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The Evolution of Thin-Film Structure in pi-Conjugated System

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Final Report

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14. ABSTRACT
Printed, flexible electronics have the potential to be produced at sufficiently low cost to enable ubiquitous electronic control and monitoring in health care, environmental quality, national security, and systems integrity. We developed fundamental understanding of materials and devices using a systematic approach to identify how structure and processing impact morphology, interfaces, and devices. We investigated how rigid rod -conjugated systems interact and in solution and during the film formation process. These interactions are the antecedent to the - stacked networks that are crucial for charge transport. In situ spectroscopic experiments identified specific molecular interactions and processes required for the development of effective -conjugated systems that allow efficient intra- and intermolecular charge transport. Knowledge concerning how these systems associate to form effective -conjugated networks informs the design and development of materials and processes for viable, robust, flexible electronics.

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Contract/Grant #: FA9550-12-1-0248

Reporting Period: May 15, 2014 – May 14, 2015

Annual accomplishments (200 words max):

We discovered fundamental mechanisms of π-conjugated polymer assembly and alignment into ordered structures required for macroscopic charge transport. Simultaneous spectroscopic and electrical interrogation of drop-cast P3HT provided direct correlation of structural changes during thin-film formation with the incidence of drain current (*ChemNanoMat*, 2015). Polarized optical microscopy, micro-Raman, UV-vis, DLS and cyro-TEM definitively showed time-dependent, polymer self-assembly (*Chem Matls*, 2015). The results provide vital insights into factors leading to organized conjugated polymer nanostructures and how they may be manipulated for performance.

Building on our discovery that low-dose UV induces conjugated polymer anisotropic supramolecular assembly, we found that aggregation can be manipulated by ultrasound induced nucleation site formation which facilitates growth of high mobility nanofiber assemblies (*ACS AMI*, 2014). Transport characteristics can also be optimized through judicious choice of molecular additives (*ACS AMI*, 2015). Our fundamental process studies led to identification of conjugated-insulating polymer blends with superior charge transport characteristics (*ACS AMI*, 2015). We also demonstrated that optimization of thermodynamic factors during microfluidic processing of π-conjugated polymer solutions can afford over order of magnitude increases in macroscopic charge transport (*ACS Nano*, in revision).

We demonstrated how conjugated polymer solution behavior and the evolution of thin-film morphology can be controlled and manipulated.

Archival publications (published) during reporting period:

1. Chang, M.; Lee, J.; Chu, P.-H.; Choi, D.; Park, B.; Reichmanis, E. “Anisotropic Assembly of Conjugated Polymer Nanocrystallites for Enhanced Charge Transport” ***ACS Applied Materials and Interface***s (2014) 6, 21541−21549; DOI:10.1021/am506546k
2. Min Sang Park, Avishek Aiyar, Jung Ok Park, Elsa Reichmanis*, Mohan Srinivasarao*, “Drain Current in Poly (3-hexylthiophene) Solutions during Film Formation: Correlations to Structural Changes”, ***ChemNanoMat*** (2015), 1(1), 32-38; DOI: 10.1002/cnma.201400003
3. Ping-Hsun Chu, Lei Zhang, Nicholas Colella, Boyi Fu, Jung Ok Park, Mohan Srinivasarao, Alejandro Briseno, Elsa Reichmanis*, “Enhanced Mobility and Effective Control of Threshold Voltage in P3HT-Based Field Effect Transistors via Inclusion of Oligothiophenes", ***ACS Applied Materials and Interfaces*** (2015), 7(12), 6652-6660.
4. Nabil Kleinhenz, Cornelia Rosu, Sourav Chatterjee, Mincheol Chang, Karthik Nayani, Zongzhe Xue, Eugenia Kim, Jamilah Middlebrooks, Paul Russo, Jung Ok Park, Mohan Srinivasarao*, and Elsa Reichmanis*, "Liquid Crystalline Poly(3-hexylthiophene) Solutions Revisited: Role of Time-

dependent Self-Assembly", ***Chemistry of Materials*** (2015), 27(7), 2687-2694; DOI: 10.1021/acs.chemmater.5b00635
5. Chang, M., Choi, D., Wang, G., Kleinhenz, N., Persson, N., Park, B., and Reichmanis, E., "Photoinduced Anisotropic Assembly of Conjugated Polymers in Insulating Polymer blends" ***ACS Applied Materials and Interfaces*** (2015); DOI: 10.1021/acsami.5b03310
6. Wang, G., Persson, N., Chu, P.-H., Kleinhenz, N., Fu, B., Chang, M., Deb, N., Mao, M., Wang, H., Grover M., and Reichmanis, E., "Microfluidic Crystal Engineering of π-Conjugated Polymers", ***ACS Nano****, in revision*.

Changes in research objectives, if any: none

Change in AFOSR program manager, if any: none

Extensions granted or milestones slipped, if any: none

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none):

For the first time, we demonstrated that π-conjugated polymers self-assemble and exhibit liquid crystal ordering when confined to rectangular capillaries. Using the representative semiconductor, poly(3-hexylthiophene) (P3HT) in trichlorobenzene (TCB), it was shown that the relative proportion of polymer assemblies increased with time. Polarized optical microscopy (POM) revealed development of birefringence and monodomain-like long-range ordering, while micro-Raman spectroscopy allowed for calculation of the orientational order parameters, $<P_2>$ and $<P_4>$ of the liquid crystalline solutions. Notably, $<P_2>$ increased with time up to 0.35, indicating increased anisotropy. The calculated depolarization ratio (ρ_v) from depolarized dynamic light scattering measurements (DDLS) points to the time-dependent formation of highly ordered P3HT nanostructures, while cryogenic transmission electron microscopy facilitated direct visualization of the rod-like assemblies. POM shows that the observed anisotropy can be preserved in P3HT films drawn from aged solutions. The fundamental insights revealed through this investigation suggest that conjugated polymers self-assemble to afford liquid crystalline solution based aggregates. This discovery will provide the foundation for optimized processes for organic electronic device applications.

Expanding on our solution based studies, we successfully achieved oriented crystallization of conjugated polymers directly in solution. Significantly, we found that solution crystallization of conjugated polymers in a microfluidic system produces tightly π-stacked fibers with commensurate improved charge transport characteristics. For P3HT films, processing under flow caused exciton bandwidth to decrease from 140 to 25 meV, π-π stacking distance to decrease from 3.93 to 3.72 Å and hole mobility to increase from an average of 0.013 to 0.16 $cm^2 V^{-1} s^{-1}$, versus films spin coated from pristine, untreated solutions. Variation of the flow rate affected thin-film structure and properties. The flow process included sequential cooling followed by low-dose ultraviolet irradiation that promoted growth of conjugated polymer fibers. Image analysis coupled with mechanistic interpretation supports the supposition that "*tie chains*" provide for charge transport pathways between nanoaggregated structures. The "microfluidic flow enhanced semiconducting polymer crystal engineering" was also successfully applied to a representative electron transport polymer and a non-halogenated solvent. The process can be applied as a general strategy for the fabrication of high-performance polymer devices.

Having demonstrated that semiconductor blends facilitate formation of charge transport pathways in conjugated polymers, we extended our study of blends to semiconductor-insulator systems. Notably, "pre-processing" P3HT-insulating polymer (polystyrene (PS) or polyisobutylene (PIB)) blend solutions led to the formation of highly ordered P3HT nanofibrillar structures in solidified thin-films. The P3HT nanofibers were interconnected through P3HT islands phase-separated from insulating polymer regions in blend films to form effective charge transport pathways. Significantly, even films prepared with a P3HT content as low as 5 wt% exhibited excellent macroscopic charge transport characteristics. The impact of PS on P3HT intra- and intermolecular interactions was systematically investigated. The presence of PS chains

appeared to assist in the pre-processing of blend solutions to facilitate molecular interactions of the semiconductor component, and to enhance P3HT chain interactions during spin coating.

The fundamental insights derived from our solution phase investigations and process oriented studies are leading to a cohesive understanding of conjugated polymer behavior in solution and importantly, during the solvent evaporation process. Our AFOSR funded research has provided a foundation that we believe will allow us to directly visualize important features of solution processed semiconducting polymer films that to date have only been the subject of speculation, namely the preponderance of semiconducting polymer 'tie chains'. Further, our discovery that active-insulating polymer blends where the active component comprises only 5 wt% of the film can preserve the excellent charge carrier transport characteristics of the parent semiconductor allows us to explore a wide range of insulators selected for their own properties. For instance, we can envision using insulators optimized for their barrier or mechanical properties.

1.

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Elsa Reichmanis

Program Manager
The AFOSR Program Manager currently assigned to the award

Charles Lee

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Abstract

We discovered fundamental mechanisms of π-conjugated polymer assembly and alignment into ordered structures required for macroscopic charge transport. Simultaneous spectroscopic and electrical interrogation of drop-cast P3HT provided direct correlation of structural changes during thin-film formation with the incidence of drain current (ChemNanoMat, 2015). Polarized optical microscopy, micro-Raman, UV-vis, DLS and cyro-TEM definitively showed time-dependent, polymer self-assembly (Chem Matls, 2015). The results provide vital insights into factors leading to organized conjugated polymer nanostructures and how they may be manipulated for performance.

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macroscopic charge transport (ACS Nano, in revision).

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Archival Publications (published) during reporting period:

1. Chang, M.; Lee, J.; Chu, P.-H.; Choi, D.; Park, B.; Reichmanis, E. “Anisotropic Assembly of Conjugated Polymer Nanocrystallites for Enhanced Charge Transport” ACS Applied Materials and Interfaces (2014) 6, 21541–21549; DOI:10.1021/am506546k
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Program Officer

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Equipment/Facilities			
Supplies			
Total			

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Appendix Documents

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