The Effects of Side Chains on the Charge Mobilities and Functionalities of Semiconducting Conjugated Polymers beyond Solubilities

Yizhou Yang, Zitong Liu,* Guanxin Zhang, Xisha Zhang, and Deqing Zhang*

1. Introduction

Recent decades have witnessed the rapid development of organic and polymeric semiconductors. A number of p-, n- and ambipolar semiconductors with high charge mobilities have been reported through the design and synthesis of new conjugated molecular systems and optimization of their solid state structures. Moreover, these organic and polymeric semiconductors have been successfully used to fabricate various devices such as organic field-effect transistors (OFETs), organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). Light-weight and flexible devices have also been demonstrated with organic and polymeric semiconductors. In this regard, semiconducting conjugated polymers have been extensively investigated due to their merits of flexibility and solution processability, in addition to their high charge mobilities.

Semiconducting polymers entail both conjugated backbones and flexible side chains, which enable the polymers to be dissolved in organic solvents. The charge transporting behaviors of semiconducting polymers are determined by the structures of conjugated backbones and the interchain \(\pi-\pi\) interactions. For this reason, significant attention has been paid to the design and synthesis of various conjugated moieties and the covalent linkage of them into conjugated polymers. Conjugated frameworks, such as diketopyrrolopyrrole (DPP), isodindigo (IID), naphthalenediimide (NDI), and benzodifurandione-based oligo(p-phenylene vinylene) (BDOPV), have been widely used as building blocks for semiconducting conjugated polymers. Meanwhile, our group and others have shown that side alkyl chains not only endow the polymers with solubilities in organic solvents and solution processability, but also affect the interchain packing at the microscopic level, and thin film crystallinity and morphology at the macroscopic level, resulting in the modulation of charge transporting property of the polymer thin films. Therefore, modification of side alkyl chains has gradually become an efficient approach to boost the charge mobilities of semiconducting conjugated polymers.

Furthermore, heteroatoms and functional groups are incorporated...
into the side chains of conjugated polymers, not only for improving the semiconducting property but also for endowing the polymers with sensing and responsive functionalities.\textsuperscript{[64-69]} Increasing numbers of results demonstrate that i) the semiconducting performances of conjugated polymers can be improved by varying the side chains without changing the conjugated backbones, ii) highly selective and sensitive FET-based sensors can be achieved by incorporating functional groups in the side chains of conjugated polymers, and iii) stimuli-responsive semiconductors can be generated by linking photoresponsive groups in the side chains of conjugated polymers.

In this review, we will first discuss conjugated polymers with side alkyl chains of different structures and investigate the effects of side alkyl chains on the charge transporting properties of the conjugated polymers. Then, conjugated polymers containing heteroatom or functional groups in the side chains will be discussed. These include the tuning of interchain packing, thin film crystallinity, and the enhancement of charge mobilities for conjugated polymers after incorporating heteroatoms or functional groups in the side chains. In addition, we will show that the incorporation of functional groups in the side chains can endow the conjugated polymers with sensing and stimuli-responsive functionalities and such conjugated polymers can be utilized to fabricate highly selective and sensitive FET-based sensors and memory devices. Finally, we will discuss side chain modification as a molecular design strategy in general for the further development of organic and polymeric semiconductors with high performances.

2. Alkyl Chains with Different Structures

2.1. The Alkyl Chain Contents

The contents of alkyl chains in the conjugated polymers affect not only their solubilities in organic solvents but also the interchain interaction and packing order.\textsuperscript{[70-75]} DeLongchamp and co-workers found that P1 and P2 (Scheme 1) exhibit more ordered film structures and higher charge carrier mobilities than P3HT (Table 1).\textsuperscript{[70]} As shown in Scheme 1, P1 and P2 contain the 2,2’-bithiophene and thieno[3,2-b]thiophene units without the attachment of alkyl chains, respectively. As a result, P1 and P2 entail fewer alkyl chain attachment densities than P3HT (Figure 1a). DeLongchamp and co-workers investigated the interchain packing modes for P1 and P2 with XRD, polarized IR transmission spectroscopy and near-edge X-ray fine-structure spectroscopy (NEXAFS), and they concluded that the interdigitation of side chains in P1 and P2 can occur efficiently, leading to 3D order, because of the low side chain attachment densities. In comparison, the interdigitation of alkyl chains in P3HT is not favorable due to the high side chain density, and accordingly, the thin film of P3HT has a two-dimensionally ordered, smectic like structure.

Müllen and co-workers showed that P3 shows a two orders of magnitude improvement of hole mobility in comparison with P4 (Scheme 1).\textsuperscript{[73]} P3 and P4 have the same electron acceptor (DPP) and electron donor (BTT: benzothiophenes) moieties in their backbones. Two alkyl chains are connected to the BTT units in P4, while there are no alkyl chains in the BTT units within P3. Steric hindrance is expected to generate among the two alkyl chains linked to the BTT units and those attached to the DPP units in P4, resulting in a twist of the polymer backbone and therefore in decreased order. For P3, however, the steric interactions among the alkyl chains can be prevented. The removal of the alkyl chains in P3 also leads to the variation of the arrangement of polymer chains on the hydrophobic surface. The polymer chains

Yizhou Yang received his B.S. degree from Wuhan University in 2014. He is currently pursuing his Ph.D. degree under the supervision of Prof. Deqing Zhang at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS), which he began in 2014. His current research focuses mainly on design, synthesis and self-assembly of organic conjugated polymers for high semiconducting performance, and exploration of organic optoelectronic devices with new functionalities.

Zitong Liu is an associate professor at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS), China. He received his Ph.D. from ICCAS in 2008 under the supervision of Prof. Qinghua Fan, after receiving the B.S. degree from Jilin University in 2003. His current research focuses on the design and synthesis of conjugated materials, self-assembly behaviors, and their semiconducting properties.

Deqing Zhang is currently a research professor at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in Beijing, China. He received his Ph.D. from Ruprecht-Karls University Heidelberg in 1996 under the supervision of Prof. H. A. Staab. His research interests include the design and synthesis of organic conjugated molecules toward opto-electronics, and the development of external stimuli-responsive molecular systems for molecular switches, logic gates, and chemo/biosensors.
of P3 are adopted an edge-on packing mode, which is beneficial for charge transporting,[76,77] whereas the polymer chains of P4 are arranged predominately in the face-on mode. As a result, the polymer chains of P3 are orderly packed and its thin film shows improved charge transporting performance.

Park and co-workers developed a new approach to boost the charge transporting performance of polythiophene by reducing the number of alkyl chains.[74] They synthesized series of polythiophenes (P5–P7, Scheme 1) with different contents of alkyl chains, which are randomly distributed along the backbones. Interestingly, random polymers P5–P7, which have with low alkyl chain density and low thin film crystallinity compared with P3HT, display greatly enhanced field-effect mobilities up to 1.37 cm² V⁻¹ s⁻¹ (Table 1). This is attributed to i) the backbone planarity being improved after reducing the number of alkyl chains; and ii) the formation of localized aggregates in the amorphous regions, as illustrated in Figure 1b, which increases the connectivity of the polymer chains, facilitating both intrachain and interchain charge transport. They further reported DPP-based conjugated polymers P8 and P9, which have different alkyl chain contents.[75] The alkyl chain content influences the orientation of polymer chains on the substrate. The polymer chains of P8 are orientated in the edge-on mode on the substrate after thermal treatment. However, the polymer chains of P9, in which two alkyl chains are attached to each phenyl moiety, are packed dominantly in the face-on mode after thermal treatment, but it transforms into the edge-on mode after undergoing thermal treatment above the melting temperature.

2.2. The Substitution Position of Alkyl Chains

For certain conjugated polymers, the substitution positions of alkyl chains also influence the backbone coplanarity, electronic structure, interchain packing and thin film morphology, and accordingly the charge transporting performances are varied.[78–83] Li and co-workers investigated two conjugated polymers, i.e., P10 and P11, in which the two alkyl chains attached to the bithiophene moiety are positioned differently (Scheme 2).[79] The two n-dodecyl chains are placed in tail-to-tail (TT) and head-to-head (HH) manners for P10 and P11, respectively. The results reveal that the TT placement of two alkyl chains causes the distinct twisting of the junction of the acceptor and donor moieties because of the steric congestion of n-dodecyl groups and the adjacent hydrogen atoms. As a result, P10 shows a larger optical bandgap and a lower HOMO level than P11. In comparison, the HH positioning of alkyl chains in P11 can weaken the steric hindrance, and consequently, the twisting of the donor and acceptor units is reduced. However, a larger dihedral angle between the two thiophene moieties occurs as a result. The less twisting of the acceptor and donor units in P11 facilitates the orderly packing of polymer chains. In fact, the thin film of P11 exhibits higher crystallinity than that of P10, which agrees well with the observation that P11 shows high ambipolar charge transport performance with µe and µh up to 0.33 and 0.15 cm² V⁻¹ s⁻¹, respectively, outperforming those of P10 (Table 1). Similarly, Qiu and co-workers reported three conjugated polymers, i.e., P12, P13, and P14 (Scheme 2), in which the two n-dodecyl chains linked to the bithiophene moiety are positioned in HH, head-to-tail (HT), and TT manners, respectively.[79] P12, with HH placement of two n-dodecyl chains, shows better backbone coplanarity and thin film crystallinity. The backbone of P13, with HT positioning of two n-dodecyl chains, has the most twist, and the resulting thin film displays poor crystallinity. These three polymers show ambipolar semiconducting performances and the electron and hole mobilities decrease in the following order: P12 > P14 > P13. However, this trend does not hold true for polymers P15 and P16.[80] In this case, the steric hindrance due to the alkyl chains at the two central

![Scheme 1. Chemical structures of semiconducting polymers P1–P9 with different alkyl chain contents.](image-url)
Table 1. OFET performances of polymers P1–P123.

| Polymers | HOMO [eV] | LUMO [eV] | Device structure | Deposition process | $\mu_{\text{on}}$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $\mu_{\text{off}}$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $I_{\text{on}}/I_{\text{off}}$ | $\phi_{\text{on}}$ [Å] | Ref. |
|----------|-----------|-----------|-----------------|-------------------|--------------------------|--------------------------|----------------|----------------|-----|
| P1       | −         | −         | BGTC            | Spin-coating      | 0.14                     | 10$^2$                    | −             | −             | 3.8 [71] |
| P2       | −         | −         | BGBC            | Spin-coating      | 0.3                      | 10$^6$                   | −             | −             | 3.72 [72] |
| P3       | −5.35a    | −3.55a    | BGBC            | Drop-casting      | 0.007b                  | 5 × 10$^5$               | −             | −             | 3.7 [73] |
| P4       | −5.45k    | −3.44a    | BGBC            | Drop-casting      | 0.2h                    | 5 × 10$^5$               | −             | −             | 3.8 [73] |
| P5       | −4.91c    | −         | Spin-coating    | −                  | 0.9                      | 2 × 10$^5$               | −             | −             | 3.77 [74] |
| P6       | −4.91c    | −         | Spin-coating    | −                  | 0.94                     | 4 × 10$^5$               | −             | −             | 3.77, 3.63 [74] |
| P7       | −4.92k    | −         | Spin-coating    | −                  | 1.37                     | 10 × 10$^5$              | −             | −             | 3.63 [74] |
| P8       | −5.40a    | −3.83i    | TGBC            | Spin-coating      | 0.41i                   | −                        | −             | −             | [75] |
| P9       | −5.25c    | −3.82c    | TGBC            | Spin-coating      | 0.011i                  | −                        | −             | −             | [75] |
| P10      | −5.76a    | −3.78a    | BGBC            | Spin-coating      | 0.017j                  | 10$^2$                   | 0.0217         | 10$^4$         | −             | [78] |
| P11      | −5.68a    | −3.77a    | BGBC            | Spin-coating      | 0.15                     | 10$^2$                   | 0.33           | 10$^4$         | −             | [78] |
| P12      | −5.63a    | −4.06a    | BCTC            | Spin-coating      | 0.37                     | −                        | 1.23           | −             | 3.55 [79] |
| P13      | −5.68a    | −4.05a    | BCTC            | Spin-coating      | 0.018                   | −                        | 0.175          | −             | 3.61 [79] |
| P14      | −5.73k    | −4.01c    | BCTC            | Spin-coating      | 0.17                     | −                        | 0.70           | −             | 3.55 [79] |
| P15      | −5.32a    | −4.07a    | TGBC            | Spin-coating      | 4.9 × 10$^{-4}$         | 10$^2$–10$^3$            | −             | −             | [80] |
| P16      | −5.39a    | −4.09a    | TGBC            | Spin-coating      | 10$^{-4}$–10$^{-4}$     | 10$^{-2}$–10$^2$         | −             | −             | [80] |
| P17      | −4.97a    | −         | TGBC            | Spin-coating      | 4.6                      | 10$^{-2}$–10$^3$         | −             | −             | [81] |
| P18      | −5.08a    | −         | TGBC            | Spin-coating      | 0.4                      | 10$^{-4}$–10$^{-4}$      | −             | −             | [81] |
| P19      | −5.11a    | −         | TGBC            | Spin-coating      | 0.1                      | 10$^{-2}$–10$^2$         | −             | −             | [81] |
| P20      | −5.2a     | −3.5a     | BCTC            | Drop-casting      | 1.69                     | >10$^4$                   | −             | −             | 3.65 [82] |
| P21      | −5.1a     | −3.3a     | BCTC            | Drop-casting      | 0.90                     | >10$^4$                   | −             | −             | 3.60 [82] |
| P22      | −5.05a    | −         | BCTC            | Spin-coating      | 1.29                     | 10$^{-2}$–10$^2$         | −             | 3.74 [83] |
| P23      | −5.07a    | −         | BCTC            | Spin-coating      | 0.15                     | 10$^{-2}$–10$^2$         | −             | −             | 3.63 [83] |
| P24      | −5.06a    | −         | BCTC            | Spin-coating      | 0.011                   | 10$^3$                   | −             | −             | 3.67 [83] |
| P25      | −         | −         | BCTC            | Spin-coating      | 2.10 ± 0.13i            | 3.8 × 10$^4$             | −             | 3.6 [85] |
| P26      | −         | −         | BCTC            | Spin-coating      | ≈2.50k                  | 10$^4$                   | −             | 3.6 [85] |
| P27      | −         | −         | BCTC            | Spin-coating      | ≈2.50k                  | 10$^4$                   | −             | 3.5 [85] |
| P28      | −         | −         | BCTC            | Spin-coating      | 3.69 ± 0.42i            | 5.0 × 10$^4$             | −             | 3.5 [85] |
| P29      | −         | −         | BCTC            | Spin-coating      | 1.38 ± 0.21i            | 7.5 × 10$^4$             | −             | 3.5 [85] |
| P30      | −         | −         | BCTC            | Drop-casting      | −                        | 1.90                     | 6.63 × 10$^4$ | 3.84 [86] |
| P31      | −         | −         | BCTC            | Drop-casting      | −                        | 1.22                     | 6.92 × 10$^4$ | 3.90 [86] |
| P32      | −         | −         | BCTC            | Drop-casting      | −                        | 0.39                     | 1.80 × 10$^4$ | 3.89 [86] |
| P33      | −5.32b    | −3.90b    | TGBC            | Spin-coating      | 1.64                     | 588–1357                 | 1.89 × 10$^{-2}$ | − | ≈3.7 [87] |
| P34      | −5.36a    | −3.91a    | TGBC            | Spin-coating      | 0.606                    | 347–520                  | 1.49 × 10$^{-2}$ | − | ≈3.7 [87] |
| P35      | −5.35a    | −3.91a    | TGBC            | Spin-coating      | 0.108                    | 49–92                    | 1.63 × 10$^{-2}$ | − | ≈3.7 [87] |
| P36      | −5.23c    | −3.60c    | BGTC            | Spin-coating      | 0.012                    | 4.98 × 10$^5$            | −             | 3.6 [88] |
| P37      | −5.38a    | −3.62a    | BGTC            | Spin-coating      | 5.26                     | 1.57 × 10$^6$            | −             | 3.8 [88] |
| P38      | −5.39a    | −3.66a    | BGTC            | Spin-coating      | 0.00104                  | 3.85 × 10$^4$            | −             | −             | [88] |
| P39      | −4.97a    | −         | BCTC            | Spin-coating      | 0.47                     | ≈10$^3$                  | −             | −             | 3.7 [89] |
| P40      | −5.16a    | −         | BCTC            | Spin-coating      | 0.042                    | ≈10$^4$                  | −             | −             | 3.6 [89] |
| P41      | −5.26c    | −         | BCTC            | Spin-coating      | 0.026                    | ≈10$^4$                  | −             | −             | [89] |
| P42      | −         | −         | (TOF method)    | Drop-casting      | 7.5 × 10$^{-3}$         | −                        | −             | −             | [90] |
| P43      | −         | −         | Drop-casting    | −                  | 2.2 × 10$^{-4}$         | −                        | −             | −             | [90] |
| P44      | −         | −         | Drop-casting    | −                  | 6.6 × 10$^{-5}$         | −                        | −             | −             | [90] |
| Polymers | HOMO a–c) [eV] | LUMO a–c) [eV] | Device structure d) | Deposition process | Max $\mu_h$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $I_{on}/I_{off}$ | Max $\mu_L$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $I_{on}/I_{off}$ | $d_{opt}$ [Å] | Ref. |
|----------|----------------|----------------|--------------------|-------------------|-----------------|----------------|----------------|----------------|----------------|-----|
| P45      | −5.70 a)       | −3.70 b)       | BGTC               | Spin-coating      | 1.06            | $>10^6$        | −              | −              | 3.75           | [91]|
| P46      | −5.60 a)       | −3.70 b)       | BGTC               | Spin-coating      | 0.40            | $>10^5$        | −              | −              | 3.61           | [91]|
| P47      | −5.52 a)       | −3.74 b)       | BGTC               | Spin-coating      | 3.62            | $>10^6$        | −              | −              | 3.57           | [91]|
| P48      | −5.50 a)       | −3.74 b)       | BGTC               | Spin-coating      | 1.76            | $>10^6$        | −              | −              | 3.57           | [91]|
| P49      | −5.49 a)       | −3.89 b)       | BGTC               | Spin-coating      | 1.89            | $10^6$–3       | −              | −              | 3.99           | [92]|
| P50      | −5.44 a)       | −3.86 b)       | BGTC               | Spin-coating      | 4.07            | $10^1$         | −              | −              | 3.81           | [92]|
| P51      | −6.16 a)       | −4.01 b)       | TGBG               | Spin-coating      | −              | 0.90           | $>10^3$        | 3.52           |                | [93]|
| P52      | −6.15 a)       | −4.07 b)       | TGBG               | Spin-coating      | −              | 0.60           | $>10^4$        | 3.48           |                | [93]|
| P53      | −6.16 a)       | −4.01 b)       | TGBG               | Spin-coating      | −              | 1.40           | $>10^3$        | 3.45           |                | [93]|
| P54      | −6.15 a)       | −3.97 b)       | TGBG               | Spin-coating      | −              | 0.05           | $>10^4$        | 3.38           |                | [93]|
| P55      | −6.16 a)       | −4.02 b)       | TGBG               | Spin-coating      | −              | 0.76           | $>10^3$        | 3.38           |                | [93]|
| P56      | −6.12 a)       | −4.01 b)       | TGBG               | Spin-coating      | −              | 0.44           | $>10^3$        | 3.38           |                | [93]|
| P57      | −5.31 a)       | −3.74 b)       | BGBC               | Spin-coating      | 2.8            | $>10^6$        | −              | −              | >3.7           | [94]|
| P58      | −5.25 a)       | −3.78 b)       | BGBC               | Spin-coating      | 10.54          | $>10^6$        | −              | −              | 3.62           | [94]|
| P59      | −5.33 a)       | −3.78 b)       | BGBC               | Spin-coating      | 4.4            | $>10^6$        | −              | −              | >3.7           | [94]|
| P60      | −5.27 a)       | −3.78 b)       | BGBC               | Spin-coating      | 12.04          | $>10^6$        | −              | −              | 3.58           | [94]|
| P61      | −5.34 a)       | −3.74 b)       | BGBC               | Spin-coating      | 0.77           | $10^6$–10^6    | −              | −              | 3.73           | [95]|
| P63      | −5.27 a)       | −3.78 b)       | BGBC               | Spin-coating      | 2.95           | $10^5$–10^6    | −              | −              | 3.6            | [95]|
| P66      | −4.95 a)       | −3.67 b)       | BGTC               | Drop-casting      | 8.32           | $10^5$–10^6    | 1.26           | 10^2–3        | 3.60           | [96]|
| P68      | −4.87 a)       | −3.52 b)       | BGTC               | Drop-casting      | 5.20           | $10^5$–10^6    | 0.19           | 10^2–3        | 3.67           | [96]|
| P69      | −5.01 a)       | −3.38 b)       | BCBB               | Drop-casting      | −              | 0.004         | $10^4$         | −              | −              | [99]|
| P70      | −5.13 a)       | −3.54 b)       | BCBB               | Drop-casting      | −              | 0.090         | $10^4$         | 3.65           |                | [99]|
| P71      | −5.25 a)       | −3.78 b)       | BCBB               | Drop-casting      | 0.00044        | −              | −              | 3.8            |                | [100]|
| P73      | −5.59 a)       | −3.82 b)       | BGTC               | Spin-coating      | −              | 0.034         | $>10^5$        | 4.1            |                | [101]|
| P75      | −5.59 a)       | −3.82 b)       | BGTC               | Spin-coating      | −              | 0.093         | $>10^6$        | 4.0            |                | [101]|
| P76      | −5.56 a)       | −3.85 b)       | BGTC               | Spin-coating      | −              | 0.142         | $>10^6$        | 3.9            |                | [101]|
| P77      | −5.59 a)       | −3.86 b)       | BGTC               | Spin-coating      | −              | 0.217         | $>10^6$        | 4.0            |                | [101]|
| P78      | −5.02 a)       | −3.76 b)       | TGBG               | Spin-coating      | 0.29           | −              | 0.31           | −              | −              | [102]|
| P79      | −4.99 a)       | −3.78 b)       | TGBG               | Spin-coating      | 0.11           | $10^2$–10^2    | 1.01           | 10^4–5        | 3.59           | [102]|
| P80      | −4.99 a)       | −3.77 b)       | TGBG               | Spin-coating      | 0.20           | −              | 0.99           | −              | −              | [102]|
| P81      | −4.99 a)       | −3.76 b)       | TGBG               | Spin-coating      | 0.13           | $10^2$–10^2    | 1.04           | 10^4–5        | 3.58           | [102]|
| P82      | −4.97 a)       | −3.74 b)       | TGBG               | Spin-coating      | 0.52           | −              | 3.11           | −              | −              | [102]|
| P83      | −5.02 a)       | −3.78 b)       | TGBG               | Spin-coating      | 0.38           | $10^1$         | 0.63           | 10^4–5        | 3.60           | [102]|
| P84      | −5.02 a)       | −3.78 b)       | TGBG               | Spin-coating      | 0.090         | $5.2 \times 10^2$ | 0.0020         | 8.14           | −              | [98]|
| P85      | −5.15 a)       | −3.84 b)       | BGTC               | Spin-coating      | 0.110         | $4.8 \times 10^2$ | 0.0020         | 3.47           | −              | [98]|
| P86      | −5.15 a)       | −3.84 b)       | BGTC               | Solution-shearing | 4.59           | $>10^4$        | −              | −              | 3.60           | [103]|
| P87      | −5.13 a)       | −3.86 b)       | BGTC               | Solution-shearing | 0.5            | $>10^4$        | −              | −              | 3.61           | [103]|
| P88      | −5.19 a)       | −3.93 b)       | BGTC               | Solution-shearing | 4.23           | $>10^3$        | −              | −              | 3.61           | [103]|
| P89      | −5.17 a)       | −3.92 b)       | BGTC               | Solution-shearing | 0.54           | $>10^4$        | −              | −              | 3.57           | [103]|

Table 1. Continued.
thiophenes of the quaterthiophene segment becomes weak for the TT positioning, as in P15, compared with the HH positioning, as in P16. Thus, P15 shows better backbone coplanarity. Further field-effect transporting studies reveal that the hole charge mobility for the thin film of P15 is higher than that of P16.

The steric hindrance of alkyl chains can be reduced by lengthening the spacers between the alkyl chains. For instance, Heeney and co-workers reported three isomeric conjugated polymers, i.e., P17, P18, and P19, which possess the same conjugated backbone with thieno[3,2-b]thiophene, and (E)-2-((2-thiophen-2-yl)-vinyl)thiophene (TVT) moieties (Scheme 2 and Figure 2a). However, the alkyl chains are positioned differently. While the distinct twisting of the thieno[3,2-b]thiophene and thiophene moieties exists along the backbones of P18 and P19, the backbone of P17 is more planar, on the basis of cyclic voltammetry. LUMOs were calculated from HOMOs and optical bandgap (\(E_g^{opt}\)) with the following equation: 

\[
E_{	ext{LUMO}} = E_{	ext{HOMO}} + E_g^{opt}.
\]

Table 1.

| Polymers | HOMO \[\text{eV}\] | LUMO \[\text{eV}\] | Device structure | Deposition process | Max \(\mu_H\) \[\text{cm}^2\text{V}^{-1}\text{s}^{-1}\] | \(I_{	ext{on}}/I_{	ext{off}}\) | Max \(\mu_E\) \[\text{cm}^2\text{V}^{-1}\text{s}^{-1}\] | \(I_{	ext{on}}/I_{	ext{off}}\) | \(d_{	ext{sat}}\) \[\text{Å}\] | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| P90 | -5.14 | -3.91 | BGTC | Solution-shearing | 17.8 | >10^4 | – | – | 3.60 | [103] |
| P91 | -5.16 | -3.93 | BGTC | Solution-shearing | 10.3 | >10^4 | – | – | 3.61 | [103] |
| P92 | -5.12 | -3.87 | BGTC | Solution-shearing | 7.27 | >10^4 | – | – | 3.61 | [103] |
| P93 | -5.17 | -3.93 | BGTC | Solution-shearing | 4.75 | >10^4 | – | – | 3.57 | [103] |
| P94 | -5.28 | -3.97 | BGTC | Solution-shearing | 4.10 | >10^4 | – | – | – | [104] |
| P95 | -5.26 | -4.03 | BGTC | Solution-shearing | 0.80 | >10^4 | – | – | – | [104] |
| P96 | -5.27 | -3.98 | BGTC | Solution-shearing | 4.69 | >10^4 | – | – | – | [104] |
| P97 | -5.27 | -3.90 | BGTC | Solution-shearing | 1.20 | >10^4 | – | – | – | [104] |
| P98 | -5.25 | -3.97 | BGTC | Solution-shearing | 8.74 | >10^4 | – | – | – | [104] |
| P99 | -5.27 | -4.00 | BGTC | Solution-shearing | 1.23 | >10^4 | – | – | – | [104] |
| P100 | -5.26 | -3.94 | BGTC | Solution-shearing | 6.69 | >10^4 | – | – | – | [104] |
| P101 | -5.27 | -3.97 | BGTC | Solution-shearing | 4.85 | >10^4 | – | – | – | [104] |
| P102 | -5.0 | -3.5 | BGTC | Spin-coating | 0.54 | 5 \times 10^3 | – | – | – | [105] |
| P103 | -4.9 | -3.4 | BGTC | Spin-coating | 0.007 | 3 \times 10^3 | – | – | – | [105] |
| P104 | -4.9 | -3.4 | BGTC | Spin-coating | 1.05 | 2 \times 10^3 | – | – | – | [105] |
| P105 | -4.9 | -3.4 | BGTC | Spin-coating | 0.32 | 8 \times 10^3 | – | – | – | [105] |
| P106 | -5.27 | -3.53 | BGBC | Spin-coating | 3.5 | 10^{6–10^7} | – | – | 3.79 | [107] |
| P107 | -5.26 | -3.56 | BGBC | Spin-coating | 5.7 | 10^{6–10^7} | – | – | 3.76 | [107] |
| P108 | -5.25 | -3.57 | BGBC | Spin-coating | 6.1 | 10^{6–10^7} | – | – | 3.73 | [107] |
| P109 | -5.20 | -3.64 | BGBC | Spin-coating | 8.1 | 10^{6–10^7} | 0.48 | 10^{2–3} | 3.69 | [108] |
| P110 | -5.21 | -3.66 | BGBC | Spin-coating | 9.4 | 10^{6–10^7} | 0.79 | 10^{2–3} | 3.67 | [108] |
| P111 | -5.28 | -3.64 | BGBC | Spin-coating | 1.35 | 10^{6–10^7} | 0.19 | 10^{2–3} | 3.68 | [108] |
| P112 | -5.43 | -4.01 | BGBC | Spin-coating | 0.53 | 10^4 | – | – | 3.51 | [109] |
| P113 | -5.42 | -4.01 | BGBC | Spin-coating | 2.22 | 10^4 | – | – | 3.52 | [109] |
| P114 | -5.42 | -4.01 | BGBC | Spin-coating | 0.43 | 10^4 | – | – | 3.53 | [109] |
| P115 | -5.15 | -3.90 | TGBC | Spin-coating | 2.8 | >10^4 | 2.4 | – | 3.7 | [110] |
| P116 | -5.13 | -3.81 | TGBC | Spin-coating | 0.48 | >10^4 | 0.31 | – | 3.6 | [110] |
| P117 | – | – | TGBC | Spin-coating | 0.075 | >10^4 | 0.073 | – | 3.6 | [110] |
| P118 | – | – | TGBC | Spin-coating | 0.011 | >10^4 | 0.018 | – | – | [110] |
| P119 | -5.8 | -3.8 | TGBC | Spin-coating | – | – | 0.0011 | 2300 | 4.19 | [111] |
| P120 | -6.1 | -4.1 | TGBC | Spin-coating | – | – | 0.0092 | 38 000 | 4.05 | [111] |
| P121 | -5.7 | -4.0 | TGBC | Spin-coating | – | – | 0.016 | 41 000 | 3.81 | [111] |
| P122 | -4.9 | -3.19 | TGBC | Spin-coating | 1.51 | 10^4 | – | – | 3.62 | [112] |
| P123 | -4.9 | -3.18 | TGBC | Spin-coating | 2.58 | 10^4 | – | – | – | [112] |

\(^{a}\)HOMOs or LUMOs were calculated by cyclic voltammetry. \(^{b}\)LUMOs were calculated from HOMOs and optical bandgap \(\left(E_{g}^{opt}\right)\) with the following equation: 

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}^{opt};
\]

\(^{c}\)HOMOs were calculated by ultraviolet photoelectron spectroscopy (UPS), and LUMOs were calculated from HOMOs and optical bandgap \(\left(E_{g}^{opt}\right)\) with the following equation: 

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}^{opt};
\]

\(^{d}\)BGBC: bottom gate bottom contact; BGTC: bottom gate-top contact; TGBC: top gate bottom contact; \(^{e}\)Average saturated mobility.
Figure 1. a) Schematic diagram showing the edge-on arrangement of polymer chains for P3HT, P1, and P2 in the terraces; b) schematic illustration of the microstructure aggregates of P5 and the homopolymer. a) Reproduced with permission. Copyright 2007, American Chemical Society; b) Reproduced with permission. Copyright 2016, American Chemical Society.

Scheme 2. Chemical structures of P10–P24 by modifying the substitution positions of the alkyl chains.
of the DFT calculations. Thus, P17 shows the lowest degree of conformational disorder and the longest effective conjugation length. This is well correlated with its redshifted absorption compared to those of P18 and P19. The planar conjugated backbone of P17 is favorable for interchain orderly packing. In fact, P17 shows excellent performance in field-effect transistors with hole mobilities up to 4.6 cm² V⁻¹ s⁻¹ (Figure 2a and Table 1). The conjugated polymers P20 and P21 described by Yang and co-workers also contain TVT moieties. They found that the positioning of two n-hexyl chains attached to the TVT moiety has a significant effect on the interchain packing and charge transporting behavior. The polymer chains of P20 are orientated in both the edge-on and face-on modes on the substrate, which is favorable for 3D charge transporting. In comparison, the polymer chains of P21 only show the edge-on packing mode (Figure 2b). Thin film of P20 exhibits high hole mobility up to 1.69 cm² V⁻¹ s⁻¹, being twofold larger than that in the thin film of P21. Li and co-workers also substantiated that the alkyl chain positioning plays an important role in determining the polymer chain packing, thin film morphology and semiconducting performance with P22, P23, and P24 (Scheme 2). They grouped the alkyl chains attached to both electron donor and acceptor moieties into clusters, and claimed that the large space between the clusters of the alkyl chains is favorable for the interdigitations of the side chains and the formation of lamellar stacking structures for P22. Accordingly, P22 shows the highest thin film charge mobility among the three polymers (Table 1).

2.3. The Length of Alkyl Chains

Long alkyl chains are favorable for increasing the solubilities of conjugated polymers, and thus improving solution processability. However, alkyl chains are not intrinsically semiconducting. Thus, short alkyl chains are, in principle, beneficial for boosting the charge transporting performances of semiconducting polymers. Increasingly studies are demonstrating that differences in the alkyl chain length can alter the lamellar packing of polymer chains, resulting in the variation of lamellar d-spacing and thin film crystallinity and morphology (Scheme 3 and Table 1). For instance, P25–P29, as reported by Bao and co-workers, possess the same conjugated backbone and similar branching alkyl chains, and they are different only in the length of one alkyl chain arm. As shown in Figure 3a, P25–P26 with short alkyl chain arms preferentially adopt a dominant edge-on orientation on the substrate. For instance, P25, with the shortest alkyl chain shows entirely the edge-on orientation. By lengthening the alkyl chain arm, the polymer chains of P27–P28 are packed in both the edge-on and face-on packing modes with an increased percentage of the face-on fraction. The coexistence of the face-on and edge-on orientations is beneficial for charge transport, as they provide 3D conducting pathway and allow charges to travel both in the planes perpendicular and parallel to the substrate. Among the polymers, P28, with the most balanced edge-on/face-on orientation, shows the highest hole mobility of 3.69 ± 0.42 cm² V⁻¹ s⁻¹ (average mobility). Kim and co-workers investigated P30–P32.
with branching alkyl chains of different lengths. A close interchain packing with short lamellar spacing (22.47 Å) and π–π stacking distance was observed for P30 with short alkyl chains. P30, with 2-hexyldecyl as the side chains, displays the best semiconducting property with thin film electron mobility of 1.9 cm² V⁻¹ s⁻¹. A similar trend with regard to interchain packing and charge mobility was also reported for semiconducting polymers P33–P35.

When the alkyl chains are adjacent along the backbones, the lengths of the alkyl chains can affect the backbone coplanarity and thus interchain packing. As shown in Scheme 3, the same alkyl chain (2-butyloctyl) is attached to each dithieno[3,2-b:6,7-b’]fluorene, the unit in P37 and P38, but the alkyl chain (2-octyldodecyl) linked to each DPP moiety in P38 is longer than that (2-ethylhexyl) in P36 and P37. The steric congestion of neighboring alkyl chains along the backbone of P38 jeopardizes efficient intramolecular conjugation and intermolecular stacking. As a result, the thin film of P38 shows a less ordered morphology and a much lower mobility compared with P37, which displays a high thin film mobility of 5.26 cm² V⁻¹ s⁻¹ (Table 1). A similar steric hindrance effect owing to long linear alkyl chains was also observed for naphthodithiophene-based polymers P39–P41, as reported by Takimiya and co-workers.

As an interesting case, poly(3-alkylthiophene) (P42, P43, and P44) with different linear alkyl chain (CnH2n+1) lengths of n = 4, 6, 12 shows increased mobilities up to fivefold after rubbing, as the alkyl side chains become longer (Figure 3b). Polarized absorption and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements indicate that the P44 with the longest alkyl chains has a highly oriented structure in the in-plane direction and increased stacking in the out-of-plane direction after rubbing due to a low tensile modulus from the long alkyl chain.

2.4. The Branching Point Position of Side Chains

Branching alkyl chains are usually attached to the donor and/or acceptor moieties of conjugated D–A polymers to improve their solubilities in organic solvents. Many groups have investigated

Scheme 3. Chemical structures of polymers P25–P44 with alkyl chains of different lengths.
the effect of the branching point position of branching alkyl chain on the solid state structures and charge transporting behaviors of conjugated polymers (Scheme 4). In most cases, the polymer backbones become more planar, and the interchain packing and charge mobilities are improved after moving the branching points away from the backbones. For instance, as shown in Scheme 4 and Table 1, Pei and co-workers reported on isoindigo-based conjugated polymers P45, P46, P47, and P48, which entail the same conjugated backbone and different branching alkyl chains. The branching point is gradually moving away from the backbone and the spacer between the branching point and the N-position is lengthened in the following sequence: P45 < P46 < P47 < P48. The backbones of P47 and P48 become more planar after moving the branching point positions further away from the backbones. This explains well the observed redshifted absorptions of P47 and P48 in comparison with those of P45 and P46. The planar backbones are favorable for the dense interchain packing. In fact, the interchain π–π stacking distances for P47 and P48 are shorter than those of P45 and P46. Importantly, P47 and P48 exhibit higher field-effect charge mobilities than P45 and P46. In particular, the thin film of P47 shows an exceptionally high mobility of 3.62 cm² V⁻¹ s⁻¹. These results clearly demonstrate that a subtle change of branching point of the branching side chains can exert a significant effect on the interchain stacking and semiconducting performance of conjugated polymers.

Choi and co-workers come to a similar conclusion with the isoindigo-based conjugated polymers P49 and P50, in which TVT is utilized as the electron donor unit. The branching point is separated from the N-position by –(CH2)6 for P49, while the corresponding spacer is –(CH2)3 for P50. As expected, P49 shows a shorter interchain π–π stacking distance and higher charge mobility than P50. Pei and co-workers prepared conjugated polymers P51–P56 (Scheme 4 and Figure 4a) with benzodifurandione-based poly(p-phenylene vinylene) (BDPPV) as the backbone. In P51–P56, the branching points of the side chains are gradually moved away from the respective N-positions. For P45–P50, the interchain π–π stacking is strengthened by prolonging the spacer between the branching points of the side chains and the corresponding N-positions. As shown in Figure 4a, P54, P55, and P56, for which the spacers are –(CH2)4, –(CH2)5, and –(CH2)6, respectively, show an unprecedentedly close π–π stacking distance, i.e., as low as 3.38 Å on the basis of GIWAXS data. P51–P56 are air-stable n-type semiconductors. Unfortunately, the electron mobilities are not well correlated to the interchain packing distances. Actually, other factors including the polymer packing conformation, thin film crystallinity, and morphology show significant influence on the device performance. Among P51–P56, the thin film of P53 shows the highest electron mobility, i.e., up to 1.40 cm² V⁻¹ s⁻¹.

The effect of branching point of side chains on the interchain packing and semiconducting performance was also
explored for DPP-based conjugated polymers. Chung and co-workers prepared DPP-based conjugated polymers P57–P60 with either TVT or the selenophene analog as the electron acceptors. P57 and P58 possess the same conjugated backbone, but there are differences in the spacers that link the corresponding N-position and the branching chains. This holds true for P59 and P60. In comparison with P57 and P59, P58, and P60 exhibit improved backbone coplanarity and thin film crystallinity. The interchain π–π stacking distance is shortened from 3.7 Å for P57 and P59 to 3.62 Å for P58 and 3.58 Å for P60. Eventually, high hole mobilities of 10.54 and 12.04 cm² V⁻¹ s⁻¹ are achieved for the thin films of P58 and P60, respectively, after thermal annealing. The improvement of thin film crystallinity and enhancement of charge mobility were also reported for DPP-based polymers P61–P66 and P84–P85 and other semiconducting polymers P67–P83 by varying the branching point in the side chains. For conjugated polymers P84–P85, however, the effect of side alkyl chains with different branching positions on their charge transporting properties is not distinct.

An interesting odd–even characteristic was observed for the DPP-based conjugated polymers P86–P93 and P94–P101 regarding the dependence of their semiconducting performances on the lengths of the spacers between the branching points and the corresponding N-positions (Scheme 4 and Figure 4b). P86, P88, and P90, with spacer groups containing even numbers of carbon atoms exhibit higher charge mobilities than P87 and P89, with odd numbers of carbon atoms in
the respective spacers. Among P86–P93, P90, with a C6 spacer, shows the highest hole mobility up to 17.8 cm² V⁻¹ s⁻¹ after optimization. Similarly, P98 exhibits the best semiconducting property with charge mobility up to 8.74 cm² V⁻¹ s⁻¹, among P94–P101. It is noted that the odd–even trend fails when the spacer groups are longer than −(C₆H₁₂) for P91–P93. Such an odd–even effect of the branching point on the chain packing, morphology, and charge transporting performance has also been demonstrated by Liu and co-workers with the quinoidal para-azaquinodimethane-based conjugated polymers P102–P105.[105]

2.5. The Partial Replacement of Branching Alkyl Chains with Linear Ones

The steric hindrance owing to the bulky branching chains can be weakened by moving the branching points of side chains away from the conjugated backbones as discussed in the above section. However, the respective alkyl halogens, which are used for the synthesis of the respective monomers in which the branching points of side chains are gradually moved away from the conjugated frameworks, are not commercially available. Their syntheses involve three or more reaction steps and purifications.[99,97,106] This will add additional cost for the preparation of the conjugated polymers with branching alkyl chains.

Alternatively, some of us devised a new approach to reduce the steric hindrance of branching alkyl chains and improve the interchain packing by replacing partial branching alkyl chains with linear ones (Scheme 5).[107,108] Initially, we prepared P106–P108 by co-polymerization of the bis-stannyl compound with two DPP monomers with the respective branching alkyl chains and linear chains.[107] The ratio of the branching alkyl chain versus the linear chain in P106–P108 can be tuned by varying the feed ratio of the two DPP monomers. By increasing the content of linear chains, the GIWAXS signal intensities due to the interchain lamellar and π–π packing increase; thus, the thin film crystallinity is improved. As a result, the partial replacement of branching alkyl chains with linear ones leads to obvious charge mobility enhancement. Recently, we designed and studied P109 and P110, in which each DPP unit contains one branching alkyl chain and one linear chain.[108] Both theoretical calculation and experimental studies (UV–vis, Raman and Photothermal deflection spectra) reveal that the backbone of P110 is more planar than that of P111, in which two branching alkyl chains are attached to each DPP unit. Furthermore, the thin films of P109 and P110 exhibit the edge-on packing mode, while the thin film of P111 exhibits the face-on packing mode (Figure 5). Both the hole and electron mobilities are boosted for P109 and P110 compared to those of P111.

Mei and co-workers reported on P112, P113, and P114, in which both the linear and branching alkyl chains are attached to the backbones.[109] They found that the sequence of the arrangement of alkyl chains along the backbone has a significant effect on the aggregation behaviors of polymer chains. P112, with the “linear-branching-branching-linear (LBBL)” arrangement sequence of alkyl chains, shows the largest ordered domains and smooth fibrillar intercalating network morphology, and thus, the thin film of P112 exhibits the highest hole mobility, i.e., 2.22 cm² V⁻¹ s⁻¹. In comparison, P114 in which the branching and linear chains are randomly arranged along the backbone shows the lowest thin film hole mobility.

As shown in Scheme 5, in P115–P118, both branching and linear alkyl chains are attached to different repeat units.[110] The side chains were reported pronounced effects on the thin film structures and semiconducting performances of these polymers.

Figure 4. a) Schematic illustration of the microstructure of the conjugated polymer film, the edge-on packing model observed for conjugated polymer chains in good π–π stacking zones (up), and the average electron mobilities with error bars and π–π distances for P51–P56; b) The average mobilities and d(100)-spacing of the thin films of P86–P93. a) Reproduced with permission,[93] Copyright 2014, Wiley-VCH; b) Reproduced with permission.[103] Copyright 2015, American Chemical Society.
Sirringhaus and co-workers examined the effect of side chains with P115–P118, P115, P116, and P117, in which linear alkyl chains are attached to the DPP units, show better thin film crystallinity based on the GIWAXS data than P118. As anticipated, P115, P116, and P117 display better ambipolar semiconducting performance with higher hole and electron mobilities.
Among these four polymers, P115, with linear and branching chains on the DPP and benzotriazole (BTZ) moieties, respectively, exhibits excellent ambipolar charge transfer performance with $\mu_e$ and $\mu_h$ values of 1.5 and 2.4 cm$^2$ V$^{-1}$ s$^{-1}$, which are much higher than those of P116–P118, with linear chains on BTZ. Similarly, the way that the branching and linear chains are attached to the NDI and benzene moieties affects the electron transporting performance of P119–P121.[111] P121, in which the branching and linear chains are linked to NDI and benzene units, respectively, exhibits the highest electron mobility.

The effects of the side chains can be complex. For instance, the pristine thin film of P122, in which the linear chains are attached to the benzotriazole units, shows higher charge mobility than that of P123, which entails branching chains on the benzotriazole units.[112] Interestingly, after thermal annealing P123 shows better semiconducting property than P122. It is noted that conjugated polymers with chiral alkyl chains were investigated for chiroptical properties,[113–115] but the effects of chiral groups on their semiconducting performances were not examined.

3. Side Chains with Heteroatoms and Functional Groups

3.1. Fluoroalkyl Chain

Fluoroalkyl chains including perfluorinated and semifluorinated alkyl chains own unique properties coming from the fluorine atoms, which have strong electron affinity. These include chemical and thermal stability, hydrophobicity and a self-assembly ability.[116–119] For this reason, fluoroalkyl chains are attached to conjugated polymers to tune their solid state structures and improve their semiconducting performances.[7,10,66,120–123] The studies reveal that the unique fluorophbic interactions due to the fluoroalkyl chains can promote the polymer chains to form more orderly assembly structures and thus boost their charge transporting properties. Furthermore, the hydrophobic feature and the closely packed structure of fluoroalkyl chains are beneficial to inhibit the diffusion of moisture and oxygen into the semiconducting films, thereby enhancing the stability of the polymers in air.

As shown in Scheme 6 and Table 2, polythiophenes (P124–P128) with perfluoroalkyl, semifluoroalkyl, alternating alkyl/perfluoroalkyl and alternating alkyl/semifluoroalkyl chains were prepared and investigated.[120] The polymer chains of P124–P128 are spontaneously assembled into highly ordered bilayer lamellar structures due to segregation of the hydrocarbon and semifluorinated chains. The field-effect hole mobilities can reach $1.45 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for these polythiophenes with regioregularly substituted alkyl and semifluorinated chains. Polyquaterthiophene P129, with semifluorinated alkyl groups as side chains can be self-assembled into worm like fibrils (Figure 6a).[121] The formation of such orderly self-assembly structures is attributed to the attractive interaction between polymer chains and repulsive interaction between the polymer and the nonfluorous solvent. The worm like fibril morphology offers an excellent carrier transfer pathway for efficient hole transfer and results in mobilities up to 0.36 cm$^2$ V$^{-1}$ s$^{-1}$, which is more than two times higher than that for the respective polymers with pure alkyl chains. In particular, P129 shows a unique thermally reversible soluble-insoluble property, which enables the formation of a solution-processed bilayer structure and orthogonal processing, which are essential for the fabrication of ambipolar transistors and patterned complementary inverters.
Table 2. OFET performance of polymers P124–P126.

| Polymers | HOMO[a–c] [eV] | LUMO[a–c] [eV] | Device structure[s] | Deposition process | Max $\mu_h$ [cm² V⁻¹ s⁻¹] | $I_{on}/I_{off}$ | Max $\mu_d$ [cm² V⁻¹ s⁻¹] | $I_{on}/I_{off}$ | $d_{on}–d_{off}$ [Å] | Ref. |
|----------|----------------|----------------|--------------------|-------------------|--------------------------|----------------|--------------------------|----------------|------------------------|------|
| P124     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [120]|
| P125     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [120]|
| P126     | –              | –              | BGBC               | Spin-coating      | $1.45 \times 10^{-2}$    | $> 10^4$      | –                        | –              | –                      | [120]|
| P127     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [120]|
| P128     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [120]|
| P129     | –              | –              | TGBC               | Dip-coating       | –                        | –             | –                        | –              | –                      | [121]|
| P130     | –              | –              | BGTC               | Spin-coating      | –                        | –             | $6.5 \times 10^5$         | 4.1            | –                      | [66] |
| P131     | –              | –              | BGTC               | Spin-coating      | –                        | –             | $5.64 \times 10^5$        | 4.1            | –                      | [66] |
| P132     | –              | –              | BGTC               | Spin-coating      | $0.246$                 | $1.11 \times 10^4$ | –                        | –              | –                      | [122]|
| P133     | –              | –              | TCBC               | Off-center spin-coating | $1.02$               | $10^4$        | –                        | –              | 3.63                    | [123]|
| P134     | –              | –              | BGTC               | Spin-coating      | $2.48$                   | $> 10^4$      | –                        | –              | 3.58                    | [65] |
| P135     | –              | –              | BGTC               | Spin-coating      | $0.57$                   | $> 10^4$      | –                        | –              | 3.76                    | [65] |
| P136     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [125]|
| P137     | –              | –              | –                  | –                 | –                        | –             | –                        | –              | –                      | [125]|
| P138     | –              | –              | BGTC               | Spin-coating      | $1.9$                    | $10^6$        | –                        | –              | 3.413                   | [125]|
| P139     | –              | –              | BGTC               | Spin-coating      | $3.2$                    | $10^4$        | –                        | –              | 3.402                   | [125]|
| P140     | –              | –              | BGTC               | Spin-coating      | $3.2$                    | $10^6$        | –                        | –              | 3.414                   | [125]|
| P141     | –              | –              | BGTC               | Spin-coating      | $3.0$                    | $10^5$        | –                        | –              | 3.393                   | [125]|
| P142     | –              | –              | BGTC               | Spin-coating      | $4.8$                    | $10^6$        | –                        | –              | 3.392                   | [125]|
| P143     | –              | –              | BGTC               | Spin-coating      | $2.0$                    | $10^5$        | –                        | –              | 3.392                   | [125]|
| P144     | –              | –              | BGTC               | Spin-coating      | $1.8$                    | $10^5$        | –                        | –              | 3.379                   | [125]|
| P145     | –              | –              | BGBC               | Spin-coating      | $5.1$                    | $> 10^5$      | –                        | –              | 3.58                    | [127]|
| P146     | –              | –              | BGC               | Spin-coating      | $7.8 \times 10^{-2}$     | $10^3$        | –                        | –              | 3.51                    | [128]|
| P147     | –              | –              | BGC               | Spin-coating      | $4.7 \times 10^{-3}$     | $10^{3}$      | $1.5 \times 10^{-3}$      | $10^3$         | 3.59                    | [128]|
| P148     | –              | –              | BGC               | Spin-coating      | $1.1 \times 10^{-3}$     | $10^{4}$      | $1.2 \times 10^{-1}$      | $10^4$         | –                      | [128]|
| P149     | –              | –              | BGC               | Drop-coating      | $4.55$                   | $> 10^6$      | –                        | –              | 3.62                    | [129]|
| P150     | –              | –              | BGC               | Solution-shearing | $6.16$                   | $> 10^4$      | $3.07$                   | $> 10^3$       | 3.70                    | [131]|
| P151     | –              | –              | BGC               | Solution-shearing | $8.84$                   | $> 10^4$      | $4.34$                   | $> 10^3$       | 3.66                    | [131]|
| P152     | –              | –              | BGC               | Solution-shearing | $3.97$                   | $> 10^4$      | $2.20$                   | $> 10^3$       | 3.65                    | [131]|
| P153     | –              | –              | BGBC              | Spin-coating      | $0.74$                   | $10^2$        | $0.87$                   | $10^3$         | –                      | [132]|
| P154     | –              | –              | BGBC              | Spin-coating      | $0.52$                   | $10^3$        | $0.35$                   | $10^{3}$       | –                      | [132]|
| P155     | –              | –              | TGBC              | Spin-coating      | $1.04$                   | $10^1$        | $3.88$                   | –              | –                      | [133]|
| P156     | –              | –              | TCBC              | Spin-coating      | $0.93$                   | $10^1$        | $3.85$                   | –              | –                      | [133]|
| P157     | –              | –              | TGBC              | Spin-coating      | $3.22$                   | $10^6$        | –                        | –              | 3.61                    | [134]|
| P158     | –              | –              | TGBC              | Spin-coating      | $8.06$                   | $10^6$        | –                        | –              | 3.55                    | [134]|
| P159     | –              | –              | TGBC              | Spin-coating      | $1.76$                   | $10^5$        | –                        | –              | –                      | [135]|
| P160     | –              | –              | TGBC              | Spin-coating      | $1.98$                   | $10^7$        | –                        | –              | 3.61                    | [135]|
| P161     | –              | –              | TGBC              | Spin-coating      | $1.33$                   | $10^5$        | –                        | –              | –                      | [135]|
| P162     | –              | –              | TGBC              | Spin-coating      | $0.78$                   | $8 \times 10^5$ | –                        | –              | 3.5                     | [136]|
| P163     | –              | –              | TGBC              | Spin-coating      | $0.33$                   | $2 \times 10^4$ | –                        | –              | 3.5                     | [136]|
| P164     | –              | –              | TGBC              | Spin-coating      | $0.22$                   | $8 \times 10^4$ | –                        | –              | 3.5                     | [136]|
| P165     | –              | –              | TGBC              | Spin-coating      | $0.063$                  | $3 \times 10^4$ | –                        | –              | 3.5                     | [136]|
| P166     | –              | –              | TGBC              | Spin-coating      | $< 10^{-7}$              | $10^1$        | –                        | –              | –                      | [136]|
| P167     | –              | –              | TGBC              | Spin-coating      | $1.58 \times 10^{-4}$    | $10^1$        | –                        | –              | –                      | [139]|
| P168     | –              | –              | TGBC              | Spin-coating      | $3$                      | $10^4$        | $3.6$                    | –              | –                      | [140]|

---

*a*–*c* Ref. **Mater.**
Cho and co-workers demonstrated that the n-type charge transporting performance of NDI-based conjugated D–A polymers P130 and P131 can be significantly improved by attaching the semifluorinated alkyl chains to the NDI units.\[66\] The presence of semifluoroalkyl side chains increases the backbone rigidity and the crystalline order of the thin films.
of P130 and P131 largely. They claimed that the strong self-organization of semifluoroalkyl side chains induced the polymer chains to form a superstructure composed of “backbone crystals” and “side-chain crystals” (Figure 6b). Electron mobilities of 3.93 and 3.75 cm² V⁻¹ s⁻¹ were measured with the respective field-effect transistors for P130 and P131, respectively. After introducing chloronaphthalene into the thin films of P130 and P131 as an additive, their electron mobilities were further boosted to 6.50 and 5.64 cm² V⁻¹ s⁻¹, respectively. It is noted that the electron mobilities of P130 and P131 are much higher than those of the analogous polymers with the same backbones and pure alkyl chains. Moreover, the devices with P130 and P131 display superior ambient stability because of the presence of semifluoroalkyl side chains. The beneficial effects of fluoroalkyl side chains were also explored for other semiconducting polymers such as P132 and P133 (Scheme 6).

3.2. Side Chains with Silicon Atoms

The widely used side chains with silicon atoms for semiconducting polymers are alkyl siloxane-terminated side chains with 1,1,1,2,5,5,5-heptamethyltrisiloxane as the terminal group. This siloxane unit has the following structural characteristics: i) a long Si–O bond length (1.64 Å), which is longer than the C–C bond length (1.53 Å); and ii) a large Si–O–Si bond angle (143°), which is larger than the usual tetrahedral angle (110°). These structural features are expected to produce good solubilities for conjugated polymers. The linear alkyl chain as the spacer between the terminal siloxane group and the conjugated backbone can be finely tuned to endow good solubilities and simultaneously to promote the interchain orderly packing. Additionally, the synthesis of monomers with siloxane-terminated side chains can be synthesized in a straightforward way. In comparison, the synthesis of the respective monomers containing branching alkyl chains with different spacers involves multistep synthetic efforts.

As shown in Scheme 7 and Table 2, Bao and co-workers first introduced hybrid siloxane terminated alkyl chains to the isoindigo-based conjugated D–A polymer P134. Based on the reference polymer P135, P134 shows good solubilities in organic solvents because of the bulky siloxane group. As the bulky siloxane group is separated by –CH₂)₆ from the backbone in P134, the interchain packing distance is shortened to 3.58 Å. As a result, a hole mobility up to 2.48 cm² V⁻¹ s⁻¹ was achieved for the thin film of P134. They further prepared a series of isoindigo-based polymers, i.e., P136–P144, with siloxane terminated side chains in which the lengths of linear alkyl spacers are systematically varied from –(C₃H₆) to –(C₁₁H₂₂). For P136–P144, the interchains are more closely packed and the thin film crystallinities are improved by gradually increasing the lengths of spacers in the same way as with the conjugated polymers with branching alkyl chains discussed in Sections 2–4. However, different from conjugated polymers with branching alkyl chains, P136–P144 with siloxane chains tend to take bimodal (face-on and edge-on) orientations for their polymer chains to pack on the substrate. The thin film hole mobilities of P138–P144 are higher than 1 cm² V⁻¹ s⁻¹, which is one order of magnitude higher than the polymer
with the same backbone but pure branched alkyl side chains. Among these polymers, P142 shows the highest mobility, i.e., up to 4.8 cm² V⁻¹ s⁻¹.

Kim and co-workers studied the temperature-dependent nanostructure and electrical conduction of polymers with siloxane side chains, and they concluded that the bimodal packing of polymer chains can enhance 3D charge transport.[126] Mei and co-workers prepared P145, in which each isoindigo unit contains one siloxane side chain and one alkyl chain, to tune the interchain packing mode.[127] The presence of two side chains at the isoindigo units in P145 resulted in a balanced bimodal orientation and high charge mobility of 5.1 cm² V⁻¹ s⁻¹, outperforming with reference polymers with either pure alkyl side chains or pure siloxane side chains (Table 2). The interchain packing was also reported to be reinforced for P146–P148 (Scheme 7), with the thienoisindigo and thiophene-flanked DPP in their backbones by moving the siloxane groups away from the backbones.[128]

The siloxane chains were introduced to the DPP-based conjugated polymers P149–P152.[129–131] Bimodal interchain packing was also observed for P149.[129] In comparison, the reference polymer with the same backbone, to which branching alkyl chains with −(CH₂)₄ as the spacer are attached, shows the predominant edge-on packing mode. Nevertheless, P149 shows similar thin film mobility as the reference polymer. It is interesting to note that the field-effect devices with P149 display unexpectedly good air stability. P150–P152 exhibit ambipolar semiconducting behavior, and their hole and electron mobilities are dependent on the length of the linear alkyl spacer in the siloxane chains.[130,131] Unprecedentedly high hole and electron mobilities of 8.84 and 4.34 cm² V⁻¹ s⁻¹ are achieved for the solution-sheared thin film of P151, which have the siloxane-terminated side chains with −(C₆H₁₀) as the spacer. Some of us reported that bipyrrylidene-2,2′(1H,1′H)-dione (BPD)-based conjugated polymers P153 and P154 exhibit more balanced hole and electron mobilities by using the siloxane terminated chains.[132]

Hybrid siloxane terminated hexyl chains are attached to the NDI units of the n-type semiconductor polymers P155 and P156, in which bithiophene and TVT are the respective electron donor moieties.[133] It was found that the edge-on and face-on packing modes were influenced by the solvents used to dissolve and process the polymers. When chloroform was used as the solvent, the polymer chains adopted balanced edge-on and face-on packing modes, resulting in a high thin film electron mobility of 1.04 cm² V⁻¹ s⁻¹ (Figure 7a and Table 2). In comparison, the polymer chains of P156 were predominantly oriented in edge-on mode and its thin film electron mobility was measured to be 0.93 cm² V⁻¹ s⁻¹.

Apart from siloxane, carbosilane was also utilized as side chains for semiconducting polymers.[134] Chen and co-workers reported on the isoindigo-based polymers P157 and P158, with carbosilanes as the side chains.[134] A thin film mobility up to 8.06 cm² V⁻¹ s⁻¹ was achieved for P158. In particular, the presence of branching carbosilane chains endows them to possess superior thin film ductility with a low tensile modulus in the range of 0.27–0.43 GPa. The charge mobility of P158 remained over 1 cm² V⁻¹ s⁻¹, even under a 60% strain along the parallel or perpendicular direction to the tensile strain. In addition, the polymer thin film can be simultaneously operated over 400 stretching/releasing cycles and maintain stable electronic characteristics. These results show that semiconducting polymers with carbosilane side chains possesses great potential for next-generation skin-inspired wearable electronic application with high charge transfer mobility, low tensile modulus, and stable device characteristics during stretching.

Bao and co-workers devised an innovative method to induce elasticity and enhance the stretchability of semiconducting polymers (P159–P161), to which alkene-terminated linear side chains are attached, by cross-linking with siloxane oligomers, as illustrated in Figure 7b.[135] The cross-linking network increases the elasticity and improves the fracture strain. The crosslinked polymers produce stretchable films that are stable up to a strain of 150 and 500 stretching/releasing cycles of 100% strain without the formation of cracks. Importantly, a thin film charge mobility of 0.40 cm² V⁻¹ s⁻¹, which is comparable to an average hole transfer mobility of 0.66 cm² V⁻¹ s⁻¹ under 0% strain, can be obtained after 500 stretching/releasing cycles of 20% strain. Alternatively, the mechanical properties of semiconducting polymers (P162–P166) can be improved by partial replacement of siloxane-terminated side chains with poly(butyl acrylate) (PBA) chains by taking advantage of the low glass transition temperature and high softness of the PBA segment.[136]

3.3. Oligo (Ethylene-Glycol) (OEG) Side Chain

OEG chains are nonionic, highly polar, hydrophilic, and flexible.[137,138] The incorporation of OEG chains into semiconducting polymers can improve their solubilities in polar solvents (in particular in water) on one hand, and alter the interactions of side chains and thus tune the aggregate structures of polymers on the other hand.[139–145] As shown in Scheme 8 and Table 2, polythiophene P167 with triethylene glycol as side chains can be dissolved in water, and thus a thin film of P167 can be prepared with its aqueous solution.[139] The as-prepared thin film was found to be less ordered, but a wormlike nanofibrillar morphology was obtained after thermal annealing above the glass transition temperature. However, the charge mobility of the thermally annealed thin film was in the order of 10⁻⁵ cm² V⁻¹ s⁻¹. Patil and co-workers reported on the DPP-based conjugated polymer P168, in which the branching alkyl chains and OEG chains are alternatively attached to the DPP units.[140] The introduction of hydrophilic OEG chains induce the polymer chains to assemble and form large crystalline domains. Intriguingly, the top gate bottom contact (TGBC) devices with thin films of P168 show n-type transporting behavior with a maximum electron mobility of 3 cm² V⁻¹ s⁻¹. However, the corresponding bottom gate bottom contact (BGBC) transistors exhibit clear ambipolar transport with balanced electron and hole mobilities in the order of ±0.01 cm² V⁻¹ s⁻¹.

The side chains of P169 and P170 entail the linear alkyl chain and OEG segment.[141] While the OEG segment is at the end of the side chain in P169, the OEG segment is directly connected to the backbone of P170 (Scheme 8). In comparison with NDI-based polymers with pure alkyl side chains that often show bimodal packing, P169 and P170, with hybrid alkyl and OEG chains, predominantly display the edge-on packing mode
after thermal annealing. This is likely owing to the hydrophilic feature of the OEG segments which induce the polymer chains to take the edge-on orientation on the hydrophobic octadecyltrichlorosilane (OTS) modified SiO$_2$/Si substrate. Both the thin films of P169 and P170 display good crystalline ordering with superior polymer-chain rigidity. As expected, transistors with thin films of P169 and P170 show typical n-type behavior. In particular, the thin film of P169 exhibits higher electron mobility of 0.51 cm$^2$ V$^{-1}$ s$^{-1}$, which is further boosted to 1.64 cm$^2$ V$^{-1}$ s$^{-1}$, after introducing 1-chloronaphtalene as an additive. Thin film of P170, however, possesses comparably low electron mobility.

Some of us incorporated OEG chains into the DPP-based polymers P171 and P172.$^{[14]}$ While the OEG and branching alkyl chains are randomly distributed along the backbone of P171, each DPP unit in P172 entails one branching alkyl chain and one OEG chain. On the basis of the GIXRD data, the edge-on orientation is favored for the polymer chains of

Scheme 7. Chemical structures of P134–P166 with silicon atom containing side chains.
both P171 and P172 on the hydrophobic substrate (Figure 8a). This is likely due to the presence of hydrophilic OEG chains in P171 and P172. P172, with uniformly distributed OEG chains shows spontaneous self-assembly behavior with more ordered packing, resulting in a higher hole mobility of $2.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ without any post treatment.

**Figure 7.** a) Chemical structures of P155 and P156, and the edge-on and face-on orientation population of the annealed films at 300 °C. b) Chemical structure of P159–P161 containing crosslinkable linear side chains, the crosslinker, and hydrosilylation reaction scheme. a) Reproduced with permission.© 2015, American Chemical Society; b) Reproduced with permission.© 2016, Wiley-VCH.
We prepared another DPP-based polymer, i.e., P173 in which each DPP unit is linked to tetra(ethylene glycol) (TEEG) and decyldodecyl side chains.[143] Monolayer and ultrathin films from bilayer to five-layer were successfully prepared through the assembly of P173 at an air–water interface by using the Langmuir–Schaefer method (Figure 8b). These ultrathin films were further utilized for the fabrication of FETs. The monolayer FET device shows p-type transporting behavior with a hole mobility of 0.014 cm² V⁻¹ s⁻¹. The device’s hole mobility increases by increasing the thickness of the ultrathin films, and it reaches 0.04 cm² V⁻¹ s⁻¹ for the three-layer FET device. The FET devices with ultrathin films of P173 were examined for alcohol sensing. In particular, the monolayer FET with P173 displays ultrahigh sensitivity toward ethanol vapor with detectable current variation at a concentration of 1 ppb. Moreover, the device shows good selectivity toward alcohol vapor, and the device current variation is extremely small after exposure to other solvent vapors and gases, such as CO₂, CH₂Cl₂, ethyl acetate, and acetone. This can be attributed to the interactions of hydrophilic TEEG chains in P173 and hydroxyl groups of alcohols.

It should be noted that FET-based sensors have been intensively explored.[67,144–154] However, they are mainly based on the physical adsorption/de-adsorption mechanism, and thus, the selectivity is still an open issue. The sensitivity issue has been addressed by incorporating functional groups in the side chains of semiconductors. For instance, Katz and co-workers prepared poly(alkylthiophene) P174 with tetrathiafulvalene (TTF) groups in the side chain.[144] The introduction of tetrathiafulvalene groups in the side chains in P174 resulted in the loss of hole mobility. However, the device with P174 shows a current-increase response to trinitrotoluene (TNT) as an analyte. This can be understood as follows: i) the electron donating TTF groups in the side chains of P174 can act as hole traps; ii) the electron donor–acceptor interactions between TNT as electron acceptor and TTF as electron donor can weaken the charge trapping effect. As a result, the device current increases after exposure of the P174-based FETs to TNT vapor.

### 3.4. Hydrogen Bonding Type Chain

Hydrogen bonding (H bonding) has been widely used to tune intermolecular interactions and self-assembly structures by considering its relative bonding strength and directionality.[155–163] On the basis of this consideration, as shown in Scheme 9 and Figure 9, some of us incorporated urea groups in the side chains of DPP-based polymers P175–P177[155] The formation of H bonding among the urea groups in P175–P177 were confirmed by the ¹H NMR and Fourier transform infrared spectroscopy (FTIR) studies. The lamellar packing of side chains is improved and the interchain π–π stacking is strengthened for P175–P177 compared with the reference polymer with the same backbone and pure alkyl chains with no urea groups (Figure 9a). Moreover, the sizes of the fibrillar domains within their thin films increase by increasing the contents of the urea groups in the side chains. The thin film hole mobilities of P175–P177 are higher than those of the reference polymer with
pure alkyl chains. Thin film charge mobility of P175, in which the molar ratio of the side chain with the urea group versus the branching alkyl chain is 1:10, can reach 13.1 cm$^2$ V$^{-1}$ s$^{-1}$ after thermal annealing. The studies of P175–P177 clearly demonstrate that appropriate modification of side chains by introducing functional groups is an efficient approach to improve the interchain packing order and boost the charge mobilities for semiconducting polymers.

We further extended this strategy to ambipolar semiconducting polymers, i.e., P178–P180, which entail different urea groups in the side chains. Pre-aggregation in solutions for P178–P179 occurs due to the interchain hydrogen bonding

![Figure 8.](image_url)

Figure 8. a) Chemical structures of P171–P172, and a schematic illustration of the interchain packing in the presence of hydrophilic oligo (ethylene-glycol) side chains. b) The chemical structure of P173, and a schematic illustration for the fabrication of FETs with the monolayer and ultrathin films by using the Langmuir–Schaefer technique. a) Reproduced under the terms of the Creative Commons Attribution 4.0 International (CC-BY-4.0) license.[142] Copyright 2017, the Authors. Published by Wiley-VCH. b) Reproduced with permission.[143] Copyright 2017, Wiley-VCH.
among the urea groups. GIWAXS characterizations indicate that the polymers chains of P178–P179 are more densely packed because both the π–π stacking and lamellar stacking distances are shortened compared to the reference polymer without urea groups in the side chains. Moreover, the polymer chains of P178–P179 are orientated in bimodal modes (edge-on and face-on) on the substrate, resulting in the formation of a 3D conduction channel for efficient carrier transfer. Both the hole and electron mobilities of P178–P179 are boosted compared to those of the reference polymer with only alkyl chains. The hole and electron mobilities of P179 are ≈25 and 3 times those of the reference polymer.

Rondeau-Gagné and co-workers introduced urea groups in the side chains of isoindigo-based polymers P181–P183.^[157] They show that the charge mobility enhancement is not obvious for these polymers when the contents of urea groups
are low. However, the thin film charge mobility for P183 with 20 mol% urea moieties in the side chains increases to 0.032 cm² V⁻¹ s⁻¹, which is ≈50 times of that for the analog polymer with branching and linear alkyl chains. These studies again demonstrate that the incorporation of urea moieties in the side chains is a promising strategy to control the nanoscale morphology, solubility, and polarity of conjugated polymers without reducing their semiconducting performances. They also incorporated amide groups in the side chains of conjugated polymers P184–P187. The results show that the additional interchain interactions due to H bonding among the amide groups can affect the interchain packing, thin film morphology and, thus, the charge transporting performance of conjugated polymers. Charge mobility enhancement was observed for P184, in which the molar ratio of amide-containing chains versus branching alkyl chains is 5:95. However, the charge mobility starts to decrease when more amide groups are incorporated, as in P185–P187. This was attributed to the reduction of aggregation of polymer chains and thin film crystallinity by increasing the contents of amides in the side chains based on the absorption spectral and morphological (with atomic force microscope (AFM)) studies. The authors claimed that hydrogen bonds due to amide groups in the side chains could induce a mismatch in the side chain aggregation and further disrupt the self-assembly of the side chains. Notably, P187, with high contents of amide groups in the side chains still maintain good solubility in

![Figure 9. a) Illustration of design rationale for the incorporation of urea groups in the side chains of P175–P177. b) Illustration of T–T intermolecular hydrogen bonding and the coordination with Pd(II) and Hg(II) (left), and a schematic illustration of the fabrication of FETs with thin films of P188–Pd(II) or P188–Hg(II) for sensing CO and H₂S, respectively. a) Reproduced with permission. Copyright 2016, American Chemical Society; b) Reproduced with permission. Copyright 2019, Wiley-VCH.](image-url)
organic solvents. They also demonstrated that the introduction of imide groups in the side chains could effectively enhance the mechanical properties of polymers P184–P186 to afford stretchability and morphology healing.\[159]\n
Apart from urea and amide groups, thymine, which is known as one of nucleobase units, was utilized as a H bonding unit to incorporate into the side chains of conjugated polymers, as reported very recently by some of us.\[168]\n
Similarly, the presence of thymine units in P188 promotes the lamellar packing of alkyl chains and the interchain π−π stacking, resulting in the improvement of thin film crystallinity and, thus, the charge transporting performance. Thymine groups can not only form H bonding, but also coordinate with certain metal ions (Figure 9b). By using this feature of thymine, the thin films of P188 with Pd(II) and Hg(II) ions were successfully prepared with the air–water interfacial coordination method. Furthermore, the resulting thin films of P188, with either Pd(II) or Hg(II) ions, were employed to fabricate thin film transistors, which can sense CO or H2S with rather high sensitivity and good selectivity. CO with a concentration as low as 10 ppb can be detected with the field-effect transistor with the P188-Pd(II) thin film, whereas the device current variation is still detectable. Thymine units in the side chains of the polymer without the insertion of a PDCA unit with the same device structure. Remarkably, high charge transport abilities are retained for these conjugated polymers upon application of strain. For instance, the charge mobility of the thin film of P195 can remain at 1.12 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 100% along the direction perpendicular to the strain. Moreover, the thin film shows a considerable self-healing ability. The semiconducting performances of the damaged devices can be almost fully recovered after a solvent and thermal healing treatment. Recently, they incorporated PDCA units into the side chains of P197–P200.\[163]\n
On the basis of FTIR studies, they concluded that the PDCA units in the side chains as in P197–P200, are more favorable for the formation of H bonding compared with those in P194–P196, in which the PDCA units are positioned in the backbones. Again, the incorporation of H bonding units (PDCA) in the side chains results in no charge mobility enhancement for P197–P200. This is due to the fact that P198–P200 exhibit lower thin film crystallinity in comparison with P197 which contains no PDCA units in the side chains. This was verified by the observation that the full width at half-maximum (FWHM) increased by increasing the PDCA contents in P198–P200 based on grazing incidence angle X-ray diffraction (GIXD) data. The H bonding among PDCA groups in the side chains of P198–P200 may prevent the polymer chains from having maximal π−π interaction. However, the thermal and mechanical properties of these conjugated polymers are improved by increasing the contents of the PDCA units in their side chains. Both the tan delta intensity and temperature, at which softening of film crosslinking occurs, increase linearly with the contents of the PDCA units in the side chains of P197–P200. P194–P196 and P198–P200 contain PDCA groups, but they exhibit different mechanical properties. The PDCA groups are incorporated in the backbones of P194–P196, while side chains of P198–P200 entail PDCA groups. The authors reported that the location (backbone versus side chain) of PDCA units in polymers affected the amounts of hydrogen bonds formed among PDCA groups and the temperature at which the H bonding breaking occurred. PDCA groups in side chains of P198–P200 are more favorable to form hydrogen bonds than those in backbones of P194–P196.

### 3.5. Side Chains with Ionic Groups

Conjugated polymers with pendant ionic groups, which are usually referred as to conjugated polyelectrolytes (CPEs), have been extensively investigated.\[164,165]\n
In particular, the light-emitting CPEs have been widely explored for biosensing and imaging.\[166–168]\n
In recent years, new CPEs have been designed and investigated to improve charge injection in OLEDs,\[169–171]\n
charge extraction in OPVs,\[172–175]\n
and OFETs.\[176–178]\n
CPEs were also used as sensitizers in dye-sensitized solar cells.\[179,180]\n
As shown in Scheme 10, Seo and co-workers reported on conjugated polymers, i.e., P201 and P202, with cationic groups in their side chains.\[176\] The spectroscopic studies indicate that the HOMO and LUMO energy levels are lowered for P201 and P202 in comparison with those of similar polymers but with neutral side chains, hinting that the charged groups in the side chains can influence the electronic structure of the polymer backbone. Unexpectedly, the thin film of P202 shows n-type transporting
behavior. In marked contrast, similar polymers with the same backbone as P202, but with neutral side chains, display a characteristic p-type transporting property. They hypothesized the reasons for the transformation of p-type into n-type transporting behavior observed for P202 as follows: i) the ionic groups can generate electrostatic dipoles at the electrode, and such dipoles are expected to reduce barriers for charge injection, and ii) P202 is expected to be easily reduced and the resulting radical anion becomes more stable because of the lower LUMO level. This finding suggests that the unique structures of CPEs may offer new possibilities to design materials with unusual properties.

3.6. Photochromic Chain

More and more studies show that the interchain packing and thin film crystallinity and, thus, semiconducting properties of conjugated polymers can be affected by the structures of side
chains.\cite{62-64} On the basis of this finding, we and other groups incorporated photochromic groups in the side chains of semiconducting polymers, aiming to generate photoresponsive semiconductors and fabricate optically tunable transistors, by taking advantage of the fact that photochromic molecules can be reversibly interconverted between two states with different structures.\cite{69,181,182} Müllen and co-workers prepared conjugated polymers P203, P204, and P205, which possess the same conjugated backbone, but with different side chains (Scheme 10).\cite{181} The side chains of P204 and P205 entail cis- and trans-alkene moieties. The GIWAXS studies reveal that the trans-alkenes in the side chains in P205 are beneficial for interchain close packing. In comparison, the cis-alkenes in P204, which are curved and show a less regular shape, are not favorable to form ordered structures of polymer chains. While the transformation of trans-alkenes into the cis-isomers were not explored for P204 and P205, the respective cis-to-trans isomerization was conducted for P204 under UV light (365 nm) irradiation in the presence of diphenyl sulfide. The cis-to-trans transformation leads to tighter interchain packing and the increase of the coherence length of the crystalline domains, resulting in the improvement of transistor performance in terms of lower off-current and a higher on/off ratio.

Some of us have recently reported on the DPP-based polymer P206, which contains side chains with azobenzene groups and branching alkyl chains.\cite{69} The design and synthesis of P206 is motivated for the development of photoresponsive semiconductors and optically tunable field-effect transistors. The interconversion between the trans- and cis-forms of azobenzene units in P206 is expected to affect the interchain packing and charge transporting behavior by considering the fact the isomerization is accompanied by large conformation and dipole moment changes (Figure 10a). The absorption spectral studies for the thin film of P206 show that the photoisomerization of azobenzene units of P206 can take place in a fast and reversible way. This is likely because bulky branching alkyl chains are present along the backbone of P206 and, accordingly, the dense packing of azobenzene units can be prevented. As depicted in Figure 10b–d, the transfer characteristics of the FET with thin film of P206 were reversibly tuned after UV light irradiation, followed by visible light irradiation. Accordingly, the thin film charge mobility and the drain–source current can be reversibly modulated by alternating between UV and visible light irradiations for several cycles. Such device current variation agrees very well with the change of the absorption intensity owing to the photoisomerization of azobenzene groups, indicating that the photomodulation of the semiconducting property of P206 can be ascribed to the photoisomerization of azobenzene groups in P206. In fact, the control experiment was performed with a similar DPP-based polymer without azobenzene groups, and the device current could not be modulated by light irradiations under the same conditions for P206. On the basis of theoretical calculations and GIWAXS analysis, we hypothesize that the conformation and dipole moment changes in association with the photoisomerization of azobenzene groups can influence the intrachain and interchain charge transport.

Furthermore, the dynamic photomodulation of the device current was successfully demonstrated (Figure 10d) by recording the current during the light irradiations for which the UV and visible light sources were switched alternatively. Clearly, the current variation upon UV and visible light

Figure 10. a) Photoisomerization of azobenzene. b) Variation of transfer curves of FET with thermally annealed thin film of P206 upon alternating UV and visible light irradiations. c) The reversible modulation of device current and charge mobility for five light irradiation cycles. d) The dynamic variation of device current after successive UV and visible light irradiations for five cycles and the enlarged panel, showing the detailed variation of I_{DS} versus the irradiation time with UV or visible lights. a–d) Reproduced with permission.\cite{69} Copyright 2019, Wiley-VCH.
irradiations is rather fast. To our delight, the FET with P206 displays the fastest photosensitivity among the reported optically tunable FETs.\textsuperscript{[180–188]} This can be attributed to i) the azobenzene units being covalently linked to the flexible alkyl chains and separated by branching alkyl chains in P206 and, as a result, the photoisomerization can be carried out easily, and ii) the active layer in the device contains only the thin film of P206 without further blending of an additional photoresponsive component and the need for interface modification.\textsuperscript{[183–191]} It should be noted that physical blending and interface modification with photochromic molecules were reported previously for photoresponsive devices.\textsuperscript{[183–191]} However, self-aggregation of photochromic molecules is likely to occur within the blending thin films. This can yield a large-scale phase segregation, and accordingly the device stability and photoreversibility can be affected. Sophisticated procedures are needed for electrode or dielectric layer modifications with photochromic molecules.

Meng and co-workers recently reported on the anthracene-derived organic semiconductor containing photochromic azo-unit in the conjugated backbone.\textsuperscript{[182]} The isomerization of the trans-form into the cis-form occurs after UV light irradiation based on the absorption spectroscopic studies. The filed-effect mobility enhancement was observed after UV light irradiation, but it required long time (up to 1.0 h) UV light irradiation.

4. Summary and Outlook

In this review, we show that the side chains of semiconducting polymers are not only able provide solubility of conjugated polymers in organic solvents, but also affect the interchain packing, thin film morphology and, thus, the semiconducting performances. In the first section of this review, we discuss the effects of the contents and substitution positions of alkyl chains and the structures of alkyl chains in terms of length, linear, or branching conformation on the aggregate structures and charge transporting properties of semiconducting polymers with many recent examples. It is generally favorable for interchain close packing and charge transporting of semiconducting polymers when the contents of alkyl chains are reduced and the lengths of alkyl chains are shortened. The positioning of alkyl chains can affect the planarity of the backbones of conjugated polymers and, thus, the charge mobilities of conjugated polymers. Modification of branching alkyl chains by moving the branching points from the backbones results in significant improvement of the thin film crystallinity and charge mobilities of semiconducting polymers. The partial replacement of branching alkyl chains with linear ones has been demonstrated to be an efficient and simple approach to boost the charge mobilities of conjugated polymers by weakening the steric hindrance of alkyl chains and promoting the close packing of polymer chains.

In the second section of this review, we summarize and discuss semiconducting polymers with side chains containing heteroatoms and functional groups. By taking advantage of the self-assembly property of fluorinated alkyl chains because of the strong and unique physical properties of the C–F bond and hydrophobicity, conjugated polymers with fluorinated alkyl chains show an improved interchain packing order and semiconducting performances. In particular, the presence of fluorinated alkyl chains can prevent the diffusion of moisture and oxygen into the semiconducting layers, resulting in the improved air stability of the resulting transistors. The application of siloxane-terminated side chains with different lengths of linear alkyl spacers leads to p-type, n-type, and ambipolar semiconductors with high charge mobilities. Incorporation of H bonding groups, such as urea, amide, and thymine, into the side chains can effectively improve thin film crystallinity of conjugated polymers and boost the charge mobilities. The sensing performances of FETs with semiconducting polymers containing functional groups, such as glycol, tetrathiafulvalene, and thymine, have been investigated, and the results demonstrate that the incorporating of functional groups in the side chains can improve the selectivity of FET-based sensors. The attachment of side chains with photochromic azobenzene groups into the conjugated polymers successfully leads to photoresponsive semiconductors and optically tunable FETs with fast responsiveness. The effects of side chains on the mechanical properties of semiconducting polymers have been studied for the development of stretchable polymeric semiconductors and devices.

These studies reveal that side chain modification is becoming a powerful molecular design tool to develop polymeric semiconductors with high performances and multifunctionalities. Further studies with regard to the modifications of side chains of semiconducting polymers include the following: i) further optimization of the structures of side chains to generate polymeric semiconductors with high charge mobilities, good solubilities, and air stabilities in combination with the design and synthesis of new conjugated frameworks, ii) development of new synthetic strategies to attach various targeting groups in the side chains of conjugated polymers for the construction of FET-based biosensors, iii) rational incorporation of different responsive units into the side chains of conjugated polymers to attain responsive semiconductors with multistable states and construct unique functional devices, iv) design of new side chains to enable orthogonal processing and patterning of semiconducting polymers, v) design of new side chains for stretchable polymeric semiconductors and devices with high performances, and vi) incorporation of chiral groups in the side chains of conjugated polymers to investigate the effects of chiral groups on the interchain packing and semiconducting properties.

Acknowledgements

This article is part of the Advanced Materials Hall of Fame article series, which recognizes the excellent contributions of leading researchers to the field of materials science. The authors thank the financial support from NSFC (21790363, 61890943, and 21661132006), the Youth Innovation Promotion Association CAS (No. 2015024), the National Key R&D Program of China (2017YFA0204701), and the Strategic Priority Research Program of the CAS (XDB12010300).

Conflict of Interest

The authors declare no conflict of interest.
Keywords

charge mobility, field-effect transistors-based sensors, modifications of side chains, semiconducting conjugated polymers, side chains with functional groups

Received: May 15, 2019
Revised: July 5, 2019
Published online: September 4, 2019
[184] H. Zhang, X. Guo, J. Hui, S. Hu, W. Xu, D. Zhu, Nano Lett. 2011, 11, 4939.
[185] Q. Shen, L. Wang, S. Liu, Y. Cao, L. Gan, X. Guo, M. L. Steigerwald, Z. Shuai, Z. Liu, C. Nuckolls, Adv. Mater. 2010, 22, 3282.
[186] E. Orgiu, N. Crivillers, M. Herder, L. Grubert, M. Pätzel, J. Frisch, E. Pavlica, D. T. Duong, J. A. Hutchison, C. Ruzié, G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu, P. Samorì, Nat. Chem. 2012, 4, 675.
[187] Y. Li, H. Zhang, C. Qi, X. Guo, J. Mater. Chem. 2012, 22, 4261.
[188] Y. Ishiguro, R. Hayakawa, T. Chikyow, Y. Wakayama, J. Mater. Chem. C 2013, 1, 3012.
[189] H. Zhang, J. Hui, H. Chen, J. Chen, W. Xu, Z. Shuai, D. Zhu, X. Guo, Adv. Electron. Mater. 2015, 1, 1500159.
[190] M. E. Gemayel, K. Börjesson, M. Herder, D. T. Duong, J. A. Hutchison, C. Ruzié, G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu, P. Samorì, Nat. Commun. 2015, 6, 6330.
[191] T. Leydecker, M. Herder, E. Pavlica, G. Bratina, S. Hecht, E. Orgiu, P. Samorì, Nat. Nanotechnol. 2016, 11, 769.