

# Toward intrinsically stretchable organic semiconductors: mechanical properties of high-performance conjugated polymers

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## ABSTRACT

This paper describes several approaches to understanding and improving the response of  $\pi$ -conjugated (semiconducting) polymers to tensile strain. Our principal goal was to establish the design criteria for introducing elasticity and ductility in conjugated (semiconducting) polymers through a rigorous analysis of the structural determinants of the mechanical properties of this type of material. We elucidated the details of the effect of the alkyl side chain length on the mechanical properties of regioregular polythiophene and used this analysis to select materials for stretching and transfer printing of organic solar cells to hemispherical substrates. This demonstration represents the first time that a conjugated polymer device has ever been stretched and conformally bonded to a complex 3D surface (i.e., other than a cone or cylinder, for which flexibility—as opposed to stretchability—is sufficient). We then further explored the details of the dependence of the mechanical properties on the side chain of a semiconducting polymer by synthesizing a series of hybrid materials (block and random copolymers) containing both short and long side chains. This analysis revealed the unusual semiconducting polymer, poly(3-heptylthiophene), as having an excellent combination of mechanical and electronic properties. In parallel, we explored a new method of producing “blocky” copolymers using a new procedure based on random segmentation of conjugated monomers. We found that introduction of structural randomness increased the elasticity without having detrimental effects on the photovoltaic performance. We also describe methods of synthesizing large volumes of conjugated polymers in environmentally benign ways that were amenable to manufacturing.

## KEYWORDS

Mechanical properties, organic solar cells, bulk heterojunction, polythiophene, P3HT, PCBM, conjugated polymer, stretchable electronics, green chemistry, transfer printing

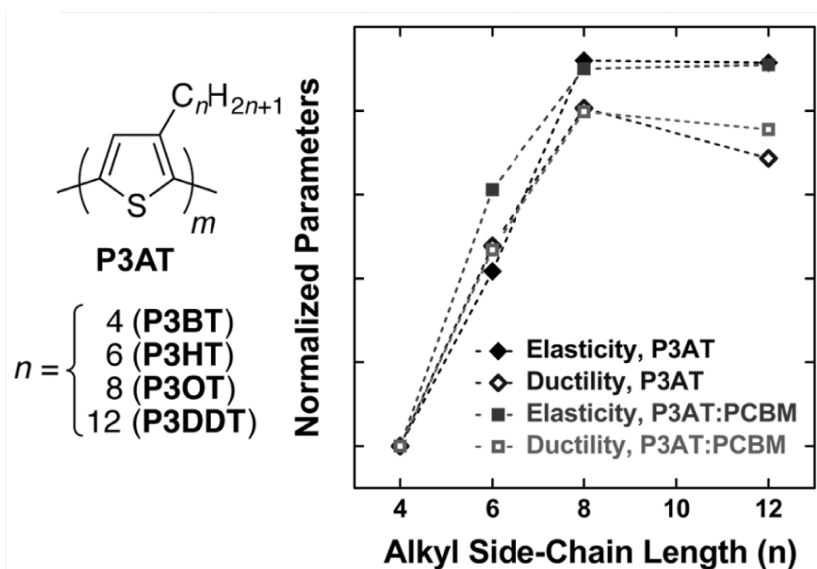
## 1. MECHANICAL PROPERTIES OF CONJUGATED POLYMERS AND POLYMER-FULLERENE COMPOSITES AS A FUNCTION OF MOLECULAR STRUCTURE

Although mechanical compliance is touted as a distinct advantage of semiconducting polymers, the relationship between the structural parameters of these materials and their mechanical properties is not often emphasized. To explore this relationship, we began by studying the effect of the length of the side chain on the tensile modulus and brittleness for a number of regioregular poly(3-alkylthiophenes) (P3ATs) (Figure 1), as well as their blends with a soluble fullerene derivative, Phenyl-C61-butyric acid methyl ester (PCBM).<sup>[1]</sup> We found that as the alkyl side chains were made to be shorter, the tensile modulus of the pure P3AT films dramatically increased, from 0.16 GPa for dodecyl side chains to 1.87 GPa for butyl side chains.<sup>[1]</sup> As expected, the addition of PCBM increased the moduli of the films, and blended P3AT:PCBM films generally demonstrated moduli greater than those of the pure polymers by factors of 2–4.<sup>[1]</sup> Moduli were measured using the strain-induced elastic buckling instability, wherein films of relatively high modulus are bonded to relatively soft materials, and the buckling wavelength,  $\lambda_b$ , is related to the thickness of the film,  $d_f$ , the Poisson ratios of the two materials,  $\nu_f$  and  $\nu_s$ , and the tensile moduli of the film and the substrate,  $E_f$  and  $E_s$ , by equation (1):<sup>[1]</sup>

$$E_f = 3E_s \left( \frac{1 - \nu_f^2}{1 - \nu_s^2} \right) \left( \frac{\lambda_b}{2\pi d_f} \right)^3 \quad (1)$$

Values of moduli produced from this calculation agree well with values obtained by traditional methods and dynamic mechanical analysis.<sup>[1]</sup> In addition, a semi-empirical theoretical model of the dependence of the moduli on alkyl side chain length was made, taking into account the molecular structure as well as empirical relations involving the glass transition temperature, the molecular volume, Poisson's ratio, and the cross sectional area of the molecules. The resulting trends agreed well with the experimental data.<sup>[1]</sup>

Brittleness correlated with the tensile modulus; for example cracks appeared in films with octyl side chains (P3OT) strained > 60%, but films with butyl side chains (P3BT) only withstood strains up to 6%.<sup>[1]</sup> While the brittleness appeared to increase from P3OT to P3DDT (dodecyl side chain), this was attributed to adhesion of the film to the polydimethylsiloxane (PDMS) substrate.<sup>[1]</sup> RMS roughness was also measured with tapping mode AFM and observed to decrease with increasing side chain length, and it has been suggested that the increasingly degrees of crystallinity with decreasing side length, as evidenced by the increasing roughness, play a role in the stiffening of the films.<sup>[1]</sup> In addition the effect of various additives on the mechanical and photovoltaic properties of P3ATs was investigated. 1,8-Diiodooctane (DIO) had the effect of reducing the modulus of P3HT:PCBM blend by a factor of 3, while small additions of PDMS slightly lowered the tensile modulus at the expense of the efficiency of a solar cell made using the material.<sup>[1]</sup> These results hold the promise of enabling mechanically robust, stretchable, and flexible electronics. This work was previously described in the paper by Savagatrup et al.,<sup>[1]</sup> from which some elements of this section were adapted.

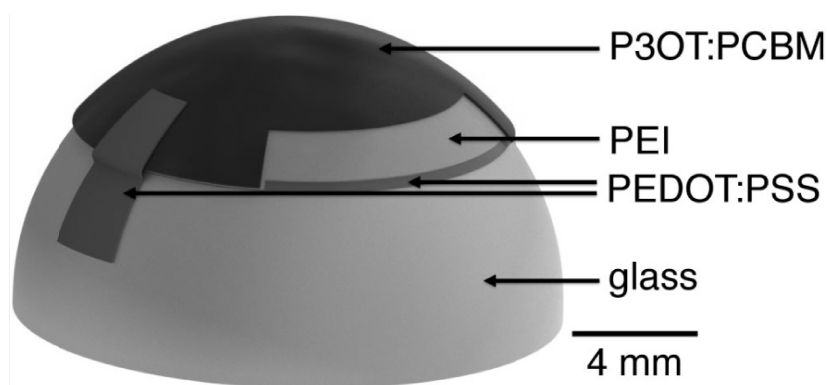


**Figure 1.** Structure of regioregular poly(3-alkylthiophene) (P3AT) and plot of normalized elasticity (inverse tensile modulus) and ductility (crack-onset strain) as a function of the alkyl side chain length,  $n$ . Reproduced with permission from Ref. 1. Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA.

## 2. STRETCHING AND CONFORMAL BONDING OF ORGANIC SOLAR CELLS TO NON-PLANAR SUBSTRATES

One of the advantages of organic materials and devices over traditional inorganic semiconductors is the promise of elastic and plastic deformation of the materials without fracture. For applications in organic solar cells, mechanical compliance would facilitate roll-to-roll fabrication, integration with the moving parts of machines or the body, bonding to non-planar surfaces such as vehicles and buildings, and robustness to the stresses encountered in the outdoor environment and in portable applications. However, organic semiconductors are generally optimized solely on the basis of electrical properties, often neglecting mechanical compliance or leaving it as an afterthought, meaning many materials and devices crack at relatively small strains.<sup>[2]</sup> Using the insights we developed in the previous section, we demonstrated stretching and conformal bonding (i.e., decal-transfer printing) of organic solar cells in both the “inverted” and “conventional” configurations to hemispherical glass surfaces with radii of 8 mm (Figure 2).<sup>[2]</sup> The solar cells were strained by this process by equivalent biaxial tensile strains of 24%, which would surpass what many materials used in

organic electronics can accommodate without fracture.<sup>[2]</sup> As in the previous section, the elasticity and ductility of regioregular polythiophenes were closely related to a single parameter—the length of the alkyl side chain. The electronic and photovoltaic properties of the solar cells were measured at various points on the hemisphere representing various amounts of biaxial strain.<sup>[2]</sup> This analysis demonstrates the ability of these materials to function while bonded to a generally curved surface producing a moderate amount of strain, and allows selection of materials that can accommodate such strain for non-planar applications. While solar cells based on the relatively brittle P3HT exhibited extensive cracking, degrading the photovoltaic properties significantly (due to short circuiting), the elastic and ductile P3OT exhibited typical photovoltaic properties when bonded to the hemispherical glass substrate.<sup>[2]</sup> Two classes of unconventional form factors require stretchable electronic systems: those that require repeatedly reversible strain for applications involving moving parts of a machine, the body, or a temporary or portable device, and applications involving the one-time bonding to a non-planar surface. This analysis has shown P3ATs to be a viable candidate for the later application, though they show promise for both areas. The results suggested that mechanical properties should be considered on an equal footing with electronic properties when designing and selecting organic semiconductors for applications that demand significant deformation. This work was described in the work of O'Connor et al.,<sup>[2]</sup> from which some elements of this section were adapted.



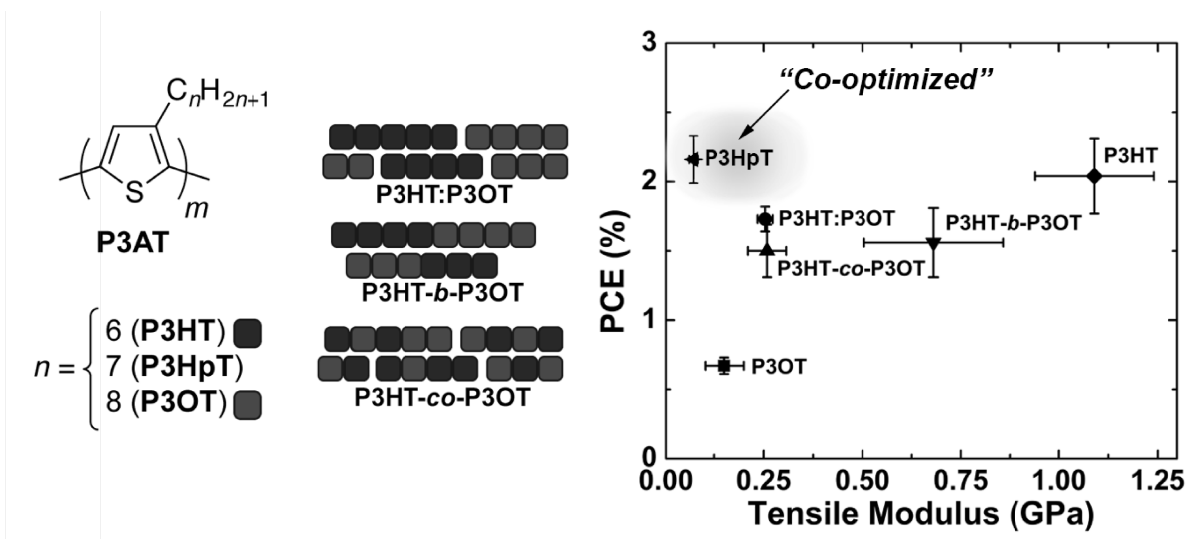
**Figure 2.** Schematic diagram of all-organic solar cell stretched and conformally bonded to a hemispherical glass substrate. Reproduced with permission from ref. 2. Copyright 2014 American Chemical Society.

### 3. BEST OF BOTH WORLDS: CONJUGATED POLYMERS EXHIBITING GOOD PHOTOVOLTAIC PROPERTIES AND HIGH COMPLIANCE

Based on our observations described in Sections 2 and 3, it appeared as though elasticity and ductility were incompatible with good semiconducting properties. We therefore undertook experiments to ascertain whether or not we could co-engineer stretchability and good charge-transport properties in a single material.<sup>[3]</sup> We thus further examined P3ATs, a class of materials for which electrical and mechanical performance have been observed to be in competition. P3ATs with short side chains ( $n \leq 6$ ) exhibit good electronic performance, as seen in composites soluble fullerene derivatives, but poor elasticity and ductility, while those with longer side chains ( $n \geq 8$ ) exhibit high elasticity and ductility but significantly worse electronic performance. We therefore tested a series of polymer films, each having an average side chain length of  $n = 7$ , using photovoltaic device based, mechanical, microscopic, and spectroscopic measurements to determine the possibility, in principle, to maximise simultaneously the mechanical and electronic performance in a single organic semiconductor (the "best of both worlds"). The four polymer samples tested were (1) poly(3-heptylthiophene) (P3HpT,  $n = 7$ ), (2) a physical blend of equal parts P3HT and P3OT (P3HT:P3OT,  $n = 6$  and  $n = 8$ ), a random copolymer (P3HT-co-P3OT), and (4) a block copolymer (P3HT-b-P3OT) (Figure 3).<sup>[3]</sup>

As described briefly in Section 1, we measured the buckling wavelength of the films to determine the modulus, and compared the results to the weakly interacting H-aggregate model.<sup>[3]</sup> The order observed in spectroscopic data was used to compare trends in conjugation length from the UV-vis absorption spectra of the polymers, in an attempt to correlate these values with the mechanical stiffness and device performance, with the results correlating well with the

tensile moduli obtained by mechanical buckling data.<sup>[3]</sup> The maximum compliance was exhibited by P3HpT ( $70 \pm 10$  MPa), while block copolymer was the stiffest of the hybrid samples ( $680 \pm 180$  MPa). P3HpT also exhibited power conversion efficiency (PCE =  $2.16 \pm 0.17\%$ ) similar to that of P3HT, using a 1:1 blend with PCBM and stretchable electrodes. As in previous sections, the blends with PCBM exhibited higher tensile moduli than the pure films, but the increase was generally more pronounced for the films with average side length  $n = 7$  than the P3HT or P3OT films.<sup>[3]</sup> One explanation for the sharply reduced moduli of the P3HpT films as compared to the P3HT films is that P3HpT is the P3AT with the shortest side chain whose glass transition temperature is below room temperature ( $12\text{--}25$  °C). These analyses may lead to the design of organic semiconductors exhibiting both improved mechanical and electrical properties for stretchable and mechanically robust applications. This work was presented in the paper by Savagatrup et al.,<sup>[3]</sup> from which some elements of this section were adapted.



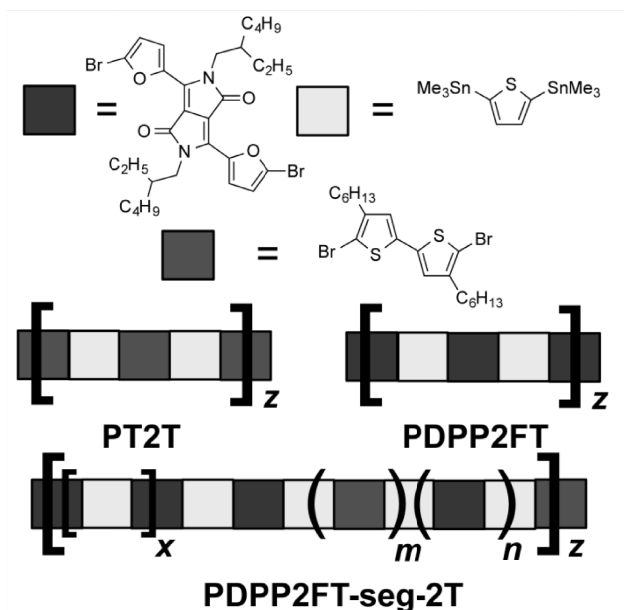
**Figure 3.** Schematic representation of three homopolymers (P3HT, P3HpT, and P3OT) and three hybrid systems, the physical blend (P3HT:P3OT), the block copolymer (P3HT-*b*-P3OT), and the random copolymer (P3HT-co-P3OT). The power conversion efficiency of the materials mixed with PC<sub>61</sub>BM is plotted on the right-hand side as a function of the tensile modulus of the pure polymer. The upper-left quadrant of the plot represents the most elastic materials with the best electronic properties, and P3HpT thus embodies the co-optimized “best of both worlds.” Reproduced with permission from ref. 3. Copyright 2014 American Chemical Society.

#### 4. INCREASED COMPLIANCE OF A LOW-BANDGAP CONJUGATED POLYMER BY RANDOM SEGMENTATION FOR MECHANICALLY ROBUST SOLAR CELLS

While P3ATs are a good starting point in research of mechanically compliant organic semiconductors, many other materials and synthesis methods remain to be investigated to optimize both electronic properties and mechanical compliance.<sup>[4]</sup> One promising material is an N-alkylated diketopyrrolopyrrole (DPP) unit flanked by two furan rings (2F) alternating with thiophene (T, altogether PDPP2FT), an alternating copolymer synthesized by the Stille polymerization.<sup>[4]</sup> We then PDPP2FT modified by exchanging the DPP for a tail-to-tail coupled unit of two 3-hexylthiophene rings (bithiophene, 2T) in an average of one of approximately five repeat units, producing the (“segmented”) polymer, PDPP2FT-seg-2T (Figure 4). Ultraviolet-visible spectroscopy, <sup>1</sup>H NMR spectroscopy, and gel-permeation chromatography confirmed the presence and covalent incorporation of the 2T units within the conjugated backbone of the segmented polymer.<sup>[4]</sup> While the tensile modulus of the homopolymer was  $2.17 \pm 0.35$  GPa, the segmented polymer exhibited a lower modulus of  $0.93 \pm 0.16$  GPa.<sup>[4]</sup> Blended with PCBM, the segmented polymer produced devices with PCEs of  $2.82 \pm 0.28\%$ , which was similar to that of devices utilizing PDPP2FT ( $2.52 \pm 0.34\%$ ).<sup>[4]</sup>

Semi-empirical theoretical calculations of the tensile modulus, based again on the molecular structure as well as the glass transition temperature of the materials, agreed well with the data for the homopolymers, PT2T and PDPP2FT.<sup>[4]</sup> However, this simple theoretical model failed to predict the reduction in modulus of PDPP2FT-seg-2T

relative to that of the homopolymer, PDPP2FT, perhaps due to its inability to fully incorporate the effects of randomness in the polymer chain.<sup>[4]</sup> As in Section 1, we measured the RMS roughness using tapping mode AFM. We observed PDPP2FT-seg-2T had an RMS roughness of  $1.25 \pm 0.08$  nm and that PDPP2FT had an RMS roughness of  $1.13 \pm 0.09$  nm.<sup>[4]</sup> The similarity of these values suggests that the correlation between tensile modulus and roughness (as a manifestation of crystallinity) —as observed in other systems— is not general. These results suggest that it is possible to increase the mechanical resiliency of semiconducting polymers for solar cells without causing negative effects on the photovoltaic properties. This work was described in the paper by Printz et al.,<sup>[4]</sup> from which some elements of this section were adapted.



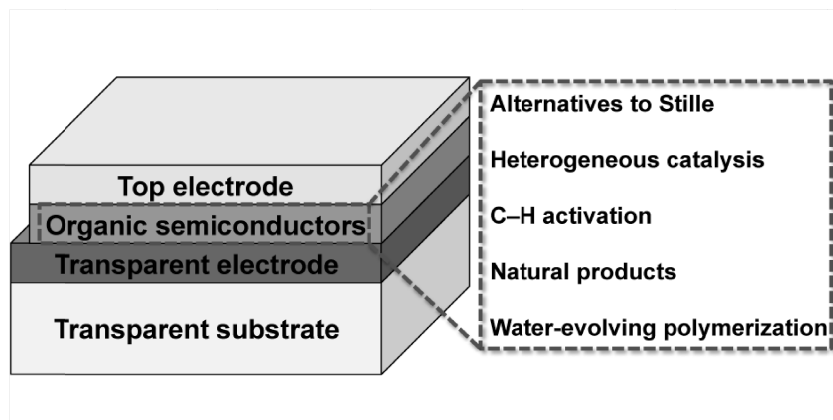
**Figure 4.** Schematic diagram the structure of a homopolymers PT2T (elastic but not efficient), PDPP2FT (not elastic but efficient), and a polymer containing random segments of PDPP2FT interspersed by units of alkylated bithiophene, PDPP2FT-seg-2T, which exhibited good elastic behavior and high photovoltaic efficiency. Reproduced with permission from ref. 4. Copyright 2014, Royal Society of Chemistry.

## 5. GREEN CHEMISTRY FOR ORGANIC SOLAR CELLS

All current methods of energy production (i.e., hydroelectric power, recovery of oil and natural gas, and mining rare elements for solar cells) are associated with some degree of environmental degradation.<sup>[5]</sup> Organic solar cells (OSCs) have the promise of providing potentially environmentally benign sources of power at a relatively low cost. Semiconducting  $\pi$ -conjugated polymers (i.e., the active components of OSCs) are not typically synthesized in ways that are amenable to manufacturing with low environmental impact.<sup>[5]</sup> Methods such as the Stille coupling have poor atom economies and other metrics of “greenness.” One theme in both green chemistry and process research is that when costs of disposing wastes are high, low cost can be achieved in parallel with environmentally benign methods. Five synthetic strategies that satisfy several or all of the criteria of green chemistry, and which are particularly amenable to the synthesis of  $\pi$ -conjugated polymers, are (1) polymerization involving activation of C–H bonds; (2) polycondensation reactions that evolve water as a byproduct; (3) the use of heterogeneously catalyzed polymerizations; (4) use of biofeedstock-derived starting materials; and (5) polymerization using metal-mediated cross- coupling reactions that reduce or eliminate stoichiometric organotin waste (Figure 5).<sup>[5]</sup>

Choices and optimizations based on these strategies can dramatically reduce the environmental impact of production of necessary chemicals for OSCs, for example the embodied energy and costs of synthesizing and purifying organic semiconductors (conjugated polymers and fullerenes) is well known.<sup>[5]</sup> Other materials could significantly reduce this energy cost. The methods mentioned above have a variety of benefits depending on the specific method but

including the reduction of toxic waste by-product, simplified removal of catalysts, reduction of contamination in the products, simple implementation, as well as lower cost and energy usage. This topic was reviewed in the paper by Burke and Lipomi,<sup>[5]</sup> from which some elements of this section were adapted.



**Figure 5.** Schematic diagram of an organic solar cell in which the active semiconducting polymers are produced using industrially viable and “green” synthetic methodologies. Reproduced with permission from ref. 5. Copyright 2013, Royal Society of Chemistry.

## 6. CONCLUSIONS

We have established many of the design criteria for semiconducting polymers that exhibit both high tensile elasticity and good photovoltaic behavior. We are currently exploring new molecular architectures that exhibit extreme elasticity. Implicit in this goal is to gather fundamental insights into the ways in which mechanical softness and chemical responsiveness—i.e., elasticity and perhaps other attributes, such as self-repair—can coexist with state-of-the-art charge-transport properties in a single material.

## ACKNOWLEDGEMENTS

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