

Anisotropic Properties of Conducting Polymers Prepared by Liquid Crystal Templating**

By James F. Hulvat and Samuel I. Stupp*

Conducting polymers receive considerable attention due to their combination of useful mechanical, optical, and electronic properties. In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) is widely studied because it is transparent, flexible, easy to prepare, highly conductive, and more environmentally stable than most other conducting polymers.^[1] PEDOT is already employed in several commercial applications, but its greatest potential impact is on organic light-emitting diodes (OLEDs), in the form of PEDOT coated indium tin oxide (ITO) anodes.^[2,3] Aqueous PEDOT dispersions with the polyelectrolyte poly(styrene sulfonate) (PSS) have become a standard hole transport layer for OLEDs.^[4,5] Due to its low lying highest occupied molecular orbital (HOMO) level, PEDOT facilitates charge injection from ITO anodes into emissive polymers.

The formation of PEDOT occurs through chemical or electrochemical oxidation of the 3,4-ethylenedioxythiophene (EDOT) monomer. EDOT has been electropolymerized in polar organic solvents, in aqueous solutions of micellar surfactants, in polymer electrolytes, and in nanoporous membranes.^[3,6–9] Recently, we reported a novel method to prepare PEDOT films within a nanoscale, self-organized template.^[10] This approach utilizes an aqueous, lyotropic liquid crystal (LC) with a hexagonal mesophase to solubilize the monomer and direct its electropolymerization, leading to PEDOT films that replicate the texture and birefringence of the LC template. We have proposed that the structure observed in these templated films results from a directed aggregation of the oriented polymer chains, which collapse together when the LC template is removed.^[10] This is illustrated schematically in Figures 1a,b. Here we examine the optical absorption and conductivity of these films, which exhibit anisotropy arising from the ordered nanostructure of the LC template.

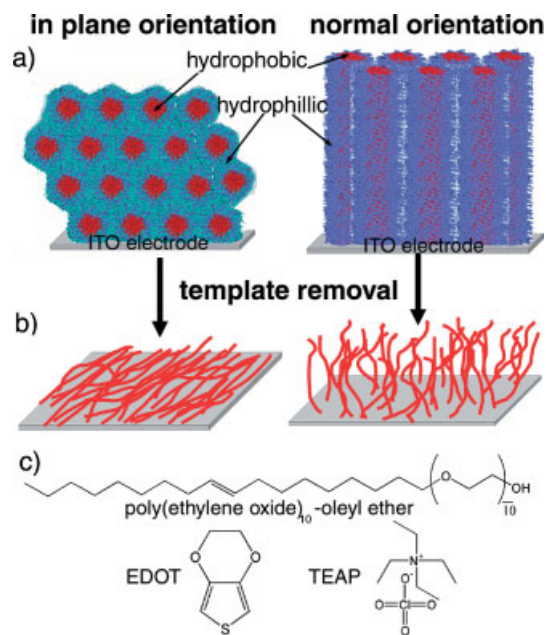


Figure 1. a) Illustration of a hexagonal (H1) lyotropic liquid crystal mesophase showing two possible orientations relative to the substrate. Cylindrical hydrophobic cores (red) solubilize EDOT monomer and direct electropolymerization. b) After LC template removal, PEDOT polymers adhered to the ITO retain a net orientation from the template, leading to either in-plane (left) or normal orientation (right). c) Chemical structure of the poly(ethylene oxide)₁₀-oleyl ether amphiphile, tetraethylammonium perchlorate (TEAP) supporting electrolyte and 3,4-ethylenedioxythiophene (EDOT) monomer.

Conductivity and optical properties of PEDOT films vary dramatically with preparation conditions. Reported conductivities range from ~ 0.1 to 1000 S cm^{-1} , depending on doping level, counter ion, and the incorporation of various other additives during film formation.^[2,5,7,11] Anisotropy in conducting polymers has been attributed to the influence of polymer morphology and orientation on the effective conjugation length and the rate of interchain charge transfer.^[9,12] Several conduction mechanisms have been proposed for PEDOT, and ordering of polymer chains within a film ultimately determines which mechanism dominates.^[1,13] Understanding and improving the conductivity of PEDOT has been complicated in part by the difficulty in controlling the nanoscale structural order of PEDOT films. Unlike many well studied systems which are soluble or formed from soluble polymer precursors, such as poly(3-alkylthiophene) or poly(phenylene vinylene), PEDOT is insoluble, complicating film processing.

Conducting polymers such as PEDOT prepared by chemical or electrochemical polymerization are poorly ordered, consisting of amorphous material mixed with nanoscale crystalline domains.^[12,14,15] Spin-coating and chemical polymerization of PEDOT films can orient polymer chains parallel to the substrate, however orientation within the plane is generally random.^[11,13,16] Conducting polymer thin films have been aligned in-plane by Langmuir–Blodgett techniques, by stretching, rubbing, or with alignment layers.^[12,15,17] However,

[*] Prof. S. I. Stupp, J. F. Hulvat
Department of Materials Science & Engineering
Department of Chemistry
Feinberg School of Medicine
Northwestern University
Evanston, IL 60208–3108 (USA)
E-mail: s-stupp@northwestern.edu

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these techniques add additional processing steps and can present obstacles to incorporation in device architectures. In this work, we use a self-organized template to direct polymerization of EDOT, resulting in oriented polymer chains without the need for rubbing, stretching, or other mechanical alignment. Organizing soluble monomers in a template and locking order in during polymerization eliminates the need for subsequent processing to align PEDOT films. With this approach one can form large, uniform domains of PEDOT, molecularly oriented either in-plane or normal to the substrate, which is not possible with other alignment techniques.

LC templated PEDOT films were prepared as described previously.^[10] Briefly, ITO-glass substrates were used as the working electrode in an electrochemical cell filled with an aqueous, liquid crystalline gel of the amphiphile poly(ethylene oxide)₁₀-oleyl ether, EDOT, and tetraethylammonium perchlorate (Fig. 1c). The LC gel was heated to isotropization and then cooled, allowing the hexagonal mesophase to self-organize at the ITO interface. EDOT was then polymerized under a constant potential within the LC template, which was subsequently removed by washing in water, acetone, and dichloromethane and dried under vacuum. PEDOT was optically birefringent and adhered to the ITO surface. Its domains were commensurate with those of the LC template from which it was grown, and this birefringent texture was stable up to the decomposition temperature of PEDOT.^[10] Non-templated PEDOT films were prepared for comparison as above with the addition of acetonitrile to disrupt the LC mesophase and thus form an isotropic solution. These films were of the same chemical composition as the templated ones but showed no birefringence. Powder X-ray diffraction indicated no significant crystallinity for either templated or non-templated films. PEDOT film thickness was controlled by varying the charge density passed during the electropolymerization.

Figure 2a shows a polarized optical micrograph of a uniaxially birefringent domain in the templated PEDOT film, with its optic axis parallel to the substrate. The film was reduced at -0.3 V to shift its absorption peak (λ_{\max}) into the visible range. To quantify the optical anisotropy, a $200\ \mu\text{m}$ aperture was placed over the domain. Figures 2b,c shows the film switching uniformly from dark to bright upon 45° rotation between crossed polarizers, consistent with uniaxial, in-plane orientation. The UV-vis absorption spectrum in Figure 2d has a λ_{\max} at 520 nm, and the LC template with EDOT monomer tested before polymerization was transparent in this range. This observation indicates the absorption observed arises only from the PEDOT film. At the same time, absorption at 520 nm as a function of polarization angle was measured, revealing a sinusoidal variation in absorption with a period of 180° and thus confirming uniaxial orientation of the PEDOT film in the plane of the sample. Non-templated films showed no variation in absorption with polarization angle, indicating the PEDOT alignment observed arises directly from the self-organized LC template. The dichroic ratio A_{\parallel}/A_{\perp} was found to be 2.6 ± 0.3 , averaged for five spots with thicknesses of ~ 500 nm. This in-plane anisotropy is comparable to what has

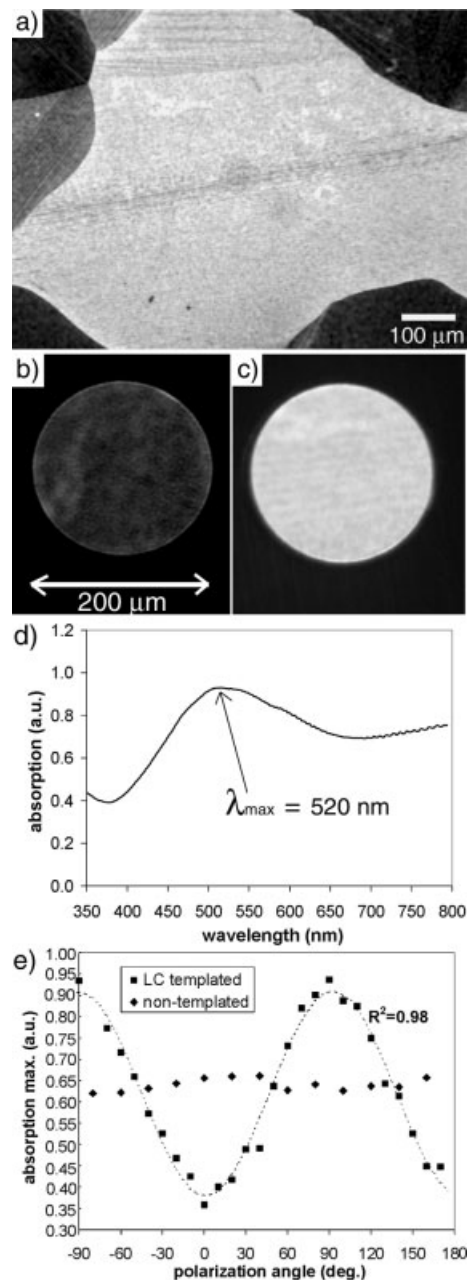


Figure 2. a) Optical micrograph of PEDOT film between crossed polarizers. Observed through an aperture, the film switches from b) dark to c) bright on 45° rotation between crossed polarizers, indicating uniaxial orientation. d) UV-vis absorption spectrum of LC templated PEDOT film. e) Absorption at 520 nm versus incident light polarization relative to the substrate (0° arbitrarily defined).

been reported for stretched polythiophene films on 400% drawing.^[12] With further optimization, this approach may prove useful to prepare PEDOT films as polarizing filters or alignment layers for OLEDs.

The in-plane conductivity of self-organized, templated PEDOT films was measured using a four-probe technique after transferring PEDOT films from ITO to an insulating sub-

strate. The average conductivity (without further doping) in the self-organized films was found to be nearly tripled relative to non-templated films of similar composition, $27 \pm 7 \text{ S cm}^{-1}$ versus $10 \pm 3 \text{ S cm}^{-1}$, respectively. Higher variability in LC templated films is not surprising, as each film was measured across multiple domains differing in orientation and separated by higher resistance boundaries. Despite this drawback, the threefold increase in conductivity due to LC templating indicates improved molecular ordering in the plane of films, in spite of the polydomain structure.

To investigate conductivity within single domains of the LC templated PEDOT film and exclude the effect of domain boundaries, a grid patterned ITO electrode was fabricated

(Fig. 3a). PEDOT was polymerized on the ITO grid and transferred to an insulating substrate. Each intersection could be isolated, allowing resistance measurement along two orthogonal directions in the plane of the film. Using polarized optical microscopy, intersections coinciding with templated PEDOT domains, with an optic axis aligned in-plane parallel to one measurement direction (Fig. 3b,c), as well as domains oriented normal to the surface, were identified. To analyze these measurements, we assumed that the optical axes of the film corresponded to the principle axes of the resistivity tensor and approximated $\sigma_{\parallel}/\sigma_{\perp} = R_{\perp}/R_{\parallel}$, which may not be valid for larger anisotropies. Domains oriented in-plane exhibited anisotropic conductivity ($\sigma_{\parallel}/\sigma_{\perp} = 2.4 \pm 0.2$) and showed similar absolute conductivity to that measured above ($\sigma_{\parallel} = 22 \pm 4 \text{ S cm}^{-1}$) (see Fig. 3e). This confirms alignment of the conductive polymer chains within the templated film. As expected, domains oriented normal to the substrate showed somewhat lower conductivity and no in-plane anisotropy ($\sigma_{\parallel} = 15 \pm 2 \text{ S cm}^{-1}$, $\sigma_{\parallel}/\sigma_{\perp} = 1.1 \pm 0.1$). These results are consistent with a conduction mechanism in which intra-chain transport dominates. In this system, inter-chain transport is likely hindered by the lack of crystallinity and the possible presence of residual amphiphile, which may create insulating regions between bundles of conducting polymers.

X-ray photoelectron spectroscopy (XPS) was used to determine the film composition and doping level.^[3] The chlorine/sulfur ratio (Cl/S) estimates the chlorine doping from ClO_4^- counter ions in the film after electropolymerization. LC templated and non-templated PEDOT films had Cl/S ratios of 0.52 and 0.54, respectively, indicating a similar doping level. The carbon/sulfur ratio (C/S) for templated PEDOT was 14.3, compared with 13.4 for non-templated films, and higher than the C/S value of 6 in pure PEDOT. This indicates ~45% of the LC amphiphile is entrapped in the film during polymerization. The film likely consists of a network of highly conductive PEDOT in an insulating matrix. Since a similar amount of amphiphile is present in both templated and non-templated films, however, any effect on conductivity must be due to the self-organized structure of the LC template.

Self-organized films of PEDOT electropolymerized in a hexagonal, lyotropic liquid crystalline template exhibit anisotropic absorption and conductivity, indicating alignment of the polymer by nanoscale hydrophobic channels in the liquid crystal. This facile, aqueous technique provides a unique and potentially useful method to modify the optical and electronic properties of conducting polymer films. Oriented layers of electroactive polymers could improve hole injection and increase efficiency of OLEDs, or serve as polarizing alignment layers for OLED backlighting of liquid crystal displays (LCDs). Further work is needed to control orientation, improve ordering, and minimize domain boundaries within the LC template. However, the ability to consistently produce aligned PEDOT domains as large as $500 \mu\text{m}$ in diameter demonstrates the feasibility of incorporating these anisotropic structures, formed with self-assembly techniques, into novel device architectures.

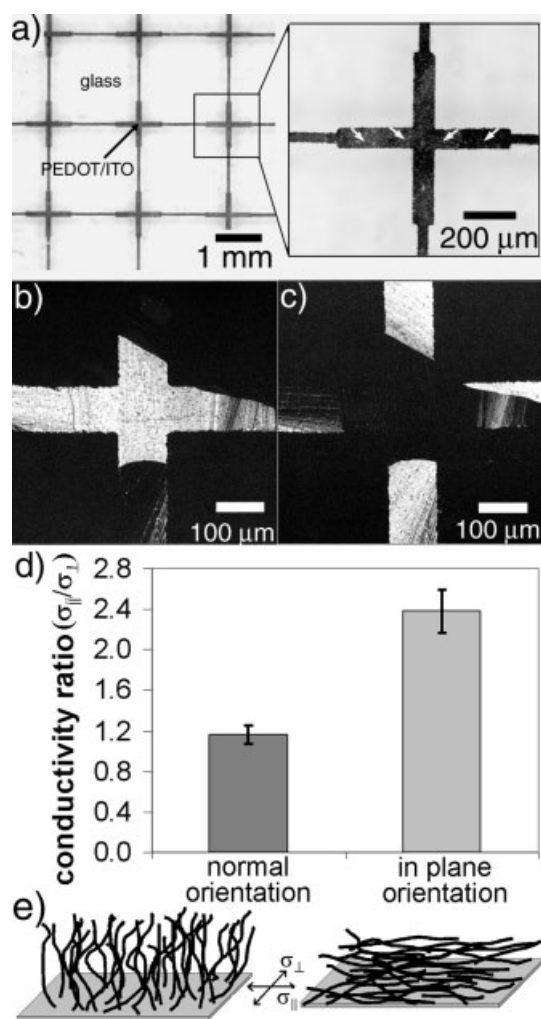


Figure 3. a) Optical micrograph of an LC templated conductive polymer film grown on a grid pattern. Resistivity at each intersection ($100 \mu\text{m} \times 100 \mu\text{m}$) can be measured independently along the vertical and horizontal direction. White arrows (inset) illustrate placement of a four-point probe for the horizontal measurement. Polarized optical microscopy shows a uniform, birefringent PEDOT domain at the intersection, switching from b) bright to c) dark upon 45° rotation. d) Conductivity anisotropy for different domain orientations. e) Schematic illustration of normal (left) and in-plane (right) orientation.

Experimental

A detailed procedure for growing LC templated PEDOT films on ITO is given elsewhere [10]. Absorption spectra were collected on a Cary 500 UV/VIS/NIR spectrometer in double beam mode with a linearly polarizing filter (Edmund Optics A43-785) mounted on a rotating goniometer in the sample beam. Spectra were normalized to the baseline absorption of the filter and the ITO substrate. Substrates for four-probe conductivity measurements were photolithographically patterned using Clariant AZ1518 photoresists and the exposed ITO was removed with HCl. Patterned substrates were cleaned and polymerized as above. After washing and removal of the LC template, PEDOT films were cast with a 20 wt.-% solution of a thermosetting poly(amide-imide) (42827-2, Aldrich) in 1-methyl-2-pyrrolidinone (NMP), heated to 150 °C for 2 h; the resulting film was lifted off, transferring the PEDOT film from ITO to the insulating polyamide substrate. For multi-domain film conductivity measurements, Au electrodes were e-beam evaporated through a shadow mask across narrow strips of PEDOT. For single domain measurements, probes were contacted directly to the PEDOT film (Fig. 3a). A Keithley 2400 source meter was used to measure I - V curves for LC templated and non-templated PEDOT, and both exhibited ohmic behavior. Uncertainty values given are a 95 % confidence interval for the mean based on ten samples. Film thickness was measured with a Tencor P10 profilometer. 30 nm thick PEDOT films for XPS were polymerized on Au coated Si substrates and studied using an Omicron ESCA Probe XPS with an AlK α source operating at 14 kV. Binding energies were calibrated using the Au $_{4f}$ peak (84.0 eV). After background subtraction, relative atomic composition was determined by integrating the C $_{1s}$ (286.0 eV), S $_{2p}$ (163.7 eV) and Cl $_{2p}$ (200.4 eV) peaks and multiplying by instrument sensitivity factors determined for C, S, and Cl from known standards.

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A Poly(vinyl alcohol)/Carbon-Black Composite Film: A Platform for Biological Macromolecule Incorporation**

By Lawrence L. Brott, Sophie M. Rozenzhak, Rajesh R. Naik, Shawn R. Davidson, Ronald E. Perrin, and Morley O. Stone*

Protein responses to stimuli can be extremely difficult to detect due to the fact that the secondary and tertiary structure conformational changes tend to be minute, often on an angstrom scale. Therefore, a challenge exists with respect to measuring and real-time coupling of these molecular-scale changes into a format that can be easily integrated with existing device architectures. Most studies of biomolecules focus on amplifying structural changes through light diffraction,^[1] changes in light polarization,^[2] changes in fluorescence,^[2] or through flexing of microsensor cantilevers.^[3] One limit to these techniques is that they require a stable environment

*] Dr. M. O. Stone, Dr. L. L. Brott, S. M. Rozenzhak, Dr. R. R. Naik, S. R. Davidson, R. E. Perrin
Materials and Manufacturing Directorate
Air Force Research Laboratory
3005 Hobson Way
Wright-Patterson Air Force Base, OH 45433-7702 (USA)
E-mail: morley.stone@wpafb.af.mil

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