable according to regioregularity, molecular weight and end groups of P3HT, temperature and methods in the device fabrication, and affinity with surface of substrates. Recently, many researchers have discussed the effects of their factors [11–22]. However, in their discussion, they adopted P3HT with less molecular weight than 100,000 as high molecular weight P3HT, then they assumed that the structure at the surface is the same as that at bulk. The control of P3HT structure is highly controversial for their prominent performance in the organic devices.

Herein, we evaluated and compared the structure of P3HT thin films with various molecular weight (from 13 k to 828 k) in the bulk and at the surface. The P3HT in this research had high molecular weight as well as high head-to-tail regioregularity (>95%). We prepared thin films under various conditions such as molecular weights, solvents, temperature, rotational speeds in spin-casting and surface properties of substrates, and their effects on the structure of P3HT were investigated using small angle incidence/grazing incidence X-ray diffraction.

2. Experimental section

2.1. Materials

All P3HT were synthesized with nickel catalysts according to our

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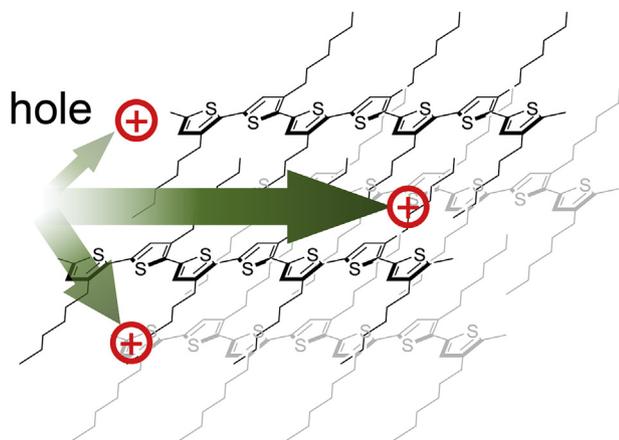


Fig. 1. P3HT structure in crystallite and direction of hole mobilities.

previous report [23]. All the reagents were obtained from commercial sources and used without further purification. ^1H (400 MHz) NMR spectra were recorded on JEOL ECZ400. ^1H NMR spectra were obtained with tetramethylsilane (TMS) as an internal standard in CDCl_3 at room temperature (Fig. S1 in the Supplementary Data). Gel permeation chromatography (GPC) was carried out on JASCO LC-2000 Plus with UV-vis detector (at 254 nm) using Shodex GPC KF-404HQ and KF-402HQ using chloroform as an eluent after calibration with 6 polystyrene standards.

2.2. Preparation of hydrophilic and hydrophobic silicon wafer substrates

Hydrophilic silicon wafers were prepared in a piranha solution (sulfuric acid (H_2SO_4)/hydrogen peroxide (H_2O_2) = 3: 1). After immersing in piranha solution for 15–20 min at room temperature, the substrates were rinsed with deionized water and dried.

The hydrophobic substrates were prepared with silane coupling treatment to piranha-treated silicon wafers. The piranha-treated silicon wafers were immersed in 1-propanol and water (9: 1) solution containing 3 wt% dodecyltriethoxysilane for 3 h. After immersion, the substrates were washed with 1-propanol and dried at 100°C for 1 h.

The surfaces of the modified silicon wafers were characterized with XPS (8 kV, 30 mA and pressure 5×10^{-6} Torr) and contact angles of water. The characterization data of both substrates were shown in Fig. S2 in the Supplementary Data.

2.3. Preparation of P3HT thin films

On the silicon wafer substrates, 650 μL chloroform or chlorobenzene solution containing 0.3 wt% P3HT at 50°C was dropped on SPIN COATER IMC-7094. The standard condition of spin-casting was 800 rpm for 5 s and 3000 rpm for 1 min. Only when the rotational speed in spin-casting was compared, the condition was 500 rpm for 5 s and various rotating speeds (500, 1000, 2000, 3000, 4000 and 5000 rpm) for 1 min. The cast thin films were prepared by casting 0.3 wt% P3HT solution, then dried at room temperature for 24 h.

2.4. Measurement of thickness of P3HT thin films

The thickness of P3HT thin films were measured by the X-ray reflection methods or the AFM. In the X-ray reflectivity carried on RIGAKU X-ray Diffractometer SmartLab, the power were 40 kV and 30 mA. The GXRR3 package was used for the curve fitting of the X-ray reflectance profiles (Fig. S3 in the Supplementary Data) and

then their thickness and roughness were evaluated. The thin films were scratched by sewing needles and P3HT layers were removed, then P3HT thickness was also estimated from the AFM height images by SII NanoTechnology, Navi E-sweep. The measurements were carried out in the dynamic force mode using silicon cantilevers. The surface roughness of the thin films was estimated from the AFM images. The roughness was presented by the root-mean-square (RMS) values using equation (1):

$$\text{RMS}(\text{nm}) = \sqrt{\frac{1}{X_{\text{max}}Y_{\text{max}}} \int_0^{Y_{\text{max}}} \int_0^{X_{\text{max}}} \{F(X,Y) - Z_0\}^2 dXdY} \quad (1)$$

where X_{max} , Y_{max} are 20 μm , $F(X,Y)$ is height at the pixel (X,Y) and Z_0 is the average of the height.

2.5. Measurement of X-ray diffraction

For the investigation of structure beneath the surface of thin films, X-ray diffraction was measured in the grazing incidence angles of X-ray beams ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$). The diffraction from the bulk structure in the thin films is observed in the measurement of small incidence angle X-ray diffraction with a little larger incidence angle than the critical angle (α_c). The total reflection of X-ray beams occurs below the critical angle (α_c). With the lower incidence angles than α_c , the evanescent wave is observed and the structure within several nanometers from the surface is investigated. In contrast, with a little larger incident angles, the diffraction from the bulk structure is observed. In this work, we measured X-ray diffraction at the incidence angles 0.20° or below α_c . This 0.20° was an angle between the critical angles of P3HT (0.16°) and silicon wafer (0.23°). Therefore, the diffraction originated from silicon wafer substrates was inhibited.

For the investigation of the crystallite orientation in P3HT thin films on the silicon wafer substrates, the X-ray diffractions were detected by the scintillation counter with two different geometry; one was scanned in the direction perpendicular to the sample surface and the other was in the parallel direction. The former is called “Out-of-plane” measurement and the later is “In-plane” measurement. In the “Out-of-plane” geometry, the lattice planes nearly parallel to the surface of thin films are detected. In contrast, in the “In-plane” geometry, the lattice planes nearly perpendicular to the surface are observed.

The penetration depth of X-ray beam from the surface was around 1.7 μm at $\alpha = 0.20^\circ$. (see the section “Penetration depth of X-ray beam” and Fig. S4 in the Supplementary Data).

3. Results and discussion

3.1. Characterization

All the P3HT were synthesized through the deprotonative polymerization with the Knochel-Hauser base (TMPMgCl·LiCl) catalyzed by $\text{CpNiCl}(\text{SiPr})$ in the reported method [23–25]. The molecular weight and molecular weight distribution are shown in Table 1. The distribution of several P3HT samples were larger relatively. However, there was no effect of the PDI on the following investigation in this work. The obtained P3HT had high head-tail regioregularity (>95%) from their ^1H NMR spectra (Fig. S1 in Supplementary Data). From the height images of AFM, the thickness and roughness of P3HT thin films are shown in Table 1. All the spin-coated films had similar thickness and high smoothness. The film prepared by casting method had larger thickness than 100 μm . In only the X-ray reflectivity profile of the thin film of lowest

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