

Effects of Thermal Annealing On the Morphology of Polymer–Fullerene Blends for Organic Solar Cells

As worldwide energy consumption continues to increase, there is a pressing need to reduce our dependence on non-renewable and environmentally harmful fossil fuels. Achieving this goal will require a variety of solutions to provide energy in a wide range of settings. The development of solution processable organic solar photovoltaics (OPVs) shows promise as one route for providing inexpensive, flexible solar energy conversion devices.

Polymer-fullerene bulk heterojunctions (BHJ) have been intensely studied over the past decade for use as the active layer in such OPV devices (Figure 1). These BHJs typically consist of blends of the two components, where the domain size of each component is on the nanometer length scale. In these devices, optical photons are absorbed in the polymer component creating excitons (bound electron-hole pairs). The excitons then diffuse to the polymer-fullerene interface where charge separation occurs. Current is generated when the resulting free electrons and holes are transported through the donor polymer and acceptor fullerene, respectively, to the electrodes.

The molecular packing and crystallite size of both the acceptor and donor, within their respective domains, must be optimized for exciton transport (diffusion) and maximum charge carrier mobilities for efficient transfer of electrons and holes to their respective electrodes. Thus, an understanding of how to manipulate the molecular arrangement of the materials is critical for the design of more efficient solar cell devices.

Thermal annealing is frequently used to process BHJs, but currently, there is incomplete knowledge about how annealing processes affect the morphology of each component within the blend and the phase segregated domain size. Gaining a deeper understanding of these effects will allow for more efficient optimization of the processing conditions required to achieve the maximum performance from such devices.

We have developed techniques which use grazing incidence X-ray scattering (GIXS) to rapidly and systematically characterize the morphological evolution of polymer–fullerene BHJ blends during thermal annealing. These techniques are widely applicable for the rapid characterization of new materials systems where the thermal phase behavior is not well understood. Understanding how to control the morphology of such systems through thermal processing steps is critical for maximizing the solar cell device performance.

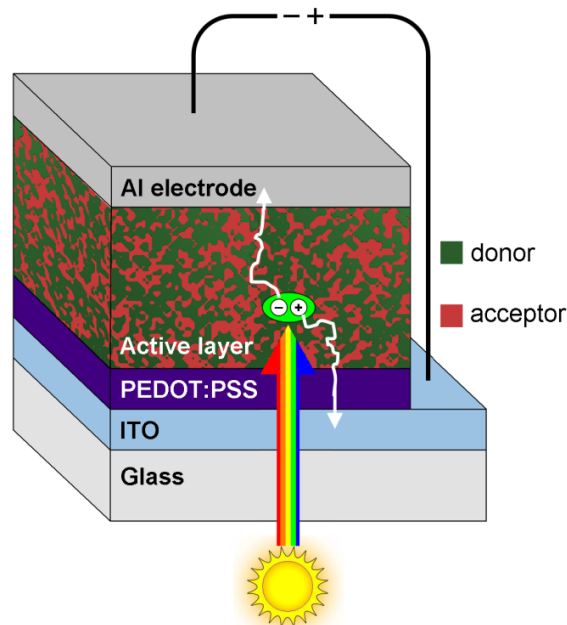


Figure 1: Architecture of an organic photovoltaic device. The negative electrode is aluminum, indium tin oxide (ITO) is a common transparent electrode, and the substrate is glass. The schematic depicts a bulk heterojunction (BHJ) active layer where the donor and acceptor blend forms phase segregated domains within the active layer. The structure of the BHJ is critical to the performance of the solar device.

In this work we have investigated the morphology of the BHJ blends and their individual components with GIXS both *during* the thermal annealing process (in-situ heating) and *after* annealing over a range of temperatures. One of the most popular blends consists of poly(3-hexylthiophene) (P3HT), as the electron donor phase, and phenyl-C61-butyric acid methyl ester (PCBM), as the electron acceptor phase. In-situ heating allows for the observation of molecular rearrangements during annealing, for both the P3HT and PCBM components, providing critical insights into the dynamics of the morphological evolution.

Figure 2 shows 2-D GIXS images of neat P3HT, neat PCBM, and blends with P3HT:PCBM blending ratios of 3:1, 1:1 and 1:3 both as-cast and after thermal annealing at 220°C. For each thin film composition significant morphological rearrangements are observed after thermal annealing.

The as-cast P3HT thin films display crystallites that have π - π stacking primarily perpendicular to the substrate (the π -face parallel to the substrate; see Figure 3). GIXS during in-situ heating revealed an increase in the P3HT layer spacing and the coherence length of the crystallites with increasing temperature, until approaching the melting point (T_m), observed at 205 °C. GIXS and AFM of P3HT thin films annealed with a thermal gradient (and subsequently cooled to room temperature) suggest two distinct crystallization mechanisms that occur for annealing above and below the P3HT T_m . As the annealing temperature is increased up to the P3HT T_m , existing P3HT crystallites grow with increasing annealing temperatures. In contrast upon cooling the P3HT films from the melt (after annealing above the P3HT T_m), heterogeneous nucleation at the substrate interface results in a massive reorientation of the P3HT crystallites. The melt crystallized P3HT has the P3HT lamellae and the π - π stacking direction preferentially oriented parallel to the substrate.

Annealing of amorphous PCBM thin films above the glass transition temperature (T_g) results in cold crystallization, as evidenced by the appearance of crystalline diffraction peaks and an increased surface roughness. In-situ GIXS of PCBM films above the T_g provides a quantitative measurement of the fraction of crystallization as a function of time and allows for the determination of crystallization mechanisms. Using the Avrami equation we were able to determine that PCBM cold crystallization occurs through heterogeneous nucleation at the substrate, and for temperatures above 155 °C the growth is limited to one dimension due to impingement of neighboring crystallites in the plane of the substrate.

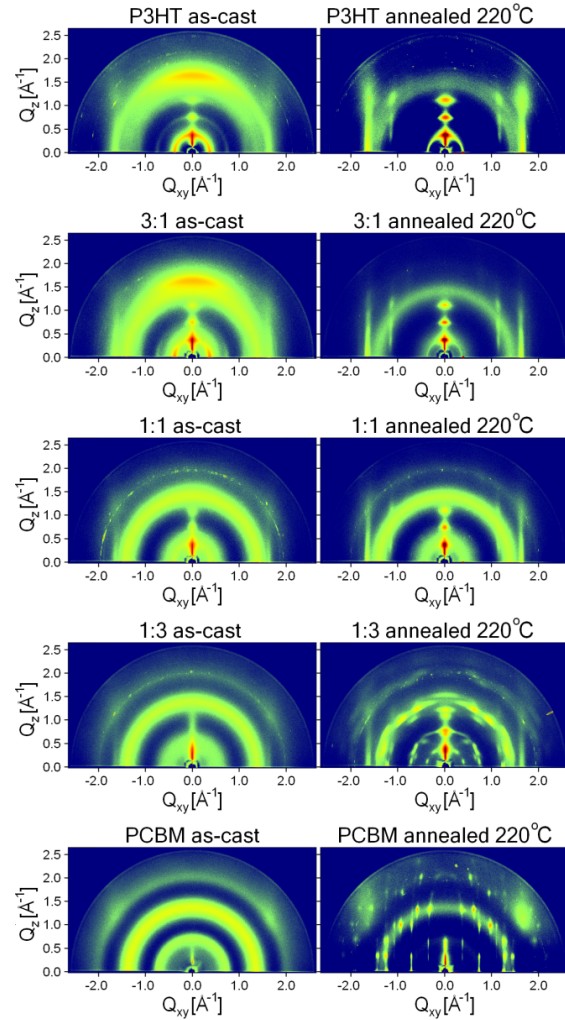


Figure 2. 2-D GIXS images of neat P3HT, 3:1 P3HT – PCBM blend, 1:1 P3HT – PCBM, 1:3 P3HT – PCBM blend, and neat PCBM films, each as-cast and annealed at 220°C.

By applying the same characterization techniques to a series of P3HT - PCBM BHJs, we were able to investigate the effects of incorporating each component into the blend as a function of blend composition and annealing temperature. The P3HT component in the 3:1 and 1:1 P3HT - PCBM blends displays similar behavior as the pure P3HT film; growth of existing crystallites for films annealed below the T_m and a reorientation of the P3HT crystallites due to heterogeneous nucleation at the substrate interface when cooled from the melt. However, increasing PCBM content leads to a reduction in the P3HT crystallite size and a corresponding reduction in the P3HT melting point. Similarly, a reduction in the PCBM T_g is observed with increasing P3HT content for the 1:3 and 1:1 blend films. The shift in these key transition temperatures as a function of blend composition underscores the importance of determining the optimal thermal annealing conditions for a given BHJ blend.

Understanding how various annealing conditions affect morphology of polymer - fullerene BHJ blends is critical for the design and optimization of systems for use in high performance solar cell devices. This work provides insights into the nature of the crystallization processes of both P3HT and PCBM as pure components and in BHJ blends, and illustrate the need to understand the thermal phase behavior of each component as a function of blend composition. The techniques demonstrated in this work can be implemented to identify key transition temperatures for new polymer - fullerene blend combinations, thus guiding the optimization of the processing conditions for solar cell device fabrication.

Primary Citation

E. Verploegen, R. Mondal, C. J. Bettinger, S. Sok, M. F. Toney and Z. Bao, "Effects of Thermal Annealing Upon the Morphology of Polymer-Fullerene Blends", *Adv. Funct. Mater.* **20**, 3519 (2010) doi: 10.1002/adfm.201000975

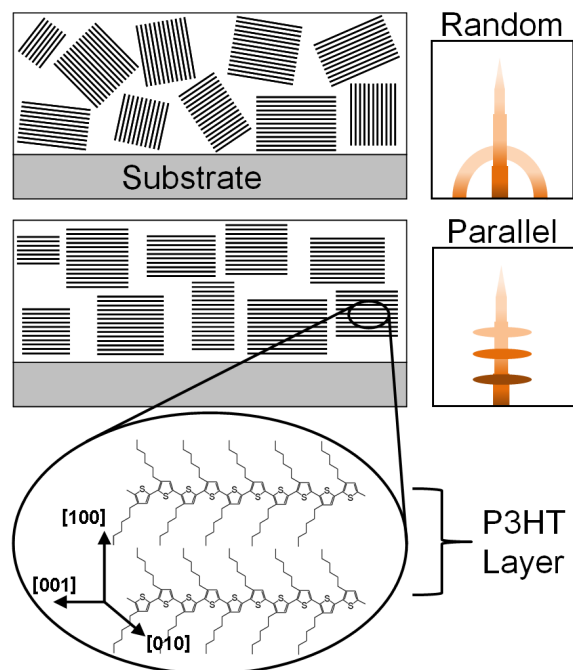


Figure 3. Top: Cartoons of P3HT thin films with random and parallel P3HT layer orientations and representative scattering patterns for each morphology. Bottom: The crystallographic directions are shown relative to the molecular structure.