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# 論文要旨

## THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Due to the versatility of synthesis and solution processability, semiconducting polymers are promising materials for organic field-effect transistor (OFET) applications. Structure of a semiconducting polymer strongly affects its optoelectronic and film-forming properties. These in turn determine the charge transport characteristics of the polymer films. Therefore, optimization of polymer design is essential to achieve the best possible OFET performances. This thesis focuses on optimization of polymer backbone structures and understanding its relationship with the polymer properties. Particularly, three sets of polymers were studied, covering backbone planarity tuning, alkyl side group substitution, random copolymerization and cross-linking methods.

Five novel [1,2,5]Thiadiazolo[3,4-f]benzotriazole (TBZ) and bis(thieno[3,2-b]thiophenyl) ethylene (DTTE)-based conjugated polymers with different alkyl group positions were synthesized. The effect of substituent position on the optical, electrochemical, and charge-transporting properties in OFETs was comprehensively studied. Placing alkyl groups on neighboring units, so that they face into a common space, created high steric hindrance and resulted in a polymer with the highest backbone torsion. This polymer gave amorphous films, which exhibited hole mobility ($\mu_h$) of $2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (P2). Polymers with moderate backbone planarity that had alkyl groups concentrated on one part of the polymer gave $\mu_h$ in the range of 0.01–0.08 cm$^2$ V$^{-1}$ s$^{-1}$ (P1 and P3). By spreading the substituents as equally as possible, polymers with similar backbone planarity but higher crystallinity were obtained, and the $\mu_h$ increased to 0.15–0.18 cm$^2$ V$^{-1}$ s$^{-1}$ (P4 and P5). Unfortunately, all these polymers exhibited face-on molecular packing, which is deemed unfavorable for OFET applications. Density functional theory (DFT) calculations showed that the thiophene "spacers", which have traditionally been present in the TBZ-based copolymers (and many other copolymers), were the source of the backbone torsion. Hence, another polymer without the thiophene units was synthesized and characterized (P6). The polymer had an almost planar copolymer backbone giving thin-films with an edge-on and bimodal molecular packing. Chloroform and chlorobenzene soluble fractions of the copolymer (**P6-CF** and **P6-CB**, respectively) exhibited the improved $\mu_h$s exceeding 0.2 and 0.4 cm$^2$ V$^{-1}$ s$^{-1}$, respectively.

When incorporated into bithiophene units, methoxy groups can act as so-called "conformational" locks through O⋯S interactions and induce high backbone planarity. In addition, electron-donating nature of methoxy group can improve the p-type charge transport properties of polymers. However, some methoxy-substituted polymers were shown to acquire face-on molecular packing. In order to find an optimized extent of incorporation, random copolymers based on diketopyrrolopyrrole (DPP) and quaterthiophene (4T) copolymer was synthesized by step-by-step incorporation of 3,3'-dimethoxy-2,2'-bithiophene (P7–P11). Enhanced $\pi$-conjugation was evidenced in light absorption spectra, which was attributed to the planarization of the polymer backbone. At a 25mol% loading, a random copolymer (P8) exhibited a $\mu_h$ of ~0.3 cm$^2$ V$^{-1}$ s$^{-1}$, which was comparable to that of the original polymer (P7). Further increasing the methoxy-substituted bithiophene resulted in limited number averaged molecular weights ($M_n$). Nevertheless, among these low-$M_n$ copolymers, $\mu_h$ was enhanced from 0.02 cm$^2$ V$^{-1}$ s$^{-1}$ for 50mol% loading (P9) to 0.07 cm$^2$ V-1 s-1 for 100mol% loading (P11). The enhancement was attributed to the formation of pre-aggregates in deposition solution with stronger interchain interactions, which could be caused by improved backbone coplanarity. Eventually, this resulted in edge-on dominant and bimodal molecular packing orientations. Tetramethyl ammonium iodide had been shown to enhance the crystallinity of DPP-based polymers when added into deposition solutions as an ionic additive. In this work, its effect on the methoxy-substituted random copolymers was also investigated. Surprisingly, incorporation of the additive into polymer films had no effect on charge transport properties, whereas the original polymer displayed a noticeable improvement of $\mu_h$.

In-film thermal or photochemical 1,4-coupling reactions of butadiyne units have been reported to be effective method to prepare polymer films with high degree of long-range ordering. The examples in literature were limited to small molecules and polymers with butadiyne moieties in the side groups. On the other hand, poly(arylenebutadiynylene)s are solution-processable polymers with butadiyne moieties incorporated into the conjugated backbone. Over the past few years these polymers have gained research interest for applications in organic electronic devices. The effects of the topochemical cross-linking reactions of the main chain backbone on the electronic device performances have not been reported to date. To shed light on the possible outcomes of these reactions, poly(thieno[3,2-b]thiophen-2,5-diylbutadiynelene) (PDETT) and poly(thiophen-2,5-diylbutadiynelene) (PDET) were prepared and their topochemical cross-linking was comprehensively studied. Grazing-incident wide-angle X-ray scattering (GIWAXS) measurements revealed that PDET was completely amorphous, while PDETT had high degree of crystallinity. In addition, DFT calculations and GIWAXS results further showed that PDETT had the required alignment of butadiyne moieties for the topochemical reaction. Thus, thermal annealing of PDETT films generated cross-links, which formed perpendicularly to the polymer backbone plane. Despite the expected disruption of backbone planarity and degradation of charge transport properties, cross-linked PDETT exhibited improved $\mu_h$. This was attributed to the low extent of cross-links inhibited by the rigidity of polymer backbone. This allowed the remaining parts of the film to crystallize into a tightly packed motif. PDET produced cross-links by both thermal and UV-induced topochemical reactions. Due to its zigzagged backbone and amorphous nature, cross-links eliminated the $\pi$-$\pi$ stacked regions in the film, which led to complete loss of charge transport.