

Orientation Control of Regioregular-Poly(3-dodecylthiophene) Films Formed by the Friction-Transfer Method and the Performance of Organic Photovoltaic Devices Based on These Films

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ABSTRACT: Control of the molecular orientation of regioregular poly(3-alkylthiophene)s (RR-P3ATs) improves the performance of field-effect transistors and organic photovoltaic devices (OPVs). However, most thiophene ring planes of the RR-P3AT molecules (except RR-poly(3-butylthiophene)) in films formed by the conventional spin-coating method stand on the substrate, that is, edge-on orientation. Orientation control of RR-poly(3-dodecylthiophene) (RR-P3DDT) molecules in films formed by the friction transfer method is reported and the performance of OPVs based on friction-transferred RR-P3DDT films is compared to that of OPVs based on spin-coated films. The films are investigated by polarized ultraviolet–visible light absorption spectroscopy, Fourier transform infrared spectroscopy, and grazing-incidence X-ray diffraction measurement. For friction-transferred films, the RR-P3DDT molecular chain is uniaxially aligned parallel to the substrate plane. In addition, the thiophene ring planes of the RR-P3DDT molecules are also oriented parallel to the substrate plane, that is, face-on orientation. The power conversion efficiency (PCE) and fill factor of the RR-P3DDT/C₆₀ bilayer OPVs based on the friction-transferred RR-P3DDT films are higher than those of devices based on spin-coated films. The PCE and photocurrent of the device based on the friction-transferred film are larger under irradiation with polarized light parallel to the RR-P3DDT molecular chain direction than with polarized light orthogonal to the chain direction. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40136.

KEYWORDS: friction transfer; regioregular-poly(3-dodecylthiophene); orientation; organic photovoltaic devices; conducting polymers

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INTRODUCTION

Poly(3-alkylthiophene)s (P3ATs) are promising materials for application in organic optoelectronic devices, such as field-effect transistors (FETs)¹ and organic photovoltaic devices (OPVs).²

Molecular orientation of regioregular (RR)-P3ATs has been reported to significantly affect the performance of devices based on these materials. Therefore, control of molecular orientation is a key issue to improve the performance of these FETs and OPVs based on RR-P3AT films. For example, Sirringhaus et al. investigated FETs based on poly(3-hexylthiophene) (P3HT), the thiophene ring planes of which stood vertically on the substrate, that is, edge-on orientation, and showed that molecular orientation of these polymers significantly improves charge transport, considering that it occurs along the π - π overlapping direction of thiophene rings.¹ This is because, the larger intermolecular π - π overlap between the thiophene rings formed in the substrate plane leads to higher mobility in the direction parallel to

the substrate, resulting in an increase in FET performance. Conversely, for OPV devices, where charge transport takes place between top and bottom electrodes, the increase in mobility in the direction perpendicular to the substrate should lead to improved power conversion efficiency. This can be achieved if thiophene ring planes of the RR-P3AT molecules are oriented parallel to the substrate plane, that is, face-on orientation, which allows π - π stacking in the vertical direction and leads to improvement of carrier mobility in the direction perpendicular to the substrate.^{3,4}

When RR-P3HT films are formed by the conventional spin-coating method, most RR-P3AT molecules have an edge-on orientation on the substrate. A mechanical rubbing method for film production was reported to promote face-on orientation of most macromolecules, including RR-P3DDT, on the substrate⁵⁻⁷; however, a much lower ratio of face-on to edge-on crystallites was observed in the lower part of these films (close

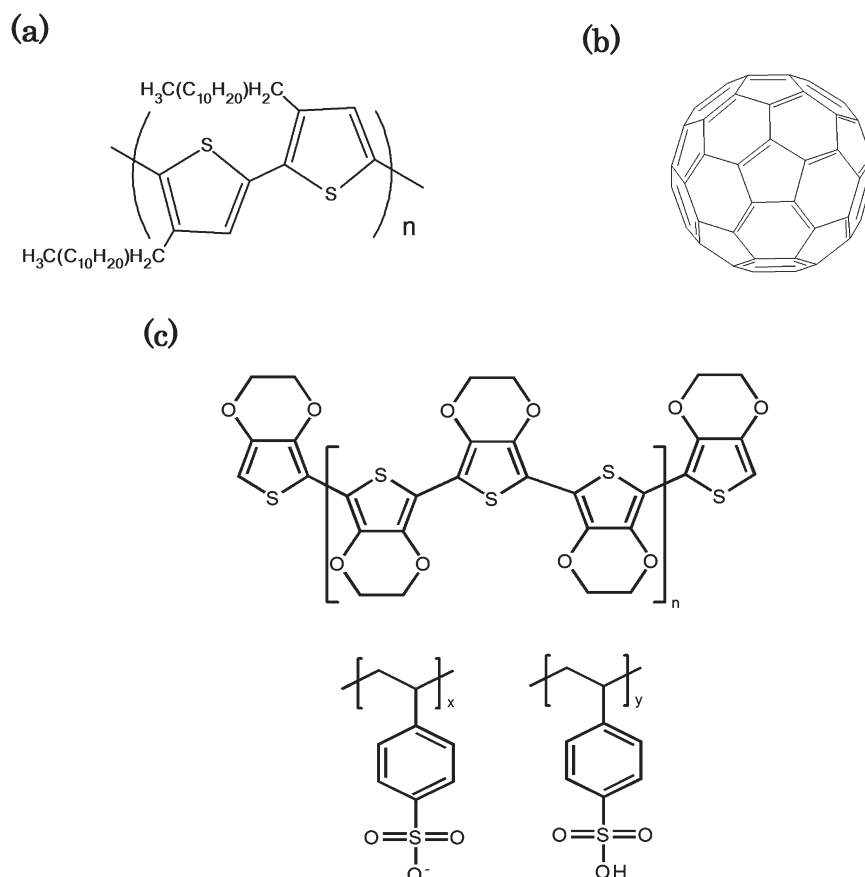


Figure 1. Chemical structures of (a) RR-P3DDT, (b) C_{60} , and (c) PEDOT:PSS.

to the substrate).⁵ Control of P3HT was also achieved by applying a DC or AC electric field perpendicular to the substrate^{8,9}; however, the face-on to edge-on crystallite ratio did not change significantly. Therefore, a technique that leads to face-on orientation of RR-P3AT molecules in the whole film is needed to improve the performance of OPVs based on RR-P3AT films.

Previously, we reported use of the friction transfer method for formation of oriented thin films of various conjugated polymers, in which polymer chains were aligned uniaxially.^{10–13} In this study, we applied this method for preparation of thin films of RR-P3AT molecules and observed a high degree of orientation of the RR-P3AT molecular chains parallel to glass, quartz, SiO_2/Si , Si , and indium tin oxide (ITO) substrates.¹² In addition, most RR-poly(3-butylthiophene) (RR-P3BT) molecules showed edge-on orientation,¹³ while most RR-P3HT and RR-poly(3-dodecylthiophene) (RR-P3DDT) molecules showed face-on orientation on these substrates.¹²

Here, we report the characterization of oriented RR-P3DDT thin films formed by the friction transfer method, and also the improvement of OPV performance based on these oriented RR-P3DDT films, which act as p-type semiconductor layers. For comparison, RR-P3DDT films with various thicknesses were also formed by the spin-coating method. Film characterization was performed by polarized UV–vis absorption spectroscopy,

Fourier transform infrared (FTIR) spectroscopy, and grazing-incidence X-ray diffraction measurement (GIXD). RR-P3DDT/fullerene (C_{60}) devices were fabricated to evaluate the effects of RR-P3DDT orientation on OPV performance, and the results indicated that devices based on friction-transferred RR-P3DDT films with the face-on orientation on ITO substrates showed better performance than those based on spin-coated RR-P3DDT films with the edge-on orientation on these substrates.

EXPERIMENTAL

Materials

RR-P3DDT (Lot No. 20620CH, M_w : ~27,000), C_{60} and BCP were purchased from Aldrich Chemical, MER, and Tokyo Chemical Industry, respectively, and were used without further purification. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) aqueous solution (PEDOT:PSS, Clevis P VP. AI 4083) was purchased from Heraneus. Chemical structures of some of these materials are shown in Figure 1.

Film Preparation

The RR-P3DDT powder was compressed into a pellet under vacuum. The friction transfer process was then carried out by squeezing and drawing this RR-P3DDT pellet on various substrates, including glass, Si , and 100 nm-thick gold-coated Si (Aldrich Chemical), heated between 90 and 150°C. The applied load for squeezing was 2 MPa and the drawing speed was 0.66 m/min.

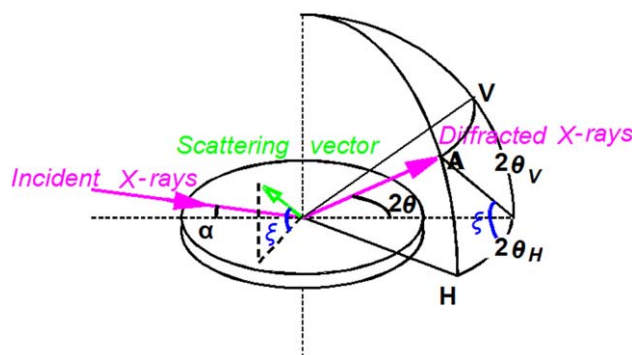


Figure 2. Schematic diagram of ED-GIXD geometry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For comparative analysis, RR-P3DDT films were also prepared by spin-coating (1500 rpm, 30 s) from a solution obtained by dissolving 0.20 wt % RR-P3DDT in chloroform. RR-P3DDT films prepared under these conditions showed maximum absorbance (without polarizer) of around 0.12, which was almost the same as that for RR-P3DDT films formed by the friction transfer method. This shows that the films formed by both methods had almost the same thickness.

Film thickness of the spin-coated RR-P3DDT film was measured with a surface profilometer (P. 15; KLA Tencor).

Evaluation of Orientation

UV–vis absorption spectra were measured with a Shimadzu UV-3150 spectrophotometer using glass substrates at an incidence angle of 0° . For polarized UV–vis measurement, a Glan–Taylor polarizing prism (GYPC-10-8AN; Sigma Koki) was used.

Fourier transform infrared (FTIR) spectra were taken with a Bio-Rad FTS175C FT-IR spectrometer with a wire-grid polarizer. Si and 100 nm-thick Au-coated silicon wafers were used as substrates for transmission infrared (IR) and reflection absorption (RA) spectroscopy, respectively.

Energy-dispersive (ED) GIXD measurements were performed to evaluate the orientation of the crystallites of RR-P3DDT in the films. The details of the experimental setting were as described previously.^{14,15} The ED-GIXD system was constructed by Rigaku. White X-rays (non-monochromatized X-rays) generated by a molybdenum (Mo) target tube (2.0 kW) were used as incident X-rays. Typically, incident X-rays were set up at a glancing angle of about 0.1° . The diffracted X-rays were detected with an energy-dispersive pure germanium solid-state detector (SSD) (Canberra GL0210R). Bragg's condition was rewritten using the X-ray energy E as in the following equation¹⁶:

$$E = \frac{hcn}{2d \sin \theta} \quad (1)$$

where h , c , n , d , and θ are Planck's constant, the velocity of light, order of reflection, lattice spacing, and the scattering angle, respectively. In ED-GIXD, the direction (orientation) and size (spacing) of the scattering vector in the reciprocal space can be measured separately. The energy dispersive system is advantageous for evaluation of the crystal orientation because the measurements can be performed with fixed X-ray optics.

Figure 2 shows a schematic diagram of ED-GIXD geometry. The SSD is movable in two directions, that is, horizontal ($2\theta_H$) and vertical ($2\theta_V$) directions. Reflections in any direction can be measured with the coupling of $2\theta_H$ and $2\theta_V$. To characterize the relation between a crystal plane and its substrate plane, the tilt angle ξ is defined as that between the horizontal plane (the sample plane) and the scattering vector, which is normal to the diffracting plane. To evaluate the preferred orientation distribution of the crystallites in relation to the substrate plane, the series of diffractions were measured with fixed 2θ and with variation of $2\theta_H$ and $2\theta_V$ combinations, corresponding to various tilt angles ξ . The accumulation time for measuring an ED-GIXD spectrum was 600 s.

OPV Performance Characterization

Glass substrates with ITO films were purchased from Geomatec. The ITO films were about 150-nm thick, with sheet resistance of about $8 \Omega/\text{sq}$.

PEDOT:PSS was spin-coated (2000 rpm, 90 s) on the ITO films and subsequently heated at 100°C for 1 h under vacuum. The resultant thickness of the PEDOT:PSS film was about 40 nm.

A RR-P3DDT film, used as a p-type semiconductor layer, was then prepared on top of these PEDOT:PSS/ITO films by the friction transfer method at a substrate temperature of 90°C . For comparison, RR-P3DDT was also spin-coated (1500 rpm, 30 s) on the ITO with PEDOT:PSS films, from a solution obtained by dissolving 0.15 wt % RR-P3DDT in chloroform. The thickness of the RR-P3DDT film was 25 nm.

C_{60} , used as an n-type semiconductor layer, was then deposited with a thickness of 20 nm in a vacuum better than 2×10^{-4} Pa, followed by vacuum evaporation of a 55 nm-thick Al cathode to complete the OPV cells. The cells were then encapsulated with glass sheets by epoxy resin in a nitrogen atmosphere.

To measure the photovoltaic J – V characteristics, an Air Mass 1.5 Global (AM 1.5G) solar simulator (XES-5025; Kansai Kagaku Kikai) was used as the light source, calibrated to $100 \text{ mW}/\text{cm}^2$ using a crystalline Si reference cell with an amorphous Si optical filter (Bunkoukeiki). A Keithley semiconductor parameter analyzer was used to measure the J – V characteristics. The effective cell area was 4 mm^2 . The short circuit photocurrent action spectra of the OPV devices were measured using the incident light of a halogen lamp passing through a monochromator (Sumitomo Heavy Industries) at wavelengths between 400 and 800 nm.

A polarizing plate was placed between the outlet of the incident light and the OPV devices for measurement of the J – V and the action spectra with incident light polarized parallel and orthogonal to the direction of friction to investigate the effects of polarization of the incident light on OPV performance. The polarized light powers for the J – V and the action spectra were $51.2 \text{ mA}/\text{cm}^2$ and $4 \mu\text{A}/\text{cm}^2$, respectively.

RESULTS AND DISCUSSION

UV–Vis Absorption Spectroscopy

Figure 3(a) shows the polarized UV–vis spectra of the RR-P3DDT film formed by the friction transfer method at 90°C for

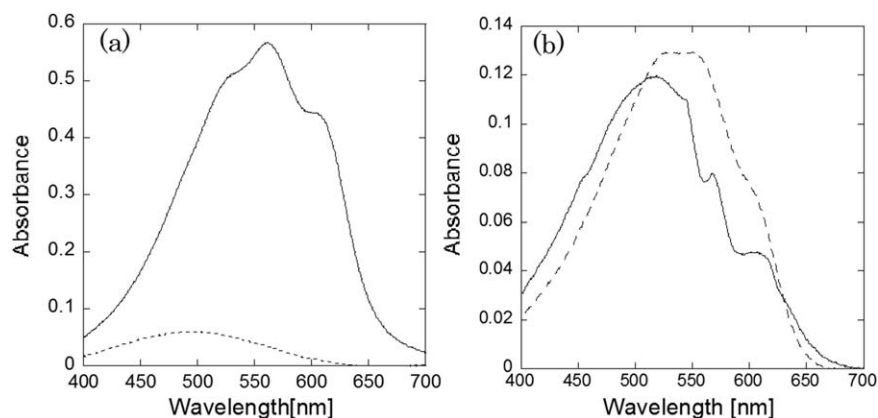


Figure 3. (a) Polarized UV-vis spectra of RR-P3DDT film formed by the friction transfer method at 90°C for optical polarization both parallel (solid) and orthogonal (dashed) to the direction of friction; (b) UV-vis spectra (without polarizer) of the RR-P3DDT films formed by friction transfer method (solid) and spin-coating method (dashed).

optical polarization parallel (solid) and orthogonal (dashed) to the direction of friction. It can be seen that there was greater absorption around 525, 560, and 610 nm, derived from RR-P3DDT, for parallel compared to orthogonal polarization. The dichroic ratio, that is, the ratio of the parallel component to the orthogonal component of the integrated absorbance, in the range between 300 and 800 nm, of the polarized UV-vis spectra provides information about the anisotropy of the absorption process. In this case, the large dichroic ratio observed from the RR-P3DDT oriented films shows large anisotropy, which is due to the RR-P3DDT molecular orientation in the films.

The electron transition probability is maximized when the transition dipole moment of the molecule lies parallel to the direction of the electronic vector of the light.¹⁷ The transition dipole moment of RR-P3DDT molecules is nearly parallel to their molecular long chains. The dichroic ratio of the friction-transferred RR-P3DDT films formed at 90°C was 10.3. This result indicates that most RR-P3DDT molecular chains are aligned in the friction direction in the friction-transferred RR-P3DDT films. We produced friction-transferred RR-P3DDT films at substrate temperatures between 90 and 150°C, and the highest dichroic ratio was achieved for those formed at 90°C; therefore, we fixed the substrate temperature to 90°C for formation of the friction-transferred RR-P3DDT films used in this study.

In Figure 3(a), the peaks at 525 and 560 nm were attributed to the intrachain π - π^* transition of the RR-P3DDT and to ordered stacking of the backbones of the RR-P3DDT in the film, respectively.¹⁸ The shoulder peak at 610 nm results from the interchain π - π interaction, and its intensity is correlated with the degree of interchain order.¹⁸ All the peaks were attributed to the orientation of the main chains of RR-P3DDT molecules in the crystalline phase, indicating crystallization of the RR-P3DDT film formed at 90°C.

Conversely, the dichroic ratio of a RR-P3DDT film prepared by spin-coating was about 1.0, indicating that the RR-P3DDT molecular chains were not aligned in the plane of the substrate (data not shown).

Figure 3(b) shows UV-vis spectra (without polarizer) of the RR-P3DDT films formed by friction transfer and spin-coating methods. The maximum absorbance of the films formed by both methods was almost the same, which indicated that these films had almost the same thickness. The film thickness formed by the spin-coating method was between 20 and 25 nm. Peaks around 525, 560, and 610 nm, derived from crystallization of RR-P3DDT, were not clearly observed when RR-P3DDT film was formed by the spin-coating method, compared to the spectrum of the film formed by the friction transfer method, indicating that spin-coated films were less crystallized.

FTIR Spectroscopy

Figure 4 shows FTIR-RA spectra of the RR-P3DDT film formed by the friction transfer method [Figure 4(a)] and that formed by the spin-coating method [Figure 4(b)], on 100-nm-thick Au-coated Si substrates.

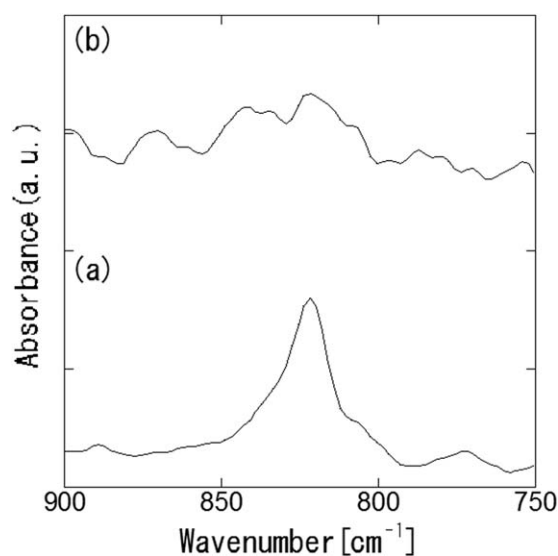


Figure 4. FTIR-RA spectra of RR-P3DDT films formed by the friction transfer method (a) and by the spin-coating method (b), on 100-nm-thick Au-coated Si substrates.

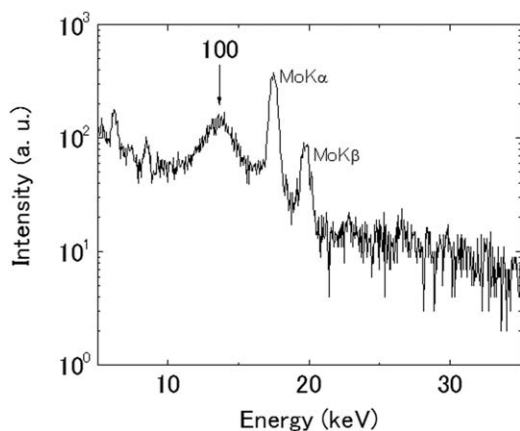


Figure 5. A typical energy-dispersed diffraction spectrum of the friction-transferred P3DDT film, with tilt angle $\xi = 0^\circ$ and $2\theta = 1.8^\circ$.

IR spectra derived from molecular vibration were used to obtain information about the molecular structure. The band around 820 cm^{-1} of polythiophene derivatives is assigned to the C—H out-of-plane deformation bands ($\delta(\text{C—H})$) (the hydrogen atom is attached to the thiophene ring).^{19,20} As the transition moment of the $\delta(\text{C—H})$ mode is approximately normal to the thiophene ring planes, analyzing this band is a good means of probing the orientation direction of thiophene ring planes on the substrate. In the case of RR-P3DDT film formed by the friction transfer method, a strong $\delta(\text{C—H})$ band peak in the RA spectrum was observed around 820 cm^{-1} [Figure 4(a)]. The relative intensity of this $\delta(\text{C—H})$ band was determined from the ratio of the integrated intensities of the $\delta(\text{C—H})$ to the $\nu(\text{CH}_2)$ bands. This is because the band derived from C—H stretching bands ($\nu(\text{CH}_2)$) that appear around 2924 cm^{-1} (not shown here) can be independent of the RR-P3DDT orientation, considering that the hydrogen atom is attached to the carbon atom in alkyl chains of the RR-P3DDT. This ratio of $\delta(\text{C—H})$ to $\nu(\text{CH}_2)$ bands for the friction-transferred film was 0.17. Furthermore, considering that the RA spectrum is sensitive to the bands with a transition moment normal to the reflection plane, it can be concluded that most RR-P3DDT molecules in the friction-transferred film show the face-on orientation on the substrate plane. Conversely, the $\delta(\text{C—H})$ band of the RR-P3DDT film formed by the spin-coating method was not clearly observed in the RA spectrum [Figure 4(b)]. The ratio of $\delta(\text{C—H})$ to $\nu(\text{CH}_2)$ bands for the spin-coated film was 0.071, which was much lower than that for the friction-transferred film. These results suggest that most RR-P3DDT molecules in the spin-coated film show the edge-on orientation on the substrate plane.

Moreover, in transmission IR measurements, the ratio of $\delta(\text{C—H})$ to $\nu(\text{CH}_2)$ bands of the spin-coated film was about twice that of the friction-transferred film. This result also indicated that RR-P3DDT molecules in the spin-coated film preferentially show the edge-on orientation, whereas RR-P3DDT molecules in the friction-transferred film preferentially show the face-on orientation (data not shown).

GIXD Measurement

To confirm the orientation in relation to the substrate plane, we performed ED-GIXD measurements of diffraction by varying the angles between the scattering vector and the substrate plane. In this measurement, the diffractions were measured not only in the “in-plane” direction (Q_x , Q_y) and the “out-of-plane” direction (Q_z), but also in some intermediate directions. In ED-GIXD, because the directions (orientation) and sizes (*d*-spacing) of the scattering vectors in the reciprocal space can be measured separately, the orientation distribution of the crystallites in relation to the substrate can be evaluated quantitatively. Therefore, more detailed analyses of the preferred orientation were performed by ED-GIXD than reported previously by conventional GIXD with synchrotron radiation.^{12,13} Figure 5 shows a typical energy-dispersive diffraction spectrum of the friction-transferred P3DDT with 2θ fixed at 1.8° . A relatively strong broad peak can be seen at 13.7 keV, which was assigned as 100 diffraction ($d = 2.88\text{ nm}$) of P3DDT crystallites, at $E = 17.4$ and 19.6 keV with very strong characteristic X-rays of Mo (K_α and K_β , respectively). In this measurement system, as we used white X-rays from a tube as the source, the scattering intensities were very weak and only the 100 reflection, which is the strongest, could be observed.

The orientation distribution of the (100) plane of P3DDT was compared between spin-coated and friction-transferred films. The 100 diffractions with various tilt angles ξ between the scattering vectors and the film plane were measured. Figure 6 shows the changes in 100 diffraction intensity with variation in tilt angle ξ for the spin-coated film. The intensity depends strongly on the angle ξ and shows that the (100) plane assumes preferential orientation. The intensity is the strongest at $\xi = 90^\circ$ and the weakest at $\xi = 0^\circ$. This result indicated that the *a*-axis is normal to the substrate plane with the edge-on orientation being observed. The distribution width is broad. It was reported that solution-processed regioregular P3ATs (especially poly(3-hexylthiophene)) show self-organized edge-on orientation.¹ The orientation distribution was evaluated quantitatively. Conversely, 100 intensity dependence on the tilt angle ξ of the friction-

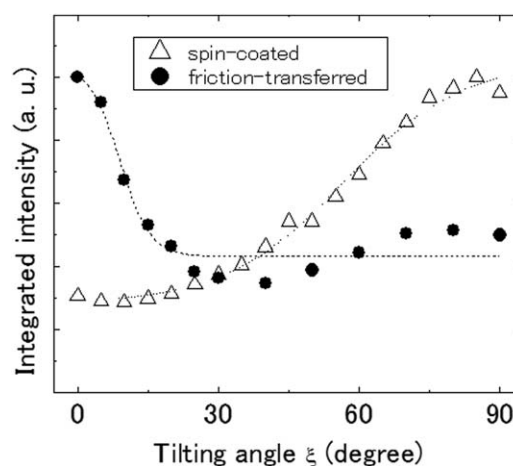


Figure 6. Integrated intensity of 100 diffraction with variation in tilt angle ξ for spin-coated film (triangles) and friction-transferred film (filled circles).

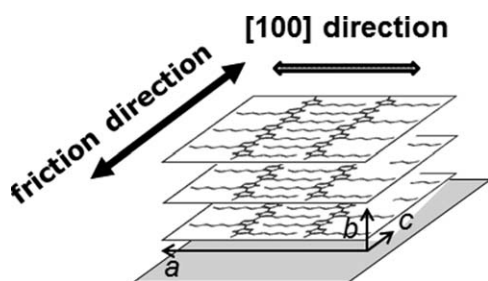


Figure 7. Image of proposed molecular orientation of P3DDT in thin films.

transferred film is shown in Figure 6. The intensity was the strongest at $\zeta = 0^\circ$ and weakest at $\zeta = 90^\circ$. This shows that the *a*-axis is parallel to the substrate plane, that is, the face-on orientation, as shown in Figure 7. The width of the distribution was narrower than that of the spin-coated film. This suggests that the crystallites in the friction-transferred film are strongly oriented. These results (crystallite orientation in the spin-coated and friction-transferred films) were in agreement with those obtained by IR measurements (molecular orientation). More detailed ED-GIXD evaluation will be reported in a separate paper.¹⁵

Performance of RR-P3DDT/C₆₀ Bilayer OPV Devices

Figure 8(a,b) shows the current density–voltage (*J*–*V*) characteristics of RR-P3DDT/C₆₀ bilayer OPV cells formed by the friction transfer and spin-coating methods, respectively. The cell formed by the friction transfer method shows the following OPV characteristics: power conversion efficiency (PCE) of 0.35%, short circuit current density (*J*_{sc}) of 2.1 mA/cm², open circuit voltage (*V*_{oc}) of 0.43, and fill factor (F.F.) of 0.38 at AM1.5G 100 mW/cm². Conversely, the cell formed by the spin-coating method shows lower OPV characteristics: PCE of 0.17%, *J*_{sc} of 1.9 mA/cm², *V*_{oc} of 0.48, and F.F. of 0.18 at AM1.5G 100 mW/cm². The *V*_{oc} and *J*_{sc} of these devices were almost the same; however, the PCE and F.F. of the OPV cell formed by the friction transfer method were about double those of the cell formed by the spin-coating method, indicating that the increase in F.F. would lead to an increase in the PCE.

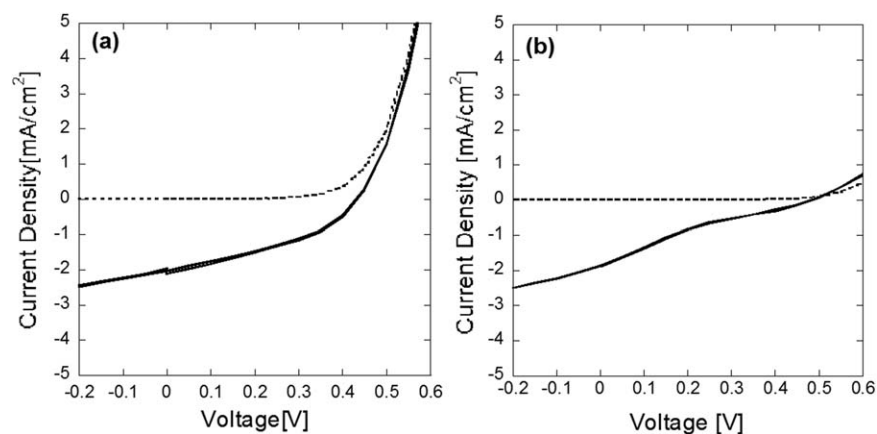


Figure 8. *J*–*V* characteristics in the dark (dashed) and under AM1.5G 100 mW/cm² (solid) for RR-P3DDT/C₆₀ bilayer OPV devices based on RR-P3DDT film formed by (a) the friction transfer method and (b) the spin-coating method.

In the following experiment, we investigated whether the increase in PCE was due to the orientation or crystallization of the RR-P3DDT films.

RR-P3DDT films formed by the spin-coating method were subsequently annealed at 90°C for comparison with the friction-transferred films that were formed on the substrate at 90°C, and the annealing resulted in enhancement of RR-P3DDT crystallization. OPV devices were then fabricated with these films. The PCE of the device did not increase significantly with crystallization of the RR-P3DDT film. Therefore, not crystallization but the orientation effect may be the main cause of the improvement in PCE of our devices.

From these results, we concluded that the RR-P3DDT orientation plays an important role in the improvement of F.F., resulting in improvement of PCE; that is, RR-P3DDT molecules with face-on orientation on the substrates affect intermolecular π – π stacking, which leads to increased carrier mobility in the direction perpendicular to the substrate. Osaka et al.²¹ reported that the edge-on rich orientation of semiconducting polymers improves OFET performance, whereas the face-on rich orientation improves OPV performance, indicating that the orientation control of polymers significantly affects OPV performance.

Figure 9(a) shows current–voltage (*I*–*V*) characteristics in the dark and under irradiation with white light (51.2 mW/cm²) polarized parallel and orthogonal to the direction of friction of the RR-P3DDT/C₆₀ bilayer OPV device based on the RR-P3DDT film formed by the friction transfer method. The photocurrent was enhanced when white light polarized parallel to the direction of friction was used for irradiation compared to that when white light polarized orthogonal to the direction of friction was used due to the orientation of the RR-P3DDT molecular chains parallel to the direction of friction. Conversely, the photocurrent of the OPV device based on the RR-P3DDT film formed by the spin-coating method was almost the same under white light irradiation polarized in any direction on the substrate plane, showing that the RR-P3DDT molecules absorb white light polarized along both parallel and orthogonal directions (data not shown).

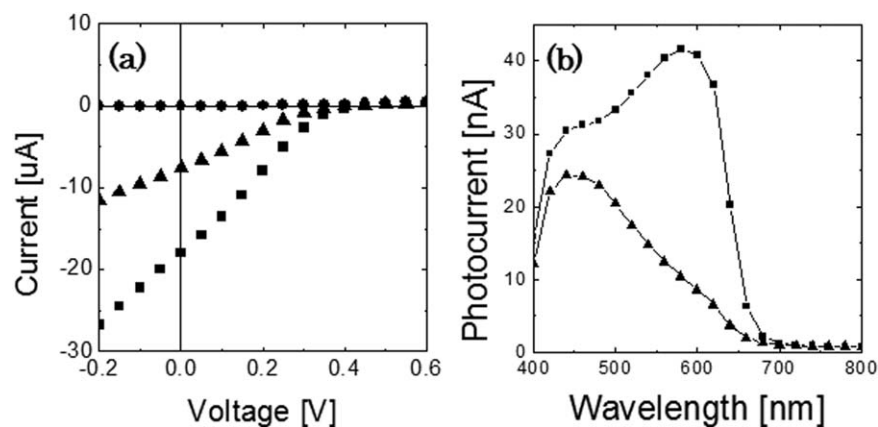


Figure 9. (a) I - V characteristics in the dark (solid circles) and under irradiation with white light (51.2 mW/cm^2) polarized parallel (solid squares) and orthogonal (solid triangles) to the direction of friction and (b) short circuit photocurrent action spectra under irradiation with monochromatic light ($4 \mu\text{W/cm}^2$) polarized parallel (solid squares) and orthogonal (solid triangles) to the direction of friction, for the RR-P3DDT/ C_{60} bilayer OPV device based on the RR-P3DDT film formed by the friction transfer method.

Figure 9(b) shows the action spectra of the same device used in Figure 8(a) under irradiation with light polarized parallel (solid squares) and orthogonal (solid triangles) to the direction of friction. In the action spectra, peaks around 440 and 580 nm were derived from C_{60} and RR-P3DDT molecules, respectively. The peak intensity around 580 nm was higher under irradiation with light polarized parallel compared to that polarized orthogonal to the direction of friction, also due to the orientation of the RR-P3DDT molecules parallel to the direction of friction, which led to the increase in photocurrent intensity. Conversely, a peak around 480 nm was observed under irradiation with light polarized orthogonal to the RR-P3DDT chain direction, even though there was no distinct absorption peak around 480 nm under irradiation with light polarized orthogonal to the RR-P3DDT chain direction in Figure 3(a). This may have been because the C_{60} layers of the OPV also generate excitons,²² which affect the peak around 440 nm in the action spectrum.^{23–25}

These results indicate that the uniaxially oriented RR-P3DDT molecules absorb more light that is polarized parallel to the RR-P3DDT molecular chain direction. RR-P3DDT/ C_{60} bilayer OPV devices based on RR-P3DDT films formed by the friction transfer method can be used not only as OPV devices but also as detectors of polarized light.^{3,4,26–28} Moreover, our polarizing OPVs can be used in liquid crystal displays, where backlight energy ($\sim 75\%$) is lost due to the orthogonal polarizers, as an alternative energy recycling system.²⁹

CONCLUSION

Orientation control of RR-P3DDT molecules in films was achieved by the friction transfer method. Analyses of the films were performed by polarized UV-vis absorption spectroscopy, transmission and RA FT-IR spectroscopy, and GIXD measurement. The results showed that the a -axis of the RR-P3DDT crystallites in the spin-coated film is normal to the substrate plane, that is, edge-on orientation, and that the RR-P3DDT molecular chains do not align in any direction in the substrate plane, whereas the RR-P3DDT crystallites in the friction-

transferred film are parallel to the substrate plane, that is, face-on orientation, and that the RR-P3DDT molecular chains are aligned parallel to the direction of friction (i.e., parallel to the substrate plane).

We also showed that the OPV performance of the RR-P3DDT/ C_{60} bilayer devices based on the friction-transferred RR-P3DDT films was higher than that of those based on the spin-coated RR-P3DDT films. This may have been because the intermolecular π - π stacking due to the P3DDT molecules with the face-on orientation on the substrate leads to an increase in carrier mobility in the direction perpendicular to the substrate.

In addition, the OPV devices based on the friction-transferred RR-P3DDT films showed a response to polarized light, indicating that the OPV devices based on the friction-transferred RR-P3DDT films can be used not only as OPV devices but also as detectors of polarized light.

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