“Face-On” Oriented $\pi$-Conjugated Polymers Containing 1,3,4-Thiadiazole Moiety Investigated with Synchrotron GIXS Measurements: Relationship between Morphology and PSC Performance

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The detailed morphology was investigated on 1,3,4-oxadiazole (OXD) and 1,3,4-thiadiazole (TD) containing $\pi$-conjugated polymer films based on synchrotron GIXS measurements. Grazing-incidence wide-angle X-ray scattering (GIWAXS) proved that TD-containing polymers showed face-on orientation, which is, in general, favor for the polymer solar cell (PSC) application. Density function theory calculation suggests that the favorable orientation is probably induced by the curvature of TD-containing polymer main chains. In addition, the bulk-heterojunction structure were evaluated by grazing-incidence small-angle X-ray scattering (GISAXS) and atomic force microscope (AFM). As a result, it was also found that the $\pi-\pi$ stacking distance, correlation length and PC$_{61}$BM cluster size had good relationship with the short circuit current density ($J_{sc}$) and fill factor (FF) in the PSC application.

Keywords: polymer solar cell, organic photovoltaic, morphology, synchrotron X-ray scattering, $\pi$-conjugated polymer, thiadiazole.

1. Introduction

The polymer solar cell (PSC) is one of the photoelectric conversion devices utilizing a composite film as a photoactive layer with an interpenetrating network, namely, a bulk-heterojunction structure composed of a polymeric semiconductor and a fullerene derivative. Owing to the excellent film-forming property of polymeric materials, the PSC has attracted much expectation as a physically flexible device with a much lower fabrication cost via a continuous coating, i.e., roll-to-roll solution process [1]. The feasibility of PSC fabrication fundamentally comes from the amorphenous nature of polymeric materials, however, such a non-crystallinity simultaneously induces an undesirable structural disorder in the composite film that causes a localization and loss of photocurrent carriers. In order to achieve both the processability and effective photoelectrical conversion, it is essential to understand the relationship between the device performance and...
morphological properties of the composite film, e.g., the degree of crystallization, domain size, polymer orientation, connectivity of each separated p/n domain, etc. Therefore, the morphology has been investigated in detail for high performance p-type polymers, such as benzothiadiazole (BT) containing polymers which are representative semiconductors showing high open-circuit voltage ($V_{oc}$) for the PSC applications [2-6].

We have previously developed novel π-conjugated polymers with 1,3,4-oxadiazole (OXD) and 1,3,4-thiadiazole (TD) units (P1-P4) focusing on their high electron-withdrawing property and more compact structure than the BT unit. These properties would provide more densely packed structures, hence, a high charge mobility in the polymer films with high $V_{oc}$ values for the PSC (Figure 1) [7,8]. In fact, the TD-containing polymer, P2, showed the high hole mobility of $8.81 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ in an organic field-effect transistor. Among them, the PSC utilizing P2/PC$_{61}$BM achieved the high $V_{oc}$ of 0.80 V and power conversion efficiency (PCE) of 3.0%.

However, the detailed morphological properties of the OXD- and TD-containing polymers have never been investigated. Therefore, the relationship between the morphology and PSC performance is still not clarified.

We now report the systematic morphological study of the OXD- and TD-containing π-conjugated polymers based on synchrotron grazing-incidence wide-/small-angle X-ray scattering (GIWAXS/GISAXS) measurements. GIWAXS is often used as a promising method to investigate the orientation of polymer thin films and quantify the average $d$-spacing of the π-π stacking and crystal lattice, which are significant factors for carrier mobility. On the other hand, the p/n phase separated structures can be evaluated by GISAXS, which affects the efficiency of the elementary steps of the photoelectric conversion, such as exciton diffusion, carrier dissociation and carrier transportation.

2. Experimental

2.1 Sample preparation

Synthesis, molecular weight, polydispersity, electrical and thermal properties of P1-P4 are described elsewhere [7,8]. The samples were prepared according to the following method. 4.0 mg of polymer or polymer/PC$_{61}$BM (1:1 = w:w) were dissolved in 0.4 mL of chloroform. These solution were drop-cast on Si wafers with filtration (pore size = 0.40 μm) followed by air-drying for 30 min. Then, the samples were completely dried under vacuum at r.t. (as-cast sample) or 150 °C (annealed sample) for 1 h. The thickness of films were almost 1 μm.

2.2 GIXS

GIWAXS measurements were conducted at beamline BL19B2 of Spring-8, Japan. The sample was irradiated at a fixed incident angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.39 keV (X-ray wavelength $\lambda = 0.10$ nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300K) with the sample-to-detector distances of 174 mm. GISAXS were measured at beamline BL46XU of Spring-8, Japan. The monochromated energy of the X-ray source was 10.314 KeV (λ = 0.12 nm) and the incidence angle was 0.15°. GISAXS patterns were recorded with a 2D image detector (Pilatus 300K) with the sample-to-detector distances of 3133 mm. To obtain the average radius R of the PC$_{61}$BM clusters, we use the polydispersed sphere model with the Schultz size distribution for GISAXS data fitting. In low-q region 0.01-0.03 nm$^{-1}$, a scattering term described by the Debye-Anderson-Brumberger model was included to account for the upturn scattering [9].

2.3 Atomic force microscope

Tapping mode AFM observation was performed with an Agilent AFM 5500, using microfabricated cantilevers with a force constant of 34 N/m.
3 Results and Discussion

3.1 GIWAXS

The 2D-GIWAXS patterns of the as-cast films are displayed in the upper part of Figure 2. We focused on the reflection at about $|q| = 16-18$ nm$^{-1}$ which corresponds to the $d$-spacing of the $\pi-\pi$ stacking. While $P_1$ and $P_2$ show a weak ring-shaped reflection at $|q| \approx 15.0$ nm$^{-1}$ (Figure 2a, b), $P_3$ and $P_4$ exhibit an arc concentrated at $|q| = 15.4$ nm$^{-1}$ and 15.8 nm$^{-1}$, respectively, on the $q_z$ axis (Figure 2c, d). The large $\pi$-conjugated units, such as dithienopyrrole and benzodithiophene incorporated in $P_3$ and $P_4$, respectively, can induce the orientation of the polymer backbone in the as-cast film. Annealing the $P_2$ film induced a reflection at $\sim q_z = 17.9$ nm$^{-1}$ concentrated on the meridian while no obvious scattering in the same region was found for the annealed $P_1$ film (Figure 2e). The peaks observed for the $P_3$ and $P_4$ films were enhanced by annealing. Thus, annealing the $P_2$-$P_4$ films develops a highly crystalline lamellar structure characteristic for the $\pi$-conjugated polymers. The reflection direction indicates that the $\pi$ planes of the polymer backbones lie parallel to the substrate (face-on orientation). This is the first report of a face-on orientation for the $\pi$-conjugated polymers. Such an unusual face-on orientation may be attributed to the curvature along the main chain due to the bent structure of the 2,5-bis(3′,4′-dihexylthien-2′-yl)-1,3,4-thiadiazole (BTTD) unit. Z. Bao et al. reported that the annealed poly(3,4-dihexyl-2,2′-bithiophene) (PDHBT) adopts a hexagonal lattice from the helical conformation caused by its twisted polymer backbone [10]. Compared to PDHBT, $P_2$ has a similar structure except for the TD unit which is more compact than the thiophene unit on account of the absence of hydrogen atoms at the 3- and 4-positions. Thus, it is possible that the twisting of the BTTD unit is partly relaxed so that the polymer backbone has a greater planar, but curved conformation, as illustrated in Figure 3. In fact, the density functional theory calculations at the oB97XD/6-311G(d,p) level suggests that the TD unit reduces the dihedral angle between the TD and neighbor 3,4-diethylthiophene units, and thus the curvature of the backbone is induced for the dimer of BTTD (Figure 4). L. Chen et al. also reported that, unlike the rod-shaped polymer as represented by the regioregular poly(3-hexylthiophene) (rrP3HT) which aligns
perpendicular to the substrate (edge-on orientation), the polymer having a curved backbone is likely to exhibit a face-on orientation [11]. Such a face-on orientation is generally favorable for PSC applications because the direction of the π-π stacking is the same as that of the charge transport in PSC devices. Indeed, P1 without the face-on orientation had the lowest PCE of the PSC characteristics among all the polymers (Table 1).

The d-spacings of the π-π stackings for the annealed P2-P4 films calculated from each ~qz value were 0.351 nm, 0.369 nm, and 0.400 nm, respectively (Table 1). Thus, it was confirmed that P2 has the most densely packed crystalline structure in the present polymers. It should be noted that the π-π stacking distance of P2 (0.351 nm) is much shorter than that of rrP3HT, 0.38 nm, which is a typical high hole-mobility polymer [12]. It was also found that the d-spacings of the π-π stacking for P2-P4 strongly affect short-circuit current densities (Jscs) and the fill factors (FFs) in their PSC applications, that is, narrowing the π-π stacking distances results in the increased Jscs and FFs. This finding implies an improvement of the carrier transport between the polymer chains [13,14] and across the polymer/anode interface [11].

In addition to the d-spacings, the crystal correlation lengths, L, were determined from the width of the scattering peak using the Scherrer equation (Table 1). L is the distance over which the periodical packing of the polymer is preserved, and it is reported that the PCEs have a positive correlation with the L values which are changed by solvent additives [4], annealing treatments [9], weight ratio of PC61BM [15] and alkyl side chains [16]. However, since P2-P4 have different π-π stacking distances, we calculated the L/d values to evaluate the periodicity for the polymers independent of their π-π stacking distances, which corresponds to the average number of lamellas in the L length (Table 1). The L/d values were improved in the following order: P4 (L/d = 9.8) < P3 (L/d = 15) < P2 (L/d = 17), which indicates that P2 has the highest periodicity in the π-π direction among all the polymers. As well as the π-π stacking distance, the L/d values also have a strong correlation with Jsc, FFs, and thus the PCEs. This correlation is reasonable because the high periodicity of the face-on oriented polymers in the π-π direction would be helpful for charge transport in the PSCs. Consequently, P2 shows the best performance due to the shortest π-π stacking distance and the largest L/d value in the π-π stacking direction.

### 3.2 GISAXS and AFM

Figure 5 shows the in-plane GISAXS profiles of (1:1, w/w) films. While the SAXS of the polymer, the annealed polymer and the polymer/PC61BM films are attributed to hetero-

### Table 1. PSC performance and morphological properties of the annealed P1-P4 films

<table>
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<tr>
<th></th>
<th>PCE [%]</th>
<th>( J_{sc} ) [mJcm(^{-2})]</th>
<th>FF</th>
<th>( L ) [nm]</th>
<th>( L/d )</th>
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<tr>
<td>P1</td>
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<tr>
<td>P2</td>
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<td>0.351</td>
<td>6.0</td>
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<tr>
<td>P3</td>
<td>1.2</td>
<td>3.6</td>
<td>0.42</td>
<td>0.369</td>
<td>5.5</td>
<td>15</td>
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<tr>
<td>P4</td>
<td>0.67</td>
<td>1.9</td>
<td>0.41</td>
<td>0.400</td>
<td>3.9</td>
<td>9.8</td>
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\( ^{a} \) PSC performance of polymer/PC61BM (1:1, w/w) annealed at 100 °C for 10 min. Other detail information is reported in ref 7 and 8. \( ^{b} \) The average PCE of P2/PC61BM (1:1, w/w) without annealing.

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geneity arising from the crystalline and amorphous phases, that of the polymer/PC 61BM films can be related to the PC 61BM clusters in the range of 10^0-10^2 nm ($q_{xy} = 0.01-1$ nm$^{-1}$) [9]. The average size of the clusters can be estimated from the model fitting for the GISAXS profiles. The estimated mean cluster radius, $R$, is 32 nm for the P1/PC61BM film. Such a relatively large segregation may cause an inefficient charge separation because the exciton diffusion lengths are normally around 10-20 nm for the PSCs. As a result, a quite low $J_{sc}$ (0.60 mAcm$^{-2}$, Table 1) was indeed exhibited for the PSC using the P1/PC61BM film. On the other hand, for the P2/PC61BM, P3/PC61BM, and P4/PC61BM films, $R$ values of 11 nm, 15 nm, and 21 nm are calculated respectively, which correspond to the exciton diffusion length, resulting in the increase of $J_{sc}$ values. Therefore, the PSC performances depend on the phase separated morphology of blended films with PC61BM as well as the orientation of the polymer backbone, the $\pi-\pi$ stacking distance and the periodicity in the $\pi - \pi$ stacking direction as already mentioned.

Figure 6 show AFM height and phase images of the annealed blend films. We attributed the bright area to the polymer-rich phase in the phase images (Figure 6b, d, f, h) and the dark area to the PC61BM-rich phase, respectively. Focusing on the PC61BM-rich area, the size in P1/PC61BM (Figure 6b) is obviously larger than that in P2-P4/PC61BM (Figure 6d, f, h), which supports the result of GISAXS.

Figure 6. AFM height (a,c,e,g) and phase (b,d,f,h) images of annealed films which are P1 (a,b), P2 (c,d), P3 (e,f) and P4 (g,h) blended with PC61BM.
4 Conclusion

In this study, we reported the detailed morphological studies of OXD- and TD-containing polymer thin films, P1-P4, utilizing the synchrotron GIWAXS, AFM and GISAXS in order to understand the hierarchical relationship between the molecular design, morphology and device performance. Unlike the OXD-containing polymer (P1), the TD-containing polymers (P2-P4) exhibited the characteristic 2D-GIWAXS patterns indicating a “face-on” orientation which was observed for the first time. This is probably due to their curved polymer backbone caused by the bent structure of the BTTD units. The GISAXS experiments revealed that there are PC61BM clusters (R = 11-32 nm) in the P2-P4/PC61BM. The cluster size in P2-P4/PC61BM are enough small for effective charge separation, however, P1/PC61BM shows relatively large aggregation of PC61BM. As a result, it was concluded that the PSC performance using the P1-P4/PC61BM films are influenced by the phase separated morphology, the orientation of the polymer backbone, the π-π stacking direction and the periodicity in the π-π stacking direction.

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