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Elucidating Mechanisms for Electron Beam Damage in Conjugated Polymers

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Conjugated polymers are poised to play an important role in emerging organic electronic applications because they are soft and flexible, chemically versatile, and can be solution processed [1]. This unique combination of properties enables conjugated polymers to be used in various applications, such as organic light-emitting diodes (OLEDs) [2], electrolytic capacitors [3], antistatic coatings [4], organic photovoltaics (OPVs) [5], organic field-effect transistors (OFETs) [6], and biosensors [7]. However, while the electronic properties of conjugated polymers and their blends are intimately tied to their morphology, characterizing the complex morphology of these materials is difficult.

Characterizing the morphology of conjugated polymers through TEM remains a challenge because imaging of soft materials is limited by their sensitivity to the electron beam and low contrast between domains. Contrast and sensitivity to the beam are related because the latter limits the number of electrons that can be used for imaging. In more quantitative terms, the number of electrons Q incident on an area d^2 will be $Q = Jd^2$, where d is the smallest resolvable feature size and J is the electron dose. The noise of an image is then $\sqrt{Q}/Q$ or, equivalently, $1/\sqrt{Jd^2}$. In other words, resolution is limited by the electron dose the sample can handle [8-10]. Unfortunately, beam damage of soft materials in the TEM is currently not well understood.

In the present study, we investigate the beam damage of poly(3-hexylthiophene) (P3HT) by calculating the critical dose D_C from the fading of electron diffraction rings at dose rates ranging from 1 e/Å^{2}s to 20 e/Å^{2}s. 10 mg/mL solutions of P3HT were made with chlorobenzene in a nitrogen glove box and stirred overnight at 45°C. Silicon wafers were cleaned through sonication for 20 minutes in acetone and 20 minutes in isoproponal followed by 15 minutes of ultraviolet light ozonation. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was spin-cast onto the silicon wafers in air, after which P3HT is spin-cast onto the PEDOT:PSS film inside a nitrogen glove box. Films were floated off in deionized water and then picked up with copper TEM grids. Samples were dried overnight at room temperature under vacuum and then annealed in a nitrogen glove box at 165°C for 3 hours.

Diffraction experiments were carried out on the FEI Tecnai G20 XTWIN at the Penn State Materials Characterization Lab operating at 200 kV with a camera length of 330 mm at room temperature. Dose rates were measured in areas of vacuum in the sample, after which a selected area aperture and beam stop were inserted and diffraction patterns were collected at fixed time intervals using the Digital Micrograph Acquire Series plug-in. Figure 1a shows the first and last diffraction pattern collected during a series taken at a dose rate of 1 e/Å^{2}s. Time intervals and exposure times were varied based on dose rate, but the sample was exposed to the beam during the entire series acquisition. To calculate D_C, peak intensities are plotted as a function of accumulated dose and fitted to an exponential function (Figure 1b). D_C can then be calculated by taking the inverse of the decay rate.

We observe that D_C first increases then decreases with dose rate (Figure 2). We propose that this trend is consistent with radiolysis followed by diffusion. We speculate that we are outrunning damage as dose rate

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is increased, implying slow processes. In the case of P3HT, for example, if reacting species are being generated from broken side chains, they would slowly diffuse throughout the sample since the T_g of P3HT is slightly below room temperature. At some threshold dose rate, we hypothesize that local heating from the electron beam causes a rise in temperature that speeds up diffusion, thus causing a drop in D_C at higher dose rates [11].

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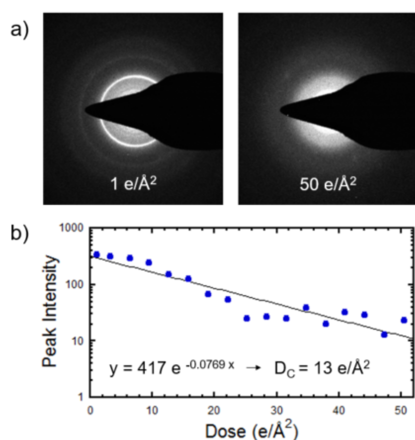

Figure 1. (a) First and last diffraction pattern of a series taken at 1 e/Å^{2}s. Diffraction ring intensity fades with accumulated dose. (b) Critical dose can be calculated by fitting an exponential to the peak intensity vs accumulated dose.

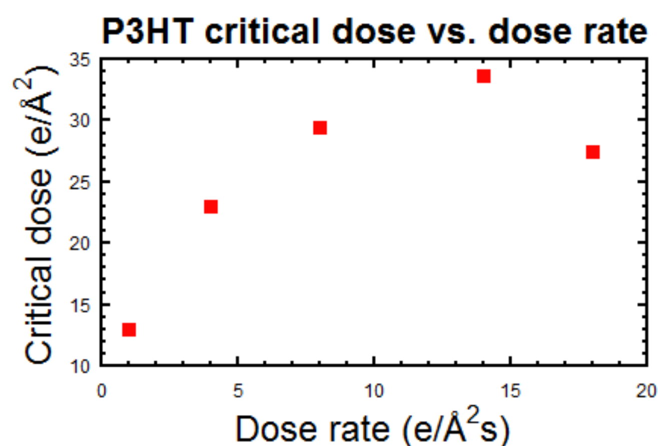

Figure 2. Critical dose first increases then decreases with dose rate. The initial increase in critical dose reflects a diffusion-limited damage mechanism. At higher dose rates, local heating causes the critical dose to decrease again.

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