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Stretchable Conjugated Polymers: A Case Study in Topic Selection for New Research Groups

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Conspectus

Our research group has spent much of the past six years studying the mechanical properties of π -conjugated (semiconducting) polymers. The field of organic electronics—of which conjugated polymers are a part—has been underwritten because of the promise of flexible (and increasingly stretchable) devices for energy and healthcare. Mechanically robust materials can extend the lifespans of devices such as solar cells and OLED panels, and enable high throughput processing techniques such as roll-to-roll printing. Additionally, wearable and implantable devices, including electronic skin, implantable pressure sensors, and haptic actuators, benefit by having moduli and extensibilities close to those of biological tissue. At the time of our laboratory's inception, however, the optoelectronic properties of conjugated polymers were understood in much greater depth than their mechanical properties. We therefore set out, as our laboratory's first research topic, to understand the molecular and microstructural determinants of the mechanical properties of conjugated polymers. This is an Account not only of our scientific findings but also of the pragmatic aspects—including personnel, funding, and time constraints—behind our studies as a nascent research group. We hope that this Account will provide information to newly independent scientists about the process of starting a new research laboratory. We identify three main stages of our scientific growth. (1) We began by conducting proof-of-concept experiments to identify basic correlations between chemical structure and mechanical properties, and to determine whether high optoelectronic performance and mechanical robustness were mutually exclusive. (2) We then added new metrological techniques to enable more rapid and robust measurements, such as obtaining full stress-strain curves for conjugated polymer thin films, characterizing modes of thin film failure, and simplified identification of the glass transition temperature. (3) Finally, we incorporated new capabilities—such as organic synthesis and molecular dynamics simulations—into the toolkit of our group. These stages corresponded with increased funding, personnel commitment, and flexibility to take on long-term projects. Our research efforts identified polythiophene-based semiconducting polymers capable of achieving both high power conversion efficiencies and accommodating high degrees of strain. Additionally, we identified several chemical and microstructural determinants of the mechanical properties of conjugated polymer films, such as the chemical composition and structure of side chains and a high degree of dependence on amorphous packing structure. While the field has not yet produced stretchable materials that retain state-of-the-art electronic properties with high elastic range and repeated

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deformation, we hope that our work and the work of others in the field has provided a foundation for future advances.

Graphical Abstract

1. Introduction

Selecting one's first research topic is the most important decision one makes at the start of an independent career. It influences the types of students attracted to the research group and thus the laboratory culture. By creating "institutional knowledge," it creates inertia that influences the selection of future projects. A lab's first research topic also provides the basis for which one is invited to participate in collaborative projects. It is the criticality of the decision that makes selecting this topic so difficult. This difficulty is compounded by the scientific community's tendency to avoid public discussion of the non-technical aspects of research. The realities which often govern much of science are often not well understood by postdocs on the job market until after they have been working at their independent positions for several months. While some of these factors depend on the locale of the research group in question—for research groups based in the United States, this includes the "tenure clock" and the collection of preliminary data for grants—many are universal, such as the need to establish a group's reputation with limited resources and equipment. We thus describe our group's first research topic—the mechanical properties of organic semiconductors—with special attention paid to the practicalities that guided our selection of experiments.

When picking our first research topic, we looked for unstated assumptions in fields in which our principal investigator had experience, including nanofabrication, stretchable electronics, and organic synthesis.^{1–3} One field which combined these interests was π -conjugated polymers. The stated purposes of conjugated polymers have nearly always included printed solar cells, light-emitting devices, RFID devices, and wearable or implantable biosensors. All of these applications were thought to benefit from mechanical deformability. It seemed reasonable to believe that the molecular and packing structure of the solid films would have a substantial effect on their deformability. We believed that measuring the effects of systematic modifications of the molecular structures of conjugated polymers on the mechanical properties of their solid films (the "physical-organic approach") would be a good way to generate new knowledge.⁴

We were aided by early literature on the mechanical behavior of conjugated polymer films. The first studies of the mechanical properties of conjugated polymers were performed by Heeger, Smith, and Wudl on polyacetylene, regiorandom polythiophene, and other relatively simple structures in the 1980s and early 1990s.^{5–8} Upon the discovery of the polymer solar cell, however, the interest of the field shifted from thermomechanical to optoelectronic properties.^{9,10} Many advances in the field focused on new chemical structures, charge-transport in disordered media, microstructural investigations, and device-level engineering.^{11,12} This focus on optoelectronic properties meant there was little literature between the early 1990s and late 2000s on the thermomechanical properties of polymer structures and morphologies central to modern conjugated polymer research, especially for low-bandgap materials.¹³

Interest in deformability of organics seemed to be renewed by the successes of Wagner, Suo, Rogers, and others in making flexible and stretchable devices out of metals and inorganic semiconductors.^{14–19} Evidence of a high degree of deformability in modern semiconducting polymers was demonstrated in 2007, when Müller et al. synthesized bulk samples of a block copolymer of regioregular P3HT and polyethylene that was tough and stretchable, and which retained its charge-carrier mobility even when the insulating fraction reached 90%.²⁰ This study was followed by another in 2010 by O'Connor et al., which showed a negative correlation between the deformability and charge transport properties of polythiophenes.²¹ The elastic moduli of thin film devices of conjugated polymers was first explored by Tahk et al. in 2009 using a technique based on surface buckling instability, described by Hutchinson and Whitesides and then transformed into a metrological technique by Stafford and coworkers.^{22–24} Implementation of conjugated polymers into fully stretchable devices was also explored. Drawing inspiration from the Rogers laboratory, our principal investigator used the buckling technique to make a stretchable organic solar cell as member of the Bao laboratory.² Pei followed with a report of an intrinsically stretchable light emitting electrochemical device, which may be the first semiconducting device in which the active components themselves accommodated tensile strain without strain-relief features (e.g., buckles).²⁵

What seemed to be absent, however, was control over molecular structure, particularly for the emerging family of low-bandgap materials. The mechanical properties of newly synthesized polymers were rarely reported, and structure-property relationships were significantly less developed for mechanical properties than for optoelectronic properties. Additionally, most articles were not concerned with the mechanisms of storage and dissipation of mechanical energy in conjugated polymer films, instead focusing on the extent to which the materials could be strained without failure (the “stretchability”). We therefore chose structure-mechanical property relationships in conjugated polymers as one of our primary research thrusts.

2. Side Chain Length in Polythiophenes: Proof of Concept

It was unclear initially whether conjugated polymers could retain high optoelectronic performance while increasing their deformability, as some early work suggested good optoelectronic properties and deformability were incompatible.²⁶ Many of the characteristics

of conjugated polymers that give rise to charge transport, an optical bandgap, and the ability to be processed from solution make them structurally unlike most engineering plastics. Characteristics found in semiconducting polymers include solubilizing side chains, stiff π -conjugated cores, large and chemically heterogeneous monomer residues, and relatively low degrees of polymerization (Figure 1). Additionally, high degrees of order and crystallinity were thought to be necessary for optoelectronic properties comparable to amorphous silicon (mobility $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, power conversion efficiency $\sim 10\%$), the most commonly used intrinsically flexible inorganic semiconductor.²⁶

We therefore required a proof of concept to determine whether it was, in principle, possible to obtain the “best of both worlds” in electronic performance and mechanical deformability. We chose to perform our experiments on the family of polymers known as the poly(3-alkylthiophene)s (P3ATs). The P3ATs presented several characteristics ideal for a new lab. Being in an engineering department, we initially did not have access to students trained in synthetic organic chemistry, and therefore needed to use existing materials or materials for which synthesis was relatively straightforward. The P3ATs were nearly an order of magnitude less expensive than many low-bandgap polymers and were available in large quantities from general chemical suppliers, which was ideal for a lab functioning exclusively on startup funding. Additionally, there was a large body of literature describing the morphologies and optoelectronic properties of the P3ATs under a wide range of different processing and structural conditions, ready to be matched to mechanical properties.²⁷ Moreover, the quasi-living Grignard metathesis polymerization provides some control over the molecular weights and dispersities of P3ATs.^{28,29}

Our initial experiments focused on the relation between the mechanical and electronic properties of P3ATs and side chain length. Determining even basic mechanical properties presented challenges. Conjugated polymers are usually synthesized in small quantities and almost always cast into thin films. These constraints demanded the use of metrological techniques that used material sparingly. One such technique is the buckling-based metrology.^{23,30} To obtain the elastic modulus using this method, one transfers a film of interest to a prestrained ($\sim 5\%$) elastomeric substrate. Upon release of the prestrain, sinusoidal wrinkles appear in the film. The wavelength of these wrinkles increases with the modulus and the thickness of the film. It is thus possible to extract the modulus from the slope of a plot of buckling wavelength vs. thickness. This technique only required a microscope and time, making it ideal for our research group, which at the beginning consisted in large part of undergraduate volunteers.

We found a sharp decrease in elastic modulus and increase in ductility when we increased the side chain length of P3ATs from a hexyl group to an octyl group, as the glass transition temperature (T_g) of the polymer drops substantially below room temperature.^{31–33} This transition corresponded to a significant decrease in electronic properties as measured by both the field-effect mobility of thin-film transistors and PCE of bulk heterojunction solar cells. The electronic performance of solar cells can be measured by the power conversion efficiency (PCE), which represents the percentage of solar energy converted to electrical energy. A more general measurement of semiconductor performance is the charge-carrier mobility, which is a measurement of how quickly charges can move through a

semiconductor when an electric field is applied. We began investigating the space between hexyl and octyl side chains, hoping to find a middle ground (Figure 2a).³⁴ Both block and statistical copolymers, as well as the physical blend of P3HT and P3OT, were found lacking in either deformability or power conversion efficiency when mixed with [60]PCBM (Figure 2c). However, we were surprised to find that using a heptyl side chain (P3HpT) blended with phenyl-C61-butyric acid methyl ester ([60]PCBM) gave power conversion efficiencies as high as P3HT and a tensile modulus lower than P3OT in the neat form, thus suggesting the existence of a “best of both worlds” (Figure 2b).^{33,34} We took this result as proof that rubbery conjugated polymers need not have poor optoelectronic properties and decided to devote our group’s full research efforts to this topic.

3. New Metrological Techniques: Improving Data Collection

With greater focus within our group on the mechanical properties of conjugated polymer films, we needed more accurate and efficient methods to characterize their elastic moduli and fracture behavior. We had additionally now obtained outside funding for this research topic, giving the long-term stability required to explore more foundational work such as metrological techniques. Until this point, we had carried out all our experiments with our thin films adhered to an elastomer (PDMS). We used these “film-on-elastomer” methods as handling freestanding thin films was highly impractical. However, we had to carry our measurements of each mechanical property separately—we performed one test to find the elastic modulus of the polymer,³⁴ one to find the yield point,³⁵ and one to find the strain at failure (crack-onset-strain).³⁶ Several films for each test had to be cast, and several locations on each film were measured to obtain proper statistics. For the measurements of strain at failure, each sample had to be examined by optical microscopy for each 1% increment of strain. For highly stretchable films, this was impractical. Additionally, the buckling method for testing the elastic modulus used a combination of compressive and tensile forces rather than the more commonly reported tensile modulus.³⁷ Even with all these tests, we could still only approximate the stress-strain curve by estimating a perfectly linear increase corresponding to the elastic modulus until the yield point, and then constant stress until failure (Figure 2a).

In comparison, conventional pull tests of a bulk sample reveal the modulus, the elastic range, the tensile strength, and the fracture strain of a material in a single measurement. Around the time we were finishing our proof-of-concept experiments, Kim and coworkers published a method for performing a conventional pull test of a thin film suspended on water.³⁸ The adoption of this technique in our own experiments allowed us to directly measure stress-strain curves for conjugated polymers. We found significant differences between properties measured by this “film-on-water” method compared to our previous “film-on-elastomer” techniques (Figure 3).³⁷ For example, the modulus measured using the buckle test is higher, and the crack-onset test tends to underestimate the film’s stretchability as it is simply the first formation or expansion of a crack or hole, as opposed to complete bifurcation of the film.

While this new “film on water” technique gave us new insight into the properties of the isolated semiconducting polymer films, the mechanical behavior of semiconducting films on

elastomers was still of interest for fabrication of actual stretchable devices. As such, we looked to improve our “film on elastomer” techniques. In particular, we aimed to improve our understanding of the failure of thin films of semiconducting polymers. We looked to a method pioneered by Stafford and coworkers that related crack density to fracture stress in brittle films.³⁹ We sought to use this method to characterize conjugated polymer films, and wondered whether it would be possible to develop an analogous technique for measuring the behavior in ductile films. Our previous experiments had shown that in ductile films diamond-shaped microvoids appeared at the crack-onset strain which increased in aspect ratio with increasing strain (Figure 4). We were able to correlate the rate of change in aspect ratio to strain to find a microvoid propagation number, m .⁴⁰ This number corresponds to the crack-onset-strain of the polymeric film, and is a more robust measurement as it does not depend on human judgement of small changes in the sizes of defects.

Our work on P3HpT had demonstrated the importance of T_g on the mechanical properties of conjugated polymer films.³⁶ However, the structure of conjugated polymers can make the measurement of T_g difficult.⁴¹ The glass transition is a second-order phase transition that occurs concomitantly with a change in the heat capacity and rate of change in density with temperature. A conjugated polymer, however, comprises both a conjugated backbone and (usually) aliphatic side chains. Given that the side chains are liquid-like even at temperatures well below the operating temperatures of most devices, the additional heat capacity upon reaching the glass transition of the side chains is only incremental and thus hard to detect. Moreover, for materials that form liquid crystalline phases, the transition from the liquid crystal glass to the liquid crystal melt may not enable sufficient molecular motion to produce a measurable increase in heat capacity by calorimetry.⁴¹

A number of techniques already existed to overcome the challenges of measuring the T_g . These approaches included variable temperature ellipsometry,⁴² along with a technique in which the conjugated polymer film is cast on a film of metallic nanoparticles and changes in density are recorded based on changes in the localized surface plasmon resonances of the nanoparticles.⁴³ However, these techniques required specialized materials, equipment, and training, making them difficult to access for a young laboratory. We therefore developed a method to determine the T_g based on the intrinsic optoelectronic changes of π -conjugated polymers that occur upon thermally activated aggregation.⁴⁴ The technique only requires a hot plate and an ultraviolet-visible (UV-vis) spectrometer. Briefly, one takes a film and anneals it on a hotplate at a relatively low temperature. The sample is then allowed to cool to room temperature, and its UV-vis spectrum is measured. The process is then iterated at increasing temperatures. A quantity called the deviation metric is calculated (DM , equation 1), and defined as the mean-squared deviation between the as-cast and annealed films:

$$DM \equiv \sum_{\lambda_{min}}^{\lambda_{max}} [I_{RT}(\lambda) - I_A(\lambda)]^2 \Delta\lambda \quad (1)$$

Here, $I_{RT}(\lambda)$, $I_A(\lambda)$ are the normalized absorption intensity of the as-cast and annealed films as a function of the wavelength, λ . $\Delta\lambda$ is the wavelength increment of the UV-Vis

spectrophotometer ($\lambda = 1 \text{ nm}$), and $\lambda_{min/max}$ are the bounds for the optical sweep. This quantity is plotted against the temperature and a change in slope corresponds to the location of the T_g . The values obtained by this process agree with the results of other methods of obtaining T_g for polymers with semicrystalline microstructures (Figure 5).

4. Synthesis and Simulation: Expanding Our Techniques

The success of our proof-of-concept experiments, along with the refinement of our metrological techniques, gave us the stability and increased funding necessary to incorporate new techniques into our group, such as organic synthesis and molecular dynamics simulations. We found increased funding particularly important at this stage as this required hiring additional students and postdocs who specialized in these techniques, and personnel were by far the largest expense for our research group. While we had improved our techniques of measuring mechanical properties, we still relied on indirect methods of analyzing the mesoscale morphology of our thin films such as UV-vis spectroscopy. Given the complexity of the ways in which the molecular structure of a polymer ultimately determines the mechanical properties of a solid sample, we wanted to probe the evolution of mesoscale morphology in as much detail as possible. Therefore, we turned to molecular dynamics simulations in collaboration with Prof. Gaurav Arya. We additionally believed that including molecular dynamics simulations would help diversify our lab by incorporating both experimental and computational projects, which would help our future funding efforts.

We had two goals with our molecular dynamics simulations: to predict the thermomechanical properties of semiconducting polymers, and to understand how nanoscale features affect a film's mechanical properties. We chose to simulate three materials—PDTSTPD, PTB7, and TQ1—because they occupy a range of microstructures (semicrystalline, ordered over short length scales, and amorphous, respectively) and because they are well known in the literature (Figure 6).⁴⁵ We employed molecular models of these polymers developed by Jackson et al.⁴⁶ We were able to predict the T_g of all the pure polymers and its increase upon the addition of PCBM by monitoring the density of a simulated polymer film under constant pressure and decreasing temperature.

Another finding from these computational studies was the primacy of solid-state microstructure—as opposed to molecular structure—in determining the mechanical properties of the film. For example, in these studies, our solid films were produced to mimic either thermodynamically equilibrated or highly kinetically trapped morphologies. We initialized “melt quenched” films by simulating the film at a high temperature, then gradually bringing it to room temperature. This process produced a film with a high density, high incidence of entanglements, and high elastic modulus. Conversely, a “self-aggregated” morphology was produced by simulating the conformations in a poor solvent and allowing the polymers to rapidly condense into a film. This morphology was characterized by high free volume, low elastic modulus, and reduced density of entanglements. Tellingly, the simulated mechanical properties of the three materials, PDTSTPD, PTB7, and TQ1, depended far more on the method of deposition than on the molecular structure of the materials. This result implied that the importance of molecular structure in determining the

mechanical properties of solid films arises principally from its effect on conformation during the process of solidification, at least for glassy films.

We also began to incorporate chemical synthesis into our group's toolkit. We were initially cautious about synthesizing new materials, as fine-tuning a synthetic process could add a substantial amount of time before materials characterization could begin. This made synthesis unideal for our proof-of-concept experiments. As our research progressed, however, we found that furthering our understanding of the relationships between chemical structure and mechanical properties in semiconducting polymers nearly required inclusion of synthetic chemistry, particularly to measure structure-property relations in donor-acceptor polymers. As such, we synthesized our own library of donor-acceptor polymers with varying side chain structures to examine whether the softening effects of long side chains held in a stiffer, higher- T_g donor-acceptor polymer (Figure 7a).⁴⁷ We additionally looked at the effects of different side chain structures, particularly branched and polyethylene oxide (PEO) motifs.

We chose the PDPP2F-T structure developed by the Fréchet group as our backbone due to its high planarity and good optoelectronic properties.⁴⁸ We found that while longer side chains did soften films, branching had greater effect, and PEO side chains produced the softest films of all (Figure 8b). Interestingly, while all our polymers were found to have T_g significantly above room temperature (using our technique described in Section 4), some polymers were found to have greater ductility and lower elastic moduli than the P3ATs we had previously studied with T_g below room temperature. This result suggested that for donor-acceptor polymers, branched or PEO side chains can produce soft, ductile films.

Synthetic techniques additionally allowed us to expand our applications beyond simply stretchable electronics. For example, stretchable organic electronic devices are potentially appealing to the field of implantable bioelectronics, as stretchable electronics can maintain intimate contact with the skin and internal organs. For many implantable devices, it would also be beneficial for the device to eventually degrade under physiological conditions into harmless byproducts. We decided to engineer a block copolymer that was both stretchable and biodegradable via a chain extension reaction of semiconducting polymers bearing DPP acceptor units flanked by two furan units (DPP2F) and thiophene donor units, separated by biodegradable units based on poly(caprolactone) (PCL).⁴⁹ The semiconducting units would provide the charge transport, while the PCL units would provide the mechanical deformability and biodegradability.

Our approach is illustrated in Figure 8. The block copolymer was substantially tougher and more stretchable than both the neat semiconducting polymer and the physical blend of the semiconducting polymer and the PCL. Moreover, when the fused thienothiophene unit was used to couple the DPP2F units together—as opposed to a single thiophene unit—charge mobility as measured in thin-film transistors was retained up to loading fractions of 90% PCL. Additionally, we found that the polymer degraded in a slightly basic phosphate buffered saline (PBS) solution which we used to mimic biological conditions. This approach thus constitutes a promising way to develop implantable materials that have favorable electronic and mechanical properties.

5. Conclusions

When we started our research program in 2012, the work described in this Account—the mechanical properties of conjugated polymers—was one of three research thrusts, which incidentally corresponded to the proposals in our principal investigator’s faculty applications. It later became the basis of his tenure dossier and remains the foundational topic of the group. We believe there are three reasons why this ended up being our ideal initial topic. (1) There was a large field of researchers and previous literature in the field of the synthesis and microstructure of conjugated polymers from which to draw inspiration and to connect our findings. (2) The initial experiments did not require specialized equipment and for the most part could be done inexpensively. (3) There was an adjacent field (mechanics, especially of polymeric materials) that rarely interacted with the central field (organic electronics), and thus much knowledge to be created by bridging the fields.

Six years into our research mission, understanding and predicting the mechanical properties of conjugated polymers is still by no means a “solved problem.” For example, “stretchable” in the field of composite materials—metal traces and integrated circuits embedded in elastomers—typically means “elastic.” Most “stretchable” organic semiconductors, however, have a limited elastic range ($\sim$ 10%). Additionally, the rheological behavior (time-dependent mechanical properties) of high-performance organic semiconductors with complex molecular structures is still unknown. It is our hope that the work described here influences others to engage with aspects of this important topic, and that our experiences are instructive to newly independent scientists at the outset of their careers.

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Biographical Information

Andrew Kleinschmidt earned his BS in chemical engineering from Stanford University in 2014. He began his PhD work at UC San Diego in 2016 under the supervision of Darren Lipomi. His research interests include computational approaches to understanding the mechanical properties of conjugated polymers.

Darren Lipomi earned his PhD in chemistry from Harvard University with George Whitesides in 2010. Following a postdoctoral fellowship at Stanford University with Zhenan Bao, he began his independent career at UC San Diego in 2012. His research interests include the work described in this Account, along with materials for human-machine interfaces.

References

- (1). Lipomi DJ; Martinez RV; Whitesides GM Use of Thin Sectioning (Nanoskiving) to Fabricate Nanostructures for Electronic and Optical Applications. *Angew. Chemie Int. Ed* 2011, 50, 8566–8583.
- (2). Lipomi DJ; Tee BC-K; Vosgueritchian M; Bao Z Stretchable Organic Solar Cells. *Adv. Mater* 2011, 23, 1771–1775. [PubMed: 21491510]
- (3). Darren J. Lipomi; Neil F. Langille, and; Panek* JS Total Synthesis of Basiliskamides A and B. 2004, 6, 3533–3536.
- (4). Whitesides GM Physical-Organic Chemistry: A Swiss Army Knife. *Isr. J. Chem* 2016, 56, 66–82.
- (5). Tokito S; Smith P; Heeger AJ Mechanical and Electrical Properties of Poly-(2,5-thienylene vinylene) Fibers. *Synth. Met* 1990, 36, 183–194.
- (6). Cao Y; Smith P; Heeger AJ Mechanical and Electrical Properties of Polyacetylene Films Oriented by Tensile Drawing. *Polymer* 1991, 32, 1210–1218.
- (7). Cao Y; Smith P; Heeger AJ Mechanical and Electrical Properties of Highly Oriented Polyacetylene Films. *Synth. Met* 1991, 41, 181–184.
- (8). Wudl F; Srdanov G Conducting Polymer Formed of Poly(2-methoxy,5-(2-ethyl-hexyloxy)-p-phenylvinylene) U.S. Patent 5189136A, 12 12, 1990.
- (9). Tang CW Multilayer Organic Photovoltaic Elements U.S. Patent 4164431A, 5 18, 1978.
- (10). Tang CW Two-layer Organic Photovoltaic Cell. *Appl. Phys. Lett* 1986, 48, 183–185.
- (11). Li G; Zhu R; Yang Y Polymer Solar Cells. *Nat. Photonics* 2012, 6, 153–161.
- (12). Günes S; Neugebauer H; Sariciftci NS Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev* 2007, 107, 1324–1338. [PubMed: 17428026]
- (13). Boudreault P-LT; Najari A; Leclerc M Processable Low-Bandgap Polymers for Photovoltaic Applications. *Chem. Mater* 2011, 23, 456–469.
- (14). Lu N; Wang X; Suo Z; Vlassak J Metal Films on Polymer Substrates Stretched beyond 50%. *Appl. Phys. Lett* 2007, 91, 221909.
- (15). Li T; Huang Z; Suo Z; Lacour SP; Wagner S Stretchability of Thin Metal Films on Elastomer Substrates. *Appl. Phys. Lett* 2004, 85, 3435–3437.
- (16). Suo Z; Ma EY; Gleskova H; Wagner S Mechanics of Rollable and Foldable Film-on-Foil Electronics. *Appl. Phys. Lett* 1999, 74, 1177.
- (17). Lacour SP; Wagner S; Huang Z; Suo Z Stretchable Gold Conductors on Elastomeric Substrates. *Appl. Phys. Lett* 2003, 82, 2404–2406.
- (18). Kim R-H; Kim D-H; Xiao J; Kim B-H; Park S-I; Panilaitis B; Ghaffari R; Yao J; Li M; Liu Z; Malyarchuk V; Kim D-G; Le A-P; Nuzzo RG; Kaplan DL; Omenetto FG; Huang Y; Kang Z; Rogers JA Waterproof AlInGaP Optoelectronics on Stretchable Substrates with Applications in Biomedicine and Robotics. *Nat. Mater* 2010, 9, 929–937. [PubMed: 20953185]
- (19). Lee J; Wu J; Shi M; Yoon J; Park S-I; Li M; Liu Z; Huang Y; Rogers JA Stretchable GaAs Photovoltaics with Designs That Enable High Areal Coverage. *Adv. Mater* 2011, 23, 986–991. [PubMed: 21226014]
- (20). Müller C; Goffri S; Breiby DW; Andreasen JW; Chanzy HD; Janssen RAJ; Nielsen MM; Radano CP; Sirringhaus H; Smith P; Stingelin-Stutzmann N Tough, Semiconducting Polyethylene-Poly(3-Hexylthiophene) Diblock Copolymers. *Adv. Funct. Mater* 2007, 17, 2674–2679.
- (21). O'Connor B; Chan EP; Chan C; Conrad BR; Richter LJ; Kline RJ; Heeney M; McCulloch I; Soles CL; DeLongchamp DM Correlations between Mechanical and Electrical Properties of Polythiophenes. *ACS Nano* 2010, 4, 7538–7544. [PubMed: 21080648]
- (22). Tahk D; Lee HH; Khang D-Y Elastic Moduli of Organic Electronic Materials by the Buckling Method. *Macromolecules* 2009, 42, 7079–7083.
- (23). Whitesides GM; Bowden N; Brittain S; Evans AG; Hutchinson JW Spontaneous Formation of Ordered Structures in Thin Films of Metals Supported on an Elastomeric Polymer. *Nature* 1998, 393, 146–149.

- (24). Stafford CM; Harrison C; Beers KL; Karim A; Amis EJ; VanLandingham MR; Kim HC; Volksen W; Miller RD; Simonyi EE A Buckling-Based Metrology for Measuring the Elastic Moduli of Polymeric Thin Films. *Nat. Mater* 2004, 3, 545–550. [PubMed: 15247909]
- (25). Yu Z; Niu X; Liu Z; Pei Q Intrinsically Stretchable Polymer Light-Emitting Devices Using Carbon Nanotube-Polymer Composite Electrodes. *Adv. Mater* 2011, 23, 3989–3994. [PubMed: 21796688]
- (26). O'Connor B; Chan EP; Chan C; Conrad BR; Richter LJ; Kline RJ; Heeney M; McCulloch I; Soles CL; DeLongchamp DM Correlations between Mechanical and Electrical Properties of Polythiophenes. *ACS Nano* 2010, 4, 7538–7544. [PubMed: 21080648]
- (27). Kleinschmidt AT; Root SE; Lipomi DJ Poly(3-Hexylthiophene) (P3HT): Fruit Fly or Outlier in Organic Solar Cell Research? *J. Mater. Chem. A* 2017, 5, 11396–11400.
- (28). McCullough RD The Chemistry of Conducting Polythiophenes. *Adv. Mater* 1998, 10, 93–116.
- (29). McCullough RD; Lowe RD; Jayaraman M; Anderson DL Design, Synthesis, and Control of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-Alkylthiophenes). *J. Org. Chem* 1993, 58, 904–912.
- (30). Tahk D; Lee HH; Khang DY Elastic Moduli of Organic Electronic Materials by the Buckling Method. *Macromolecules* 2009, 42, 7079–7083.
- (31). O'Connor TF; Zaretski AV; Shiravi BA; Savagatrup S; Printz AD; Diaz MI; Lipomi DJ Stretching and Conformal Bonding of Organic Solar Cells to Hemispherical Surfaces. *Energy Environ. Sci* 2014, 7, 370–378.
- (32). Savagatrup S; Makaram AS; Burke DJ; Lipomi DJ Mechanical Properties of Conjugated Polymers and Polymer-Fullerene Composites as a Function of Molecular Structure. *Adv. Funct. Mater* 2014, 24, 1169–1181.
- (33). Savagatrup S; Printz AD; Wu H; Rajan KM; Sawyer EJ; Zaretski AV; Bettinger CJ; Lipomi DJ Viability of Stretchable Poly(3-Heptylthiophene) (P3HpT) for Organic Solar Cells and Field-Effect Transistors. *Synth. Met* 2015, 203, 208–214.
- (34). Savagatrup S; Printz AD; Rodriguez D; Lipomi DJ Best of Both Worlds: Conjugated Polymers Exhibiting Good Photovoltaic Behavior and High Tensile Elasticity. *Macromolecules* 2014, 47, 1981–1992.
- (35). Printz AD; Zaretski AV; Savagatrup S; Chiang AS-C; Lipomi DJ Yield Point of Semiconducting Polymer Films on Stretchable Substrates Determined by Onset of Buckling. *ACS Appl. Mater. Interfaces* 2015, 7, 23257–23264. [PubMed: 26437763]
- (36). Savagatrup S; Printz AD; Wu H; Rajan KM; Sawyer EJ; Zaretski AV; Bettinger CJ; Lipomi DJ Viability of Stretchable Poly(3-Heptylthiophene) (P3HpT) for Organic Solar Cells and Field-Effect Transistors. *Synth. Met* 2015, 203, 208–214.
- (37). Rodriguez D; Kim J-H; Root SE; Fei Z; Boufflet P; Heeney M; Kim T-S; Lipomi DJ Comparison of Methods for Determining the Mechanical Properties of Semiconducting Polymer Films for Stretchable Electronics. *ACS Appl. Mater. Interfaces* 2017, 9, 8855–8862. [PubMed: 28220705]
- (38). Kim J-H; Nizami A; Hwangbo Y; Jang B; Lee H-J; Woo C-S; Hyun S; Kim T-S Tensile Testing of Ultra-Thin Films on Water Surface. *Nat. Commun* 2013, 4, 2520. [PubMed: 24084684]
- (39). Chung JY; Lee J-H; Beers KL; Stafford CM Stiffness, Strength, and Ductility of Nanoscale Thin Films and Membranes: A Combined Wrinkling–Cracking Methodology. *Nano Lett* 2011, 11, 3361–3365. [PubMed: 21761850]
- (40). Alkhadra MA; Root SE; Hilby KM; Rodriguez D; Sugiyama F; Lipomi DJ Quantifying the Fracture Behavior of Brittle and Ductile Thin Films of Semiconducting Polymers. *Chem. Mater* 2017, 29, 10139–10149.
- (41). Snyder CR; DeLongchamp DM Glassy Phases in Organic Semiconductors. *Curr. Opin. Solid State Mater. Sci* 2018, 22, 41–48.
- (42). Müller C; Andersson LM; Peña-Rodríguez O; Garriga M; Inganäs O; Campoy-Quiles M Determination of Thermal Transition Depth Profiles in Polymer Semiconductor Films with Ellipsometry. *Macromolecules* 2013, 46, 7325–7331.
- (43). A Nugroho FA; Diaz de Zerio Mendaza A; Lindqvist C; Antosiewicz TJ; Mu C; Langhammer C Plasmonic Nanospectroscopy for Thermal Analysis of Organic Semiconductor Thin Films. *Anal. Chem* 2017, 89.

- (44). Root SE; Alkhadra MA; Rodriquez D; Printz AD; Lipomi DJ Measuring the Glass Transition Temperature of Conjugated Polymer Films with Ultraviolet-Visible Spectroscopy. *Chem. Mater* 2017, 29, 2646–2654.
- (45). Root SE; Jackson NE; Savagatrup S; Arya G; Lipomi DJ Modelling the Morphology and Thermomechanical Behaviour of Low-Bandgap Conjugated Polymers and Bulk Heterojunction Films. *Energ. Environ. Sci* 10, 558–569.
- (46). Jackson NE; Kohlstedt KL; Savoie BM; Olvera de la Cruz M; Schatz GC; Chen LX; Ratner MA Conformational Order in Aggregates of Conjugated Polymers. *J. Am. Chem. Soc* 2015, 137, 6254–6262. [PubMed: 25920989]
- (47). Sugiyama F; Kleinschmidt AT; Kayser LV; Rodriquez D; Finn M; Alkhadra MA; Wan JM-H; Ramírez J; Chiang AS-C; Root SE; Savagatrup S; Lipomi DJ Effects of Flexibility and Branching of Side Chains on the Mechanical Properties of Low-Bandgap Conjugated Polymers. *Polym. Chem* 2018, 9, 4354–4363. [PubMed: 30873221]
- (48). Woo CH; Beaujuge PM; Holcombe TW; Lee OP; Fréchet JMJ Incorporation of Furan into Low Band-Gap Polymers for Efficient Solar Cells. *J. Am. Chem. Soc* 2010, 132, 15547–15549. [PubMed: 20945901]
- (49). Sugiyama F; Kleinschmidt AT; Kayser LV; Alkhadra MA; Wan JM-H; Chiang AS-C; Rodriquez D; Root SE; Savagatrup S; Lipomi DJ Stretchable and Degradable Semiconducting Block Copolymers. *Macromolecules* 2018, 51, 5944–5949. [PubMed: 30930487]

Figure 1.

Features of the molecular structure (left) and microstructure (right) of conjugated polymers that can differ from those of commodity polymers and engineering plastics that have profound effects on the mechanical properties.

Figure 2.

Summary of initial P3AT experiments. (a) Molecular structures of P3HT-P3OT hybrid polymers. (b) Relationship between optoelectronic and mechanical properties of P3HT-P3OT hybrid polymers. (c) Tensile moduli of P3HT-P3OT hybrid polymers. Reproduced with permission from Ref. 34. Copyright 2014, American Chemical Society.

Figure 3.

Comparison of methods of testing on the mechanical properties of conjugated polymer films. (a) Reconstructed stress-strain curves of four different molecular weights of P3HT using the film-on-elastomer methods. (b) Results of pull testing of quasi-free standing films of the same samples as shown in (a) obtained using the film-on-water method. (c) Results of coarse-grained molecular dynamics simulations showing the effect of increasing molecular weight on the entanglement density of a polymer film, which is correlated to its extensibility. The high-molecular weight system (top) had a degree of polymerization of 300; the low molecular weight system (bottom) had a degree of polymerization of 50, and one-sixth the density of entanglements. Reproduced with permission from Ref. 37. Copyright 2017, American Chemical Society.

Figure 4.

Fracture behavior of brittle and ductile films. (a) Schematic diagram of brittle (left) and ductile (right) fracture of conjugated polymer films on PDMS substrates. Ductile fracture is characterized by diamond-shaped microvoids. The rate at which the aspect ratio (l/w) grows with strain is named the microvoid propagation number (m) and plotted vs. the log of the elastic mismatch of the PDMS and a (relatively stiff) film of poly(3-butylthiophene) (P3BT) in (b). The elastic mismatch has a smaller effect on the crack-onset strain (COS). (c) Stress- vs. strain curves for the four structures shown in (d). The inset plotting $\log(m)$ vs. the fracture stress (σ^*) shows linear behavior, and connects m , determined optically, to a force σ^* , determined mechanically. Reproduced with permission from Ref. 40. Copyright 2017, American Chemical Society.

Figure 5.

Determination of the glass transition temperature (T_g) using a hot plate and UV-vis spectroscopy. (a) Time course of the experiment. Samples were placed on a hotplate, cooled, and measured by UV-vis. (b) UV-vis spectra. Vibronic structure begins to shift at ~600 nm as the temperature crosses T_g . (c) Visualization of the evolution in vibronic structure by plotting the deviation metric vs. temperature. The change in slope corresponds to the T_g obtained using other techniques, when available. Reproduced with permission from Ref. 44. Copyright 2017, American Chemical Society.

Figure 6. Atomistic dynamics simulations of the mechanical properties of donor-acceptor (low-bandgap) conjugated polymers. (a) Chemical structures. (b) Slices of the melt-quenched and self-aggregated morphologies. (c) The melt-quenched morphology exhibits a higher modulus than the self-aggregated morphology, largely because of the greater density and density of entanglements for the melt-quenched morphology. Reproduced with permission from Ref. 45. Copyright 2017, Royal Society of Chemistry.

Figure 7.

A library of donor-acceptor polymers (PDPP2F-T) with different side chain structures and compositions. (a) Chemical structures of the donor-acceptor backbone and side chain structures. C8 and C14 side chains were obtained with very low molecular weight and were not characterized. (b) Thermomechanical properties of the library of polymers. (c) Optoelectronic properties of the library of polymers. Reproduced with permission from ref 47. Copyright 2018, Royal Society of Chemistry.

Figure 8. Stretchable and degradable block copolymers. (a) Chemical structure of a polymer comprising a semiconducting component and a stretchable, degradable, insulating component, poly(caprolactone) (PCL). (b) Stress-strain behavior of one family of the polymers shown in (a). (c) Hole mobility for thiophene-donor (BCP-T) and thienothiophene-donor (BCP-TT) polymers vs. PCL content. The maintenance of mobility is consistent with increased aggregation (order) of BCP-TT as measured by the ratio of A_{0-0} to A_{0-1} absorption by UV-vis (d). Reproduced with permission from Ref. 49. Copyright 2018, American Chemical Society.