



# Enhanced thermal stability of a polymer solar cell blend induced by electron beam irradiation in the transmission electron microscope

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## ABSTRACT

We show by in situ microscopy that the effects of electron beam irradiation during transmission electron microscopy can be used to lock microstructural features and enhance the structural thermal stability of a nanostructured polymer:fullerene blend. Polymer:fullerene bulk-heterojunction thin films show great promise for use as active layers in organic solar cells but their low thermal stability is a hindrance. Lack of thermal stability complicates manufacturing and influences the lifetime of devices. To investigate how electron irradiation affects the thermal stability of polymer:fullerene films, a model bulk-heterojunction film based on a thiophene-quinoxaline copolymer and a fullerene derivative was heat-treated in-situ in a transmission electron microscope. In areas of the film that exposed to the electron beam the nanostructure of the film remained stable, while the nanostructure in areas not exposed to the electron beam underwent large phase separation and nucleation of fullerene crystals. UV–vis spectroscopy shows that the polymer:fullerene films are stable for electron doses up to 2000 kGy.

## 1. Introduction

It is well known that it is crucial to understand and control the effects of electron beam irradiation during transmission electron microscopy (TEM) and in particular during in situ microscopy. The electron beam can, for example, cause transitions from a crystalline to amorphous structure, generate Frenkel pairs, and in polymers it can give rise to polymeric chain scission, crosslinking or atomic/molecular motion leading to mass loss [1–4]. The mechanisms responsible for the beam induced changes are knock-on displacements and ionization damage [2,4,5]. In our study, we address the effect of thermal annealing on the functional nanostructure of polymer solar cells and illustrate that the effect is beneficial for their performance.

During the last years a large amount of research has been dedicated to exploring the possibility of using organic solar cells (OSC) as a source for cost effective, environmentally friendly energy [6]. Significant progress has been made, devices made in the lab have today reached power conversion efficiencies (PCE) of over 10%, but further research is still needed before OSC can be regarded as economically viable [7–10]. A factor that complicates up-scaling the

production of OSC is the fact that the PCE of a device heavily depends on the nanostructure of the active layer in the device. Changes in the nanostructure of an active layer can lead to a dramatic decrease in efficiency for a device. It is thus of high importance to ensure that the nanostructure of an active layer is stable during all production steps and throughout the lifetime of an OSC.

To optimize PCE, the most common choices for active layer in an OSC are polymer:fullerene bulk hetero junction (BHJ) blends, where a polymer and a fullerene form a bicontinuous network on the nanoscale. Most polymer:fullerene BHJ blends are not in thermal equilibrium, giving them a low thermal stability. As a consequence, at temperatures above the glass transition temperature ( $T_g$ ) of a blend, the polymer and fullerene phase will start to phase separate [11]. The coarsening of a blend's nanostructure induced by the phase separation is commonly connected with a dramatic drop in photovoltaic performance for the blend [12–15]. Depending on the polymer and fullerene are used as electron acceptor and donor, other degradation mechanism can be relevant at elevated temperatures, such as the nucleation and growth of fullerene crystals. Many different fullerenes and fullerene derivatives have been used in OSC. The fullerene derivative (6,6)-phenyl-C<sub>61</sub>-

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butyric acid methyl ester, (PCBM), is one of the most frequently used fullerenes in high performance polymer:PCBM blends. PCBM will not only undergo phase separation in a polymer:PCBM blend at elevated temperatures, PCBM will also nucleate and grow crystals in a polymer:PCBM blend. PCBM crystals can easily grow to be over a micron in lateral size, which strongly decreases the photovoltaic performance of the blend [16,17].

One strategy for increasing the thermal stability of a BHJ polymer:fullerene blend is to induce crosslinking between the molecules in the blend. Various approaches to generate crosslinking have been tested with varying degrees of success [18]. Many of the approaches involve a modification of the electron donor or acceptor. For example exchanging some of the monomers in the polymer that serves as electron donor with monomers bearing side chains which can be crosslinked under specific conditions, such as a specific pH value, temperature or exposure to UV radiation. Another strategy is to add functional groups that enable direct crosslinking with the fullerene derivatives that serve as electron acceptor [16,19–29]. Yet another approach is to add an extra component to the blend that can serve as a crosslinker when the blend is exposed to the right trigger [22,29–34]. One potential problem with many of these approaches is that the modification of the molecular structure of the electron donor or acceptor, or the addition of an extra component, changes the overall physico-chemical properties of the blend, whereby the OSC performance degrades. Another potential problem is that even if the approach for stabilizing the blend morphology is successful, additional material needed and/or production steps will likely increase the manufacturing cost, thus hampering application on an industrial scale. A potential approach that avoids these problems is to use electron irradiation to induce crosslinking between the molecules in polymer:fullerene blends.

While electron irradiation is an established technique widely used in industry for crosslinking of polymers, only a limited amount of research has been done on using electron irradiation to induce crosslinking of BHJ OSC blends. Krebs et al. irradiated films spin coated from three different polymer:fullerene blends, P3HT:PCBM, PV-D4610:PCBM and PBDTTTz-4:PCBM, to investigate the possibility of using electron irradiation to stabilize the nanostructure of BHJ blends [35]. All three blends have the potential to be used in OSC but show lack of thermal stability [36]. By comparing the UV–vis absorption spectra of irradiated films and pristine films they found that films of these blends could withstand relatively high doses, around 200 kGy, before optical properties started to degrade. Furthermore, optical microscopy revealed that electron irradiation affected the nucleation rate and growth of PCBM crystals in films that had been thermally annealed at 140 °C for 24 h. Exposure to higher electron doses was found to yield smaller and/or fewer PCBM clusters compared to non-irradiated films, indicating an increased thermal stability for the irradiated films. What Krebs et al. could not investigate was how electron irradiation affected the stability of the films' nanostructure, due to the length scale of the features of the nanostructure being below the spatial resolution of optical microscopy. To investigate if the nanostructure of polymer:fullerene films stabilizes under electron radiation is of high interest due to the strong connection between the nanostructure of a polymer:fullerene BHJ film and the PCE of the corresponding OSC utilizing the polymer:fullerene BHJ film as an active layer.

In this study we use Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) to investigate how electron irradiation can be used to enhance the thermal stability of polymer:fullerene BHJ blends. We also use UV–vis spectroscopy to investigate if our polymer:fullerene blends are stable under electron irradiation or if the polymer and fullerene starts to break down when irradiated. A model blend system composed of poly(2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl) (TQ1) and PCBM is used to investigate the effect of electron radiation on the thermal stability of the system. The electron beam in a transmission electron microscope is

used to induce crosslinking in a TQ1:PCBM film and a TEM heating holder allows annealing of the TQ1:PCBM film at temperatures above the  $T_g$  of the film, which is roughly 110 °C [14,17,37]. In this way, the evolution of the nanoscale morphology upon annealing can be directly compared between areas with or without prior exposure to the electron beam. Our results show that those areas that have been exposed to the electron beam show higher thermal stability compared to areas that have not been exposed to the beam.

## 2. Experimental

### 2.1. Materials

PC<sub>61</sub>BM (purity > 99%) was purchased from Solenne BV. TQ1 was prepared according to previously published procedures [38]. (number-average molecular weight of  $M_n \sim 34 \text{ kg mol}^{-1}$ ). PEDOT:PSS was purchased from Heraeus (Clevious P VP Al 4083) and used as received.

### 2.2. Thin film preparation

Films, with a thickness of around 100 nm, were spin-coated from chlorobenzene (CB) solutions (total material content  $20 \text{ g L}^{-1}$ ). PEDOT:PSS coated glass substrates were used, where the PEDOT:PSS had been annealed at 120 °C for 10 min prior to film deposition. Spin-coated films were allowed to dry for at least 15 h to remove residual solvent. Annealing was carried out at ambient atmosphere but absence of light. A heating plate was calibrated with K-type self-adhesive thermocouples from Omega (estimated error  $\pm 5 \text{ }^\circ\text{C}$ ; time to reach stable temperature  $\sim 30 \text{ s}$ ).

### 2.3. Electron beam exposure

Low-energy electron beam treatment was carried out in an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland). Samples were subjected to different doses ranging from 10 kGy to 2000 kGy under nitrogen (< 200 ppm oxygen), employing an acceleration voltage of 150 kV and a maximum dose of 50 kGy per pass at a transport speed of 12 m/min and an air gap of 10 mm.

### 2.4. Transmission electron microscopy

Samples were prepared by floating off spin-coated films on PEDOT:PSS coated glass substrates in water, followed by collection with either TEM copper mesh grids or sample chips for a heating holder from DENSsolutions. TEM bright field images were recorded with a G2 Tecnai microscope operated at an acceleration voltage of 200 kV. For the TEM bright field images, an under focus of 8  $\mu\text{m}$  was used to enhance the contrast in the images.

### 2.5. Scanning electron microscopy

Images were taken using a LEO Ultra FEG 55 SEM. The acceleration voltage used was 3 kV and a secondary electron detector was used for collecting images. No further sample preparation were done, glass substrates with spincoated TQ1:PCBM films were imaged directly in the microscope.

### 2.6. UV–vis spectroscopy

The UV–vis absorption spectra were recorded using a Perkin-Elmer Lambda 900 spectrophotometer relative to a reference glass substrate.

## 3. Results and discussion

UV–vis spectroscopy was used to investigate whether TQ1:PCBM films are stable under electron irradiation or if TQ1 and PCBM will

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