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学 位 論 文 題 名

Synthesis of Bio-based Block Copolymers with Conjugated Segments and Their Applications
in Electronic Devices
(バイオベース共役ブロックコポリマーの合成と電子デバイス応用)

Conjugated polymers have widely been used as active components of organic electronic devices including organic field-effect transistors (OFETs), light-emitting diode (LEDs) and memory devices. In particular, conjugated block copolymers (BCPs) with soft segments possess advanced mechanical properties, which are promising for the development of stretchable devices. However, most of the reported conjugated BCPs were synthesized from petroleum resources. Thus, the fabricated devices could have a huge impact on the environment after being discarded. To address this issue, the author proposed green electronics made from bio-based polymers. In this dissertation, a series of bio-based and stretchable semiconducting BCPs with linear and branched soft segments of poly(δ -decanolactone) (PDL) was presented. PDL was chosen as the green and soft block in the target BCPs since it is a bio-based, flexible polymer obtained through a metal-free and living ring-opening polymerization process. Conjugated-insulating BCPs were prepared through Cu-catalyzed azido-alkyne click reaction (CuAAC) between azido-functionalized PDLs and typical conjugated polymers with alkyne functional group including poly(3-hexylthiophene) (P3HT) and poly(9,9-di-*n*-hexyl-2,7-fluorene) (PF). Thermal, morphological, mechanical and electronic properties were studied to understand the structure-property correlations of the novel conjugated BCPs. Such polymers have demonstrated high potential to be used in stretchable transistor and memory applications.

In Chapter 1, the author summarized the current state of research on development of stretchable semiconducting polymers and their electronic applications, followed by introduction of bio-based materials for green electronic devices. A bio-based and soft polyester, PDL, was then introduced regarding its synthesis methods and BCP architecture design. Finally, research objectives for this dissertation were proposed, with the molecular design of target polymers, synthesis schemes, strategy to evaluate polymer properties, and potential device applications.

In Chapter 2, the author proposed soft-hard-soft type triblock BCPs with P3HT and branched PDL segments for stretchable semiconducting layer of OFET. The BCPs with AB, AB₂, B₂AB₂ and B₃AB₃ structure (A: P3HT, B: PDL) were designed to confine molecular assembly of P3HT while tailoring crystallinity and phase separation of the BCP. The prepared polymers exhibited OFET mobility of 0.045-0.089 cm² V⁻¹ s⁻¹, which is comparable to the pristine P3HT homopolymers. This was attributed to the confined P3HT assembly through the triblock architecture design, as evidenced by atomic force microscopy (AFM) and grazing incidence X-ray scattering (GIXS). Interestingly, stretchability of the BCPs increased by introducing soft-hard-soft structure and the branched soft segments, as investigated by optical microscopy (OM) and amplitude modulation-frequency modulation AFM (AM-FM AFM). This can be attributed to more random phase separation and smaller P3HT crystallites of the branched triblock BCPs. Finally, OFETs with the stretched and transferred semiconducting layer of the BCPs were fabricated and the B₃AB₃ device showed the highest mobility retention among all the synthesized BCPs (72-75%) under 100% strain, and 71-75% mobility retention after 500 stretch-release cycles at 50% strain. In summary, the author demonstrated a novel conjugated BCP architecture design to advance its stretchability without sacrificing charge mobility.

In Chapter 3, the author proposed poly(9,9-di-*n*-hexyl-2,7-fluorene)-*block*-poly(δ -decanolactone)s (PF-*b*-PDLs) with AB, AB₂ and AB₃ structures (A: PF, B: PDL) as stretchable charge-storage layer of OFET memory. The polymer thin films exhibited extraordinary stretchability with no cracks observed by OM under up to 100% strain owing to the incorporated PDL soft segments. Meanwhile, the trapping density of the electret film of the branched polymers was boosted by the tailored phase separation and higher crystallinity of the BCPs. Quantitative analysis of the polymer thin films on the AFM images was performed to correlate thin film morphology with memory device performance. The PF-*b*-PDL₃ film possessed condensed PF nanofibers with the highest coverage area. Due to the highest coverage area of PF nanofibers, the OFET memory device based on PF-*b*-PDL₃ electret exhibited the largest memory window (102 V) and the highest memory ratio (3.5×10^4). Finally, the performance of the charge-storage layer under stretching was investigated. The OFET memories made by the stretched and transferred BCPs can retain their memory performance under up to 100% strain, and the PF-*b*-PDL₃ device can endure 500 stretch-release cycles at 50% strain with 84% memory window retention. Based on these results, the author demonstrated the importance of BCP architecture design on modulating electronic properties and stretchability of conjugated BCP.

Throughout this dissertation, the author successfully demonstrated the design and synthesis of conjugated BCPs for stretchable device applications utilizing bio-based soft segments of PDL, and highlighted the effect of branch polymer architecture on the electronic properties and device performance of conjugated BCP. Such knowledge will greatly contribute to the fields of organic electronic device and bio-based functional materials. In conclusion, this dissertation can be recognized to be awarded a Ph.D. degree in Chemical Sciences and Engineering.