Controlled Electropolymerization

Liquid-Crystal Templating of Conducting Polymers**

*James F. Hulvat and Samuel I. Stupp**

In organic electronics, conducting polymers have a number of advantages over small molecules, particularly because of their stability, mechanical properties, and ease of processing.[1,2] However, performance of some conducting polymers is limited by their high degree of disorder.[3,4] Molecular ordering improves carrier mobility in organic field-effect transistors and enhances charge injection in organic light-emitting diodes (OLEDs).[5] For this reason, vapor-sublimated crystalline films of small molecules are often used,[3] but alternative strategies to obtain molecular ordering would reduce cost and simplify fabrication of organic electronic devices. One possible way to achieve this is through molecular self-organization. Toward this goal we developed an aqueous, low-temperature technique for preparing conducting polymer films in a self-organized template.

Films of poly(3,4-ethyldioxythiophene) (PEDOT) are commonly used as hole injection layers in OLEDs. PEDOT can be polymerized in organic solvents or in an aqueous suspension with a soluble copolymer or surfactant, leading to amorphous films.[6] We have studied here the formation of PEDOT films by electropolymerization within a liquid crystalline template.

The well-known hexagonal (H1) lyotropic liquid crystal (LC) consists of cylindrical hydrophobic cores parallel to one another and separated by a hydrophilic continuum (see Figure 1 in the Supporting Information).[7] LCs have been used by us and others to template inorganic minerals as well as in the formation of mesoporous silica.[8] With regard to conducting polymers, template chemistry has been used to incorporate chains within the channels of mesoporous silica[9] or in aqueous channels of an inverse hexagonal LC.[10] These approaches, however, are limited to soluble, chemically polymerized polymers or to water-soluble monomers such as aniline or pyrrole. Our approach described here is novel in two key respects. First, polymerization occurs in the hydrophobic domain of the LC, allowing use of less polar

---

[*] Prof. S. I. Stupp, J. F. Hulvat
Department of Materials Science and Engineering
Department of Chemistry
Feinberg School of Medicine
Northwestern University
Evanston, IL 60208-3108 (USA)
Fax: (+1) 847-491-3010
E-mail: s-stupp@northwestern.edu

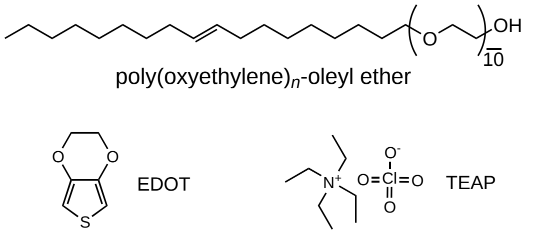
[**] This work made use of the Electron Probe Instrumentation Center at Northwestern University and was funded by a DoE grant (DE-FG02-00ER45810/A001). J.F.H. is supported by an NDSEG fellowship. We thank M. Kern for assistance with XRD and Prof. I. Koltover for helpful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

0044-8249/03/11507-0802 $ 20.00+.50/0

monomers with potentially more useful electronic properties, such as 3,4-ethyldioxythiophene (EDOT) and bithiophene.[2,11] In addition, the polymers formed within the template need not be soluble since the nanoscale distribution of monomers in the LC is locked-in during polymerization. Incorporation of bulky substituents to solubilize the polymer is avoided, simplifying preparation and possibly improving electronic properties.[12]

Poly(oxyethylene)–alkyl amphiphiles form various LC phases in water.[13] Poly(oxyethylene)$_n$–oleyl ether ($n \sim 10$) (Scheme 1) forms a self-supporting gel at concentrations in water in the range of 35—60 wt %. This gel is a hexagonal LC



Scheme 1. Amphiphile, monomer, and supporting electrolyte for liquid crystal templating system.

with 3 nm hydrophobic cores spaced 7.7 nm apart, as determined by small-angle X-ray diffraction (XRD) (see Figure 2 in the Supporting Information). The aliphatic cores solublize hydrophobic molecules such as EDOT, which is only sparingly soluble in water (< 0.002 M), but up to 0.25 M EDOT can be incorporated in the hexagonal LC phase. This strongly suggests that the monomer becomes localized within the 3 nm hydrophobic cores. We use tetraethylammonium perchlorate (TEAP) as a supporting electrolyte to facilitate electropolymerization in the LC. Small-angle XRD shows no significant change in LC structure upon incorporation of 0.2 M EDOT and TEAP (see Figure 2 in the Supporting Information). Differential scanning calorimetry (DSC) indicates that EDOT- and TEAP-doped gels are thermally stable with an isotropization point (T_i) of 46 °C compared with 49 °C for undoped gels (see Figure 3 in the Supporting Information).

We polymerized EDOT-doped gels potentiostatically on gold- or ITO(indium-tin oxide)-coated glass substrates. In this procedure, the electrochemical cell is sealed, heated to 60 °C, cooled slowly (0.03 °C min^{-1}), and annealed just below T_i. This allows the LC to self-organize forming large, uniaxial domains ~500 µm in size. EDOT electropolymerizes anodically at 1.3 V versus Ag/AgCl in the LC template, with a mean current density of 2.0 mA cm^{-2}. After polymerization, the LC gel is removed by washing in water, acetone, and CH_2Cl_2. Heating to 110 °C in vacuum (~10 mbar) removes any remaining solvent.

Figure 1a shows the polymer thickness t obtained as a function of time at different potentials, as measured by profilometry. Film growth in the LC is shown to be diffusion-limited given the observed quadratic growth rate, whereas in isotropic solutions it follows a linear, reaction-limited rate (Figure 1b). This is likely due to the confinement of EDOT molecules in the hydrophobic cores of the LC template. Figure 1c shows cyclic voltammetry of the EDOT- and TEAP-doped LC. The electrochemical behavior is similar to that described in the literature for PEDOT polymerization.[14]

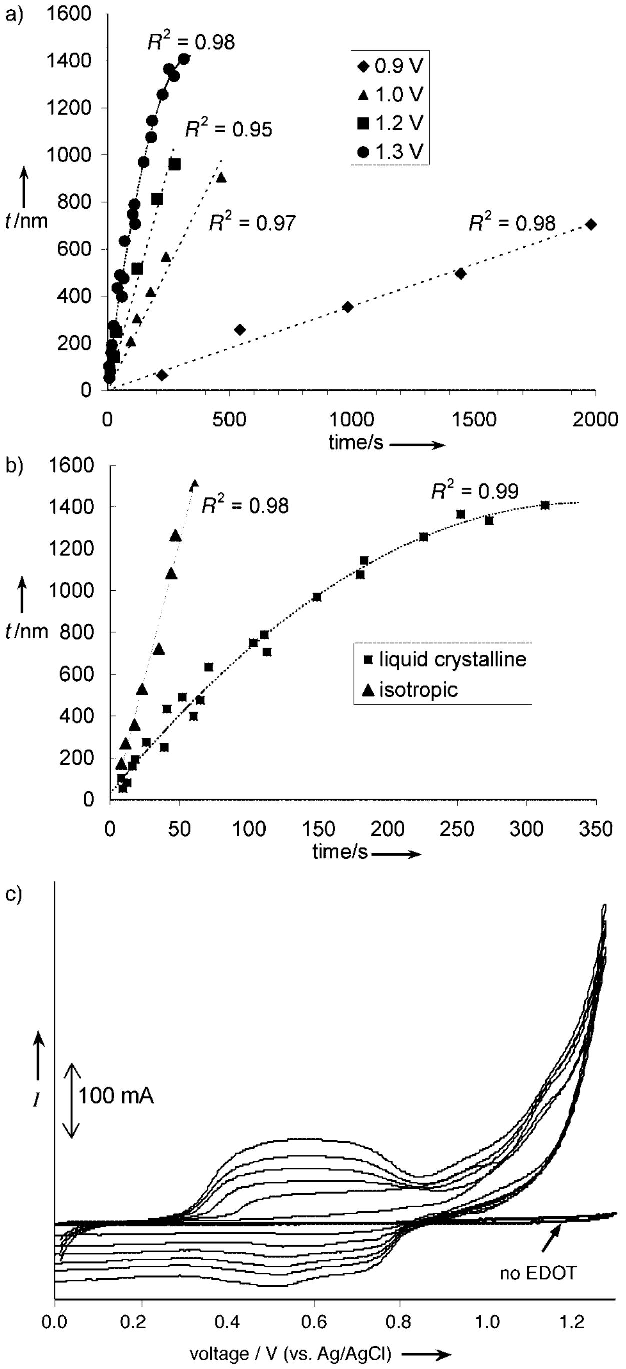


Figure 1. EDOT electropolymerization: a) PEDOT film thickness t as a function of time and potential. b) Film growth within the liquid crystalline template and in an isotropic solution of similar composition (at 1.3 V versus Ag/AgCl). Quadratic behavior (dashed line) indicates diffusion-limited growth. c) Cyclic voltammetry of EDOT and TEAP in LC gel of **1**. Arrow indicates LC gel without EDOT.

We observed in situ the film formed during electropolymerization using a two-electrode setup with transparent ITO glass sandwiched around a teflon spacer filled with LC gel. Blue domains of PEDOT grow commensurate with domains of the LC template (Figure 2), and polymer thick-

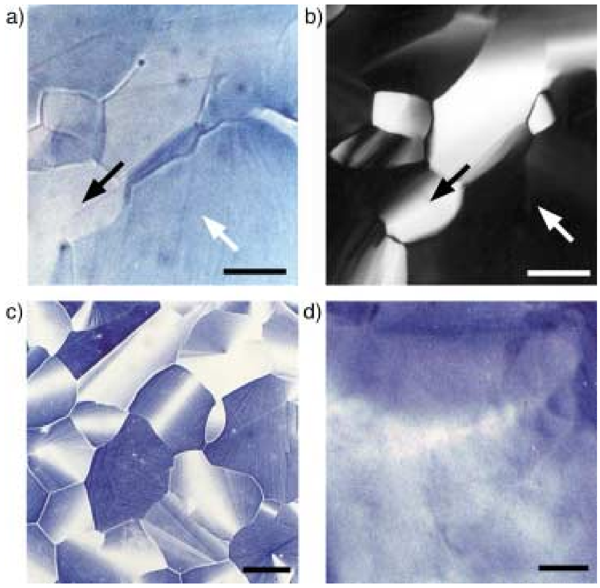


Figure 2. Optical micrographs of PEDOT electropolymerized on ITO (bars = 100 μm): a) nonpolarized and b) cross-polarized images of PEDOT in LC template during polymerization. Black arrows show a domain with director parallel to the substrate (slow PEDOT growth), and white arrows point to domains with director normal to substrate (rapid growth). c) Domain structure of a similarly grown PEDOT film after the LC template is removed. d) PEDOT polymerized in isotropic solution has no domain structure.

ness was found to vary with LC director orientation. Domains with director orientation parallel to the substrate result in less polymer growth, while those with a director oriented normal to the electrode surface exhibit the most rapid and thickest polymer growth. This indicates that the anisotropic LC environment mediates polymerization, that is, if monomer diffusion is confined to hydrophobic cores, the polymer should grow fastest in cores aligned normal to the substrate, that is, parallel to the electric field.

After the LC template is washed away, PEDOT films remain adhered to the electrode with no change in microstructure. Interestingly, these polymeric films essentially "copy" the LC texture, revealing birefringent domains that match those of the LC medium (Figure 3). We propose that polymerization within the confined nanoscale environment of hydrophobic cores produces polymer chains oriented parallel to the director of the LC. Thus, the optical anisotropy of the LC template is transferred to the PEDOT film during polymerization. Anisotropy is of course locked-in due to the polymer's insolubility. Similar films prepared from EDOT and TEAP in CH_3CN or in an LC mixture heated above the isotropization temperature (Figure 2d) lead to amorphous films with no domain structure or birefringence, confirming that the optical anisotropy of the PEDOT arises directly from the self-organized nature of the LC template. Figure 4 shows scanning electron microscopy (SEM) images of the PEDOT film after removal of the LC gel. Templated films show a texture consisting of ~50 nm nodules (Figure 4a–c) the size and height of which creates the observed domain structure. Amorphous films (Figure 4d,e) show no similar features. We propose that the structure observed in the templated films results from a directed aggregation of oriented polymer chains that collapse together when the LC template is removed (Figure 4f).

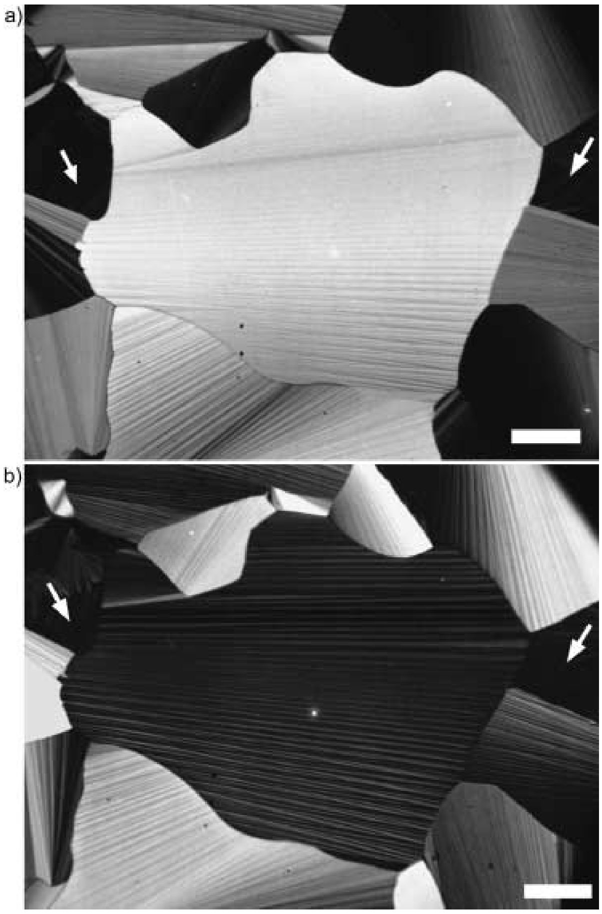


Figure 3. Polarized optical micrographs showing birefringence of templated PEDOT film after removing the LC template (bar = 100 μm). Center domain has its optical axis oriented parallel to the substrate: a) 45° relative to polarizer, b) 0° relative to polarizer. Arrows indicate domains with their optical axis oriented normal to the substrate.

The method reported here offers a simple, novel way to control and lock-in molecular orientation in conducting polymers using a self-assembled medium of surfactant molecules. EDOT electropolymerization in an organized template yields films exhibiting optical anisotropy commensurate with the LC template. Molecular alignment in these films might be used to improve charge injection from conducting polymer layers in OLEDs or otherwise enhance film properties in organic electronic devices.

Experimental Section

LC gels were prepared by dissolving 0.1 M EDOT (99%, Bayer AG) and 0.1 M TEAP (95%, Acros Organics) in poly(oxyethylene)$_n$–oleyl ether (1.0 g; 95%, Aldrich, $n \sim 10$). Deionized water (1.0 g) was added. Samples were heated in a closed vial to 80°C, vigorously mixed, and cooled, forming a transparent gel.

Electrode substrates were either e-beam evaporated (40 nm Au/10 nm Ti/glass) at ~10^{-6} Torr or on an ITO glass (120 nm thick, Applied Thin Films). Substrates were cleaned by sonication (15 min) in acetone, CH_2Cl_2, CH_3OH, 6 N HCl (30 s), and deionized water.

0044-8249/03/11507-0804 $ 20.00+.50/0

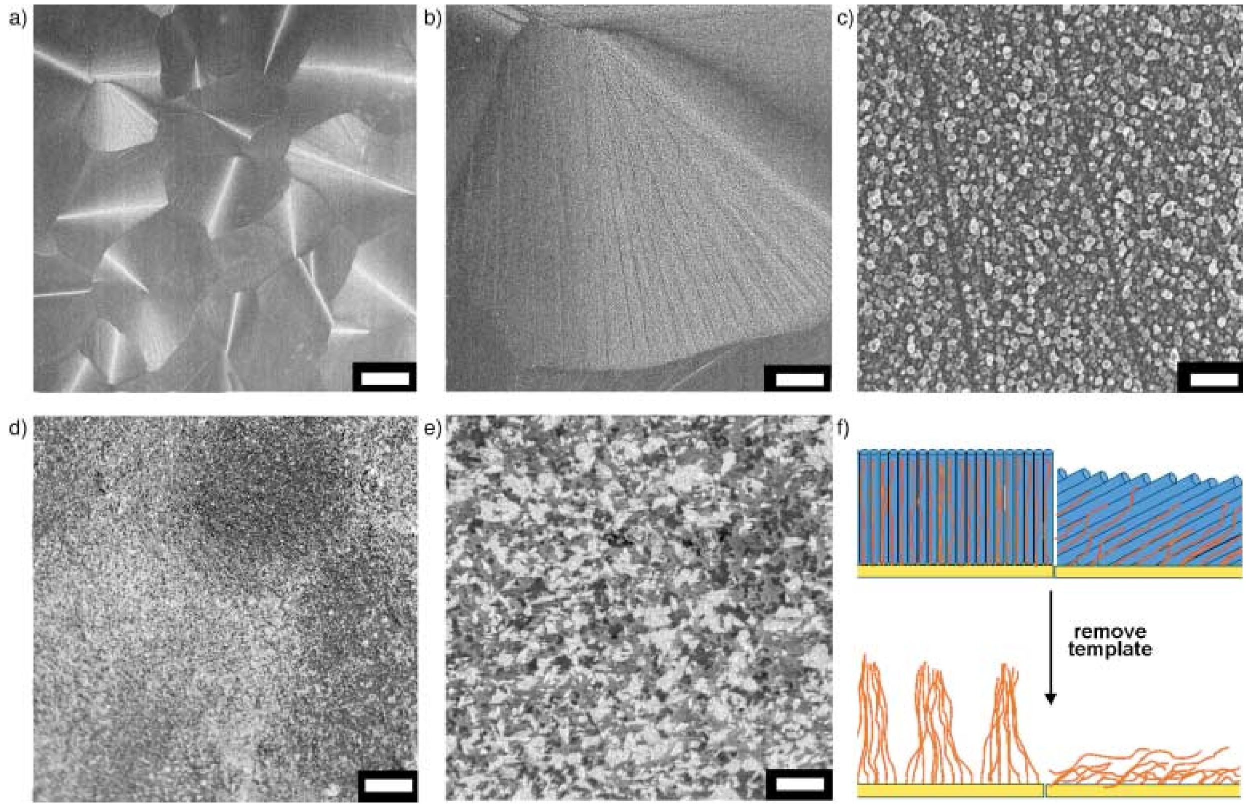


Figure 4. SEM images of PEDOT film after removal of the LC template. Templated polymer films have textures similar to focal conic textures of liquid crystals: bar = a) 50 µm, b) 10 µm, c) 1 µm. Nontemplated film grown from isotropic solution d) bar = 50 µm, e) bar = 5 µm. f) Schematic diagram depicting directed aggregation of oriented conducting polymer chains.

1.0 cm^2 substrates were placed in a glass cell 5 mm from a Pt counter electrode with a Ag/AgCl reference electrode (BAS Inc. model RE-5B). Electropolymerization and cyclic voltammetry used an E&G Princeton Applied Research potentiostat model 263A. For cyclic voltammetry, the potential was swept 0.0 to 1.3 V at 50 mV s^{-1}.

Small-angle XRD was performed in transmission geometry by sealing LC gel (~5 mg) in a polycarbonate holder using a Rigaku $Cu_{K\alpha}$ source and a 2D Bruker CCD detector calibrated with silver behenate. T_i of the LC was measured by using a TA Instruments 2920 diferential scanning calorimeter. For this purpose, 10 mg was hermetically sealed in Al pans and cycled at 5 °C min^{-1}. The thickness of the PEDOT film was measured with a Tencor P10 profilometer, and five measurements per sample were averaged. Optical micrographs were prepared by using a Leitz Laborlux 12POL polarizing microscope with a heating stage and either a 35 mm film camera or a Sony XC-ST70 CCD camera. SEM was performed on a Hitachi S-4500FE operating at 2 kV. PEDOT films conducted sufficiently and therefore did not require any coating prior to imaging.

Received: October 29, 2002 [Z50457]

---

[1] a) J. Pei, W. L. Yu, W. Huang, A. J. Heeger, *Macromolecules* **2000**, *33*, 2462; b) L. J. Rothberg, A. J. Lovinger, *J. Mater. Res.* **1996**, *11*, 3174; c) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo, *Science* **2000**, *290*, 2123.

[2] K. Gurunathan, A. Vadivel Murugan, R. Marimuthu, U. P. Mulik, D. P. Amalanerkar, *J. Mater. Chem.* **1999**, *61*, 173.

[3] Z. N. Bao, J. A. Rogers, H. E. Katz, *J. Mater. Chem.* **1999**, *9*, 1895.

[4] T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, W. J. Feast, *Appl. Phys. Lett.* **1999**, *75*, 1679.

[5] a) R. Osterbacka, C. P. An, X. M. Jiang, Z. V. Vardeny, *Science* **2000**, *287*, 839; b) P. Markart, E. Zojer, S. Tasch, R. Smith, D. Gin, G. Leising, *Synth. Met.* **1999**, *102*, 1155; c) P. K. H. Ho, J. S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli, R. H. Friend, *Nature* **2000**, *404*, 481.

[6] B. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481.

[7] P. J. Collins, *Liquid Crystals*, Princeton University Press, Princeton, NJ, **1990**.

[8] a) P. V. Braun, P. Osenar, V. Tohver, S. B. Kennedy, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 7302; b) A. Sayari, S. Hamoudi, *Chem. Mater.* **2001**, *13*, 3151.

[9] a) T. Q. Nguyen, J. J. Wu, V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652; b) J. J. Wu, A. F. Gross, S. H. Tolbert, *J. Phys. Chem. B* **1999**, *103*, 2374.

[10] a) D. Gin, R. Smith, H. Deng, G. Leising, *Synth. Met.* **1999**, *101*, 52; b) L. M. Huang, Z. B. Wang, H. T. Wang, X. L. Cheng, A. Mitra, Y. X. Yan, *J. Mater. Chem.* **2002**, *12*, 388; c) X. H. Li, X. G. Zhang, H. L. Li, *J. Appl. Polym. Sci.* **2001**, *81*, 3002.

[11] A. Greiner, *Polym. Adv. Technol.* **1998**, *9*, 371.

[12] a) M. A. Sato, M. A. Sakamoto, M. Miwa, M. Hiroi, *Polymer* **2000**, *41*, 5681; b) O. Stephan, P. Schottland, P. Y. Le Gall, C. Chevrot, C. Mariet, M. Carrier, *J. Electroanal. Chem.* **1998**, *443*, 217.

[13] H. Kunieda, G. Umizu, Y. Yamaguchi, *J. Colloid Interface Sci.* **1999**, *218*, 88.

[14] a) Q. B. Pei, G. Zuccarello, M. Ahlskog, O. Inganas, *Polymer* **1994**, *35*, 1347; b) M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electroanal. Chem.* **1994**, *369*, 87.