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Oriented Thin Films of the Low-Band-Gap Polymer PTB7 by Friction Transfer Method

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Low-band-gap polymers are promising materials for organic photovoltaic application. We prepared an oriented thin film of a low-band-gap polymer, PTB7, by friction transfer method. The oriented film showed a strong dichroic absorption in the whole visible range. The orientation of molecular chain was characterized by two-dimensional grazing incident X-ray diffraction (2D-GIXD) with synchrotron radiation. 2D-GIXD results showed PTB7 molecular plane parallel to the substrate plane, i.e.*, "face on orientation."*

Keywords low-band-gap polymer; thin films; polarized light; molecular alignment; X-ray diffraction

Introduction

Recently, importance of molecular orientation is emphasized for organic photovoltaic devices (OPV). Especially, arrangement of π-stacking is important because it strongly affects on carrier transporting [1]. The orientation in which aromatic planes in conjugated molecules is parallel to the substrate, namely 'face-on' orientation, is favorable for OPV. We have been studying on orientation control of conjugated polymers by mean of friction transfer method [2-5]. The friction transfer is a fabrication method of oriented polymer films reported an improvement on the photovoltaic properties of regioregular-poly(3-dodecylthiophene) devices in which 'face-on' orientation was raised by the friction transfer [6]. A low-band-gap polymer poly{4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl} (PTB7) (Figure 1(a)), which is promising materials for OPV [7, 8], is known to show preferential orientation of 'face-on' in the neat film and the blend film with [6,6]-phenyl-$C_{61(71)}$-butyric acid methyl ester (PCBM)

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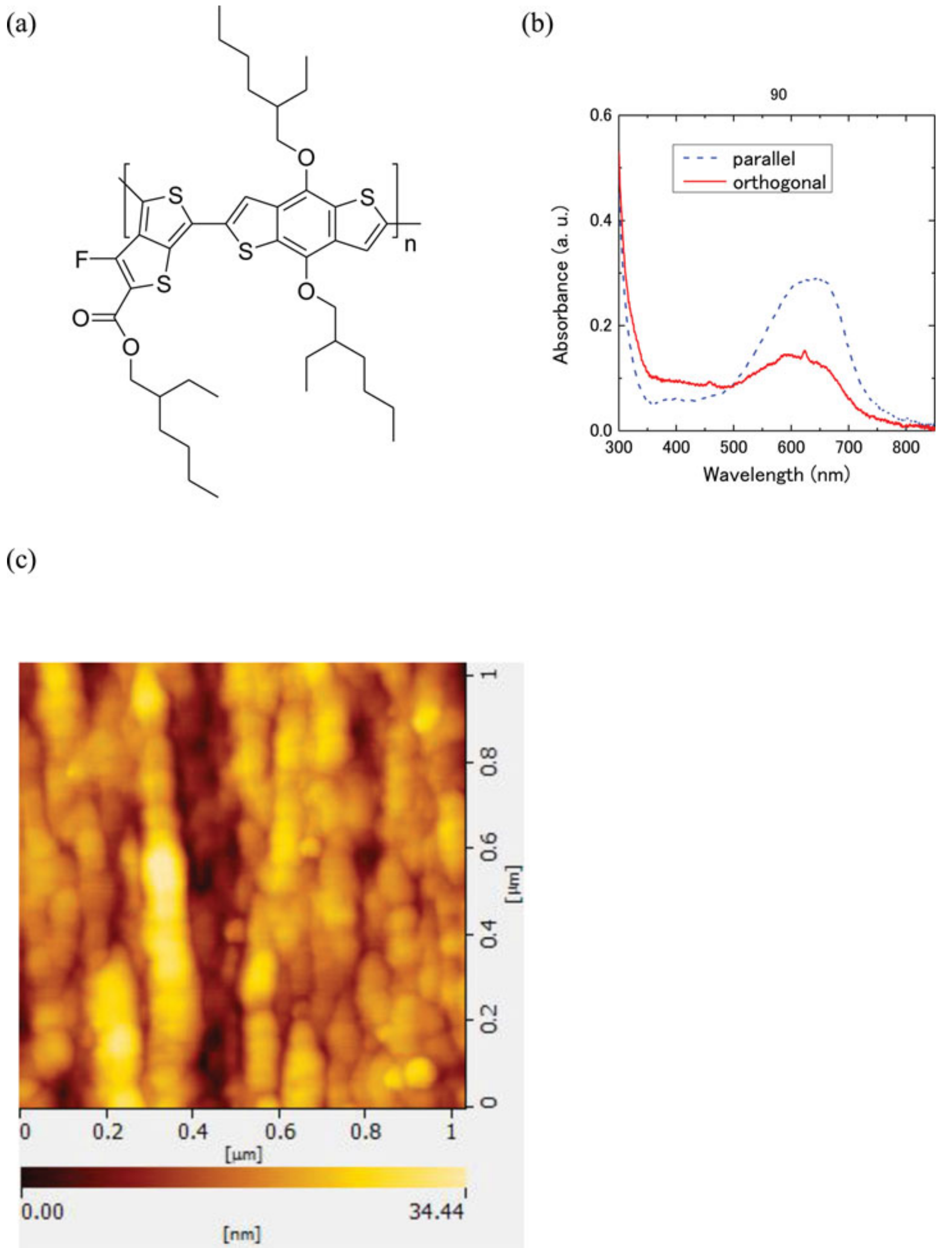

Figure 1. (a) Chemical structure of PTB7, (b) Polarized UV-vis spectra of friction-transferred PTB7, (c) an AFM image of the friction-transferred PTB7 film.

[9, 10]. In this study, we prepared PTB7 oriented films by the friction transfer method and evaluated their orientation.

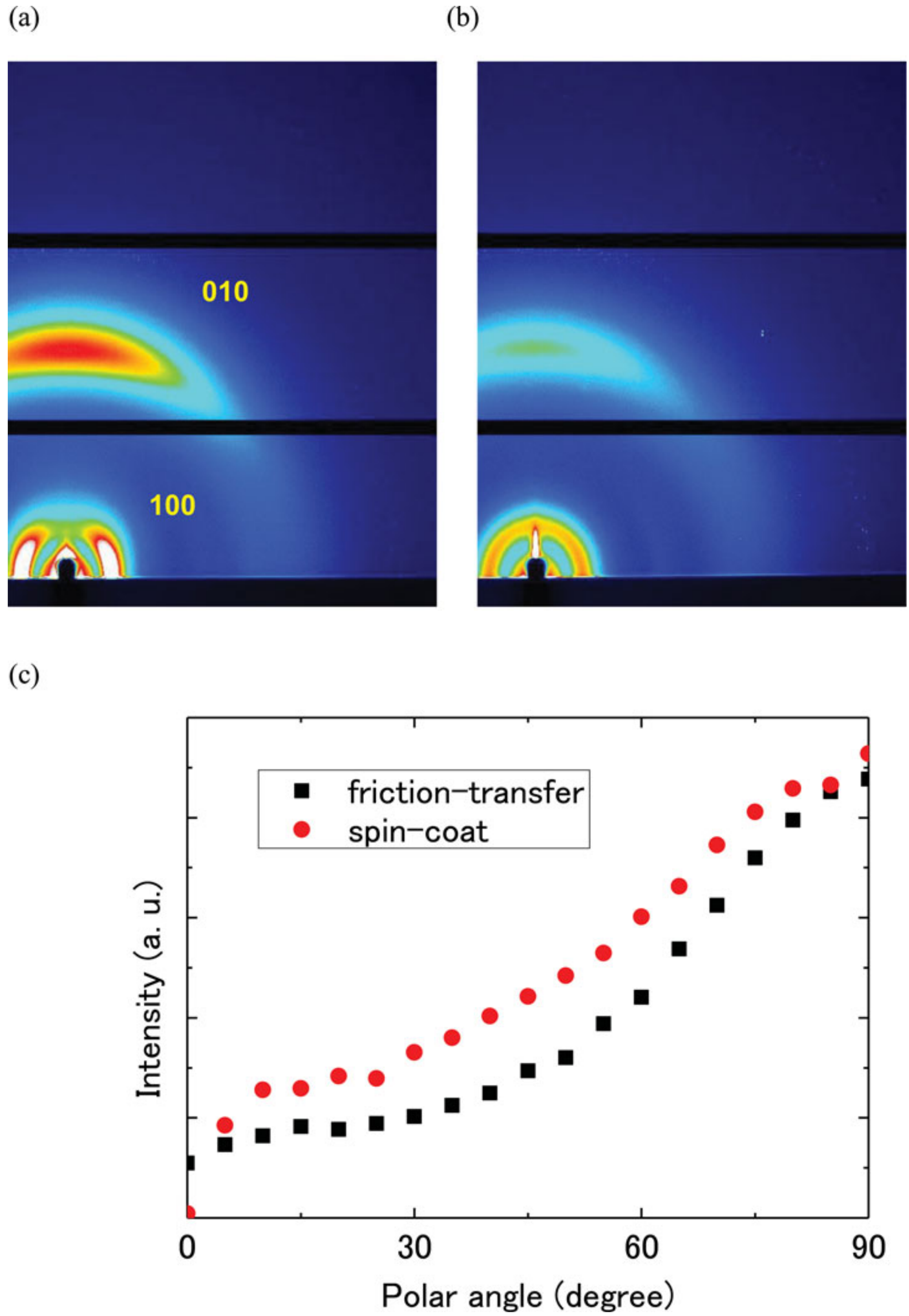

Figure 2. 2D-GIXD patterns of PTB7 film: (a) friction-transferred film, (b) spin-coated film. (c) Intensity variation of 010 reflection of friction-transferred and spin-coated films with various angles between the equatorial and radial line.

Experimental

In this study, PTB7 [molecular weight (MW) is 10,000-60,000, purchased from Luminance Technology Inc.] were used without any further purification. Glass slides were used as substrates after washing in alkaline ethanol. The friction transfer was carried out as follows [2-5]: A polymer block, which was produced by compressing polymer powder, was slid on the substrate at controlled temperature, pressure, and sliding speed, forming a polymer film onto the substrate's surface. The substrate temperature was varied in a range between ambient temperature and 150°C. The applied pressure was lower than 2.1 MPa. The sliding speed was ranging between 25 and 100 cm/min. Spin-coated films were fabricated from chlorobenzene solution as the reference sample.

The polymer films were characterized by optical absorption spectroscopy using a Shimadzu UV-3150 spectrophotometer. Polarized spectra were measured with a Glan-Taylor polarizing prism. X-ray diffraction measurements performed at the SPring-8 on the beamline BL46XU. Two-dimensional grazing incident X-ray diffraction (2D-GIXD) data were recorded with a 2D image detector (Pilatus3 300K) equipped on a Huber diffractometer. Incident angle of X-rays (energy: 12.398keV, wavelength: 0.1000nm) were fixed 0.12º.For characterization of in-plane orientation, diffraction patterns were measured with sample rotating (φ) in the substrate plane with an interval angle of 2º.

Results and Discussion

Preparation of PTB7 Oriented Films

Oriented films of PTB7 were obtained by friction transfer method at all substrate temperatures between ambient and 150°C. Orientation of the films was characterized with polarized optical microscopy and polarized UV-vis spectroscopy. As whole area of the films changed bright and dark for every 45º rotation in polarized micrograph under crossed Nicol condition, the whole films were uniaxially oriented. However, the films prepared at lower temperatures were discontinuous, then proper temperature is determined to be higher than 70°C. Figure 1(b) shows the polarized UV-vis spectra of the oriented PTB7 film. The films showed strong dichroism in the whole range of visible light region. The dichroic ratios are around 3, and these values are smaller than the case of friction-transferred films of other conjugated polymers already reported [2-5]. Figure 1(c) shows an atomic force micrograph of the oriented PTB7 film. It could be seen ridge structure along the friction direction. Typical film thickness was ca. 100nm.

Evaluation of Orientation by GIXD

Though PTB7 is a low crystalline polymer, 100 and 010 reflection can be used for evaluation of orientation from X-ray diffraction [11]. The 100 and 010 reflections correspond to molecular packing in lamellar structures and p-stacking of the lamellae, respectively. Figure 3 shows 2D-GIXD patterns of PTB7 films ((a) friction-transferred and (b) spin-coated film). As the 010 reflection was observed in meridian for both samples, the *b*-axis was normal to the substrate plane. Because the *b*-direction is almost parallel to the π-stacking direction, PTB7 assumed 'face-on' orientation, in which their aromatic plane parallel to the substrate for both samples. For the friction-transferred film the 100 reflection appeared distinctly on equator, however, the 100 reflection was almost ring for the spin-coated one. For evaluation

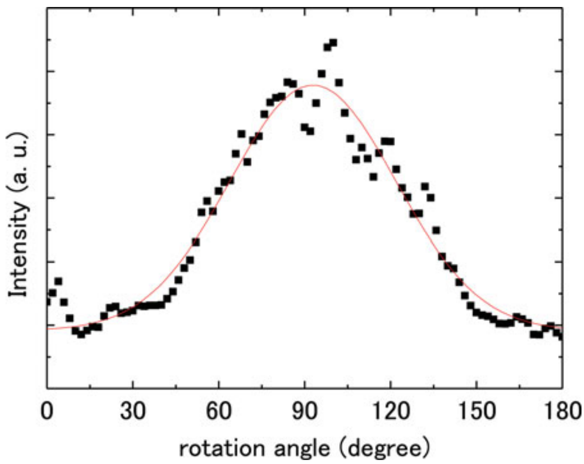

Figure 3. Variation of integrated intensity of 100 reflection of PTB7 with azimuthal rotation angle of the sample in the substrate plane.

of orientation distribution, 2D-diffraction patterns were analyzed as following: We evaluated the 010 reflection intensity from the profiles of scattering intensity along some radial lines. The intensities of the 010 reflection were plotted with angles between the equator and the line (Figure 2(c)). Comparison of the distribution of 010 reflection suggests that the friction-transferred film showed little bit more strongly oriented than the spin-coated film.

In order to evaluate the distribution of alignment molecular chains along the friction direction we measured a series of diffraction patterns with rotation of the samples in the substrate plane. We can use 100 reflection for this purpose because the *a*-direction is normal to the molecular chain axis and lies in-plane for ‘face-on’ orientation. Figure 3 shows the intensity variation of 100 reflection plotted with in-plane rotation angles. Distribution of 100 reflection and distribution of molecular chain orientation are in agreement. The full width at half maximum is 68.3º. This distribution is wider than those of already obtained for other friction-transferred polymers [4, 5]. This seems to be due to the fact that the molecular unit of PTB7 is not linear but bending shaped.

Conclusion

We can successfully prepared oriented films of PTB7, which is first example of low-band-gap polymer with large aromatic unit. The friction-transferred film showed ‘face-on’ orientation like spin-coated one. This orientation is benefit for photovoltaic application. We are studying on the photovoltaic application of the PTB7 oriented film.

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