Development of N-Type Semiconducting Polymers for Transistor Applications

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The recent development of n-type semiconducting polymers in the author’s group is reviewed. Fullerene polymers are initially described. By introducing a specially designed alkylated comonomer and using the Cu(I)-catalyzed azide-alkyne cycloaddition reaction, highly soluble but high-molecular-weight fullerene polymers with a high fullerene content are obtained. Next, a new attempt to produce n-type polymers by a postfunctionalization reaction is shown. The [2+2] cycloaddition-retroelectrocyclization (CA-RE) between electron-rich alkynes and electron-deficient olefins is employed to construct acceptor units in the polymers. The frontier energy levels of typical p-type polymers containing electron-rich alkynes are lowered by the [2+2] CA-RE with cyano acceptors, such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). Finally, rational design of high mobility n-type semiconducting polymers based on benzobisthiadiazole (BBT) and its analogues are described. A series of polymers are designed and synthesized, and their thin film transistor (TFT) performances are investigated. Although the BBT unit is suitable for TFT applications, the comonomer must be carefully selected in order to create unipolar n-type charge-transport properties. Thus, naphthalenediimide (NDI) with a deep highest occupied molecular orbital (HOMO) level is copolymerized with the BBT monomer to produce high-performance n-type polymers.

Keywords: Acceptor, Cycloaddition, Fullerene, Semiconducting polymer, Thin film transistor

1. Introduction
The development of high-mobility n-type semiconducting polymers is an urgent demand in the field of organic electronics [1-5]. Studies over the past decade have succeeded in producing excellent p-type semiconducting polymers, which are used in organic thin-film transistors (TFTs) and organic photovoltaics (OPVs). However, the state-of-the-art and next generation devices require counter n-type polymers. Examples include complementary metal oxide semiconductor (CMOS)-like circuits, all-polymer solar cells (all-PSCs), organic thermoelectrics, and TFT-based sensors [6,7].

The electronic properties of organic semiconducting polymers can be tuned by chemical structures. It is well-known that π-conjugated chromophores in the polymer backbone significantly affect the charge carrier transport properties. For example, when conventional organic dyes and pigments, such as diketopyrrolopyrrole (DPP), indigo, carbazole violet, and quinoxaline, were employed, good to excellent TFT performances were readily obtained [8-11]. However, most of these performances were based on an ambipolar charge-transport. In other words, both hole and electrons flowed due to these π-chromophores, which made it rather difficult to achieve unipolar n-type charge-transport properties.

In order to efficiently block the hole transport and realize a unipolar n-type behavior, it is important to use the π-conjugated chromophores with deep highest occupied molecular orbital (HOMO) levels. The HOMO levels of most organic dyes and pigments are shallow due to their
narrow band gaps. With these problems in mind, three approaches were attempted in my group to develop high-performance n-type semiconducting polymers.

2. Fullerene polymers

Fullerene (mainly C\textsubscript{60} and C\textsubscript{70}) derivatives are well-known n-type semiconductors used in organic photovoltaic devices. There have been many reports about fullerene polymers since the 1990s, but high-molecular-weight soluble polymers with high fullerene contents have been elusive due to the synthetic difficulty and strong aggregation nature of the fullerene moieties [12]. In order to solve these problems, the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction was found to be a useful reaction to functionalize fullerenes [13]. In addition, highly-branched substituents based on the 1,3,5-tris(alkyloxy)benzene unit were serendipitously found to prevent the fullerene aggregation [14,15]. With the increasing alkyl chain length, the melting points of the fullerene derivatives gradually decreased to form room-temperature liquid fullerenes. These interesting features were applied to synthesize new fullerene polymers. The dialkyne-substituted C\textsubscript{60} monomer and 1,3,5-tris(dodecyloxy)benzene-based diazide comonomer were subjected to click polymerization at room temperature overnight, yielding the corresponding C\textsubscript{60} polymers (Fig. 1) [16]. The dodecyloxy group was one of the most appropriate alkyl chains that lower the melting point and viscosity of fullerene derivatives. Interestingly, the solubility of the formed C\textsubscript{60} polymers depended on the alkylene spacer [17]. PolyC\textsubscript{60} (x = 1) demonstrated a very high molecular weight with the number-average molecular weight ($M_n$) of 130,000 and polydispersity index ($M_w/M_n$) of 2.42, while the other two polymers, PolyC\textsubscript{60} (x = 2) and PolyC\textsubscript{60} (x = 3), were only slightly soluble in common organic solvents.

PolyC\textsubscript{60} (x = 1) showed an absorption maximum at 253 nm in CHCl\textsubscript{3} and the first reduction potential at -1.05 V (vs. Fe/Fe\textsuperscript{2+}). These properties are ascribed to the substituted C\textsubscript{60} moiety and confirm the formation of the target fullerene polymers. However, unfortunately, the n-type semiconducting properties of these polymers were not demonstrated by the TFT performances probably due to the low electron mobilities. An excellent n-type performance was displayed by the operation of electrical memory devices [16]. The memory device based on PolyC\textsubscript{60} (x = 1) exhibited nonvolatile n-type memory performances with the remarkable shelf-storage stability of over 1.5 years.

3. Postfunctionalization of p-type polymers

Polymer reactions are useful techniques even in industry for the creation of functional polymers. However, there have been few effective reactions in the field of the postfunctionalization of organic semiconducting polymers. The author’s group noticed the unique reactivity of electron-rich alkynes toward tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), forming highly cyanated acceptor units. The reactions are the [2+2] cycloaddition-retroelectrocyclization (CA-RE), which efficiently proceeds even at room temperature in air [18-22]. Therefore, a new click postfunctionalization was proposed to produce n-type polymers. The postfunctionalization methodology was indeed similar to the semiconducting polymer doping, as TCNE and TCNQ are well-studied p-type dopants. However, in contrast to the semiconducting polymer doping, the postfunctionalization using the [2+2] CA-RE reactions provideschemically stable, neutral products.

Poly(aryleneethynylene), poly(arylenebutadiynylene), and platinum(II) polyyne polymers are an important class of conjugated polymers, whose optical and electrical properties have been studied for decades [23-33]. Most of these polymers are composed of electron-rich substances in the main chain, and accordingly, the [2+2] CA-RE with TCNE was attempted. For example, 3,6-carbazole-based poly(arylenebutadiynylene) derivative was reacted with TCNE at 100 °C in 1,2-dichloroethane, furnishing the corresponding donor-acceptor type polymer with the narrower band gap of 1.46 eV (Fig. 2) [34]. Similar to this result, alkyne-containing
organometallic polymers, such as ferrocene-based poly(arylenebutadiynylene)s and platinum(II) polynye polymers, were converted into donor-acceptor type polymers [35-39]. Although these polymers did not show high TFT performances, they were initially tested as an n-type semiconductor in OPVs.

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unoccupied molecular orbital (LUMO) levels importantly, both the HOMO and lowest frontier energy levels decreased due to the strong electron-withdrawing nature of the formed tetracyanated acceptor unit (Fig. 3) [49-53]. More chain alkynes were reacted with TCNE, the frontier energy levels decreased due to the strong electron-withdrawing nature of the formed tetracyanated acceptor unit (Fig. 3) [49-53]. More importantly, both the HOMO and lowest unoccupied molecular orbital (LUMO) levels gradually decreased as more TCNE was added.

The fully TCNE-added polyamine, PA-TCBD, eventually demonstrated an n-type energy level almost comparable to that of methyl [6,6]-phenyl-C61 butyrate (PCBM) [54,55]. This result suggested that the frontier energy level of aromatic polymers could be converted from p-type to n-type ones by the [2+2] CA-RE click postfunctionalization. Moreover, the relationship between the energy levels and TFT performances was investigated. As the added TCNE amount increased, the hole mobility decreased due to the decrease in the HOMO level. It was expected that the n-type charge transport properties are produced when all the monomer units were functionalized by the [2+2] CA-RE. However, electron-transport was not observed in the TFTs probably due to the significantly enhanced amorphous nature of the thin films. This situation did not change even when the stronger cyano-acceptor of TCNQ was employed in place of TCNE [56].

Furthermore, other polymers, such as P3HT, were also subjected to the [2+2] CA-RE postfunctionalization. Starting from the commercially-available P3HT, three high-yielding postfunctionalization reactions based on the bromination, Stille cross-coupling, and [2+2] CA-RE afforded P3HT-TCBD in high yields (Fig. 3) [57]. Interestingly, the tetracyanated moieties were readily reduced to form the corresponding anionic radicals, which ferromagnetically interacted with each other through the regioregular P3HT backbone. Since the [2+2] CA-RE reactions are efficient, they are employed to synthesize many donor-acceptor type molecules and polymers [58-83].

![Figure 2](image2.png)

Fig. 2. Donor-acceptor polymers synthesized by [2+2] CA-RE postfunctionalization.

The postfunctionalization of polymer side chains is another powerful approach in controlling the energy levels of conjugated polymers. Aromatic polyamines and poly(3-hexylthiophene) (P3HT) are typical hole-transporting materials or p-type semiconductors [40-48]. However, when the side chain alkynes were reacted with TCNE, the frontier energy levels decreased due to the strong electron-withdrawing nature of the formed tetracyanated acceptor unit (Fig. 3) [49-53].

4. Benzobisthiadiazole-based polymers

Benzobisthiadiazole (BBT), initially reported by Yamashita et al. in 1994 [84], is a very strong acceptor unit. BBT polymers were for the first time synthesized by Wudl et al. in 2011 [85-87]. They found that the BBT polymers are suitable for use in ambipolar transistors with the maximum mobility reaching 2.5 cm² V⁻¹ s⁻¹. In order to further improve the TFT performances, the author’s group started to optimize the main chain structure. We initially synthesized PBBT-FT, which demonstrated the ambipolar TFT performances with the hole mobility ($\mu_h$) of 1.3×10⁻¹ cm² V⁻¹ s⁻¹ and electron mobility ($\mu_e$) of 3.1×10⁻³ cm² V⁻¹ s⁻¹ (Fig. 4) [88]. Insertion of electron-poor thiazole spacers into the main chain resulted in PBBT-Tz-FT with the $\mu_h$ of 6.8×10⁻³ cm² V⁻¹ s⁻¹ and $\mu_e$ of 1.5×10⁻² cm² V⁻¹ s⁻¹. This result suggested that the π-spacer can alter the charge polarity of the polymers. Electron-poor spacers enhance the n-type character, while electron-rich spacers improve the p-type charge-transport properties. This general design principle has been widely recognized for the synthesis of high-performance
polymers used in TFTs, OPVs, and other related organic electronic devices. Another powerful method of controlling the charge polarity was heteroatom substitution. One of the sulfur atoms of BBT was substituted by a nitrogen (N) or selenium (Se) atom. The former improved the p-type character, while the latter strengthened the n-type TFT performances. PSeS is the Se substitution version of PBBT-Tz-FT (Fig. 4) [89]. PSeS displayed n-type dominant charge-transport properties with the $\mu_e$ of 0.087 cm$^2$ V$^{-1}$ s$^{-1}$, which is much higher than that of PBBT-Tz-FT.

![Fig. 4. BBT-based ambipolar polymers.](image)

In order to achieve excellent TFT mobilities, polymer packing orientation is one of the most important parameters. Since the carrier transport direction in TFTs is parallel to the substrate, the edge-on orientation is more promising than the corresponding face-on orientation. However, there have been few effective approaches to control the polymer packing orientation. In other words, it has been postulated that the packing orientation of semicrystalline polymers in thin films cannot be determined by the chemical structure. A significant finding was reported by Osaka and Takimiya in 2012 [90]. If there are two different alkyl side chains in the repeat unit of the semicrystalline copolymers and these alkyl chain lengths are similar, the polymers tended to form a face-on orientation. In contrast, if there is a well-defined difference in the alkyl chain lengths, such polymers formed an edge-on orientation. In order to verify the generality of this rule, two SNT-based polymers were designed and synthesized. **PSNVT-DTC16** and **PSNVT-DTC8** possessed the same backbone structure, and the only difference was the alkyl chain length of the thiophene spacers (Fig. 5) [91]. **PSNVT-DTC16** contained a hexadecyl group on the thiophene ring, of which its length was similar to that substituted on the SNT unit (tetradecyl). On the other hand, **PSNVT-DTC8** possessed the octyl chain on the thiophene ring, which was much shorter than the tetradecyl group. Interestingly, the grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis of **PSNVT-DTC16** demonstrated the face-on orientation, and accordingly, the $\mu_e$ of this polymer was limited to 0.13 cm$^2$ V$^{-1}$ s$^{-1}$ [91]. However, it was found that **PSNVT-DTC8** formed an edge-on orientation and displayed the significantly improved $\mu_e$ of 3.22 cm$^2$ V$^{-1}$ s$^{-1}$. This result is consistent with a previous report [90], highlighting the significant technique of controlling the polymer packing orientation.

![Fig. 5. SNT-based p-type polymers with different alkyl side chains.](image)

As already described, semiconducting polymers based on BBT and its heteroatom-substituted derivatives are excellent structural units for high-mobility polymers [92-96]. However, the reported charge polarity was mainly the p-type or at most the ambipolar type. In order to realize unipolar n-channel TFTs, the comonomers must be carefully selected. Among the many promising comonomer structures, naphthalenediimide (NDI) was one of the most suitable units as it can efficiently block the hole injection and transport due to the deep HOMO level. Thus, three NDI copolymers, namely, **PSN-NDI, PSeN-NDI, and PBBT-NDI**, were synthesized (Fig. 6) [97]. As anticipated from the frontier energy levels, the TFT performances of these polymers exhibited unipolar n-type charge-transporting properties. The $\mu_e$ values increased with the decreasing LUMO energy levels. Hence, **PSN-NDI** with the LUMO of -3.85 eV showed the $\mu_e$ of $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, while **PSeN-NDI** with the LUMO of -3.95 eV displayed the $\mu_e$ of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and **PBBT-NDI** with the deepest LUMO of -4.01 eV exhibited the improved $\mu_e$ of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. The lifetime or shelf-storage stability of the TFT devices also increased with the decreasing LUMO levels. Among the three polymers, **PBBT-NDI** produced the most stable TFT device. Even after one-month storage in air, 80% of the original mobility was retained. This result indicated that the air-stable n-channel TFT operation could be realized by the design of the
LUMO levels. It should be noted that the development of air-stable n-type organic materials is more difficult than that of the counter p-type materials due to the intrinsic instability of the reduced state of organic materials.

![Fig. 6. SNT-based unipolar n-type polymers.](image1)

A further improvement of the \( \mu_e \) values can lead to the advanced applications of high-performance n-type semiconducting polymers. Computational studies of PBBT-NDI suggested the significant twist of the main chain backbone mainly caused by the alkyl side chains on the flanking thiophene spacers. PBBT-NDI required the branched bulky alkyl side chains in order to achieve a sufficient solubility in organic solvents. Therefore, the alkyl side chains on the thiophene spacers of PSN-NDI were removed, resulting in pSNT (Fig. 7) [98]. Due to the improved planar backbone structure, the pSNT film showed a highly-crystalline bimodal morphology, and at the same time, the remarkable \( \mu_e \) of 4.87 cm² V⁻¹ s⁻¹ in the TFT with the octadecyltrimethoxysilane (OTMS) self-assembled monolayer (SAM) as a dielectric. Since the OTMS SAM is almost neutral, a marginal \( \mu_h \) of 0.01 cm² V⁻¹ s⁻¹ was observed. In order to perfectly block the hole transport and realize unipolar n-channel TFTs, a SAM of [3-(N,N-dimethylamino)propyl]trimethoxysilane (NTMS) was employed in place of the OTMS-SAM. As the NTMS-SAM trapped all holes due to the dimethylamino groups, the unipolar n-channel TFT could be realized and the \( \mu_e \) was improved to 5.35 cm² V⁻¹ s⁻¹. Very recently, a further improvement was achieved by utilizing the intramolecular hydrogen bonding. The vinylene spacers were introduced into pSNT, producing P4 [99]. The backbone planarity of P4 was higher than that of pSNT due to the intramolecular hydrogen bonding between the vinylene hydrogen atom and NDI oxygen atom. The GIWAXS of the P4 thin film revealed the extremely short \( \pi-\pi \) stacking distance of 3.40 Å. Finally, the TFT performances of P4 demonstrated the very high unipolar \( \mu_e \) of 7.16 cm² V⁻¹ s⁻¹. This value is among the highest for unipolar n-type semiconducting polymers reported to date.

![Fig. 7. High-mobility SNT-based n-type polymers.](image2)

5. Conclusion

Studies of high-mobility n-type semiconducting polymers are significant due to the future applications in organic electronics. Simple C₆₀ polymers and highly-cyanated polymers displayed n-type frontier energy levels, but they were not suitable for TFT applications. In contrast, BBT-based semiconducting polymers were found to be some of the most promising TFT materials. Both backbone and side chain engineering approaches were adopted to optimize the backbone planarity and solubilities in common organic solvents. Further mobility enhancement of the n-type semiconducting polymers will be realized in the near future.

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