

NEW CONDUCTING AND SEMICONDUCTING POLYMERS FOR ORGANIC PHOTOVOLTAICS

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INTRODUCTION

In the emerging field of printable organic electronics, such as emissive displays and organic photovoltaics (OPVs), there is a significant need for improved conducting and semiconducting materials. This paper reports our recent progress in two fields: 1) the development of solvent-based dispersions of the intrinsically conducting polymer (ICP) poly(3,4-ethylenedioxythiophene) (PEDOT) and 2) the synthesis of new electron-deficient (acceptor) semiconducting polymers.

PEDOT COPOLYMERS IN ORGANIC SOLVENT DISPERSIONS

ICPs are polymers with extended pi conjugation along the molecular backbone, and their conductivity can be changed by several orders of magnitude from a semiconducting state to a metallic state by doping. P-doping is achieved by partial oxidation of the polymer by a chemical oxidant or an electrochemical method, and causes depopulation of the bonding pi orbital (HOMO) with the formation of "holes" [1].

Despite the promises of ICPs since their discovery in the 70s, relatively few commercial products have succeeded, primarily because of their limited performance and inherent insolubility, which makes processing difficult. PEDOT is one of the most commonly used ICPs because of its good electrical conductivity, environmental stability in the doped (conducting) form, and reasonable optical transparency when used as a thin film [2]. A common way to apply a PEDOT coating is to use a water dispersion consisting of a blend of PEDOT and the polyanion poly(styrene sulfonate) or PEDOT-PSS. Doped PEDOT-PSS blends are manufactured by H.C. Starck and are marketed under the trade name of Clevios® P. Several grades of Clevios® P are available from Sigma-Aldrich (655201, 483095, 560596). A low-conductivity grade has been successfully employed as the hole injection layer in organic LEDs (OLEDs) and OPVs and the high conductivity grades are being evaluated as transparent conductors with work functions of ca. 5.1 eV [3,4].

Despite the success of the PEDOT-PSS blends, it has been shown that the presence of the strongly acidic and hygroscopic PSS can sometimes degrade device lifetime and performance [5-7]. With recent advances in flexible, printed electronic devices, there is increasing interest in optically transparent conducting polymer materials that can be processed from non-hygroscopic solvents and that will wet hydrophobic plastic substrates.

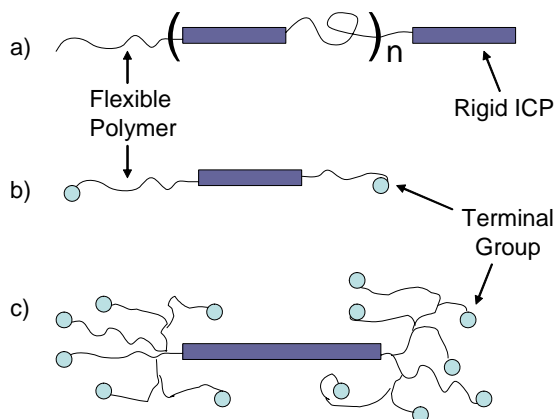


Fig. 1. Various structures of TDA block copolymers: linear multiblock (a), linear triblock (b), and hyperbranched (c): the dark blue rectangles represent the rigid blocks of doped PEDOT, and the curly lines represent blocks of PEG.

TDA Research, Inc. (TDA) developed and manufactures solvent-dispersible forms of PEDOT. Selected grades of these materials are available through Sigma-Aldrich under the trademark Aedotron™ materials. Our approach is to synthesize block copolymers of doped PEDOT and a flexible, soluble polymer such as poly(ethylene glycol) (PEG) [8]. We have developed a number of block copolymer geometries (Fig. 1) and found that through careful control of block composition, molecular weight, block ratio, and dopant type, we can vary the bulk conductivity of the copolymers from 10^{-4} S/cm to 60 S/cm. Fig. 2 shows the chemical structure of both a multi-block and tri-block structure of PEDOT-PEG copolymer. We

have developed methods to purify and process our copolymers to form stable colloidal dispersions in organic solvents. These dispersions are neither acidic nor corrosive, and can be used to spin cast or otherwise apply non-hygroscopic thin films of the copolymers on a variety of inorganic and organic substrates. These colloidal dispersions are stabilized by the highly solvated PEG chains which sterically limit the aggregation of the PEDOT blocks. Our copolymers easily disperse in polar aprotic solvents; we have selected propylene carbonate for applications that require a high boiling solvent, and nitromethane for applications that require a volatile solvent. Other solvents are being explored, especially for the low conductivity materials.

Since the colloidal stabilization mechanism in our products is independent from the polymer doping, the dopant can be controllably varied to tune the bulk conductivity and the work function of our copolymers. Typically, *para*-toluenesulphonate (PTS) doped copolymers (Aedotron™ P polymers) have a lower conductivity, making them useful for antistatic dissipation applications and as an electrode interface layer in OLEDs.

Aedotron™ P polymers typically have larger particle sizes in suspension and are somewhat amenable to being dispersed in less polar solvents. Perchlorate-doped copolymers (Aedotron™ C polymers) typically have a higher conductivity with thin films that are more transparent. With the improved tri-block copolymer (Aedotron™ C-3 polymer, Fig. 2B) we can spin cast thin films with 1000 Ohms/square sheet resistance at 80% transmittance (400-800 nm average) with good wetting properties on polycarbonate and other plastic films.

Fig. 3 shows the UV-vis spectra for 1, 2, and 3-layer films spun on glass at 1000 RPM, and each data trace is labeled with the measured sheet resistance for that film. These properties meet requirements for a transparent conductor that can be used in touch sensitive displays and electroluminescent lamps and displays. The tri-block

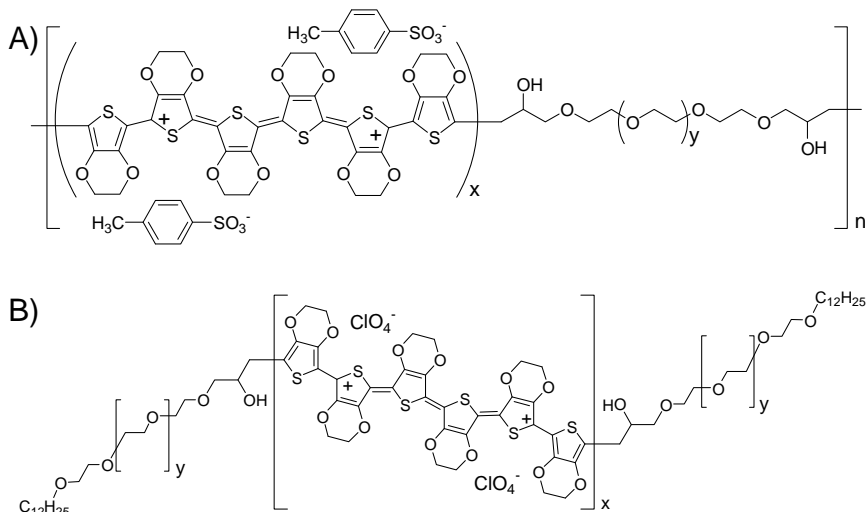


Fig. 2. Chemical structure of TDA's multi-block (a) and tri-block (b) PEDOT-PEG block copolymers.

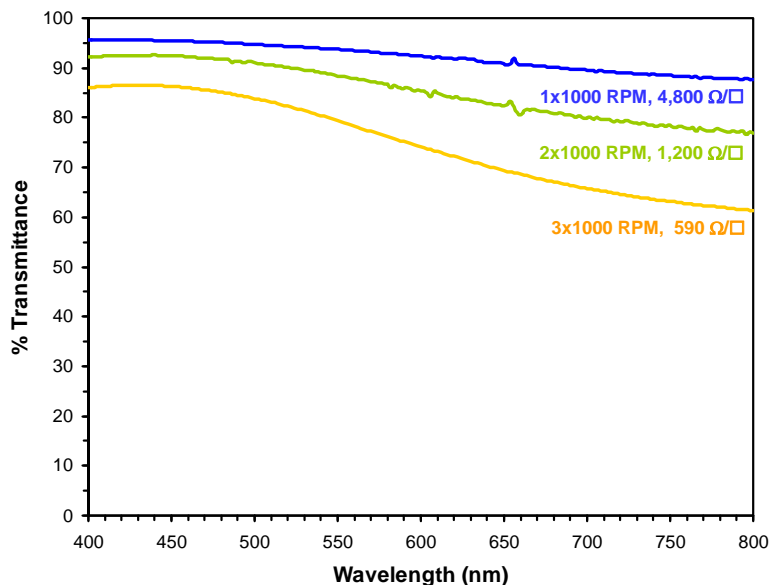


Fig. 3. UV-visible spectra of TDA's new, high-conductivity, tri-block copolymer spin cast at 1000 RPM; 1, 2, & 3-layer films are shown and labeled with the corresponding sheet resistance.

copolymer has smaller particle size (290 nm) in suspension than our multi-block copolymers, and form thin films with lower surface roughness (<10 nm), as determined by contact-mode Atomic Force Microscopy.

Relative electronic band energies of materials in different layers are important to consider in designing multilayer devices. The work functions of our multi-block copolymers were measured using x-ray photoelectron spectroscopy and were found to be lower than the work function of PEDOT-PSS blends (~4.2 eV for Aedotron™ P polymers and 4.3 eV for Aedotron™ C polymers) [9]. This lower work function must be taken into account when fabricating thin film electronic devices in which the alignment or overlap of electronic bands is crucial.

Table 1 summarizes the properties of the commercial grades of our Aedotron™ copolymers that are commercially available.

Table 1. Comparative Table of TDA's Conducting Polymer Products.

Trade Name	Aedotron™ C-NM	Aedotron™ C-PC	Aedotron™ P-NM	Aedotron™ C3-NM
Basic Description	Perchlorate-doped multiblock copolymer in nitromethane	Perchlorate-doped multiblock copolymer in propylene carbonate	PTS-doped multiblock copolymer in nitromethane	Perchlorate-doped triblock copolymer in nitromethane
Bulk conductivity (S/cm)	0.5-5	0.5-5	10^{-2} - 10^{-4}	10-60
Sheet resistance, Spin Cast Thin Films* (Ohms/square)	10^4 - 10^5			600-3000
Average transmittance** (%T)	70-85%			70%-85%
Particle size in suspension (nm)	600-1000			200-600
RMS roughness spin cast thin films (nm)	40			10
Work Function (eV)	4.33		4.19	
Main Characteristics	General purpose, moderate conductivity dispersion in volatile solvent	General purpose, moderate conductivity dispersion in low-volatility solvent	Hole Injection Layers and low conductivity applications	High transparency and high conductivity dispersion in volatile solvent

* Typically 1-3 layers spun at 1000 RPM or higher

** %T averaged from 400-800 nm, background to Corning Glass

NEW POLYMERIC ACCEPTORS

The unifying basic requirement of most thin-film, organic electronic devices like OLEDs and OPVs is that they contain at least two semiconducting materials with offsets in their molecular orbital (HOMO-LUMO) energetic levels. In the organic semiconductor world, one can create such an energy offset by forming an interface between a more electron-rich (donor) semiconductor and an electron-poor (acceptor) material. It is at this interface where charge separation or recombination typically occurs. Moreover, the extent of the offset and the proper alignment of the HOMO-LUMO bands of the donor and acceptor semiconductors are critical to the efficient operation of the device. It is therefore important to have a wide variety of donor and acceptor materials to choose from. There are a number of available classes of relatively electron-rich, semiconducting donor molecules and polymers. In contrast, there are few electron-poor, semiconducting acceptor molecules, like metalloporphyrins and methanofullerenes. Even rarer are the semiconducting, pi conjugated acceptor polymers like cyano-derivatives of poly(p-phenylenevinylenes).

Our group has been working to develop and produce new semiconducting, pi conjugated, acceptor polymers and oligomers. Our approach is quite similar to what has been done for many years to produce electron-rich, donor conducting polymers; we introduce a heteroatom to the pi conjugated backbone that can alter the electron density of the overall polymer. The heteroatom that we add is boron, whose vacant p orbitals are conjugated to the pi electronic system of unsaturated repeat units of the polymer. Because of the absence of electrons in the boron p orbitals, the overall pi electronic system of the polymer becomes inherently electron-deficient and, therefore, the polymer has acceptor-like electronic properties.

Several different synthetic methods are available to prepare air stable pi conjugated organoboron polymers [10-15]. Our group has prepared a number of both new and previously reported pi conjugated organoboron polymers and oligomers. Fig. 4 shows representative chemical structures of the polymers we have been studying. Over the past few years we have refined their synthesis and purification, characterized their properties as organic semiconductors, and evaluated their performance in thin film devices [16]. TDA just begun manufacturing selected pi conjugated organoboron polymers and oligomers under the trade name of Boramer™ materials, which are available at Sigma-Aldrich. Additional pi conjugated organoboron structures are currently under development and investigation with funding from NASA.

We have found that careful purification of the polymers is critical to preserve the solubility of these materials. Chloroform and chlorobenzene are preferred solvents for most of these polymers. All the prepared organoboron polymers are colored and the majority are strongly photoluminescent in the blue to green region of the visible spectrum (see Fig. 5). Air-stability has not been fully assessed yet, but preliminary evidence indicates that it varies with the polymer structure. Boramer™ T01 polymer is more sensitive to air than Boramer™ TC03 polymer. Since we have yet to quantify their air-stability, we prefer to handle both materials under an inert atmosphere.

The electronic band structure of selected Boramer™ materials was characterized via ultraviolet photoelectron spectroscopy (UPS) at Colorado State University (Fort Collins, CO). UPS gives a direct measure of the electron energies of the HOMO level to Fermi level gap at the low binding energy end of the spectrum. UPS results conclusively prove that our polymers are in fact acceptor semiconductors and that their valence band (VB) resides at a similar energy to the VB of other common acceptor organic semiconductors including methanofullerenes (PCBM) and cyano-PPV. The polymer bandgap was estimated from UV-Vis spectra and was found to be in the range of 2.6-2.9 eV. Fig. 6 shows the HOMO-LUMO levels of two of our boron-containing, pi conjugated polymers (orange) along with familiar donor (blue) and other acceptor organic materials (green). The energy level data clearly indicate their acceptor-like character, with Boramer™ T01 having the lowest lying work function and HOMO-LUMO levels.

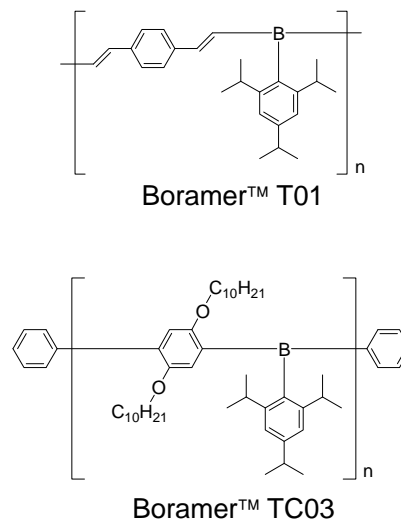


Fig. 4. Chemical structure of TDA's boron-containing, n-type polymers.

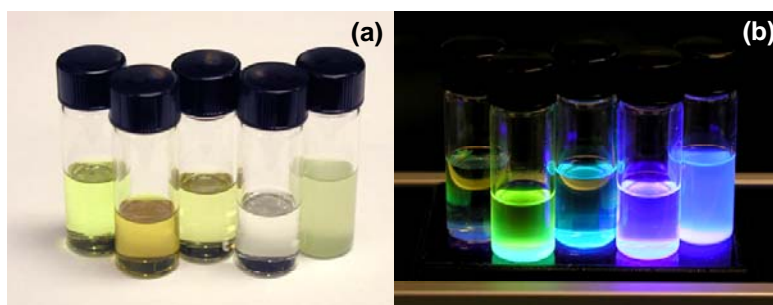


Fig. 5. Chloroform solutions of TDA's boron-containing, n-type polymers under ambient (a) and ultraviolet (b) lighting.

During our work on these new acceptor materials we collaborated with the National Renewable Energy Laboratory (NREL, Golden, CO) to evaluate the properties of our polymers for use in OPV prototypes. NREL carried out photoluminescence quenching (PLQ) experiments and built OPV devices with two of the materials supplied by TDA. Results from PLQ indicated that our polymers efficiently quench the excited state of a typical donor semiconductor (MDMO-PPV) with efficiencies up to 83%. This indicates that, in fact, efficient electron transfer occurs from this donor semiconductor to our material. One of the prepared polymers was also used as the electron-transmitting and light-emitting layer for the fabrication of an OLED prototype. Bright green light emission was observed (similar in color to the solid-state luminescence of our polymer) at a turn-on voltage of ca. 6 Volts.

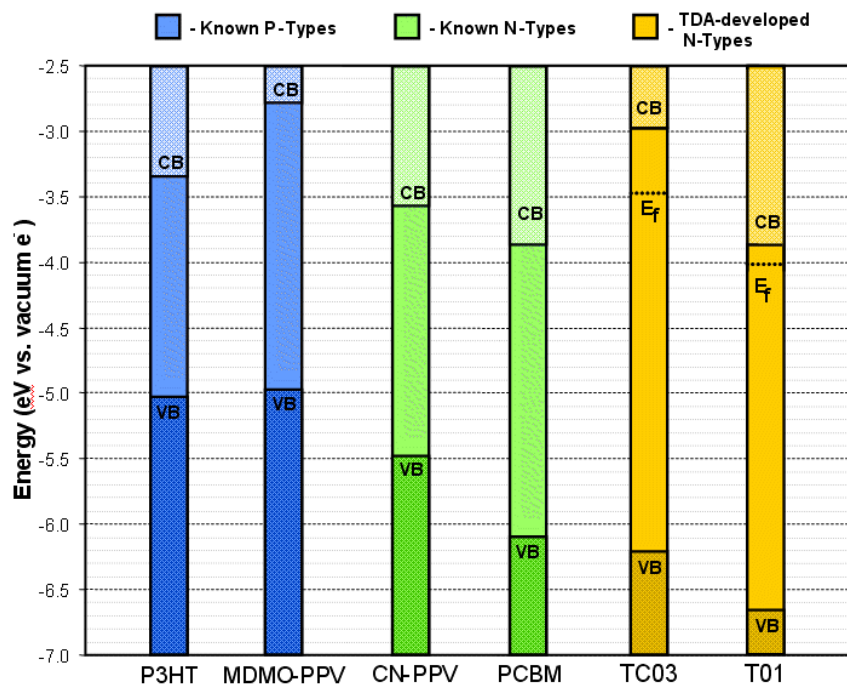


Fig. 6. Energy level diagram of HOMO-LUMO levels for known donor and acceptor organic semiconducting materials, including TDA's new acceptor materials.

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REFERENCES

- [1] MacDiarmid, A.G. *Angew. Chem. Int. Ed.*, **40**, 2581-2590, 2001.
- [2] Groenendaal, L.; Dhaen, J.; Manca, J.; Van Luppen, J.; Verdonck, E.; Louwet, F.; Leenders, L. *Synth. Met.*, **135-136**, 115-117, 2003.
- [3] Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature*, **395**, 257-260, 1998.
- [4] Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A.J. *Synth. Met.*, **87**, 171-174, 2003.
- [5] Kawano, K.; Pacios, R.; Poplavskyy, D.; Nelson, J.; Bradley, D.; Durrant, J. R. *Solar Energy Materials & Solar Cells*, **90**, 3520-3530, 2006.
- [6] Danier Van Der Gon, A.W.; Birgerson, J.; Fahlman, M.; Salaneck, W.R. *Org. Electr.*, **3**, 111-118, 2002.
- [7] Greczynski, G.; Kugler, T.; Keil, M.; Osikowicz, W.; Fahlman, M.; Salaneck, W. R. *J. Elec. Spectr. & Rel. Phenom.*, **121**, 1-17, 2001.

- [8] Luebben, S.; Elliott, B.; Wilson, C. "Poly(heteroaromatic) Block Copolymers with Electrical Conductivity," U.S. Patent 7,361,728 B1 Issued on April 22, 2008.
- [9] Sapp, S.; Luebben, S.; Jeppson, P.; Shulz, D.L.; Caruso, A.N. *Appl. Phys. Lett.*, **88**, 152107(1-3), 2006.
- [10] Chujo, Y.; Miyata, M.; Matsumi, N. *Polymer Bulletin*, **42**, 505-510, 1999.
- [11] Chujo, Y.; Miyata, M.; Matsumi, N. *Macromolecules*, **32**, 4467-4469, 1999.
- [12] Chujo, Y.; Naka, K.; Matsumi, N. *J. Am. Chem. Soc.*, **120**, 10776-10777, 1998.
- [13] Chujo, Y.; Umeyama, T.; Matsumi, N. *Polymer Bulletin*, **44**, 431-436, 2002.
- [14] Jäkle, F.; Sundararaman, A.; Victor, M.; Varughese, R. *J. Am. Chem. Soc.*, **127**, 13748-13749, 2005.
- [15] Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.*, **128**, 12879-12885, 2006.
- [16] Luebben, S.; Sapp, S.A. "Use of Pi-conjugated Organoboron Polymers in Thin-film Organic-Polymer Electronic Devices" PCT Patent Application PCT/US07/64328.