

17

Conjugated Polymer Thin Films for Stretchable Electronics

Aristide
Gumyusenge,
William McNutt,
and Jianguo Mei

17.1	Introduction	535
17.2	Engineering Approach for Stretchable/Flexible Electronics	536
	Criteria for Flexible Electronics • Designing Stretchable Electronics	
17.3	Molecularly Stretchable Polymers for Organic Electronics	543
	Introduction of Section • Design Strategies and Structure-Property Relationship of Polymers • Backbone Engineering • Crosslinks and Dynamic Bonds • Sidechain Engineering • Additives	
17.4	Closing Remarks	554
	References	554

17.1 Introduction

Conjugated polymers have attracted tremendous attention in the past few decades owing to their optical and electronic properties achievable via material design and engineering.¹⁻⁶ In addition to these properties, conjugated polymers present features not readily found in inorganic counterparts: facile processability, biocompatibility, flexibility, and stretchability.⁷⁻¹² In that regard, the use of conjugated polymers for the manufacturing of thin film-based electronics has been widely studied for various applications. For organic thin film electronics, polymers that can be processed by solution- or melt-processing are of great interest. A wide library of polymers that can be processed at ambient conditions with performances comparable to that of the inorganic counterparts have been achieved.¹³

An emerging and attractive feature is the ability of conjugated polymers to be used in flexible and stretchable electronics. This feature has promised the manufacturing of next-generation electronics featuring wearables, e-skins, and self-healing electronics.^{8,14-18} For this class of electronics, materials able to sustain strain while retaining their intrinsic properties are required. Engineering approaches have been utilized to attain ultra-flexible and stretchable electrodes as well as dielectric layers thus making the organic semiconductor (OSC) layer, the limiting component towards achieving flexible and stretchable electronics.¹⁹ This limitation was first believed to be intrinsic to most organic high-performers. Most high-performance semiconducting polymers had historically exhibited rigid backbones, high crystallinity, and high aggregation behavior in solid-state.^{13,20-22} This rendered the resulting thin films to be fragile and not suitable for deformable electronics. Recently, engineering approaches and materials designs have demonstrated that it is possible to deviate from this seemingly quintessential rigidity of conjugated polymers (i.e. crystallinity) without sacrificing the desired electronic properties.

The focus of this chapter is to investigate both engineering and materials design principles to achieve the mechanical excellence complementing the electronic properties in conjugated polymer thin films. We first discuss the mechanical requirements for ultra-flexible and stretchable devices as well as the ubiquitous metrology. We will then discuss two successful approaches able to lift the trade-off between mechanical and electronic properties in conjugated polymers. The use of strain engineering and nanocomposites are first overviewed as the two successful engineering tools towards stretchability. The design principles of molecularly stretchable polymers will then be discussed. In this polymer chemistry approach, we mainly focus on backbone and sidechain engineering, crosslinking, as well as the use of additives.

17.2 Engineering Approach for Stretchable/Flexible Electronics

Thin materials can flex; wavy materials can stretch. These two engineering approaches have served as a platform to afford unconventional mechanical behaviors for organic electronics. Ultrathin polymer substrates have allowed for the fabrication of lightweight devices with unprecedented conformability.^{9,23,24} Most conjugated polymers do not show sufficient mechanical deformability; by processing these semiconductors into thin films which can then be deposited onto elastic substrates, device arrays with improved mechanical properties can be realized. To attain stretchability, strain engineering is often utilized. By introducing wavy patterns on the substrates, the Poisson ratio can be reduced in directions perpendicular to the applied mechanical strain.²⁵ With the success of strain engineering for substrates, the ongoing efforts in the field of organic electronics have shifted towards designing organic semiconductors able to intimately conform with the plastic substrates. In that regard, notable success has been realized with the use of nanocomposites in thin film processing. The confinement effect on semiconducting polymers into nanoscale environments has shown to amplify their mechanical properties while preserving the electrical behavior.²⁶

In this section, we first discuss the requirements for thin, therefore flexible, systems, mainly semiconducting polymer-based thin films. We will then address ways to compensate for Poisson effect in polymer thin films by the introduction of wavy structures. The use of polymer nanocomposites in stretchable arrays will be discussed before we tackle the design of intrinsically stretchable semiconductors.

17.2.1 Criteria for Flexible Electronics

17.2.1.1 Metrology

Two parameters are to be considered in materials design for flexible and stretchable electronics: how much bending (bending radius, i.e. flexibility) and strain (Poisson effect, or stretchability) the material can tolerate. For conjugated polymer thin films, several methodologies on measuring the bending radius have been demonstrated.²⁷ One of the ubiquitous methods is the buckling method, first demonstrated by Stafford et al.²⁸ By forming waves on the surface of a pre-strained substrate, a layer of the active material is deposited, and the strain on the substrate is released. The periodicity of the formed buckles is then used to extract the bending radius as well as the Young modulus. First, in order to be studied using the buckling method, the semiconducting films ought to adhere well onto the flexible substrate, most commonly polydimethylsiloxane (PDMS). In the cases of rigid and stiff films, initial failure resulting in microcracks or even de-bonding is often observed (Figure 17.1 A)). Depending on the device geometry, the organic thin film then must sustain tensile strain, compressive strain, or shear stress, as shown in Figure 17.1 B), without losing its electronic properties. For organic thin films, the integrity between soft slabs of PDMS and the semiconducting layer tends to be excellent allowing most OSCs to pass the initial film failure. Methods allowing for the evaluation of this adhesive or cohesive ability have been developed for laboratory scale initial measurements.¹⁵ Organic thin films, notably conjugated polymer thin films, are thus attractive for applications as they exhibit excellent interfacing with soft supports

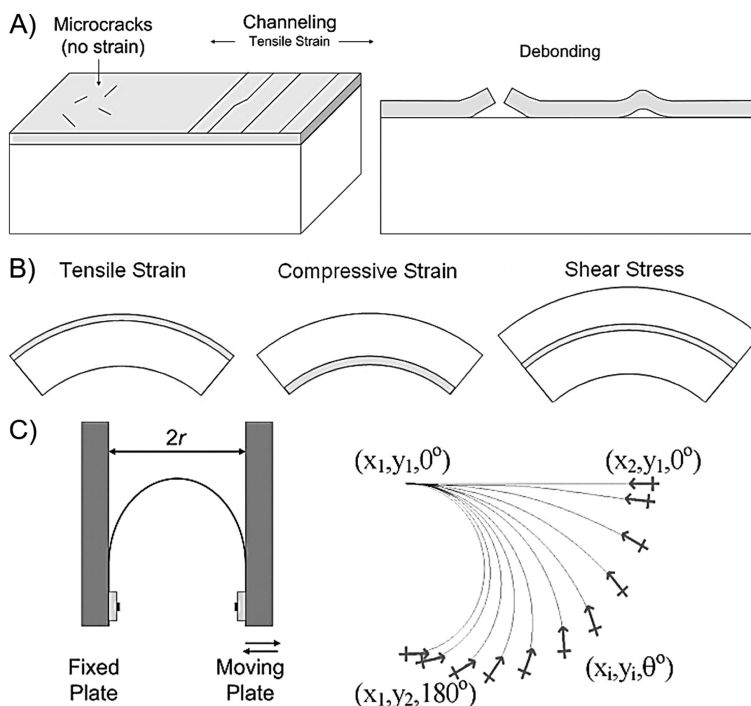


FIGURE 17.1 Thin film flexibility metrology. A) Initial failure evaluation. B) Typical geometries of flexible devices and corresponding strain type experienced by the thin films upon bending. C) Evaluation of thin-film flexibility via the collapsing radius test and the X-Y-θ test. From Lewis, *Mater. Today* 2006, 9, 38–45.

for evaluation.²⁹ A more detailed discussion on recent advances in semiconducting polymer thin films’ mechanical properties and measurements can be found in Chapter 7.

Alternatively, thin film flexibility can also be directly tested using the bending curvature and the X-Y-θ techniques, as shown in Figure 17.1 C).³⁰ These two methods are more advantageous for materials which cannot form buckles easily to be studied using the aforementioned buckling method. In the bending (or collapsing) radius set-up, the sample is clamped between two parallel plates whose separation distance is controlled by a linear actuator. Initially, the sample is mounted between the plates in a curved shape of a relatively large radius (larger than the one corresponding to the onset of cracking of the substrate coating) and is subsequently squeezed between the plates. The bending radius experienced by the sample in such a geometry is then given, in a first approximation, by half of the distance between the plates, L_p , i.e. $r = L_p/2$. For the X-Y-θ test, the sample is clamped in a flat position between a fixed plate and a co-planar plate mounted on top two linear and one rotary motorized actuators. These actuators control the spatial coordinates of the sample end in X-Y-θ space so that the sample end is positioned on the coordinates of a circumference. The angle θ is defined as the angle between the tangent to the mobile sample end and the X-axis. The length of the sample that is being bent, L_0 , remains fixed during the measurement, and it is defined as the initial distance between the clamps, $X_2 - X_1 = L_0$. With assumed perfectly elastic behavior of the substrate, the bending moment is uniform across the length of the sample and the sample is bent uniformly at the corresponding radius. In order to have the sample bent to a radius r , the coordinates become $\theta = L_0/r$, $X = (L/\theta) \sin(\theta)$, $Y = (L_0/\theta) [1 - \cos(\theta)]$.³¹ Both methods illustrated here can be used to extrapolate how far a thin film can bend before cracking or collapsing. The smaller the collapsing radius, the more flexible the film is. For conjugated polymer thin films, a bending radius of a few tens of micrometers is typically desired for flexible electronics.

17.2.1.2 Achieving Flexibility

Device flexibility can be achieved in almost all materials with lowered thickness. Semiconducting polymers which have shown to be easily processed into thin-films thus present a great platform towards achieving this thickness-dependent flexibility.^{5,24,32–34} Assuming intimate adhesion between the film and the substrate, the periodicity of the formed buckles, λ_e , depends on the thickness of the deposited film (Figure 17.2). For instance, in a systematic study by Stafford et al., the size of the formed equilibrium wavelengths, λ_e , was found to depend on three parameters in a bilayer setup: membrane strain energy in the film, bending energy of the film, and near-surface strain energy in the substrate. Long wavelengths were shown to be suppressed due to the large strain energy associated with deformation of the soft substrate, and the short wavelengths due to the sizable bending energy associated with the stiff film.³⁵ Thus, the system undergoes periodic buckling with an intermediate wavelength to minimize the total strain energy. For an elastic film on an elastic substrate, the equilibrium wavelength, λ_e , of buckling is given by Equation (17.1) below and the associated elastic modulus is given by Equation (17.2):

$$\lambda_e = 2\pi h_f \left(\frac{\bar{E}_f}{3\bar{E}_s} \right)^{1/3} \quad (17.1)$$

$$\bar{E}_f = 3\bar{E}_s \left(\frac{\lambda_e}{2\pi h_f} \right)^3 \quad (17.2)$$

Where λ_e is the wavelength of the formed buckles, h_f the film thickness, \bar{E}_f and \bar{E}_s are the plane-strain moduli of the film and the supporting substrate, respectively. As shown in Figure 17.3 A), thin film flexibility depends, almost linearly, on its thickness especially for sub-40 nm thick films. By minimizing the film thickness, the curvature radius can be lowered to only a few nanometers, and the resulting Young's modulus can significantly deviate from that of the bulk.³⁵ The measured Young's modulus, $\bar{E}_{f,app}$, for bilayer configurations was further shown to be independent of material's molecular weight once below film thickness of 40 nm (Figure 17.3 A)). When approaching then finite film thickness, composite model (Figure 17.3 A) and B)), the Young modulus exponentially deviates from that of the bulk, reaching as low as 10% of bulk value for a thickness of 7.5 nm. This method has then been adopted for semiconducting thin films as a tool to quickly demonstrate how far the processed layers can buckle.^{27,29}

17.2.1.3 Flexible Device Architecture

Several efforts in the field have then successfully utilized ultrathin structures to demonstrate light-weight functional device arrays by deviating from the bulk thickness as much as possible.^{9,23,24,36–38} By

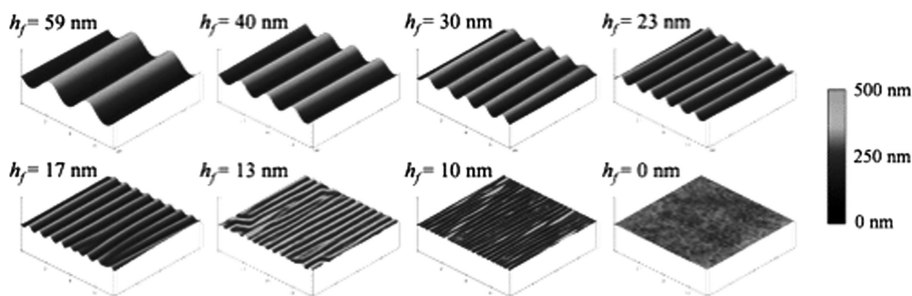


FIGURE 17.2 AFM height images showing the dependence of buckles on film thickness. For film thickness below 40 nm, a substantial deviation from the bulk behavior is observed. From Stafford et al., *Macromolecules* 2006, 39, 5095–5099.

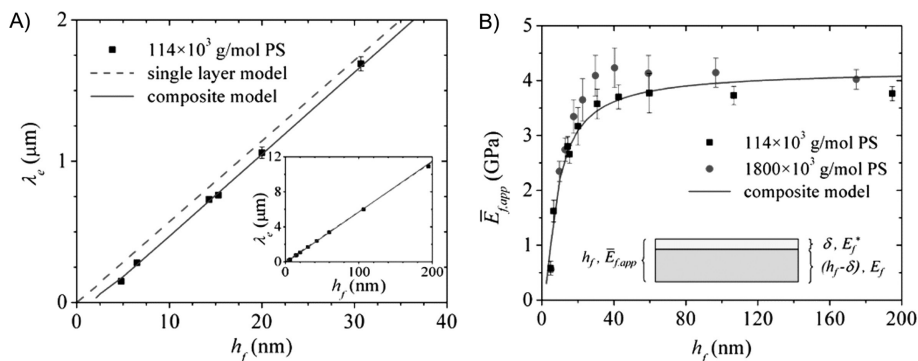


FIGURE 17.3 A) A linear dependence of buckle periodicity on the film thickness in sub-100 nm films for polystyrene films with agreement to single layer and composite models. B) The influence of film thickness on the measured Young's modulus. Sub-100 nm films thicknesses show an exponential deviation from the bulk behavior. From Stafford et al., *Macromolecules* 2006, 39, 5095–5099.

incorporating polymer thin films onto thin plastic substrates, ultra-light and highly flexible devices could be achieved. Upon multi-directional deformations, these devices can retain their original functionalities when made tough with the assistance of the mechanical properties of the substrate. Figure 17.4 A) shows an example of a solar cell device using poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) as the active material deposited on ultrathin polyethylene terephthalate (PET) substrates. The assembled device could achieve a bending radius of $35 \mu\text{m}$ as it could easily wrap around a human hair. By using thin substrates, these solar cells could sustain wrinkling and shuffling, and recover to their original state. The scanning electron microscopy images revealed the formation of ultra-fine buckles/wrinkles without cracking the surface (Figure 17.4 B)). With the overall thickness being well under $2 \mu\text{m}$, these devices also showed to be ultra-lightweight, making these kinds of assemblies attractive for various applications. The limiting factor for flexible electronics would thus become achieving finite film thickness.

17.2.2 Designing Stretchable Electronics

While soft elastic substrates can be used to attain excellent conformability, other components of the organic device, especially the semiconducting layer, must display the same mechanical behavior to attain overall device stretchability. As discussed above, device thickness has been the most prominent tool for achieving flexibility, but this does not accommodate the desired stretchability. In order to achieve all-stretchable arrays, one ought to consider materials and devices that are capable of accommodating for the Poisson effect under strain. To design a stretchable array for organic electronics, the force in the directions perpendicular to the stretching direction has to either be dissipated or consumed by the material's ability to contract in that direction. Rubber-like materials would render intrinsic stretchability, but most semiconductors tend to be more rigid, and those with excellent elasticity show poor electronic performance. In that regard, engineering approaches have been used to demonstrate rubbery systems. For instance Zhao et al. demonstrated that by processing semiconducting polymers into free standing thin microwires could improve their ductility while retaining the semiconducting properties.³⁹ Figure 17.5 A) shows a melt-drawn semiconducting polymer microfiber, and B) and C) the mechanical behavior of the wire during stretch/release cycling. Zhao et al. showed that the polymeric material could stretch elastically up to 10% of the original length as the yield point. The fibers could further be stretched plastically up to 180% while retaining their semiconducting abilities. Within the fibers, with the elastic stress regime, polymer chains could reversibly align and could dissipate the straining force. Notably, this stretchability could be tuned via the molecular design using sidechain engineering as well as conjugation breaking.

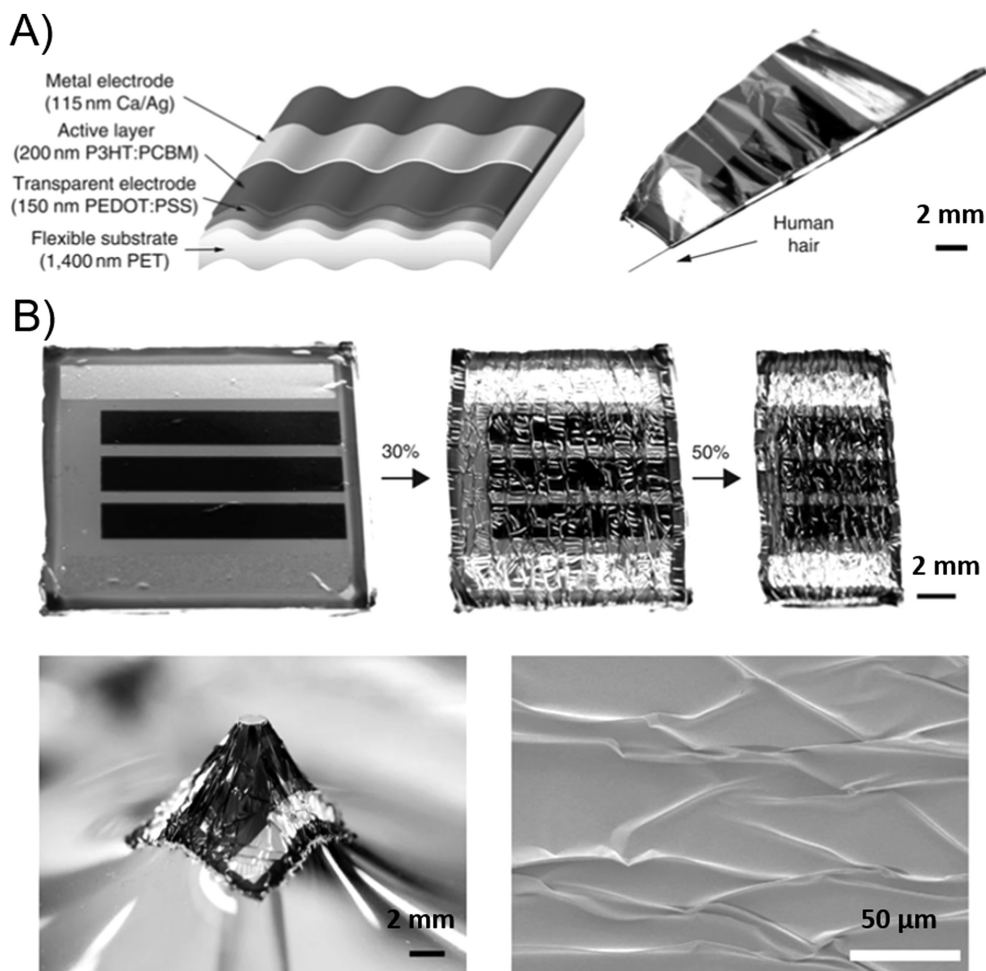


FIGURE 17.4 A) Device structure of an ultra-flexible device on thin substrates with extremely low bending radii. B) Illustration of mechanical conformability of the devices fabricated on ultra-thin substrates. From Kaltenbrunner et al., *Nat. Commun.* 2012, 3, 770.

By changing the conjugation break spacer (CBS) length from three, to five, and seven methylene units, Zhao and coworkers could demonstrate that CBS length has a large influence on the yield point and that sidechains could assist the fiber elongation. The design of sidechains and conjugation breakers will be revisited in the molecular design portion of this chapter as a tool for rendering intrinsic stretchability.

Before we tackle intrinsic stretchability, we discuss engineering approaches to attaining stretchability for rigid systems. To account for the Poisson effect in organic electronics, engineering approaches, including patterning, are normally utilized.³⁶ Recent strategies in designing stretchable electrodes and substrates were reviewed by Trung et al.⁴⁰ In this section, we only present a few examples that were able to use strain engineering for substrate and electrode patterning, and we focus on the use of nanocomposites as tools to attain overall device stretchability.

17.2.2.1 Strain Engineering

Material systems able to compensate for the Poisson effect are ideal for building stretchable electronics. Patterning remains the most prominent tool for tuning the Poisson effect in functional materials. The introduction of wavy, serpentine, and multi-axial patterns has been demonstrated to yield

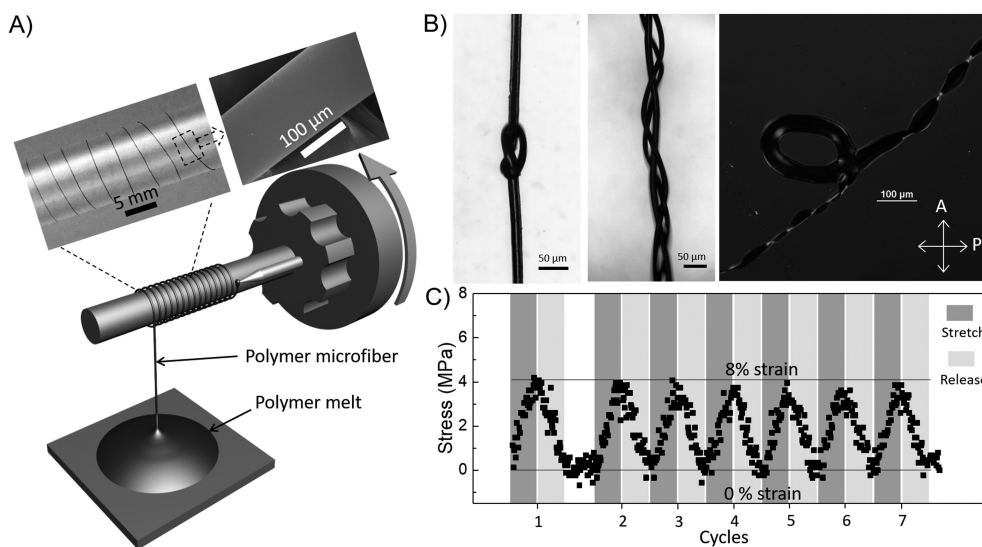


FIGURE 17.5 A) Illustration of the polymer microfiber continuous drawing from semiconducting polymer melts. B) Optical images of the drawn microfibers demonstrating fiber conformability as they can be easily bent, twisted, and tied into knots. C) Mechanical properties of a melt-drawn single fiber during stretch/release cycles. Plotted is the stress supported by the fiber under different strain levels. The fiber shows excellent elasticity below 10% strain levels. From Zhao et al., *Adv. Funct. Mater.* 2017, 1705584.

stretchable arrays, even those on metallic electrodes.^{25,41} Figure 17.6 shows the concept of pre-patterned multi-directional wavy structures of a thin film to achieve stretchability. By having interlocked buckles oriented in different directions, this assembly becomes capable of absorbing the forces in directions orthogonal to the applied strain. This patterning design could be utilized for silicon-based structures to render the intrinsically rigid surfaces significantly malleable. Serpentine shapes have been utilized especially for metallic substrates and engineered stretchability could be achieved (Figure 17.6). Stretching induces, by the Poisson effect, a compressive strain in the orthogonal direction roughly equal to half of the tensile strain. This compressive strain can be accommodated by compression of the wavy structures in the orthogonal direction. Upon release of the applied tensile strain, the original herringbone waves can recover to their original state. This combination of engineered stretchable substrates and electrodes can thus allow for the deposition of conjugated polymer thin films atop the pre-patterned assemblies to achieve overall device deformability. Since the deposited organic layers are ultrathin, they tend to be able to adapt to the shape of patterned substrates allowing for device stretchability.

17.2.2.2 Nanocomposites

With the quasi-linear relationship between mechanical properties and thickness mentioned above, the subsequent task for conjugated polymer thin films becomes attaining finite thicknesses. Nanocomposite formation, a feature that is well mastered in natural tissues, including collagen and keratin, to name a few, has thus been studied for mechanical property tunability at finite size. Nature achieves the toughest yet most ductile tissues by self-assembling building blocks into nanofibers that are then tailored together. This tailoring of nanostructures to build large assemblies hence became an inspiration for flexible and stretchable electronics applications. By confining polymer chains in microfibers or even nanofibers, their mechanical properties can be greatly altered.^{6,42,43} This use of polymer fibers to attain ductile assemblies has long served the textile industry, where electrospinning is a commonly used route for the mass production of polymer microfibers. For semiconducting polymers, electrospinning, carbon nanotubes formation, and nanopatterning have been studied for their use in flexible electronics.

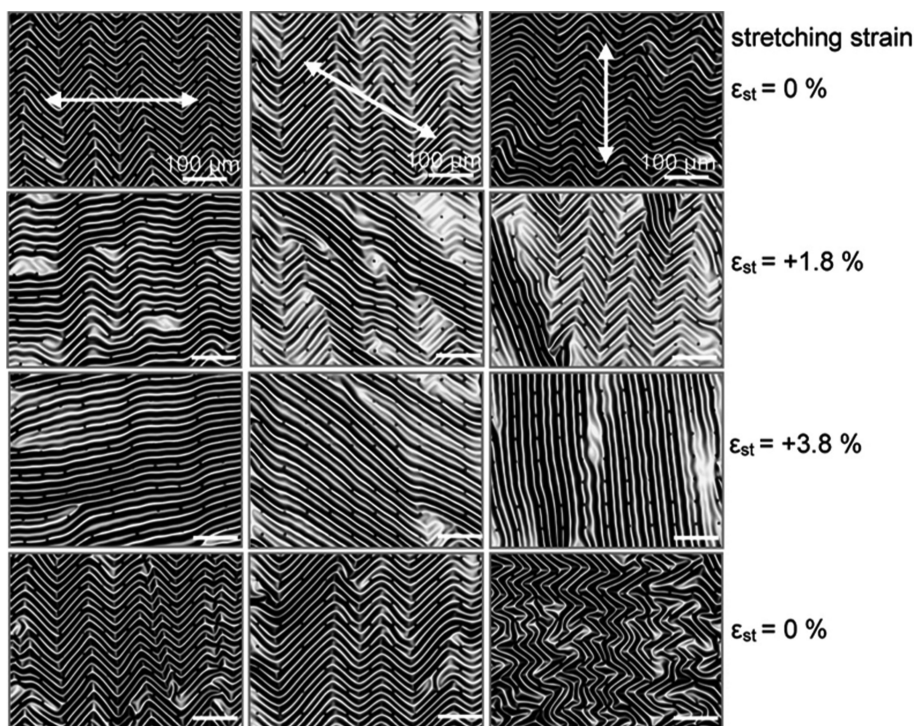


FIGURE 17.6 Demonstration of stretchability in prepatterned wavy structures. Upon application of strain, the Poisson effect in the direction orthogonal to that of applied strain and the assembly is able to elastically recover to the original state. From Choi et al., *Nano Lett.* 2007, 7, 1655–1663.

More notably, self-assembled conjugated polymer nanocomposites have been realized via nanopatterning techniques,^{43,44} solution aging and UV-curing,^{45,46} as well as phase separation.^{26,47–49} In the following sections, we discuss self-assembly of semiconducting of polymers into nanocomposites as the robust way of achieving thin film stretchability via the nanoconfinement effect.

17.2.2.3 Nanoconfinement Effect

As discussed in sections above, polymer chains' mechanical properties are amplified at the nano-scale level. This feature becomes of great significance for attaining stretchability, especially for intrinsically rigid semiconducting polymers. Polymer nanocomposites notably include nanotubes, nanoparticles, and nanofibers. For stretchable electronics, we focus on the use nanofibers to form nano-tailored thin films. The size-dependent molecular motion of polymer chains has been discovered, especially for thermal transition analysis in polymer thin films.^{50–53} At the nano-scale, mechanical properties of conjugated polymers show to deviate greatly from that of the bulk. To confine conjugated polymers a common strategy is to blend the semiconductor with a host matrix. The segmental motion of the conjugated system can thus be guided by the host medium which induces the long-range aggregation of the former due to structural incompatibility. This long-range vitrification often results in the formation of nanofibers of the conjugated polymer dispersed within the host matrix. High glass transition temperature matrices including polystyrene (PS), polymethyl methacrylate (PMMA), as well as polyacrylonitrile (PAN) are often used as they can pull the polymer chains bundles apart and allow for long range crystallization.^{26,46,54–57} Oftentimes, due to structural incompatibility, the polymer wires can easily phase separate and settle at the substrate interface. Once assembled into long range fiber networks, improved electronic performances are often obtained due to longer range crystallization.

The current consensus on the nanoconfinement effect remains that the neighboring effect observed in the bulk can be lowered by confining polymer chains to nano-scale habitats.⁵⁸⁻⁶¹ Segmental motion of individual polymer chains becomes nearly independent of that of corresponding neighbors, and the observed mechanical behaviors approach that of the ultimate polymer flexibility: a single chain. For instance, Xu et al. recently demonstrated the design of a block copolymer elastomer, within which a rigid fully conjugated polymer could crystallize into long fibers via the nanoconfinement effect.^{26,62} In this case poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-alt-thieno[3,2-b]thiophen) (DPPT-TT) was used as the conjugated component. A polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) was used as the soft elastomer. The aggregation of DPPT-TT at the nanometer scale led to peculiar thermodynamically and kinetically driven properties. Figure 17.7 A), B) illustrates the aggregation of DPPT-TT within the SEBS elastomer and the nanoconfined fibers. When subjected to strain levels up to 100%, films of pristine DPPT-TT showed large imprints due to film cracking, while the “CONPHINE” morphology could mechanically sustain the same level of strain. These amplified mechanical properties in nanoconfined polymers were exploited in fabricating a highly stretchable organic device array as illustrated in Figure 17.7 C). Upon stretching, twisting, and poking, the fabricated devices showed stable electrical behaviors for the CONPHINE morphology.

To probe the effect of the nanoconfinement effect on thin film properties, key physical properties including glass transition temperature and crystallinity ought to be investigated. Within confined environments, the motion of polymer chains differs from that of the bulk. In the bulk state, each polymer chain has a large number of neighboring chains. The motion of each chain is thus influenced by its neighbors, and the propagation goes on depending on the stimulus. The degree of freedom of each polymer is therefore limited in the bulk due to this neighboring effect.⁵⁸ When “CONPHINED” however, this neighboring effect can be greatly reduced as only a few polymer chains can aggregate within the formed nanofiber. The nanoconfinement effect has thus been shown to greatly lower the glass transition of thin films. This improvement in local polymer chains freedom has shown to induce overall mechanical properties for thin films based on self-assembled nanoconfined fibers.

17.3 Molecularly Stretchable Polymers for Organic Electronics

17.3.1 Introduction of Section

In the previous section of this chapter, we discussed how to utilize strain-engineering and nanocomposite architecture to divert from the rigid/brittle active layers in flexible and stretchable organic electronics. An alternative approach towards achieving device stretchability would be the use of “intrinsically” or “molecularly” stretchable components. In this section, we thus focus on conjugated polymer systems that combine electronic properties with the ability to intrinsically absorb mechanical strain. Even though rigid backbones and large brittle crystalline domains have historically shown to be beneficial for semiconducting properties, efforts have been demonstrated towards reducing this rigidity at the molecular level without significantly interfering with the electronic properties. Molecular structure designs employing conjugation breaking and sidechain engineering, the use of inter-molecular dynamic bonds, as well as additives, are some of the tools for attaining intrinsic stretchability of in conjugated polymers. In the following sections, we will highlight works that were able to correlate the molecular structure to mechanical properties with minimal compromise on the electronic properties.

17.3.2 Design Strategies and Structure-Property Relationship of Polymers

In the field of organic electronics, it has long been believed that large crystalline domains are essential for high performance, especially in semiconducting polymer thin films.^{113,22,63} Most conjugated polymers are semicrystalline and form complex microstructures of ordered crystalline and amorphous domains.

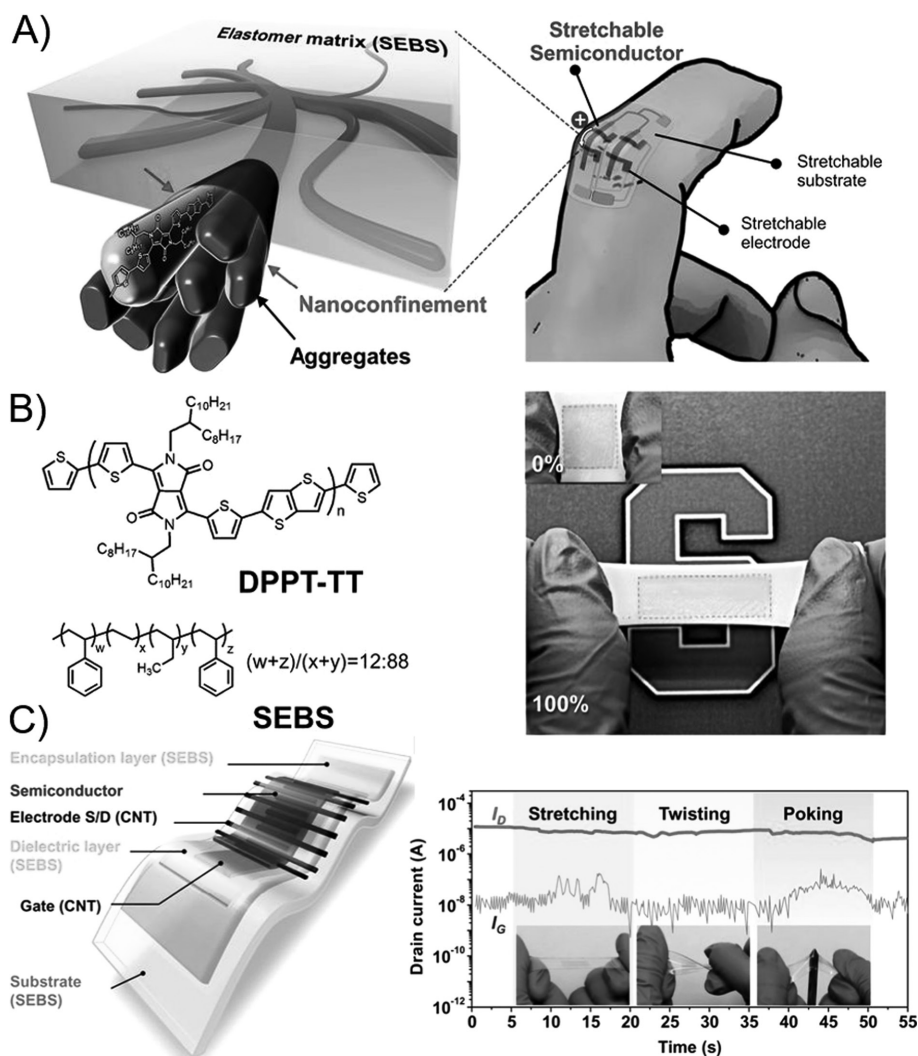


FIGURE 17.7 A) Nanoconfinement design for flexible electronics: conjugated polymer chains are self-assembled within a host elastomer. B) Molecular structures of the semiconducting polymer as well as the designed elastomer for nanoconfinement. Stretchable films based on the blends can be demonstrated C) Device assembly using all-organic components with excellent stability under stretching, twisting, and poking. From Wang et al., *Acc. Chem. Res.* 2018, 51, 1033–1045.

A high degree of π -orbital overlap between polymer chains will form ordered crystalline domains. This π - π stacking feature commonly translates to efficient transport in the polymer active layer. In the case of amorphous domains, random configurations where π -orbital overlap is limited are observed due to the free rotation of sidechains restricting close packing. Intrachain transport is superior to interchain transport but both are necessary for high mobilities.^{64–67} Interchain hopping allows charge carriers to avoid dead ends and high energy traps formed in amorphous domains due to poor orientation of π -orbitals on backbones. The ordered crystalline domains with π -orbital overlap facilitate charge transport and thus it was thought that increasing crystallinity in polymers would lead to the best charge transport properties. This drove the field into increasing the crystallinity of polymer thin films to improve charge transport, but even highly crystalline P3HT shows limited crystallinity and mobilities less than $1.0 \text{ cm}^2 / \text{Vs}$.

This crystallinity requirement has thus recently been challenged since it leads to poor mechanical properties unsuitable for flexible and stretchable electronics.^{27,68–70}

For instance, Son et al. recently demonstrated that localized aggregation could be sufficient in P3HT random copolymers to attain high charge mobilities.⁷¹ Instead of solely relying on large crystalline domains, within which charge transport might be efficient but the assistance from charge carrier hopping is difficult, local and smaller aggregations were employed in random copolymers. Interconnectivity between polymer chains could be increased by forming localized aggregates in amorphous regions. By controlling the density of hexyl sidechains, which play an important role in molecular–molecular interaction, large-scale crystallinity could be intentionally decreased. This could be achieved by reducing the density of sidechains-bearing units to induce structural irregularity (Figure 17.8). The copolymers which exhibited the lowest crystallinity showed a greatly enhanced field-effect mobility, compared with the high-crystallinity P3HT, reaching $1.37 \text{ cm}^2/(\text{V}\cdot\text{s})$. This enhancement was attributed to the increased backbone planarity and the existence of localized aggregates in amorphous regions, giving rise to enhanced intra- and interchain charge transport, respectively, leading to lowered activation energy needed for efficient charge transport. This demonstration challenges the required rigidity (i.e. high crystallinity) and thus makes it feasible to design conjugated polymers with unprecedented mechanical properties.

17.3.3 Backbone Engineering

It seems intuitive that the starting point for attaining molecularly stretchable semiconducting polymers would be the breaking of the conjugated backbone. Unfortunately, this conjugated backbone, being the main cause of polymer rigidity, is also the main path and literal backbone of organic materials' electrical properties. Therefore, directly breaking the backbone can quickly lead to diminished electrical properties. The necessary mechanical compliance for ultra-flexible and stretchable electronics can be enhanced through the incorporation of more flexible building blocks into the backbone. The flexible building blocks would reduce crystallinity and increase the fraction of amorphous domains, leading to a decrease in the elastic modulus. The insertion of methylene units along the backbone was first believed to be an excellent starting point for this backbone breakage. Zhao et al. utilized the spacer length tunability to design a

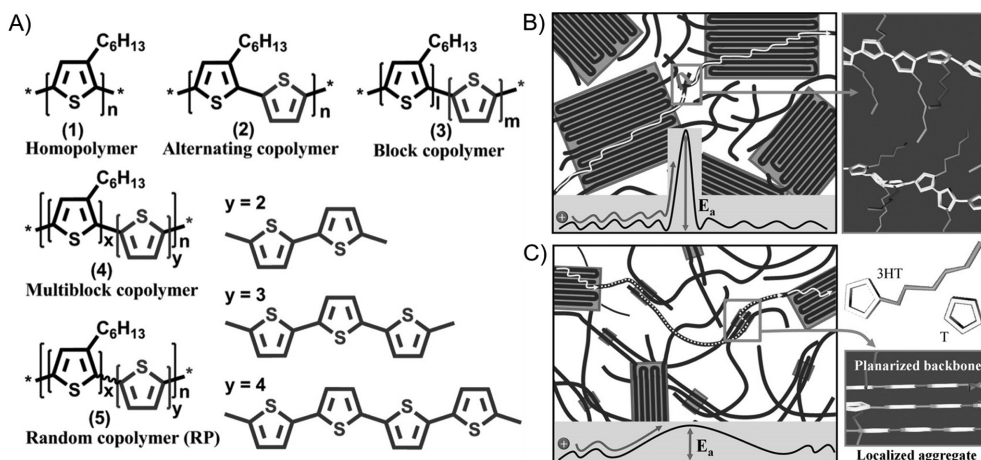


FIGURE 17.8 A) Molecular design of alternating copolymers for lowered overall thin film crystallinity. The alkyl chains density could be tuned by varying the block copolymers ratio. B) Illustration of the thin film packing of the homo-P3HT exhibiting large crystalline domains accompanied with large activation energy barrier for carriers hopping. C) Packing mechanism in the random copolymer where only local aggregates are favored even within the amorphous regions. The efficient interconnectivity leads to lowered activation for carriers hopping. From Son et al., *J. Am. Chem. Soc.* 2016, 138, 8096–8103.

library of DPP-based matrices which showed retention of modest hole transporting properties with up to five carbons inserted.^{72,73} The matrices showed excellent processability compared to the fully conjugated DPP parents and could be used in the “tie-chain model” analogous to the local aggregation demonstrated by Son and colleagues. In the tie-chain model, instead of relying on the fully conjugated polymers to achieve efficient charge transport, a small portion (as low as 1 wt% of the fully conjugated polymer) is used to serve as “tie-molecules” in the blends with a complementary matrix polymer. The tie-polymer showed to serve as connecting bridges between the crystalline domains of the matrix and restore the efficient charge transport, which is intentionally interrupted in the matrix by breaking the conjugation. (Figure 17.9). These binary blends display performances nearly as good as the pure conjugated polymer with excellent processability.^{72–74} This blending system could be used to readily process flexible free-standing thin films as well as microfibers (mentioned above), owing to the processability of the designed matrices.^{39,75}

To correlate the mechanical properties to the spacing between the conjugated components, Savagatrup et al. used a DPP-based copolymer with varied contents of the DPP-C3 component along the main chain as illustrated in Figure 17.10 A).⁷⁶ By incorporating the fully conjugated component and the spacer-bearing block in the copolymer, electronic properties were envisioned to be preserved, while tuning the mechanical behaviors with varying content of the flexible unit.⁷⁷ Figure 17.10 B) shows the mechanical properties of the thin films of the obtained copolymers. Non-intuitively, the alkyl chains did not appear to completely impede the long-range aggregation that is observed in the fully conjugated analogs. This unavoidable crystallinity in these copolymers thus leads to unpredicted tensile moduli and crack-onset results revealing that the aliphatic groups alone cannot dictate the packing of the partially conjugated polymers. Larger yet flexible conjugation breakers would thus be desired.

17.3.4 Crosslinks and Dynamic Bonds

The insertion of large groups able to compete with the aggregation of the conjugated domains would be the ideal case for intrinsically stretchable polymers. However, the density of non-conjugated components

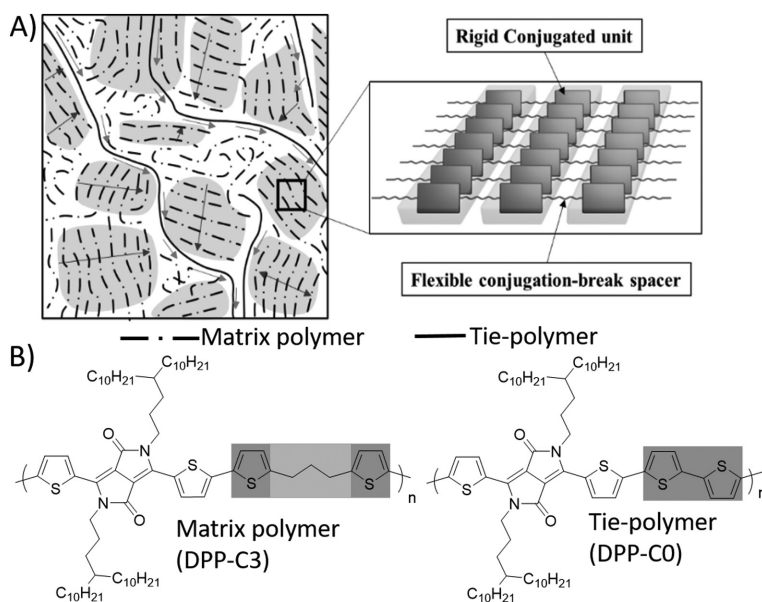


FIGURE 17.9 A) Illustration of the tie-chain model: alternating rigid and flexible components are used to design as semiconducting matrix polymer. The fully conjugated analog chains are used in small ratios to serve as connecting bridges for efficient charge transport. B) The molecular structures of the matrix polymer with a tri-methylene spacer, as well as the fully conjugated tie-chain analog. From Zhao et al., *Chem. Mater.* 2015, 27, 7164–7170.

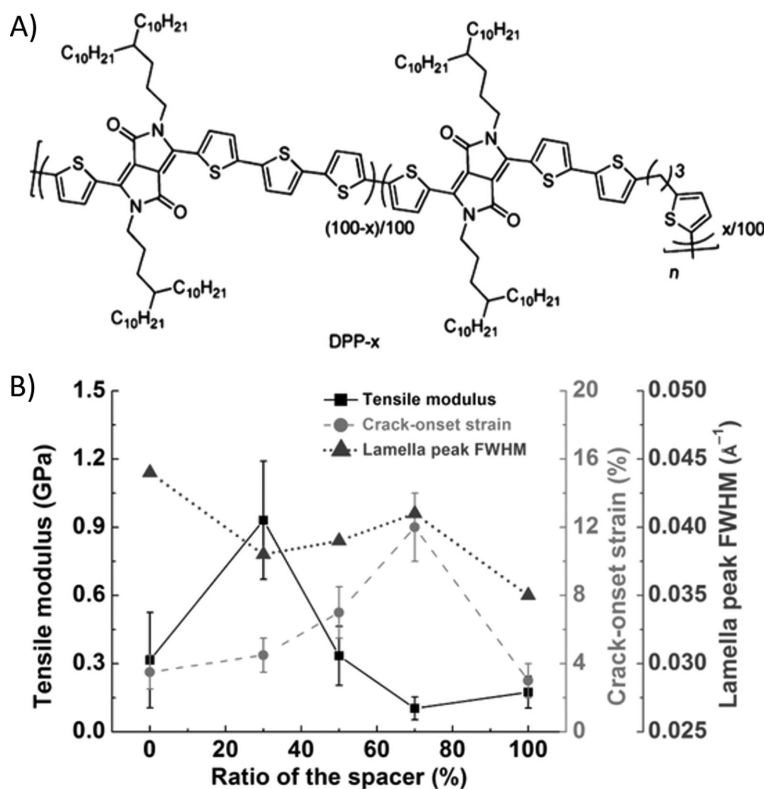


FIGURE 17.10 A) Molecular design of DPP copolymers incorporating the spacer-bearing matrix into the main chain. B) Tensile modulus, crack-onset, and crystallinity evaluation of the copolymers with varying spacer ratio. Non-intuitive mechanical properties observed especially with the larger loading of the spacer component in the copolymer. From Savagatrup et al., *Macromol. Rapid Commun.* 2016, 37, 1623–1628.

seems to be linearly disproportional with the electronic properties. One way to achieve this competing feature would be the use of molecular recognition. i.e. the use of groups that can interact with their analogs between the neighboring molecules without greatly affecting the main chain conjugation. The use of hydrogen bonding and metal–ligand/metal– π bond interactions are two successful examples of conjugation breakers able to allow crosslinking without immensely impeding the backbone. The use of these dynamic bonds thus becomes a vital tool for increasing the mechanical compliance in conjugated polymers. These non-covalent bonds are easily broken upon strain, thus becoming a route to dissipate the mechanical force and improve the strain tolerance.¹⁶ Since the broken dynamic bonds can spontaneously reform upon strain release, it adds a self-healing element to these materials, in addition to increasing the cycling stability. Dynamic bonds essentially create a reversible crosslinked network.

17.3.4.1 Hydrogen Bonding

The most familiar dynamic bond in chemistry is hydrogen bonding, owing to its being weaker than covalent bond but having the ability to dissociate and reform. Hydrogen bonding plays a vital role in macromolecules and finds significant impact among elastic materials for self-healing properties. However, hydrogen bonding remains understudied in semiconducting polymers since these bonds were originally thought to be detrimental to the electronic properties. The networking formation can interrupt electronic delocalization. However, recent efforts have shown that charge-transport can readily move in materials that contain hydrogen bonding. For instance, Oh et al. (2016) demonstrated semiconducting DPP-based copolymers that incorporated 2,6-pyridine dicarboxamide (PDCA) directly

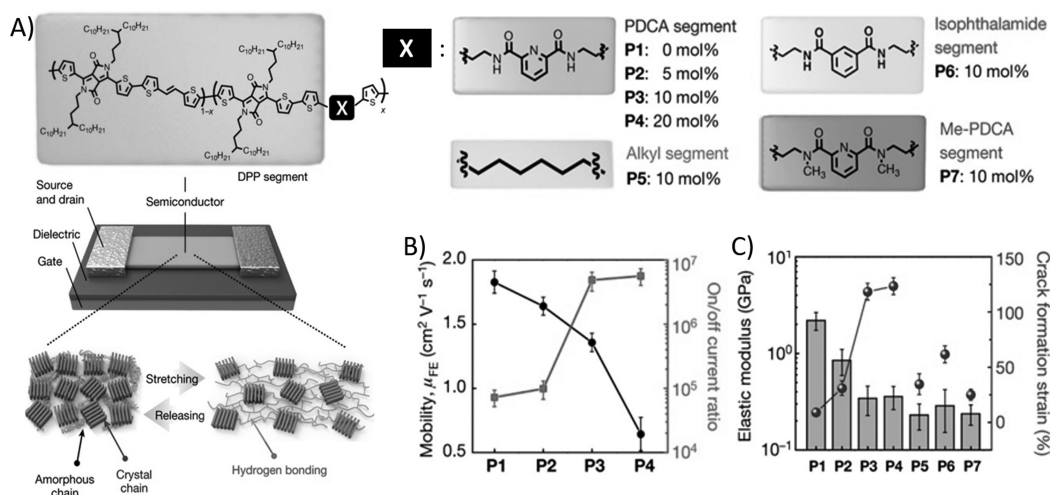


FIGURE 17.11 A) Molecular structure of the random copolymer encompassing fully conjugated segments, and conjugation breaking bearing hydrogen bonding sites. Also illustrated is the working mechanism of the solid-state device where the stretching amorphous domains containing hydrogen bonds can lead to overall film stretchability without compromising the crystalline regions. B) Electrical properties of the studied copolymers and C) their mechanical properties compared to the non-hydrogen assisted analogs. From Oh et al., *Nature* 2016, 539, 411–415.

into the backbone (Figure 17.11 A)). The PDCA segment contains two amide bonds capable of including hydrogen bonds between polymer chains. The copolymers were able to maintain electrical performance even at 100% strain levels over multiple cycles. The electrical performance of the copolymers exhibited a slight decrease with increased strain, but could fully be recovered after strain was removed. The work further demonstrated that increase in the PDCA content along the main chain is indeed detrimental to the overall electronic properties, but low contents (below 10 mol%) can yield polymers with excellent mobilities and excellent conformability (Figure 17.11 B)). Additionally, in comparison to the analogs containing aliphatic groups (discussed above), the PDCA containing polymers display improved mechanical behaviors (Figure 17.11 C)) to complement their electronic properties.

Since the incorporation of hydrogen bond containing groups seems to be detrimental to the overall electronic properties, the alternative would be to use the crosslinking units as the sidechains. The molecular designs and use of sidechains to attain stretchability will later be revisited in full. Baek et al. incorporated moieties capable of hydrogen bonding on the sidechains of a graft polymer showing to establish efficient crosslinking without interfering with the fully conjugated polymer backbone.⁷⁸ Figure 17.12 A) shows the use of hydrogen bond containing groups flanking the conjugated main chain to attain stretchability and healability in a graft polymer. By utilizing poly(acrylate urethane) (PAU) as the crosslinking unit flanking the semiconducting polythiophene (PTh) units, a copolymer with excellent mechanical and electronics properties could be designed and synthesized. The copolymer synthesis could be readily carried out via an atomic-transfer radical polymerization (ATRP) mechanism. The crosslinking properties of the synthesized copolymer could be directly tuned by varying the ratio between the PAU containing and the aliphatic containing PTh blocks. Figure 17.12 B) shows the electrical conductivity of the graft polymers containing varied crosslinking units after doping. Figure 17.12 C) shows the mechanical properties of the thin films based on the graft polymers. The hydrogen bonding could allow films toughness (indicated by the strain-at-break) without comprising its ductility (Young's modulus). As proposed for crosslinked polymers, the graft polymers could further be healed upon rupture, even at room temperature (Figure 17.13). This polymer material system could thus demonstrate unprecedented applicability for ultimate stretching in organic electronics, i.e. self-healing.

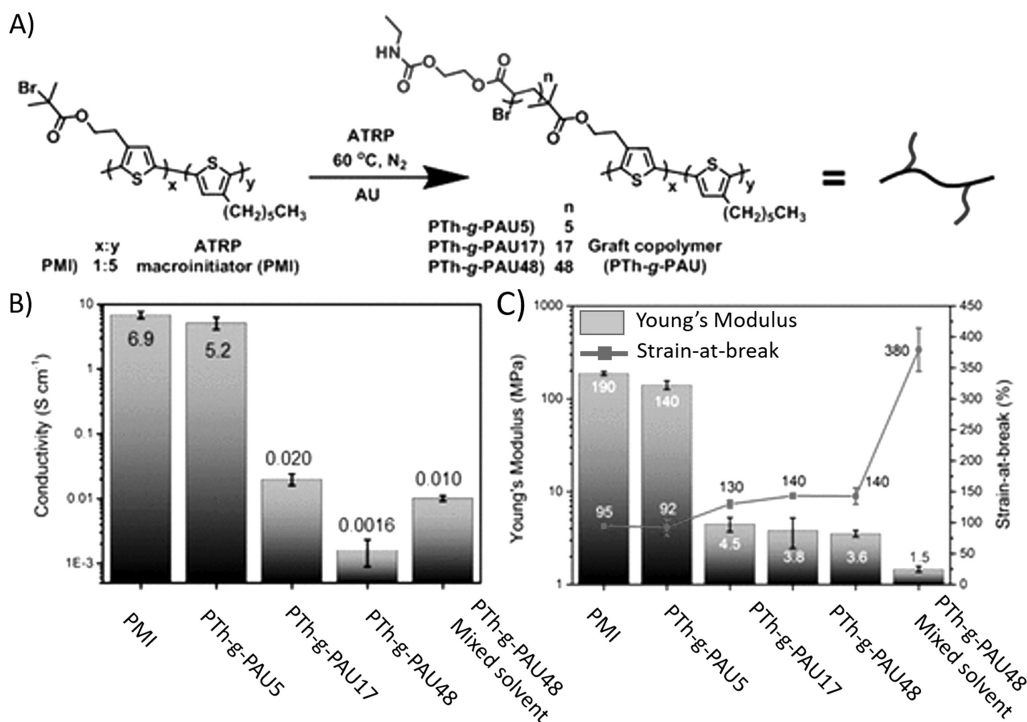


FIGURE 17.12 A) Design and synthesis of H-bond containing sidechains for a crosslinked graft polymer. PAU units are used to tune the hydrogen-bonding within the copolymer. B) Conductivity of doped films showing electrical properties comparable to the non-crosslinked parent (PMI) especially for the graft polymer containing low amounts of PAU. C) Mechanical properties of the graft polymer thin films showing excellent combination of film ductility (modulus) and film toughness (strain-at-break). From Baek et al., *Chem. Mater.* 2017, 29, 8850–8858.

17.3.4.2 Metal–Ligand/Metal– π bond Coordination

Another class of dynamic bonds studied for crosslinking ability in molecularly stretchable polymers is the metal–ligand/metal– π bond coordination. Given the ability of these bonds to readily break and re-form, metal–ligand interactions have attracted intensive attention in designing materials able to dissipate energy upon a mechanical stimulus—stretchable and even self-healing materials.^{79,80} The use of this weak interaction was recently demonstrated in designing a stretchable and self-healing dielectric elastomer by Rao et al.¹⁷ By incorporating zinc and iron–bipyridine coordination as crosslinking sites in nonpolar polydimethylsiloxane (PDMS) polymers, the kinetically labile bonding could allow for the design and synthesis of a highly elastic and healable dielectric polymer (Figure 17.14). Owing to the dynamic nature of the bonds, the dielectric material could readily dissipate mechanical energy. When used to fabricate stretchable OFET devices, the metal–ligand containing polymer exhibited ideal hysteresis-free transfer characteristics, while the gate leakage current remained low, even after 1000 cycles under 100% tensile strain. Upon extreme stretching and breakage, the dielectric layer showed to self-heal as the metal coordination interactions could reform, even at ambient conditions. This use of metal–ligand coordination thus shows to be an excellent tool in designing intrinsically stretchable (semi)conducting polymers. The external mechanical forces can be readily dissipated owing to the weak interactions provided by the reversible breaking of the coordination.

17.3.5 Sidechain Engineering

A more commonly explored approach in molecular properties tuning is the use of sidechains. Sidechain engineering offers the ability to tune the polymeric material's properties without necessarily affecting

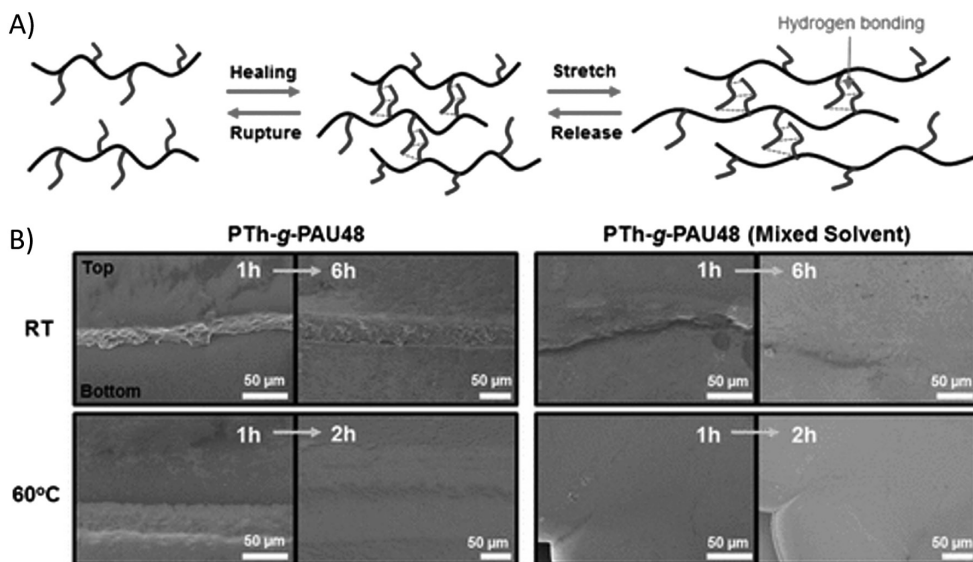


FIGURE 17.13 A) Illustration of the self-healing mechanism using H-bonded crosslinking units. B) Demonstration of the healing process of two free-standing polymer strips being pressed together. After a few hours, the strips show to intimately merge owing to the hydrogen combining recognition, even at room temperature. From Baek et al., *Chem. Mater.* 2017, 29, 8850–8858.

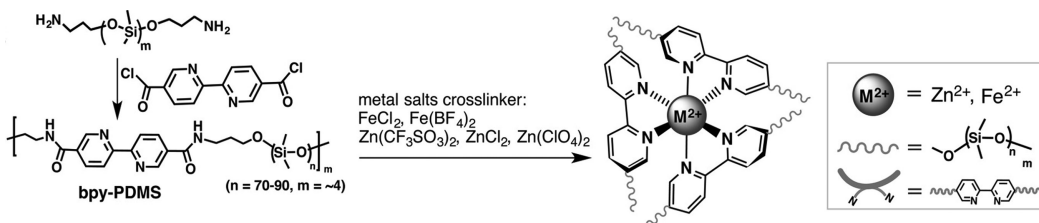


FIGURE 17.14 Molecular design and synthetic route of a PDMS-based dielectric polymer containing metal-bipyridine coordination as the crosslinking site. From Rao et al., *J. Am. Chem. Soc.* 2016, 138, 6020–6027.

the conjugated main chain. Functionalized moieties are able to offer molecular stretchability can thus be utilized to flank the polymer backbone. The use of sidechain engineering is commonly used to improve the processability of organic semiconductors; moieties ranging from aliphatic groups to electron donating/withdrawing, conjugated, oligoethers, fluoroalkyls, and latent reactive groups are often utilized.⁸¹ As previously mentioned, sidechains able to compete with the long-range π -conjugates aggregation have been utilized to attain thin films stretchability. To reduce the effect of the sidechains on the backbone's properties, the softening sidechains ideally would be placed as far away from the backbone as possible. This approach was recently demonstrated by Wang et al. to induce thin film elasticity using oligo-siloxane sidechains in DPP-based copolymers. By placing an elongated aliphatic group bearing a siloxane terminus, the crosslinking between neighboring molecules could be induced to attain excellent thin film mechanical properties (Figure 17.15).⁸² The content of the siloxane-bearing blocks in the copolymer could be tuned to engineer the thin film's elasticity. This use of siloxane as covalent crosslinkers showed to induce elasticity in thin films without greatly sacrificing the charge transporting abilities. For instance, the crosslinked random copolymer with 20 mol% of the crosslinker-bearing units was shown to sustain up to 150% strain (Figure 17.16 A)). These mechanical behaviors were complemented by the electrical behaviors of the copolymer. Further increase of the polymer's crosslinking ability appears

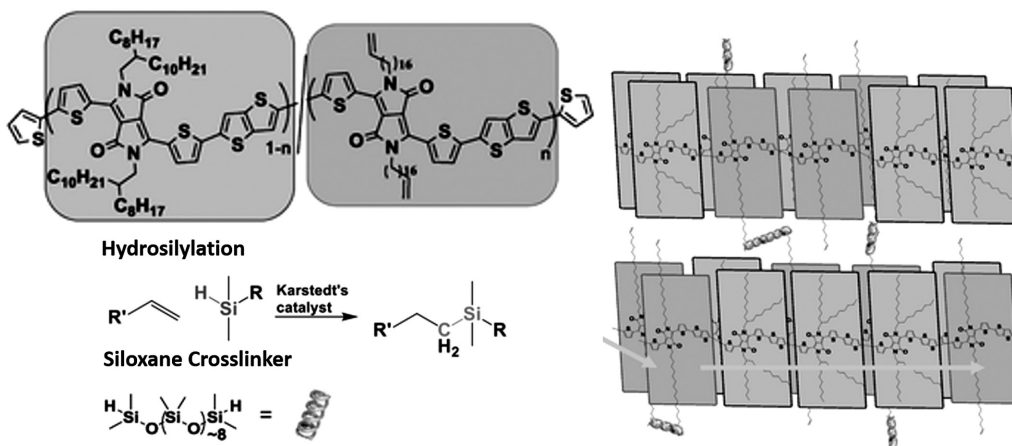


FIGURE 17.15 Molecular structure of DPP-based copolymers with siloxane-terminated alkyl chains as the cross-linking sites between adjacent molecules. From Wang et al., *Adv. Funct. Mater.* 2016, 26, 7254–7262.

slowly detrimental to the charge transport, but it remains a great tool for tuning the polymer thin film's elasticity (Figure 17.16 B, C)).

17.3.6 Additives

As discussed in previous sections, the ideal situation for molecularly stretchable organic material would be to achieve stretchability without impeding the electronic properties, i.e. without interfering with the charge carrier pathways. So far, we have discussed strategies inserting benign moieties within the molecular structures to tune the elasticity of the polymers. An alternative approach would be the physical blending of the (semi)conducting polymer with tolerant hosts able to physically interact with the polymer and tune its mechanical behavior. Non-ionic plasticizers, as well as ionic liquids, are commonly used.

17.3.6.1 Plasticizers

The case of nanoconfined polymer fibers is an excellent example to show that the blending of conjugated polymers with other structurally foreign materials can yield different mechanical behaviors. In

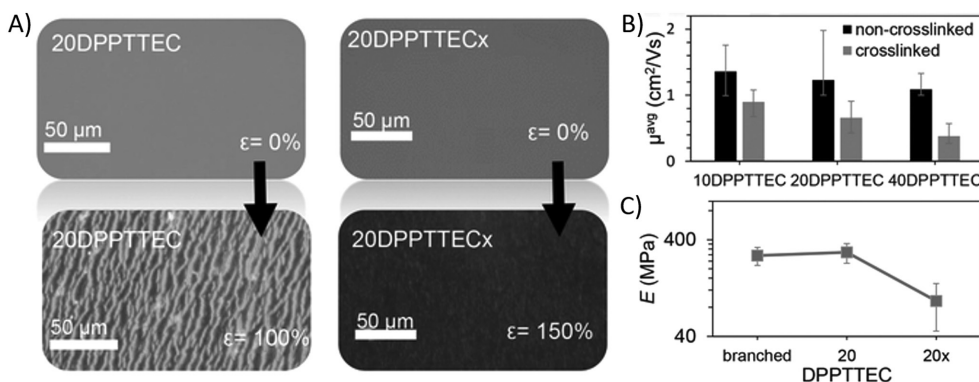


FIGURE 17.16 A) Optical microscope images demonstrating thin film elasticity of the crosslinked DPP-copolymer with siloxane terminated sidechains as the crosslinking sites. The influence of crosslinking of B) the charge carrier mobility and C) the Young modulus. The increase in crosslinked units within the films greatly increases the elasticity without greatly deteriorating the electronic abilities. From Wang et al., *Adv. Funct. Mater.* 2016, 26, 7254–7262.

the absence of nanoconfinement, one can also envision the use of softer components to form blends with improved elasticity combined with the charge transporting ability. For instance, Scott et al. demonstrated that blends of the rigid poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt-[1,2,5]thiadiazolo[3,4-c]pyridine] (PCDTPT) with the much softer P3HT show excellent thin film ductility and inherent charge mobility.⁸³ Films based on the blends could retain their electronic behavior under strain levels as high 75% compared to 10% for the pristine PCDTPT. Plasticizers thus become an attractive class of materials to be blended with the rigid conjugated semiconductors to combine the mechanical and electrical properties in the resulting blends.

Besides binary polymer systems, the addition of plasticization components has been demonstrated to yield great film elasticity. For instance, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) thin films have been demonstrated to be softened when mixed with common plasticizers. This was done by the addition of high boiling point solvents, namely dimethylsulfoxide (DMSO), Zonyl fluorosurfactant, as well as amine-containing polymers (PEI) (Figure 17.17).^{84,85} DMSO, commonly used as a “secondary dopant” for PEDOT:PSS, and believed to fully evaporate upon film formation, was shown by Savagatrup et al. to greatly impact the mechanical behaviors of PEDOT:PSS films with optimized processing conditions.⁸⁴ Similarly, Zonyl which is commonly used to improve the wetting between hydrophobic substrates and PEDOT:PSS was found to have an impact on the mechanical behavior. Not only did Zonyl show to act as a “tertiary dopant” by coalescing the conductive grains of PEDOT within the insulating, continuous phase of PSS,^{85,86} the fluorosurfactant was also demonstrated to significantly lower the tensile modulus and improve the crack-onset strain in PEDOT:PSS films. Contrarily, PEI, a “universal” tool for lowering the work function on conducting materials,⁸⁷ was shown to rigidify the PEDOT:PSS films (Figure 17.18). These findings by Savagatrup and coworkers thus revealed that for stretchable electronics applications, a careful selection of additives that do not impede the targeted ductility ought to be considered.

17.3.6.2 Ionic Additives

Ionic liquids present another class of materials able to provide a plasticizing effect in solid-state devices. For instance, Wang et al. demonstrated a class of stretchability and electrical conductivity (STEC) enhancers for PEDOT:PSS films.^{18,62} To retain the electrical conductivity, good connectivity between PEDOT-rich domains must be conserved. This could be achieved by weakening the electrostatic interaction between PEDOT and PSS to allow PEDOT to partially aggregate forming “hard” conductive network inside a soft PSS.^{88,89} Through an extensive investigation, Wang and coworkers identified a class of materials containing sulfonate or sulfonimide anions that can act as effective STEC enhancers

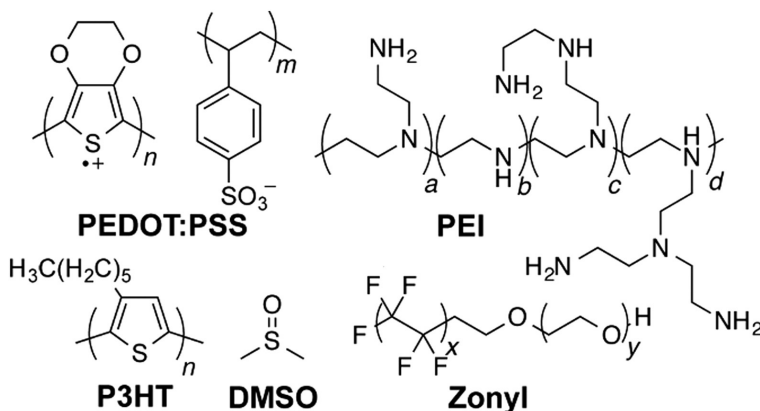


FIGURE 17.17 Molecular structures of PEDOT:PSS and the commonly used additives that exhibited to affect the mechanical properties of the conducting films. From Savagatrup et al., *Adv. Funct. Mater.* 2015, 25, 427–436.

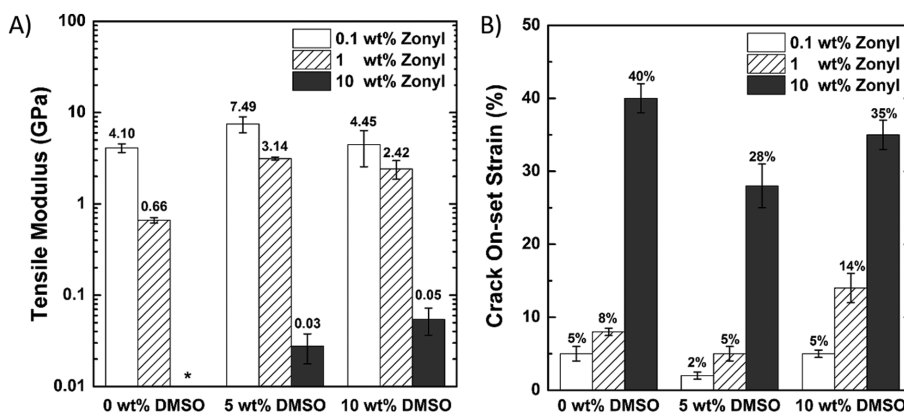


FIGURE 17.18 Influence of DMSO and Zonyl on the A) the tensile modulus and B) the toughness (crack-on-set strain) of PEDOT:PSS thin films. From Savagatrup et al., *Adv. Funct. Mater.* 2015, 25, 427–436.

for PEDOT:PSS. These enhancers include dioctyl sulfosuccinate sodium salt, sodium dodecylbenzenesulfonate, dodecylbenzenesulfonic acid, and ionic liquids (Figure 17.19 A)). These ionic additives were shown to alter the charge transfer doping, crystallinity, and morphology in the conductive material. The presence of the ionic enhancers is known to provide a charge screening effect,^{89–91} which results in an improved aggregation of PEDOT-rich domains into long nanofibrous units, leading to improved planarity of the PEDOT backbone (Figure 17.19 B)).^{92,93} This planarity would thus contribute to more efficient charge delocalization and a higher packing order. PEDOT:PSS/STEC films exhibiting improved mechanical toughness when the ionic additives were added can be fabricated. In addition, the conductivity of PEDOT:PSS could first be increased upon addition of STEC enhancers, and then retained under high strain levels (Figure 17.19 C)). This mechano-electrical enhancement from ionic additives is thus an

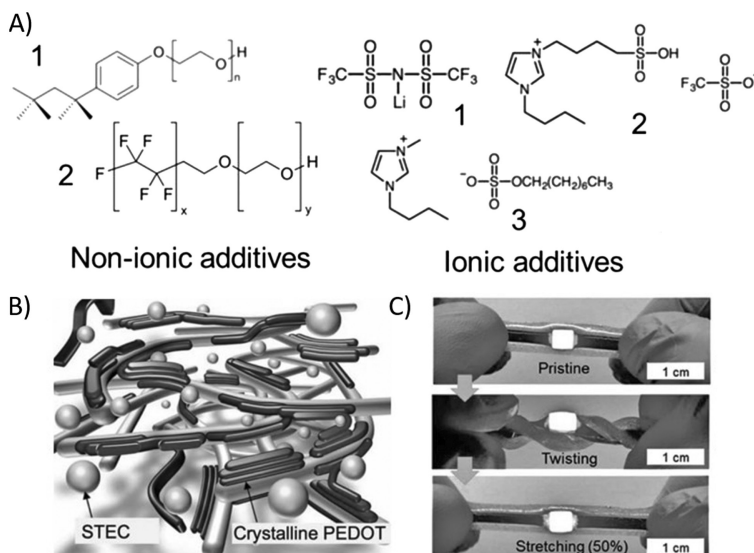


FIGURE 17.19 A) Representative stretchability and electrical conductivity (STEC) enhancers. B) The illustration of the packing mechanism of PEDOT domains within PSS with the presence of ionic enhancers. C) Mechanical and electrical behaviors of PEDOT:PSS films containing sulfonate (or sulfonimide)-rich additives. From Wang et al., *Acc. Chem. Res.* 2018, 51, 1033–1045.

attractive feature that can be extended to other (semi)conducting polymers for stretchable electronics applications.

17.4 Closing Remarks

The field of organic electronics has seen tremendous advancements in understanding the device physics, developing new processing and synthetic methods, and designing new classes of materials. Conjugated polymers, specifically, have promised to constitute a class of materials that can be integrated in next-generation electronics, with promising applications in health monitoring and treatment, energy conversion and storage, circuitries, and environmental sustainability. With the availability of ultra-flexible and stretchable substrates, the research work on the semiconductors that display excellent mechanical conformability and stretchability without sacrificing the electronics properties seemed, for several decades, to be lagging. This chapter has provided an overview of the design principles for achieving such high performers. We focused on the engineering approaches utilizing strain engineering and nanocomposites. The chemist's approach of designing materials with intrinsic mechanical deformability was also presented. We provided representative works that successfully combined the mechanical and electrical features in (semi)conducting polymers. We hope that the chapter paints a promising image of where the research field stands towards the large-area manufacturing of flexible and stretchable electronics. Challenges remain where no specific guidelines exist relating material structure to properties, and each class of materials seems to require a specific processing method for the desired properties. Nonetheless, conjugated polymer thin films remain of intensive interest for stretchable electronics and ongoing efforts in the field continue to bring about unprecedented features, both from the engineering and the chemistry viewpoints.

References

1. Reese, C.; Roberts, M.; Ling, M.-M.; Bao, Z., Organic thin film transistors. *Mater. Today* 2004, 7, 20–27.
2. Bao, Z.; Locklin, J., *Organic Field-Effect Transistors*. CRC Press, Inc. 2007; p. 640.
3. Facchetti, A., π -Conjugated polymers for organic electronics and photovoltaic cell applications. *Chem. Mater.* 2011, 23, 733–758.
4. Facchetti, A.; Yoon, M. H.; Marks, T. J., Gate dielectrics for organic field-effect transistors: new opportunities for organic electronics. *Adv. Mater.* 2005, 17, 1705–1725.
5. Forrest, S. R., The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* 2004, 428, 911–918.
6. Heeger, A. J., Semiconducting and metallic polymers: the fourth generation of polymeric materials. *Synth. Met.* 2001, 125, 23–42.
7. Gelinck, G. H.; Huitema, H. E. A.; van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; van der Putten, J. B. P. H.; Geuns, T. C. T.; Beenhakkers, M.; Giesbers, J. B.; Huisman, B.-H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; van Rens, B. J. E.; de Leeuw, D. M., Flexible active-matrix displays and shift registers based on solution-processed organic transistors. *Nat. Mater.* 2004, 3, 106–110.
8. Hammock, M. L.; Chortos, A.; Tee, B. C. K.; Tok, J. B. H.; Bao, Z., 25th anniversary article: the evolution of electronic skin (e-skin): a brief history, design considerations, and recent progress. *Adv. Mater.* 2013, 25, 5997–6038.
9. Kaltenbrunner, M.; White, M. S.; Glowacki, E. D.; Sekitani, T.; Someya, T.; Sariciftci, N. S.; Bauer, S., Ultrathin and lightweight organic solar cells with high flexibility. *Nat. Commun.* 2012, 3, 770.
10. Khodagholy, D.; Doublet, T.; Gurfinkel, M.; Quilichini, P.; Ismailova, E.; Leleux, P.; Herve, T.; Sanaur, S.; Bernard, C.; Malliaras, G. G., Highly conformable conducting polymer electrodes for in vivo recordings. *Adv. Mater.* 2011, 23, H268–H272.

11. Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A.; Yu, K. J.; Kim, T.-I.; Chowdhury, R.; Ying, M.; Xu, L.; Li, M.; Chung, H.-J.; Keum, H.; McCormick, M.; Liu, P.; Zhang, Y.-W.; Omenetto, F. G.; Huang, Y.; Coleman, T.; Rogers, J. A., Epidermal electronics. *Science* 2011, 333, 838–843.
12. Leleux, P.; Badier, J.-M.; Rivnay, J.; Bénar, C.; Hervé, T.; Chauvel, P.; Malliaras, G. G., Conducting polymer electrodes for electroencephalography. *Adv. Healthc. Mater.* 2014, 3, 490–493.
13. Mei, J.; Diao, Y.; Appleton, A. L.; Fang, L.; Bao, Z., Integrated materials design of organic semiconductors for field-effect transistors. *J. Am. Chem. Soc.* 2013, 135, 6724–6746.
14. Chou, H.-H.; Nguyen, A.; Chortos, A.; To, J. W. F.; Lu, C.; Mei, J.; Kurosawa, T.; Bae, W.-G.; Tok, J. B. H.; Bao, Z., A chameleon-inspired stretchable electronic skin with interactive colour changing controlled by tactile sensing. *Nat. Commun.* 2015, 6, 8011.
15. Lipomi, D. J.; Bao, Z., Stretchable and ultraflexible organic electronics. *MRS Bull.* 2017, 42, 93–97.
16. Oh, J. Y.; Rondeau-Gagné, S.; Chiu, Y.-C.; Chortos, A.; Lissel, F.; Wang, G.-J. N.; Schroeder, B. C.; Kurosawa, T.; Lopez, J.; Katsumata, T.; Xu, J.; Zhu, C.; Gu, X.; Bae, W.-G.; Kim, Y.; Jin, L.; Chung, J. W.; Tok, J. B. H.; Bao, Z., Intrinsically stretchable and healable semiconducting polymer for organic transistors. *Nature* 2016, 539, 411–415.
17. Rao, Y.-L.; Chortos, A.; Pfattner, R.; Lissel, F.; Chiu, Y.-C.; Feig, V.; Xu, J.; Kurosawa, T.; Gu, X.; Wang, C.; He, M.; Chung, J. W.; Bao, Z., Stretchable self-healing polymeric dielectrics cross-linked through metal–ligand coordination. *J. Am. Chem. Soc.* 2016, 138, 6020–6027.
18. Wang, Y.; Zhu, C.; Pfattner, R.; Yan, H.; Jin, L.; Chen, S.; Molina-Lopez, F.; Lissel, F.; Liu, J.; Rabiah, N. I.; Chen, Z.; Chung, J. W.; Linder, C.; Toney, M. F.; Murmann, B.; Bao, Z., A highly stretchable, transparent, and conductive polymer. *Sci. Adv.* 2017, 3, e1602076.
19. Choi, S.; Lee, H.; Ghaffari, R.; Hyeon, T.; Kim, D. H., Recent advances in flexible and stretchable bio-electronic devices integrated with nanomaterials. *Adv. Mater.* 2016, 28, 4203–4218.
20. Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y.; Di, C.-A.; Yu, G.; Liu, Y.; Lin, M.; Lim, S. H.; Zhou, Y.; Su, H.; Ong, B. S., A stable solution-processed polymer semiconductor with record high-mobility for printed transistors. *Sci. Rep.* 2012, 2, 754.
21. Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; Yan, H., Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nat. Commun.* 2014, 5, 5293.
22. Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D., Semiconducting π -conjugated systems in field-effect transistors: a material odyssey of organic electronics. *Chem. Rev.* 2012, 112, 2208–2267.
23. Yokota, T.; Inoue, Y.; Terakawa, Y.; Reeder, J.; Kaltenbrunner, M.; Ware, T.; Yang, K.; Mabuchi, K.; Murakawa, T.; Sekino, M.; Voit, W.; Sekitani, T.; Someya, T., Ultraflexible, large-area, physiological temperature sensors for multipoint measurements. *PNAS* 2015, 112, 14533–14538.
24. Kaltenbrunner, M.; Sekitani, T.; Reeder, J.; Yokota, T.; Kuribara, K.; Tokuhara, T.; Drack, M.; Schwodiauer, R.; Graz, I.; Bauer-Gogonea, S.; Bauer, S.; Someya, T., An ultra-lightweight design for imperceptible plastic electronics. *Nature* 2013, 499, 458–463.
25. Choi, W. M.; Song, J.; Khang, D.-Y.; Jiang, H.; Huang, Y. Y.; Rogers, J. A., Biaxially stretchable “wavy” silicon nanomembranes. *Nano Lett.* 2007, 7, 1655–1663.
26. Xu, J.; Wang, S.; Wang, G.-J. N.; Zhu, C.; Luo, S.; Jin, L.; Gu, X.; Chen, S.; Feig, V. R.; To, J. W. F.; Rondeau-Gagné, S.; Park, J.; Schroeder, B. C.; Lu, C.; Oh, J. Y.; Wang, Y.; Kim, Y.-H.; Yan, H.; Sinclair, R.; Zhou, D.; Xue, G.; Murmann, B.; Linder, C.; Cai, W.; Tok, J. B.-H.; Chung, J. W.; Bao, Z., Highly stretchable polymer semiconductor films through the nanoconfinement effect. *Science* 2017, 355, 59–64.
27. Root, S. E.; Savagatrup, S.; Printz, A. D.; Rodriguez, D.; Lipomi, D. J., Mechanical properties of organic semiconductors for stretchable, highly flexible, and mechanically robust electronics. *Chem. Rev.* 2017, 117, 6467–6499.
28. Stafford, C. M.; Harrison, C.; Beers, K. L.; Karim, A.; Amis, E. J.; VanLandingham, M. R.; Kim, H.-C.; Volksen, W.; Miller, R. D.; Simonyi, E. E., A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nat. Mater.* 2004, 3, 545–550.

29. Tahk, D.; Lee, H. H.; Khang, D.-Y., Elastic moduli of organic electronic materials by the buckling method. *Macromolecules* 2009, *42*, 7079–7083.
30. Lewis, J., Material challenge for flexible organic devices. *Mater. Today* 2006, *9*, 38–45.
31. Grego, S.; Lewis, J.; Vick, E.; Temple, D., Development and evaluation of bend-testing techniques for flexible-display applications. *J. Soc. Inf. Disp.* 2005, *13*, 575–581.
32. Bao, Z.; Dodabalapur, A.; Lovinger, A. J., Soluble and processable regioregular poly(3-hexylthiophene) for thin film field-effect transistor applications with high mobility. *Appl. Phys. Lett.* 1996, *69*, 4108–4110.
33. Dimitrakopoulos, C. D.; Malenfant, P. R. L., Organic thin film transistors for large area electronics. *Adv. Mater.* 2002, *14*, 99–117.
34. Gelinck, G. H.; Geuns, T. C. T.; de Leeuw, D. M., High-performance all-polymer integrated circuits. *Appl. Phys. Lett.* 2000, *77*, 1487–1489.
35. Stafford, C. M.; Vogt, B. D.; Harrison, C.; Julthongpiput, D.; Huang, R., Elastic moduli of ultrathin amorphous polymer films. *Macromolecules* 2006, *39*, 5095–5099.
36. Rogers, J. A.; Someya, T.; Huang, Y., Materials and mechanics for stretchable electronics. *Science* 2010, *327*, 1603–1607.
37. Sekitani, T.; Zschieschang, U.; Klauk, H.; Someya, T., Flexible organic transistors and circuits with extreme bending stability. *Nat. Mater.* 2010, *9*, 1015–1022.
38. Someya, T.; Kato, Y.; Sekitani, T.; Iba, S.; Noguchi, Y.; Murase, Y.; Kawaguchi, H.; Sakurai, T., Conformable, flexible, large-area networks of pressure and thermal sensors with organic transistor active matrixes. *PNAS* 2005, *102*, 12321–12325.
39. Zhao, Y.; Gumyusenge, A.; He, J.; Qu, G.; McNutt, W. W.; Long, Y.; Zhang, H.; Huang, L.; Diao, Y.; Mei, J., Continuous melt-drawing of highly aligned flexible and stretchable semiconducting microfibers for organic electronics. *Adv. Funct. Mater.* 2017, *28*, 1705584.
40. Trung, T. Q.; Lee, N.-E., Recent progress on stretchable electronic devices with intrinsically stretchable components. *Adv. Mater.* 2017, *29*, 1603167.
41. Qian, Y.; Zhang, X.; Xie, L.; Qi, D.; Chandran, B. K.; Chen, X.; Huang, W., Stretchable organic semiconductor devices. *Adv. Mater.* 2016, *28*, 9243–9265.
42. Luo, C.; Kyaw, A. K. K.; Perez, L. A.; Patel, S.; Wang, M.; Grimm, B.; Bazan, G. C.; Kramer, E. J.; Heeger, A. J., General strategy for self-assembly of highly oriented nanocrystalline semiconducting polymers with high mobility. *Nano Lett.* 2014, *14*, 2764–2771.
43. Lee, B. H.; Hsu, B. B. Y.; Patel, S. N.; Labram, J.; Luo, C.; Bazan, G. C.; Heeger, A. J., Flexible organic transistors with controlled nanomorphology. *Nano Lett.* 2016, *16*, 314–319.
44. Chang, J.-F.; Gwinner, M. C.; Caironi, M.; Sakanoue, T.; Siringhaus, H., Conjugated-polymer-based lateral heterostructures defined by high-resolution photolithography. *Adv. Funct. Mater.* 2010, *20*, 2825–2832.
45. Wang, G.; Chu, P.-H.; Fu, B.; He, Z.; Kleinhenz, N.; Yuan, Z.; Mao, Y.; Wang, H.; Reichmanis, E., Conjugated polymer alignment: synergisms derived from microfluidic shear design and UV irradiation. *ACS Appl. Mater. Interfaces* 2016, *8*, 24761–24772.
46. Persson, N. E.; Chu, P.-H.; McBride, M.; Grover, M.; Reichmanis, E., Nucleation, growth, and alignment of poly(3-hexylthiophene) nanofibers for high-performance OFETs. *Acc. Chem. Res.* 2017, *50*, 932–942.
47. Qiu, L.; Xu, Q.; Chen, M.; Wang, X.; Wang, X.; Zhang, G., Low-temperature melt processed polymer blend for organic thin-film transistors. *J. Mater. Chem.* 2012, *22*, 18887–18892.
48. Qiu, L.; Lim, J. A.; Wang, X.; Lee, W. H.; Hwang, M.; Cho, K., Versatile use of vertical-phase-separation-induced bilayer structures in organic thin-film transistors. *Adv. Mater.* 2008, *20*, 1141–1145.
49. Qiu, L.; Lee, W. H.; Wang, X.; Kim, J. S.; Lim, J. A.; Kwak, D.; Lee, S.; Cho, K., Organic thin-film transistors based on polythiophene nanowires embedded in insulating polymer. *Adv. Mater.* 2009, *21*, 1349–1353.

50. Priestley, R. D.; Broadbelt, L. J.; Torkelson, J. M., Physical aging of ultrathin polymer films above and below the bulk glass transition temperature: effects of attractive vs neutral polymer–substrate interactions measured by fluorescence. *Macromolecules* 2005, 38, 654–657.
51. Mataz, A.; Gregory, B. M., Effects of confinement on material behaviour at the nanometre size scale. *J. Phys. Condens. Matter* 2005, 17, R461.
52. Starr, F. W.; Schröder, T. B.; Glotzer, S. C., Effects of a nanoscopic filler on the structure and dynamics of a simulated polymer melt and the relationship to ultrathin films. *Phys. Rev. E* 2001, 64, 021802.
53. Roth, C. B.; Dutcher, J. R., Glass transition and chain mobility in thin polymer films. *J. Electroanal. Chem.* 2005, 584, 13–22.
54. Lei, Y.; Deng, P.; Li, J.; Lin, M.; Zhu, F.; Ng, T.-W.; Lee, C.-S.; Ong, B. S., Solution-processed donor-acceptor polymer nanowire network semiconductors for high-performance field-effect transistors. *Sci. Rep.* 2016, 6, 24476.
55. Lei, Y.; Deng, P.; Lin, M.; Zheng, X.; Zhu, F.; Ong, B. S., Enhancing crystalline structural orders of polymer semiconductors for efficient charge transport via polymer-matrix-mediated molecular self-assembly. *Adv. Mater.* 2016, 28, 6687–6694.
56. Chen, H.-L.; Wang, S.-F., Crystallization induced microstructure of polymer blends consisting of two crystalline constituents. *Polymer* 2000, 41, 5157–5164.
57. Hopkins, A. R.; Reynolds, J. R., Crystallization driven formation of conducting polymer networks in polymer blends. *Macromolecules* 2000, 33, 5221–5226.
58. Keddie, J. L.; Jones, R. A. L.; Cory, R. A., Size-dependent depression of the glass transition temperature in polymer films. *EPL* 1994, 27, 59.
59. Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R., Interface and chain confinement effects on the glass transition temperature of thin polymer films. *Phys. Rev. E* 1997, 56, 5705–5716.
60. Ellison, C. J.; Torkelson, J. M., The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nat. Mater.* 2003, 2, 695–700.
61. Si, L.; Massa, M. V.; Dalnoki-Veress, K.; Brown, H. R.; Jones, R. A. L., Chain entanglement in thin freestanding polymer films. *Phys. Rev. Lett.* 2005, 94, 127801.
62. Wang, S.; Oh, J. Y.; Xu, J.; Tran, H.; Bao, Z., Skin-inspired electronics: an emerging paradigm. *Acc. Chem. Res.* 2018, 51, 1033–1045.
63. Siringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M., Two-dimensional charge transport in self-organized, high-mobility conjugated polymers. *Nature* 1999, 401, 685–688.
64. Wang, S.; Fabiano, S.; Himmelberger, S.; Puzinas, S.; Crispin, X.; Salleo, A.; Berggren, M., Experimental evidence that short-range intermolecular aggregation is sufficient for efficient charge transport in conjugated polymers. *PNAS* 2015, 112, 10599–10604.
65. Salleo, A.; Kline, R. J.; DeLongchamp, D. M.; Chabinyc, M. L., Microstructural characterization and charge transport in thin films of conjugated polymers. *Adv. Mater.* 2010, 22, 3812–3838.
66. Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A., A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* 2013, 12, 1038–1044.
67. Mollinger, S. A.; Krajina, B. A.; Noriega, R.; Salleo, A.; Spakowitz, A. J., Percolation, Tie-molecules, and the microstructural determinants of charge transport in semicrystalline conjugated polymers. *ACS Macro Lett.* 2015, 4, 708–712.
68. Onorato, J.; Pakhnyuk, V.; Luscombe, C. K., Structure and design of polymers for durable, stretchable organic electronics. *Polym. J.* 2016, 49, 41–60.
69. Kim, J.-S.; Kim, J.-H.; Lee, W.; Yu, H.; Kim, H. J.; Song, I.; Shin, M.; Oh, J. H.; Jeong, U.; Kim, T.-S.; Kim, B. J., Tuning mechanical and optoelectrical properties of poly(3-hexylthiophene) through systematic regioregularity control. *Macromolecules* 2015, 48, 4339–4346.

70. Gargi, D.; Kline, R. J.; DeLongchamp, D. M.; Fischer, D. A.; Toney, M. F.; O'Connor, B. T., Charge transport in highly face-on poly(3-hexylthiophene) films. *J. Phys. Chem. C* 2013, *117*, 17421–17428.
71. Son, S. Y.; Kim, Y.; Lee, J.; Lee, G.-Y.; Park, W.-T.; Noh, Y.-Y.; Park, C. E.; Park, T., High-field-effect mobility of low-crystallinity conjugated polymers with localized aggregates. *J. Am. Chem. Soc.* 2016, *138*, 8096–8103.
72. Zhao, X.; Zhao, Y.; Ge, Q.; Butrouna, K.; Diao, Y.; Graham, K. R.; Mei, J., Complementary semi-conducting polymer blends: the influence of conjugation-break spacer length in matrix polymers. *Macromolecules* 2016, *49*, 2601–2608.
73. Zhao, Y.; Zhao, X.; Zang, Y.; Di, C.-A.; Diao, Y.; Mei, J., Conjugation-break spacers in semiconducting polymers: impact on polymer processability and charge transport properties. *Macromolecules* 2015, *48*, 2048–2053.
74. Zhao, Y.; Zhao, X.; Roders, M.; Qu, G.; Diao, Y.; Ayzner, A. L.; Mei, J., Complementary semiconducting polymer blends for efficient charge transport. *Chem. Mater.* 2015, *27*, 7164–7170.
75. Zhao, Y.; Zhao, X.; Roders, M.; Gumyusenge, A.; Ayzner, A. L.; Mei, J., Melt-processing of complementary semiconducting polymer blends for high performance organic transistors. *Adv. Mater.* 2017, *29*, 1605056.
76. Savagatrup, S.; Zhao, X.; Chan, E.; Mei, J.; Lipomi, D. J., Effect of broken conjugation on the stretchability of semiconducting polymers. *Macromol. Rapid Commun.* 2016, *37*, 1623–1628.
77. Schroeder, B. C.; Chiu, Y.-C.; Gu, X.; Zhou, Y.; Xu, J.; Lopez, J.; Lu, C.; Toney, M. F.; Bao, Z., Non-conjugated flexible linkers in semiconducting polymers: a pathway to improved processability without compromising device performance. *Adv. Electron. Mater.* 2016, *2*, 1600104.
78. Baek, P.; Aydemir, N.; An, Y.; Chan, E. W. C.; Sokolova, A.; Nelson, A.; Mata, J. P.; McGillivray, D.; Barker, D.; Travas-Sejdic, J., Molecularly engineered intrinsically healable and stretchable conducting polymers. *Chem. Mater.* 2017, *29*, 8850–8858.
79. Yang, Y.; Urban, M. W., Self-healing polymeric materials. *Chem. Soc. Rev.* 2013, *42*, 7446–7467.
80. Li, C.-H.; Wang, C.; Keplinger, C.; Zuo, J.-L.; Jin, L.; Sun, Y.; Zheng, P.; Cao, Y.; Lissel, F.; Linder, C.; You, X.-Z.; Bao, Z., A highly stretchable autonomous self-healing elastomer. *Nat. Chem.* 2016, *8*, 618–624.
81. Mei, J.; Bao, Z., Side chain engineering in solution-processable conjugated polymers. *Chem. Mater.* 2014, *26*, 604–615.
82. Wang, G.-J. N.; Shaw, L.; Xu, J.; Kurosawa, T.; Schroeder, B. C.; Oh, J. Y.; Benight, S. J.; Bao, Z., Inducing elasticity through oligo-siloxane crosslinks for intrinsically stretchable semiconducting polymers. *Adv. Funct. Mater.* 2016, *26*, 7254–7262.
83. Scott, J. I.; Xue, X.; Wang, M.; Kline, R. J.; Hoffman, B. C.; Dougherty, D.; Zhou, C.; Bazan, G.; O'Connor, B. T., Significantly increasing the ductility of high performance polymer semiconductors through polymer blending. *ACS Appl. Mater. Interfaces* 2016, *8*, 14037–14045.
84. Savagatrup, S.; Chan, E.; Renteria-Garcia, S. M.; Printz, A. D.; Zaretski, A. V.; O'Connor, T. F.; Rodriguez, D.; Valle, E.; Lipomi, D. J., Plasticization of PEDOT:PSS by common additives for mechanically robust organic solar cells and wearable sensors. *Adv. Funct. Mater.* 2015, *25*, 427–436.
85. Vosgueritchian, M.; Lipomi, D. J.; Bao, Z., Highly conductive and transparent PEDOT:PSS films with a fluorosurfactant for stretchable and flexible transparent electrodes. *Adv. Funct. Mater.* 2012, *22*, 421–428.
86. Lipomi, D. J.; Lee, J. A.; Vosgueritchian, M.; Tee, B. C. K.; Bolander, J. A.; Bao, Z., Electronic properties of transparent conductive films of PEDOT:PSS on stretchable substrates. *Chem. Mater.* 2012, *24*, 373–382.
87. Zhou, Y.; Fuentes-Hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Fenoll, M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Brédas, J.-L.; Marder, S. R.; Kahn, A.; Kippelen, B., A universal method to produce low-work function electrodes for organic electronics. *Science* 2012, *336*, 327–332.

88. Oh, J. Y.; Kim, S.; Baik, H.-K.; Jeong, U., Conducting polymer dough for deformable electronics. *Adv. Mater.* 2016, 28, 4455–4461.
89. Ouyang, J., “Secondary doping” methods to significantly enhance the conductivity of PEDOT:PSS for its application as transparent electrode of optoelectronic devices. *Displays* 2013, 34, 423–436.
90. Xia, Y.; Ouyang, J., Salt-induced charge screening and significant conductivity enhancement of conducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). *Macromolecules* 2009, 42, 4141–4147.
91. Kim, Y. H.; Sachse, C.; Machala, M. L.; May, C.; Müller-Meskamp, L.; Leo, K., Highly conductive PEDOT:PSS electrode with optimized solvent and thermal post-treatment for ITO-free organic solar cells. *Adv. Funct. Mater.* 2011, 21, 1076–1081.
92. Garreau, S.; Louarn, G.; Buisson, J. P.; Froyer, G.; Lefrant, S., In situ spectroelectrochemical raman studies of poly(3,4-ethylenedioxythiophene) (PEDT). *Macromolecules* 1999, 32, 6807–6812.
93. Garreau, S.; Duvail, J. L.; Louarn, G., Spectroelectrochemical studies of poly(3,4-ethylenedioxythiophene) in aqueous medium. *Synth. Met.* 2001, 125, 325–329.