Morphological Study of Blend Thin Films of Poly(3-hexylthiophene)-*block*-polyisobutylene-*block*-poly(3-hexylthiophene):Poly(3-hexylthiophene) and Their Application to Photovoltaics

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The detailed morphological studies of poly(3-hexylthiophene)(P3HT)-*b*-polyisobutylene(PIB)-*b*-P3HT:P3HT blend thin films by grazing incidence X-ray scattering (GIXS) were reported. The results of GIXS experiments indicated the formation of phase separation between P3HT and PIB domains even after blending the P3HT homopolymer below 30 wt%. The change in d-spacing values of the phase-separated under strains was suppressed by increasing the weight ratio of the P3HT homopolymer, probably due to the disruption of the microphase separation. The blending the P3HT homopolymer induced the edge-on orientation during the strain process below 75%, probably by improving the interaction between P3HT domains in the blend thin films. The OPV characteristics were obtained with the device structure of ITO/PEDOT:PSS/P3HT-*b*-PIB-*b*-P3HT:P3HT:PC61BM/Ca/Al, significantly improving the JSC and FF values by increasing the P3HT homopolymer weight ratio. The excellent elongation behavior of P3HT-*b*-PIB-*b*-P3HT:P3HT blend bulk films (P3HT < 30 wt%) could be achieved, probably due to the formation of microphase separation between semi-crystalline P3HT and rubbery PIB domains.

Keywords: Morphology, Block copolymer, Organic photovoltaic, Synchrotron X-ray scattering, π-Conjugated polymer, Elastomer

1. Introduction

Flexible and even stretchable optoelectronic devices have received much attention to realize mass production of wearable devices for medical and healthcare uses, owing to their low cost R2R processability based on printing technologies. Focusing on the stretchable organic electronics, many examples of organic thin film transistors (OTFTs) have been reported [1-8], yet the ones of organic photovoltaics (OPV) application are rare. Stretchable OPVs are also expected important as lightweight and codeless electric power supplies for operating the stretchable chemical/bio sensors.

Lipomi et al. reported the stretchable OPV devices based on a bulk-heterojunction (BHJ) system of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) by introducing the buckle structures onto a poly(dimethylsiloxane) (PDMS) substrate to achieve a power conversion efficiency (PCE) of 1.2% under the applied strain of 18.5% [9]. Kaltenbrunner et al. also reported the BHJ-based ultrathin OPV devices to achieve a PCE of 4.2% under the strain of 400% [10]. However, trend has
recently shifted to pursue flat and intrinsically stretchable devices without buckle or any wavy device structures.

The high performance stretchable OTFTs could be achieved based on the blend system of diketopyrrolopyrrole (DPP)-based semiconducting polymer and a typical thermoplastic elastomer of polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS), reaching 0.55 cm²V⁻¹s⁻¹ under the strain of 100% [7]. Recently, an array of ABA triblock copolymers has been developed where A and B are a semiconducting polymer and an elastomer with low glass transition temperature (Tg) [11-13] expecting more thermodynamically stable morphology than the blend system.

We have succeeded in the synthesis of a novel ABA triblock copolymer where A and B were P3HT and polyisobutylene (PIB) segments, P3HT-b-PIB-b-P3HT [14] (Fig. 1). The detailed morphological study of the P3HT-b-PIB-b-P3HT thin films by grazing incidence X-ray scattering (GIXS) showed the changes of the phase-separated domain sizes as well as P3HT crystalline orientation, while maintaining the P3HT crystalline structure under the strains from 0 to 200%. The OTFT performance of P3HT-b-PIB-b-P3HT thin films was determined to be 3.0 × 10⁻³ cm²V⁻¹s⁻¹ (without stretching) comparable to a pristine P3HT film, although P3HT-b-PIB-b-P3HT contained 70 wt% of the insulating PIB segment. This is an indirect evidence of the existence of well-connected phase-separated domains of P3HT segments in the P3HT-b-PIB-b-P3HT thin film between source and drain electrodes in the OTFT device.

In this work, the morphological studies of the blend system of P3HT-b-PIB-b-P3HT:P3HT thin film varying the blend ratios of P3HT from 0 to 50 wt% to apply to BHJ-OPV for the first time. The aim of blending with a P3HT homopolymer is to elucidate the criteria of maintaining stretchability of the semiconducting materials while improving light absorption and networks for charge transportation to apply to OPV systems.

2. Experimental

2.1. Materials

P3HT-b-PIB-b-P3HT (Mn = 54,200, Dm = 1.34, P3HT:PIB = 30:70, by wt.) was prepared according to our previous paper [14]. P3HT (Mn = 36,100, Dm = 1.07) was prepared by modifying Kumada-Tamao catalyst-transfer polymerization method described in the literature [15]. PC61BM (E100) was purchased from Frontier Carbon Corp., Japan and used as received.

2.2. Measurements

The tapping mode AFM observation was performed with an Agilent AFM 5500, using microfabricated cantilevers with a force constant of 34 N/m.

The grazing incidence small angle X-ray scattering (GISAXS) patterns were obtained at beamline BL46XU of SPring-8, Japan. The monochromated energy of the X-ray source was 12.398 keV (λ = 0.12002 nm) and the incidence angle α of was 0.15°. GISAXS patterns were recorded with a 2D image detector (Pilatus 2 M) where the sample-to-detector distances were 2981 mm. The grazing incidence wide angle X-ray scattering (GIWAXS) measurements were also conducted at the beamline BL46XU of SPring-8, Japan. The sample was irradiated at a fixed incident angle α on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.398 keV (λ = 0.10002 nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300 K) with the sample-to-detector distances of 174.1 mm. The scattering vectors qy and qx for GIXS are defined in Eq. (1).

\[
\begin{align*}
(q_y, q_x) &= \frac{2\pi}{\lambda}\left(\sin \psi \cos \alpha_f - \sin \alpha_t \sin \alpha_f \right)
\end{align*}
\]

where ψ is an out-of-plane angle and αi is an exit angle.

To prepare the thin film samples for AFM and GIXS, the films were transferred onto PDMS substrates from PEDOT:PSS-coated glasses. The transferred films on PDMS substrates were then stretched at certain strains (ε = 0, 25, 50, 75, 100, and 200%) and retransferred onto a Si wafer according to the reported method [16].

For thermomechanical analysis (TMA) experiments, the P3HT-b-PIB-b-P3HT:P3HT bulk
standing films (W 5.0 mm × L 10 mm) with a thickness around 70 μm were prepared by drop casting onto glass substrate, followed by peeling off in water. The tensile modulus of the film was measured by a TMA8311 Thermo plus EVO2 at 25 °C.

2.3. Solar cell characterization
The solution for the active layer was prepared by dissolving P3HT-b-PIB-b-P3HT:P3HT (30 mg/mL) and PC61BM in o-dichlorobenzene, adjusting total P3HT:PC61BM = 1:0.8 by wt. The glass–indium tin oxide (ITO) substrates (obtained from Lumtec, Ltd. (7 Ω/sq.)) were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, subsequently dried on a hot plate at 120 °C for 5 min, and finally treated with oxygen plasma for 15 min. Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron P VP A14083) was passed through a 0.45 μm filter before being deposited on ITO spin-coating at 3,500 rpm for 60 s in the air, and dried at 140 °C for 20 min inside a glovebox. The blended films of the P3HT-b-PIB-b-P3HT:PC61BM were prepared by spin-coating the active layer solution on the top of the PEDOT:PSS layer at 430 rpm for 60 s. After drying for 1 h, the devices were completed by thermal evaporation of Ca (30 nm) and Al (100 nm) under high-vacuum condition. The active area of the device is 4 mm². The current density−voltage (J−V) measurement was conducted by a computer-controlled Keithley 2400 source measurement unit (SMU) with an Oriel solar simulator (Newport Corp.) under the illumination of AM 1.5G, 100 mW/cm². The illumination intensity was calibrated by a standard Si photodiode detector with KG-5 filter.

3. Results and discussion
First of all, the AFM surface phase images of pristine P3HT-b-PIB-b-P3HT thin films were observed (Fig. 2). The as-spun film showed periodic finger-like images for nanophase separation (Fig. 2(a)). However, after the double transfer process, the phase separated images got unclear to some extent, although nanofibril domains are still observed (Fig. 2(b)). After applying the strains from 0 to 100%, the nanophase separation seems to be distorted as expected (Figs. 2(c)-2(f)). However, it is hard to quantify the degree of deformation of P3HT-b-PIB-b-P3HT thin films only from AFM observation.

Previously, our group reported the detailed deformation of the morphology of pristine P3HT-b-PIB-b-P3HT thin film by GIXS [14]. The self-assembled hierarchical nanostructure of the P3HT-b-PIB-b-P3HT thin film with vertically-aligned microphase separation was clearly observed. In addition, it was turned out that some of PIB domains enlarged when applying the strain from 0 to 200% parallel to the polymer main chains, while the PIB domains shranked with applying the strain vertical to the polymer main chains. On the other hand, P3HT crystalline orientation was also found deformable between bimodal and edge-on when applying the strain parallel and vertical to the polymer main chains, respectively.

We have further evaluated the morphology of the P3HT-b-PIB-b-P3HT blend thin films varying the weight ratios of P3HT from 0 to 50 wt% by GISAXS. Figure 3 shows the in-plane GISAXS profiles of the P3HT-b-PIB-b-P3HT thin film after the double transfer process under the strain of 0%.

Increasing the blend ratio of the P3HT homopolymer, we still confirm the existence of scattering peaks for periodic distances of the phase segregation, although the scattering peaks became broaden in the in-plane GISAXS profiles especially over 30 wt% P3HT loading. This implies that the phase separation between P3HT and PIB domains are somewhat disturbed by P3HT homopolymers.

The d-spacing values of the nanofibril structures of P3HT-b-PIB-b-P3HT:P3HT blend (P3HT: 0, 10, 20, and 30 wt%) thin films could be determined by in-plane GISAXS profiles measured with an X-ray beam parallel to the strain direction (Fig. 4). As a result, the value decreased by increasing the strains from 0 to 100% when the P3HT blend ratio was less
than 20 wt%. This is probably due to the shrinking forth vertical to the strain direction followed by the compression of phase-segregated PIB domains to decrease the \(d\)-spacing values. In contrast, increasing the P3HT blend ratio to 30 wt% caused less changing in \(d\)-spacing values under the strain, presumably because of the disturbed phase separation of PIB domains.

The in-plane GIXS profiles measured with an X-ray beam vertical to the strain direction showed the increase in the \(d\)-spacing values by increasing the strains from 0 to 25% (Fig. 5). However, after applying the strains more than 25%, the \(d\)-spacing values of blend films did not change much probably due to the disruption of the phase separation by blending. Note that \(d\)-spacing values of the pristine P3HT-b-PIB-b-P3HT film splitted over 25% strain and one of \(d\)-spacing value increased significantly following the tensile stress. This result may support the partial enlargement of phase-segregated PIB domains of the pristine P3HT-b-PIB-b-P3HT film without blending.

Figure 6 shows 1D in-plane and out-of-plane GIWAXS profiles of the P3HT-b-PIB-b-P3HT:P3HT blend (P3HT: 0, 10, 20, 30, 40, and 50 wt%) thin films after the double transfer process under the strain of 0%. As can be seen, there is no difference in the scattering peak positions of P3HT(100) and P3HT(010) which indicates no difference in the P3HT crystalline structure itself independent on the P3HT blend ratio from 0 to 50 wt%. However, the intensity of the scattering peak increased compared to that of amorphous halo by increasing the P3HT blend ratio. This result can be simply explained by the increase of semi-crystalline P3HT wt% toward the amorphous PIB segment.
Fig. 6. 1D in-plane (left) and out-of-plane (right) GIWAXS profiles of the P3HT-b-PIB-b-P3HT:P3HT blend (P3HT: 0, 10, 20, 30, 40, and 50 wt%) thin films after the double transfer process under the strain of 0%.

The azimuthal plots of P3HT(100) scattering patterns were taken from 2D GIWAXS profiles of the P3HT-b-PIB-b-P3HT:P3HT blend (P3HT: 0, 10, 20, and 30 wt%) thin films after the double transfer process under the strains from 0% to 100% (Fig. 7). The pristine P3HT-b-PIB-b-P3HT film causes the broadening of azimuthal plots by increasing the strains from 0 to 100%, indicating the disruption of the edge-on orientation of P3HT crystallines. Interestingly, by blending with P3HT (10, 20, and 30 wt%), such disruption of the edge-on orientation was somewhat suppressed, although the high strain levels >75% induced again the disruption. The blending of P3HT into P3HT-b-PIB-b-P3HT may suppress the disordering of P3HT crystalline orientation by strengthening the interaction between P3HT domains.

Figure 8 shows the J-V curves of the classic BHJ OPV devices with the structure of ITO/PEDOT:PSS/P3HT-b-PIB-b-P3HT:P3HT:PC_{61}BM/Ca/Al with varying P3HT homopolymer weight ratio from 0 to 50 wt% with maintaining the total weight of P3HT:PC_{61}BM=1:0.8 by wt.

The OPV device showed similar open-circuit voltage ($V_{oc}$) values of 0.518-0.544 V independent on the blend ratio. On the other hand, the short-circuit current density ($J_{sc}$) (0.302 to 4.96 mA/cm$^2$) and fill factor (FF) (38.1 to 60.7%) significantly increased by increasing the P3HT homopolymer weight ratio. The light absorption as well as the connections of charge transporting pathways would be much improved by the addition of P3HT homopolymer to P3HT-b-PIB-b-P3HT which possesses totally insulating PIB segments. The OPV performances under strains are now under investigation.

Fig. 7. Azimuthal plots of P3HT(100) scattering patterns taken from 2D GIWAXS profiles of the P3HT-b-PIB-b-P3HT:P3HT blend (P3HT: 0, 10, 20, and 30 wt%) thin films after the double transfer process under the strains from 0% to 100%. The profiles were obtained with an X-ray beam parallel to the strain direction.

Fig. 8. Organic photovoltaic characteristics of ITO/PEDOT:PSS/P3HT-b-PIB-b-P3HT:P3HT:PC_{61}BM/Ca/Al (P3HT: 0, 10, 20, 30, and 50 wt%, total weight of P3HT:PC_{61}BM=1:0.8, w:w).

The tensile modulus increased from 1.41, 2.46, 3.19, 7.86, and 23.9 MPa by increasing the P3HT homopolymer weight ratio from 0 to 50 wt%, respectively (Fig. 9). Below 30 wt% blend ratios, the film remains tolerable even for 50% strain. The excellent elongation behavior of the blend bulk film would be attributed to the existence of microphase separation between semi-crystalline P3HT and rubbery PIB domains even after blending P3HT homopolymer below 30 wt% as also supported by the results of GIXS experiments.
4. Conclusion

In this study, we reported the detailed morphological studies of P3HT-b-PIB-b-P3HT blend thin films by GIXS. The results of GISAXS experiments indicated that the existence of phase separation even after blending the P3HT homopolymer below 30 wt%. Also, the deformation behavior of the microphase separation, especially for $d$-spacings of the nanofibril structures, was affected by increasing the weight ratio of the P3HT homopolymer, probably due to the disruption of the microphase separation. The GIWAXS results showed the interesting phenomena that the blending the P3HT homopolymer improved the edge-on orientation during the strain process below 75%, probably by improving the interaction between P3HT domains in the blend thin films. The OPV devices were fabricated and characterized with the structure of ITO/PEDOT:PSS/P3HT-b-PIB-b-P3HT:PC$_{61}$BM/Ca/Al with varying P3HT homopolymer weight ratio from 0 to 50 wt%. As a result, the $J_{SC}$ and FF significantly increased by increasing the P3HT homopolymer weight ratio. The mechanical properties of the P3HT-b-PIB-b-P3HT:PC$_{61}$BM/Ca/Al with varying P3HT homopolymer weight ratio from 0 to 50 wt% showed the excellent elongation behavior, presumably owing to the existence of microphase separation between semi-crystalline P3HT and rubbery PIB domains which is comparable to the results from GIXS experiments.

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