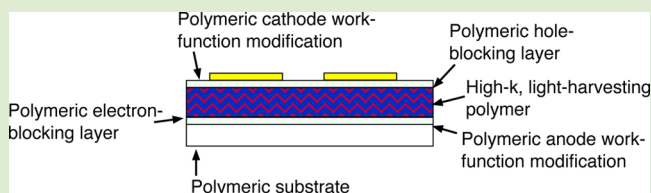


Polymer Electronics, Quo Vadis?

Ryan C. Chiechi* and Jan C. Hummelen*

Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ABSTRACT: At the heart of polymer electronics lies more than three decades of research into conjugated polymers. The future of these materials is intimately tied to the development of organic photovoltaic (OPV) devices that can compete with traditional, inorganic devices in efficiency and cost. In addition to functioning as light-harvesting materials, polymers, conjugated or not, are increasingly being used at interfaces in thin-film OPV and other electronic devices, reprising the successes of poly(ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS). The push toward more efficient OPV devices is moving chemists to think beyond band-gaps and toward charge, dielectric properties, and new synthetic methods.



Since the discovery of doping and metallic conduction in poly(acetylene),¹ researchers have been anticipating new technological applications that combine the electronic properties of semiconductors with the physical properties of plastics. Polymer electronics has since grown into a robust field of research largely at the intersection between chemistry, physics, and materials science. It is both frustrating and exhilarating because the applications are to a large degree presupposed, replicating the functionality of inorganic semiconductors using polymers, but modern semiconductor technology sets a very high bar, and while progress in polymer electronics should not be measured against mature technologies, commercialization is undoubtedly an important goal for the field and progress toward that goal is a reasonable measure of success.

When asking quo vadis, we should first look a posteriori at the three decades that have transpired since poly(acetylene). One of the most ubiquitous and, arguably, successful polymers in electronics is actually a blend of two polymers, poly(ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS).² This material, rather than leveraging the semiconducting properties of PEDOT, packaged it in its doped form, blended with PSS, in an aqueous suspension. Early applications of PEDOT/PSS exploited its optical transparency, where it found use as an antistatic coating in roll-to-roll photographic film manufacturing. Of course, charge-coupled device (CCD) detectors have all but completely replaced photographic film, but the ubiquity of PEDOT/PSS persists because of its useful electronic properties, namely, that the position of its conduction band renders it an ideal material to match organic conductors to transparent conducting oxides. Thus, PEDOT/PSS exists at the interface between the active layer and the transparent conducting oxide (TCO) electrode of virtually any organic device in which light enters or exits. The ubiquity of PEDOT/PSS in electronic devices also gives a hint at the future of polymer electronics, as it defied the conventional wisdom that the electroactive polymers would find commercial success by exploiting their bulk properties as

semiconductors in which they comprise the active layer of devices.

A more recent application of PEDOT/PSS in electronic devices, though not necessarily considered polymer electronics, is at the interface between self-assembled monolayers (SAMs) and vapor-deposited gold electrodes in large-area molecular junctions.³ These devices are fabricated on silicon wafers using standard photolithographic procedures to produce crossbar structures of gold/SAM/PEDOT/PSS/gold in remarkably high yields. The devices are highly reproducible and, importantly, stable for long periods of time. A similar approach uses an ultrathin layer of poly(*para*-phenylenevinylene) in its undoped, semiconducting state to protect the SAM from the top electrode.⁴ These applications of conjugated polymers in tunneling-based electronic devices have proven successful because of the mechanical properties of the polymers, which allow them to conform to the topology of the SAM while, due to surface tension and viscosity, not penetrating pinholes. With the application of a metallic top-contact, the conjugated polymer then acts as a plastic electrode that encapsulates the fragile SAM, leading to extraordinarily stable, robust devices. As molecular electronics matures, these hybrid polymer/molecular electronic devices may see commercial applications, spurring the development of new polymeric materials that are tailored to this specific application. These applications are again indicative of an important role for polymers in electronics as interfacial materials.

The epitome of modern polymer electronics is organic photovoltaics (OPV), not because polymer light-emitting devices, field-effect transistors, tunneling junctions, and so on are less interesting or important, but because of the (sudden) societal relevance of research into renewable energy and the commensurate implications of the commercialization of

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polymers for OPV. In a world increasingly concerned with the development of renewable sources of electricity, the potential of devices that combine the mechanical properties of plastics with the light-harvesting properties of solar cells is incalculable. Wearable OPV materials, photovoltaic threads woven into clothing,⁵ PV paint for your house, self-charging electronic devices—there is limitless room for innovation. A commercially viable OPV device must be compatible with current manufacturing methods, which require films of sufficient thickness for industrial, roll-to-roll processing. These devices have, however, not yet met with the unbridled commercial success that one might expect, due largely to the inability to match the cost/efficiency ratio of inorganic PV. A major hurdle yet to be overcome is the ability of charges to escape the active layer after generation, which directly affects the maximum thickness at which a device can operate efficiently. The two bottlenecks for the extraction of these charges are the charge-carrier mobility in the active layer and the interfaces with the electrodes, both of which can be overcome by tailoring the polymers that these devices comprise. To that end, remarkable progress has been made in the optimization of the electronic properties of conjugated polymer donors, pushing efficiencies in bulk-heterojunction (BHJ) devices into double digits.⁶ Conjugated polyelectrolytes have proven well suited to this task because, like PEDOT/PSS, they are cast from water (or other polar, protic solvents) and are not affected by organic solvents used to spin-cast the active layer.⁷ They can also be installed and controlled precisely using layer-by-layer dip coating and other orthogonal-processing techniques, which allows for systematic studies and fine-tuning of the properties of this interface. Unlike PEDOT/PSS, however, the electronic properties of polyelectrolytes can be tuned via organic synthesis. Thus, they can serve as hole or electron blocking layers by manipulating the band gap and ionization potentials to match perfectly the bands/orbitals of the active layers. In combination with future advances in the light-harvesting polymers in the active layer, the challenges of commercializing OPV may exist entirely in the development of polymeric materials.

Another major hurdle in OPV devices is stability; a solar cell must last for years in all kinds of weather and, of course, direct sun. The organic materials themselves are surprisingly robust, given proper encapsulation; however, conventional devices use low work function metals as cathodes to match the Fermi energy of the electrode to the LUMO of the acceptor. These metals are easily oxidized in air, react with water, and harm the environmental stability of OPV devices. An obvious, though nontrivial, solution to this problem is to invert the architecture: use a high work function metal as an anode and the TCO as the cathode. This is another problem that is largely solvable using polymers. Conjugated polyelectrolytes and other highly charged or highly polar polymers can alter the effective work function of an electrode by affecting a shift in the vacuum level, which will allow the efficiencies of inverted OPV devices to converge with noninverted devices. This shift is typically accomplished by installing aligned dipoles at the surface of an electrode and has largely been accomplished using SAMs; however, recent work on a “universal method” for altering work functions with polymers highlights just how fast this area of polymer electronics is progressing.⁸ In this work, Zhou et al. demonstrate a remarkable $5.9 \pm 0.3\%$ power conversion efficiency using the benchmark, poly(3-hexylthiophene) (P3HT)/indene-C60 bis adduct (ICBA) blend, which is

robust, but far from the most efficient polymer/fullerene combination, and a Ag cathode. Given the limits of even the most sophisticated encapsulation techniques and the associated costs, it is unlikely that commercialized OPV devices will employ reactive cathode materials such as Ca. Thus, inverted cells are likely the future of commercialized OPV and the key technological challenge to inverted OPV devices catching up to the efficiencies of the current record-holders may very well have been solved by the inclusion of a polymeric material at the interface between the cathode and the active layer, and, by fabricating these devices on polymeric substrates, they embody true polymer electronics; the only nonpolymeric components are the electrodes and the fullerene (though even these can in principle be replaced by polymeric materials).

The maximum efficiency of an inorganic photovoltaic cell is subject to the Shockley–Queisser limit, which states that, given certain (reasonable) assumptions, a single p/n junction cannot be more efficient than $\sim 33\%$ (under standard solar irradiation). The mechanism of charge-generation in OPV devices differs from that of inorganic devices in that the absorption of light results in the formation of bound electron–hole pairs (excitons) as opposed to free charge-carriers. A major factor in this difference in mechanism is the dielectric constant of organic polymers, which are typically <4 as opposed to Si, which is ~ 11 . The low dielectric medium of the active layer increases the exciton binding energy (it does not effectively screen charges), which impinges on the efficiency of the generation of free carriers from photon absorption events. While still a new concept in the design of materials for OPV devices, increasing the dielectric constant of the active layer is predicted to lead to a dramatic increase in efficiency, approaching the Shockley–Queisser limit.⁹ This insight proposes an intriguing challenge to synthetic chemists as it demands conjugated polymers that retain the high charge mobility and small band gaps of current state-of-the-art materials but with dielectric constants that are at least three times larger than that of a typical conjugated polymer. As shown in Figure 1, starting from a BHJ device that is optimized to 12% efficiency, increasing the dielectric constant from 3 (a typical value) to 10 pushes the efficiency to 22% without any changes to the band gap, interface layers, mobility, and so on, but how does one affect the dielectric constant of a conjugated polymer? It is presumably by incorporating freely rotating dipoles and polarizable groups, but the real challenge is doing

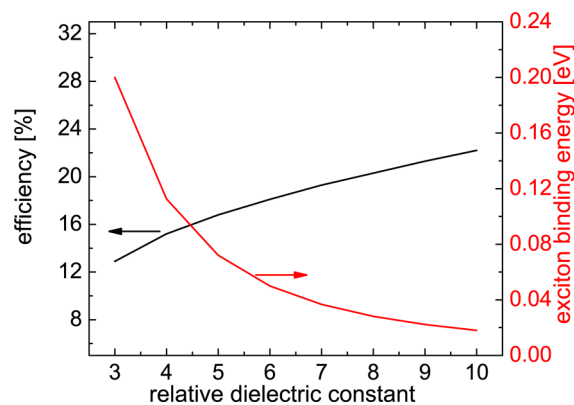


Figure 1. Plot of the predicted influence of the dielectric constant on the exciton binding energy (right axis) and power conversion efficiency (left axis) of an optimized organic photovoltaic cell.

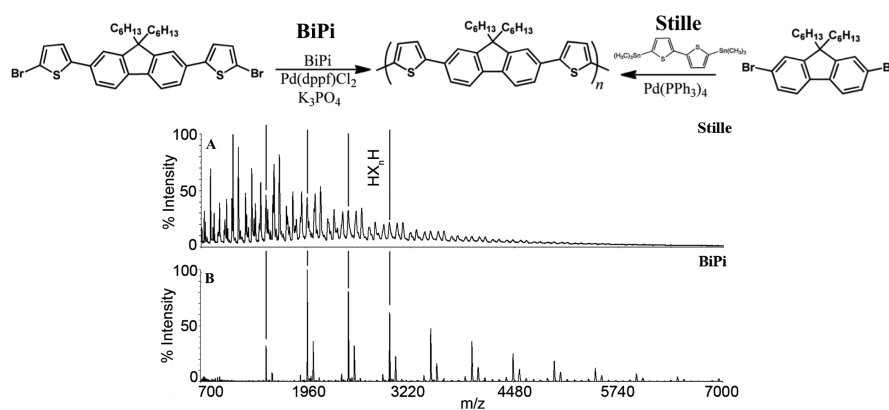


Figure 2. Two synthetic methods (top) to prepare the same copolymer; the new BiPi (left to right) and the traditional Stille (right to left) polymerizations. The MALDI-TOF spectra (bottom) of the resulting polymers show that, although they have the same structure on paper, in reality they are very different materials. The Stille polymerization (A) produces side-reactions, branching, and homocouplings while the BiPi method (B) produces chains that differ only by end-group (Br or H).

so without perturbing the band gap, orbital energies, and mobility. Highly efficient OPV devices of the (near) future will almost certainly have to take advantage of this additional parameter, ushering in a new class of polymeric materials.

Regardless of whether OPV devices are ultimately constructed in inverted architectures, with or without interfacial charged polymers, or what the dielectric constant is, no conjugated polymer will see commercial application without an industrially viable synthetic route. For instance, some of the better-known commercialized conjugated polymers, poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV), P3HT, and PEDOT/PSS, are synthesized via a Gilch reaction (initiated with an alkoxide base), a Grignard metathesis reaction (or using Rieke Zn), and oxidatively (using inorganic peroxides), respectively. These are all scalable polymerization reactions because they do not involve stoichiometric amounts of expensive metals or highly toxic intermediates. The current generation of donor polymers for OPV devices comprise A-B copolymers that incorporate electron-rich and poor monomers to tailor the band gap and energy levels; however, many of these copolymers are synthesized via Stille (stannane/arylhalide) cross-coupling reactions. While this synthetic strategy produces record-breaking OPV devices in the laboratory, the toxicity of stannanes adds unnecessary cost to manufacturing these materials on an industrial scale. Moreover, Stille-derived copolymers contain a high degree of defects, branch sites, and homocoupling, which may not negatively impact the performance of these materials in OPV devices (in fact, it may help in some cases), but it hinders reproducibility and adds considerable complexity to device-modeling. These effects can be seen clearly in Figure 2, which compares the MALDI-TOF spectra of a copolymer synthesized via a Stille polymerization to the same polymer prepared via the “BiPi” polymerization, which combines the Miyaura reaction with a Suzuki polycondensation to directly polymerize arylbromides.¹⁰ The BiPi polymerization is currently limited to symmetrical “macro-monomers,” but it shows that there are ways of synthesizing copolymers that are objectively of higher quality than those prepared by conventional routes and that eliminate the use of stannanes. Berrouard et al. recently reported an exceedingly simple strategy for eliminating stannanes in donor/acceptor copolymers: omit them.¹¹ For copolymers between electron-

rich and electron-poor monomers, the electron-poor coupling partner can be sufficiently activated to undergo direct arylation with a bromothiophene. This approach effectively omits the use of tin and the need to halogenate one of the coupling partners but, as the authors demonstrate, produces polymers with ideal, if not slightly better, properties than their Stille-synthesized analogs.

Past is prologue for polymer electronics; the early vision of materials that combine the properties of semiconductors and plastics has become a reality in the 21st century, but the remarkable innovation of researchers in silicon/inorganic semiconductor technology has reduced the quest for the large-scale commercial success of polymer electronics to cost/performance ratios. This axiom is particularly evident for OPV devices, which are currently the most likely vehicle for the widespread application of electroactive polymers and true polymer-electronic devices. The prevalence of charged and interfacial polymers indicate that state-of-the-art conjugated polymers (and devices) have learned from the successes of PEDOT/PSS, leveraging charge and water compatibility for functionality that is unique to polymeric materials. The near future will almost certainly yield methods for tailoring the dielectric properties of conjugated polymers, which will directly benefit all polymer electronics as light-emitting devices, field-effect transistors, sensors, and so on, all benefit from the enhanced screening of charge-carriers. Further, in the future, the chemistry underlying conjugated polymers will likely experience a renaissance as the push toward carbon-neutral technologies excludes organic solvents from thin-film processing and more chemistry moves into renewable solvents. Perhaps we will someday realize conjugated polymers that are synthesized with the precision of DNA, possibly even enzymatically, but in the mean time, conjugated polymers and polymer electronics, in general, have a bright future full of exciting innovation ahead.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: r.c.chiechi@rug.nl; j.c.hummelen@rug.nl.

Notes

The authors declare no competing financial interest.

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