Enhancing Electron Mobility and Mechanics in Optoelectronic Devices via Conjugated Blends

Motivation: Interest in flexible optoelectronic devices has burgeoned recently in both the academic and industrial communities due to potential applications in advanced soft robotics and health monitoring devices.[1] Cutting-edge applications of conductive elastic materials promise the availability of robust, low-cost electronics in the near future, but achieving high mechanical deformability and high charge transport simultaneously in polymer semiconductors remains a major challenge. Conjugated polymers, which are prime candidates for flexible technologies due to their high electron mobility and potential for mechanical compliance, possess two modes of charge transport: *intra*molecular (along the conjugated backbone) and *inter*molecular transport (between π-stacked units). The intermolecular π-π stacking and high degree of fused aromatic rings in conjugated polymers result in exceptional electron mobility, but also result in highly rigid materials.[2] In an effort to solve this problem, recent developments in polymer research have provided perspectives on the role of backbone flexibility in thin film mechanics. In a recent study published by the Gu research group, the backbone flexibility of an n-type naphthalene diimide-based conjugated polymer (NDI) was shown to significantly increase upon addition of conjugation break spacers (CBS) - or linear alkyl units - into the conjugated backbone (>400% strain before failure).[3] Though a mechanical understanding of some CBS containing polymers has been achieved, the conductivity of the materials is limited due to the interruption of electron mobility in the polymer backbone. Thus, *the goal of the research outlined in this proposal is to optimize the electrical contributions of the parent NDI polymer as well as the mechanical contributions afforded by a CBS matrix in a compatible blend system*.

Intellectual Merit: NDI based polymers have the potential to serve as promising candidates for flexible optoelectronic devices, as they exhibit considerable excimer-like emission in aggregates or in the solid state and show outstanding performance in n-type transistors.[4] The efficacy of NDI in widespread applications, however, relies on its capability to maintain a satisfactory electric charge and its ability to exhibit robust mechanical properties. While NDI polymers have been tuned for mechanical favorability, there remains a need to balance both mechanical and electrical properties *simultaneously*, as information regarding the electron mobility with increasing CBS content in NDI-based polymers is lacking.[5] **Therefore, I propose to investigate blends of partially conjugated NDI polymers (containing CBS of up to ten carbon atoms) with their fully conjugated parent polymers (Fig. 1).** By varying the CBS-to-parent polymer ratios in these blends, I aim to develop a fundamental understanding of blend morphology for these similar components through establishing the framework for how they deform with strain. I also intend to expand this information by examining the effect of tensile chain alignment on the electrical properties of the blends. In order to promote the widespread use of CBS materials, a comprehensive characterization of these blend systems must be conducted through rheological and conformational analysis methods. Thus, my goal is to study the effects of CBS blend systems on polymer morphology and, in turn, the morphology's impact on mechanical and electrical properties. By blending the unaltered NDI component with its CBS counterpart, I aim to achieve high ductility while maintaining electrical performance of the inherently conductive NDI polymer in a two-polymer blend system.

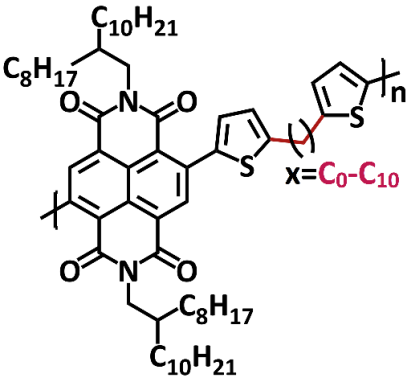

Figure 1. Naphthalene diimide (NDI-Cx) based polymers under investigation.

Research Plan: To determine the mechanical and electrical properties of these blends and the potential for chain alignment upon stretching, I will utilize my previous research experience to: 1) Perform grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis on thin film NDI blends

to monitor the crystalline alignment, 2) Perform pseudo-free-standing tensile testing to examine mechanics, 3) Perform atomic force microscopy (AFM) to monitor surface alignment, and 4) Fabricate devices to quantify electron mobility. For X-ray scattering, The Stanford Synchrotron Radiation Lightsource (SSRL) offers the most rapid means of collecting the necessary data with its 12.7 keV, 11-3 beam line. The results of GIWAXS will enable clarification on whether there will be an increase in the alkyl packing distance upon addition of C_0. Additionally, GIWAXS data will elucidate if the blends possess π-π stacking and demonstrate co-crystallization, which would clarify whether the blends favor the CBS containing matrix polymer or the fully conjugated component. To confirm mechanical deformability, pseudo-free-standing tensile testing will be performed following X-ray characterization by patterning the thin-film polymers in question into a dog-bone shape and then floating the films on water before pulling unidirectionally until the film fractures. I hypothesize that, as more of the fully conjugated polymer is introduced, the tensile data will reveal a shortened strain before fracture. However, if the strain prior to failure remains exceedingly high, and the Young's Modulus for the blends is maintained near the disposition of the softer C_{10} component despite an increase in the fully conjugated component in the blend system, this would reinforce the flexible properties of partially/fully conjugated blends and give a clearer understanding of their mechanical capabilities.

AFM will then be performed to investigate topographically how the blends organize to form a given morphology. Depending on the resulting pattern, phase separation of the individual components can be visualized, and it can be deduced whether the modulus for these materials is impacted due to the morphology of the blend components. Finally, device fabrication will proceed by patterning gold source/drain electrodes onto a Si substrate via photolithography, after which the NDI blend systems will be deposited via spin coating. Using a Keithley 4200 parameter analyzer available at Stanford, I will be able to acquire quantitative information regarding the electron mobility, which I hypothesize to be maintained due to long range percolation of conjugated units via a robust π-π stacked network. Given the similarity between NDI-C_0 and its partially conjugated counterparts, there is a potential challenge in determining the contribution of each component towards the morphology. I anticipate employing deuterated polymers, which have a specific infrared absorption that will allow us to distinguish between the two polymers in question within a given AFM-infrared (IR) image. I also plan to use polarized UV-Vis spectroscopy to monitor the chain backbone alignment throughout tensile deformation. Blends of NDI-C_0 and polystyrene will then be compared to determine if the partially conjugated polymer is ultimately beneficial as the ductile component (i.e., promotes the desired morphology for enhanced mechanics and electrical properties).

Broader Impacts: In summary, this work will establish the use of flexible partially conjugated polymers as the ductile matrix in blend systems and develop a fundamental understanding of blend morphology for similar components. This design further provides a simple approach to modulating polymer solution processability and offers a promising strategy to prepare melt-processable semiconducting polymers **without the use of toxic and environmentally harmful solvents**.[5] The mechanical and morphological information obtained in this study will prove invaluable to the field of biomimetics, as well as optoelectronic devices, where the need for ductile electronics prepared via environmentally friendly processes is paramount.

References:

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