Perspective

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Molecularly Stretchable Electronics

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TOC Graphic

Biography

Darren J. Lipomi earned his BA in chemistry with a minor in physics from Boston University in 2005. Under Prof. James S. Panek, his research focused on total synthesis and heterogeneous catalysis for efficient asymmetric synthesis. He earned his PhD in chemistry at Harvard University in 2010, with Prof. George M. Whitesides, where he developed unconventional, green approaches to fabricate nanostructures for electronic and optical applications. From 2010 – 2012,
he was a postdoctoral fellow in the laboratory of Prof. Zhenan Bao at Stanford University, where
his research was directed toward increasing the mechanical compliance of organic photovoltaic
devices. He is now an assistant professor in the Department of NanoEngineering at the
University of California, San Diego. The interests of his research group include the mechanical
properties of organic semiconductors for robust and stretchable devices, and green chemistry and
nanoengineering.

Abstract

This Perspective describes electronic materials whose molecular structure permits
extreme deformation without the loss of electronic function. This approach—“molecularly
stretchable” electronics—is complementary to the highly successful approaches enabled by
stretchable composite materials. We begin by identifying three general types of stretchable
electronic materials: (1) random composites of rigid structures sitting atop or dispersed in an
elastic matrix, (2) deterministic composites of patterned serpentine, wavy, or fractal structures on
stretchable substrates, and (3) molecular materials—non-composite conductors and
semiconductors—that accommodate strain intrinsically by the rational design of their chemical
structures. We then identify a short-term and a long-term goal of intrinsically stretchable organic
electronics: the short-term goal is improving the mechanical stability of devices for which
commercialization seems inevitable; the long-term goal is enablement of electronic devices in
which every component is highly elastic, tough, ductile, or some combination thereof. Finally,
we describe our and others’ attempts to identify the molecular and microstructural determinants
of the mechanical properties of organic semiconductors, along with applications of especially
deformable materials in stretchable and mechanically robust devices. Our principal conclusion is
that while the field of plastic electronics has achieved impressive gains in the last several years in terms of electronic performance, all semiconducting polymers are not equally “plastic” in the sense of “deformable,” and thus materials tested on glass substrates may fail in the real world and may not be amenable to stretchable—or even modestly flexible—systems. The goal of this Perspective is to draw attention to the ways in which organic conductors and semiconductors specifically designed to accommodate large strains can enable highly deformable devices, which embody the original vision of organic electronics.

1. Electronics in the 21st century

1.1. Plastic electronics. Advances in two branches of materials science in the twentieth century left virtually no aspect of modern life untouched: plastics and semiconductors. It is little wonder that the advent of the hybrid technology, plastic electronics, in the form of conducting and semiconducting polymers—for which Heeger, MacDiarmid, and Shirakawa were awarded the Nobel Prize in Chemistry in 2000—excited researchers in fields as diverse as condensed matter physics and biomedical engineering. Early work focused on improving the conductivity of polyacetylene and unsubstituted polymers of aromatic compounds. This period was also characterized by an interest in the bulk properties familiar to polymer scientists, namely mechanical and thermal properties, and processability. The early 1990s, however, saw the discovery of the polymer solar cell and light-emitting device, and substantial development of the polymer field-effect transistor. Research in the area turned toward improving the performance of these devices, while bulk properties became less prominent. As work on devices began in earnest, researchers have attained electronic figures of merit that might have been difficult to predict a decade ago. Among other achievements, organic semiconductor devices
have been prepared with charge-carrier mobilities well over 10 cm$^2$ V$^{-1}$ s$^{-1}$, and efficiencies of organic solar cells have surpassed ten percent.$^{16}$

Investigating organic semiconductors and devices with the goal of improving the electronic figures of merit however, has left important aspects such as mechanical compliance behind. The names “plastic electronics” and “flexible electronics” are virtually synonymous with organic and polymer electronics,$^{17-19}$ but the descriptors mask the wide variety of mechanical properties possessed by organic conductors and semiconductors.$^{20}$ Evaporated films of pentacene$^{20}$ and drawn fibers of polyacetylene,$^1$ for example, have tensile moduli $>$10 GPa, while polyaniline films can have moduli around 10 MPa (though these films were likely plasticized by residual solvent).$^{20}$ The mechanical properties of semiconducting polymers with common structural characteristics, such as polythiophenes, vary with a strong dependence on factors such as the length of the alkyl side chain.$^{21,22}$ We previously found large differences in elasticity and ductility between polythiophenes whose structures differed by a single carbon atom on the alkyl side chain.$^{22}$ We measured a tensile modulus of 1.15 GPa for poly(3-hexylthiophene) (P3HT, Figure 1) and 90 MPa for poly(3-heptylthiophene) (P3HpT), and the stiffer material was also significantly more brittle.$^{21,22}$ The transparent conductive polymer PEDOT:PSS also exhibits a large dependence of mechanical compliance on the presence of common additives (e.g., surfactants and secondary dopants),$^{23,24}$ and the modulus and ductility of polymer:fullerene composites for organic solar cells are strongly dependent on the identity of the polymer$^{21,22,25,26}$ and the conditions used to cast the thin films.$^{27}$ In the design of new organic electronic materials, however, mechanical properties are generally not considered, but almost certainly occupy a range of values that is relevant to the stability of devices in the solid state.
Figure 1. Chemical structures of conjugated polymers discussed in the text.

There are at least two reasons to increase the priority of mechanical compliance in research on organic semiconductors. The first reason is to improve the mechanical stability of flexible organic devices that now seem destined for commercialization.\textsuperscript{28-31} Nominally flexible devices, especially those for portable outdoor use, will be subjected to bending, tensile, and shear stresses produced by roll-to-roll fabrication, manipulation, thermal expansion and contraction, and the forces produced by wind, rain, and snow.\textsuperscript{28} Even small forces will produce large strains if the devices are fabricated on ultra-thin substrates,\textsuperscript{19,32} which are required to obtain significant reductions in cost\textsuperscript{32} and embodied energy\textsuperscript{33} possible with organic devices. Encapsulating these devices in glass will surrender essentially all of the advantages that define the field. The second reason to understand and improve the intrinsic mechanical properties of organic semiconductors is for the burgeoning field of stretchable electronics.\textsuperscript{34-39} That is, electronic materials and devices designed for form factors inaccessible to conventional metals and semiconductors on stiff, planar substrates.\textsuperscript{36} These applications include consumer devices and textiles,\textsuperscript{40} systems for energy conversion and storage,\textsuperscript{28,38,41,42} and biomedicine, such as implantable sensors,\textsuperscript{43,44} artificial
retinas,\textsuperscript{45,46} artificial skin for prostheses,\textsuperscript{19,47-50} and sensors for soft robotics.\textsuperscript{51,52} Compared to inorganic semiconductors, an ability that remains mostly unique to organics is facile chemical functionalization,\textsuperscript{53,54} which can tune the bandgaps of individual semiconductors for multijunction solar cells,\textsuperscript{55,56} provide chemoselectivity for chemical and biological sensors,\textsuperscript{57} allow electrochromic behavior for all perceptible colors,\textsuperscript{58-61} and tailor the mechanical compliance for specific applications in portable displays,\textsuperscript{62} solar cells,\textsuperscript{21,22,25,26} and biomedical devices.\textsuperscript{19,45}

1.2. Limitations of conventional semiconductors and devices. Silicon integrated circuits (ICs) are man-made devices of unmatched sophistication.\textsuperscript{63} Technological advancements—e.g., purification of silicon, resolution of photolithography, and design of integrated circuits—combined with enormous economic driving forces have rendered these devices ubiquitous. The scale of investment, performance metrics, and extraordinarily low rate of error present in a silicon IC suggest that achieving the same level of computational sophistication could take decades to accomplish with nanocarbon, nanowires, nanocrystals, and organics.\textsuperscript{64} Silicon ICs are, however, relatively expensive, and the contribution of cost and embodied energy of a typical device is dominated by the complexity of the manufacturing phase of its life cycle (it consumes comparatively little energy during the “use phase”).\textsuperscript{65,66} They are also generally limited to rigid substrates and planar geometries. For applications in chemical and biological sensing, displays, and energy, it may be permissible to sacrifice computational speed and other performance metrics for the sake of another attribute, such as low cost or mechanical compliance.

2. Stretchable electronics
2.1. Stretchable (not just flexible) systems. Stretchable electronics are both an extension and significant departure from flexible electronics.\textsuperscript{36,67-71} Flexible systems are characterized by active materials that can withstand small bending radii by virtue of their thinness (though greater bending strains can be applied if the thin material is itself highly elastic).\textsuperscript{19,32,72,73} For thin substrates under bending deformation, the tensile strain imposed on the apex of the bend, $\varepsilon_{\text{peak}}$, is equal to the ratio of the thickness of the substrate, $d_s$, to the diameter of curvature, $2r$, or $\varepsilon_{\text{peak}} = d_s/2r$.\textsuperscript{72,74} For films whose thickness is small compared to that of the substrate and whose mechanical properties are similar to those of the substrate,\textsuperscript{72} it is clear that even very brittle materials (such as crystalline silicon, which fractures at 0.7\% strain\textsuperscript{74}) can be bent to operationally small values of $r$, but this ability is, nevertheless, critically dependent on the thinness of the substrate.\textsuperscript{32} In one of the most impressive demonstrations of the flexibility of organic semiconductors to date, Kaltenbrunner et al. fabricated an organic solar cell based on a composite of poly(3-hexylthiophene) and [6,6]-phenyl C\textsubscript{61} butyric acid methyl ester (P3HT:PCBM) on a 1.4-\textmu m polyester foil and achieved bending radii $\sim$35 \textmu m (Figure 2a and 2b).\textsuperscript{32} To render this device stretchable, the authors bonded it to a pre-strained elastomeric substrate. Release of the pre-strain generated wrinkles that accommodated further cycles of strain.\textsuperscript{32}
Figure 2. Organic solar cells fabricated on ultra-thin polyester substrates. (a) Schematic diagram. (b) Device partially wrapped around a human hair. (c) Power-to-mass ratio for several photovoltaic technologies. This plot highlights the potential cost savings of OPV devices, which are 5–10 times more efficient than the second-most efficient technology per unit mass. Reproduced with permission from ref. 32, copyright 2012 Nature Publishing Group.

The seminal studies that characterized the behavior of metallic and other thin films on compliant substrates for ultra-flexible and stretchable applications were those of Hutchinson and Whitesides;75,76 Lacour, Suo, and Wagner;34,77,82 and Lu and Vlassak.83,84 Rogers and coworkers, in addition to substantially furthering the fundamental thin-film mechanics and the design criteria of the geometries intended to accommodate strain in flexible and stretchable form factors,35-


also demonstrated several successful applications, including a hemispherical electronic eye camera, the first stretchable solar module, electrotactile devices, and conformable devices for in vivo use in brain and cardiac electrophysiology. Recently, tattoo-like and bioresorbable materials have added significantly to the toolkit of stretchable devices. Someya and coworkers have pioneered the use of stretchable layouts and conductive elastomers to confer stretchability to organic electronics, and have made substantial progress in the areas of electronic skin-like sensors, solar cells, and conformable light-emitting devices. These authors and others realized that devices exhibiting only flexibility were limited to bending deformations and cylindrical or conical form factors. In order to enable deformation in response to tensile and compressive stresses, elasticity and ductility—i.e., stretchability—is required.

2.2. Methods of making electronics stretchable. Methods of rendering otherwise brittle materials stretchable fall into three broad categories that can be differentiated, with some overlap, on the size scale at which they accommodate strain. The first approach, based on random compositing (Figure 3a – 3c), depends on percolated pathways for charges. This method is broad and includes intentionally fractured thin films and bulk composite materials that contain conductive nanoparticles. The second method, based instead on deterministic compositing (Figure 3d and 3e), converts global tensile strains to local bending strains using laterally or topographically patterned thin films. These two- or three-dimensionally patterned structures include fishnet or fractal geometries that accommodate strain by out-of-plane twisting. A related technique includes exploiting the micron-scale sinusoidal wrinkles that form on a thin film on an elastic substrate under compressive strain; these waves accommodate tensile strains by local unbending. The third method—the focus of this Perspective—does not in principle rely on composite structures. Rather, the conducting and
semiconducting materials accommodate strain by virtue of their molecular structures and morphology in the solid state (Figure 3f and 3g). The borderline between composite stretchable materials and molecularly stretchable materials is not always distinct. An exemplary case is the loudspeaker reported by the groups of Suo and Whitesides fabricated from a stretchable, transparent, ionic conductive membrane.\textsuperscript{106}

**Figure 3.** Images of representative examples of mechanisms for producing stretchable electronic materials: percolation through random networks (a–c), deterministic patterning of waves and fractals (d, e), and use of elastic molecular materials. (a) High-contrast photograph of a stretchable, transparent pressure sensor based on wavy films of carbon nanotubes embedded in a silicone elastomer (scale bar, 1 cm). (b) Photograph exhibiting extreme flexibility and transparency. (c) Atomic force micrograph, phase contrast, of bundles of buckled carbon nanotubes (scale bar, 600 nm). (d) Photograph of metallic wires in a fractal pattern adhered to skin (scale bar, 1 cm). A blow-up within the region indicated by the red box is shown in the optical micrograph (scale bar, 1 mm) and (e) in the scanning electron micrograph (scale bar, 500 \(\mu\)m). (f) Photographs of an ultra-flexible and stretchable organic light-emitting device fabricated using carbon nanotube-based top and bottom electrodes and an intrinsically stretchable emissive layer based on a stretchable polyfluorene conjugated polymer (PF-B), PEO-DMA, and LiTf (g). (a–c) Reproduce with permission from ref. \textsuperscript{107}, copyright 2011 Nature Publishing Group. (d, e) Reproduced with permission from ref. \textsuperscript{88}, copyright 2014 Nature Publishing Group. (f, g)
2.3. Random composites for stretchable electronics. One method of producing a material that is on the whole stretchable is to start with an intact material—e.g., a film on a stretchable substrate—and stretch it to fracture it deliberately. Many materials naturally form fractured surfaces that nonetheless maintain uninterrupted pathways for conducting charge. This approach has enabled stretchable interconnects as well as devices whose active components require only conductivity, such as capacitive tactile sensors. The mechanism of reversible deformation and evolution of conductivity under cyclic loading has been characterized by Lacour and coworkers for metals. A later study determined that intentional fracture is also an effective strategy for producing stretchable transparent electrodes from the transparent conductor PEDOT:PSS (see Figure 1 for structure) on polydimethylsiloxane (PDMS) substrates. The authors, however, noted that the relationship between strain and conductivity was critically dependent on the method by which the hydrophobic substrate was activated: brittle plasma-oxidized surfaces cracked upon straining and propagated these cracks through the PEDOT:PSS film. These cracks rendered the film non-conductive upon very small strains. Another type of stretchable random composite can be produced from micro- or nanostructures, such as two-dimensional plates or one-dimensional wires, which sit atop or are mixed into an elastomeric matrix. Such materials comprising graphene, conductive nanowires, or other conductive particles retain percolated pathways while absorbing strain, presumably by sliding motions of the components or by dynamic reconfiguration—loss and reformation—of electrical connections with strain within or on top of the stretchable matrix. In one study, stretchable transparent conductive films of carbon nanotubes were spray-coated on PDMS substrates, stretched, and
then relaxed. The first cycle of stretch-and-release generated buckles whose amplitudes were parallel to the substrate, and which accommodated subsequent cycles of stretching. Films of this type have among the most favorable combinations of elasticity, conductivity, and transparency of any material in the literature, and have been used for transparent, elastic pressure and strain sensors.

2.4. Deterministic composites for stretchable electronics. The most successful stretchable electronic devices produced so far have used a deterministic strategy that combines photolithography and soft lithographic printing of metals and semiconductors on elastic substrates, which may or may not bear relief structures to localize strain to specific areas of the device. One method is to exploit the topographic buckles that form when an elastic substrate bearing a relatively rigid film is compressed. This approach has been developed and utilized with extraordinary success by Rogers and coworkers. While the use of buckled silicon nanomembranes and patterns of metals as interconnects are well known, the method has also been used on semiconducting polymers for the first stretchable organic solar cell, stretchable organic thin-film transistors, and stretchable supercapacitors based on thick buckled films of carbon nanotubes. Another approach is to use serpentine or fractal patterns, which accommodate strain by out-of-plane bending and twisting. This approach has been used in optoelectronic devices, along with epidermal, tattoo-like biosensors, electrotactile fingertip sensors, and biologically resorbable devices. A common element to both random and deterministic compositing is that an elastic substrate provides the restoring force, and that typically the most sensitive components (e.g., the semiconductors) are located near mechanically neutral planes or on thicker regions of the substrate. Thus, most of the strain is absorbed in
the regions containing the conductors, whose function is not generally sensitive to bending strains.

2.5. Molecular materials for stretchable electronics. A complementary approach to random and deterministic compositing is to design and use materials that can accommodate strain by virtue of their molecular structure and morphology, as opposed to topology. These intrinsically—or “molecularly”—stretchable materials could simplify patterning (e.g., by printing on elastomeric sheets) and in principle would not require design of relief structures to direct strain away from sensitive semiconducting components. Molecularly stretchable materials based on π-conjugated polymers and small molecules would have additional advantages associated with their organic nature, including low-cost, facile manufacturing, and tunability by synthesis. The remainder of this Perspective focuses on work by our group and by other researchers (1) to understand the molecular structural parameters that determine the mechanical properties of organic semiconductors and (2) to apply this knowledge toward the realization of mechanically robust and intrinsically stretchable optoelectronic devices.

3. Mechanical properties of organic semiconductors

3.1. Plastic electronics. The promise of organic—especially polymeric—conductors and semiconductors is, somewhat obviously, to produce plastic electronic devices. The common perception is that all organic electronic materials are already highly flexible and elastic. The origin of this notion, we believe, arises from both the small bending radii allowable by the thinness of organic semiconductors, along with the now-synonymous relationship of the words “polymer” and “plastic.” While these words are interchangeable in everyday speech, the word
plastic implies deformable, and is an adjective that does not describe all π-conjugated polymers to the same extent.\textsuperscript{20,21,119} Conjugated polymers exhibit a range of mechanical behavior that depends on the presence of fused or isolated rings in the main chain,\textsuperscript{114,119} length and composition of any pendant groups,\textsuperscript{21,22} propensity to form crystallites,\textsuperscript{27,119} and microstructural order.\textsuperscript{26} The work of Heeger, Smith, and Wudl characterized the mechanical properties of early conjugated and other comb-like polymers,\textsuperscript{5} but the discovery and development of the polymer light-emitting device by Friend,\textsuperscript{10} and the discoveries of the bulk heterojunction solar cells by Heeger and Wudl,\textsuperscript{7,120} and independently by Friend,\textsuperscript{9} combined with the steady increase in performance of the organic thin-film transistor\textsuperscript{12,13} in the 1990s, refocused attention from mechanical properties to electronic ones. New polymers with bandgaps that can be dialed in by synthesis,\textsuperscript{15,118,121} computational tools that relate charge transport to molecular structure and packing in the solid state,\textsuperscript{122} and spectroscopic, micrographic, and synchrotron-based methods of linking morphology to charge-transport characteristics are the subject of an enormously successful literature\textsuperscript{123} that has propelled organic devices from laboratory curiosities to modules that can compete with or outmatch other thin-film technologies in several important metrics.\textsuperscript{124} In the field of “plastic electronics,” the focus on the second word may have come, however, at the expense of the first. There are, we believe, both near-term and long-term goals for increasing the elasticity, toughness, and ductility of organic semiconductors.\textsuperscript{21,22,29,30,125-130}

The first, near-term goal, is to enable organic electronic devices—e.g., roll-to-roll fabricated organic solar modules—to survive the rigors of manufacture, transportation, installation, and manipulation in portable applications and environmental forces in utility-scale applications.\textsuperscript{131} Indeed, the “Workshop on Key Scientific and Technological Issues for Development of Next-Generation Organic Solar Cells,” sponsored by the National Science
Foundation and Office of Naval Research in 2012, identified mechanical behavior as an important component of future research.\textsuperscript{31}

\textit{“Do organic cells fracture cohesively or at interfaces when temperature cycling causes some layers to thermally expand more than others? What has to be done to prevent solar cells from failing mechanically?”}  –NSF/ONR Workshop Report, September 2012\textsuperscript{31}

As a matter of fact, the most popular active material for organic solar cells is a blend of P3HT and a fullerene derivative (PCBM), which fractures at \(\leq 2.5\%\) tensile strain on PDMS substrates.\textsuperscript{119} Krebs et al. noted that for portable organic solar modules deployed in rural Africa:\textsuperscript{132}

\textit{“...mechanical failure mechanisms were dominant during the field test and therefore these would have to be improved significantly before the photochemical stability of the [semiconducting] polymer becomes a problem.”}  –Krebs et al.\textsuperscript{132}

For portable and outdoor applications, it is likely that mechanical degradation is a principal route by which organic solar cells fail. Mechanical routes of degradation include cracking and cohesive failure\textsuperscript{29,127,129} of the individual components, and interfacial failure\textsuperscript{30,128} (e.g., between the organic semiconductor and the electrodes). Molecular control over the elasticity, ductility, toughness, and surface energy would seem to be a priority for research in organic solar cells, but has received relatively little attention in the body of literature concerned with the stability of devices\textsuperscript{133,134} (a notable exception is the work of the Dauskardt laboratory\textsuperscript{29,30,127-129}). Proposed solutions that involve manufacturing and encapsulating devices using thick polymeric or glass layers abandon many of the advantages of organics, not the least of which is the low production energy of conjugated polymers and semiconducting small molecules, and the minute quantities required.\textsuperscript{33,116,135} Indeed, the analysis by Anctil et al. has shown that the 130-\(\mu\)m poly(ethylene
terephthalate) (PET) substrates and encapsulants most commonly employed for flexible organic solar cells make up around twenty percent of the embodied energy of conventional modules and by extrapolation around forty percent in modules that do not contain ITO. Exploitation of the extraordinarily favorable ratio of power to mass possible with organics cannot proceed using thick substrates and encapsulants, but thin substrates will endure large strains even with relatively small forces. The use of thin substrates and encapsulants is thus contingent on favorable mechanical properties of organic semiconductors. A complete picture of the factors that describe the interplay between mechanical and charge-transport properties of organic semiconductors, however, has yet to emerge.

The second, longer-term goal that drives our interest in intrinsically stretchable electronics is to access form factors that are unavailable to conventional semiconductors. Despite the intuitive notion that applications requiring elasticity, toughness, and ductility appear to be a problem for which organic materials are an ideal fit, devices based on inorganic materials using deterministic composites described in Section 2.4 have overtaken organics in terms of electronic and mechanical performance metrics. There are, however, several compelling reasons to explore molecularly stretchable materials for applications that are complementary to inorganic-elastomeric hybrid systems. Such molecularly stretchable devices could, if necessary, sacrifice state-of-the-art performance for one or more of the following characteristics for which organics may have advantages: tunability of absorption, emission, and chemical sensitivity by synthesis; simplification of fabrication by roll-to-roll printing on planar elastomeric sheets; the potential for melt processing and embossing; relaxed standards of purity; low embodied energy; low cost; extreme thinness and light weight; disposability; self-healing and other forms of response to stimuli; thermally activated charge transport;
semitransparency\textsuperscript{142} and aesthetic considerations;\textsuperscript{136} and the fundamental knowledge that could be created en route to the development of elastomeric materials that are also high-performance semiconductors.

3.2. Stretchable conjugated polymers. The effect of stretch aligning on conjugated polymers such as polyacetylene is to increase both conductivity and tensile strength.\textsuperscript{1-3} For polymers with alkyl solubilizing groups such as P3HT, stretch aligning has also been shown to increase field-effect charge-carrier mobility along the strained axis.\textsuperscript{143,144} The mechanism for increased strength and charge transport is by alignment of chains, a phenomenon that is confirmed by X-ray diffraction and by polarization-dependent absorption.\textsuperscript{130,144} Other microstructural changes can occur with strain, as O’Connor and coworkers recently reported a reorientation of crystallites in P3HT films from predominantly edge-on to highly face-on after uniaxial\textsuperscript{144} and biaxial\textsuperscript{145} stretching. The mechanism for this reorientation has not yet been elucidated, but the effect has important implications for solar cells, in which it may be beneficial to have the axis of \( \pi \) stacking perpendicular to the electrodes\textsuperscript{145} (though it may be better still to have the \textit{molecular} axes of the polymers perpendicular to the electrodes\textsuperscript{14}).

One of the most successful synthetic attempts to date to produce a tough, stretchable semiconducting polymer was that of Müller et al., who synthesized a P3HT-block-polyethylene copolymer capable of undergoing elongations of 600\% (\textit{Figure 4a}).\textsuperscript{126} Remarkably, this material retained a high value of field-effect mobility even with weight fractions of the insulating component as high as 90\%.\textsuperscript{126} While the ductility of this material was impressive (\textit{Figure 4b}), elastic semiconductors that do not have such a high weight percentage of an insulating component will be desirable. To this end, we believe an effective strategy would be to
understand the structural determinants of the mechanical properties of well-known conjugated polymers, while applying the insights generated toward the synthesis of new materials that exhibit the “best of both worlds”—favorable mechanical and electronic properties.

![Stress-strain curves](image)

**Figure 4.** Tough, stretchable diblock copolymers of polythiophene and polyethylene. (a) Stress vs. elongation for the block copolymers and for the homopolymers. (b) Images exhibiting the mechanical behavior of the block copolymers, and wide-angle X-ray diffraction pattern of a highly stretch-aligned sample. Reproduced with permission from ref. 126, copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

### 3.3. Mechanical properties of regioregular polythiophene: A case study

We began our investigations by considering the effect of the side chain on the mechanical properties of the poly(3-alkylthiophene)s (P3ATs). The P3ATs are probably the most well characterized class of organic electronic materials, and the effects of the length of the side chain is their most widely explore aspect. While the P3ATs have been the subject of numerous studies, the low production energy, ease of derivatization, reports of new benchmarks in efficiency,
and research investment suggests that they will continue to be an important part of research, and also of future commercial products.\textsuperscript{156} We began by measuring the elasticity and ductility of a series of P3ATs where $A =$ butyl, hexyl, octyl, and dodecyl.\textsuperscript{21} We chose this sequence because the length of the side chains that separate butyl, octyl, and dodecyl is a constant four atoms apart, and hexyl because P3HT is the standard material in the literature. We measured the elasticity using the buckling-based metrology,\textsuperscript{102} which relates the wavelength of the sinusoidal wrinkles that form when a film is compressed on an elastic substrate to the tensile modulus of the film.\textsuperscript{103} This method avoids the difficulties in preparing sub-100-nm, free-standing thin films for tensile testing and effects of the substrate in nanoindentation of ultra thin films.\textsuperscript{102} Our results, plotted in Figure 5a, show a dramatic decrease in tensile modulus with increasing length of the alkyl side chains, with the difference between polymers with hexyl and octyl chains being nearly an order of magnitude. This trend was predicted by a semi-empirical theory reported by Seitz,\textsuperscript{157} used for the first time on conjugated polymers by Tahk et al.,\textsuperscript{20} and applied to polythiophenes with different alkyl side chains by us.\textsuperscript{21} The explanation for the overall trend is familiar in the field of comb-like polymers, where longer alkyl side chains dilute the volume fraction of load-bearing, main-chain bonds and a concomitant reduction in secondary interactions between the main chains,\textsuperscript{5} which are responsible for the high strength of oriented polyacetylenes.

We note that an examination of the early literature reveals a reversal in attitudes regarding the desirability of high mechanical compliance. For polyacetylenes, a tensile modulus $>10$ GPa was regarded as favorable,\textsuperscript{1} while the inclusion of alkyl pendant groups on comb-like polymers was described as paying the “ultimate penalty” for processability (i.e., a substantial lowering of the tensile modulus).\textsuperscript{5} If one places value on elasticity and ductility however, as is implied in plastic electronics, the ability to deform without fracture should be maximized. The
The design of molecularly stretchable electronic materials is tantamount to having charge mobilities and other electronic figures of merit that are as large as possible with tensile moduli that are as low as possible.

![Figure 5](image)

**Figure 5.** Tensile modulus (a) and crack-onset strain (b) as a function of the length of the alkyl side chain for \( n = 4, 6, 8, \) and 12. Reproduced with permission from ref. 21, copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

We also discovered a trend in ductility for P3ATs that followed a similar trend to that of the elasticity. 21 In a measurement of crack-onset strain for the same sequence of materials (Figure 5b), we observed a curious reduction in strain (increase in effective brittleness) between polythiophenes with octyl and dodecyl side chains, which is unexpected based on the similarity of the tensile moduli. We attributed this effect, however, to reduced adhesion to the substrate. 21 Indeed, surface energy, as manifested in water contact angle, decreased with increasing length of the side chain. 21 Locally delaminated areas experienced large strains, and thus effective brittleness increased with reduced adhesion. The presence of PEDOT:PSS, however, seemed to serve as an adhesion layer for conjugated polymers to stick to PDMS, and increased the crack-onset strain. 25,114 Lu et al. observed the same effect in copper films on polyimide foils with and without chromium adhesion layers. 73,83 Adhesion is thus an important design consideration for devices intended for flexible and stretchable applications. 30
3.4. Stretchable solar cells. To examine the differences in photovoltaic properties between two P3AT:fullerene composites with disparate mechanical properties, we fabricated devices on PDMS substrates and measured the current density vs. voltage ($J-V$) characteristics before stretching and at ten percent uniaxial tensile strain.\textsuperscript{21} Extensive cracking visible in the P3HT:PCBM film (Figure 6a) correlated with short circuits (Figure 6c), whereas the P3DDT:PCBM film, which exhibited completely ductile behavior (Figure 6b), produced normal photovoltaic plots (Figure 6d).\textsuperscript{21} The resistor-like behavior was probably produced by the liquid eutectic gallium-indium (EGaIn, Figure 6e) seeping through the cracks and making contact directly with the PEDOT:PSS in the P3HT:PCBM devices. The electrodes, along with the active materials, were strained during these experiments. While uniaxial deformation is important to measure mechanical properties and to characterize the evolution in photovoltaic properties with strain, resiliency in response to biaxial deformation is more consistent with realistic applications and potential routes of mechanical failure.\textsuperscript{25}
Figure 6. Photographs and photovoltaic properties of uniaxially stretched devices based on P3HT:PCBM (a) and P3DDT:PCBM (b). The more brittle active layer based on P3HT exhibits behavior resembling a short circuit (c) while that based on the elastic and ductile P3DDT exhibits a photovoltaic effect in both the equilibrium and strained states (d). The insets are optical micrographs of the device surfaces; the scale bars are 0.5 cm. (e) Schematic diagram of the geometry used to collect the photovoltaic data, in which eutectic gallium-indium (EGaIn) served as the low-work-function electrode. (a-d) Reproduced with permission from ref. 21, copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

3.5. Conformal bonding to hemispheres. Conformal bonding of organic electronic devices has long been a goal of the community concerned with plastic electronics. Bonding to
3D surfaces other than conical and cylindrical ones, however, requires biaxial stretchability, not just flexibility. A hemisphere is one of the simplest curvilinear surfaces that requires biaxial stretchability for a device to make conformal, wrinkle-free contact. Our goal was to bond an all-elastomeric solar cell to the convex surface of a glass hemisphere (Figure 7a). We began by calculating the strain that would be generated by bonding such a cell to a hemisphere with a 16-mm diameter, and determined from a finite-element analysis that the greatest equivalent strain of 24% would occur 4 mm from the apex (Figure 7b). Based on our previous measurements of elasticity and ductility, we reasoned that P3OT:PCBM films would survive the transfer, but that P3HT:PCBM would not. Visual inspection revealed significant cracking in the more brittle composite, while as predicted, the more elastic composite remained intact. The photovoltaic responses (Figure 7c) showed similar behavior when the light was shone from the convex (device-incident) or concave (glass-incident) surface, which exhibited similar qualitative features as the device fabricated on planar glass. The P3HT:PCBM device produced plots resembling short circuits. The low short-circuit current density and fill factor of devices based on P3OT (or all alkyl chains ≥ octyl) is well known and struck us as unfortunate that the best performing polymer mechanically would be among the worst electronically. This apparent competition between mechanical and electronic properties led us to investigate the interplay of mechanical and electronic behavior more closely.
Figure 7. Hemispherical solar cells. (a) Schematic diagram of an all-organic “inverted” solar cell on a hemispherical glass substrate. (b) Computational model of the strain produced on the concave and convex surface of the solar cell. (c) Photovoltaic properties of the device when the light was incident on the concave surface (glass-incident), convex surface (device-incident), and on planar glass. Reproduced with permission from ref. 25, copyright 2014 Royal Society of Chemistry.

3.6. Trade-off between electronic and mechanical properties. The all-sp$^2$ hybridization of the carbon atoms in the main chain of a conjugated polymer is responsible for semiconducting behavior, but also produces high stiffness.$^{157}$ Furthermore, crystallinity in materials is generally regarded as beneficial for charge transport, but also reduces the compliance of materials within groups having similar molecular structures.$^{119}$ The trend has been observed in
polythiophenes, where the copolymer PBTTT (Figure 1) forms a highly crystalline structure after thermal annealing, which also increases the modulus and the charge-carrier mobility.\textsuperscript{119} The O’Connor group has shown that slow evaporation of the solvent when casting P3HT:PCBM active layers produce devices that are not only more efficient, but also stiffer and more brittle than their counterparts produced by fast evaporation.\textsuperscript{27} These differences were directly correlated to order in the conjugated polymer film from UV-vis absorption spectra\textsuperscript{27} using the weakly interacting H aggregate model proposed by Spano and coworkers.\textsuperscript{158} Our measurements, combined with the fact that the trend in field-effect mobility of P3ATs,\textsuperscript{159} along with photovoltaic efficiency in polymer:polymer\textsuperscript{153} and polymer:fullerene\textsuperscript{160} bulk heterojunction solar cells follows the opposite trend as compliance, further supported the notion that mechanical compliance and electronic performance tend to be in competition.\textsuperscript{21}

3.7. Best of both worlds? We initially believed that, like transparency and conductivity, compliance and charge mobility (or photovoltaic efficiency) might be properties that were fundamentally incompatible, and that only by compositing would we be able to maximize both properties in a single material. We examined more closely the sharp drop-off in modulus that we observed between P3ATs with hexyl and octyl side chains by preparing films of several “hybrid” materials whose side chains average to seven carbon atoms: a physical blend (P3HT:P3OT), a block copolymer (P3HT-\textit{b}-P3OT), a statistical copolymer (P3HT-\textit{co}-P3OT), and poly(3-heptylthiophene) (P3HpT, whose side chain contains exactly seven carbon atoms, Figure 8).\textsuperscript{22} The results of our mechanical measurements are shown in Figure 9, which exhibits three salient features. The first feature is that P3HpT (C\textsubscript{7}) has a modulus of a similar order of magnitude as that of P3OT (C\textsubscript{8}), P3DT (C\textsubscript{10}), and P3DDT (C\textsubscript{12}). The second feature is the modulus of poly(3-pentylthiophene) (P3PT, C\textsubscript{5}), which lies on the line connecting P3BT (C\textsubscript{4}) and P3HT (C\textsubscript{6}). This
placement suggests that the low modulus of P3HpT is probably not a consequence of an odd number of carbon atoms in the side chain. The third feature is the relative placement of the other “hybrid” materials. The block copolymer falls on the line connecting P3HT and P3OT—the “synergistic” modulus—while the statistical copolymer and the physical blend lie below this line. We hypothesized that the P3HT and P3OT domains are not cocrystallized in either the block copolymer or the physical blend. We based this hypothesis on the spectroscopic similarity of the block copolymer and the physical blend and the overlap in the spectra of both of these systems to that of a mathematical superposition of the spectra of the pure homopolymers. The lack of cocrystallization suggests that in the block copolymer, compliant domains of P3OT are tethered by rigid domains of P3HT due to covalent connectivity, while no such connectivity exists in the physical blend, whose mechanical properties appear to be dominated by the more compliant P3OT. The statistical copolymer, which could only exhibit one possible form of crystalline packing, had a modulus similar to that of the physical blend.

**Figure 8.** Chemical structures of the P3ATs with \( n = 6–8 \) and “hybrid” polymers including a physical blend of P3HT and P3OT (P3HT:P3OT), a block copolymer (P3HT-b-P3OT), and a statistical copolymer (P3HT-co-P3OT). Reproduced with permission from ref. \(^{22}\), copyright 2014 American Chemical Society.
Figure 9. Elaborated plot of tensile modulus vs. alkyl side chain length that includes the hybrid materials whose number of carbon atoms in the side chain averages to \( n = 7 \). Reproduced with permission from ref. \(^22\), copyright 2014 American Chemical Society.

We also performed a detailed microstructural analysis of the films formed by these polymers of UV-vis spectra in the solid state.\(^22\) According to the weakly interacting H aggregate model, the extent of order is correlated to the relative intensities of absorption of the \(0 \rightarrow 0\) to \(0 \rightarrow 1\) vibronic transitions.\(^158\) Awartani et al. found a direct correlation between the extent of crystallites in the solid state to the mechanical compliance in P3HT:PCBM films.\(^27\) In comparing the physical blend and the block copolymer, we found nearly identical spectroscopically determined order, but a substantially different mechanical response.\(^22\) We also found substantially similar mechanical behavior between the physical blend and the statistical copolymer, yet different structural order.\(^22\) We did not observe a correlation between thin-film order and mechanical compliance in our samples, probably because of the insensitivity of the UV-vis spectra to spatial distribution and covalent connectivity of the compliant and rigid blocks within the film. The correlation between the crystalline order and the photovoltaic parameters, however, was roughly present in the physical blend, block copolymer, and statistical copolymer.

Figure 10 plots the power conversion efficiency of the P3AT:PCBM blend as a function of
tensile modulus of the polymer. A pure correlation between efficiency and stiffness would place all data points on a line connecting P3OT in the bottom left quadrant to P3HT in the top right one.\textsuperscript{22}

The observation that some of the hybrid materials lie above and to the left of this line—that is, in the “favorable” quadrant—strongly suggests that mechanical and electronic properties need not always be in competition. This notion is exemplified by the presence of P3HpT in the extreme top-left corner, which is simultaneously the most efficient and most elastic material studied. We attribute the uniqueness of P3HpT to its tendency to produce crystallites that are similarly well ordered as those of P3HT, while its glass transition temperature is the first in the series of P3ATs with increasing side-chain length to be extrapolated to be significantly below room temperature (most measurements of $T_g$ of P3HT place it near or just below 25 °C).\textsuperscript{161} The electronic absorption spectra and the photovoltaic properties appear thus to be manifestations of the crystalline regions in the film, while the mechanical properties seem to be dominated by the amorphous regions. These observations may underpin design criteria for truly “rubber” semiconductors.\textsuperscript{22}
Figure 10. Plot of power conversion efficiency (PCE) of a P3HT:PCBM vs. tensile modulus of the pure polymer. The position of P3HpT in the upper-left quadrant suggests that photovoltaic performance and mechanical compliance need not be in competition. Reproduced with permission from ref. 22, copyright 2014 American Chemical Society.

3.8. Segmented copolymers. While P3ATs will almost certainly have a role in the future of organic electronics, they are not the highest-performing materials in the literature in terms of charge-carrier mobility in OTFTs and efficiency in solar cells. Donor-acceptor copolymers comprising alternating units of electron-rich (e.g., thiophene, benzodithiophene) and electron poor (e.g., benzothiadiazole, diketopyrrolopyrrole) heterocycles produce low bandgaps and high mobilities for both holes and electrons. We were inspired by the fact that low-bandgap conjugated polymers can exhibit high mobilities and photovoltaic efficiencies even with high disorder. We hypothesized that structural randomness, intentionally introduced by a new type of synthetic strategy based on random segmentation, could produce a material that might have increased elasticity without deleterious effects on the photovoltaic properties.

We began our investigation by considering the structure PDPP2FT (see Figure 1), which was first reported by the Fréchet group. This material exhibited good electronic performance (PCE ~ 5.0%) and a high solubility that is thought to be an effect of the furan units in the main chain. We started by preparing oligomers of PDPP2FT by the Stille polymerization. After a short reaction time (ca. 15 min) in which we observed the first formation of coupled species by color change, we introduced bithiophene (2T) units, which were included randomly in the polymer backbone (Figure 11a). Analysis by $^1$H NMR and UV-vis spectroscopy and gel permeation chromatography was consistent with the presence of one 2T unit for approximately every 4.4 DPP units. Spectroscopic and chromatographic evidence suggested that there was little contamination by the homopolymers, PDPP2FT and the poly(terthiophene), PT2T. The
segmented sample, PDPP2FT-seg-2T, exhibited substantial broadening of features in the UV-vis spectra, which is consistent with reduced structural order in the solid state (X-ray diffraction studies, which are forthcoming, will be needed to verify this hypothesis). We then made a similar plot of PCE vs. tensile modulus of the pure polymer (Figure 11b). Our hypothesis that it would be possible to increase the elasticity by intentionally randomizing the structure is consistent with the plot, in which the segmented material was both more elastic and similarly efficient to the unsegmented homopolymer, PDPP2FT. This synthetic strategy might also be useful for the preparation of functional copolymers analogous to block copolymers by polycondensation of two types of macromonomers. Typical block copolymers are synthesized by living, chain-growth mechanisms, and thus materials that follow step-growth kinetics, as do low-bandgap conjugated polymers, are generally not amenable to block copolymerization. We note that efficiencies of our devices based on PDPP2FT (≤3%) were lower than those originally reported for this material (~5.0%). We attribute the lower efficiencies of our devices, in part, to our use of stretchable materials for the electrodes (PEDOT:PSS for the anode and EGaIn for the cathode), because of our ultimate interest in systems in which every component is compliant.
Figure 11. Mechanical and photovoltaic properties of segmented polymers. (a) A strategy based on Stille polycondensation reactions produces a randomly segmented, low-bandgap polymer, PDPP2FT-seg-2T. (b) A plot of power conversion efficiency (PCE) vs. tensile modulus places this material in the “favorable” quadrant of the plot. Reproduced with permission from ref. 26, copyright 2014 Royal Society of Chemistry.

3.9. Intrinsically stretchable light-emitting devices. Our studies and those of others have revealed several structural characteristics that influence the mechanical properties of conjugated polymers, including the length of the alkyl side chain, the presence of fused vs. isolated rings in the main chain, structural randomness, and the ability of the side chains to...
interdigitate in the crystallites.\textsuperscript{119} Another route may be to replace methylene units with oxygen atoms in the side chain that permit a high range of motion.\textsuperscript{108} This route can be predicted by a preliminary application of the semi-empirical theory of Seitz to increase the modulus significantly, probably owing to increased configurational entropy of the side chains under strain.\textsuperscript{157} The laboratory of Pei and coworkers used a polyfluorene copolymer that incorporated side chains with ethylene oxide units as light emitting devices that maintained their performance up to strains as high as 45 percent \textbf{(Figure 3f and 3g)}.\textsuperscript{108} The authors also introduced one of the first stretchable transparent electrodes based on carbon nanotubes embedded in an elastic substrate as both the top and bottom electrodes of this device.\textsuperscript{108} Later, the same group produced a stretchable light-emitting device with an active emissive layer comprising a poly(phenylenevinylene) derivative, SuperYellow, and electrodes made of stretchable films of silver nanowires.\textsuperscript{110} This approach suggests it is possible to combine stretchable random composites (i.e., silver nanowire films on elastic substrates) with intrinsically stretchable conjugated polymers \textbf{(Figure 12)}. The mechanism of reversible deformation in this system, that is, whether the emissive layer absorbs the strain elastically or plastically, is an open question, as the substrate supplies the restoring force. Furthermore, it is likely that the addition of non-electroactive polymers and ionic species to the conjugated polymers increased the compliance of the emissive layer, and thus the electroactive polymer may not have absorbed the strain on its own.
**Figure 12.** Intrinsically stretchable light-emitting devices. A stretchable device uses SuperYellow, a polyphenylenevinylene derivative, as the emissive material. In this device, stretchable films of silver nanowires are used as both the top and bottom electrodes. Reproduced with permission from ref. 110, copyright 2013 Nature Publishing Group.

**4. Outlook**

This Perspective began by describing the value of stretchable electronics, and how the field of plastic—that is, organic—electronics may have fallen behind the significant progress made by stretchable composite systems. The two approaches are, however, complementary, and there are many compelling reasons for pursuing intrinsically stretchable electronic materials and devices whose molecular structures permit truly elastic and plastic behavior. The field of molecularly stretchable electronics is in its infancy, but significant progress on understanding how molecular structure influences the electronic properties has already been made. Such fundamental insights are necessary to develop a predictive framework so that, ideally, a device engineer can specify the mechanical and electronic properties needed for a particular application, and a chemist can synthesize a material that will exhibit these properties. Synthetic techniques will always constrain available structures, but the several methods identified to produce elastic-yet-high-performance materials suggest that there may be many functionally equivalent materials with different molecular structures. Several general strategies for imparting intrinsic stretchability to semiconducting materials are emerging from work in this area. For example, polymers exhibiting low-$T_g$ amorphous domains but well-ordered crystalline domains (e.g., P3HpT), along with high-mobility polymers with structural randomness to reduce crystalline order (e.g., PDPP2FT-seg-2T), could represent general strategies for producing materials with favorable combinations of mechanical and electronic properties. From the standpoint of integration, molecularly stretchable materials may offer advantages over deterministic
composites because most of the engineering takes place at the molecular level, as opposed to at the level of the device (i.e., it is relatively easy to swap out a rigid semiconducting polymer for an elastic one in the context of an existing manufacturing process).

The principal challenge in the field is to obtain a better predictive understanding of the ways in which molecular structure simultaneously influences electronic and mechanical properties. The ability to obtain good electronic properties from highly amorphous films seems to represent a way forward. Another strategy, which involves preparing stretchable nanowire “fabrics” from solution processing\textsuperscript{168} or electrospinning,\textsuperscript{169} represents a middle ground between composite and molecular approaches to elastic semiconductors. A concerted effort involving a five-way (at least) collaboration between device engineers, materials scientists, synthetic chemists, and theorists specializing in both electronic structure calculations and the mechanical behavior of soft materials will be required to meet the challenges represented by high-performance molecular semiconductors with predictable mechanical properties. There is a significant intellectual draw to multifunctional materials in which the properties are regarded as antithetical. Stretchable semiconductors join transparent conductors as examples of this class of materials. Another class of multifunctional materials that will be required to commercialize stretchable organic (and some inorganic) devices is stretchable encapsulants against water and oxygen. Significant work will be required to address this challenge, because elastomers generally permit significant diffusion of gases. We hope this Perspective will be successful in identifying the importance, preliminary results, and potential way forward in this technologically and intellectually exciting field.

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