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From stretchable and healable to self-healing semiconducting polymers: design and their TFT devices

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Flexible thin-film transistor (TFT) devices are essential elements of future flexible electronics owing to their promising applications in various fields ranging from lighting and display, sensors, communication, and smart textiles to medical devices. Currently, these state-of-the-art electronic devices are not only struggling from “brittle” to “stretchable”, but are also expected to advance to “autonomous self-healable”. However, to integrate these features into flexible and stretchable devices, the first requirement to consider is compatibility between their mechanical and electrical properties given that the self-healing ability is associated with mechanical compliance but is incompatible with existing electronic technologies. Therefore, the first step closer to achieve is due to the recent progress in the field of stretchable semiconducting polymers, which thus far consists of two strategies: (1) structural engineering of conjugated polymers and (2) physical blending of conjugated polymers in soft insulating polymers. Together with the emphasis on additional functionalization in novel modified-semiconducting materials to boost large mechanical deformation without damaging their electronic properties, structural engineering can also provide targeted features (*i.e.*, self-healing ability). Finally, we highlight the chemical aspects of self-healing materials (from non-covalent to reversible covalent-based mechanisms) that have been successfully integrated in TFT devices.

1. Introduction

Since the discovery of polythiophenes and related conductive organic polymers by Heeger, MacDiarmid, and Shirakawa

(Nobel Prize in Chemistry 2000),^{1–3} numerous conjugated polymers have been developed as a new class of organic semiconductors, setting out to renew the semiconducting industry, which has been dominated by their inorganic counterparts such as traditional silicon-based materials over the last 50 years.⁴ The fruit of this effort is reflected in the electronics revolution from heavy and cumbersome to compact and mobile and rigid



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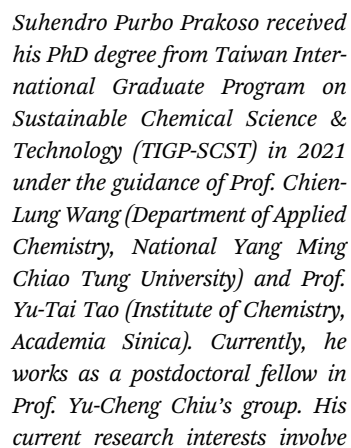


In this progress report, we comprehensively review the various approaches employed by different research groups to develop stretchable semiconducting polymers with emphasis on the design and manipulation of semiconducting polymers toward deformable stretchable electronics, a field which has grown significantly in the past few years.^{17,18} We also provide an update on the current strategies developed toward intrinsically stretchable semiconducting materials as a starting point, among which two main strategies for diverse structural

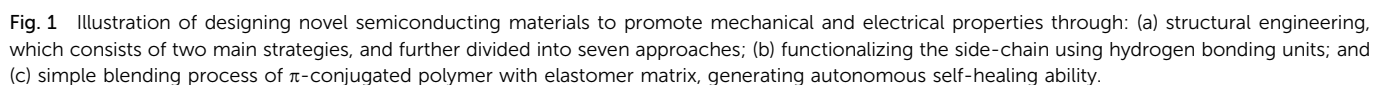
modifications have been adopted, as follows: (1) backbone engineering and (2) side-chain engineering, with each strategy having several unique approaches, as depicted in Fig. 1a. Then, highlighting the strong impact in the hydrogen bonding units incorporated in the conjugated polymer, intramolecular conformational locks can be established, resulting in increased backbone planarity, enhanced π -delocalization and field-effect mobility ($\mu_{\text{FET}}^{\text{FET}}$).^{19–22} This elegant strategy also creates new properties and functions, one of which is self-healing ability (Fig. 1b).^{23–25} The exceptionally successful building blocks that will be discussed in this review are exemplified by a range of different conjugated materials, including thiophene, diketopyrrolopyrrole (DPP), and isoindigo (IDG), containing polymers.^{26–30} Furthermore, to outweigh the extra complexity introduced in modifying structural polymers, the simplicity of the physical blending of conjugated polymers in an elastomeric matrix for TFTs has been exploited (Fig. 1c).^{31–33} Therefore, surveying the advances from extrinsically stretchable semiconducting polymer blends to self-healing capability is also necessary. We anticipate that the integration of these approaches will be crucial for the development of future-generation stretchable and self-healable polymer semiconductors.

2. Stretchable semiconducting polymers

Inspired by the overwhelming feature of elastomeric materials, many efforts have been devoted to replicating the mechanical properties of elastomers by integrating conjugated polymers in TFT applications to attain sufficiently high elasticity for stable



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P3HT has emerged as a second-generation conjugated polymer that has successfully improved the performance of organic TFT devices.⁴ Starting from the dedication of scientists to analyze and characterize the structural properties of P3HT, it was revealed that one of the most compelling properties of P3HT is its ability to form highly ordered π -stacks and side-chain lamella stacks.^{39,41,42} Transmission electron microscopy (TEM) has been used to demonstrate the structural evolution from

Focusing on the typical semicrystalline P3HT morphology composed of anisotropic crystalline regions bridged by tie chains (Fig. 2a),^{47,48} the possibility of intrinsic stretchability can be expected. As the first step in investigating the strong correlation between the strain-alignment and charge mobility of P3HT thin films, O'Connor *et al.* proposed an innovative strategy to align the crystalline phase in P3HT, which was achieved by laminating a P3HT spin-coated film on a stretchable poly(dimethylsiloxane) (PDMS) substrate, and then stretching to various extents.⁴⁹ Upon stretching, the crystallites in the P3HT films were reoriented with the polymer backbones aligned in the direction of the applied strain. The mobility of P3HT increased in the applied strain direction and decreased in the perpendicular direction. This strain-induced alignment



Fig. 2 Structure engineering of polythiophene derivatives. (a) Atomic force microscopy (AFM) image of P3HT film (left), schematic of molecular structure consisting of anisotropic crystalline region bridged by amorphous regions (middle), and crystallographic molecular structures of the semicrystalline P3HT packing behavior showing directions of π -stacking and lamellar-stacking (right). (left and middle)⁴⁷ Copyright: 2005, the American Chemical Society. (right)⁴⁸ Copyright: 2017, the American Chemical Society. (b) Illustration of the P3HT backbone stacking orientation before and after strain. The polymer crystallites reorient to align in the direction of the applied strain, transforming the edge-on crystallites into face-on crystallites.⁵⁰ Copyright: 2013, the American Chemical Society. (c) Hole mobilities and stress–strain curves of P3HT tapes as a function of M_n . Copyright: 2013, Elsevier. (d) stress–strain curves and tensile moduli of P3HT thin films at different M_n obtained by film-on-water (FOW) technique.⁵³ Copyright 2017, the American Chemical Society. (e) Schematic showing three possible coupling modes and chemical structure of regioregularity (RRe) and regiorandom (RRA) of P3HT. (f) stress–strain curves and hole mobilities of P3HT films with respect to the degree of regioregularity M_n obtained by the FOW technique.⁵⁸ Copyright: 2015, the American Chemical Society. (g) Schematic illustration of *block*-P3HTs with increasing lengths of RRA-blocks added for mechanically robust and high-performance TFTs, the stress–strain curves of *block*-P3HTs (the inserted picture of the RR_{block} 60 film shows that no damage occurred even after stretching above 30% strain), and hole mobility values as a function of RRe-*block*-P3HTs.⁵⁹ Copyright: 2019, the American Chemical Society.

transformed the predominant edge-on oriented (100) polymer crystallites to face-on orientation (010) crystallites (Fig. 2b). Alternatively, 100% biaxially stretched films showed an increase in facial alignment, but the charge mobility anisotropy was not significant.⁵⁰ These results suggest that mechanical strain on the micrometer scale can produce changes in texture, anisotropy in

elastic modulus, and alter charge transport. Furthermore, molecular engineering seeks to attain the integration of different features by focusing on the structure–property relationship at the molecular level such as molecular weight (M_w), regioregularity (RRe), and other considerations related to solution processing and fabrication techniques. In the following section, we specifically

2.1.2 Regioregularity effect. P3HT exhibits three possible orientations when two thiophene rings are coupled (*i.e.*, head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT)) (Fig. 2e). P3HT with mainly the HT orientation ($\geq 95\%$) is referred to as a regioregular (RRe) structure, leading to ordered interchain packing. In contrast, other configurations such as HH and TT coupling lead to distributed chain conformations of the regiorandom (RRa) P3HT owing to the steric hindrance between the nearest hexyl side chains. Early studies reported that RRe P3HT resulted in higher crystallinity and higher charge mobility compared to RRa isomers.^{36,39,54–57} As an example, Sirringhaus *et al.* revealed that 96% RRe P3HT possessed a high carrier mobility of up to $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas less RRe P3HT ($\sim 80\%$) exhibited low mobilities of about $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{56,57} Since the regioregularity (RRe) of a polymer can control the crystallinity of thin films, it may also influence their mechanical properties. Kim *et al.* reported that the mechanical and electrical properties of P3HT could be effectively controlled by tuning the degree of RRe.⁵⁸ P3HT was synthesized *via* Grignard metathesis (GRIM) polymerization, which allows excellent control of the RRe

Considering the disadvantages of using a homopolymer with randomly coupled HH defects, in the case with a limited extent of ordered domains, the same research team continued the development of mechanically robust and high-performance TFT using a P3HT regiorandom copolymerization strategy (*block*-P3HTs).⁵⁹ The authors prepared a series of *block*-P3HTs consisting of RRe and RRa P3HTs with various M_n values of RRa blocks (from 3 to 33 kg mol⁻¹) and a fixed M_n of RRe blocks (11–12 kg mol⁻¹) *via* a catalyst-transfer polycondensation strategy (Fig. 2g). Briefly, *block*-P3HT thin films with longer RRa blocks enhanced the mechanical ductility due to the fact that the amorphous moiety in regiorandom copolymers promotes the formation of an entangled and/or folded structure. For example, the elongation at break of the thin films was remarkably enhanced by 100-fold (*i.e.*, from 0.3% to 30.2%) as the M_n of the RRa block increased. Amazingly, all the *block*-P3HT possessed a similar high μ_h^{FET} of 1.5×10^{-1} cm² V⁻¹ s⁻¹ to that of the high RRe P3HT homopolymer. The discovery of the mechanical ductility of *block*-P3HTs, which can be dramatically enhanced without sacrificing the electrical properties, becomes one of the promising candidate strategies to fabricate high-performance soft electronics, considering the trade-off between electronic properties and mechanical flexibility often encountered by scientists.

2.1.3 Solution processing and fabrication effect. The mobility together with the deformability of polymer packing by altering the film preparation or processing conditions, such as annealing temperature and solvent choice, have also been considered.^{36,60–65} These considerations are based on the relationship between the film morphology and mechanical compliance by M_n and regioregularity effects. An early study by Bao *et al.* reported both high carrier mobilities (*i.e.* $4.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the accumulation mode and $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the depletion mode) and on/off current ratios close to 10^4 for their RRe P3HT ($\geq 95\%$) using solution casting.³⁶ The mobility of RRe P3HT was found to vary by two orders of magnitude depending on the choice of solvent used. This investigation confirmed that the mobility of RRe P3HT varied greatly with the solvent employed for its fabrication. The

2.2 Conjugated polymer engineering

Considering the high crystallinity and amorphous nature of conjugated polymers, it is assumed that their electrical-mechanical properties are mutually exclusive. However, through the continuous efforts and exploration by researchers, it was discovered that conjugated polymers based on isoindigo (IDG), naphthalene diimides (NDI), and diketopyrrolopyrrole (DPP)^{26–30} exhibit impressive charge mobilities of over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ although their long-range order is relatively poorer than that of P3HT and PBTTT. These observations have led to a new way of generating conjugated polymer thin films for effective charge mobility, thus facilitating the optimum intra- and intermolecular charge transport at the device length scale, improving the interconnectedness between aggregated domains, and reducing the amount of disorder in the conjugated segments (making rigid backbones) seem to be the key rather than inducing high crystallinity.^{74–76} Hence, two main strategies of diverse structural modifications have been adopted, *i.e.*, backbone engineering and side-chain engineering (Fig. 1a). Backbone engineering involves the introduction of conjugated and non-conjugated units into the main chain of a polymer, which is generally classified into three approaches, mainly block copolymerization, molecular spacer, and terpolymerization. Meanwhile, side chain engineering introduces non-conjugated units in the side chain of a conjugated polymer, which can also be classified into four different approaches, including symmetric/asymmetric side-chain, cross-linking, and Y-shaped side-chain. Furthermore, it was revealed that the incorporation of hydrogen bonding moieties in these novel conjugated polymer designs is particularly effective in tailoring the mechanical deformability and maintaining or even boosting the charge transport values in TFTs.^{19–22} Interestingly, the combination of dynamic H-bonds in organic semiconductors has created new properties and functions such as self-healing ability which will be explained in Section 3.^{23–25}

2.2.1 Block copolymer approach. Attaching soft and insulating segments in the conjugated backbone is a widely used approach to develop a new class of intrinsically stretchable semiconducting multiblock copolymers because the presence of a flexible insulating segment reduces the glass transition temperature (T_g) of polymers and decreases the π - π stacking and crystallinity of polymer semiconductors in the solid-state. Müller *et al.* (2007) designed semiconducting diblock copolymers containing various weight ratios of P3HT as the rigid segment and polyethylene (PE) as the soft segment (Fig. 3a).⁷⁷ The rigid P3HT homopolymer featured a high Young's modulus of up to 28 MPa and elongation at break of only 13%. However, by incorporating soft PE blocks with a content as high as 65 wt%, the diblock copolymer showed an impressive Young's modulus of 240 MPa and maximum elongation of over 600% before break. Interestingly, the 35–65 wt% P3HT-PE possessed a decent μ_h^{FET} of $5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is comparable to the maximum FET-mobility values reported for non-stretchable P3HT homopolymer.^{36,78} Thus, P3HT-PE displays very useful semiconductor properties even at a low P3HT content. Subsequently, the success of this strategy prompted the curiosity of researchers to combine P3HT with other soft-type materials. Chen and Satoh group investigated the influence of low- T_g



Fig. 3 Intrinsically stretchable semiconducting polymers developed based on the block copolymer approach. The chemical structures and mechanical and/or electrical properties of: (a) diblock copolymers with different weight ratios of P3HT and PE. The inset of the bottom image is an optical image of a dog-bone-shaped 35–65 wt% P3HT-PE under 600% stretching.⁷⁷ Copyright: 2007, Wiley-VCH. (b) P3HT-*b*-PBA rod-coil diblock copolymers.⁷⁹ Copyright: 2017, the American Chemical Society. (c) AB-type, BAB-type, and ABA-type of P3HT-*b*-POO block copolymers.⁸⁰ Copyright: 2019, The Royal Society of Chemistry. (d) Triblock copolymer P3HT-*b*-PMA-*b*-P3HT.⁸¹ Copyright: 2015, The Royal Society of Chemistry. (e) P3HT-*b*-PIB-*b*-P3HT with a photograph of the triblock copolymer film before and after stretching (upper left) and illustration of the model for the deformation of the microphase separated structure and crystalline orientation of the triblock copolymer thin film (bottom).⁸² Copyright: 2015, the American Chemical Society. (f) P3HT-*b*-P3SiHT-*b*-P3HT, where the stress–strain profile composed of the homopolymer P3HT ($M_n = 20 \text{ kg mol}^{-1}$), diblock copolymer P3HT-*b*-P3SiHT (P1–P3 where P1, P2, and P3 containing 73, 60, and 53 wt% P3HT, respectively), and triblock copolymer P3HT-*b*-P3SiHT-*b*-P3HT containing 22 wt% P3HT (P6).⁸³ Copyright: 2018, Wiley-VCH.

poly(*n*butyl acrylate) (PBA) segments in the rod-coil diblock copolymers (P3HT-*b*-PBA).⁷⁹ As expected, the tensile modulus of the P3HT-*b*-PBA thin films decreased from 0.63 GPa (P3HT-*b*-

PBA_{3k}) to 0.19 GPa (P3HT-*b*-PBA_{12k}) with an increase in the block length of PBA (Fig. 3b). Even after 100% mechanical strain, P3HT-*b*-PBA_{6k} displayed a high $\mu_{\text{th}}^{\text{FET}}$ of $2.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with



Recognizing this weakness, Miyane *et al.* (2018) fabricated fully conjugated ABA triblock polymers by utilizing a regio-regular polythiophene derivative bearing a trisiloxane group in the side chains (P3SiHT) as the soft segment.⁸³ The merits of the introduction the P3SiHT moiety in conjugated polymers have been further investigated.^{84–87} Indeed, a P3SiHT film displayed a remarkable change in characteristics such as thermal behavior, chemical stability, mechanical property, and miscibility in solvents. Especially in terms of mechanical behavior, it exhibited 2-orders of magnitude smaller Young's modulus and 20 times higher elongation at break than RRe P3HT.⁸⁷ Benefiting from the features of P3SiHT, all the block copolymers exhibited a lower tensile modulus and greater elongation as the P3SiHT content increased, which are typical characteristics of a plastic-to-rubber transition. As illustrated in

2.2.2 Molecular spacer approach. As reported by Müller's group, in P3HT-*b*-PE, it is possible for a conjugated polymer to retain favorable charge-transport properties despite the fact that most diblock copolymers are composed of insulating segments.⁷⁷ In contrast to the modification of the polymer without interfering with its conjugated units, Mei and co-workers used diketopyrrolopyrrole (DPP) donor-acceptor (D-A) polymers to improve the ductility and reduce the modulus, and simultaneously retain much of their electronic performance, while interrupting the rigid conjugated backbones with flexible 1,3-propylene (C3) spacer units.²⁶ It was revealed that the DPP-20 mol% conjugation break spacer (CBS) unexpectedly maintained relatively high charge mobility of over $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is insignificantly different from an average mobility of DPP-0 mol% CBS ($4.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The same research group collaborated with Thompson's group, introducing a concept of CBS in the polymer backbone to reduce the crystallinity and T_g , which consequently impart stretchability.^{91,92} In these reports, a series of semi-random polymers with varying spacer lengths and spacer compositions were examined (Fig. 4a).⁹² Consequently, the 10% T-10-T polymer sample exhibited relatively high hole mobility based on its space charge-limited current (SCLC) (μ_h^{SCLC}) value of $2.53 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was comparable to that of its fully conjugated counterpart (P3HT-DPP-10%) of $9.29 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Interestingly, although the hole mobility decreased with an increase in spacer composition, there is still an increment in hole mobility with respect to the length of the spacer carbon chain. Through the film-on-elastomer measurement, it was revealed that several modified polymers could be stretched beyond 80% strain, and particularly for 10% T-8-T and 10% T-10-T, they could achieve the lowest elastic modulus of 0.14 GPa and 0.15 GPa, respectively. This approach

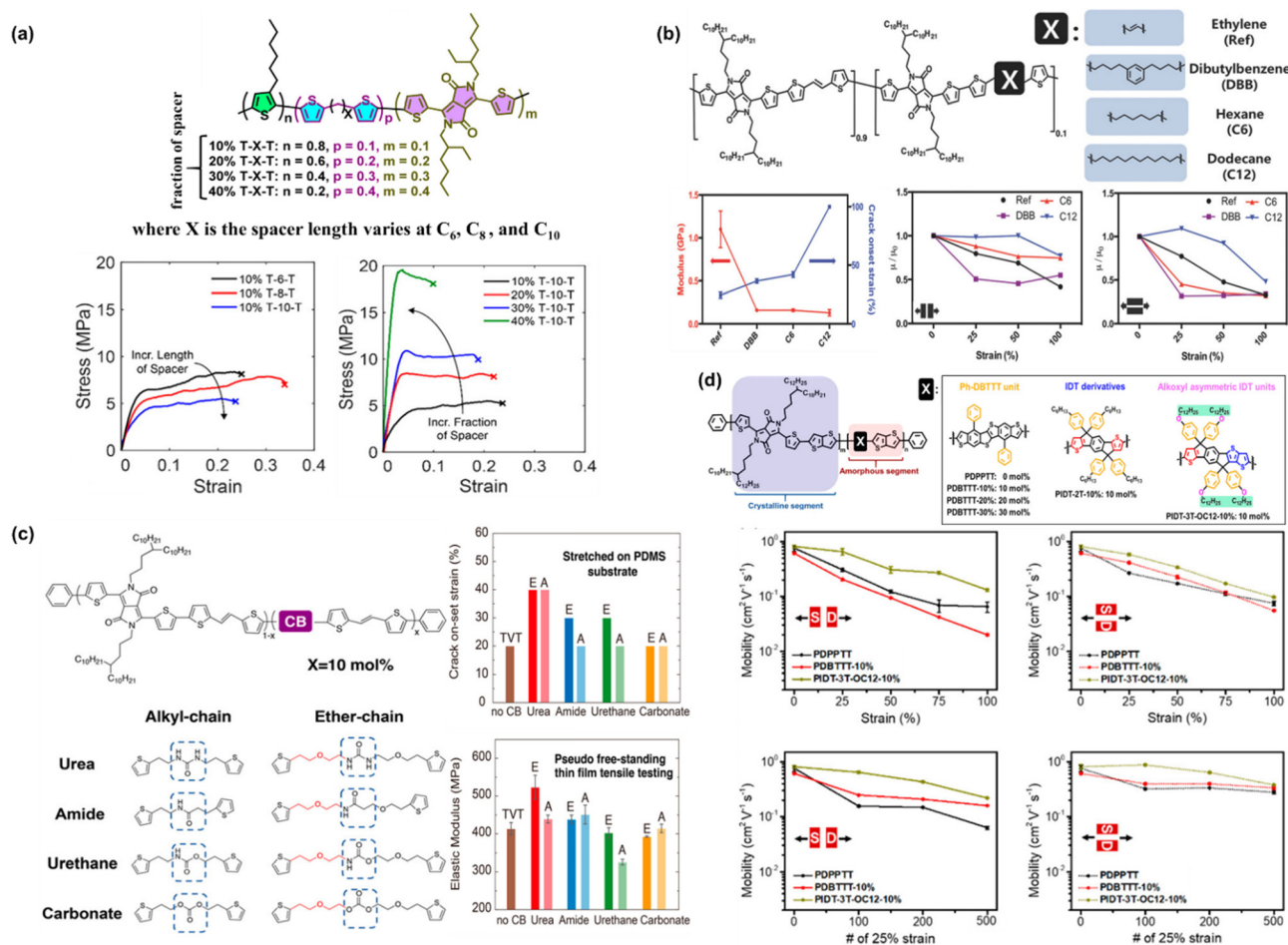


Fig. 4 (a) Chemical structure of the designed DPP-based conjugated polymer backbone and the effect of the conjugation-break spacer length and spacer composition on its mechanical and electrical properties. Representative stress-strain curves of modified P3HT-DPP polymer films obtained using the FOW technique.⁹² Copyright: 2018, the American Chemical Society. (b) Effects of chain breakers on elastic modulus and mobility under strain in DPP-TVT polymers.⁹³ Copyright: 2018, Wiley-VCH. (c) Summary of the crack on-set and elastic modulus measurements of DPP-TVT polymers as a function of the H-bonding conjugation breaker effect.⁹⁴ Copyright: 2020, the American Chemical Society. (d) Effect of conjugated rigid fused-rings with optimized bulky side groups in the conjugated polymer backbone.⁹⁵ Copyright: 2021, the American Chemical Society.

opens an avenue for researchers to overcome the most common obstacle of the tradeoff between mechanical and electronic performance.

Mun *et al.* investigated the influence of flexible conjugation breakers in the DPP/thienylene vinylene (TVT) polymer semiconductor backbone, in which three different chain breakers were used, *i.e.*, ethylene, dibutylbenzene (DBB), hexane (C6), and dodecane (C12).⁹³ Upon the incorporation of 10% molar ratio chain breaker, the non-conjugated segments could “tune” the mechanical properties, while maintaining high mobility of higher than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as shown in Fig. 4b. Remarkably, the C12-DPP/TVT polymer thin films exhibited a largely improved crack onset strain as high as 100% strain and a low modulus of 0.13 GPa, which could maintain moderate mobility ($>0.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) under 100% strain even after a hundred cycles of 50% strain. Compared to DPP/TVT-based polymer films containing other conjugation breakers, C12-DPP/TVT was revealed to exhibit the best balanced performance in terms of both mechanical and electrical properties. Moreover, the

effect of the three chain breakers on all the polymer derivatives was still more ductile with a lower elastic modulus compared to the reference polymer using ethylene as the chain breaker. It should be noted that the obtained higher stretchability of the C12-DPP/TVT thin films originates from their lower crystallinity, as confirmed by T_g measurements and X-ray diffraction. To further understand the effects of the H-bonding strength, Zheng *et al.* studied its influence on the mechanical and electrical properties of polymer semiconductor thin films using different types of H-bonding units (urea > amide > urethane > carbonate) and linker flexibilities (ether chain (E) > alkyl chain (A)) (Fig. 4c).⁹⁴ Basically, H-bonding units were incorporated as CBS into a DPP D-A conjugated polymer backbone. It was observed that E-urea and A-urea with stronger H-bonding (self-association constant of >0.7) and flexible linkers having a higher tendency for denser packing could induce higher polymer chain aggregation and crystallinity in thin films, resulting in an improvement in the modulus and crack on-set strain and less degradation in mobility during stretching. It has to be

emphasized that the E-urea/E-amide-derived polymers exhibited the highest charge transport mobilities due to their high crystallinity and intense H-bonding.

The same concept is applicable to other material systems, another example of which is the introduction two distinct classes of rigid fused-ring systems in a poly(thieno[3,2-*b*]thiophene-diketopyrrolopyrrole) (PDPPTT) backbone. The rigid fused-ring systems investigated by researchers, namely, benzene-substituted dibenzothiopheno[6,5-*b*:6',5'-*f*]thieno[3,2-*b*]thiophene (Ph-DBTTT) and indacenodithiophene (IDT) systems.⁹⁵ In fully stretchable transistors, as shown in Fig. 4d, the PIDT-3T-OC12-10% polymer showed a mobility of $0.27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 75% strain and maintained its mobility after being subjected to hundreds of stretching-releasing cycles at 25% strain. Compared to the reference polymer PDPPTT, the device showed an abrupt drop in mobility when stretched either parallel to the strain direction (\parallel) or perpendicular to the strain direction (\perp) from 0% to 75% strain, in which the initial mobility of $0.76 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ decreased to $\mu_{\text{h}\parallel}^{\text{FET}} = 7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{h}\perp}^{\text{FET}} = 1.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 75% strain. After 500 cycles at 25% strain, the tested devices all showed a low $\mu_{\text{h}\parallel}^{\text{FET}} = 6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the parallel stretching direction due to crack formation at 25% strain. These results underscore the intimate correlation between chemical structures, mechanical properties, and charge carrier mobility of polymer semiconductors.

2.2.3 Terpolymerization approach. Many previous studies revealed that the CBS approach can lower the backbone rigidity and revamp the stretchability of polymer semiconductors, despite the uncertainty in their electrical performance. Thus, to alleviate this issue, engineering conjugated monomer structures that are more complex than the binary system of conventional D-A copolymers has been pursued to enhance the stretchability without compromising charge transport.^{96–100} The most prominent example is conjugated random terpolymers, including A-D-A'-D- and/or A-D-A-D'-type copolymers. It was revealed that these conjugated random terpolymers can be used to effectively fine-tune the crystallinity and aggregation behaviors of the reference parent polymers. Owing to the mismatched geometry induced by additional components, random ternary copolymers are expected to possess reduced crystallinity compared to their reference parent polymers. Lin *et al.* utilized an elegant strategy to randomly incorporated different amounts of isoindigo (IID) unit in the reference DPP-quaterthiophene conjugated backbone.⁹⁷ As depicted in Fig. 5a, random terpolymers containing the lowest IID content such as DPP95 (95 mol% DPP and 5 mol% IID) possessed two times higher $\mu_{\text{h}\parallel}^{\text{FET}}$ ($5.5 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) value than that of the parent polymer DPP100 (100 mol% DPP and 0 mol% IID) ($2.5 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Under 100% strain, DPP95 also exhibited much higher $\mu_{\text{h}\parallel}^{\text{FET}}$ ($3.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and $\mu_{\text{h}\perp}^{\text{FET}}$ ($5.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) values

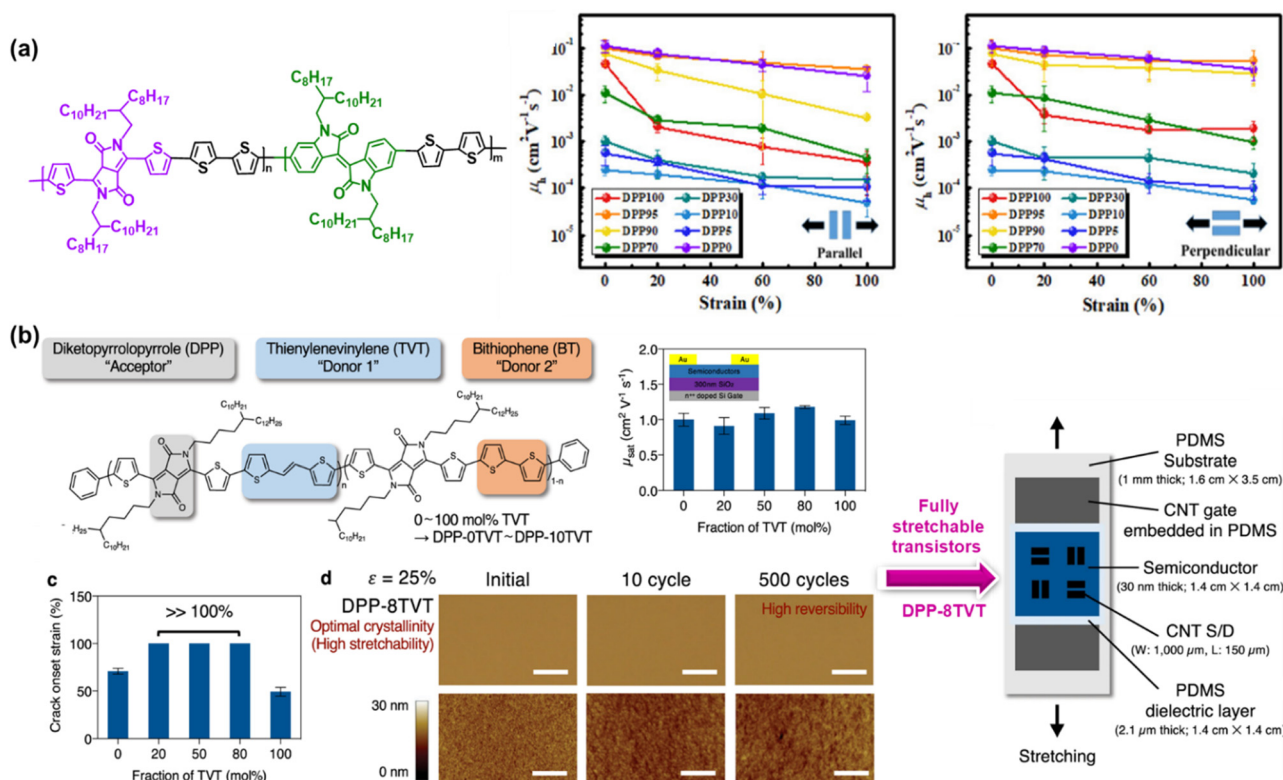


Fig. 5 Intrinsically stretchable semiconducting polymer developed based on the ternary copolymer approach. Chemical structure and mechanical and electrical performances of: (a) random terpolymers based on the diketopyrrolopyrrole-bithiophene (DPP-2T) backbone incorporating different amounts of isoindigo (IID) unit.⁹⁷ Copyright: 2020, the American Chemical Society. (b) Advances in DPP-based terpolymer semiconductors with two different fractions of TVT and BT conjugated co-monomers from observing simple semiconductor layers to fully stretchable transistors.⁹⁸ Copyright: 2021, Springer Nature.

2.2.4 Symmetric side-chain approach. The early routes for the incorporation of non-conjugated segments in the side

Alternatively, the hydrogen bonds located in the side chain also played a role in enhancing the mechanical and charge transport performance and facilitating the morphological organization. Ocheje *et al.*²² incorporated a range of amide compositions (5% to 30%) in DPP-based polymers as a direct approach to promote the intermolecular hydrogen bonding moieties between polymer chains and tune the solid-state morphology (Fig. 6c). Upon the addition of 5 mol% amide side chain, there was an enhancement in the charge mobilities to $2.46 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but the further addition of 30 mol% amide gradually decreased the

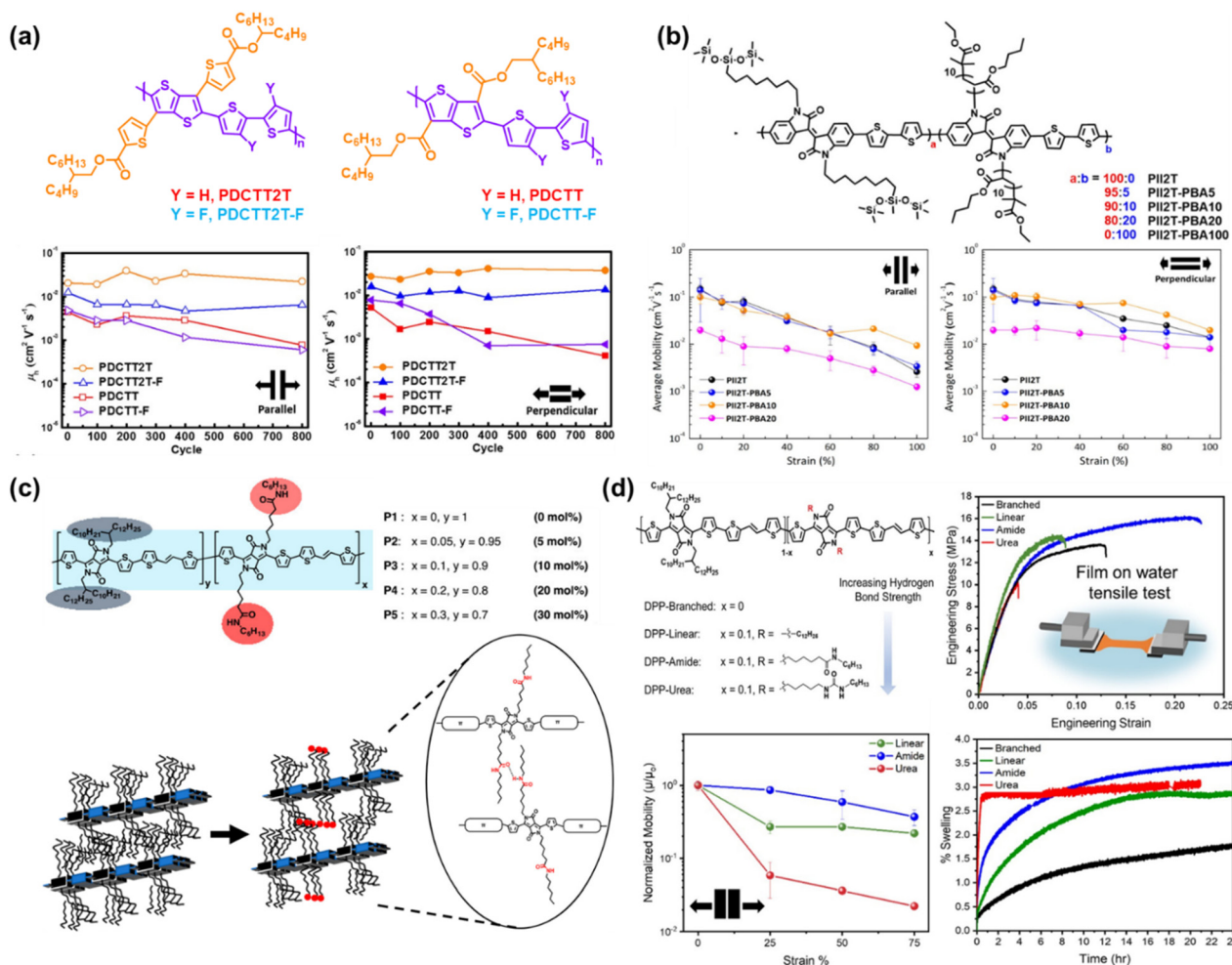


Fig. 6 Side chain engineering based on the grafting approach. (a) Charge mobility-stretchability relationship and chemical structure of PDCTT2T and PDCTT2T-F compared to their non-biaxial counterparts of PDCTT and PDCTT-F, respectively.¹⁰¹ Copyright: 2021, the American Chemical Society. (b) Influence of the amount of PBA in mol percentage on the PII2T side chain described by charge mobility-stretchability data.¹⁰³ Copyright: 2017, the American Chemical Society. (c) Structure of DPP-based conjugated polymers incorporating amide-containing side chains and schematic representation of intermolecular hydrogen bonds formed between adjacent amide-containing side chains.²² Copyright: 2018, the American Chemical Society. (d) Hydrogen bond strength described in chemical structures of DPP-TVT-based conjugated polymers and its influence on swelling, mechanical, and electrical properties as a function of maximum strain properties.²¹ Copyright: 2022, the American Chemical Society.

mobility to $0.59 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Besides hydrogen bonding, the increase in mobility can be partially influenced by the noncovalent interaction in the conjugated side chain. In comparison, Galuska *et al.*²¹ investigated the incorporation of 10% linear alkyl, amide functional, or urea functional side chains in DPP-TVT based statistical copolymers to assess the influence of hydrogen bonding on the mechanical properties of thin films (Fig. 6d). All the polymers demonstrated a similar elastic modulus with the average modulus following the order of DPP-linear > DPP-branched > DPP-urea > DPP-amide. This study showed that the hydrogen bond strength in the side chain is not linearly correlated with ductility, where DPP-urea possessed the highest hydrogen bonding strength but poor ductility due to its crystalline nature in comparison with DPP-amide, which was the best at tolerating deformation due to the disruption in crystalline packing in water. The embrittlement of DPP-urea was further confirmed in the swelling test, where

rapid swelling behavior was observed initially but quickly plateaued due to the greater crystallinity. A similar phenomenon was observed in the measurement of the respective charge transport mobility, where the charge transport of DPP-amide decayed by only 14% from $0.199 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ after being strained by 25% in the parallel stretching direction. Considering that the typical maximum strain experienced by human skin is 33%, amide functionalization may be a suitable synthetic strategy to achieve tolerable strain for wearable devices, while maintaining charge transport.

2.2.5 Cross-linking approach. The cross-linking of conjugated polymers has been demonstrated to be an effective strategy to realize the characteristics of elastomers by preventing irrevocable sliding within the polymer chains together with the ability to resist fatigue from multiple stretching. This method can also reduce polymer chain rearrangement and aggregation, thus decreasing the crystallinity. Wang *et al.*

utilized flexible PDMS oligomers for polymer crosslinking to reduce the tensile modulus and improve the fracture strain, and fatigue resistance for a high mobility DPP-based polymer (Fig. 7a).¹⁰⁴ By covalently crosslinking a DPP-based polymer with siloxane oligomers, its elasticity improved, as indicated by the absence of nanocracks after 500 strain-and-release cycles at the maximum strain of 100% and 1000 stretching-releasing cycles with 20% strain. In terms of electrical characteristics, the cross-linked films exhibited an average $\mu_{\text{h}}^{\text{FET}}$ of $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ before the strain was applied with an on/off current ratio of above 10^5 and the film could maintain an average $\mu_{\text{h}}^{\text{FET}} > 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after 500 stretching-releasing cycles of 20% strain in the direction perpendicular to the strain direction. However, the average mobility in the direction parallel to the strain was compromised due to the formation of wrinkles. Moreover, the elastic modulus significantly decreased to 0.2 GPa after cross-linking, which contributed to the mechanical toughness of the studied polymers. The studies that also focused on exploiting crosslinking reactions in conjugated polymer networks using crosslinkers with soft and flexible characteristics but not covered in this section can be found in recent reports.^{105–108}

The embedding of a cross-linked segment in the side chain conjugated polymer has been demonstrated to be an ideal approach because a high crosslinking density can be easily tuned and disruption of the charge transport is minimized. Thus, the same group investigated the importance of crosslinker crystallinity with respect to morphology, mechanical, and electrical properties of polymers by inserting urethane groups and tertiary carbon atoms into the alkyl backbone of

perfluorophenyl azide-based cross-linkers.¹⁰⁹ Similar studies have also been reported.^{94,110,111} Here, branched cross-linkers with tertiary carbon are capable of forming an evenly cross-linked network in the polymer blend, stemming from their excellent miscibility, and show a 4-fold increase in fracture strain.¹⁰⁹ Furthermore, a stable $\mu_{\text{h}}^{\text{FET}}$ of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved under 100% strain, and a stable $\mu_{\text{h}}^{\text{FET}}$ of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after 2000 stretching-releasing cycles of 25% on fully stretchable organic field-effect transistors. The charge mobility–tensile performance of each specimen in this study is presented in Fig. 7b. Another factor to be considered is the effect of fluorination on the mechanical and electrical properties of conjugated polymers, which was also evaluated by Ocheje *et al.*¹¹² Their work demonstrated the relationship between a series of fluorination and/or alkylation with benzothiadiazole-based polymer in the solid-state. The crack onset strains of the prepared polymers ranged from as low as 10% for the polymer containing only a fluorinated backbone to as high as 30% elongation for the polymer containing an alkoxy-appended backbone. Ultimately, fluorination embrittled the conjugated polymer thin films, whereas alkylation softened them.

2.2.6 Y-Shaped side-chain approach. The Y-shaped approach focuses on the modification of linear carbon chains after a bifurcate is formed. A systematic study on IID-based polymers containing branched side chains with an adjustable linear carbon spacer unit branching from a carbosilane group was conducted by Wu *et al.*¹¹³ In detail, PII2TC6 and PII2TC8 consisting of an isoindigo-bithiophene main chain and carbosilane side chain with a six or eight linear spacer plus two hexyl or octyl chains, respectively, were synthesized and assessed. The ductility

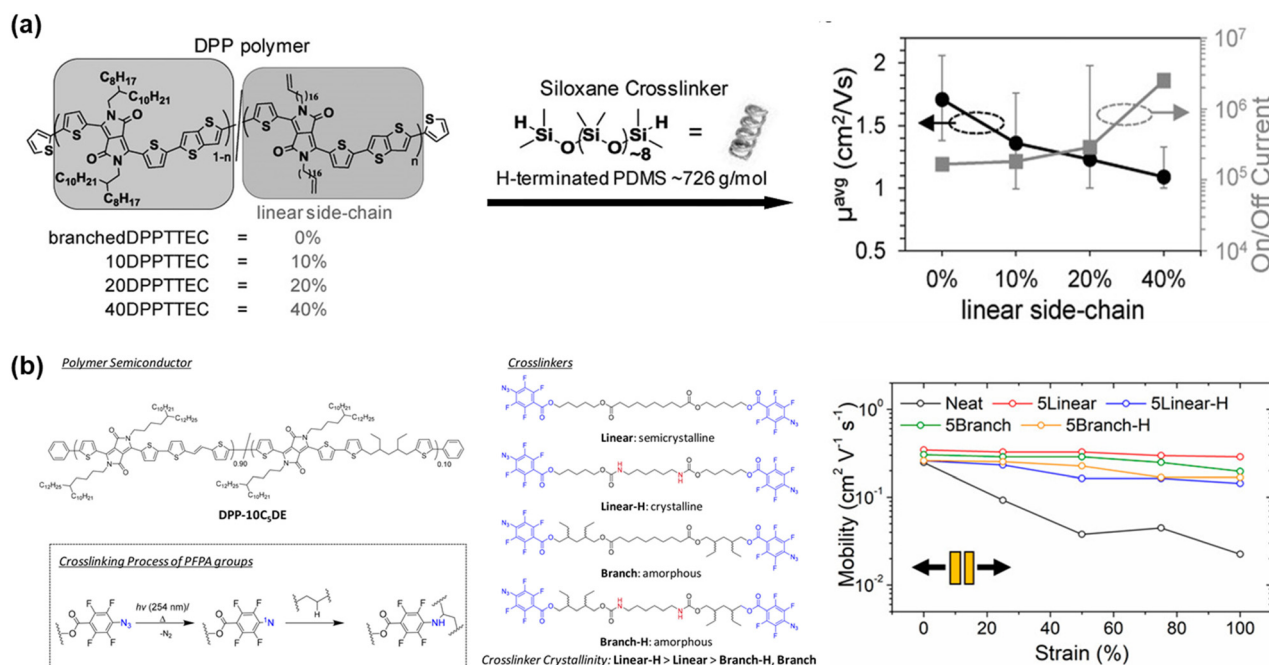


Fig. 7 Side chain engineering based on crosslinking approach. Chemical structure and the retention of mobility properties of the polymers in the stretched state. (a) DPP-based random co-polymer containing cross-linkable linear side-chains and linear H-terminated PDMS crosslinker.¹⁰⁴ Copyright 2016, Wiley-VCH. (b) Introduction of four types of cross-linkers in DPP-based polymer.¹⁰⁹ Copyright: 2019, the American Chemical Society.

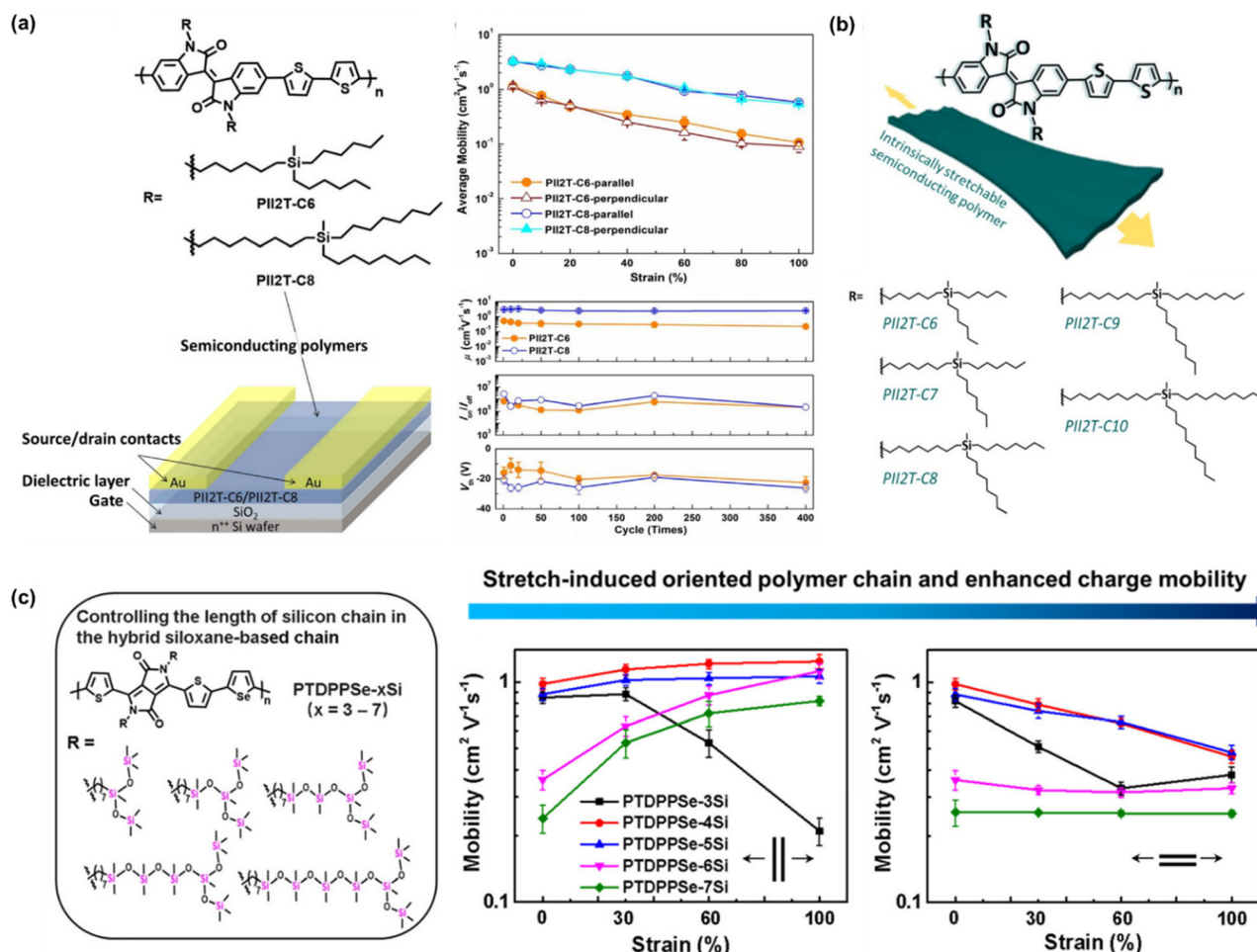


Fig. 8 Modulating the mechanical-electrical properties of conjugated polymers *via* side chain engineering based on y-shaped approach. (a) Average field-effect mobility stretched in the parallel and perpendicular directions and the mechanical-mobility resistance of the PII2T-C6 and PII2T-C8 thin films under repeated 400 stretching/releasing cycles with a maximum strain of 60% controlled parallel to the strain direction.¹¹³ Copyright: 2016, the American Chemical Society. (b) Chemical structures of PII2T-based polymers with manipulated length of carbosilane side chains, charge mobility distribution in both parallel and perpendicular directions of PII2T with carbon position ranging from C6 to C10 and normalized mobility in the parallel direction of the studied polymer thin films under strain.¹¹⁴ Copyright: 2019, the American Chemical Society. (c) PTDPSe-based conjugated polymer bearing different lengths of silicon chain.¹¹⁹ Copyright: 2022, the American Chemical Society.

measurement of PII2TC6 and PII2TC8 exhibited an impeccable mechanical performance with significant reduction in the tensile modulus at 0.43 and 0.27 GPa, respectively. The average charge carrier mobility upon annealing obtained from both specimens was 2.48 and 5.56 cm² V⁻¹ s⁻¹, respectively, with the maximum value of 8.06 cm² V⁻¹ s⁻¹ achieved by PII2TC8. A similar rate of charge transport characteristics was observed under a single stretching in the parallel and perpendicular directions (Fig. 8a). The charge mobility of the PII2TC6 thin film decreased from 1.14 to 0.11 cm² V⁻¹ s⁻¹ as the strain level increased to 100%, while the PII2TC8 thin film exhibited a higher initial charge mobility of 3.24 cm² V⁻¹ s⁻¹ with a sustained value above 1 cm² V⁻¹ s⁻¹ at 60% strain due to its better thin film ductility and denser molecular packing structure (*i.e.*, shorter π - π stacking distance). Furthermore, the PII2T-C6 and PII2T-C8 thin films showed stable performances without significant changes in their mobility, on/off ratio, and threshold voltage during 400 stretch-and-release cycles of 100% strain.

This achievement demonstrated that the newly designed IID-based polymer thin film with excellent ability to maintain stability and reproducibility under 60% tensile strain exhibits high potential to be integrated in future skin-inspired wearable electronics.

The effects of the carbon spacer present in the branch was investigated further by Chiang *et al.* (Fig. 8b).¹¹⁴ This group managed to improve the findings based on the work by Wu *et al.* by further repositioning the carbons of the side chain from 6 (PII2T-C6) to 10 carbons (PII2T-C10) to optimize the charge-transport behavior and the mechanical properties of semiconducting polymer thin films. By increasing the side chain length, the thin film modulus could be further reduced to 250 MPa with an almost unchanged $\mu_{\text{h}}^{\text{FET}}$ upon stretching of 1 cm² V⁻¹ s⁻¹ at 100% strain in both the parallel and perpendicular directions. In contrast, PII2T-C8 showed a higher initial mobility but it notably decreased upon stretching (0.7 cm² V⁻¹ s⁻¹ at 100%). The initial mobility of PII2T-C10 was not as high as that

of PII2T-C8 due to the disturbance of its backbone organization. Additionally, the length of the carbon side chain and the odd-even effect of the carbon position becomes a factor. Cracks could be seen in the PII2T-C6 and PII2T-C7 thin films under 100% strain but were significantly less in PII2T-C10. Polymers with even-numbered carbosilane side chains (C6, C8, and C10) possess smaller π - π stacking than the side chains with an odd carbon number (C7 and C9), and thus a higher mechanical and electrical performance can be achieved in even-numbered side chains.

Departing from the commonly used Y-shaped alkyl side chains, hybrid siloxane-based side chains are more easily deformed owing to their long bond lengths and large bond angles, together with low internal torsional potential barriers.^{115–117} Mei *et al.* demonstrated the effectiveness of novel siloxane-terminated solubilizing groups as a side chain in an isoindigo-based conjugated polymer (PII2T-Si) for promoting the field-effect mobility by inducing a denser π - π spacing and a larger crystalline coherence length.²⁸ The hole mobility of PII2T-Si was $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is 4 times greater than that of the reference polymer with a branched alkyl side chain (PII2T-Ref). This was explained by the polymer packing, where the new polymer exhibited a π - π stacking distance of 3.58 \AA , while PII2T-Ref showed a distance of 3.76 \AA . Starting from this discovery, other researchers tried to modify the conjugated polymer Y-shaped side chain by incorporating hybrid siloxane-based side chains.^{87,118} In the latest study by Ding *et al.*, they introduced a novel side chain engineering strategy to realize stretch-induced enhancement of the molecular orientation and charge transport in donor-acceptor conjugated polymers.¹¹⁹ Specifically, five conjugated polymers with a controlled hybrid siloxane-based side chain length were grafted on the backbone of poly-diketo-pyrrolopyrrole-selenophene: PTDPSe-*x*Si ($x = 3-7$). Considering the superior flexibility of silicon chains compared carbon chains, a series of polymers showed a progressively lower elastic modulus and increased fracture strain by increasing the silicon chain length, whereas the charge mobility could be enhanced with an appropriate increase in the silicon chain length (Fig. 8c). Interestingly, the charge mobilities parallel to the stretching direction for PTDPSe-4Si, PTDPSe-5Si, and PTDPSe-6Si were all above $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 100% strain, which were higher than that in their unstretched states. This enhancement in charge mobility is attributed to the excellent ductility and high strain-induced alignment of the polymer chains. Different from most other studies on controlling the carbon chain length in hybrid siloxane-based chains, this technique provides an alternative for manipulating the silicon chain length in hybrid siloxane-based chains.

2.2.7 Asymmetric side-chain approach. Asymmetric side-chain engineering in isoindigo-bithiophene based conjugated polymers has been reported to modulate the three-dimensional charge-transport pathways to enhance the charge mobility.^{120,121} By the simultaneous incorporation of linear and branched side chains, interchain stacking can be suppressed as a result of the increased side-chain packing. This result will be very beneficial in yielding a polymer film with high ductility. Lin *et al.* developed a series of PII2T (P1–P3) and PII2TF (P4–P6) as polymer backbones with asymmetric side chains, consisting of carbosilane side

chains (Si-C8), siloxane-terminated side chains (SiO-C8), and decyltetradecane side chains (DT), as shown in Fig. 9a.¹²² Owing to the geometric dissimilarity between the side chains, in which both SiO-C8 and Si-C8 have the same eight-carbon spacer before the branching point but with distinct branched chains after the branching point, the DT possessed a shorter spacer before the branching point, which impacts the apparent asymmetric side-chain differences in the molecular stacking and orientation of the derived polymers. Thus, it will greatly affect the resultant mobility and stretchability. The asymmetric SiO-C8/Si-C8 side chains enabled the derived polymers to possess the most balanced bimodal orientation, providing the greatest $\mu_{\text{h}}^{\text{FET}}$ values of $3.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (P1) and $1.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (P4) in their respective series. Through the Derjaguin–Muller–Toporov (DMT) model for AFM topography, the elastic modulus of PII2T was confirmed to be (0.55, 0.55, and 0.51 GPa) lower than that of the fluorinated P4–P6 (0.56, 0.67, and 0.71 GPa), respectively. The higher elastic modulus in P4–P6 is due to the higher backbone rigidity in the fluorination-based polymer. Benefitting from the advantages of twisted packing induced by the fluorinated backbone, the degree of crystallinity was reduced, indicating a favorable enhancement in stretchability and mechanical durability. Consequently, the modification of the asymmetric Si-C8/DT side chains and PII2T with a fluorinated backbone (P6) resulted in the best mobility preservation of 81% at 100% strain with the stretching force

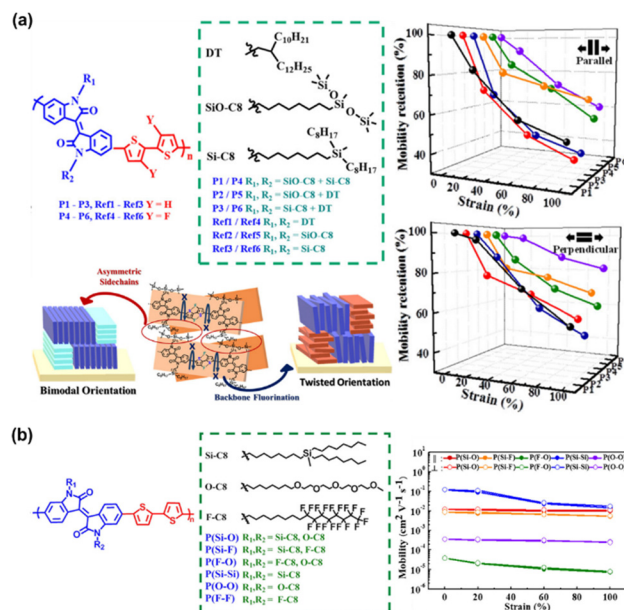


Fig. 9 Tuning the electrical-mechanical properties of conjugated polymers via asymmetric side-chain engineering. (a) Asymmetrical side-chain engineering of IID-based polymers structure; illustration of the effects of the asymmetric side-chain design and backbone fluorination on chain packing; and the mobility retention of these polymers with different strains and with the stretching force parallel and perpendicular to the charge-transporting direction.¹²² Copyright: 2019, the American Chemical Society. (b) Structure of isoindigo-bithiophene (IIT)-based conjugated polymers with three types of side chains and the orthogonal hole mobilities values of the stretched polymer films with strain ranging from 0 to 100%.¹²³ Copyright: 2021, the American Chemical Society.

2.3 Stretchable semiconducting polymer blends

In the simplest case, the widely studied semiconducting blend composed of 0.75 wt% P3HT:poly(dimethylsiloxane) (PDMS), where P3HT is prepared *via* “pre-deposition processing” became more resistance to external strain and exhibited

Liu *et al.* investigated the influence of molecular aggregation on the film morphology of conjugated polymer poly(indaceno-dithiophene-*co*-benzothiadiazole) (IDTBT)-blended-elastomer polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) at much broader parameter choices, including two types of high-boiling-point (bp) solvents such as toluene (Tol) and chlorobenzene (CB) and fast solvent evaporation from low-bp chloroform (CF) (Fig. 10b).¹³⁶ When a solvent with high-bp was utilized as the processing solvent (Tol and CB), phase

Table 1 Summary of the performance of intrinsically stretchable semiconducting polymers reported in the literature

Design Method	Materials	Engineering details	Average mobility (cm ² V ⁻¹ s ⁻¹)		Mechanical properties			Ref.	
			Before	After	Stretchability (% strain)	Elastic modulus (GPa)	Durability		
									Parallel
Block copolymer approach	P3HT	Diblock copolymers	1 × 10 ⁻²	—	—	13	0.028	—	77
	P3HT- ₃₅ -PE ₆₅	Diblock copolymers	5 × 10 ⁻²	—	—	660	0.24	—	79
	0.079		2.2 × 10 ⁻⁴ at 100% strain	1.1 × 10 ⁻⁴ at 100% strain	—	0.93 ^d	—		
	P3HT- <i>b</i> -PBA _{3k} ^a	0.073	7.9 × 10 ⁻⁴ at 100% strain	6.9 × 10 ⁻⁴ at 100% strain	—	0.63 ^d	—	$\mu_{h\parallel}^{\text{FET}}$ and $\mu_{h\perp}^{\text{FET}}$ ≥ 0.01 cm ² V ⁻¹ s ⁻¹ under 100% strain for 1000 cycles	—
	P3HT- <i>b</i> -PBA _{6k} ^a	0.061	0.025 at 100% strain	0.025 at 100% strain	—	~0.35 ^d	—		
Molecular spacer approach	P3HT- <i>b</i> -PBA _{12k} ^a	ABA triblock copolymer Diblock copolymer ABA triblock copolymer	0.014	2.1 × 10 ⁻³ at 100% strain	1.9 × 10 ⁻³ at 100% strain	—	0.19 ^d	—	81
	P3HT- <i>b</i> -PMA- <i>b</i> -P3HT		1.7 × 10 ⁻⁴	—	—	140 ^d	0.006 ^d	—	83
	P3HT- <i>b</i> -P3SiHT ^a		5.61 × 10 ⁻³	—	—	25.6	0.056 ^b	—	
	P3HT- <i>b</i> -P3SiHT- <i>b</i> -P3HT		5.14 × 10 ⁻³	—	—	118	0.003	—	
	P3HTT-DPP-10 ^a		9.29 × 10 ⁻⁴	—	—	COS ^a : 10	0.32 ^c	—	92
	10% T-10-T ^a	Semi-random polymers with CBS	2.53 × 10 ⁻⁴	—	—	COS: >80	0.13 ^b	—	93
	20% T-10-T		1.06 × 10 ⁻⁴	—	—	COS: >80	0.15 ^c	$\mu_{h\parallel}^{\text{FET}}$ = ~0.6 and $\mu_{h\perp}^{\text{FET}}$ = ~0.08 cm ² V ⁻¹ s ⁻¹ under 50% strain for 100 cycles	
	30% T-10-T		3.55 × 10 ⁻⁴	—	—	COS: >80	0.32 ^b		
	Ref-polymer ^a	2.1	0.9 at 100% strain	0.7 at 100% strain	COS: 25 ^c	0.52 ^c	$\mu_{h\parallel}^{\text{FET}}$ = 0.06 and $\mu_{h\perp}^{\text{FET}}$ = ~0.4 cm ² V ⁻¹ s ⁻¹ under 25% strain for 500 cycles		
	C12-DPP/TVT	Modified chain length and rigidity of CBS	1.3	1.0 at 100% strain	0.6 at 100% strain	COS: 100 ^c	0.33 ^b	50% strain for 100 cycles	95
	PDPPTT		0.76	0.07 at 75% strain	0.11 at 75% strain	COS: 20 ^c	0.60 ^c	$\mu_{h\parallel}^{\text{FET}}$ = 0.3 and $\mu_{h\perp}^{\text{FET}}$ = ~0.5 cm ² V ⁻¹ s ⁻¹ under 25% strain for 500 cycles	
	PDBTTT-10%		0.7	0.03 at 75% strain	0.06 at 75% strain	COS: 40 ^c	—	25% strain for 500 cycles	
Polymer approach	PID-3T-OC12-10% ^a	Introducing conjugated rigid fused-rings with optimized bulky side groups	0.9	0.27 at 75% strain	0.2 at 75% strain	COS: 60 ^c	—	25% strain for 500 cycles	96





Table 1 (continued)

Design Method	Materials	Engineering details	Average mobility (cm ² V ⁻¹ s ⁻¹)			Mechanical properties			Ref.
			Before	After		Stretchability (% strain)	Elastic modulus (GPa)	Durability	
				Parallel	Perpendicular				
Terpolymerization approach	G1 ^a	Introducing PAM-coupled alkyl side chains into the polymer backbone	0.52	0.030 at 100% strain	0.048 at 100% strain	0.85	—	$\mu_{h\parallel}^{FET} = 3 \times 10^{-3}$ and $\mu_{h\perp}^{FET} = 2 \times 10^{-4}$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles	
	G2 ^a		0.26	0.038 at 100% strain	0.052 at 100% strain				
	G3 ^a	0.38	0.10 at 100% strain	0.12 at 100% strain	0.76	—			
	G4 ^a	0.15	0.011 at 100% strain	0.031 at 100% strain	0.71	$\mu_{h\parallel}^{FET} = 0.02$ and $\mu_{h\perp}^{FET} = 3 \times 10^{-3}$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles			
	G5 ^a	0.21	0.021 at 100% strain	0.043 at 100% strain	0.36				
Symmetric side-chain approach	DPP-8TVT	A-D-A-D' type	> 1	> 1 at 100% strain	> 1 at 100% strain	COS: >> 100	0.65	98	
	PDCTT2T	Biaxially extended conjugated side chain	0.06	2 × 10 ⁻³ at 100% strain	4 × 10 ⁻³ at 100% strain	—	—	$\mu_{h\parallel}^{FET} = 0.02$ and $\mu_{h\perp}^{FET} = 0.03$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 800 cycles	
	PDCTT2T-F		0.02	2.5 × 10 ⁻⁴ at 100% strain	2.5 × 10 ⁻³ at 100% strain	—	—		$\mu_{h\parallel}^{FET} = 6 \times 10^{-3}$ and $\mu_{h\perp}^{FET} = 1.5 \times 10^{-3}$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 800 cycles
	PII2T	Introducing soft side chain	0.15	1.4 × 10 ⁻³ at 100% strain	2.6 × 10 ⁻⁴ at 100% strain	COS: <10 ^d	0.80 ^d	103	
	PII2T-PBA5	0.14	1.4 × 10 ⁻³ at 100% strain	3.4 × 10 ⁻⁴ at 100% strain	COS: ~20 ^d	0.63 ^d	$\mu_{h\parallel}^{FET} = 8 \times 10^{-3}$ and $\mu_{h\perp}^{FET} = 0.01$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles		
	PII2T-PBA10	0.10	0.02 at 100% strain	9.4 × 10 ⁻⁴ at 100% strain	COS: ~40 ^d	0.57 ^d		—	
	PII2T-PBA20	0.021	8.1 × 10 ⁻³ at 100% strain	1.2 × 10 ⁻⁴ at 100% strain	COS: 60 ^d	0.12 ^d	Stable $\mu_{h\perp}^{FET} \approx 0.4$ cm ² V ⁻¹ s ⁻¹ under 20% strain for 500 cycles		
	20DPPTTEC	Crosslinked with PDMS oligomer	1.37	—	—	COS: >150		0.28 ^d	$\mu_{h\parallel}^{FET} = 0.01$ and $\mu_{h\perp}^{FET} = 0.03$ cm ² V ⁻¹ s ⁻¹ under 25% strain for 2000 cycles
	DPP-10C ₅ DE	Tuning of the cross-linker's crystallinity	0.25	0.02 at 100% strain	0.02 at 100% strain	Pristine COS: 25 ^b	Pristine: 0.225 ^b	25% strain for 2000 cycles	
	5Linear ^a	0.34	0.29 at 100% strain	0.02 at 100% strain	Annealed ^e COS: 25 ^b	Annealed ^e : 0.225 ^b	Pristine: 0.205 ^b		$\mu_{h\parallel}^{FET} = 0.01$ and $\mu_{h\perp}^{FET} = 0.06$ cm ² V ⁻¹ s ⁻¹ under 25% strain for 2000 cycles
5Linear-H ^a	0.26	0.14 at 100% strain	0.05 at 100% strain	Annealed ^e COS ^a : 100 ^b	Annealed ^e : 0.234 ^b	Pristine: 0.234 ^b		$\mu_{h\parallel}^{FET} = 0.05$ and $\mu_{h\perp}^{FET} = 0.03$ cm ² V ⁻¹ s ⁻¹ under 25% strain for 2000 cycles	



Table 1 (continued)

Design Method	Materials	Engineering details	Average mobility (cm ² V ⁻¹ s ⁻¹)			Mechanical properties			Ref.	
			Before	After		Stretchability (% strain)	Elastic modulus (GPa)	Durability		
				Parallel	Perpendicular					
Y-Shape approach	5Branch ^a		0.30	0.20 at 100% strain	0.03 at 100% strain	Annealed ^e : COS ^a ; 75 ^b Pristine COS ^a ; 75 ^b	Annealed ^e : 0.230 ^b Pristine: 0.236 ^b	$\mu_{h\parallel}^{FET} = 0.03$ and $\mu_{h\perp}^{FET} = 0.12$ cm ² V ⁻¹ s ⁻¹ under 25% strain for 2000 cycles	113	
	5Branch-H ^a		0.26	0.17 at 100% strain	0.04 at 100% strain	Annealed ^e : COS ^a ; 100 ^b Pristine COS ^a ; 75 ^b	Annealed ^e : 0.204 ^b Pristine: 0.2 ^b	$\mu_{h\parallel}^{FET} = 0.03$ and $\mu_{h\perp}^{FET} = 0.11$ cm ² V ⁻¹ s ⁻¹ under 25% strain for 2000 cycles		
	PII2T-C6	Incorporation of branched alkyl side chain	1.14	0.11 at 100% strain	0.09 at 100% strain	> 100	0.430 ^c	$\mu_{h\parallel}^{FET} = 0.2$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles		
	PII2T-C8		3.24	0.58 at 100% strain	0.54 at 100% strain	> 100	0.270 ^c	$\mu_{h\parallel}^{FET} \geq 1$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles	114	
	PII2T-C6	Incorporation of branched alkyl side chain	2.48	0.2 at 100% strain	0.09 at 100% strain	—	0.565 ^d	—		
	PII2T-C7		2.06	0.1 at 100% strain	0.09 at 100% strain	—	0.465 ^d	—		
	PII2T-C8		4.67	0.7 at 100% strain	0.7 at 100% strain	—	0.375 ^d	—		
	PII2T-C9		0.92	0.15 at 100% strain	0.09 at 100% strain	—	0.280 ^d	—		
	PII2T-C10		2.23	2.0 at 100% strain	2.2 at 100% strain	—	0.250 ^d	$\mu_{h\parallel}^{FET}$ and $\mu_{h\perp}^{FET} = \sim 1$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 500 cycles		
	Asymmetric side-chain approach	PTDPPSe-3Si	Grafting hybrid siloxane-based side chains	0.85	0.21 at 100% strain	0.38 at 100% strain	—	0.378 ^b	—	119
		PTDPPSe-4Si		0.98	1.24 at 100% strain	0.46 at 100% strain	—	0.264 ^b	—	
PTDPPSe-5Si		0.88		1.08 at 100% strain	0.48 at 100% strain	—	0.186 ^b	—		
PTDPPSe-6Si		0.36		1.12 at 100% strain	0.33 at 100% strain	—	0.129 ^b	—		
PTDPPSe-7Si		0.24		0.82 at 100% strain	0.25 at 100% strain	—	0.087 ^b	—		
P1 ^a		Inserting asymmetric side chains	0.33	0.16 at 100% strain	0.18 at 100% strain	—	0.55	—	122	
P2 ^a			0.54	0.21 at 100% strain	0.32 at 100% strain	—	0.55	$\mu_{h\parallel}^{FET} = 0.15$ and $\mu_{h\perp}^{FET} = 0.2$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles		
P3 ^a			0.60	0.24 at 100% strain	0.29 at 100% strain	—	0.51	—		
P4 ^a			0.21	0.14 at 100% strain	0.12 at 100% strain	—	0.56	—		123
P5 ^a		0.22	0.12 at 100% strain	0.14 at 100% strain	—	0.67	$\mu_{h\parallel}^{FET} = 0.18$ and $\mu_{h\perp}^{FET} = 0.2$ cm ² V ⁻¹ s ⁻¹ under 60% strain for 400 cycles			
P6 ^a		0.26	0.16 at 100% strain	0.21 at 100% strain	—	0.71	Almost unchanged $\mu_{h\parallel}^{FET}$ under 60% strain for 1000 cycles			
P(Si-O) ^a	Inserting asymmetric side chains	0.012	9.8×10^{-3} at 100% strain	0.011 at 100% strain	> 80	0.45				
P(Si-F) ^a		8.7×10^{-3}	5.3×10^{-3} at 100% strain	5.3×10^{-3} at 100% strain	~ 60	2.09				

Table 1 (continued)

Design Method	Materials	Engineering details	Average mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		Mechanical properties			Ref.
			Before	After	Stretchability (% strain)	Elastic modulus (GPa)	Durability	
	P(F-O) ^a		3.8×10^{-5}	7.6×10^{-6} at 100% strain	8.0×10^{-6} at 100% strain	~ 20	2.79	—

^a Abbreviations: COS = crack onset strain; ref-polymer = DPP-based random copolymers incorporated with 10 mol% ethylene as the conjugation breaker; G1 = polymer with DPP-thiophenevinylene thiophene (PDPTVT) backbone with side chains consisting of methyl(8-bromooctyl)diethylsilane (SiC8); G2 = PDPTVT-SiC8-5% of poly(acryl amide) (PAM); G3 = PDPTVT-SiC8-9% PAM; G4 = PDPTVT-SiC8-16% PAM; G5 = polymer with DPP-selenophene (PDPPSe) backbone with side chains consisting of methyl(8-bromooctyl)diethylsilane (SiC8) and 5% of poly(acryl amide) (PAM); 5Linear = neat with 5 wt% semi-crystalline perfluorophenyl azide-based cross-linker blend; 5Branch = neat with 5 wt% highly crystalline perfluorophenyl azide-based cross-linker blend; 5Branch-H = neat with 5 wt% amorphous perfluorophenyl azide-based cross-linker blend ($T_g = -44.4^\circ \text{C}$); P1 = SiOC8 and Si-C8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P2 = DT/SiOC8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P3 = DT/Si-C8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P4 = SiOC8 and Si-C8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P5 = DT/SiOC8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P6 = DT/Si-C8 side chain engineered in isindigo-bithiophene (PII2T) backbone; P(Si-O) = carbosilane/oligoether side chains engineered in isindigo-bithiophene (IIT2T)-based polymer; P(Si-F) = carbosilane/semi-fluorinated side chains engineered in isindigo-bithiophene (IIT2T)-based polymer; and P(F-O) = semi-fluorinated/oligoether side chains engineered in isindigo-bithiophene (IIT2T)-based polymer. ^b Measured by film-on-water tensile test. ^c Measured by film-on-elastomer tensile test. ^d Thermally annealed at 150°C for 30 min under nitrogen.

separation of the IDTBT:SEBS blend occurred, which resulted in large isolated IDTBT domains, deterring the charge transport efficiency and mechanical deformation of the films. In contrast, the utilization of low-bp such as CF could effectively prevent the large-scale phase separation and promote the formation of a fiber network through the nanoconfinement effect in blend films. This effect enables us to achieve a stretchable film with a low elastic modulus of 72 MPa, large crack at a strain value of 326%, and negligible loss of mobility ($\mu_{\text{h}}^{\text{FET}} = 0.72 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) at 100% strain. It is envisaged that the molecular aggregation dynamics plays a critical role in the agglomeration and phase separation in conjugated polymer:elastomer blends, which offers an alternative strategy to manipulate the film morphology for a synergistic improvement in the mechanical and electrical properties of stretchable conjugated polymer films.

Nanoconfinement as the basis for the synergistic effect in semiconducting polymer (SP):insulating polymer (IP) blend systems is defined as the confinement of a material in a nanoscale region, which can cause changes in the physical properties of polymers due to interfacial and finite-size effects.³³ Several studies have reported that this confinement can result in a reduction in mechanical properties, glass transition temperature,¹³⁷ and elastic modulus,¹³⁸ increased crystalline ordering,¹³⁹ and better charge transport mobility.¹³¹ Therefore, clarifying the confinement effect of SPs and devising an effective strategy are necessary to design polymer blend composites with multi-aptitudes. Park *et al.* systematically investigated the confinement effect depending on the type of intermolecular interaction of SPs (such as P3HT, P18, DPP2T, 29-DPP, and PCDPTP) in the IP of polystyrene (PS) (Fig. 10c).¹⁴⁰ Based on the correlation between the morphological and charge transport properties on various types of SP:IP blend films, it was found that the 29-DPP-type SP exhibited an improvement in field-effect hole mobilities by 3–4 times (maximum $\mu_{\text{h}}^{\text{FET}}$ approaching $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for 60DPP:40PS blended type). The combination of temperature-dependent charge carrier mobility analysis and grazing incident wide angle X-ray spectroscopy (GIWAXS) indicated that the nanostructure of confined SPs exhibited a straight edge-on stacking structure in the blends. According to the above discussion, the capabilities of the blending method to aptly tune the electrical and mechanical properties in an easy and facile manner, coupled with its unsophisticated processing parameters (*e.g.*, blending ratio, molecular weight, and solvent), have created new avenues for many researchers to develop innovative optically transparent, stretchable, and self-healable semiconducting polymer systems for use in TFT devices.

3. Advancement from non-autonomous healing toward autonomous self-healing semiconducting polymers

According to the numerous strategic options previously reported, developing intrinsically stretchable semiconducting polymers through the insertion of bulky soft side chains or *via*



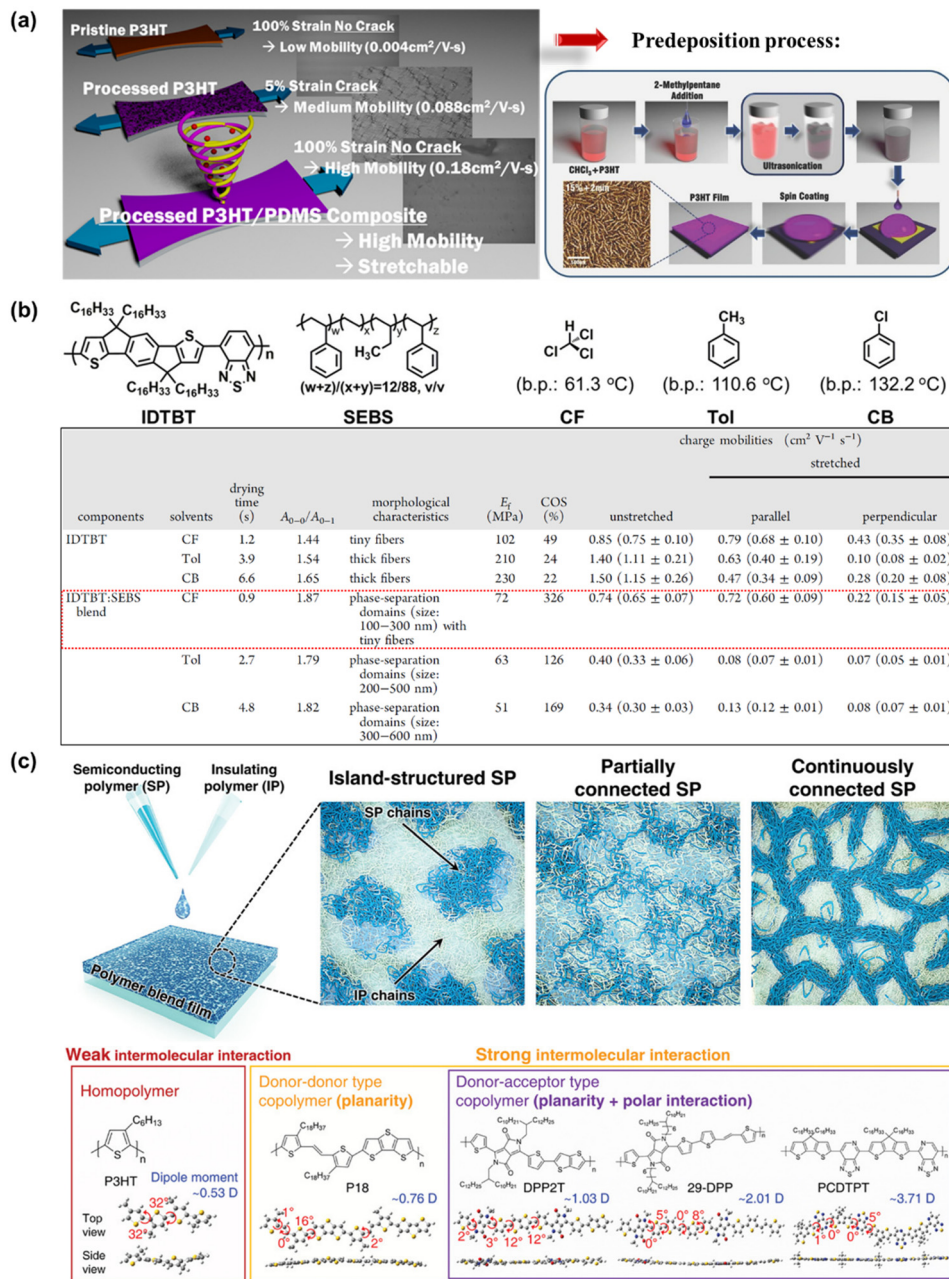


Fig. 10 (a) Schematic depicting the processed P3HT:PDMS, affording a blended semiconducting film that exhibits superior ductility and notable mobility *versus* the single-component polymer semiconductor counterpart.⁷³ Copyright: 2016, the American Chemical Society. Schematic illustration of the pre-deposition process.¹³³ Copyright: 2015, Wiley. (b) Molecular structures of the conjugated polymer IDTBT, elastomer SEBS, and the effect of different deposition treatments on the electrical and mechanical properties of IDTBT and IDTBT:SEBS blend.¹³⁶ Copyright: 2022, the American Chemical Society. (c) Representative structural morphologies of SP:IP blend and the DFT-optimized molecular models.¹⁴⁰ Copyright: 2021, Wiley.

the utilization of conjugation breaking units seems to be the preferred approach to generate materials with an increased amorphous content, reduced crystallinity, and improved resistance to mechanical failure, while maintaining good charge transport properties. As reported by Mei *et al.*, CBS can successfully reduce the backbone rigidity, and coupled with the fact that the incorporated CBS is capable of forming weak and reversible intra- and inter-chain bonds, the resulting polymer can be stretched excellently.²⁶ Furthermore, Zheng *et al.*

realized that the incorporation of H-bonding units in DPP-based conjugated polymers is a compelling manner to regulate their crystalline behaviors and mechanical properties.⁹⁴ Undoubtedly, these bonds becomes the most common and accessible types of supramolecular interactions to be implemented in π -conjugated polymeric systems. This type of non-covalent interaction is spontaneous, highly dynamic, and can be achieved through a wide variety of functional groups (amide, urea, urethane, carbonate, *etc.*), implying the versatility of the

Semiconductors			Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)			Mechanical properties		Ref.
Type	Material	f_{semi} (wt%)	Original	Parallel at 100% strain	Perpendicular at 100% strain	Crack onset strain (%)	Elongation break (%)	
p	P3HT	100	$\sim 2.3 \times 10^{-3}$	$\sim 1 \times 10^{-5}$	$\sim 2.2 \times 10^{-4}$	25	50	187
p	P3HT/PDMS	5	$\sim 1.8 \times 10^{-3}$	$\sim 1.2 \times 10^{-4}$	$\sim 2.3 \times 10^{-5}$	> 100	> 100	
p	P3HT/PDMS	0.49	0.17 ± 0.03	0.15 ± 0.01	—	—	182.1 ± 8.6	134
p	P3HT	100	0.02 ± 0.01	0.006 ± 0.001	—	32.6 ± 4.8	—	
p	DPP-DTT/PDMS	0.83	1.53 ± 0.22	1.35 ± 0.04	—	—	140.2 ± 10.2	
p	DPP-DTT	100	0.81 ± 0.11	0.18 ± 0.01	—	20.7 ± 5.2	—	
n	DPPDPyBT/PDMS	0.62	1.25 ± 0.09	1.08 ± 0.02	—	—	133.5 ± 7.6	
n	DPPDPyBT	100	0.43 ± 0.14	0.12 ± 0.01	—	22.5 ± 4.5	—	
p	Homo-P3HT NW	100	$(1.30 \pm 0.4) \times 10^{-2}$	$(1.70 \pm 0.9) \times 10^{-5}$	—	50	10	135
p	P3HT NW/PDMS	10	$(7.85 \pm 2.8) \times 10^{-3}$	$(3.74 \pm 0.7) \times 10^{-4}$	—	—	—	
p	Pristine P3HT	0.75	0.004 ± 0.0005	—	—	> 120	—	73
p	Processed P3HT	0.75	0.18 ± 0.03	—	—	> 100	—	
p	Processed P3HT/PDMS composite	0.75	0.11 ± 0.016	—	—	> 100	—	

Considering two important features, *i.e.*, the diffusion of polymer chains and the reformation of broken dynamic bonds,¹⁶⁰ a low glass transition temperature, which promotes polymer chain movement and abundant sites for dynamic interactions, is an implicit requirement in typical intrinsically self-healing semiconducting polymer systems. Since 2001, the Web of Science has listed more than 6000 publications covering

To the best of our knowledge, Bao's group was the first to successfully fabricate magnificent intrinsically stretchable and self-healable semiconducting polymers in TFT devices by utilizing hydrogen-bonding moieties,²³ wherein the nano-size cracks formed by external mechanical stress were found to heal with the assistance of solvent vapour and thermal annealing. The design concept applied was through a backbone engineering approach by synthesizing and incorporating a non-covalent crosslinking moiety of 2,3-pyridine dicarboxamide (PDCA) as a conjugation-break spacer in DPP-based conjugated polymers, namely P(DPP-TVT-X).²³ The design rationale for this intrinsically stretchable polymer was as follows: (1) the H-bonds between the non-conjugated PDCA moieties are moderate, which facilitate stress-energy dissipation during stretching, thus allowing the breaking/reforming of hydrogen bonds when strain is applied; (2) the PDCA moiety containing two amide groups markedly lowers the tensile modulus of the resulting polymer and (3) the charge transport mobility can be well-sustained due to the small loading fraction of PDCA moieties. The combination of the polymer with a small amount of 10 mol% PDCA moiety (P3) could reduce the elastic modulus from

1 GPa to 0.25 GPa without sacrificing the charge mobility compared to the pristine p(DPP-TVT)(P1). As shown in Fig. 11a, the $\mu_{\text{h}}^{\text{FET}}$ of the P3 thin-film reached up to $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and remarkably it could be maintained as high as $1.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ even with 100% elongation after a hundred cycles along the direction perpendicular to the strain. On the contrary, pristine P1 failed to maintain its mobility level under 100% applied strain, resulting in a rapid decline to $<10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. A reference conjugated polymer of P(DPP-TVT-10 mol% Me-PDCA) (P7) with the exclusion of amide-based H-bonding induced by the additional Me-PDCA chain breaker was studied. The distinct influence in mechanical behavior (25% of crack formation strain) of P7 indicates the important contribution of dynamic bonding as a sacrificial bond in the amorphous domain of these systems. Moreover, the mobility of the

damaged P3 could be almost fully recovered from $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ using a solvent/thermal healing treatment to promote the polymer chain movement. The existence of healing ability in P3 was also proven by AFM characterization, showing that the nano-cracks became less noticeable after thermal treatment.

Besides the PDCA unit, other amine-containing outermost side chains were also developed and investigated. Ocheje *et al.* confirmed the strong influence between the crystallinity, electrical, and mechanical performances of DPP-TVT derivatives with amide-containing alkyl side chains (Fig. 11b).¹⁶⁴ Indeed, the inclusion of 10% amide-containing alkyl side chains (P3) significantly promoted their stretching ability up to 75%, reduced their elastic modulus from 203 MPa to 115 MPa, and facilitated molecular alignment after stretching. Upon stretched

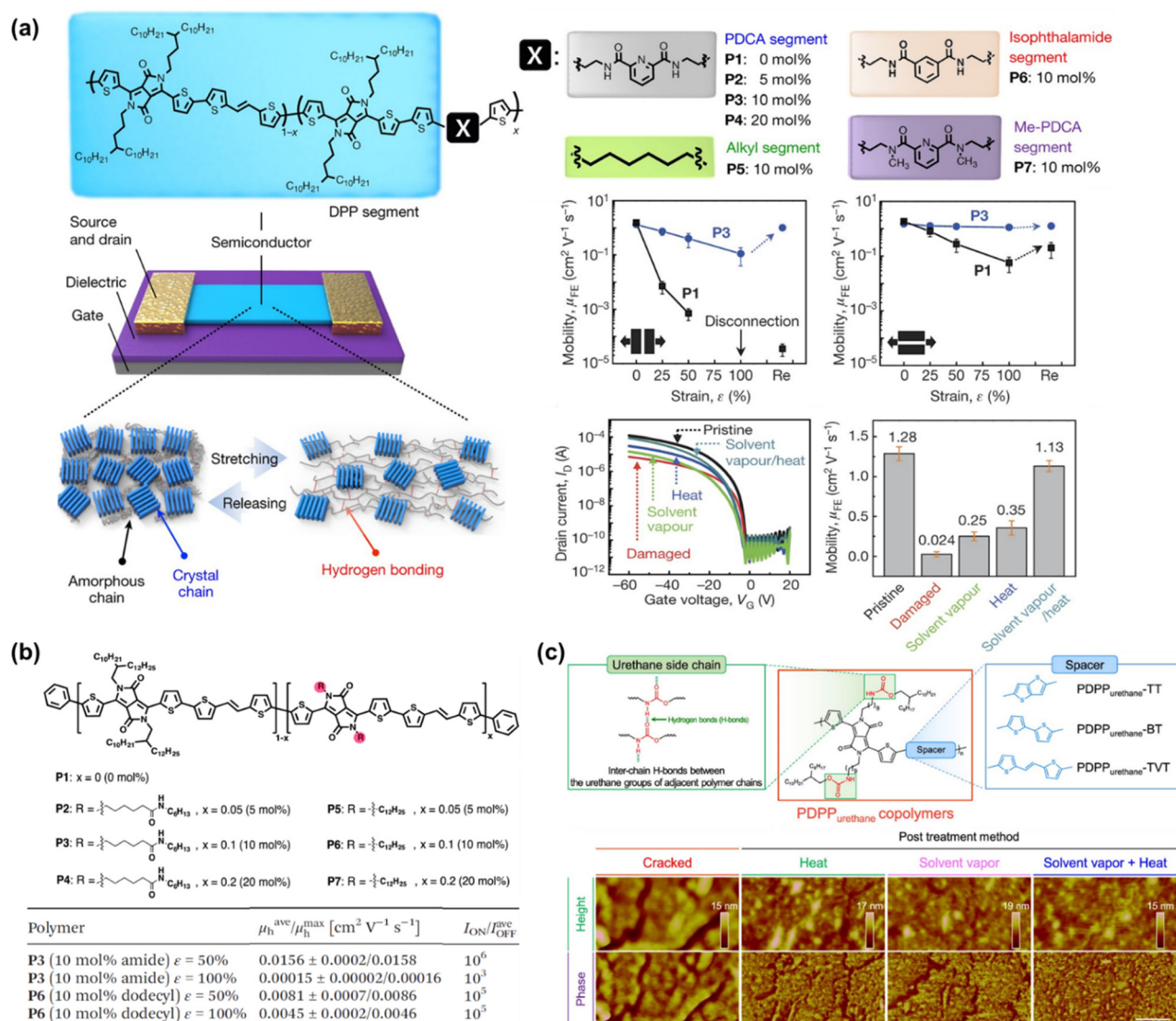


Fig. 11 Modulation and influence of the self-healing properties of conjugated polymers based on dynamic hydrogen bonding. (a) DPP-based polymer with various non-conjugated segments.²³ Copyright: 2016, Springer Nature. (b) Amide-containing alkyl chains in DPP-based conjugated polymers.¹⁶⁴ Copyright: 2018, The Royal Society of Chemistry. (c) Series of DPP-based "alternating" copolymers containing urethane side chains with different donor counterpart co-monomers, denoted as PDPP_{urethane}-TT, -BT, and -TVT.²⁴ Copyright: 2021, Wiley-VCH.

Fundamentally different from the reported IP/SP blends, in which macroscopic phase segregation is often involved, Zhao *et al.* proposed a general strategy to fabricate self-healing melt-processable semiconductors (Fig. 12a).¹⁷⁵ The complementary semiconducting polymer blends were composed of flexible DPP-C5 conjugation-break spacer as a matrix polymer due to its low melting temperature (138 °C) and a fully conjugated polymer (DPP-C0) as a tie chain. After the blend of 95 wt% DPP-C5

Recently, Zhang *et al.* also used physical blending to manufacture new self-healing semiconducting composites, but the mechanism of self-healing was different from previous reports.¹⁶⁶ Taking advantage of butyl rubber (BR) as the elastomer with outstanding elasticity (a low persistence length of 5.2 Å), strong adhesion, and excellent barrier properties to both oxygen and water, together with PDPPTVT as a p-type donor-acceptor semiconducting polymer with high charge transport mobility,¹⁷⁴ these two well-known materials were blended. A free-standing tensile tester was used to evaluate the mechanical and self-healing behavior in various blend ratios between

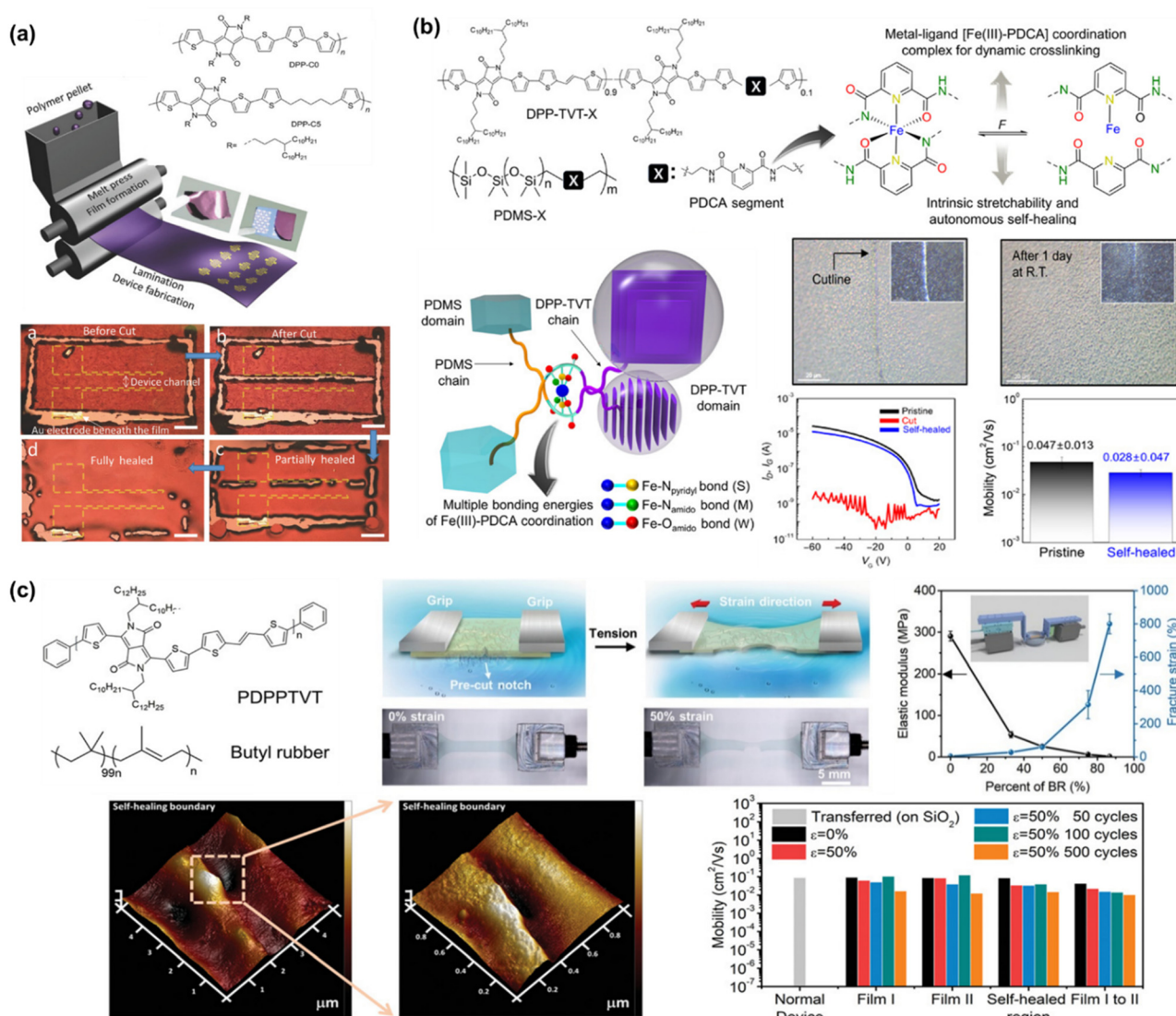


Fig. 12 Stretchable and self-healable semiconducting polymer via blending strategy. (a) Materials, fabrication procedure, and TFT characterization of melt-processing of complementary self-healable semiconducting polymer blends.¹⁷⁵ Copyright: 2017, Wiley. (b) Illustration and the mechanical-electrical properties of Fe(III)-PDCA ligand bonding of PDMS-PDCA and DPP-TVT-PDCA in the blend film.³¹ Copyright: 2019, Science Advances. (c) 3D-schematic illustration, optical images of notched film before and after tensile deformation on water surface, and the self-healing test as a function on electrical performances of 2:3 PDPPTVT/BR film.¹⁶⁶ Copyright: 2020, Wiley.

PDPPTVT and BR (Fig. 12c). As the weight fraction of BR increased to $\sim 90\%$, the semiconducting polymer composite showed a significant drop in elastic modulus to 1 MPa and great improvement in fracture strain exceeding 800%. Given that the BR polymer endows tackiness and fast segmental motion to low T_g BR polymer chains at room temperature,^{174,176} the polymer chains that reconstructed during contact led to autonomous self-healing within a few seconds at room temperature, and the film could be stretched up to 150% of its original length after healing. As is the case with electronic performance, the charge mobility was maintained on the same order of magnitude, even after 500 stretch-release cycles at 50% strain. Additionally, this new composite exhibited outstanding tear-resistant properties, which were attributed to the highly

entangled BR network being able to redistribute stress, thus preventing crack propagation and increasing the durability. From a mechanical perspective, this material successfully displayed the lowest modulus and the highest deformability compared to other polymer designs.^{33,77,81,104,177–181} Overall, these tear-resistant and room temperature self-healable semiconducting polymers feature special functionalities, which can facilitate future developments for wearable applications.

4. Perspectives

As has been elucidated from the previous sections, the presence of self-healing ability in semiconducting polymers is mainly

derived from the dynamic covalent and non-covalent interaction found in a variety of bond formations.^{142,143} However, this perspective focuses on the stretchable and self-healable semiconducting polymers that are scarce and less well-exploited in TFTs due to the limitations and challenges associated with this emerging technology. Recent advances in the performance of conjugated polymers through molecular design or physical blending have successfully exhibited field-effect mobilities $>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{23,166} similar to the electrical performance of amorphous silicon thin-film transistors.^{182–184} Furthermore, after integrating self-healable semiconducting polymers in TFT devices, they can withstand extreme mechanical behavior. However, to actualize a complete set of self-healable TFTs, three self-healable components need to be developed concurrently, *i.e.*, semiconductors, dielectrics, and three-terminal electrodes. Compared to the fabrication of self-healable semiconducting polymers, the development of other self-healable components in TFTs is simpler and has met the standards for implementation in TFTs to be integrated into sensors, memory devices, and drive circuits for displays.^{106,149,165,185,186} For example, in 2016, Bao and co-workers introduced the design of electrically stable and self-healable dielectric layers based on metal-ligand coordination interaction in a PDMS matrix.¹⁴⁹ The supramolecular non-covalent bond contained in this interaction allows impeccable self-healing property for potential applications in wearable sensors and electronic skins. Through the proper selection of counter anions, TFTs with hysteresis-free transfer characteristics can be generated. Self-healable conductive materials composed of a 3D percolation network of carbon nanotubes (CNTs) or silver nanowires (AgNWs) embedded in a self-healable polymer matrix were used as source, drain, and gate components to fabricate a fully stretchable and self-healable multi-functional electronic skin system.¹⁸⁵ This unique property was achieved by taking advantage of the low glass transition temperature and dynamic hydrogen bonding properties of an elegant elastomeric matrix,¹⁶⁰ where the broken conductive network present in the non-covalently bonded hydrogen moieties could be autonomously recovered from disconnection during the self-healing process.

Continuing the discussion in Section 3, the same group succeeded in fabricating (DPP-TVTPDCA)-blended-(PDMS-PDCA-Fe elastomer) as a stretchable and self-healable semiconducting polymer film for an active-matrix strain-sensing array.³¹ The Fe(III)-PDCA coordination complex inside the polymer blend was comprised of 3 types of bonding forces (Fe–N_{pyridyl}, strong; Fe–N_{amido}, medium; and Fe–O_{amido}, weak), which could facilitate the crosslinking process for self-healing capability based on non-covalent interaction. Fig. 13 shows that a fully stretchable 5×5 active-matrix sensor-based e-skin was capable of detecting pressure-induced deformation, with the simultaneous visualization of the applied strain. The active area of each pixel has a channel width of 1 mm and channel length of 150 μm . All devices showed good uniformity with a maximum mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an average mobility of $0.076 \pm 0.019 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It needs to be emphasized that the authors inserted a self-healing semiconducting film between stretchable sandwich layers. Thus, to construct

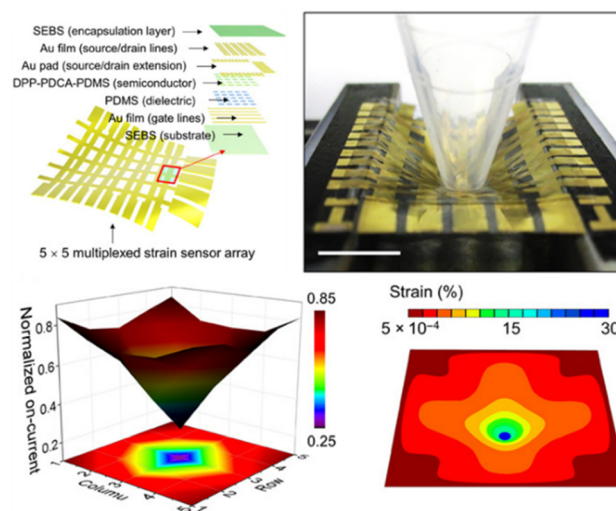


Fig. 13 Architecture, photograph, normalized on-current, and simulation results of strain applied by poking with a plastic bar to the fully stretchable active-matrix TFT array containing self-healable semiconducting polymer.³¹ Copyright: 2019, Science Advances.

skin-like sensory devices and verifiably operate within a medically safe voltage range, integration with self-healable conductors and especially high- k dielectric materials still needs to be developed.

Despite the very promising advances in the manufacture of autonomous self-healable semiconducting polymers, their implementation in real applications or commercial products is still in its infancy. To date, the application of self-healing materials in devices is still at the proof-of-concept stage. Besides the possible mismatch between self-healing ability and electrical mobility, the application of self-healable semiconducting polymers in TFT devices is currently limited due to their tedious fabrication process, which may be incompatible with existing electronic technologies established in the silicon industry. Technically, how to make them comparable in size so they can fit in the architecture of boards, especially on ultra-thin semiconductor films at the micro- and nano-scale needs to be considered. Therefore, scalable and reliable fabrication processes such as patterning or printing should be developed for the mass production of self-healing devices and electronics. It should be noted that the self-healing process remains relatively slow and the utilization of self-healing has thus far been limited to small-area damage (nano crack), and thus self-healing capabilities at damage scales larger than layer thickness, which are rapid, repeatable, and autonomous should be explored further. Lastly, the current electronic properties are not yet comparable between non-healable electronic devices and healable functional electronic devices. Thus, further perseverance in the field of new design concepts for self-healable semiconducting polymers is required.

5. Conclusions

This review presented an update on the current status and developments of stretchable to self-healing semiconducting



polymers in TFT devices. In the early stages of research, the engineering strategy focused on the fundamental morphological properties of the semiconducting polymer itself such as MW and RRe, and thus other considerations during the preparation of thin films was thoroughly reviewed. As an example, polythiophene derivatives having a high MW possess a superior synergistic relationship between mobility-stretchability properties. An enhanced chain entanglement effect and greater connectivity between crystallites in P3HT and self-aggregation of polymer chains are the advantages of utilizing high MW polymers. The main part of this report, before moving on to autonomous healing properties integrated in TFT devices, elaborated and discussed the seven main approaches and additional function compounds used to overcome the compromise between electrical-mechanical properties. Based on the range of limitations of this review, only the molecular spacer and symmetric side-chain approaches could achieve a field-effect mobility of $>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ even in the stretched state up to 100%, together with a lower elastic modulus ($<0.1 \text{ GPa}$), indicating excellent deformability and ductility to promote tolerance toward their electrical functionalities under repeated mechanical loading-unloading cycles over long-term usage. The complementary part of this report linked the chosen approaches for designing novel intrinsically stretchable semiconducting polymers with partial or full healing ability implemented with the polymers used in device technologies. Hence, the structural diversity of D-A type polymers has been well selected for the more innovative design of non-covalent interaction-induced self-healing capability. Given that most intrinsically self-healable semiconducting polymers are constructed *via* complex engineering strategies, the conjugated polymer blending approach was introduced as a modest method with fruitful advantages. This method results in autonomous self-healing capability and a remarkable enhancement in mechanical adherence for high-mobility polymer semiconductors in an easy and facile manner.

Author contributions

Y.-C. C. conceived the main concept of the review article. L. L. organized the overall manuscript and wrote the introduction, and the parts relating to fundamental properties of polythiophene derivatives, backbone-engineering approaches, the advances from non-autonomous to autonomous self-healing semiconducting polymers, perspectives and conclusions in the manuscript. A. N. wrote the parts relating to the solution processing and fabrication effect, structural engineering of polymer side chains, and preparing the summary table. S. P. P. organized the overall manuscript. The manuscript was written through contributions from all the authors. All the authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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