



The role of incident light intensity, wavelength, and exposure time in the modification of conjugated polymer structure in solution



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ABSTRACT

Our recent investigations indicate that simple white light exposure holds intriguing potential to alter the structure of conjugated polymer chains. To provide further insight into how to rationally control this process, we have employed small angle neutron scattering to investigate structural changes occurring in solutions of poly(3-hexylthiophene-2,5-diyl) upon exposure to white light. Our previous results indicate significant change in the structure of the polymer upon illumination, an effect we attribute to an alteration in the thermodynamic interactions of the polymer with the surrounding solvent. This work provides additional information to further refine our understanding of this phenomenon by studying the relationship between the magnitude of exciton creation and subsequent structural changes through a series of exposure time, light intensity, and wavelength sensitive experiments. The results demonstrate a clear and consistent relationship between the number of absorbable photons available to the conjugated polymer chain and more powerful alterations in polymer structural parameters, indicating that net exciton generation provides the fundamental driving force for this phenomenon. This points towards the feasibility of employing light exposure protocols as a powerful unobtrusive in-situ method for precise tailoring of optoelectronic active layers over a wide range of organic electronic device fabrication procedures.

1. Introduction

Conjugated polymers have presented the field of material science with exciting possibilities for advanced electronic devices possessing similar functionality as their more traditional counterparts while significantly reducing weight and cost. In order to make the organic electronic devices composed of these materials competitive on a mass market scale, work has largely focused on improving device efficiency through alterations to active layer architectures and morphologies [1–4]. Through modifications to solution casting techniques and annealing processes, varying degrees of control of active layer domain patterns and sizes can be realized, which ultimately manifest themselves in the form of changes to such crucial device characteristics as exciton dissociation lengths and heterojunction surface areas, morphological facets which have repeatedly proven to be closely tied to effective device efficiencies [5–9]. Given the clear importance of comprehensive control of these organic device functional layer morphologies, exploring and properly developing economically feasible and non-intrusive methods for directing organic layer assembly has become key.

Towards this end, recent work has studied the previously overlooked concept of light-induced changes to polymeric physical

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characteristics through simple white light exposure. Molecular dynamics simulations of simple PPV oligomers have demonstrated a rigidification of the polymer backbone upon the creation of common excited states from illumination [10]. Exploratory experiments by Reiter et al. demonstrated that exposing a polymer blend film containing a benchmark conjugated polymer to white light significantly slowed its dewetting rate and therefore increased the films viscosity, providing definitive indications that simple light-based in-situ methodologies powerfully affect conjugated polymer physical characteristics [11]. A limited collection of additional experiments has provided further instances of light exposure altering polymeric materials [12–14]. Our group has sought to further expand the understanding of the interaction between light and conjugated polymers by focusing on the structural differences observed in solution-based samples between light and dark environments, as the solution state has repeatedly proven to be a key stage within most common fabrication techniques, where modifications that exist in solution are consistently carried through to the final solid state device [15,16]. Our initial work examined the benchmark conjugated material P3HT in a single chain solution system, revealing that light exposure triggers a sharp decrease in Kuhn length and R_g along with a marked decrease in the second virial coefficient, indicating a pseudo-chain collapse upon light exposure [17]. Further experiments conducted in a much higher concentration environment during the thermally driven polymer gelation process provides further evidence of light exposure influencing conjugated polymer solution behavior, as polymer chain aggregation was substantially hindered by the presence of white illumination throughout the temperature ramp [18]. Continued studies have further clarified the nature of these light-induced physical effects and elucidate the thermodynamic mechanism behind it [19].

Specifically, this paper seeks to study the methods by which this light-based effect can be more finely controlled and tuned by way of exposure time and wavelength sensitivity, essentially studying the relationship between total net P3HT absorbable photons, the levels of structural alteration initiated by their absorbance and the subsequent generation of excitons on the polymer backbone. Together our previous work has shown that structural shifts of the conjugated polymer with illumination are not instantaneous, but rather require a given period of exposure time before full transition is achieved. By varying the amount, type, and total time of light exposure applied to a range of conjugated polymer samples, a more complete understanding of these light driven conformational effects can be attained. Moreover, this information is required to enable its future use in manipulating active layer morphologies, with the goal of developing a non-intrusive in-situ methodology for controlling device structure and ultimately boosting device performance.

2. Instrumental

Poly(3-hexylthiophene-2,5-diyl) was purchased from Osilla Chemicals with a regioregularity of ~95% and a weight average molecular weight of ~35,000 and a PDI of 1.8, per the manufacturer. This material was used as received, and was dissolved in either deuterated (d8) styrene purchased from Polymer Source, or 1,2-ortho-dichlorobenzene (d4) (ODCB) purchased from Sigma-Aldrich. The samples were kept at 60 °C throughout the scattering experiments by a thermally controlled sample holder in order to prevent localized aggregation or gelation.

Samples for use in the small angle neutron scattering experiments were assembled within 2 mm quartz solution cells. These sample cells were then either wrapped in 0.1 mm thick aluminum foil to create the dark environment or exposed to illumination provided by an optical illuminator consisting of a 125-watt halogen bulb, generating 50,000 lux at a 5 cm distance at maximum intensity. Aluminum was chosen as a barrier for light exposure due to its near total transparency to neutrons. Regardless, special care was taken during the analysis to be certain that the presence of the aluminum was accounted for in the reduction of the raw data to absolute units through such methods as separate determination of sample transmittance and empty cell scattering for the light and dark samples.

The small angle neutron scattering experiments (SANS) were conducted on instruments located at both Oak Ridge National Laboratories (ORNL) and the National Institute of Standards and Technology (NIST). ORNL experiments took place at the High Flux Isotope Reactor (HFIR) using the General Purpose SANS (CG-2) beamline. Employing three separate detector distances of 0.3, 2, and 12.5 m with a wavelength of 6 Å allowed a Q range of 0.0034 to 0.3363 Å⁻¹, where $Q = 4\pi/\lambda \sin(\theta/2)$, λ is the neutron wavelength, and θ is the scattering angle. NIST scattering data was collected at the Center for Neutron Research (NCNR) using the NGB 30 beamline using detector distances of 0.3, 4, and 13 m with a wavelength of 6 Å [20]. The raw data was reduced using NCNR macros and corrected for empty cell (with and without aluminum) scattering, dark current, and detector sensitivity [21]. Elimination of contributions from background incoherent scattering and thermal fluctuations allowed acquisition of absolute coherent scattering.

3. Results

In order to study the effects of light on the structure of conjugated polymer samples in solution, we have developed a procedure to conduct mirrored scattering experiments for each prepared solution: once under direct illumination and then again while completely isolated from ambient light via aluminum foil. We will refer to samples analyzed under these conditions as “light” and “dark” respectively throughout the text. In order to establish a control baseline we have applied this methodology to a non-conductive polymer sample in order to confirm that the effects we observe are not conflated with environmental, experimental, or methodological contributions, with the pertinent SANS data plots available in our previous publications [17]. As the data curves overlap completely, this eliminates concerns that thermal effects or the presence of aluminum foil influence our results.

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