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High-Performance Semiconducting Elastomers

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Over the course of this award, our investigations have elucidated many of the molecular and microstructural determinants of the mechanical properties of semiconducting polymers. The work has produced insights and methodologies with impacts within and beyond the field of stretchable electronics. For example, it has led to new metrological, synthetic, and computational methodologies for measuring, modifying, and predicting the mechanical properties of complex polymeric materials. The principal concerns of this proposal are to validate computational predictions and to apply the knowledge produced for semiconducting polymers broadly across polymer science.We began by performing the first measurements of the mechanical properties of a range of semiconducting polymers and have made hypotheses connecting molecular structure to mechanical properties. In parallel, we used synthetic chemistry to tune elements of the molecular structure systematically. The synthetic work was complemented with molecular dynamics simulations, whose goal is to determine how molecular structure influences solid-state structure as mediated by solvation. From the solid-state structure, it is possible to predict thermomechanical properties associated with deformability (e.g., glass transition temperature and

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High-Performance Semiconducting Elastomers

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Overview

Semiconducting polymers have always been associated with flexible applications, such as solar cells, active-matrix displays, and biomedical sensors.[1,2] Mechanical flexibility of these materials, however, is not automatic. The mechanical properties of semiconducting polymers must be engineered by tuning the structure, molecular weight, processing, and interactions with other materials in the device stack.[3,4] Despite the importance of deformability in essentially all applications of semiconducting polymers, mechanical properties have, until recently, been an afterthought. For example, the mechanical stability of organic solar cells has often been overlooked in favor of improving power conversion efficiencies. However, the development of polymers that can endure the rigors of roll-to-roll coating, survive long term against mechanical deformations in the outdoors, and withstand packing and transportation in portable devices demands an understanding of their mechanical properties. These properties—including elasticity, extensibility, strength, and toughness—are critically dependent not only on the molecular structure of the materials, but on the ways these structures pack in the solid state, which are, in turn, mediated by the conditions of processing. Prediction of the mechanical behavior of materials in a device is confounded by the fact that the properties of materials measured in the laboratory can depend on testing conditions, such as temperature, strain rate, and choice of substrate. (This paragraph is adapted from our paper, Root et al. *Chem. Rev.* **2017**, 117, 6467.)

Over the course of this award, our investigations have elucidated many of the molecular and microstructural determinants of the mechanical properties of semiconducting polymers.[5] The work has produced insights and methodologies with impacts within and beyond the field of stretchable electronics. For example, it has led to new metrological, synthetic, and computational methodologies for measuring, modifying, and predicting the mechanical properties of complex polymeric materials.[6–11] The principal concerns of this proposal are to validate computational predictions and to apply the knowledge produced for semiconducting polymers broadly across polymer science. We have taken an approach to understanding the mechanical properties of organic semiconductors that spans multiple length scales and techniques, both experimental and computational.[5] These length scales are summarized in **Figure 1**. We began by performing the first measurements of the mechanical properties of a range of semiconducting polymers and have made hypotheses connecting molecular structure to mechanical properties. In parallel, we used synthetic chemistry to tune elements of the molecular structure systematically. The synthetic work was complemented with molecular dynamics simulations, whose goal is to determine how molecular structure influences solid-state structure as mediated by solvation. From the solid-state structure, it is possible to predict thermomechanical properties associated with deformability (e.g., glass transition temperature and modulus) based on nanoscale characteristics, like entanglement density, conjugation length, and conformational classes of molecules in solution and then in the solid state. We have also performed experiments on whole, integrated devices for novel applications.[12,13] On these devices, we have used robotic testing apparatuses to predict locations of failure that can be mitigated by engineering the molecular structure or conditions of processing.[11] Continuum-scale modeling is also performed on these device architectures. The work we have performed over the last three years of AFOSR support has focused largely on three areas: (1) the connection between molecular structure and solid-state packing structure as it pertains to mechanical properties, (2) the development of computational methodologies designed to predict mechanical behavior from molecular structure, and (3) the development of new experimental tools to measure thermomechanical properties. (Paragraph reproduced and adapted from summary statement in proposal 19RT0389 submitted in March, 2019.)

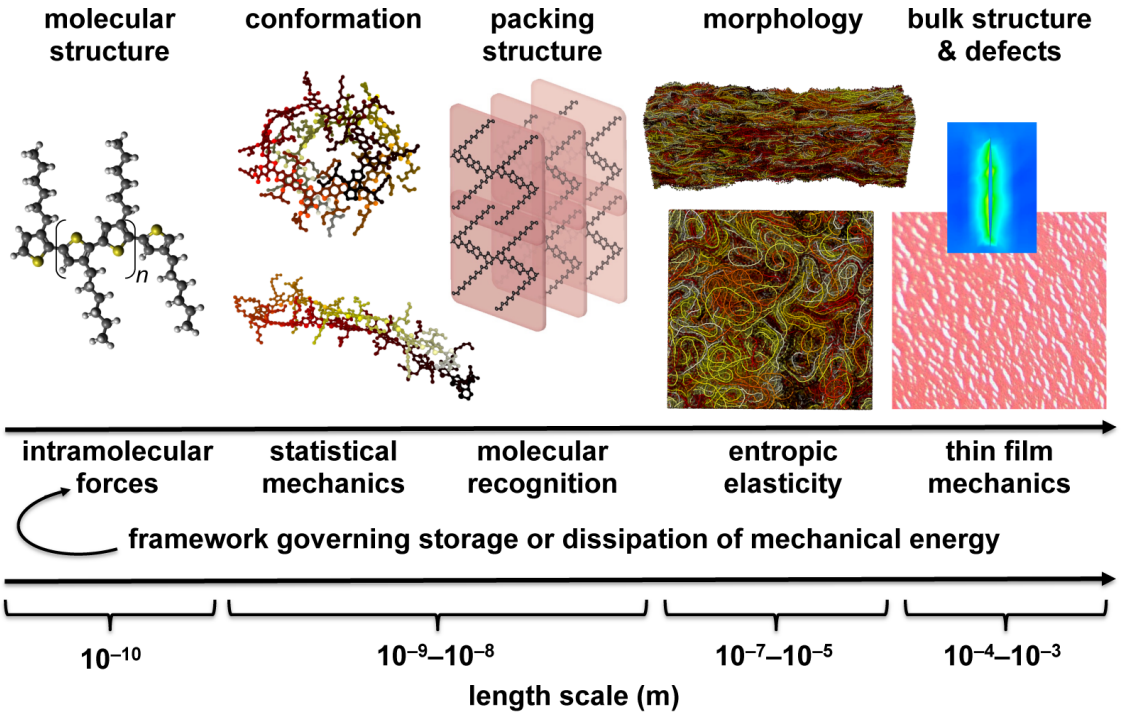

Figure 1. *Length scales—from molecular to continuum—over which mechanical energy is mediated in semiconducting polymers. Adapted from ref.*[5]

1. Connection between structure and mechanical properties.

Our initial framework for understanding the mechanical properties of solid films of semiconducting polymers relied on our assumption of the primacy of molecular structure. In other words, we believed that there would be a simple correlation between the deformability of a molecular structure and the deformability of a solid film. While we knew that the details of molecular packing would influence the bulk mechanical properties, we did not appreciate the extent to which morphological considerations would affect the mechanical properties. In a collaboration with the Mei group (Purdue), we measured the modulus and crack-onset strains of a series of low-bandgap polymers based on the diketopyrrolopyrrole (DPP) unit.[14] This series consisted of five samples with increasing content of a "conjugation-break spacer" (CBS) unit, in this case, propylene groups (**Figure 2**). The completely conjugated polymer was named DPP-0, and the polymer with completely broken conjugation was DPP-100. DPP-30, DPP-50, and DPP-70 had intermediate content of the CBS unit. The original hypothesis was that the more flexible the chain (the greater the percent incorporation of the CBS unit), the more deformable the final film would be. What we observed instead was an increase in deformability from DPP-0 to DPP-70, and a steep drop-off in deformability at DPP-100. The hypothesis for this behavior was that the greater the incorporation of CBS units, the longer the monomer residue, and thus the lower the attachment density and reduced steric demands of the side chains. The main chains were thus allowed to be closer together in the solid film at high percentages of CBS units, as determined by the decrease in the lamellar stacking signal by grazing-incidence X-ray diffraction (GIXD). The high brittleness of DPP-100 was possibly due to its structural order. Whereas the polymers with intermediate incorporation of the CBS was statistical (essentially random), the regular DPP-100 formed a well-ordered microstructure, as evident by the narrowing of the full-width at half

maximum of the lamellar reflection by GIXD.[14] We therefore hypothesized that the high brittleness of DPP-11 was due to its structural order. (Paragraph reproduced and adapted from summary statement in new 19RT0389 submitted in March, 2019.)

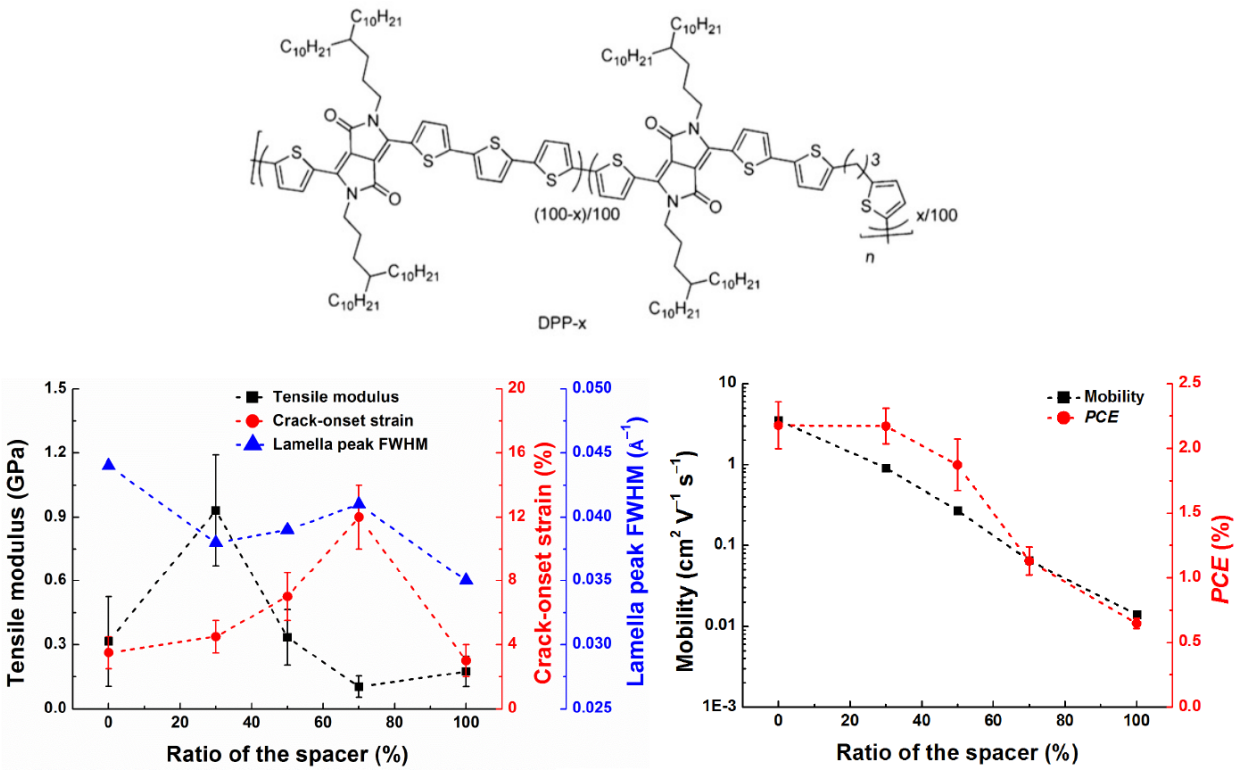

Figure 2. *Use of conjugation-break spacers (CBSs) to manipulate the microstructure and mechanical properties of semiconducting polymers. (Top) Chemical structure of a DPP-containing polymer copolymerized with a flexible propylene group (right-hand side of the structure). The structure contained between 0 and 100% of the monomer residue bearing these aliphatic units. (Bottom left) A plot showing the effect of the ratio of the spacer (flexible content) on the modulus, crack-onset strain, and lamellar full width and half maximum (FWHM) from grazing-incidence X-ray diffraction. The fully flexible polymer chain produced the most brittle film (lowest crack-onset strain). (Bottom right) A plot of mobility and power conversion efficiency (PCE) of the CBS polymers when mixed with a methanofullerene in a solar cell as a function of the ratio of the spacer. Adapted from ref.[21]*

2. Computational approaches to understanding elasticity in semiconducting polymers

The prominence of microstructure and molecular recognition in the solid state became immediately apparent in our computational studies. In our first study, done in collaboration with Prof. Gaurav Arya, we sought to see if it were possible to predict the mechanical properties of the poly(3-alkylthiophene)s (P3ATs) by molecular dynamics simulations (**Figure 3**).[15,16] We used a coarse-grained methodology in which each monomer residue was condensed into coarse-grained "beads"—one for the thiophene ring, and one for each group of three carbon atoms in the side chain. Thus poly(3-hexylthiophene) (P3HT) was modeled using a three-site model.[15] We

successfully predicted the glass transition temperature and elastic modulus for P3HT. The most interesting discovery, however, was a new mechanism of increased brittleness for polymer-small molecule composites. It is well known that fullerene molecules behave as anti-plasticizers for conjugated polymers, as they lower the T_g and increase the brittleness.[17] This is a problem for applications like solar cells and photodetectors for portable applications, which may fracture in the field. Films of pure fullerenes are known to be brittle, as crystallites are held together only by van der Waals forces, and can thus drive decohesion of a blended film of polymer and fullerene.[18] Our results suggested an additional mechanism. Namely, the high contact dissimilarity between fullerenes and semiconducting polymers causes the polymer molecules to contract, as if dissolved in a poor solvent. Evidence for this contraction was reduced radius of gyration and reduced density of entanglements. Thus fullerenes decrease the mechanical robustness of blended films in part because of the effect on the *polymer*.[15] In another study, in which we examined a series of low-bandgap polymers, we found that the way in which the film was solidified—e.g., from the melt vs. from a solution in a poor solvent—had a stronger effect on the mechanical properties than the molecular structure itself.[16]

Perhaps the most impactful consequence of the predictions of our MD simulations are the predicted effects of the conditions of processing on the mechanical properties. In particular, the mechanical properties of the film depend on the way in which the film was prepared. There are two extreme ways in which to prepare a film: "melt-quenched" and "self-aggregated" (**Figure 3e**).[16] For the melt-quenched morphology, which was generated by raising the temperature far above the melting point followed by simulated cooling, a high-density morphology was formed with a high density of entanglements. The entanglements were predicted by the intersection of the primitive paths of two segments of polymers, which has been shown to be proportional to the density of entanglements. High density results in a high cohesive energy based on van der Waals interactions (primarily influencing the modulus), while a high density of entanglements increases the extensibility and toughness. An experimental system approximating the calculated melt-quenched morphology could also be formed by casting a solid material from a good solvent, which allows the polymer chains to extend and thus entangle upon solidification. In contrast, the self-aggregated morphology simulates a scenario in which a solid film is formed from a poor solvent. That is, the polymer chains form self-aggregated structures with small radii of gyration. Upon removal (i.e., evaporation) of the solvent, the polymer chains deposit on a substrate. The pre-aggregated structure consists of increased free volume and precludes the formation of entanglements. In the simulated stress-strain curves shown in **Figure 3e**, the "bulk heterojunction" morphology consists of mixtures of the polymers and [70]PCBM, an electron acceptor commonly used in organic solar cells, and was prepared using the same technique as the "melt-quenched" morphology. (Paragraph reproduced and adapted from summary statement in new 19RT0389 submitted in March, 2019.)

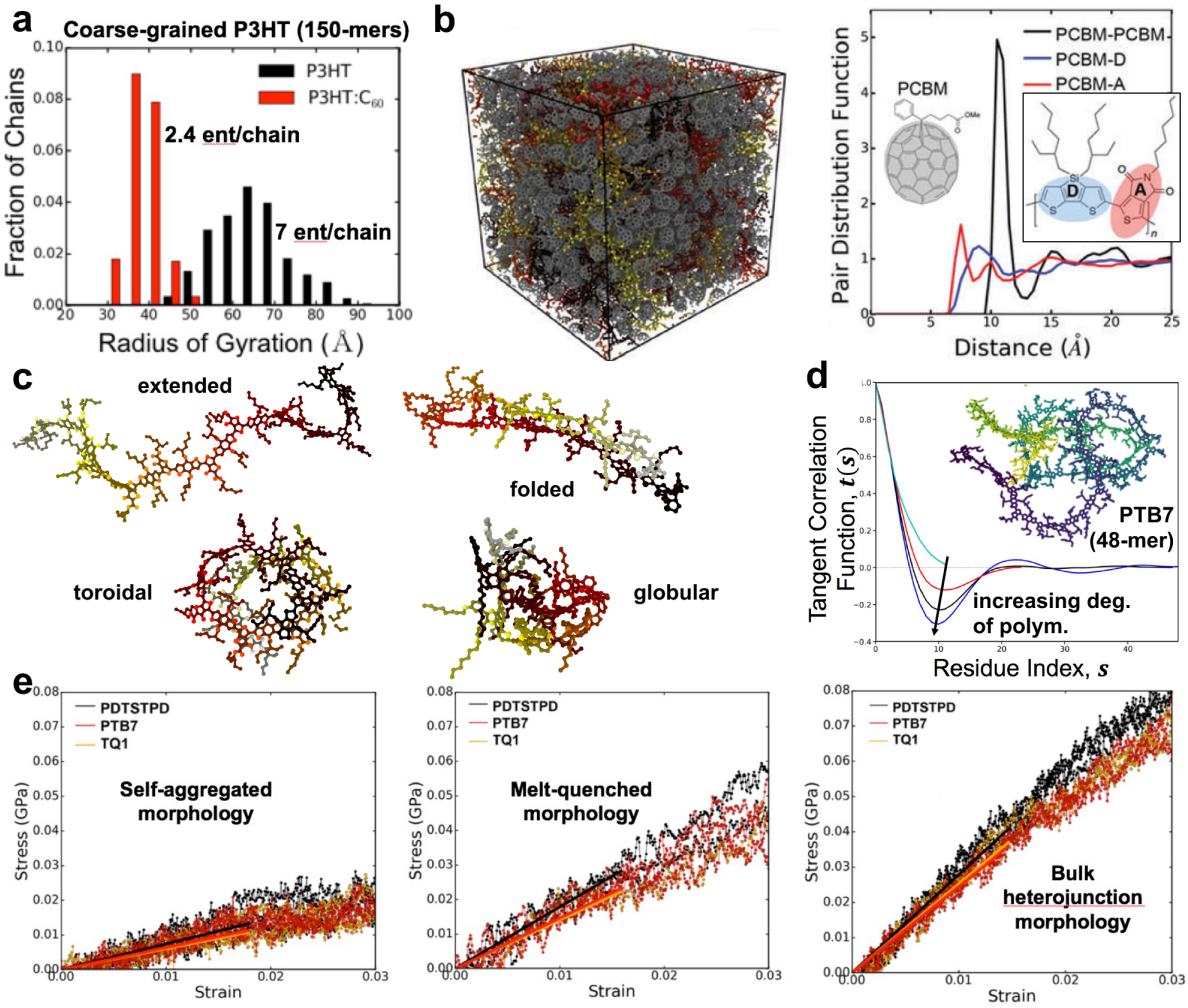

Figure 3. *Use of molecular dynamics simulations to predict the entanglements, molecular recognition, conformational classes, ribbon-like character, and mechanical behavior of conjugated polymers. (a) Blending a polymer with a fullerene (P3HT with C_{60}) decreases the radius of gyration and entanglements per chain of the polymer in the blend relative to the pure polymer and thus increases the brittleness of the blend. Adapted from ref.[35] (b) Calculated "pair distribution function" which predicts which part of the polymer the fullerene is likely to interact with. In the case of PDTSTPD, pictured, the fullerene interacts more strongly with the acceptor unit "A". Adapted from ref.[2] (c) Illustration of four conformational classes adopted by semiconducting polymers. Adapted from ref.[2] (d) Oscillatory tangent correlation function indicative of ribbon-like behavior. Oscillations increase with increasing degree of polymerization for PTB7 (48-mer). (e) Simulated stress-strain behavior. The salient feature is that the method of preparation seems to have a greater effect on the modulus and strength than the chemical structure, whose influence may manifest in the solubility. Adapted from ref.[2]*

While the force field used to generate the plots in **Figure 3e** was not able to predict the scission of covalent bonds, the plots reveal several striking characteristics. First, the melt-quenched (and bulk heterojunction) morphologies had much higher moduli and stresses (strengths) than the self-aggregated morphologies. This finding is consisted with the decreased density and number of

entanglements for the self-aggregated morphology. Second, the way in which the films were prepared appeared to be more important than the molecular structure. That is, each method of preparation produces three essentially identical stress-strain plots, regardless of the chemical structure. It seems that in a real system, the role of the molecular structure is to influence the solubility properties and thus the morphology of the film once cast. The implication is that the mechanical properties can be optimized (for stretchability, modulus, toughness, etc.) *by manipulating the conditions of processing.*[19] (Paragraph reproduced and adapted from summary statement in new 19RT0389 submitted in March, 2019.)

3. Metrology for measuring the mechanical properties of semiconducting polymers

In the course of our experiments, we also found that many existing techniques of measuring the thermomechanical properties of thin films were not able to obtain reliable measurements of these properties in conjugated polymers (**Figure 4**). For example, the glass transition temperature (T_g) is critically important in determining the mechanical properties. It is typically measured by differential scanning calorimetry (DSC) by locating the temperature at which the heat capacity changes. The signal is weak for most conjugated polymers, however, because the side chains are already liquid-like at the T_g, and thus increased thermal motion of the main chains does not add significantly to the heat capacity.[20] One characteristic of the solid material that does change, however, is the extent of aggregation. At the T_g, there is enough thermal motion for polymer chains to aggregate, and aggregation is associated with vibronic peaks that appear at lower energies as revealed by ultraviolet-visible (UV-vis) spectroscopy.[7] We hypothesized that the onset of this red shift with temperature would thus occur at the T_g. **Figure 4a** summarizes the approach and the results. For all semicrystalline materials for which the T_g was known, the method we developed was consistent with values obtained by others using established—though more difficult—techniques. Another technique we developed concerns the behavior of ductile materials after the onset of cracking. When straining films of conjugated polymers on elastomeric substrates, we often observed that cracks took the form of diamond-shaped microvoids. We found that the increase in the aspect ratio (l / w) of these microvoids was constant with strain.[8] We sought to determine if this ratio, $(\Delta l/\Delta w)/\Delta\varepsilon = m$, the "microvoid propagation number," was related to fundamental mechanical properties of the conjugated polymer film. Our results are shown in **Figure 4b**. While the samples tested differed substantially in degree of polymerization and thus it was not possible to determine specific relationships between molecular structure and mechanical properties, we did find that measurement of m could be extrapolated to the crack-onset strain, which is difficult to measure optically. It was also related to the fracture stress of the polymer. This simple optical measurement thus provides quantitative measurements of intensive mechanical properties of semiconducting polymers and requires only a microscope and a method of applying strains. This paper was selected for the "Best Paper of the Year Award" for 2018 in *Chemistry of Materials*.[8] (Paragraph reproduced and adapted from summary portion in new 19RT0389 submitted in March, 2019.)

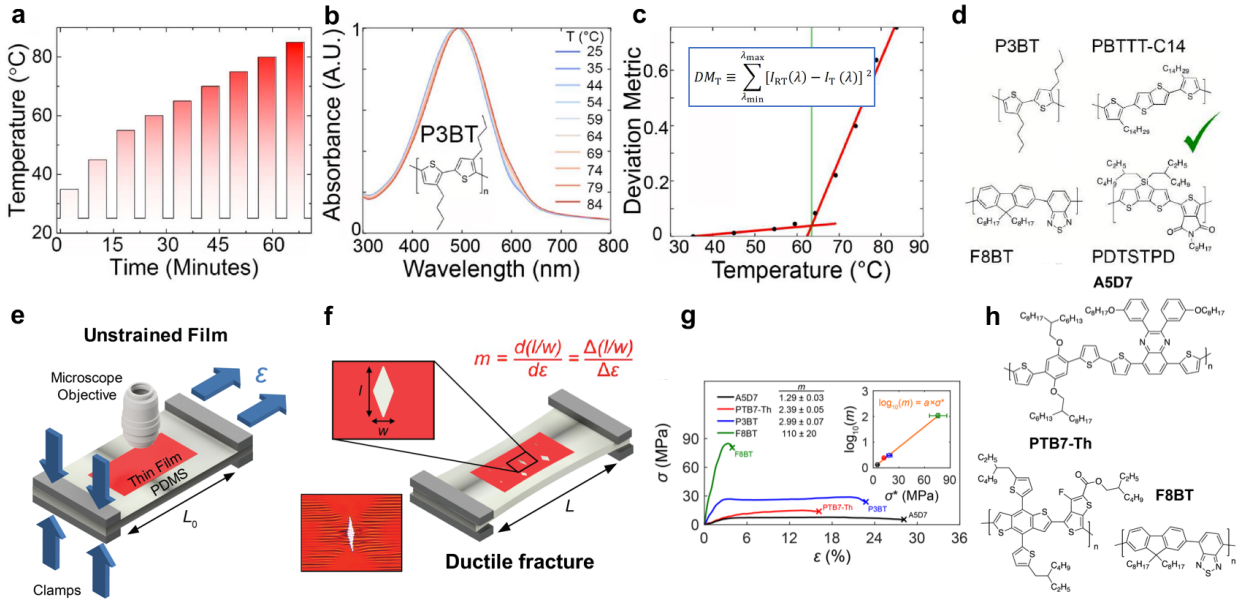

Figure 4. *Methods developed by our laboratory for measuring the glass transition temperature (a-d) and fracture stress (e-h) for materials for which these quantities are otherwise difficult to obtain. (a) Temperature profile for annealing conjugated polymer films at successively greater temperatures. (b) UV-vis spectrum of poly(3-butylthiophene) (P3BT). After surpassing the T_g, vibronic structure appears as a red shift in the spectrum. (c) The difference between plots is quantified using a thermal deviation metric (DM_T). The change in slope of a plot of DM_T vs. temperature corresponds to the location of the glass transition temperature. (d) Chemical structures of the semicrystalline materials for which this process works. The formation of π-stacked aggregates at elevated temperatures is necessary to observe the evolution in vibronic structure. Adapted from ref.*[7] *(e) Schematic diagram of the setup needed to measure the microvoid propagation number (m) in ductile films, which can be used to calculate the fracture stress (inset of panel g) which corresponds to the value obtained using a pull test of a quasi-freestanding film (g, full plot). (h) Chemical structures of the materials shown in (g). Adapted from ref.*[8]

Progressive-load scratch testing. Most advantages of organic electronic materials are enabled by mechanical deformability, as flexible (and stretchable) devices made from these materials must be able to withstand roll-to-roll printing and survive mechanical insults from the external environment. Cohesion and adhesion are two properties that dictate the mechanical reliability of a flexible organic electronic device. In this paper, progressive-load scratch tests are used for the first time to correlate the cohesive and adhesive behavior of poly(3-alkylthiophenes) (P3ATs) with respect to two molecular parameters: length of the alkyl side chain and molecular weight. In contrast to metrological techniques based on buckling or pull testing of pseudo-freestanding films, scratch tests reveal information about both the cohesive and adhesive behavior of thin polymeric films from a single procedure. Our data show a decrease in cohesion and adhesion with increasing length of the side chain. This behavior is likely due to increases in free volume and concomitant decreases in the glass transition temperature with increasing length of the side chain. In contrast, we observe increases in both the cohesion and adhesion with increasing molecular weight. This behavior is attributed to an increased density of entanglements in high

molecular weight samples, which manifests as increased plasticity. These observations are consistent with the results of molecular dynamics simulations. Interestingly, the normal (applied) forces associated with cohesive and adhesive failure are directly proportional to the number of repeat units, once the entanglement molecular weight has been surpassed. This result supports the importance of degree of polymerization—as opposed to simply the molecular weight—in improving the mechanical properties of organic electronic materials. (Paragraph reproduced and adapted from our paper, ref. [9])

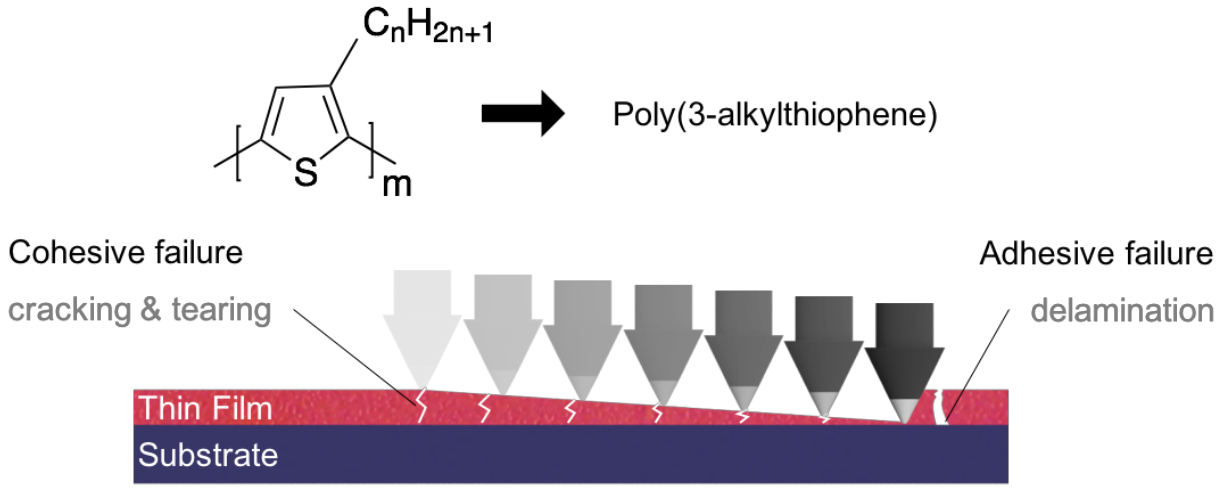

Figure 3. *Molecular structure of poly(3-alkylthiophene). Schematic diagram of nanoscratch test which quantifies the intrinsic mechanical properties of the film and also the adhesion of the film with the substrate. Reproduced from ref.* [9]

4. Conclusion

In all, this project produced fifteen peer-reviewed articles, summarized below.

- Elucidated the role of aliphatic, flexible linker units in a series of low-bandgap polymers and found that the solid-state packing structure was more important than the flexibility of the molecular structure in determining the deformability of the solid film. (Savagatrup et al. *Macromol. Rapid Commun.* **2016**, *37*, 1623).[14]

- We investigated the critical role of microstructure as compared to molecular structure in a computational paper in which we performed the first fully atomistic molecular dynamic simulations of high-performance low-bandgap polymers, in collaboration with one of our computational co-PIs, Prof. Gaurav Arya (Root et al. *Energy Environ. Sci.* **2017**, *10*, 558).[16]

- Throughout our experiments in this field, we consistently found that the glass transition temperature (T_g)—critical in determining the mechanical behavior—was not easy to measure using conventional techniques. We thus developed a simple, spectroscopic technique for determining the T_g of several high-performance, semicrystalline semiconducting polymers (Root & Alkhadra et al. *Chem. Mater.* **2017**, *29*, 2646).[7]

- In another paper, we compared two common methodologies for measuring the mechanical properties of organic thin films. That is, the combination of surface wrinkling, crack-onset, and yield of thin films supported by elastomeric slabs ("film-on-elastomer" methods), and a method in which a conventional pull test is performed on a thin film horizontally suspended on water ("film-on-water" method). This work was the first such comparison and led to important conclusions regarding the roles of voids, entanglements, and strain rates in determining the mechanical deformability (Rodriquez et al. *ACS Appl. Mater. Interfaces* **2017**, *9*, 8855).[10]

- We produced the first comprehensive review of the mechanical properties of organic semiconductors in *Chemical Reviews*, which received the Editor's Choice recognition from the American Chemical Society, an honor reserved for approximately the top 0.3% of papers published across all ACS journals. (Root et al. *Chem. Rev.* **2017**, 117, 6467)[5]

- Developed a method for determining the quantifying the fracture behavior of brittle and ductile semiconducting polymers. We found a simple relationship between the evolution of the shape of a microvoid—i.e., crack propagation—and the ultimate tensile strength of the polymer (Alkhadra & Root et al. *Chem. Mater.* **2017**, *29*, 10139, winner of the "Best Paper" award in 2017).[8]

- We then investigated device-level measurements of mechanical survivability. As such, we constructed physical and computational models to predict the long-term mechanical survivability of printed solar modules based on organic semiconductors (Finn et al. *Sol. Energy Mater. Sol. Cells* **2018**, *174*, 5).[11]

- Since constructing whole modules is not usually a practical means of testing the mechanical properties of the component materials, we also developed a technique based on nanoscratch testing for extracting the cohesive and adhesive energies of semiconducting polymers on substrates (Rodriquez et al., *ACS Macro Lett.* **2019**, *7*, 1003).[9]

- Our research laboratory has been recognized with two high-profile invitations to write about this work, first as a Commentary in *Joule* (Lipomi *Joule* **2018**, *2*, 195).[21]

- We prepared a full-length book chapter on the Mechanical Properties of Semiconducting Polymers in the *Handbook of Conducting Polymers, 3rd Ed.* CRC Press, 2019.[22]

- In a side project with UCSD colleagues Zheng Chen and Shyue Ping ong, we provided materials which led to the elucidation of the electrochemical properties of naphthalene

diimide for stable and high-rate lithium-ion battery electrodes. Shi et al. *Chem. Mater.* **2018**, *30*, 3508.[23]

- In a series of two papers, in collaboration with Prof. Barry Thompson (USC), we elucidated the role of conjugation-break spacers in determining the mechanical properties of semiconducting polymers. Melenbrink et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32426.[24]

- Similar goals to as above with a new set of materials: Melenbrink et al. *ACS Appl. Polym. Mater.* **2019** (accepted)

- This paper is an account of our work in the area of the mechanical properties of semiconducting polymers aimed at new researchers. Kleinschmidt et al. *Acc. Chem. Res.* **2018**, *51*, 3134.[25]

- This is an invited review article on stretchable forms of the permanently conductive polymer, PEDOT:PSS. Kayser et al. *Adv. Mater.* **2019**, 1806133.[26]

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