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# Stretchable Polymer Semiconductors

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Flexible organic electronics (e.g. solar cells, light-emitting diodes and field-effect transistors) have attracted considerable attention over the past decade. Despite recent progress in developing new organic semiconductors, stretchable semiconducting or conducting elastomers have yet been explored in detail. Realization of these materials will result in increased robustness and potentially new applications in wearable electronics, since these materials can be fully solution processed and provide improved form factor (e.g. arbitrary 3D shapes) for organic devices. Therefore, the goal
for this project is to develop materials chemistry and formulate an understanding to enable intrinsically stretchable electronic devices. In this work, we systematically investigated a number of molecular design approaches for realizing both good charge transport as well as good mechanical properties. Specifically, we investigated the effects of H-bonding strength, effect of additives, effects of polymer semiconductor degree of crystallinity, effects of crosslinker design. Our work advanced our understanding of stretchable polymer semiconductor design and provided guiding principles for future polymer semiconductor development for stretchable and flexible electronics,

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## Abstract:

Flexible organic electronics (e.g. solar cells, light-emitting diodes and field-effect transistors) have attracted considerable attention over the past decade. Despite recent progress in developing new organic semiconductors, stretchable semiconducting or conducting elastomers have yet been explored in detail. Realization of these materials will result in increased robustness and potentially new applications in wearable electronics, since these materials can be fully solution processed and provide improved form factor (e.g. arbitrary 3D shapes) for organic devices. Therefore, the goal for this project is to develop materials chemistry and formulate an understanding to enable intrinsically stretchable electronic devices. In this work, we systematically investigated a number of molecular design approaches for realizing both good charge transport as well as good mechanical properties. Specifically, we investigated the effects of H-bonding strength, effect of additives, effects of polymer semiconductor degree of crystallinity, effects of crosslinker design. Our work advanced our understanding of stretchable polymer semiconductor design and provided guiding principles for future polymer semiconductor development for stretchable and flexible electronics.

## Key findings:

### 1. Effects of various non-conjugated spacers on mechanical properties of polymer semiconductors:

Nonconjugated segments in polymer semiconductors have been utilized to improve the processability of semiconducting polymers. Recently, several reports have described the improvement of stretchability of polymer semiconductors by incorporating nonconjugated spacers. However, the effect of relative flexibility of such conjugation breakers on mechanical and electrical properties has not yet been studied systematically. Here, conjugation breakers with different chain length and rigidity are incorporated into the backbone of diketopyrrolopyrrole-based semiconductors. Interestingly, it is observed that the longer and more flexible conjugation breakers result in greater ductility and lower elastic modulus without significantly affecting mobility. The enhancement of stretchability is attributed to the reduced modulus and the decrease in crystallinity, as confirmed by X-ray diffraction. With this newly established molecular design, transistors are prepared with a semiconducting polymer containing dodecyl segments as conjugation breakers. It is observed that this polymer retains a mobility of >0.36 $cm^2\ V^{-1}s^{-1}$ at 100% strain, and after 100 cycles at 50% strain. Finally, its high stability against strain is also observed with a fully stretchable transistor fabricated. Taken together, the above results indicate that molecular engineering of conjugated polymers, i.e., by incorporating suitable conjugation breakers, can effectively tune mechanical properties without significantly compromising their electrical properties.

### 2. Branched crosslinker with dynamic bonding to enhance stretchability of conjugated polymers:

The cross-linking of conjugated polymers has been demonstrated to be an effective strategy to improve its elastic properties to give deformable semiconductors for plastic electronics. While there have been extensive studies of the structural requirements of the polymer host for good film ductility, no work to date has focused on the relevance of the structural design or chemistry of these cross-linker additives. In this study, urethane groups and tertiary carbon atoms are inserted into the alkyl backbone of perfluorophenyl azide- based cross-linkers to investigate the importance of cross- linker crystallinity with respect to polymer morphology and hence mechanical and electrical properties. Linear cross- linkers with hydrogen bonding from urethane groups readily phase separate and recrystallize in the polymer network to form cross-linked domains that obstruct the strain distribution of the polymer film. Branch cross-linkers with tertiary carbon on the other hand form an evenly cross-linked network in the polymer blend stemming from excellent miscibility and show a 4-fold increase in fracture strain. Furthermore, a stable hole mobility of 0.2 $cm^2 V^{-1} s^{-1}$ is achieved up to $\varepsilon = 100\%$, and a stable hole mobility of 0.1 $cm^2 V^{-1} s^{-1}$ after 2000 cycles of $\varepsilon = 25\%$ on fully stretchable organic field-effect transistors.

### 3. Investigation effects of metal-ligand coordination on mechanical and charge transport properties of polymer semiconductors:

A high performance diketopyrrolopyrrole (DPP)–based semiconducting polymer is modified with ligands to enable metal coordination, and its subsequent effect as field-effect transistors is investigated. In specific, pyridine-2,6-dicarboxamide (PDCA) units are incorporated in a DPP–based polymer backbone with a content from 0 to 30 mol%, and the resulting polymers are then mixed with Fe(II) ions. The coordination and spontaneous oxidation converts Fe(II) to Fe(III) ions to result in Fe(III)-containing metallopolymers. The resulting metallopolymers are observed to show good solubility in organic solvents and can be easily processed as thin films. The charge transport characteristics are subsequently investigated through the fabrication of field–effect transistor devices, in which an enhanced charge carrier mobility with the Fe(III)-containing metallopolymers is observed. In specific, an almost twofold improvement in the charge carrier mobility is obtained for the 20% PDCA-containing polymer after Fe coordination (from 0.96 to 1.84 $cm^2 V^{-1} s^{-1}$). Furthermore, the operation stability of the metallopolymer-based devices is found to be significantly improved with low bias stress. Its superior electrical characteristics are attributed to the doping effect of the Fe ions. This study indicates that incorporation of appropriate metallic ions to polymer presents a viable approach to enhance the performance of polymer–based transistor devices.

### 4. Characterization of hydrogen bonding formation and breaking in semiconducting polymers under mechanical strain:

Diketopyrrolopyrrole (DPP)-based donor−acceptor conjugated polymers, with increasing amount of weak H-bonding units, namely 2,6-pyridinedicarboxamide (PDCA), inserted as end groups in alkyl side chains were prepared and investigated. In contrast to previously reported DPP polymers containing PDCA units as conjugation breakers along the polymer backbone, PDCA in the alkyl side chains readily produced almost quantitative formation of intermolecular H-bonding even at low PDCA unit content (<10 mol %) as shown by Fourier transform infrared spectroscopy (FTIR). The efficient intermolecular H-bonding was further supported by the appearance of a pronounced vibronic shoulder in the UV− vis spectra and a reduction of interlamellar spacing (from 24.02 to 22.87 Å) compared to the neat DPP polymer. Increasing mol % of PDCA units in side chains of DPP conjugated polymers also has a clear effect on the thermal and mechanical properties of the films as investigated by dynamic mechanical analysis (DMA). Polymers with a high loading of PDCA showed a linear increase in both tan delta intensity and temperature at which softening of film cross-linking occurs. In particular, at a comparable mol%, polymers with PDCA units along the conjugated backbone showed a lower transition intensity and on average a 10−20 °C higher temperature required for H-bonding breaking. FTIR coupled with crack onset measurements showed that H-bonding breaking during tensile deformation happens only at strains close to crack onset. All these observations suggest that molecular engineering of conjugated polymers bearing H-bonding units has a strong influence on microstructure, thermal and mechanical properties of solution processed films, and final energy dissipation mechanisms in stretchable electronics applications.

### 5. Investigation of conjugated carbon cyclic nanorings as additives for intrinsically stretchable semiconducting polymers:

Molecular additives are often used to enhance dynamic motion of polymeric chains, which subsequently alter the functional and physical properties of polymers. However, controlling the chain dynamics of semiconducting polymer thin films and understanding the fundamental mechanisms of such changes is a new area of research. Cycloparaphenylenes (CPPs) are used as conjugated molecular additives to tune the dynamic behaviors of diketopyrrolopyrrole-based (DPP-based) semiconducting polymers. It is observed that the addition of CPPs results in significant improvement in the stretchability of the DPP-based polymers without adversely affecting their mobility, which arises from the enhanced polymer dynamic motion and reduced long-range crystalline order. The polymer films retain their fiber-like morphology and short-range ordered aggregates, which leads to high mobility. Fully stretchable transistors are subsequently fabricated using CPP/semiconductor composites as active layers. These composites are observed to maintain high mobilities when strained and after repeated applied strains. Interestingly, CPPs are also observed to improve the contact resistance and charge transport of the fully stretchable transistors. ln summary, these results collectively indicate that controlling the dynamic motion of polymer semiconductors is proved to be an effective way to improve their stretchability.

### 6. Effect of crystallinity on stretchable polymer semiconductor:

For wearable and implantable electronics applications, developing intrinsically stretchable polymer semiconductor is advantageous, especially in the manufacturing of large-area and high-density devices. A major challenge is to simultaneously achieve good electrical and mechanical properties for these semiconductor devices. While crystalline domains are generally needed to achieve high mobility, amorphous domains are necessary to impart stretchability. Recent progresses in the design of high-performance donor–acceptor polymers that exhibit low degrees of energetic disorder, while having a high fraction of amorphous domains, appear promising for polymer semiconductors. Here, a low crystalline, i.e., near-amorphous, indacenodithiophene-co benzothiadiazole (IDTBT) polymer and a semicrystalline thieno[3,2-b] thiophene-diketopyrrolopyrrole (DPPTT) are compared, for mechanical properties and electrical performance under strain. It is observed that IDTBT is able to achieve both a high modulus and high fracture strain, and to preserve electrical functionality under high strain. Next, fully stretchable transistors are fabricated using the IDTBT polymer and observed mobility ≈ 0.6 $cm^2$ $V^{-1}$ $s^{-1}$ at 100% strain along stretching direction. In addition, the morphological evolution of the stretched IDTBT films is investigated by polarized UV–vis and grazing-incidence X-ray diffraction to elucidate the molecular origins of high ductility. In summary, the near-amorphous IDTBT polymer signifies a promising direction regarding molecular design principles toward intrinsically stretchable high-performance polymer semiconductor.

### 7. Investigation of multi-scale ordering in highly stretchable polymer semiconducting films:

Stretchable semiconducting polymers have been developed as a key component to enable skin-like wearable electronics, but their electrical performance must be improved to enable more advanced functionalities. We developed a solution processing approach that can achieve multi-scale ordering and alignment of conjugated polymers in stretchable semiconductors to substantially improve their charge carrier mobility. Using solution shearing with a patterned microtrench coating blade, macroscale alignment of conjugated-polymer nanostructures was achieved along the charge transport direction. In conjunction, the nanoscale spatial confinement aligns chain conformation and promotes short-range π–π ordering, substantially reducing the energetic barrier for charge carrier transport. As a result, the mobilities of stretchable conjugated-polymer films have been enhanced up to threefold and maintained under a strain up to 100%. This method may also serve as the basis for large-area manufacturing of stretchable semiconducting films, as demonstrated by the roll-to-roll coating of meter-scale films.

8. **Investigation of stretchable and fully degradable semiconductors for transient electronics:**

The next materials challenge in organic stretchable electronics is the development of a fully degradable semiconductor that maintains stable electrical performance under strain. Herein, we decouple the design of stretchability and transience by harmonizing polymer physics principles and molecular design in order to demonstrate for the first time a material that simultaneously possesses three disparate attributes: semiconductivity, intrinsic stretchability, and full degradability. We show that we can design acid-labile semiconducting polymers to appropriately phase segregate within a biodegradable elastomer, yielding semiconducting nanofibers that concurrently enable controlled transience and strain-independent transistor mobilities. Along with the future development of suitable conductors and device integration advances, we anticipate that these materials could be used to build fully biodegradable diagnostic or therapeutic devices that reside inside the body temporarily, or environmental monitors that are placed in the field and break down when they are no longer needed. This fully degradable semiconductor represents a promising advance toward developing multifunctional materials for skin-inspired electronic devices that can address previously inaccessible challenges and in turn create new technologies.

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