

Competition between PCBM Aggregation and P3HT Crystallization upon Annealing of BHJ Solar Cells

For green energy developments, morphology of the active layer of bulk heterojunction thin films is playing an important role for performance optimization of solar cell. Concomitant development of [6,6]-phenyl-C₆₁-butyric acid methyl ester aggregation and poly(3-hexylthiophene) crystallization in solar cells of bulk heterojunction thin film has been revealed using simultaneous grazing-incidence small-/wide-angle X-ray scattering. The interesting results not only clarify the mechanistic origins of morphological development in films of poly(3-hexylthiophene)/[6,6]-phenyl-C₆₁-butyric acid methyl ester but also provide insights to the performance optimization of polymer/fullerene organic thin-film devices in general.

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Morphology of the active layer of bulk heterojunction (BHJ) thin films, comprising donor and acceptor components, is one of the critical factors in solar cell performance optimization. An ideal morphology for BHJ thin-film solar cells features in phase-separated nanodomains ca. 10 nm in size to facilitate exciton dissociation and charge transport; also relevant is the connectivity of these nanodomains in the respective phases for charge transport. With the new approach of simultaneous/time-resolved grazing incidence small-/wide angle X-ray scattering (GISAXS/GIWAXS) and the structural analysis for kinetics parameters, we have made new findings centering on the critical aggregation behavior of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in the poly(3-hexylthiophene) (P3HT) polymer composite of P3HT-PCBM blend; these include (1) the thermal equilibrium aggregation sizes and the growth kinetics of PCBM, (2) faster PCBM aggregation kinetics than that for P3HT crystallization (opposite to previous speculations), (3) a deduced activation energy for PCBM aggregation that addresses the phase separation mechanism of P3HT and PCBM (for the interacted or bi-continuous P3HT and PCBM nanodomains) in more appropriate terms of nucleation-and-growth, rather than the spontaneous spinodal decomposition (requiring no activation energy) that has been suspected for some time, and (4) closely and quantitatively correlated PCBM aggregation size and electron mobility that has long been postulated. The present results not only clarify the mechanistic origins of morphological development in P3HT/PCBM films but also provide insights to the performance optimization of polymer/fullerene organic thin-film devices in general.^{1,2}

Scattering results. The GISAXS and GIWAXS patterns exhibited concomitant and substantial changes

during the heating process from an ambient temperature to 150 °C; the scattering patterns were quickly saturated within the subsequent 100 s of isothermal annealing, revealing fast morphology development of the composite film. Specifically, the GIWAXS patterns evidenced successively enhanced P3HT lamellar peaks up to the third order in the vertical direction, corresponding to edge-on P3HT lamellae with the lamellar stacking direction perpendicular to the substrate surface. The concomitant growth of the (100) peak in the in-plane direction corresponded to the development of face-on lamellae domains with the lamellar stacking oriented parallel to the film surface. Meanwhile, the emerged GIWAXS halo at $q \approx 1.4 \text{ \AA}^{-1}$ during the annealing process revealed formation of a short-range packing of PCBM after aggregation. The PCBM aggregates also resulted in prompt and drastic increase of scattering intensity in the low- q region ($0.004 - 0.04 \text{ \AA}^{-1}$) of the corresponding GISAXS patterns simultaneously observed. Note that scattering in the low- q region was mainly dominated by large PCBM aggregates as elucidated in our previous study. With the time resolution of 5 s, these time-resolved GIWAXS/GISAXS data revealed rich structural information, especially the mutually confined growth kinetics of P3HT and PCBM nanodomains in the composite film as elucidated below.

Growths of PCBM Aggregates and P3HT Crystallites. The GISAXS profiles of the P3HT/PCBM ($c = 1.0$) film selectively extracted from the corresponding 2D patterns along the q_x direction (at the specular beam position $q_z \approx 0.018 \text{ \AA}^{-1}$), revealing the fast scattering development in the low- q region $0.004 - 0.04 \text{ \AA}^{-1}$ within the first 60 s of thermal annealing. Furthermore, the selected GISAXS profiles for 0, 96 s at 150 °C, overlapped roughly, revealing quickly saturated PCBM

aggregation. A broad interference shoulder at $q_x \approx 0.025 \text{ \AA}^{-1}$ shaped during the annealing, corresponding to formation of a liquid-like or distorted FCC-like packing of PCBM aggregates with a mean spacing of ca. 25 nm.

The evolutions of the two P3HT (100) peaks for the edge-on lamellae of the P3HT/PCBM blend film ($c = 1.0$) during 150 °C annealing. These profiles were extracted from the corresponding GIWAXS patterns along the normal-to-plane (q_z) directions. During the heating process to 150 °C, the (100) peaks sharpened concomitantly and shifted successively from $q_z = 0.388 \text{ \AA}^{-1}$ to 0.355 \AA^{-1} owing largely to thermal expansion of the lamellae; the peaks could shift back closely to 0.374 \AA^{-1} when the sample was cooled down to ambient temperature after thermal annealing, as also observed for a pristine P3HT film in a similar annealing process. After the thermal annealing, the enhanced orientation of P3HT lamellae along the surface normal direction, however, revealed straightened lamellar stacking with a slightly larger lamellar spacing of 16.8 Å than that (16.2 Å) before annealing.

Formation Mechanism. A cartoon in Fig. 1 depicts the morphological features of the P3HT/PCBM solar cell film with optimized performance; in which, PCBM is dissolved in P3HT networks, in the form of dispersed molecules or non-crystalline aggregates, forming a meta-stable phase. We demonstrate here that it is the *competition* between crystallization of P3HT nanograins and aggregation of PCBM that dictates the morphological development and hence the device performance.

Conclusions. With synchronized GIWAXS and GISAXS of enhanced spatial/time resolutions, we have captured the competing kinetics of PCBM aggregation and P3HT crystallization of the corresponding BHJ thin film solar cells. Within the first 100 s of thermal annealing at 150 °C, PCBM aggregation size in the P3HT/PCBM composite films grew quickly from 7 to 18 nm then saturated; meanwhile, the majority P3HT lamellae increased from a size of 7 to 12 nm. Both the kinetics of PCBM aggregation and P3HT crystallization could be characterized by similar Avrami exponents close to unity; the faster PCBM aggregation, however,

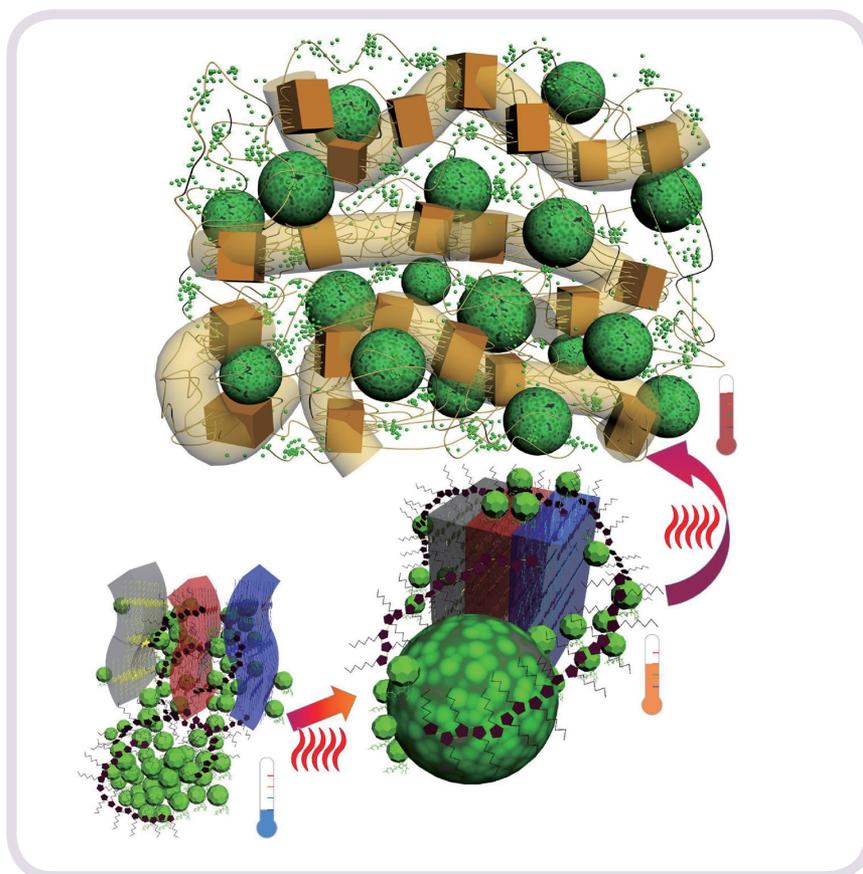


Fig. 1: Formation pathway of mutually intercalated polymer/fullerene nanograins for heterojunction thin film solar cells. Activated by thermal energy, trapped fullerene are released for aggregation, accompanied by enhanced polymer crystallization. Competition kinetics result in local phase separation with mutually confined heterogeneous nanodomains in the matrix of dispersed fullerene and polymer chains.

has a two-fold higher Avrami rate constant. The developments of PCBM and P3HT nanodomains could influence strongly and sensitively the electron and hole mobilities of the BHJ thin film solar cells. The illustrated kinetics of structural evolution and its correlation to changes in charge mobility of P3HT/PCBM composite films may bear relevance to the selection of alternative polymer/fullerene derivative combinations and in the optimization of processing conditions for future BHJ thin-film solar cells.

Beamline 23A1 SWAXS end station

References

1. W.-R. Wu, U. Jeng, C.-J. Su, K.-H. Wei, M.-S. Su, M.-Y. Chiu, C.-Y. Chen, W.-B. Su, C.-H. Su, and A.-C. Su, *ACS Nano* **5**, 6233 (2011).
2. H.-J. Liu, U. Jeng, N. L. Yamada, A.-C. Su, W.-R. Wu, C.-J. Su, S.-J. Lin, K.-H. Wei, and M.-Y. Chiu, *Soft Matter*, **7**, 9276 (2011).

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