

Simultaneous Use of Small- and Wide-angle X-ray Techniques to Analyze Nanometerscale Phase Separation in Polymer Heterojunction Solar Cells

Using grazing-incidence small-angle X-ray scattering and wide-angle X-ray diffraction techniques to analyze the nanoscale phase separation of P3HT and PCBM after annealing, the effects of the sizes of the PCBM clusters and P3HT crystallites on the power conversion efficiency of bulk heterojunction solar cells is studied. This approach allowed us to investigate the effects of the sizes of the PCBM clusters and P3HT crystallites on the power conversion efficiencies of bulk heterojunction solar cells. It appears that improved power conversion efficiency requires the value of R_g of the PCBM clusters to be greater than 20nm and the value of D_{100} of the P3HT crystallites to be greater than 16nm for an active layer thickness of ca. 100nm.

The development of conjugated polymers for use in organic optoelectronic devices has been an area of extensive investigation. Notably, poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) bulk heterojunctions display power conversion efficiencies of up ca. 5%. The improved power conversion efficiencies of these devices resulted from the use of thermal annealing and solvent annealing processes, which enhanced the film morphology relative to that of the as-cast film. The resulting improvement in performance of these systems have been attributed to a) self-organization of P3HT into a crystalline structure exhibiting enhanced absorption and high hole mobility transport and b) diffusion of PCBM molecules into PCBM-rich clusters to form large PCBM clusters. The nanostructured phase separation of P3HT/PCBM creates percolated pathways for transporting the holes and electrons to their respective electrodes. The performance of these heterojunction solar cells depends critically, therefore, on the morphology of its active layers.

Small-angle X-ray scattering (SAXS), which utilizes the elastic scattering of X-rays to probe nanostructures having sizes ranging from 1 to 100 nm, provides statistically averaged morphologies of analyzed samples. For polymer/fullerene bulk heterojunction solar cells, SAXS can provide global information regarding the internal structure of the dispersion of fullerene units within the polymer matrix much more effectively than can TEM or the other analysis techniques. In this present study, we simultaneously applied grazing-incidence small-angle X-ray scattering (GISAXS) and wide-angle X-ray diffraction (GIWAXD) to study the morphology of P3HT/PCBM bulk heterojunction solar cells after their thermal annealing. Utilizing this approach, we could therefore elucidate the relationship between the relative length scales of the PCBM clusters and P3HT crystallites and the devices' performance.

☉ Beamline

BL17B3 Small Angle X-ray Scattering

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Figure 1 displays the GIWAXD profiles of several P3HT/PCBM films. After annealing the P3HT/PCBM film at 150 °C for 15 min, a strong peak appeared representing the (100) reflections of the P3HT lamella layer structure along with two small peaks contributed by the (300) and (400) or (010) plane reflections of the P3HT lamella structure.

The sizes of the P3HT crystallites at (100) reflection (D_{100}) can be obtained using Scherrer's relation:

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos\theta} \quad (1)$$

where D_{hkl} is the apparent crystallite size along the $[hkl]$ direction and β_{hkl} is the full width at half maximum of an (hkl) diffraction (in radians). The P3HT crystallites dramatically increased in size — from 9.6 nm in the as-cast film to 18.0 nm — after annealing at 100 °C for 15 min. This phenomenon can be explained by considering that the glass transition temperature in regioregular poly(3-alkylthiophene) is ca. 100 °C.

In Fig. 1, in the low- Q range (ca. 0.006 \AA^{-1}) of the GISAXS curves for the as-cast film, we observe a small scattering peak that is possibly attributable to the presence of PCBM in P3HT. For confirming this scattering peak, we have carried out control experiments by measuring GISAXS for both the pure P3HT and the P3HT/PCBM thin films (ca. 100 nm thickness; on Si substrate). The data shows that the annealing at 150 °C for 15 min does not affect the low- Q intensity of the GISAXS profile of the P3HT film, indicating that even if there is local phase separation inside the P3HT film, it does not contribute much to the intensity change in the low- Q region. (not show here) Moreover, the GISAXS intensity of the as-cast or annealed P3HT/PCBM thin film is much larger than that of as-cast or annealed pure P3HT thin film, probably due to the large electron density difference between PCBM and P3HT (0.7 vs. $0.4 \text{ e}^-/\text{\AA}^3$). Therefore, the GISAXS features in the low- Q region of P3HT/PCBM thin film are clearly dominated by PCBM, and we attribute the large GISAXS intensity change

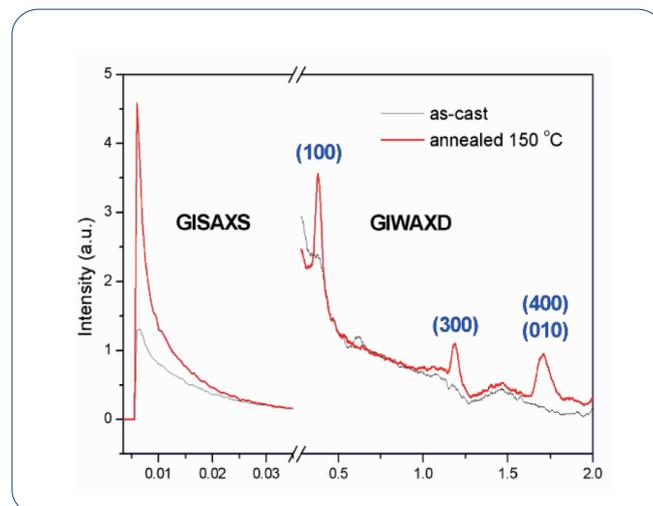


Fig. 1: GISAXS/GIWAXD curves of as-cast and annealed (150 °C, 15 min) P3HT/PCBM films (not to scale).

in the P3HT/PCBM thin film after annealing at 150 °C for 15 min to a significant growth of the PCBM aggregates. The PCBM scattering intensity increased dramatically as a result of the PCBM molecules diffusing out of the P3HT matrix and forming larger PCBM clusters.

The radius of gyration (R_g) of a PCBM cluster can be determined from the scattering peak intensity using the Guinier approximation [Equation (2)]:

$$I(Q) = I(0) \exp\left(-\frac{Q^2 R_g^2}{3}\right) \quad (2)$$

where $I(Q)$ is the scattering intensity, $I(0)$ is the zero-angle scattering intensity, Q is defined as $4\pi \sin(\theta/2)/\lambda$ in terms of the scattering angle θ and the wavelength λ , and R_g is the radius of gyration of the PCBM clusters. Figure 2 presents plots of $\ln I(Q)$ vs. Q^2 that were fit using Eq. 1 (solid lines) in the low- Q range (0.006 – 0.012 \AA^{-1}). The values of R_g can be extracted from the slopes ($-R_g^2/3$) of the fitted lines. We fitted each set of data with two slopes for two R_g values that were then used to give an averaged R_g and the spread of R_g for the aggregation size of PCBM. After annealing at 100 and 120 °C, the values of R_g of the PCBM clusters increased marginally to $16 \pm 2 \text{ nm}$ from

15 ± 2 nm in the as-cast film. After annealing at 150°C for 15 min, R_g increased dramatically to 23 ± 3 nm. Thus, it appears that large-scale diffusion of PCBM molecules into the P3HT matrix to form aggregates occurred only at temperatures at or above 150°C . The mean diameter of the PCBM clusters obtained after annealing at 150°C for 15 min was 60 ± 20 nm, as deduced from the value of R_g , assuming that the PCBM clusters were spherical.

Under 1 equivalent sun intensity (100 mW/cm^2), the power conversion efficiency (η) from our as-cast device was 0.53%, with values of J_{sc} , V_{oc} , and FF of 4.0 mA/cm^2 , 0.38 V, and 35%, respectively. After annealing at 100°C for 15 min, the value of η became 1.6%. We attribute this increase in η to the growth of the P3HT crystallites, which increased to 18.0 nm from 9.6 nm after annealing, since the hole mobility increased upon increasing the size of the P3HT crystallites, as evidenced by the current density increasing from 4.0 to 7.7 mA/cm^2 . Furthermore, the change in the morphology of P3HT/PCBM film results in increased carrier delocalization.

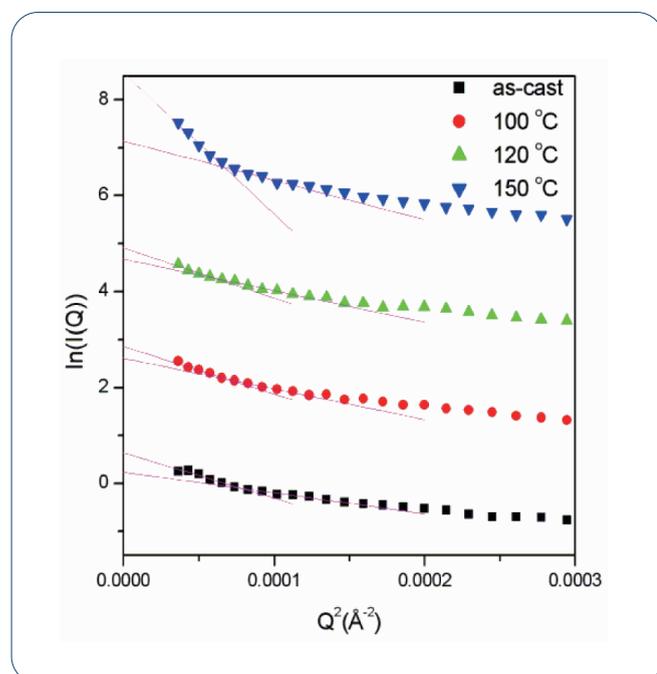


Fig. 2: Plots of $\ln I(Q)$ vs. Q^2 for P3HT/PCBM films annealed at various temperatures, fitted using the Guinier approximation (solid lines).

Annealing the P3HT/PCBM blend at 120°C for 15 min, increased the value of η to 3.0%; we believe this behavior resulted from an increase in the number of P3HT crystallites, even though the average crystallite size remained about the same as that in the sample annealed at 100°C . The sizes of the PCBM clusters remained virtually unchanged when the annealing of P3HT/PCBM was performed at either 100 or 120°C for 15 min. Annealing for 15 min at 150°C , however, led to a dramatic increase in the value of R_g of the PCBM cluster aggregates to 23 ± 3 nm; accordingly, the η increased to 4.0%, with values of J_{sc} , V_{oc} , and FF of 9.9 mA/cm^2 , 0.63 V, and 63%, respectively. In this case, the P3HT crystallite size reduced slightly relative to that for the sample annealed at 120°C , whereas the absolute intensity of the (100) reflection remained roughly the same. Therefore, we interpret the increase in J_{sc} as resulting from larger PCBM clusters forming better pathways for electron transport. Hence, different mechanisms dominate the development of the P3HT/PCBM blend morphology at different temperatures. At the glass transition temperature (100°C), increased planar stacking of P3HT chains occurred, thereby increasing the P3HT/PCBM crystallite size but not affecting the cluster size of the PCBM molecules. At 150°C , the PCBM molecules diffused to form large clusters; therefore, phase separation of P3HT and PCBM occurred to provide improved continuous pathways for the holes and electrons.

Figure 3 displays the relative length scales of the P3HT crystallites and the radii of gyration of the PCBM clusters. The value of the corresponding lattice constant, d_{100} , can be calculated using Bragg's law ($n\lambda = 2d\sin\theta$ at $2\theta = 5.3^\circ$)¹¹ to be 1.67 nm. From Scherrer's relation, the value of D_{100} is equal to md_{100} , where m is the number of layers in the P3HT lamellar structure. For the device exhibiting the optimal performance (annealing temperature, 150°C ; P3HT:PCBM blend weight ratio, 1:0.8), each P3HT crystallite contained ca. 10 layers of P3HT main chains π -stacked parallel to the substrate with their alkyl chains positioned normal to substrate at the (100) reflection, and each cluster

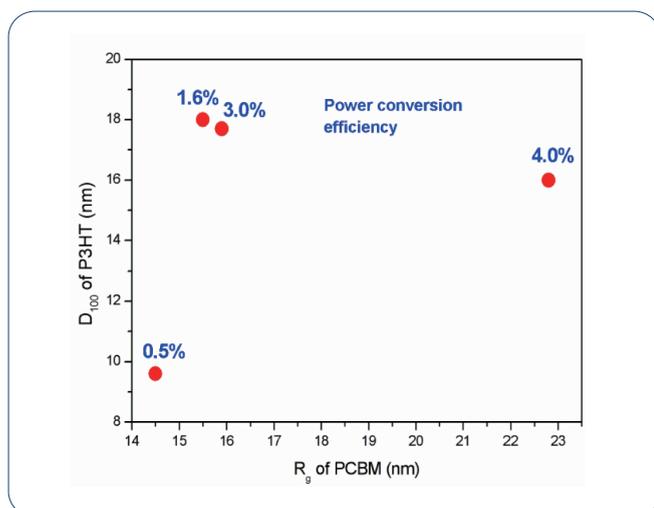


Fig. 3: Relative length scales of the P3HT crystallites, the radii of gyration of the PCBM clusters, and the power conversion efficiencies of the various P3HT/PCBM film devices.

contained ca. 39,600 PCBM molecules.

In summary, we applied GISAXS and GIWAXD simultaneously to study the morphologies of P3HT/PCBM active layers in bulk heterojunction solar cells annealed at various temperatures. This approach allowed us to investigate the effects of the sizes of the PCBM clusters and P3HT crystallites on the power conversion efficiencies of bulk heterojunction solar cells. It appears that improved power conversion efficiency requires the value of R_g of the PCBM clusters to be greater than 20 nm and the value of D_{100} of the P3HT crystallites to be greater than 16 nm for an active layer thickness of ca. 100nm.◆

Experimental Station

SWAXS endstation

Publications

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