Self-assembly of conjugated rod-coil block copolymers for organic electronics

The field of organic electronics has enjoyed increasing interest over the past decade. Organic light-emitting diodes, field-effect transistors and solar cells have a promising future, with some products already commercially available. Polymers typically offer good solution processability, paving the way for potential low-cost and large-area applications. However, the morphology always plays the decisive role in such devices since it has a large effect on the charge-transport properties.

Block copolymers are covalently linked polymers. The interconnectivity of the polymers restricts the formation of large domains, leading to so-called microphase separation. The crystallinity of one or both of the polymer blocks has a significant contribution to the enthalpy of the material system, thereby influencing the microphase separation. Rod-coil block copolymers show a further complexity because the conformational entropy is strongly influenced by the stiffer chain topology and because of the specific interactions between the conjugated moieties. The term "coil" describes the amorphous polymer segments, while the term "rod" is used for stiffer conjugated polymer segments.

A joint research study led by Professor Wen-Chang Chen in the Department of Chemical Engineering at NTU and Professor Toshifumi Satoh in the Graduate School of Chemical Sciences and Engineering of Hokkaido University designed a series of rod-coil copolymers for different kinds of organic electronic device applications. For example, main-chain conjugated, electron-donating polyfluorene (PF) rods and pendent electron-withdrawing isoindigo (Piso) coils were synthesized for resistor memories [1]. Self-assembled fibrillar nanostructures and effective charge-transport channels were formed in the polymer thin films by thermal annealing, leading to stable resistance switching behavior for memory device applications. The enhanced conjugated PF conducting channels led to stable resistance switching behavior, exhibiting volatile static random-access memory (SRAM) and nonvolatile write-once-read-many-times (WORM) memory. The results indicate that stable digital information storage could be achieved, and the charge storage volatility could be easily manipulated by tuning the PF/Piso ratio. More importantly, the memory cells were integrated on a poly(dimethylsiloxane) (PDMS) substrate to make the devices stretchable.

Moreover, poly(3-hexylthiophene) (P3HT) rod segments can potentially be coupled with coil segments to produce P3HT-coil block copolymers for field-effect transistor [2] and transistor-type memory [3] applications. Poly(3-hexylthiophene)-*block*-poly(butyl acrylate) (P3HT-*b*-PBA) thin films combined the good semiconducting properties of P3HT and the mechanical endurance of PBA to fabricate a stretchable transistor. Incorporating the low glass-transition temperature PBA block enhances the ductility of the polymer film while maintaining good charge-transport ability under 100% strain or after 100 cycles of strain due to the self-assembled fibrillar-like nanostructures and edge-on orientation of the P3HT-*b*-PBA film. Our newly synthesized P3HT-*b*-pendent Piso donor-acceptor rod-coil copolymers show dual electrical functionalities. Such block copolymer film is then introduced as both a charge-transport and charge-storage layer in an OFET memory device configuration. A p-type channel can be formed, and the memory window can be tuned by the block length of the Piso coil. From our findings, we demonstrate strategies for the synthesis of rod-coil block copolymers containing multiple electronically interesting components as well as control over their self-assembly.

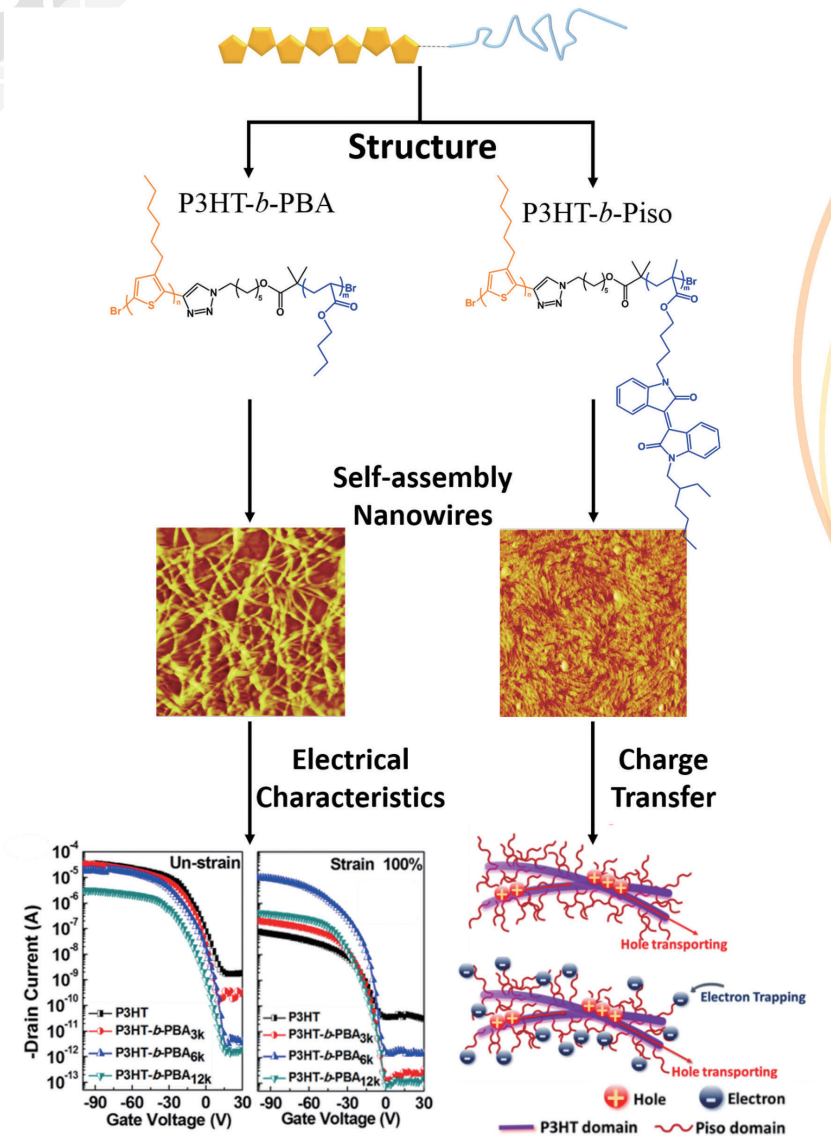

Figure 1. Synthesis, morphology, and applications of conjugated rod-coil *block* copolymers: poly(3-hexylthiophene)-*block*-poly(butyl acrylate) (P3HT-*b*-PBA) and poly(3-hexylthiophene)-*block*-poly(pendent isoindigo) (P3HT-*b*-Piso).

References

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Professor and Dean
Wen-Chang Chen
Department of Chemical Engineering, College of Engineering
chenwc@ntu.edu.tw