Revealing the molecular structure of polymer:fullerene composite solar cells by high resolution electron microscopy

Greater understanding of the nano-morphology of polymer based solar cells will greatly aid the development of more efficient and more stable OPV devices. In this chapter, a detailed study of the changes in polymer solar cell morphology at the molecular level and in real time under process conditions is presented. Using low voltage, high resolution electron microscopy (LVHREM) the mechanisms of PCBM rich domain migration have been observed in real time, and evidence for vertical segregation within the bulk heterojunction and increased crystallinity of both P3HT and PCBM is presented. The results of the study highlight the fact that P3HT:PCBM bulk heterojunction morphology should be viewed within the framework of a four phase, three dimensional, nonequilibrium system.

IV.I Introduction

Understanding the nano-morphology of polymer based solar cells has become increasingly important in recent years since the discovery that a simple post production anneal can lead to efficiency gains of over 100%.^{1,2} Although the annealing step has some interfacial benefits, ^{2,3,4} it is the changes that occur within the morphology of the photoactive layer itself that have garnered the most investigative attention. ^{5,6,7} Of particular interest is the system containing the conjugated polymer poly(3-hexylthiophene) (P3HT) and the fullerene derivative phenyl-C₆₁-butyric acid methyl ester

(PCBM) which has produced some of the most advanced plastic based solar cells to date. ^{2,8} Further advancements will be greatly assisted by techniques capable of revealing the physical effects of the annealing process and relating them to the systems electronic properties. Electron microscopy techniques are well established in the inorganic semiconductor industry for this purpose, but techniques for the determination of molecular structure in organic electronics are not well developed. This is largely due to problems with sample preparation and electron knock-on damage from high-voltage electron beams. In this set of experiments, low voltage electron microscopy was used to obtain high resolution micrographs that reveal in unprecedented detail, lateral and vertical morphologies pre, post and even during the annealing process. In the devices under investigation, P3HT and PCBM are blended in a single layer (see Figure 1a) to form a bulk heterojunction. As discussed in Chapter 2, the morphology of this layer is very important for determining the overall device efficiency. P3HT is the dominant absorbing species and absorption of a photon generates exciton which must diffuse to a P3HT:PCBM interface before it can dissociate into separate charge carriers. The exciton has a diffusion length of 10 - 20nm⁹ which sets a limit on the optimum level of P3HT-PCBM phase separation. Domain sizes greater than 20nm lead to increased germinate recombination as increasing numbers of excitons recombine before finding a P3HT/PCBM interface at which they can dissociate. Once separated, the charge carriers require a bi-continuous pathway through which they can drift to their respective electrodes; holes through the polymer and electrons through the PCBM. Increased levels of structural and electronic order within these two phases are desirable for improved charge carrier mobility and extraction and therefore device efficiency.

Consequently, understanding and controlling the distribution and mixing of P3HT and PCBM on the nanometre scale are of paramount importance for the development of high efficiency plastic solar cells. Early work that focused on optimising the P3HT:PCBM morphology used AFM to show that the choice of solvent could greatly affect the PCBMrich domain size in spin cast P3HT:PCBM films.^{6,10} More recently, low resolution TEM and optical studies have shown that annealing leads to a coarsening of the P3HT:PCBM interphase penetration² and over extended periods of time, the formation of PCBM crystallites with micrometer dimensions. ^{3,5,10,11} The formation of such large crystallites is undesirable in solar cells as the larger domain size increases the risk that an exciton will not reach a P3HT:PCBM interface before recombining, leading to increased photoluminescence and reduced photovoltaic efficiency.^{1,5,12} Nonetheless, a certain level of nano-scale coarsening does appear to improve the bi-continuous morphology necessary for efficient charge transport.² One of the questions that this work sought to address is whether this morphological change is due to phase separation, or coarsening of an already phaseseparated system.

In addition, vertical segregation within the P3HT:PCBM layer has been proposed by a number of authors^{13,14} and most recently characterised by variable angle spectroscopic ellipsometry (VASE). ⁵ This is supported by secondary ion mass spectroscopy (SIMS) experiments conducted on polyfluorene:PCBM films on silicon, which revealed a four-layer morphology with the upper layers enriched with polymer and the substrate interface enriched with PCBM.¹⁵

93

Annealing can also improve the crystallinity of both P3HT and PCBM. This has been inferred from a number of experimental techniques including absorption,³ external guantum efficiency (EQE) spectra, 5^{5} x-ray diffraction^{2,7,16,17}, transmission electron microscopy¹, electron diffraction^{16,18,19}, Raman spectroscopy²⁰ and spectroscopic ellipsometry.¹² Films of neat P3HT exhibit a natural tendency to self-organise into crystalline lamellae but this is inhibited by the addition of PCBM. ¹⁶ However, heating of P3HT:PCBM films to temperatures above the P3HT glass transition temperature facilitates phase separation which then allows the enlarged P3HT domains to crystallise. Diffraction studies^{7,16} suggest there is a preferential orientation of the P3HT lamellae with the polymer backbone parallel to the substrate and the hexyl side chains normal to the substrate. Although the cause of this preferred alignment is not fully understood, it has been hypothesised that at least in the vicinity of the substrate-polymer interface, interactions between the hydrophobic P3HT side-chains and the hydrophilic SiO₂ substrate may be causative.¹² Similar orientation has been observed in P3HT:PCBM layers spun cast on top of PEDOT:PSS. ¹⁷

The body of evidence regarding annealing-induced crystallisation of PCBM is more equivocal. Pristine PCBM is even more likely to crystallise than P3HT and has been shown to readily form thin films of densely and homogeneously distributed nanocrystals when spin cast.²¹ However, XRD analysis of P3HT:PCBM blend films has noted a distinct lack of PCBM crystallinity even after annealing,¹⁷ which suggests that the polymer chains play an inhibitory role. The failure to observe PCBM crystallites by XRD is puzzling considering that PCBM crystals have been identified in annealed P3HT:PCBM films by TEM^{1,19} and electron diffraction^{18,19} which matches well with PCBM crystallite formation reported in other conjugated polymer systems.²²

IV.II In situ TEM of the Annealing Process

The net effect of the anneal is a dramatic improvement in device efficiency as shown in Figure 1b. which presents typical JV curves for a P3HT:PCBM solar cell prepared by the author before (a) and after annealing (b). Figure 1a shows the device geometry used in this study. The dramatic increase in short circuit current, fill factor and open circuit voltage are all apparent and result in an efficiency increase from 1.3% to 4.0%.



Bias,V

Figure 1. Current voltage curves and schematic of polymer based solar cell. a) Schematic of a polymer based solar cell showing the planar layered architecture. b) Current voltage curve of a typical P3HT:PCBM solar cell pre-anneal (triangles) and post-anneal (squares). Fabrication procedures are detailed in Chapter 2. Insets are of PCBM (top left) and P3HT.

The anneal step induces an enhanced molecular mobility which allows rearrangement of both P3HT polymer chains and PCBM molecules. This leads to the coarsening of the morphology as has been shown previously by low resolution TEM.² To further investigate the dynamics of this process a P3HT:PCBM solar cell sample was annealed at 150°C while simultaneously imaging by TEM. (details can be found in Chapter 3). The time series of images in Figure 2 gives insight into how the morphological rearrangement of P3HT and PCBM occurs. At the beginning of the anneal process the morphology is dominated by sub 10nm diameter PCBM-rich domains immersed in a P3HT-rich matrix. The contrast in grey scale can be attributed to the relative densities of P3HT and PCBM¹⁸ with the denser PCBM $(1.5 \text{gcm}^{-3})^{23}$ appearing darker than the P3HT (1.10gcm^{-3}) .²⁴ Of immediate interest is that at this scale, the PCBM-rich phase is non-continuous with an average nearest neighbour distance of 1.3 ± 0.6nm. Virtually all of the excitons generated within the polymer are within diffusion range of a P3HT:PCBM heterojunction where electron transfer occurs on the picosecond timescale.²⁵ Once separated however, it appears that electron transport must be reliant on non-conductive mechanisms such as hopping and tunneling to migrate from one domain to the next.

The images show that upon annealing, the PCBM-rich domains present in the pristine film begin to agglomerate. This in turn allows larger volumes of P3HT-rich matrix to form. By analysing the presented images using VistaMetrix, it can be shown that after 12 minutes the average area of individual PCBM-rich domains increases from 143 ± 44 nm² to $350 \pm$

96

 110nm^2 . Despite this, the average nearest neighbor distance of the PCBM domains remains at $1.8 \pm 0.8 \text{nm}$ – a statistically insignificant change from the $1.3 \pm 0.6 \text{nm}$ observed in the unannealed sample. The hopping transport rate between PCBM domains scales exponentially with the inverse of the distance between domains. The upshot is that the rate-limiting charge transport step between PCBM domains is not particularly affected by the coarsening, as the nearest neighbor distance remains nearly constant. Yet the agglomeration of adjacent domains does mean that separated electrons are required to transit between domains less frequently. The net result is an improvement in electron mobility through the fullerene phase.



Figure 2. Low voltage, high resolution transmission electron micrograph time series of a P3HT:PCBM blend during the annealing process. The highlighted area shows one area of PCBM rich domain agglomeration

An analysis of the area fractions of the dark and light phases shows that the total area fractions remain constant over time. This suggests that the coarsening of the PCBM-rich domain size is not due to phase separation but instead can be accounted for solely by the agglomeration and coarsening of PCBM-rich domains present in the as-cast film. As previously discussed, little has been previously reported on the mechanism of PCBM coarsening.

Recent *in situ* ellipsometry experiments have suggested that the annealing of P3HT:PCBM blends induces immediate crystallization of P3HT followed by subsequent diffusion of PCBM.⁵ The authors hypothesized that crystallization of P3HT facilitated diffusion of PCBM through low-polymer-density pathways that are created between P3HT crystallites. However, the result presented here suggests an alternative mechanism for PCBM mobility, with entire PCBM rich nano-domains migrating and agglomerating in order to decrease the interfacial area of the morphology – a phenomenon widely reported in annealed phase separated materials.^{26,27,28,29}

In addition, the current results allow the calculation of a PCBM domain growth rate of $(350 - 142)/12 = 17.3 \text{ nm}^2/\text{min}$. The ability to determine such a metric could prove useful for quantifying and comparing the ability of different strategies to reduce the rate of physical degradation in polymer:fullerene thin films.

To ensure that the observed morphological changes were caused by the annealing process, and that the sample was stable under the electron beam, a second sample was subjected to the same imaging regime but with the heating stage turned off. The results, presented in Appendix VI.I, show that the sample is highly stable under the electron beam, with no sign of PCBM domain agglomeration.

IV.III High Resolution of Pre and Post Anneal Devices

The resolution of the micrographs in Figure 2 was limited due to the thermal motion induced by the annealing process. In order to further explore the P3HT:PCBM

98

morphology, additional, high resolution TEM images were taken of samples from pristine and post-anneal devices and representative images are presented in Figure 3.

Figure 3a shows the pristine morphology of sub 10nm PCBM rich domains in a P3HT matrix, familiar from images in Figure 2. The PCBM domain nearest neighbor distance was calculated as 1.7 ± 0.5nm. In sharp contrast to this is the morphology observed in the annealed sample (Figure 3b). The PCBM-rich regions have agglomerated into larger, denser, more irregular shapes and the average nearest neighbor distance has increased to 2.8 ± 1.1nm. There are larger unbroken volumes of P3HT-rich phase, with excitons now having to diffuse up to 20nm to reach a heterojunction. Without the thermal motion from the heating stage blurring the images, finer features of the morphology are brought into focus, such as evidence for the formation of lamellae structures within the P3HT phase, which are indicative of P3HT crystallization. The micrographs in Figure 3 bear a remarkable resemblance to schematic representations of annealing induced changes envisioned by Erb et al. ¹⁷ and the average P3HT lamellae domain size of 8.0 ± 0.5nm in Figure 3b fits nicely with the size previously calculated for P3HT lamellae from XRD measurements using Scherrer's relation.¹⁷ This result is slightly different to that observed in Figure 2, most likely due to the differences in annealing conditions between the two experiments. In Figure 2 the sample was annealed in situ, under vacuum while suspended across a hole in a carbon film, whereas in Figure 3, the anneal was ex situ, at ambient pressure while coated on a glass:ITO substrate.



Figure 3. Low voltage, high resolution transmission electron micrographs of P3HT:PCBM blends before (a) and after annealing at 150°C for 10 minutes (b). These micrographs bear striking resemblance to schematic representation of unannealed (c) and annealed (d) morphologies published in reference 16.

It is worth noting the relatively low number of observable P3HT lamella, which explains the modest P3HT crystal peaks observed in XRD spectra of P3HT:PCBM devices.² An area analysis using Vistametrix yields only 12 ± 1% P3HT crystallinity by area. This compares to a degree of crystallinity of 18.5% for films of neat P3HT drop cast from chlorobenzene.³⁰ This highlights that even for P3HT, a relatively crystalline polymer, the amorphous phase is largely dominant. It is clear that considerable opportunity exists for the development of conjugated polymers that are either capable of superior crystallinity when mixed with PCBM or that are not reliant on high levels of crystallinity in order to achieve high hole mobilities. Higher resolution TEM images were analysed to probe the various P3HT lamellae structures observed. In Figure 4 gray-scale images of a lamellae region (4b) reveal a periodicity of 1.7nm which matches reasonably well with the 1.64nm a-axis spacing of the (001) reflection, as observed in XRD studies of P3HT.^{2,17} As the hexyl side chain is only 0.75nm long, the d-spacing suggests there is no interdigitation of the side chains. In 4d we see further evidence of P3HT crystallization with an HRTEM image showing P3HT b-axis stacking which corresponds to the (002) reflection.¹¹ The d-spacing of 0.38nm, as shown in 4e and 4f, matches well with reported elsewhere in the literature.^{2,17}



Figure 4. Low voltage, high resolution, bright field transition electron micrographs, gray scale plots, 2DFFT patterns and computer models of P3HT and PCBM crystal structures. (a), (d) Bright field micrograph of a P3HT lamellae. (b) Gray scale plot of line a in (a) showing lamella spacing of 1.7nm. (c) Schematic of P3HT lamella showing a-axis spacing. (e) Gray scale plot of line b in (d) showing lamella spacing of 0.38nm, consistent with (020) spacing. (g) Computer simulation of P3HT b-axis spacing.

PCBM crystallization was also investigated and the results are presented in Figure 5. Pre anneal (5a), the morphology shows no obvious sign of long range crystalline ordering. A two dimensional fast Fourier transform (2DFFT) image of the pristine sample presents a diffuse ring with a diameter of 0.38nm. It is possible that is caused by the hexyl side chain separation of P3HT, which is 0.38nm, however the spacing is almost identical to the surrounding holey amorphous carbon that supports the specimen. As previously mentioned, spin cast PCBM readily forms homogeneous films of nanocrystals⁹ which suggests that the PCBM domains in the as-cast P3HT:PCBM film are not pure PCBM, but contain a fraction of P3HT which inhibits crystallization.



Figure 5. Low voltage, high resolution transmission electron micrographs and 2DFFT patterns

of P3HT:PCBM blends showing evidence of PCBM crystallinity. (a) Bright field micrograph of P3HT:PCBM solar cell active layer before annealing. (b) Bright field micrograph of P3HT:PCBM solar cell active layer after annealing showing a characteristic PCBM crystallite within the dotted line. (c) Two dimensional fast Fourier transforms (2DFFT) of (a). (d) 2DFFT pattern of (b) revealing a d-spacing of 0.28nm. The defocus value was kept constant for both images (a and b) to ensure a direct comparison. A through focal series was also taken to ensure that no lattice fringes were present in Figure 3a. (e) 2DFFT obtained from the central single crystal in (b) showing reflections that correspond to the 001 and 111 planes of PCBM's FCC structure. (f) 2D model of PCBM crystal packing viewed down the [100] zone axis.

The post anneal image (5b) shows the formation of PCBM crystallites, bordered by an amorphous P3HT rich matrix. The shape of the grain near the centre of the image (dotted line) suggests it has been formed by the agglomeration of two PCBM-rich domains. Furthermore, the crystalline structure is continuous, with no sign of a grain boundary which suggests that the PCBM domains agglomerated first and then crystallized as a single unit. The 2DFFT of Figure 5b is shown in Figure 5d and reveals a d-spacing of 0.28nm which matches well with previously published d-spacings for PCBM.^{21,31} The absence of the 0.28nm feature in the 2DFFT image of the pristine sample (5c) suggests a complete lack of PCBM crystallinity in the pre annealed device and suggests that the annealing step is vital for the formation of PCBM crystals in these devices.

Figure 5e shows the 2DFFT obtained from a central, single crystal in 5b. The two sets of spots present match the 001 and 111 planes for PCBM with an FCC crystal structure. The HRTEM images and 2DFFT analysis of the PCBM domains were compared to C_{60} crystals with known FCC crystal structure and it was found that the structures were similar. Figure 5f shows a schematic model of the PCBM FCC structure viewed down the [110] zone axis. These results agree well with previous studies on PCBM crystal structure. ³²

IV.IV Investigation of Vertical Segregation

The annealing-induced morphological changes in polymer composite solar cells are three dimensional. However, to date, investigations of morphological changes within the vertical plane are relatively scarce. It has been shown in both polymer-polymer blend devices³³ and vacuum deposited molecular solar cells³⁴ that vertical segregation can have beneficial effects on device efficiency with increased concentrations of the electron donor towards the anode, and increased concentrations of the electron acceptor towards the cathode. It is expected that a similar vertical segregation profile would benefit P3HT:PCBM devices. Models based on VASE have recently been developed which suggest that as-cast films of P3HT:PCBM present an undesirable, or negative, vertical

concentration profile with increased P3HT near the aluminium cathode and increased PCBM nearer the PEDOT:PSS anode. ⁵ Annealing moderately improves this profile although the concentration gradients are still mildly negative. With TEM we can build a picture of the vertical morphology by using focal series imaging. Selecting a large, flat piece of an annealed composite film overhanging a hole in the TEM grid we executed a focal series projection vertically through the film as shown in Figure 6. In order to understand the effect of defocus on the HRTEM images of P3HT lamella and ensure that structural changes are a function of depth and not the fundamental optical response of the microscope, image simulations were performed using JEMS software and are presented in Appendix VI.I.

Evidence of vertical segregation is evident with the images taken of the surface and at a focal depth of 0nm and 28nm revealing PCBM crystals, while the image taken at a focal depth of 84nm reveals P3HT lamellae. Although the particles under examination are arranged randomly on the TEM grid due to the preparation technique, by focusing on a large flat particle we can be fairly certain that the focal series penetrates perpendicular to the plane of the device, and the focal depths achieved, i.e. up to 84nm, suggest we are viewing through the entire thickness of the active layer. However, due to the random vertical orientation, we are unable to tell whether we are looking from the top down or the bottom up. Nevertheless, if one assumes that the layer is being viewed from the bottom up (i.e. the film is upside down) the images match well with the results of previously mentioned VASE experiments⁵ that suggested vertical segregation with increased PCBM concentrations near the substrate (6a and b) and increased P3HT in the upper layers (c and d). More recently, investigations using electron tomography (ET) have

allowed a three dimensional rendering of a P3HT:PCBM active layer. ¹⁹ This 3D image was then 'sliced' at regular intervals in order to investigate the vertical concentration profile for P3HT. These results contradict the previously mentioned VASE study by suggesting an increased P3HT concentration near the PEDOT:PSS anode. It is worth noting that both the current study and the VASE experiments used devices spin cast from chlorobenzene, while the ET study used devices spin cast from di-chlorobenzene. As previously mentioned, research regarding vertical segregation within these devices is relatively scarce and further investigations are warranted.



Figure 6. Low voltage, high resolution transmission electron focal series of P3HT:PCBM blend. a) and b) are PCBM crystals. c) and d) are P3HT lamella. The distances quoted refer to microscope focal depth.

The annealing induced changes to the P3HT:PCBM nano-morphology are driven by a transition from a solution based, solvent controlled phase distribution, towards a solid state equilibrium. Spin casting is a very rapid process and as such, produces a non-equilibrium phase distribution in the solid film that represents a snap-shot of the solution

phase distribution. Upon heating, the molecules attempt to establish a new, solvent-free equilibrium morphology. This equilibrium is driven by the reduction of the interface free energy of the four phases present; P3HT rich amorphous phase, PCBM rich amorphous phase, crystalline P3HT and crystalline PCBM. In this study, we have used low voltage, high resolution TEM to reveal the mechanism of PCBM domain migration which underpins this morphological rearrangement. In addition, we have presented images of unprecedented detail that give direct confirmation of P3HT and PCBM crystallization and vertical segregation within P3HT:PCBM solar cells.

IV.V Conclusions

This chapter presents the use of low voltage, high resolution TEM to reveal the mechanism of PCBM domain migration which underpins this morphological rearrangement. In addition, we have presented images of unprecedented detail that give direct confirmation of P3HT and PCBM crystallization and evidence of vertical segregation within P3HT:PCBM solar cells. The work presented shows that low voltage, high resolution electron microscopy can provide valuable insight into the molecular level organization of materials traditionally thought of as difficult from an electron microscopy point of view. While this study has focused on the P3HT:PCBM photovoltaic system, the general technique is applicable to a broad range of soft material systems.

IV.VI References

- ¹ Reyes-Reyes, M. *et al.* Meso-structure formation for enhanced organic photovoltaic cells. *Organic Letters* 7, 5749-5752 (2005).
- ² Ma, W. L., Yang, C. Y., Gong, X., Lee, K. & Heeger, A. J. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. *Advanced Functional Materials* 15, 1617-1622 (2005).
- ³ Chirvase, D., Parisi, J., Hummelen, J. C. & Dyakonov, V. Influence of nanomorphology on the photovoltaic action of polymer-fullerene composites. *Nanotechnology* 15, 1317-1323 (2004).
- ⁴ Ahn, T., Lee, H. & Han, S. H. Effect of annealing of polythiophene derivative for polymer light-emitting diodes. *Applied Physics Letters* 80, 392-394 (2002).
- ⁵ Campoy-Quiles, M. *et al.* Morphology evolution via self-organization and lateral and vertical diffusion in polymer: fullerene solar cell blends. *Nature Materials* 7, 158-164 (2008).
- ⁶ Shaheen, S. E. *et al.* 2.5% efficient organic plastic solar cells. *Applied Physics Letters* 78, 841-843 (2001).
- ⁷ Kim, Y. *et al.* A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells. *Nature Materials* 5, 197-203 (2006).
- ⁸ Kim, J. Y. *et al.* Efficient tandem polymer solar cells fabricated by all-solution processing. *Science* 317, 222-225 (2007).
- ⁹ Shaw, P. E., Ruseckas, A. & Samuel, I. D. W. Exciton Diffusion Measurements in Poly(3-hexylthiophene). *Advanced Materials* 20, 3516-3520 (2008).
- ¹⁰ Rispens, M. T. *et al.* Influence of the solvent on the crystal structure of PCBM and the efficiency of MDMO-PPV:PCBM 'plastic' solar cells. *Chemical Communications*, 2116-2118 (2003).
- ¹¹ A. Swinnen *et al.* Tuning the Dimensions of C_{60}-Based Needlelike Crystals in Blended Thin Films. *Advanced Functional Materials* 16, 760-765 (2006).
- ¹² Zhokhavets, U., Erb, T., Hoppe, H., Gobsch, G. & Sariciftci, N. S. Effect of annealing of poly(3-hexylthiophene)/fullerene bulk heterojunction composites on structural and optical properties. *Thin Solid Films* 496, 679-682 (2006).
- ¹³ Kim, Y. *et al.* Device annealing effect in organic solar cells with blends of regioregular poly(3-hexylthiophene) and soluble fullerene. *Applied Physics Letters* 86 (2005).
- ¹⁴ Waldauf, C. *et al.* Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact. *Applied Physics Letters* 89 (2006).
- ¹⁵ Bjorstrom, C. M. *et al.* Multilayer formation in spin-coated thin films of lowbandgap polyfluorene : PCBM blends. *Journal of Physics-Condensed Matter* 17, L529-L534 (2005).
- ¹⁶ Vanlaeke, P. *et al.* P3HT/PCBM bulk heterojunction solar cells: Relation between morphology and electro-optical characteristics. *Solar Energy Materials and Solar Cells* 90, 2150-2158 (2006).

- ¹⁷ Erb, T. *et al.* Correlation between structural and optical properties of composite polymer/fullerene films for organic solar cells. *Advanced Functional Materials* 15, 1193-1196 (2005).
- ¹⁸ Yang, X. N. *et al.* Nanoscale morphology of high-performance polymer solar cells. *Nano Letters* 5, 579-583 (2005).
- ¹⁹ Bavel, S. S. v., Sourty, E., With, G. d. & Loos, J. Three-Dimensional Nanoscale Organization of Bulk Heterojunction Polymer Solar Cells. *Nano Letters* 9, 507-513, doi:doi:10.1021/nl8014022 (2009).
- ²⁰ Klimov, E., Li, W., Yang, X., Hoffmann, G. G. & Loos, J. Scanning near-field and confocal Raman microscopic investigation of P3HT-PCBM systems for solar cell applications. *Macromolecules* 39, 4493-4496 (2006).
- ²¹ Yang, X. N. *et al.* Crystalline organization of a methanofullerene as used for plastic solar-cell applications. *Advanced Materials* 16, 802-+ (2004).
- Yang, X. N., van Duren, J. K. J., Janssen, R. A. J., Michels, M. A. J. & Loos, J. Morphology and thermal stability of the active layer in poly(pphenylenevinylene)/methanofullerene plastic photovoltaic devices. *Macromolecules* 37, 2151-2158 (2004).
- ²³ Bulle-Lieuwma, C. W. T. *et al.* Characterization of polymer solar cells by TOF-SIMS depth profiling. *Applied Surface Science* 203, 547-550 (2003).
- ²⁴ Prosa, T. J., Winokur, M. J., Moulton, J., Smith, P. & Heeger, A. J. X-Ray Structural Studies of Poly(3-Alkylthiophenes) - an Example of an Inverse Comb. *Macromolecules* 25, 4364-4372 (1992).
- ²⁵ Sariciftci, N. S., Smilowitz, L., Heeger, A. J. & Wudl, F. Photoinduced Electron-Transfer from a Conducting Polymer to Buckminsterfullerene. *Science* 258, 1474-1476 (1992).
- ²⁶ Kihara, H., Miura, T., Kishi, R. & Kaito, A. Morphological self-control of a phaseseparated polymer during photopolymerization in a liquid-crystalline medium. *Polymer* 45, 6357-6363 (2004).
- ²⁷ Bockstaller, M. R. & Thmoas, E. L. in *Dekker Encyclopedia of Nanoscience and Nanotechnology, Second Edition* eds James A. Schwaz, Cristian I. Contescu, & Karol Putyera) (2009).
- Finne, A., Andronova, N. & Albertsson, A.-C. Well-Organized Phase-Separated Nanostructured Surfaces of Hydrophilic/Hydrophobic ABA Triblock Copolymers. *Biomacromolecules* 4, 1451-1456, doi:10.1021/bm0341024 (2003).
- ²⁹ Lipatov, Y. S. & Alekseeva, T. *Phase-Separated Interpenetrating Polymer Networks*. (2007).
- ³⁰ Zhao, J. *et al.* Phase Diagram of P3HT/PCBM Blends and Its Implication for the Stability of Morphology. *The Journal of Physical Chemistry B* 113, 1587-1591, doi:10.1021/jp804151a (2009).
- ³¹ Reyes-Reyes, M. *et al.* Methanofullerene elongated nanostructure formation for enhanced organic solar cells. *Thin Solid Films* 516, 52-57 (2007).
- ³² Hoppe, H. & Sariciftci, N. S. Morphology of polymer/fullerene bulk heterojunction solar cells. *Journal of Materials Chemistry* 16, 45-61 (2006).
- ³³ Arias, A. C. *et al.* Vertically segregated polymer-blend photovoltaic thin-film structures through surface-mediated solution processing. *Applied Physics Letters* 80, 1695-1697 (2002).

³⁴ Barry, P. R., Jiangeng, X., Soichi, U. & Stephen, R. F. Mixed donor-acceptor molecular heterojunctions for photovoltaic applications. I. Material properties. *Journal of Applied Physics* 98, 124902 (2005).

IV.VII Appendices

IV.VII.I The Effect of the 100keV electron beam on the P3HT:PCBM sample

Without the heating stage turned on, no agglomeration of PCBM rich domains is observed over the 12 minute time period.



IV.VIII.II Image Simulation of P3HT Lamella

In order to understand the effect of defocus on the HRTEM images of P3HT lamella, image simulations were performed using JEMS software. An atomistic supercell with 5 nm x 2 nm x 0.5 nm was constructed (figure 10). The simulated microscope conditions were set as follows: Accelerating voltage = 100 kV, $C_s = 1-2$ mm, Energy spread = 1.6 eV, $C_c = 1.4$ mm and defocus spread = 42 nm.



Figure 10 Atomistic supercell of P3HT lamella

Figure 11 shows the effect of changing of defocus starting at 0 and increasing in 20 nm to 100nm at Cs=1 mm. The series of images show that at 0 defocus contrast is weak. As the defocus increases the contrast increases while the d-spacing of the structure remains relatively constant. This is primarily due to the fact that it is large d-spacing we are looking at.



Figure 11 Image simulation of lamella supercell at defocus values 0, 20 40, 60, 80 and 100nm at Cs=1 mm.

If we decrease resolution of the microscope to Cs = 2 mm as shown in figure 12 we see again that the contrast increases with defocus. The apparent structure seems to change slightly, but the major lines we are interested in stays constant in terms of d-spacing

Figure 12 Image simulation of lamella supercell at defocus values 0, 20 40, 60, 80 and 100nm at Cs=2 mm.

Finally examining only the side-chains as shown in the supercell shown in figure 13.





Figure 14 shows the effect of changing defocus starting at 0 nm and increasing in 15nm steps for 4 iterations at Cs = 1 mm. These simulations show constant d-spacing up to 60 nm defocus, with increasing contrast.



Figure 14 Image simulation of side chain supercell at defocus values 0, 15, 30, 15 and 60nm at Cs=1 mm.

In summary we find that for the imaging conditions of our JEOL 4000EX HRTEM, increasing defocus leads to an increase in contrast from the structure examined and that the d-spacing from the P3HT lamella remains relatively unchanged. Thus, when lamella is seen in the HRTEM it probably doesn't correspond to it being at 0 defocus, but rather larger defocus.