

## Organic solvent processable Oligotron™ conducting triblock copolymers for microelectronics: functional end-capped conducting oligomers.

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Over the past several years, TDA Research, Inc. has been developing solvent processable forms of poly(3,4-ethylenedioxythiophene) commonly known as "PEDOT". Our approach is to make block copolymers with alternating conducting and non-conducting blocks. The conducting segments provide the electronic properties, while the non-conducting segments are designed to promote dispersion. TDA has two lines of conducting polymer products named Aedotron™ and Oligotron™, and this paper focuses on our family of ABA end-capped oligomers (trade named Oligotron™). These capped oligomers have a center block consisting of PEDOT and two non-conducting end-capping blocks, which can contain polymerizable methacrylate groups (see Figure 1). Oligotron™ oligomers are dispersible in non-corrosive organic solvents and can be used to dip coat, spin coat or print thin films for electronic devices. The oligomers that have polymerizable methacrylate groups in the end-caps, can theoretically be printed using a lithographic technique by crosslinking the oligomers at the methacrylate groups to render them fixed in place. Alternatively, the organic dispersion containing the conducting oligomers can be formulated into inks for inkjet printing with a post photo-initiated or thermal-initiated curing step. These printing techniques could potentially be used to produce detailed patterns of PEDOT conducting materials for microelectronic applications. TDA Research has made quantities of the methacrylate end-capped oligomer (compound **2** in Figure 1) commercially available for research and development through Sigma-Aldrich as a dispersion in either propylene carbonate or nitromethane. (The propylene carbonate dispersion is Aldrich product number 649813, and the nitromethane is number 649821.)

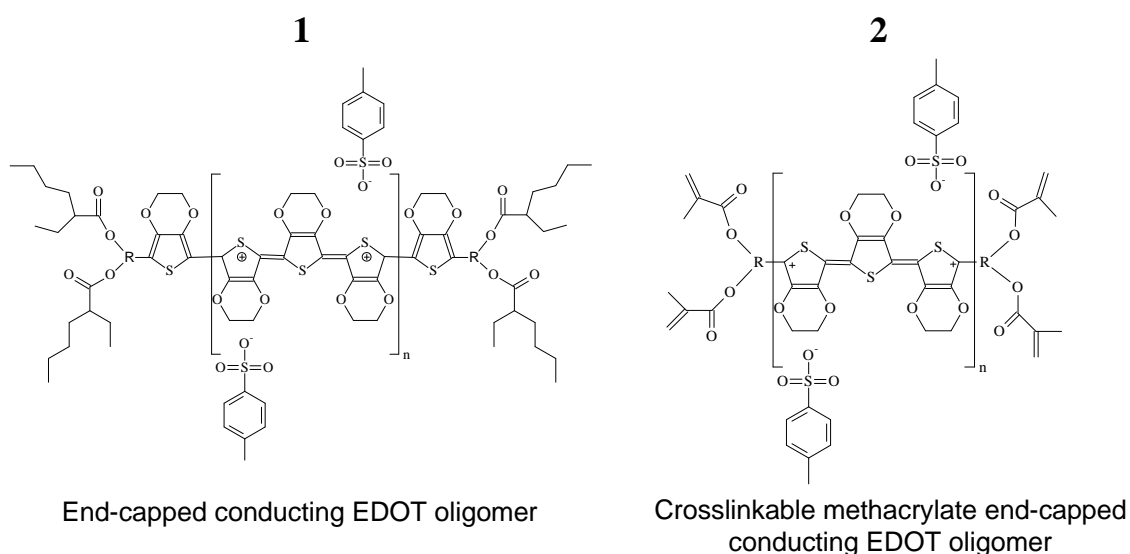


Figure 1. Structure of TDA's end-capped conducting PEDOT oligomers.

A number of versions of PEDOT are commercially available as a PEDOT / polystyrene sulfonic acid (PSS) dispersion in water (under the trade name of Baytron® P, H.C. Starck). A small portion of the PSS acts as the dopant to PEDOT and the remainder stabilizes the aqueous dispersion. This material has been used as an electrode in capacitors, as antistatic treatments for photographic film, as electrodes in thin film transistors, and as hole-injection layers in organic light-emitting diodes (OLEDs). However, in some of these applications the use of highly acidic polystyrene sulfonate causes problems. For example, in OLEDs, PEDOT/PSS is used as a smoothing and hole injection layer between the indium tin oxide anode (ITO) and the light emitting materials. OLEDs that include this hole-injection and smoothing layer outperform those without it. However, the excess acid content from the PSS has been shown to contribute to the premature failure of these devices by etching the ITO during manufacturing. Therefore, a non-corrosive solvent processable form of PEDOT would be useful in those applications where the aqueous-based dispersion is incompatible.

The fundamental problem with attempting to make an organic dispersible conducting polymer is that conducting polymers are inherently non-soluble and intractable. Conducting polymers contain an extended conjugation in the polymer backbone resulting from alternating double and single bonds. When a conducting polymer such as poly(thiophene) is doped to create holes in the valence band, the polymer becomes conductive (p-type conductor) and the conjugated double bonds align in a single plane. Extended conduction requires holes to hop frequently from one polymer chain to another. Electrons (holes) can hop from chain to chain because the planar configuration allows the polymer chains to stack tightly together with pi-pi interactions. It is this chain aggregation that helps produce the long-range electronic conductivity. Unfortunately, because conducting polymers are molecular rigid rods and form hard aggregates, they are non-soluble and non-processable.

Recognizing this, we made end-capped oligomers with a central block of PEDOT surrounded by non-conducting soluble end-caps. These end-caps render the conducting oligomer dispersible in organic solvents, presumably by preventing large, hard aggregates from forming. However, the central blocks of the oligomer can organize sufficiently to form crystalline regions of conducting polymer. As long as the volume fraction of these conducting regions is high enough to form a continuous percolating phase, and the oligomer length is long enough to allow for doping (hole formation) and conductivity, the resulting material has a conductivity similar to that of the individual conducting phase (i.e. similar to bulk homopolymerized PEDOT).

The end-capped oligomers are produced

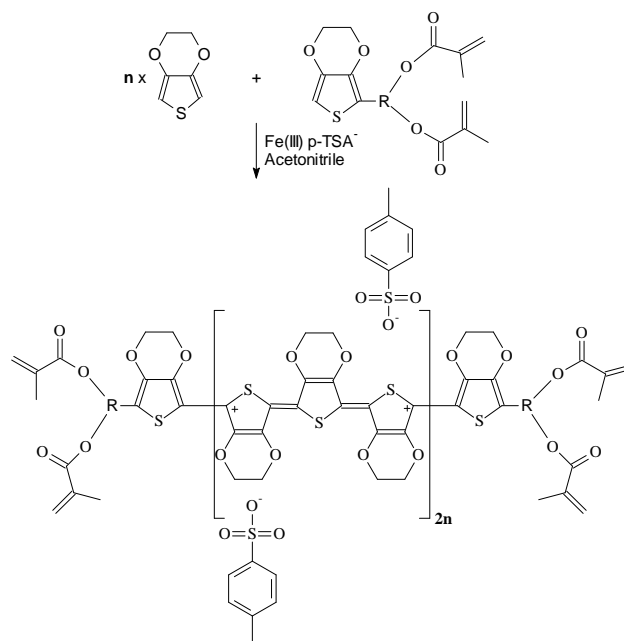


Figure 2. Oxidative polymerization forming the end-capped oligomers.

by an oxidative copolymerization of EDOT end-capping monomers and EDOT monomers (United States patent application No. US2003/0088032 A1). Figure 2 illustrates the synthesis of end-capped oligomers using EDOT monomers and pre-formed EDOT end-capping monomers. In the example illustrated the end-capping monomers contain two methacrylate groups. Iron(III) salts are used as the oxidant for the polymerization as well as for doping the formed conducting oligomer. The materials produced using this production method have a theoretical statistical average oligomer length that is set by the stoichiometry of the EDOT and end-capping monomer.

It is generally known that oligomers of PEDOT must have a certain minimum length for the formation of a conducting bi-polaron structure resulting from oxidative doping. The oligomer must be at least 6 EDOT units long to theoretically form a conducting bi-polaron. As the oligomer length increases the conductivity increases and eventually reaches a maximum conductivity (the conductivity of bulk homo-polymerized PEDOT). We have demonstrated this increase in conductivity versus oligomer length with end-capped PEDOT oligomers

(capped with the methacrylate end-cap in Figure 2). Figure 3 illustrates the conductivity of end-capped PEDOT oligomers with varying lengths (i.e. theoretical number of EDOT repeat units). As the chart shows, the conductivity for the perchlorate-doped oligomers is higher than the para-toluenesulfonate doped materials. The doping level is 0.3 mole oxidant to 1.0 mole EDOT monomer. As the length of the oligomer increases the conductivity increases sharply and then levels off. The maximum conductivity is close to the conductivity for the bulk homopolymer (PEDOT), when the homopolymer is formed and doped with either perchlorate or para-toluene sulfonate under identical conditions (but without the end-capping monomers). The bulk conductivities for the homopolymers are 95 and 11 S/cm for the perchlorate and para-toluenesulfonate doped PEDOT, respectively.

The presence of the end-capping groups renders the oligomers dispersible in some organic solvents. Specifically, the end-capped oligomers with about 30 to 50 or fewer EDOT repeat units are dispersible in nitromethane and propylene carbonate. Shorter oligomers form more stable dispersions and are easier to disperse, although the conductivity decreases as the length is shortened. Typically dispersion methods involve treating the mixture of solvent and conducting oligomer with sonication for 15 minutes to several hours (depending on the oligomer length and solvent).

Several process have been investigated for using these end-capped oligomer dispersions for electronic applications. These methods include dip and dry processing methods for producing tantalum capacitors, spin coating for forming transparent thin film electrodes or antistatic layers, blending with polymers to form antistatic materials, and either lithographic or

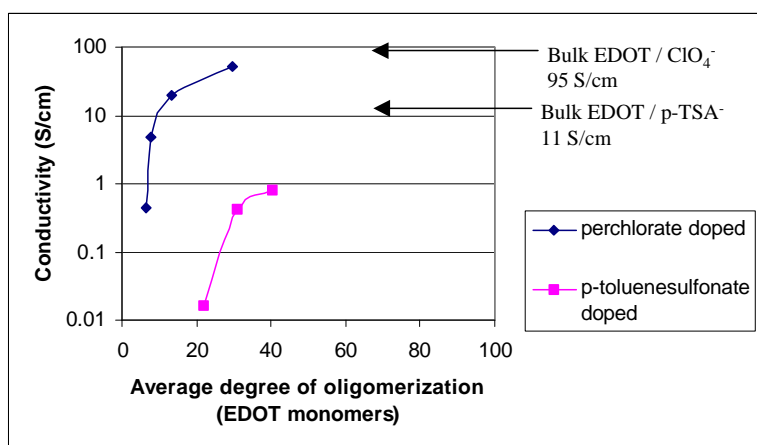


Figure 3. Conductivity vs. degree of oligomerization for end-capped PEDOT conducting oligomers doped with either perchlorate or p-toluene sulfonate.

inkjet printing to form patterned hole injection thin films for OLED displays, etc. In general dispersions in nitromethane are used when rapid evaporation is required, such as spin coating, dip coating (at room temperature). The propylene carbonate dispersions are preferred when an environmentally friendly solvent is required, or the process can be performed at elevated temperatures or under vacuum for evaporation, including for blending with other monomers and polymers, or for formulating inkjet printable inks.

Spin coating requires a fine dispersion in a volatile solvent. Particle size, evaporation rate and spinning speed are important factors affecting the quality of the spin-coated film. The methacrylate end-capped EDOT oligomer (Compound 2 in Figure 1) can be spin coated on float glass or polycarbonate from a 0.5 wt% dispersion in nitromethane. The PEDOT oligomer is doped with para-toluenesulfonate and has a bulk conductivity of 0.1 S/cm as measured by a four-point probe. (This nitromethane dispersion is Aldrich product # 649821). A 1-inch by 1-inch piece of float glass was cleaned with acetone and loaded into a spin coater. The surface was cleaned again with acetone, followed by spinning at 2,000 rpm

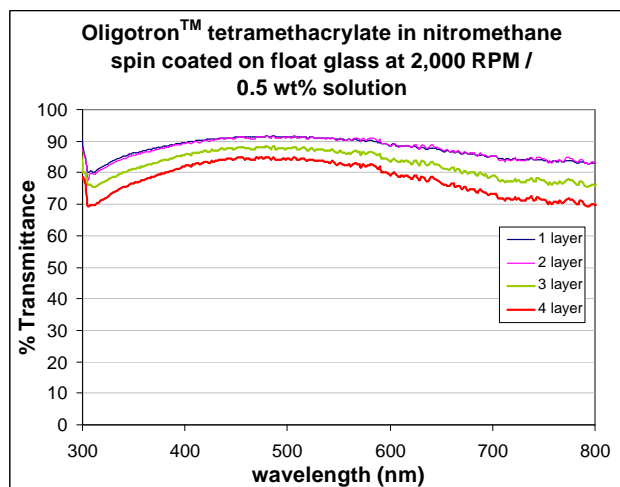


Figure 4. Visible light transmittance for spin coated Oligotron™ films.

for 25 seconds to dry. The conducting oligomer in nitromethane dispersion was first prepared by vigorous agitation and sonication for 15 minutes and then was placed on top of the float glass by pipet. Spin speeds from 400 to 3,000 rpm resulted in thin films. Slower speeds (around 400 rpm) resulted in some ridging, while higher speeds (2,000 rpm and higher) made very uniform thin films. A single layer of the film deposited at 400 rpm has a surface resistance of 33 M ohm / square (with 90% transmittance at 500 nm, and 85% transmittance at 700 nm). Films produced at 400 rpm had defects (ridging) visible to the eye. However, films made by spinning at 2,000 rpm had excellent uniformity. Multiple layers coated at 2,000 rpm resulted in films with a surface resistance lower than 10 M ohm / square. For example 2 layers spin coated at 2,000 rpm each resulted in a film with a surface resistance > 100 M ohm / square, while 3 layers at 2,000 rpm resulted in 9.2 M ohm / square, and 4 layers at 2,000 rpm resulted in 3.8 M ohm / square. The transmittance of the visible light spectrum for these films coated at 2,000 rpm are shown in Figure 4. For example, the coating made from 4 layers (3.8 M ohm / square) had a transmittance of 84% at 500 nm and 72% at 700 nm. The clarity of the films is shown in Figure 5, where the coated float glass samples on the surface of a lap top computer display. Thus, the samples are shown under back-lighting conditions.

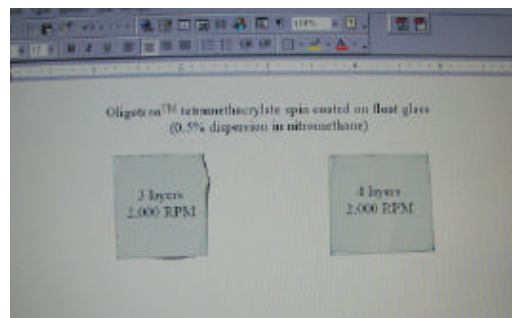


Figure 5. Samples of float glass coated with conducting PEDOT oligomers (shown on a lap top display)

Inkjet printing requires specific evaporation rates, viscosities and surface tensions for the ink. Nitromethane evaporates too quickly and would dry at the inkjet head, causing blockage. However, propylene carbonate is a suitable solvent for inkjet printing, if a heat /

vacuum step can be used to remove the propylene carbonate solvent after the image is printed. At ambient pressure the printed image must be heated to 150 - 200°C. The viscosity of a propylene carbonate 0.5% conducting oligomer dispersion (Aldrich product number 649813) must be increased to 8 -12 mPa s for proper printing. Adding dipropylene glycol (1 to 1 mass fraction) to the propylene carbonate 0.5% oligomer dispersion increases the viscosity to the required level for inkjet printing, while maintaining a stable dispersion. Alternatively, adding 0.1 to 0.5% polypropylene carbonate also increases the viscosity while maintaining a stable dispersion. We are currently investigating appropriate additives that will modify the surface tension while maintaining a stable dispersion. We will then demonstrate inkjet printing of our non-aqueous PEDOT dispersion.

Lithographic printing of a positive resist can in theory be accomplished by selectively crosslinking PEDOT oligomers containing methacrylate groups in the end-caps. The process involves formulating ink containing the oligomers dispersed in an organic solvent, combined with co-monomers and photoinitiators. Ultra-violet light is selectively exposed to the regions where PEDOT must remain, while the non-exposed regions are rinsed away.

We have demonstrated that this process is possible by mixing the propylene carbonate dispersion at a 1 to 1 mass ratio with poly(ethyleneglycol<sub>200</sub>) diacrylate containing 3 (wt)% 2,2-dimethoxy-2-phenylacetophenone. The mixture was pressed between two glass plates and selectively exposed to 5,000 mW/cm<sup>2</sup> (320-500 nm) light for 10 seconds under nitrogen. As Figure 6 illustrates, we were able to print the letters "NSF" using this conducting ink. The non-exposed regions were rinsed away, leaving the conducting printed image shown.

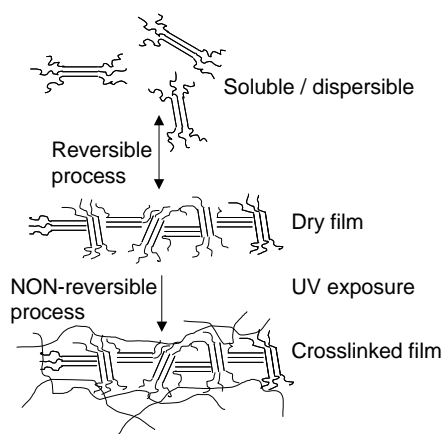


Figure 6. Demonstrating the photoprinting of a positive resist containing the organic-dispersed end-capped oligomers.

In conclusion we have developed end-capped conducting oligomers of PEDOT which are dispersible in organic solvents. We have shown how the conductivity of doped PEDOT oligomers increases with oligomer length. These organic dispersible conducting oligomer materials may overcome the problems encountered by PEDOT/PSS aqueous dispersions, which are highly acidic and degrade ITO and other materials they come in contact with during device production. The organic dispersed conducting oligomers can be used to produce electronic devices by dip and dry methods as well as spin coating, photolithography or inkjet printing. In some cases, device production methods require the addition of additives to the organic dispersion. For example, viscosity or surface tension modifiers, co-monomers and photoinitiators can be added to the organic dispersions.

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