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Synthesis and Solution- Driven Assembly of Functional Polythiophene Derivatives

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Date of Award
2-2013

Document Type
Campus Access

Degree Name
Doctor of Philosophy

Degree Program
Polymer Science and Engineering

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Keywords
Pure sciences, Functional derivatives, Fibrils, Organic photovoltaics, Polymer, Polythiophene

Subject Categories
Polymer Chemistry

Abstract

Conjugated polymers are of interest in organic photovoltaics (OPVs) for the benefits of their low cost, ease of processing, and flexible design. OPV device performance greatly depends on the morphology of the donor (conjugated polymer) and acceptor (fullerene, CdSe, etc.) materials, which should ideally promote efficient exciton formation, dissociation, and charge transport to the respective electrodes. One potentially ideal active layer morphology would consist of an interpenetrating, bicontinuous network of

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donor and acceptor materials, having domain sizes of ~10 nm (i.e., on the order of the exciton diffusion length). Such morphologies can be achieved through annealing processes (thermal or solvent) of the donor/acceptor blend, or the use of pre-formed, highly crystalline fibril nanowires of the conjugated nanowires.

This thesis outlines the design of functional polythiophene copolymers with the ability to form novel assemblies through tailored functionalities. Amphiphilic P3HT-b-poly(3-(triethyleneglycol)thiophene) (P3TEGT) diblock copolymers were synthesized that were capable of microphase separating based on the difference in polarity between the blocks. We targeted P3HT-b-P3TEGT thin-film morphologies, where we could orient [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (electron acceptor) in the polar P3TEGT domain, to allow P3HT to form pristine crystal domains. Thermal annealing P3HT-b-P3TEGT diblock copolymers led to microphase separation, as characterized by atomic force microscopy (AFM) and small-angle x-ray scattering (SAXS), and OPV devices were fabricated and characterized using P3HT-b-P3TEGT/PCBM blends.

P3HT-based diblock copolymers that had hydroxyl- and amine- functionalities were synthesized in an effort to utilize their nucleophilic nature for further functionalization. These copolymers underwent a solvent-induced crystallization that provided a P3HT nanowire decorated with the hydroxyl/amine functionalities on the fibril exterior. Previously, cross-linking mechanisms for polythiophenes had occurred in thin films upon thermal annealing or exposure to radiation, with little control over the crystallinity of the polymer. We were able to utilize fibrils formed from our functional diblock copolymers to covalently cross-link the crystalline structures by reacting with diisocyanates. This led to the formation of robust fibrils that had not previously been reported, that maintained photophysical and electronic properties to the unmodified nanowires. These nucleophilic fibrils were reacted with a bis-diisocyanate functionalized fullerene derivative to yield stabilized p-type/n-type nanowires. This process led to robust p-type/n-type fibrils that displayed photoluminescence quenching and high charge transfer characteristics that were not observed for p-type/n-type blends.

In an effort to simplify the fibril cross-linking, we designed a P3HT-based diblock copolymer that had thioacetate functionalities, which were deprotected and underwent an oxidative cross-linking process. These polymers formed nanowires by solvent induced precipitation, and upon deprotection of the thioacetate groups by reaction with dimethyl amine, experienced oxidative cross-linking to achieve robust fibrils. This provided a novel system in that the polymer was able to cross-links itself, and the cross-linking process was found to be reversible by reduction chemistry.

Recommended Citation

Hammer, Brenton A. G, "Synthesis and Solution- Driven Assembly of Functional Polythiophene Derivatives" (2013). *Doctoral Dissertations 1911-2013*. Paper 456. http://scholarworks.umass.edu/dissertations_1/456

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