

HIGHLIGHT

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Poly(3-hexylthiophene) (P3HT): fruit fly or outlier in
organic solar cell research?

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Regioregular poly(3-hexylthiophene) (P3HT) is used as a model polymer for research in organic solar cells. It is popular despite its dissimilarity in many respects to the high-performing class of polymers based on the donor–acceptor (DA) motif. For example, P3HT has a low glass-transition temperature, is highly crystalline for a semiconducting polymer, is made by a living polymerization, and contains no fused rings along the conjugated backbone; these characteristics stand in contrast to most DA polymers. These differences in structure and morphology suggest that many of the results obtained for P3HT are not directly transferable to the design and processing of new materials. This highlight proposes that focusing on a few examples of conjugated polymers based in part on the way these materials assemble in the solid state would enable greater transferability of the results from one study to another. That is, the field would benefit from having more than one “fruit fly.”

P3HT and low-bandgap polymers

Since the first independent syntheses of regioregular poly(3-hexylthiophene) (P3HT) by Rieke and McCullough in the early 1990s,¹ it has been the predominant conjugated polymer in the literature and a mainstay of research in organic solar cells (OSCs). Fig. 1a and b suggests that P3HT is the subject of a larger body of research than a group of the most well known high-performance polymers. The popularity of P3HT has significant consequences for the development of OSCs. Much of what is known about the operational principles of OSCs has been derived from devices in which the conjugated polymer is P3HT. (In most of these studies, P3HT is paired with a soluble fullerene derivative in a bulk heterojunction, BHJ.)

Since the mid 2000s, however, a class of low-bandgap semiconducting polymers based on the alternating donor–acceptor (DA) motif has achieved greater efficiencies than P3HT.² This structurally diverse class of DA polymers has challenged assumptions about the attributes necessary for high performance. For example, it was once widely accepted that long-range order was required for good charge-transport; recently developed DA polymers have, however, shown that local ordering alone is sufficient.^{3,4} Many new structurally disordered materials, which do not exhibit high mobilities in thin-film transistors (*e.g.*, TQ1), still perform well when blended with a fullerene.^{5,6} While these disordered materials do not have high charge mobilities, their ability to pack efficiently with acceptors in the solid state improves charge separation and leads to a high power conversion efficiency.^{6,7} While interest in P3HT began to

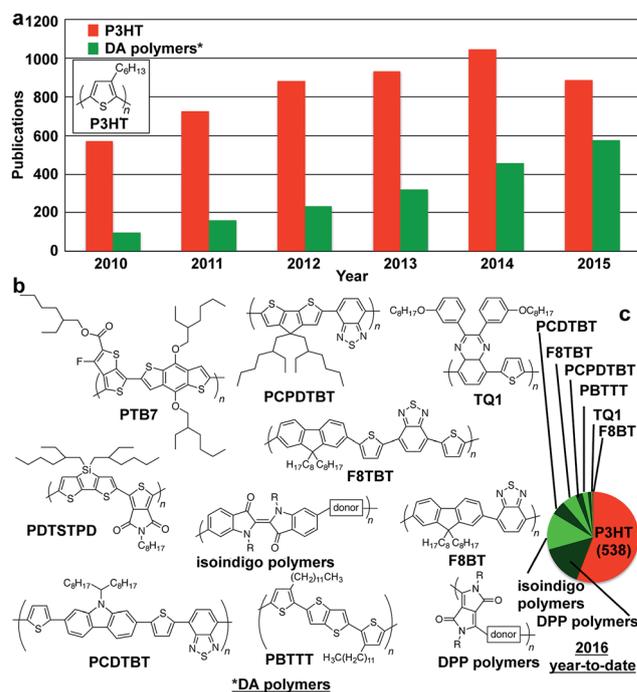


Fig. 1 (a) Number of articles published on P3HT vs. the combined citations for a representative group of donor–acceptor (DA) polymers (b) from 2010–2015. The number of publications is taken from a search for “topic” on ISI Web of Science on 22 October 2016 using the abbreviations for the materials listed. The tallies for isoindigo- and DPP-based polymers were found using a search of “isoindigo” or “DPP” and “polymer”. (c) Number of articles in 2016, year-to-date, published on P3HT and the same group of DA polymers. There were 964 published articles total and 0 articles on PDTSTPD during this period.

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decline in 2015 (Fig. 1a), it still represents the greatest fraction of articles published in 2016 (Fig. 1c).

Despite these findings, microstructural, photophysical, and device-scale measurements are performed on P3HT to a prodigious extent. The assumption in choosing P3HT is that the results will be generalizable to other materials. The central reason that P3HT remains popular is availability: of the material itself and of the results of other researchers. Moreover, the huge number of DA polymers now reported make choosing only one seem arbitrary, and thus the default choice is P3HT. Like a fruit fly, P3HT is inexpensive, has a well-known morphology, and has easily produced variants. It is, however, only one class of material. DA polymers can also be subdivided into classes on the basis of molecular, microstructural, or electronic properties. We do not know which—if any—semiconducting polymer will become predominant in commercial applications. Results obtained from P3HT, or any other semiconducting polymer, are thus most impactful if described in context. That is, the field would benefit from explicit analyses of which conclusions are likely to be true for other polymers. It may be wise for researchers to pick among a small group of widely available and well-characterized polymers as archetypes for their studies.

Synthetic procedures

The advent of regioregular P3HT was a breakthrough in research on organic semiconductors. The synthetic procedure of McCullough,⁸ a Kumada-like polycondensation often called the Grignard metathesis (GRIM) method, has two key features: (1) it produces regioregular material and (2) it proceeds by a quasi-living mechanism. The GRIM method proceeds in one pot starting with 2,5-dibromo-3-hexylthiophene.¹ The bromide at the 5-position is substituted with imperfect selectivity with a magnesium halide, whose source is usually the sacrificial isopropylmagnesium chloride. A nickel(II) catalyst reinforces the regioselectivity of the Grignard exchange. It does this by reacting preferentially with the monomer that has the Grignard at the 5-position. Regioregularities of head-to-tail couplings are usually obtained in excess of 98%. During the reaction, the nickel(II) catalyst remains associated with the end of the growing chain, and thus plays the role of an initiator in a quasi-living process. P3HT can be formed with degrees of polymerization that are unusually high (>100) for conjugated polymers. As a consequence of the control available to the GRIM method, the distribution of molecular weights of P3HT is narrow (dispersity < 1.5). The simplicity of the monomers and of the synthetic procedure is reflected in the low embodied energy (e.g., carbon footprint) of the material,⁹ which enables manufacturing on the kilogram scale.¹⁰

In comparison, almost all DA polymers are formed by step-growth polycondensation reactions using Stille or Suzuki couplings of donor and acceptor monomers.¹¹ The distribution of molecular weights of DA polymers is correspondingly broader than for P3HT and more difficult to control. The well-known theory of Carothers says that even a small stoichiometric imbalance between the starting materials—difficult to avoid on the laboratory scale—significantly reduces the theoretical

maximum degree of polymerization.¹² Difficulties in the synthesis of DA polymers, the complexity of the monomers, greater production energy, and corresponding cost have heightened the barrier to using DA polymers and thus favoured P3HT.

Conformation and chain flexibility

Both the solution-phase and solid-state conformations of P3HT and the DA polymers—which themselves are extraordinarily diverse in conformational behaviour—differ in many ways. The backbone of P3HT is made only of isolated rings and linear side chains. This structure gives the polymer chains significant freedom to sample conformational space. DA polymers, in contrast, often contain fused rings, which produce stiffer conformations. Fig. 2 shows the canonical conformational classes adopted by semiconducting polymers in solution.⁷ These classes are influenced by the stiffness of the backbones and the steric bulk of the side chains. Distributions of conformations have important effects on the structure of the film in the solid state.

P3HT in the solid state is a highly aggregated semicrystalline material.¹³ Its aggregation behaviour has been characterized extensively by analysis using the weakly interacting H-aggregate model of Spano and coworkers.¹⁴ (The ease of conducting this analysis using simple UV-vis data reinforces the popularity of P3HT.) P3HT exhibits a unique packing motif in which folded chains form needle-like crystallites with the π -stacking axis parallel to the long axis of the crystallite.¹⁵ This morphology is especially prominent by atomic force microscopy of low-molecular weight samples,¹⁶ and the effect can be used to form long nanowires when P3HT is precipitated from a poor solvent.¹⁵ Efficient π -stacking in these crystalline phases is in part responsible for the high hole mobilities of P3HT. This crystalline morphology, which requires frequent folding of the main chain, is generally not observed in the DA polymers, which are stiffer. The ribbon-like polymer poly(benzimidazo-benzophenanthroline ladder) (BBL) serves as an extreme point of comparison. It forms long nanostructures whose molecular axis is parallel to the long axis¹⁷—the opposite behaviour of P3HT.

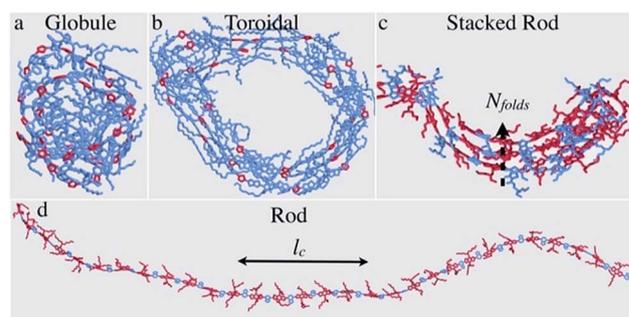


Fig. 2 Representations of the four major conformational classes of semiconducting polymers in solution. These conformations have a strong influence over the morphology of the solid film. Reproduced with permission from ref. 7 Copyright 2015, American Chemical Society.

Bulk heterojunction morphology

Much of what is known about the solid structure of the BHJ has been deduced from studies of P3HT and 6,6-phenyl C₆₁ butyric acid methyl ester (PCBM). The current model for the morphology of the P3HT:PCBM BHJ comprises a three-phase structure:¹⁸ a crystalline polymer phase, a fullerene-rich phase, and a mixed phase that forms because of the partial miscibility of PCBM in amorphous P3HT.^{19,20} Regioregular P3HT can accommodate a fraction of PCBM that is limited by tie chains between P3HT crystallites that restrict expansion.²¹ (Regiorandom P3HT, which is amorphous, can in contrast accommodate an unlimited volume fraction of PCBM.²¹) Many DA polymers, such as PBDTTPD, may follow this three-phase BHJ morphology.²² However, some DA polymers such as PTB7 have a two-phase BHJ morphology: a fullerene-rich phase and a mixed amorphous phase of PCBM and polymer.²³

The BHJ morphology of DA polymers is further distinguished from P3HT through the branching and density of attachment of side chains. Side chains are necessary to confer solubility to a π -conjugated backbone, which is intractable when unsubstituted.²⁴ P3HT has side chains on every monomer unit. This high density of alkyl chains results in the most common packing structure of P3HT, “Form I,”¹³ in which the side chains do not interdigitate.²⁵ Interdigitation can be found in the unusual “Form II” of P3HT, which can occur in samples with low degrees of polymerization (<36).²⁶ On the other hand, the side chains of many DA polymers have a lower density of attachment (*e.g.*, PBTBT), which promotes interdigitation.²⁷ Increased spacing between side chains can allow fullerene molecules to intercalate within the crystalline phase of BHJ films.²⁸ This intercalation necessitates a greater fraction of (often expensive) fullerenes to achieve bicontinuity of the phases, which is necessary in most systems for high performance. The work of Cates-Miller *et al.* describes the rules of thumb for predicting which polymers accommodate intercalation.²⁹ Side chains can also have different effects when placed on the donor monomer instead of the acceptor monomer, an effect only possible in DA polymers. Reducing steric hindrance near the acceptor (*i.e.*, by using a linear instead of a branched side chain) results in greater efficiency due to increased proximity of the acceptor to the fullerene.³⁰

Thermal and mechanical properties

The thermal³¹ and mechanical³² properties of conjugated polymers have significant effects on device stability.³³ The glass transition temperature (T_g) in particular describes the mobility of polymer chains in the solid state, which affects all of the mechanical properties.³¹ The T_g of P3HT is low by the standards of semiconducting polymers: ~ 12 °C as measured using differential scanning calorimetry³⁴ and as calculated using molecular dynamics simulations.⁵ Conjugated polymers with low T_g are susceptible to demixing of the polymer and the fullerene at elevated temperatures, which will nearly always exist in practical operation of a solar cell. P3HT is a notable exception to this effect, as the BHJ structure may be its most

thermodynamically favourable state at moderate temperatures.³⁵ High- T_g polymers often suffer from mechanical stiffness and brittleness,³⁴ which can lead to cracking or cohesive failure of devices during roll-to-roll printing, in portable applications, or in the outdoor environment.

Despite having a T_g below room temperature, P3HT has a high tensile modulus by the standards of soft materials: 200 MPa to 1 GPa depending on the method of measurement, purity of the sample, and possibly even temperature in the laboratory.³² The mechanical properties of DA polymers are highly variable. In a recent paper, our laboratory measured the modulus and crack-onset strain of each member of a library of 50 DA polymers.³⁶ In general, compliance and extensibility increased with long, branched side chains, and the absence of fused rings along the backbone. PCBM further behaves as an antiplasticizer for conjugated polymers when used as the acceptor in OSCs. For example, P3HT:PCBM blends have greater moduli and increased brittleness compared to the pure materials.³⁷ The thermomechanical stability of solar cells based on DA polymers is thus expected to be highly variable compared to those based on P3HT.

Device performance

Compared to P3HT, DA polymers exhibit lower bandgaps. Greater coverage of the solar spectrum by the absorption of the DA polymers has led to OSCs with higher efficiencies.² However, continued optimization of P3HT-based devices—possibly along with the help of outliers in the statistics of thousands of studies on this polymer³⁸—has allowed it to achieve comparable efficiencies to those obtained using designer materials. For example, Guo *et al.* produced a P3HT:fullerene solar cell with 7.4% efficiency using the indene-C₆₀ bisadduct (ICBA) and a solvent additive.³⁹ Recognizing the expense of fullerene derivatives, Holliday *et al.* achieved an efficiency of 6.4% with a non-fullerene small molecule as the acceptor.⁴⁰ These results compare well with efficiencies of $\sim 10\%$ using DA polymer-fullerene BHJ cells when one considers the low cost and embodied energy of P3HT.

Many DA polymers produce high efficiencies when coated in the laboratory in small areas under idealized conditions. However, their ability to survive roll-to-roll coating will determine their viability for large-scale production.⁴¹ P3HT is unusual in its ability to retain its efficiency even when used in fully printed, large-area modules. P3HT has advantages for printing in part because of its ability to form smooth films with relatively high thickness, which suppresses losses from shunts in large-area devices. In an effort to identify polymers that might be superior to P3HT in roll-to-roll production, Krebs and coworkers fabricated large-area (1 cm²) fully printed modules from a library of 104 DA polymers. Only 13 members of this library formed solar cells with efficiency comparable to P3HT.⁴¹ Many polymers failed during synthesis, coating, ink formulation, or exhibited poor efficiency. Our laboratory, in collaboration with the Krebs group, introduced a merit factor that accounted also for the mechanical properties of these materials (Fig. 3a and b).³⁶ This merit factor is equal to $\psi = (\text{PCE} \times \text{CoS})/$

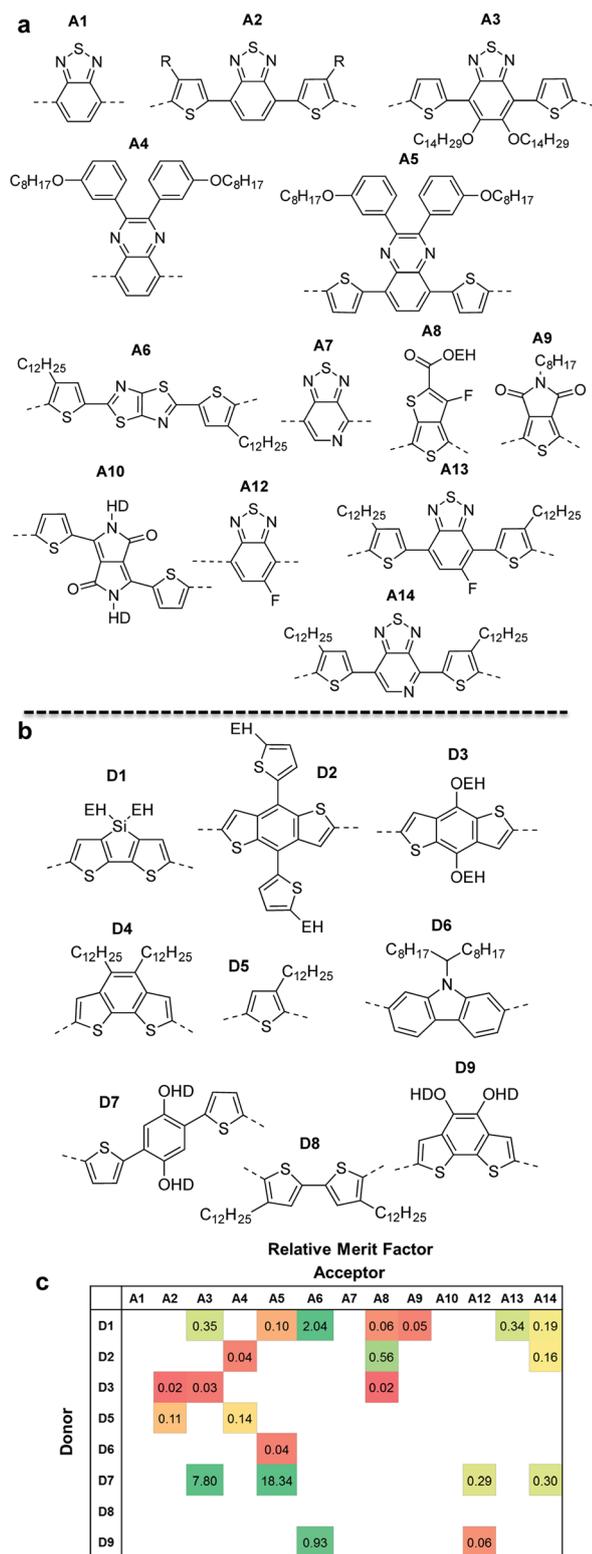


Fig. 3 Library of DA polymers and comparison of performance. The library was composed of a cross product of the acceptor residues shown in (a) and the donor residues shown in (b). The relative merit factor that combines efficiency with expected mechanical robustness, and compares this value to that obtained for P3HT, is shown in (c). See text for calculation of the relative merit factor. Reproduced with permission from ref. 36 Copyright 2016, American Chemical Society.

E_f , where PCE is the power conversion efficiency, CoS is the crack-onset strain, and E_f is the tensile modulus. Normalization of the merit factor by dividing by the merit factor of P3HT, ψ/ψ_{P3HT} (Fig. 3c), revealed four polymers that outperformed P3HT when manufacturability, performance, and expected mechanical stability were taken into account. While the mechanical properties and efficiencies were, with some arbitrariness, weighted equally, such an analysis represents a starting point for the consideration of mechanical properties along with the performance of devices.

Conclusions

The materials used in organic solar cells are characterized by a curious bimodal distribution. By far the most common material studied is P3HT. Another body of literature, however, exists for the entire class of materials known in this highlight as the DA polymers. While the future of the commercial viability of organic solar cells remains uncertain, it is likely to be dominated by a material for which every aspect is well understood. While P3HT is practical due to its wide availability, major differences make it difficult to extrapolate conclusions about P3HT to the DA polymers. The wide variability within DA polymers, moreover, hinders transfer of conclusions about one DA polymer to another. Classification of the DA polymers into groups that can be used to predict the properties of new members of the same type is needed. One suggestion is to pick a few materials that are representative of different microstructural motifs. A selection could include P3HT and a small group—say three to five—of the DA polymers, which might consist of the amorphous TQ1 (A4D5 using the notation of Fig. 3), the locally ordered PTB7 (A8D3), and the semicrystalline PDTSPD (A9D1). These materials have the additional advantages of an existing body of research (>400 publications on PTB7 alone, according to ISI), and the existence of accurate force fields for computational studies.⁷ We conclude that the availability of P3HT alone—the “fruit fly” of research on organic solar cells—may be insufficient to guarantee transfer of results from one class of materials to another. The field may also be in need of a mouse, a monkey, and a zebrafish.

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