

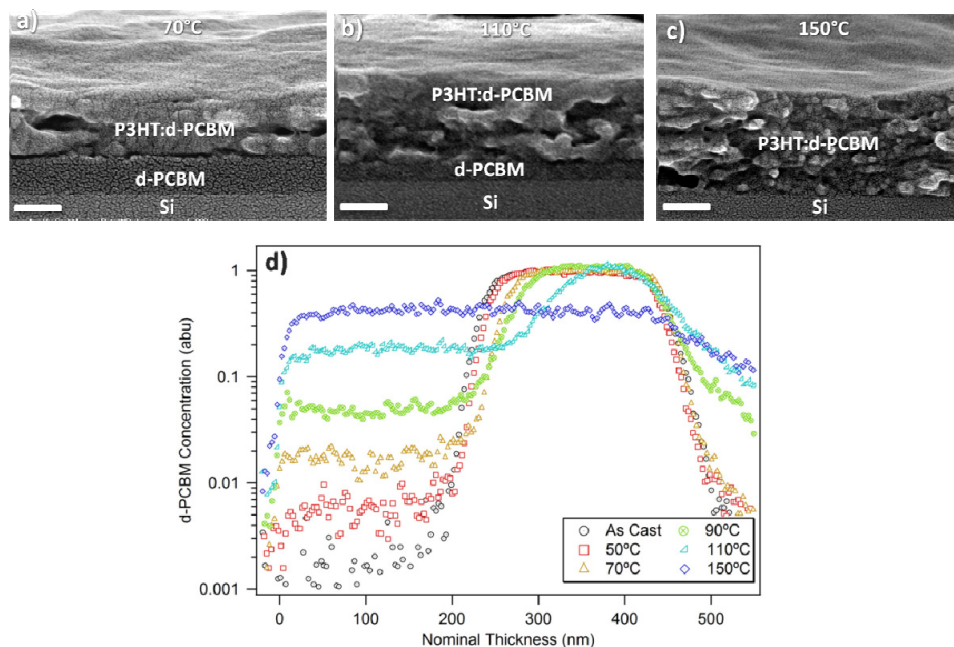
## Interdiffusion of PCBM and P3HT in Bulk Heterojunction Blends

The affordable production of the state-of-the-art silicon-based photovoltaics is limited by a need for large-area silicon substrates with low electronic defect densities.<sup>1</sup> Organic photovoltaics (OPVs) offer the potential for fabrication at low cost over virtually any size substrate due to their solution processability.<sup>2</sup> OPVs have achieved efficiencies near 8%, close to the estimated 10% needed to achieve economic viability,<sup>2,3</sup> due to the improvement in solar spectral coverage<sup>4</sup> and reduction of optoelectronic loss processes in the cells.<sup>3,5</sup> This performance is generally obtained using a bulk heterojunction (BHJ), which is a blend of an electron-donating polymer and an electron-accepting fullerene. Further improvements in efficiency require a better fundamental understanding of the morphology of the electron-donor and acceptor phases within the active layer of BHJ OPVs.

The power conversion efficiency of a BHJ is directly related to the internal morphology of the blended polymer and fullerene. Photogenerated excitons must reach the interface between the donor and acceptor materials to generate free charge carriers. In efficient devices, the photogenerated carriers must have a continuous transport path to the electrodes. There is much evidence that both the generation and collection of charges is highly dependent on the morphology (i.e. size, shape, texture, and phase distribution) of the active layer. Currently, the phase-separated morphology is difficult to control and characterize, and empirical processing methods are used to optimize OPVs.

One of the most extensively studied OPV system is formed from blends of poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric-acid-methyl-ester (PCBM). However, the internal film structure and evolution during the typical thermal annealing processing is still a topic of intense debate. The aim of this work was to develop a fundamental understanding of the miscibility of P3HT and PCBM by investigating the interdiffusion and evolution in molecular ordering starting from a pure bilayer film. By using a combination of dynamic secondary ion mass spectrometry (DSIMS) and cross-section scanning electron microscopy, we

observed interdiffusion within the P3HT/PCBM bilayers at relatively low temperatures (i.e. 50°C). Furthermore, this system rapidly (30 s) resulted in a homogeneous film (disregarding differences in interfacial concentration) when annealed at temperatures commonly used to optimize P3HT:PCBM BHJs (150°C) (Figure 1). This relatively fast rate of interdiffusion ( $2.5 \times 10^{-10}$  cm<sup>2</sup>/s - dominated by the PCBM diffusion) reveals that PCBM diffuses as molecular species or small aggregates and



**Figure 1.** Cross section SEM images of a P3HT/d-PCBM/Si bilayer annealed at a) 70°C, b) 110°C, and c) 150°C for 5 min. The scale bar represents a distance of 200 nm. d) DSIMS profiles of <sup>2</sup>H in bilayer samples of P3HT and d-PCBM annealed from 5 minutes at different temperatures. The thicknesses of the films (which differed slightly across samples) were normalized such that 0 nm is the free surface of the film and 450nm is the substrate. The deuterium concentrations were normalized such that the area under the counts versus distance for all profiles was the same after setting the normalized concentration in the d-PCBM part of the initial bilayer equal to 1.

shows that the BHJ components have significant molecular mobility during nominal thermal annealing conditions. By using 2D grazing-incidence wide-angle X-ray scattering, it was also observed that PCBM diffuses within the P3HT film without changing the P3HT crystallite structure, orientation, or growth (up to equal P3HT:PCBM weight ratios) (Figure 2).

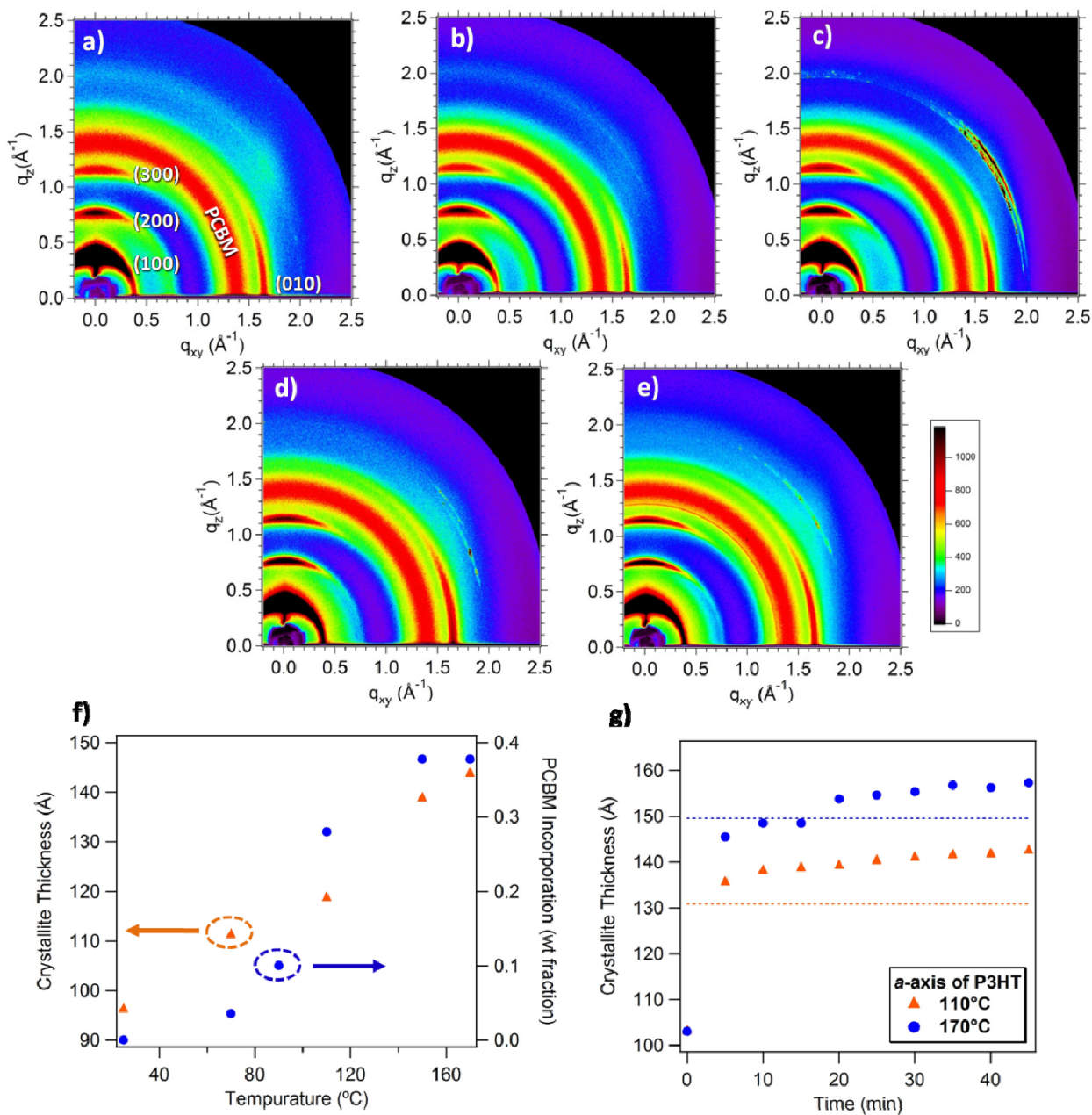


Figure 2. Two-dimensional GIWAXS of a P3HT/PCBM/Si bilayer a) as-cast and annealed at b) 70°C, c) 110°C, d) 150°C, and e) 170°C for 5 min. f) The Scherrer equation was used to extract the P3HT coherence length along the *a*-axis from the full-width-at-half-maximum of the (100) reflection corresponding to P3HT. PCBM incorporation from the DSIMS measurements was plotted for comparison at various annealing temperatures. g) Growth in the crystal thickness with time using in-situ heating 2D GIWAXS of a P3HT/PCBM/Si bilayer at 110°C (orange) and 170°C (blue). The Scherrer equation was used to determine crystal thickness from the (100) reflection corresponding to P3HT. The dotted line corresponds to a neat P3HT/Si sample heated for 5 min at 110°C (orange) and 170°C (blue).

These studies suggest that there is a clear driving force towards a three-phase mixture of P3HT and PCBM from a distinctly heterogeneous structure: pure P3HT crystallites, pure amorphous PCBM, and a mixture of disordered P3HT and PCBM. This gives strong evidence that the BHJ solar cells should have a similar structure.

### Primary Citation

N.D. Treat, M.A. Brady, G. Smith, M.F. Toney, E.J. Kramer, C.J. Hawker, M.L. Chabinyc, "Interdiffusion of PCBM and P3HT reveals miscibility in a photovoltaically-active blend," *Advanced Energy Materials*, 2011, **1**, 82-89.

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SSRL is primarily supported by the DOE Offices of Basic Energy Sciences and Biological and Environmental Research, with additional support from the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and the National Institute of General Medical Sciences.