Block copolymers of poly(3-hexylthiophene): towards better control of nanostructures

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Printable solar cells have the potential to become a disruptive solar technology that is inexpensive, efficient, and mass produced, but their power conversion efficiencies are currently lower than they could be. One of the key issues in the development of more efficient organic solar cells is to control the solar cell structure, or morphology. The optimal morphology is believed to be an interpenetrating network of two separate phases, one electron-donor phase and one electron-acceptor phase, with an interspace of 10 to 30 nm.[1] To date, the best printable solar cells are best described as bulk heterojunctions, where an electron donor (e.g. Poly(3-hexylthiophene (P3HT)) and an electron acceptor (e.g. [6,6]-phenyl-C61 butyric acid methyl ester (PCBM)) are blended together. Morphology is then optimized by the processing conditions – choice of solvents, drying time and annealing time. Although this approach was successful for the P3HT/PCBM system, it usually fails for other donor/acceptor pairs and results in bad dimensions. Other approaches to controlling nanostructures are therefore needed. Although the component's chemical structure should have a large impact on morphology, little is understood about how to design materials to optimize morphology.

Block copolymers are known to self-assemble into various nanostructures, depending on the nature and relative amounts of each block. Block copolymers consisting of P3HT (conjugated polymer, rod-like) and a non-conjugated polymer (coil-like) were found to self-assemble into conductive nanofibrils, where the P3HT segments pi-stacked with each other.[2] Changing the nature of the non-conjugated segment thus provides a way to alter the mechanical and processing properties of the conjugated block, as well as its nanostructure.

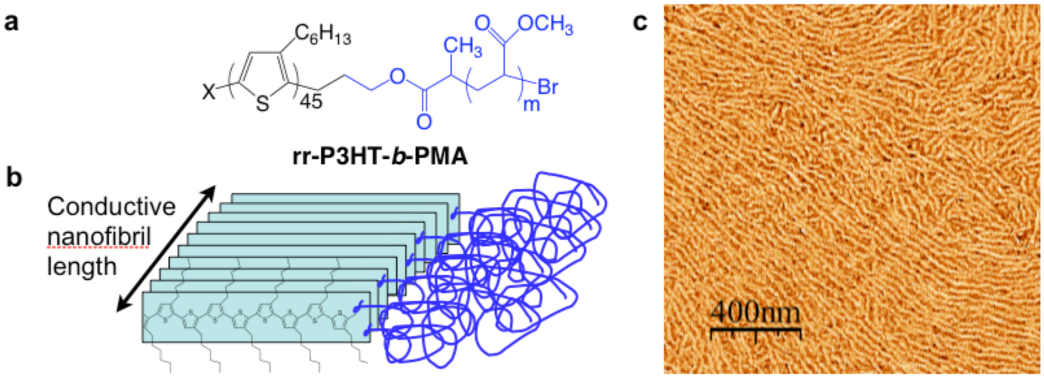

Figure 1: a) Chemical structure for the diblock copolymer of P3HT and Poly(methyl acrylate) (PMA); b) Self-assembly of P3HT-*b*-PMA, where the P3HT segment stack with each other to form long conductive nanofibrils; c) Taping Mode AFM phase image of film of P3HT-*b*-PMA (containing ~60 wt% P3HT) with a charge carrier mobility of 0.05 cm^2/Vs.[3]

Rod-coil diblock copolymers containing P3HT can have good electrical properties despite the presence of the insulating segment, because they self-assemble into long conductive nanofibrils that provide paths for charges between electrodes. A series of diblock copolymer of

P3HT and poly(methyl acrylate) (PMA) was synthesized, where the molecular weight (MW) of P3HT was kept constant and the MW of PMA block increased. To evaluate their electrical properties, bottom-contact bottom-gate field-effect transistors were fabricated and tested. The average hole-mobilities extracted for several field-effect transistors are illustrated in Figure 2. Pristine P3HT showed the largest mobility, followed by the allyl-terminated P3HT (a precursor for the synthesis of block copolymers). As the size of the insulating block increased (and P3HT content decreased), mobility of diblock copolymers filmed remained high, even at a low P3HT content of 40%.

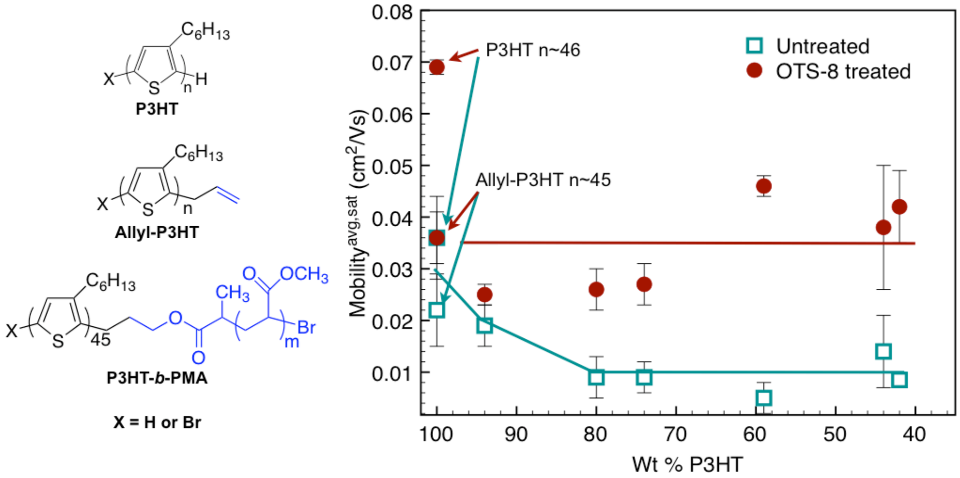

Figure 2: Charge carrier mobility in bottom-contact, bottom gate field-effect transistors for block copolymers of P3HT-*b*-PMA with different P3HT content (lower P3HT content results from larger PMA block). Mobility of P3HT and ally-terminated P3HT of similar molecular weight are added for reference. Square is untreated SiO_2 gate dielectric and circles is OTS-8 treated SiO_2 gate dielectric.

Another hypothesis to explain these high mobilities for diblock copolymers is that perhaps there is a preference for the P3HT segment at the interface. This is a reasonable hypothesis since bottom-gate bottom-contact field-effect transistors measure the charge carrier mobility of the organic semiconductor at the interface, within ~5 nm of the gate dielectic. To look at the chemical composition at the interface, Dr. Dean Delongchamp and Dr. Youngsuk Jung (National Institute of Standards and Technology, MD, USA) peeled films of P3HT-*b*-PMA (44 wt% P3HT) made on SiO_2 (with different surface energies) and examined the surface of peeled films by NEXAFS. They found relatively equal amounts of P3HT and PMA on the both sides of the peeled film. The high mobilities observed for this diblock copolymer are therefore not due to P3HT enrichment at the interface.

These diblock copolymers could be useful in organic solar cells by helping the formation of long conducting nanofibrils throughout the film. The width of these nanostructures – 20 to 30 nm – is within the target scale for ‘optimal’ morphology. The non-conjugated block also provides a way to tune solubility and other properties that could help with printing.

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(2) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. *Angew. Chem.-Int. Ed.* **2001**, *41*, 329-332.
(3) Sauvé, G.; McCullough, R. D. *Adv. Mater.* **2007**, *19*, 1822-1825.