

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Electronic Properties and Morphology of Beam-Oligomerized 3-Hexylthiophene

Heejoon Ahn^a; James E. Whitten^a

^a Department of Chemistry and Center for Advanced Materials, University of Massachusetts—Lowell, Lowell, Massachusetts, USA

Online publication date: 10 July 2003

To cite this Article Ahn, Heejoon and Whitten, James E.(2003) 'Electronic Properties and Morphology of Beam-Oligomerized 3-Hexylthiophene', *Journal of Macromolecular Science, Part A*, 40: 12, 1357 – 1368

To link to this Article: DOI: 10.1081/MA-120025315

URL: <http://dx.doi.org/10.1081/MA-120025315>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Electronic Properties and Morphology of Beam-Oligomerized 3-Hexylthiophene

Heejoon Ahn and James E. Whitten*

Department of Chemistry and Center for Advanced Materials, University of
Massachusetts—Lowell, Lowell, Massachusetts, USA

ABSTRACT

A novel means of lithographically forming fluorescent oligothiophene patterns is demonstrated. MgK α x-ray and low energy electron irradiation of 3-hexylthiophene (3HT) monomer condensed on a cold metal surface result in the formation of photoluminescent films as thick as several microns. The excitation maxima for the x-ray- and electron-formed samples are 350 and 405 nm, respectively, with corresponding emission maxima of 430 and 525 nm, indicating that the films are oligomeric rather than polymeric. Ultraviolet photoelectron spectra (UPS) of 3HT monomer and beam-formed films have been compared with theoretically simulated density-of-states spectra of 3HT, thiophene, bithiophene, terthiophene, and quaterthiophene. The radiation-induced changes in the 3HT UPS valence spectra are explained by delocalization of electrons along the oligomer backbone. Comparison of the experimental UPS and simulated spectra suggests that the average conjugation length of the beam-formed films is less than six. This is consistent with the photoluminescence results. Fluorescence and atomic force microscopies of electron-formed samples show the presence of oligomerized 3HT islands residing on a less fluorescent organic background. Electrical conductivity of the beam-formed samples is low, on the order of $10^{-9} \text{ cm}^{-1} \text{ ohm}^{-1}$, consistent with the formation of islands of conjugated material surrounded by a less electronically delocalized,

*Correspondence: James E. Whitten, Department of Chemistry and Center for Advanced Materials, University of Massachusetts—Lowell, Lowell, MA 01854, USA; Fax: 978-934-3013; E-mail: james_whitten@uml.edu.



insulating background. Lack of solubility of the beam-formed films suggests that partial crosslinking and decomposition may also occur during the oligomerization process.

Key Words: Lithography; Photoelectron spectroscopy; Photoluminescence; Polythiophene.

INTRODUCTION

Conjugated materials including oligo- and polythiophenes are finding applications in a variety of molecular electronic devices, such as organic light-emitting diodes and field-effect transistors.^[1,2] Few methods exist for lithographically forming structures of these materials. Existing techniques include using a plasma to deposit hydrophilic patterns on a surface, followed by selective adsorption of substituted conjugated polymers,^[3] and the use of a scanning tunneling microscope to lithographically polymerize spin-coated films of conjugated polymer precursors.^[4] Poly(*p*-phenylene vinylene) has been patterned with linewidths of 200 nm by Visconti et al.^[5] in a three-step process consisting of photoresist deposition on top of the conjugated polymer, multiple holographic exposures to produce a mask, and plasma etching to remove the photoresist.

First observed by Salaneck and coworkers,^[6] several studies^[7–11] have now demonstrated that x-ray and low energy electron irradiation of physisorbed thiophene condensed on cryogenically-cooled metal and metal oxide surfaces result in the formation of a film that does not desorb upon warming the substrate to room temperature. The resulting films have been characterized by x-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) and found to be similar to polymerized/oligomerized thiophenes, with clear retention of conjugation. We recently showed^[12,13] that this phenomenon also occurs for 3-hexylthiophene (3HT) condensed on gold; XPS and infrared reflection absorption spectroscopy demonstrated similarity to chemically-synthesized poly(3-hexylthiophene) (P3HT). By condensing very thick physisorbed layers of 3HT prior to electron beam irradiation, we demonstrated the lithographic formation of micron-thick conjugated oligomer patterns on gold substrates that were stable when stored in air at room temperature.

In the present study, we discuss the methodology used to lithographically pattern the films and summarize photoelectron spectroscopy and photoluminescence characterization results. We also describe for the first time atomic force microscopy studies related to the morphology of the oligothiophene films and discuss quantum mechanical simulations aimed at interpreting the valence electronic spectra of the beam-formed samples. In some cases, fluorescence from the lithographically-formed structures is bright enough to be seen with the naked eye when held under an ultraviolet lamp. Possibilities of using this methodology to form fluorescent conjugated oligomer nanostructures are briefly discussed.

EXPERIMENTAL

Gold Substrate Preparation

Approximately 1000 Å of gold was thermally evaporated onto Si(111) wafers with areas of ca. 1 cm². The wafers were attached to stainless steel or copper sample stubs



via silver conductive adhesive (Electron Microscopy Sciences) that made electrical and thermal contact to the edges of the gold surface. X-ray diffraction showed that the evaporated gold films were predominantly Au(111).

Organic Film Preparation and Photoelectron Spectroscopy

The beam-oligomerized films were prepared in a VG ESCALAB MK II photoelectron spectrometer by cryogenically cooling a gold-coated Si(111) substrate to 135–145 K with liquid nitrogen and admitting 3HT vapor (nominal doses of 2000–4000 L) via a variable leak valve. The 3HT (Aldrich, >99%) was used as received and stored in a glass reservoir connected to the leak valve. Several freeze-pump-thaw cycles were carried out to remove atmospheric gases, and the purity was verified by a residual gas analyzer. Typically, the physisorbed 3HT layers were thick enough that a white film could be seen condensed on the substrate through the viewport of the vacuum chamber. The 3HT leak valve was then closed, and the sample was irradiated either with $\text{MgK}\alpha$ ($h\nu = 1253.6$ eV) x-rays or electrons from an electron gun or from a filament in line-of-sight of the sample surface. The latter was sometimes desirable in order to be able to expose the entire surface to electrons. After irradiation, the sample was permitted to warm to room temperature, and either photoelectron spectroscopy was performed or it was removed from the vacuum chamber for further analysis. In some cases, to make very thick samples, such as those greater than 1 micron, several cycles of 3HT condensation, electron bombardment, and warming the sample to room temperature (all in vacuum) were performed. For UPS, a helium discharge lamp emitting He I radiation ($h\nu = 21.2$ eV) was used. Details of the instrument and photoelectron spectroscopic equipment are provided in Ref.^[12] The surface was electrically grounded for XPS measurements and biased at ca. -6.0 V relative to ground for UPS.

The P3HT films were spin-coated from commercially available (Aldrich) regioregular P3HT, with an average molecular weight of ca. 87,000, dissolved in chloroform. The thickness of the films was determined by profilometry.

Electron Irradiation

The higher energy electron irradiation experiments (3.5 and 5 keV) were performed with the electron gun bombarding a region of the surface having an area of ca. 0.50 cm². For those cases in which it was desirable to irradiate the entire surface so that photoelectron spectroscopy could be performed, lower energy electrons (185 eV) from a filament in line-of-sight of the sample were used.^[12]

Fluorescence Spectra and Microscopy

Excitation and emission spectra were acquired using a JY Horiba “Spex Fluorolog” instrument. The instrument was operated in reflection mode with a 22.5 angle between the excitation source and the detector. Fluorescence images were acquired with a Nikon Eclipse microscope equipped with a mercury arc lamp and emission and excitation cubes. Atomic force microscopy was performed with a Thermomicroscopes “Autoprobe CP Research” instrument.



Conductivity Measurements

In the case of the regioregular P3HT, a 2000 Å thick film was spin-coated onto an ITO/glass substrate from which a 0.5 mm stripe of ITO had been removed by chemical etching. The current flowing across the gap for a particular voltage was then measured to determine the conductivity. In the case of the electron-formed film, it was critical to keep the gap small in order to avoid charging during electron irradiation and to have good thermal contact to the sample stub. In this case, a piece of sapphire was covered with gold, except for a 0.25 mm stripe in the middle of the sample. Monomer was condensed on the substrate, and the gap and surrounding sides were bombarded with electrons. The sample was then warmed, removed from vacuum, and the conductivity was measured as for the P3HT sample.

Computational Method

Geometry optimization and orbital ionization energy calculations of gas-phase monomers and oligomers were performed using the GAUSSIAN 98 program^[14] in order to aid in interpreting the experimental spectra. The ionization potentials of gas phase 3HT, thiophene, bithiophene, terthiophene, and quaterthiophene were calculated with a restricted Hartree-Fock Outer-Valence Green's Function (ROVGF) at a 6-31G** level. The geometry optimization was carried out with a MP2/6-31G** basis. It was found empirically that the simulated density-of-valence-states (DOVS) spectra needed to be convoluted with a Gaussian function of 0.8 eV FWHM to approximate the energy resolution of the experimental UPS spectra.

RESULTS AND DISCUSSION

Reflection mode excitation and emission spectra are shown in Fig. 1 for organic films fabricated by irradiating condensed 3HT with MgK α x-rays and 5 keV electrons. For reference, corresponding data are also included for a 350 Å spin-coated film of chemically synthesized regioregular P3HT. For the x-ray-formed sample, an exposure time of 75 min, with x-ray source conditions of 12 kV and 20 mA, was used. For the electron-formed sample, the electron dose was 4×10^{16} electrons/cm². X-ray photoelectron spectroscopy signal intensity analysis^[12] or profilometry showed the thickness of the x-ray- and electron beam-formed films to be approximately 100 Å and 10 microns, respectively. The excitation maxima are 350, 405, and 510 nm for the x-ray, electron and regioregular P3HT samples, respectively. The corresponding emission maxima are 430, 525, and 640 nm. The shorter wavelengths for the beam-polymerized samples indicate shorter average conjugation lengths; this is consistent with oligomerization instead of polymerization. Comparison to photoluminescence data for films of unsubstituted thiophene oligomers^[15] suggests an average conjugation length corresponding to less than four units, with the x-ray sample being less conjugated than the electron-formed one. The emission spectra in Fig. 2 are substantially broader than those corresponding to the chemically synthesized oligomers, suggesting less homogeneous conjugation lengths. Based on emission spectra signals, the ratios of the fluorescence intensities for the samples in Figs. 1 and 2 are approximately



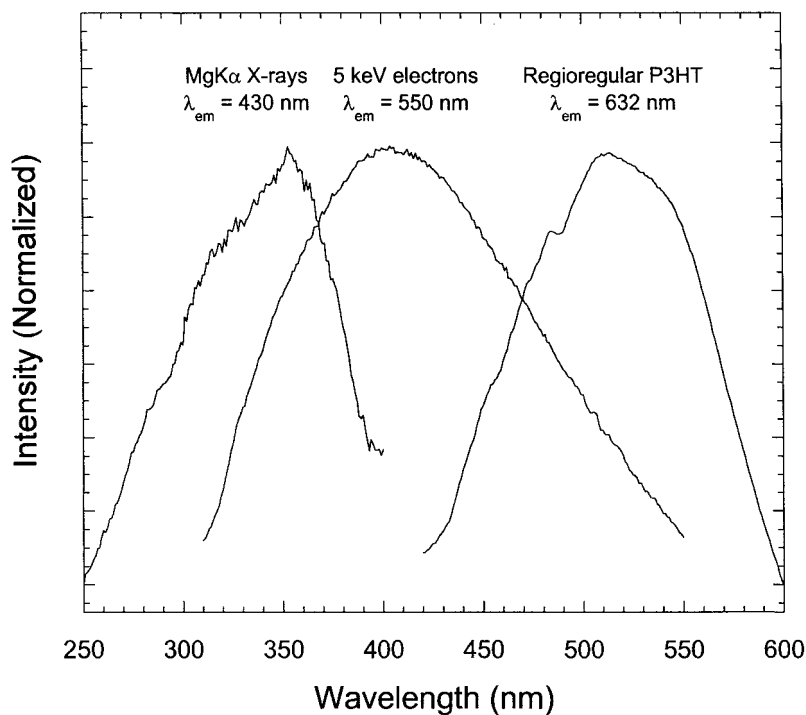


Figure 1. Fluorescence excitation spectra of x-ray and 5 keV electron-oligomerized 3HT films (4×10^{16} electrons/cm²) along with a spectrum of regioregular P3HT. The emission wavelengths were 430, 550, and 632 nm, respectively. The excitation and emission slit widths were 1 mm. Reproduced with permission from *J. Phys. Chem. B* **2002**, *106*, 11404–11405. Copyright 2002 Am. Chem. Soc.

10.5, 3.5, and 1.0 for regioregular P3HT, electron-oligomerized 3HT, and x-ray oligomerized 3HT, respectively.

Figure 3 displays He I UPS of 3HT monomer and beam-oligomerized 3HT films along with theoretically simulated gas-phase valence band states of 3HT, thiophene, bithiophene, terthiophene, and quaterthiophene. The unsubstituted thiophenes, instead of 3HT oligomers, were simulated due to software and hardware limitations in calculating the substituted oligomer valence spectra. However, the trends in the theoretical spectra as oligomer length increases are expected to be similar. All spectra are referenced to the Fermi level of the gold substrate. In the case of the theoretical gas-phase molecules, the spectra were aligned by shifting all of them by the same amount such that the frontier orbital of 3HT (spectrum labeled “DOVS of 3HT”) lined up with the experimentally measured frontier orbital of condensed 3HT (spectrum labeled “3HT”). This was accomplished by subtracting 2.85 eV from the ionization energy of each orbital. No corrections have been made to the theoretical data for ionization cross section or polarization energy effects.

The experimental UPS spectrum of 3HT monomer (i.e., no x-ray or electron exposure) shows a well-defined peak at 5.5 eV that broadens and moves toward lower binding energy



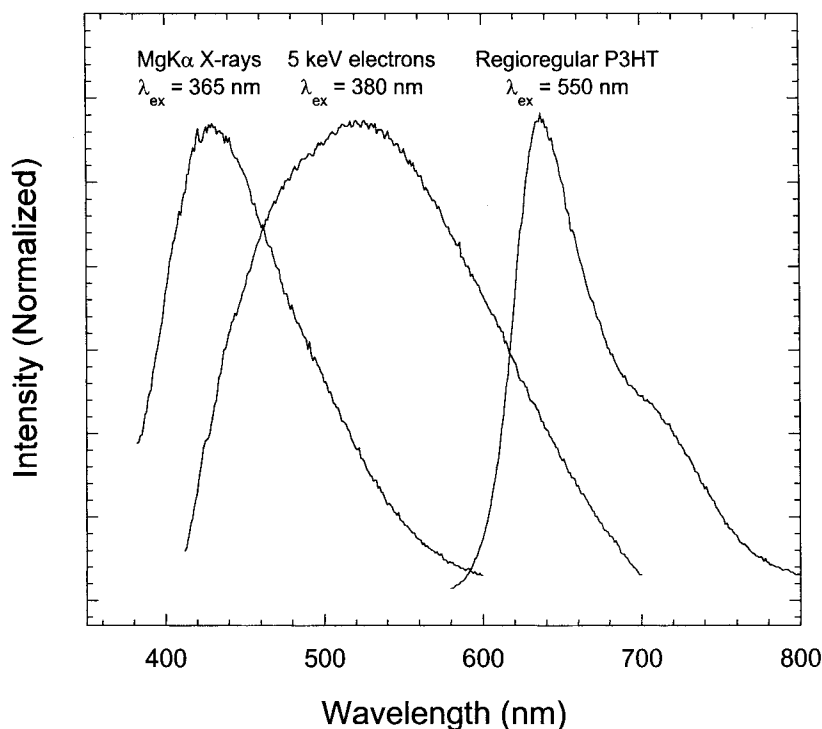


Figure 2. Fluorescence emission spectra of the same samples as in Fig. 1. The excitation wavelengths of the x-ray and electron-oligomerized 3HT and regioregular P3HT samples were 365, 380, and 550 nm, respectively. The excitation and emission slit widths were 1 mm. Reproduced with permission from *J. Phys. Chem. B* **2002**, *106*, 11404–11405. Copyright 2002 Am. Chem. Soc.

in the cases of the x-ray and electron-formed 3HT oligomer samples. The peak energies are 4.6 and 4.0 eV, respectively, for these samples. It should be noted that we have not observed oligomerization effects due to He I radiation for the conditions used for the UPS experiment.

For the monomers, the peak closest to the vacuum level (and the Fermi level) is due to electronic states localized on the thiophene rings, as previously discussed by Brédas, Salaneck, and colleagues.^[16,17] For the simulated DOVS of bithiophene, the spectrum exhibits a well-defined shoulder on the low binding energy side of the main peak. This feature, which is due to electrons delocalized along the oligomer backbone, shifts toward lower binding energy as the conjugation length increases, reaching a value of about 3.6 eV for quaterthiophene. This suggests, therefore, that the broadening and tailing toward the Fermi level of the UPS spectra of the beam-formed films is due to the formation of delocalized electronic states. The fact that the lower binding energy feature is not experimentally resolved may be due to inhomogeneities in the samples, which tend to blend the features together. In the case of the electron-formed sample, the tail extends more toward the Fermi level, consistent with a slightly longer conjugation length compared to the x-ray formed film. The x-ray and electron formed UPS spectra in Fig. 3 do not show the type of



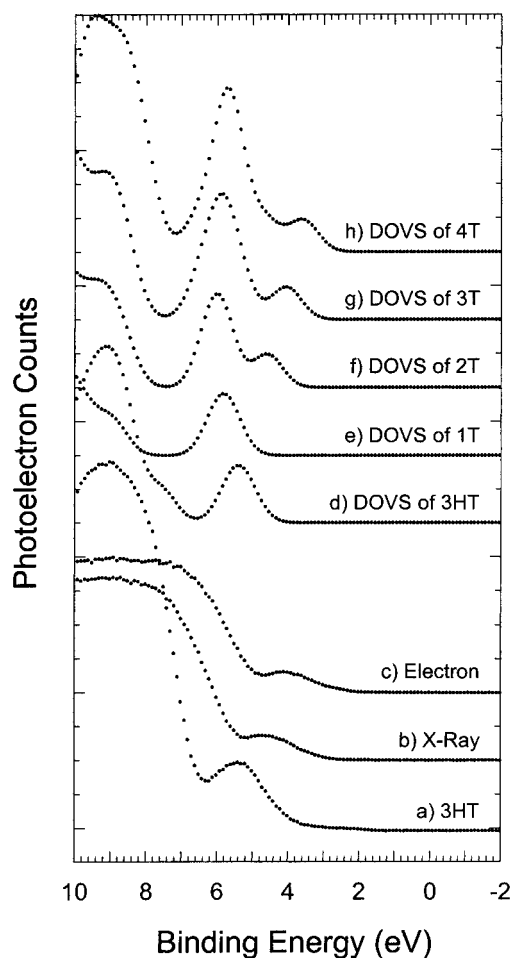


Figure 3. He I UPS of (a) 3HT monomer condensed on gold at 135–145 K; (b) MgK α x-ray formed film; (c) 185 eV electron formed film (3×10^{16} electrons/cm 2), and calculated DOVS spectra of gas phase: (d) 3HT; (e) thiophene; (f) bithiophene; (g) terthiophene; and (h) quaterthiophene. Except for spectrum (a), all experimental spectra were acquired at room temperature. The pass energy was 2 eV, and the binding energy scale is relative to the Fermi level of the gold substrate.

well-developed tail toward the Fermi level that is typically observed for P3HT.^[12] Theoretical calculations^[18] have shown that the valence spectrum is essentially fully developed for an oligomer containing six thiophene units (i.e., sexithiophene). These results thus indicate that the beam-oligomerized 3HT films have average conjugation less than six. This is consistent with the fluorescence results.

The details of the mechanism of x-ray and electron beam polymerization are presently being investigated in our laboratory. In the case of MgK α x-rays, we found that regardless of the thickness of the physisorbed 3HT layer, oligomer films of only ca. 100 Å could be formed.^[12] For 2–5 keV electrons, however, micron thick films could be fabricated. These



results, in light of the deep penetration depth of x-rays and the limited mean free path of low energy electrons in the range 50–1250 eV,^[19] suggest that photoelectrons are responsible for the oligomerization process. Condensed benzene also may be oligomerized/polymerized by electron beams, and H⁺ electron-stimulated desorption has been detected from benzene physisorbed at 90 K.^[20] A plausible oligomerization/polymerization mechanism for benzene (and thiophene) involves C–H bond cleavage and the formation of active sites on the aromatic ring. Thiophenes may be polymerized electrochemically, and it is of some interest to compare the possible operative mechanisms. In the case of electrochemical polymerization, the first step is believed to be oxidation of the monomer to its cation radical; this is followed by coupling of the radicals, which have a high concentration at the electrode, and finally C–H bond cleavage.^[21] In the case of electron irradiation, the mechanism has not been investigated but may involve as its first step C–H bond breakage. In the case of x-ray “polymerization” of condensed thiophene physisorbed on Ag(111), it has been observed that increasing the temperature of the sample, while staying below multilayer desorption temperature, increases the rate of polymerization.^[7] This suggests that a certain amount of mobility of adjacent thiophene rings may be important.

Electron beams are known to be destructive to organic films and conjugated polymers.^[22] To determine the effects of electron bombardment on electronic structure and measure possible similarity to the electron-oligomerized 3HT layer, a 350 Å film of regioregular P3HT on gold has been irradiated with 185 eV electrons, and valence and photoluminescence spectra have been measured as a function of electron dose. We have shown that electron bombardment results in destruction of delocalization of π electrons.^[23] Similar conclusions have been drawn from UPS investigations of electron irradiation of poly(*p*-phenylene vinylene) films.^[22] Poly(3-hexylthiophene) is soluble in chloroform; our attempts to dissolve electron- and x-ray-formed films in this solvent have failed to remove them completely. This lack of solubility indicates partial crosslinking, which is consistent with FT-IR results.^[12]

Figure 4 shows fluorescence microscopy of an electron-formed film. The bright worm-like features are due to oligomerized 3HT islands surrounded by a fluorescently weaker background. The less fluorescent background surrounding the oligomer islands is organic in nature (i.e., not the gold substrate), as verified by the absence of gold features in an Auger electron spectrum of the film. Profilometry reveals a very inhomogeneous overall film thickness ranging from 230 to 380 nm. Atomic force microscopy, presented in Fig. 5, reveals that the highly fluorescent structures have an average height and width of ca. 200 nm and 2–5 microns, respectively. A wide distribution of lengths is observed, ranging from less than 10 to over 100 microns, as illustrated in the figures. Vacuum-deposited short oligothiophenes are known to have high diffusion rates relative to longer ones and to form islands and crystallites on a variety of substrates,^[24,25] presumably coalescing via van der Waals forces. The results of Figs. 4 and 5 indicate that a similar type of nucleation may be occurring in the case of the beam-oligomerized samples.

To assess possible semiconducting electronic applications of this methodology, electrical conductivity measurements have been performed. For a sample made in a similar fashion as that corresponding to Figs. 4 and 5, the conductivity was on the order of $10^{-9} \text{ cm}^{-1} \text{ ohm}^{-1}$. A comparable measurement in our laboratory for (undoped) regioregular P3HT gave a value of $10^{-3} \text{ cm}^{-1} \text{ ohm}^{-1}$. The poor conductivity of the electron-formed film is consistent with the formation of electrically isolated islands, as observed in Figs. 4 and 5.



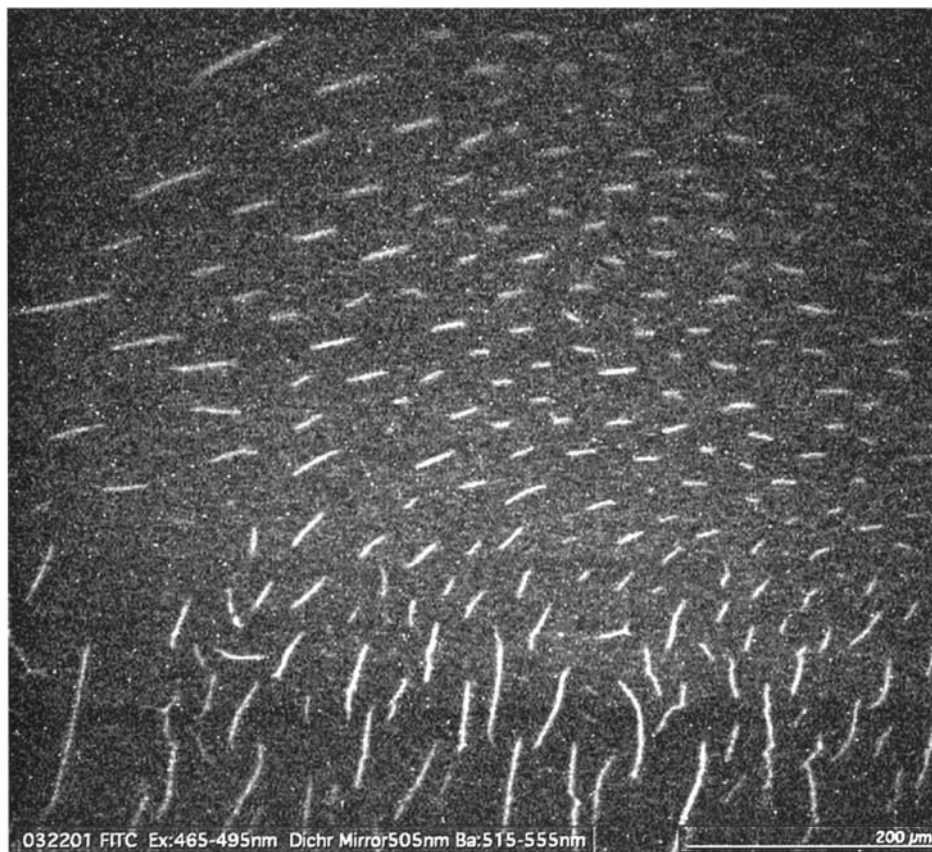


Figure 4. Fluorescence microscope image of a 670×760 micron² region of an electron-oligomerized film formed by 3.5 keV electron bombardment (1.8×10^{16} electrons/cm²) of 3HT condensed on a Au/Si(111) substrate (exposure of ca. 4000 L). The excitation and emission wavelength ranges were 465–495 and 515–555 nm, respectively. Reproduced with permission from *J. Phys. Chem. B* **2002**, *106*, 11404–11405. Copyright 2002 Am. Chem. Soc.

Further investigations of the mechanism of oligomerization, along with the fluorescent and electrical properties of these types of organic films are continuing in our laboratory. We have used electron beam lithography to write millimeter-size dots of 3HT oligomers,^[12] and Umbach and coworkers^[9] have demonstrated the writing of microstructures by apertured synchrotron irradiation of thiophene condensed on Ag(111). Decomposition of organometallic gases by electron irradiation from the tip of a scanning tunneling microscope (STM) operating in field emission mode has been used to form metallic features as small as 10 nm.^[26] If a similar procedure, with a low temperature STM, were used on a thiophene-covered sample, then fluorescent (and possibly semiconducting) nanostructures could be fabricated by this technique.



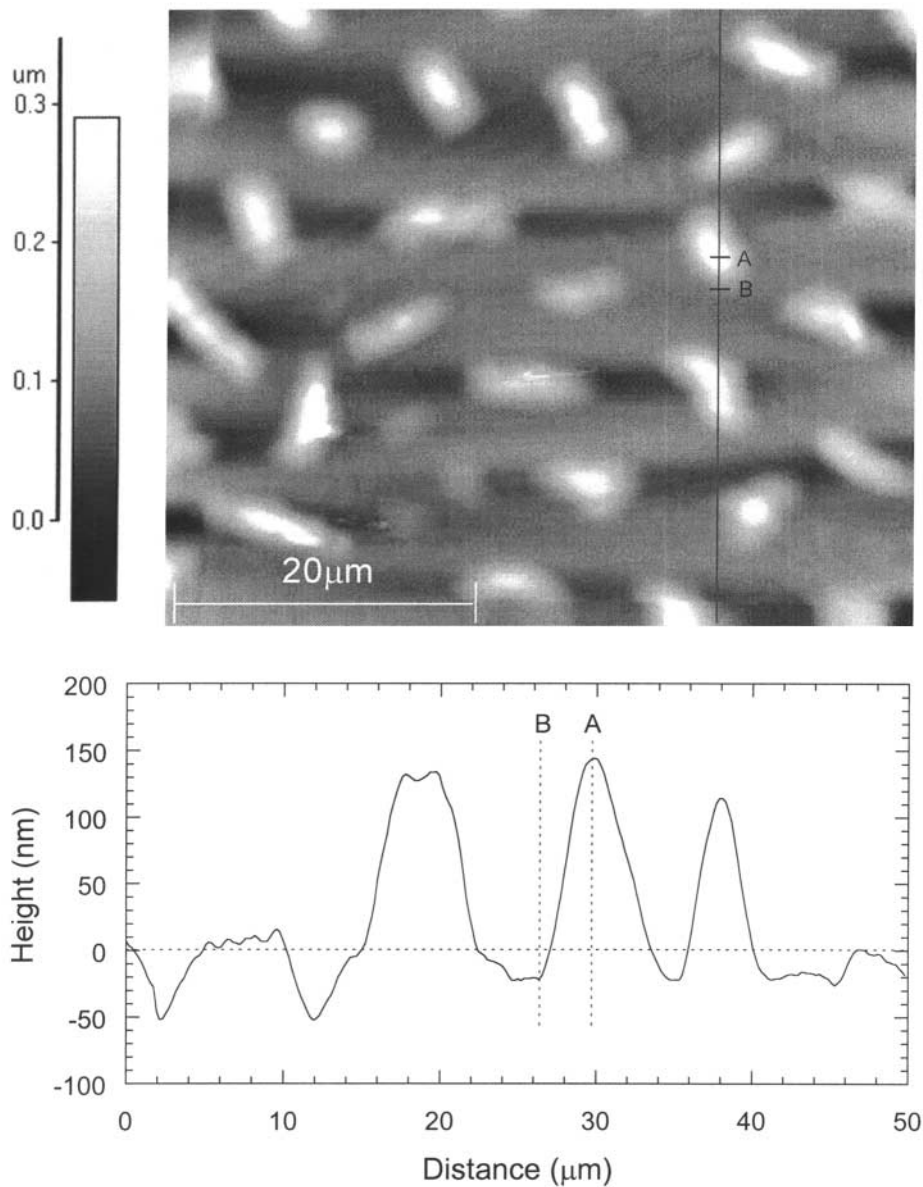


Figure 5. Atomic force microscope image of a 43×51 micron² region of the same sample as in Fig. 4. The topographic height scale is also displayed.

CONCLUSION

Either MgK α x-ray or electron beam irradiation of 3HT physisorbed on conducting surfaces results in the formation of fluorescent oligomeric films. Some crosslinking and



decomposition occurs concomitantly with oligomerization, and electrical conductivities of films are low. Fluorescence and atomic force microscopies indicate the presence of photoluminescent islands of oligomer surrounded by a non-fluorescing organic background. Possibilities exist for nanolithography to form fluorescent, conjugated nanostructures by using either a focused electron beam or the tip of a STM operating in field emission mode.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under grant DMR-0089960. The authors thank Mary McCann for performing the fluorescence microscopy analysis.

REFERENCES

1. Granström, M.; Harrison, M.G.; Friend, R.H. Electro-optical polythiophene devices. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999; 405–458.
2. Sirringhaus, H.; Friend, R.H.; Wang, C.; Leuninger, J.; Müllen, K. Dibenzothienobisbenzothiophene—a novel fused-ring oligomer with high field-effect mobility. *J. Mater. Chem.* **1999**, *9*, 2095–2101.
3. Winkler, B.; Dai, L.; Mau, A.W.H. Novel poly(p-phenylene vinylene) derivatives with oligo(ethylene oxide) side chains: synthesis and pattern formation. *Chem. Mater.* **1999**, *11*, 704–711.
4. Granström, M. Micro- and nanoscale patterning of luminescent conjugated polymer films. *Synth. Met.* **1999**, *102*, 1042–1045.
5. Visconti, P.; Turco, C.; Rinaldi, R.; Cingolani, C. Nanopatterning of organic and inorganic materials by holographic lithography and plasma etching. *Microelect. Eng.* **2000**, *53*, 391–394.
6. Salaneck, W.R.; Wu, C.R.; Nilsson, J.O.; Brédas, J.L. UHV-compatible processing of conducting polymers: polythiophene. *Synth. Met.* **1987**, *21*, 57–61.
7. Baumgartner, K.M.; Volmer-Uebing, M.; Taborski, J.; Bauerle, P.; Umbach, E. Adsorption and polymerization of thiophene on a silver(111) surface. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 1488–1495.
8. Land, T.A.; Hemminger, J.C. Photoemission and thermal desorption studies of electron beam polymerized thiophene films on platinum(111). *Surf. Sci.* **1992**, *268*, 179–188.
9. Väterlein, P.; Weiss, M.; Wüstenhagen, V.; Umbach, E. Mask-less writing of microstructures with the photon-induced scanning auger microscope (PISAM). *Appl. Surf. Sci.* **1993**, *70/71*, 278–282.
10. Raza, H.; Wincott, P.L.; Thornton, G.; Casanova, R.; Rodriguez, A. X-ray and electron beam modification of thiophene overlayers on TiO₂(100). *Surf. Sci.* **1997**, *390*, 256–260.
11. Väterlein, P.; Schmelzer, M.; Taborski, J.; Krause, T.; Viczian, F.; Bäbler, M.; Fink, R.; Umbach, E.; Wurth, W. Orientation and bonding of thiophene and 2,2'-bithiophene on Ag(111): a combined near edge extended X-ray absorption fine structure and X α scattered-wave study. *Surf. Sci.* **2000**, *452*, 20–32.



12. Hernandez, J.E.; Ahn, H.; Whitten, J.E. X-ray and electron induced oligomerization of condensed 3-hexylthiophene. *J. Phys. Chem. B.* **2001**, *105*, 8339–8344.
13. Ahn, H.; Whitten, J.E. Comment on “X-ray and electron induced oligomerization of condensed 3-hexylthiophene”. *J. Phys. Chem. B.* **2002**, *106*, 11404–11405.
14. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A.; Stratmann, R.E., Jr.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J.J.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Baboul, A.G.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Andres, J.L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. *Gaussian 98, Revision A.11.4*; Gaussian, Inc.: Pittsburgh, PA, 2002.
15. Fichou, D.; Ziegler, C. Structure and properties of oligothiophenes in the solid state: single crystals and thin films. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999; 183–282.
16. Dannetun, P.; Boman, M.; Stafström, S.; Salaneck, W.R.; Lazzaroni, R.; Fredriksson, C.; Brédas, J.-L.; Zamboni, R.; Taliani, C. The chemical and electronic structure of the interface between aluminum and polythiophene semiconductors. *J. Chem. Phys.* **1993**, *99*, 664–672.
17. Salaneck, W.R.; Inganäs, O.; Thémans, B.; Nilsson, J.O.; Sjögren, B.; Österholm, J.-E.; Brédas, J.-L.; Svensson, S. Thermochromism in poly(3-hexylthiophene) in the solid state: a spectroscopic study of temperature-dependent conformational defects. *J. Chem. Phys.* **1988**, *89*, 4613–4619.
18. Fujimoto, H.; Nagashima, U.; Inokuchi, H.; Seki, K.; Cao, Y.; Nakahara, H.; Nakayama, J.; Hoshino, M.; Fukuda, K. Ultraviolet photoemission study of oligothiophenes: π -band evolution and geometries. *J. Chem. Phys.* **1990**, *92*, 4077–4092.
19. Feldman, L.C.; Mayer, J.W. *Fundamentals of Surface and Thin Film Analysis*; Elsevier: New York, 1986; 126–130.
20. Whitten, J.E.; Gomer, R. Electron impact on benzene layers on W(100). *Surf. Sci.* **1996**, *347*, 280–288.
21. Roncali, J. Conjugated poly(thiophenes): synthesis, functionalization, and applications. *Chem. Rev.* **1992**, *92*, 711–738.
22. Bröms, P.; Johansson, N.; Gymer, R.W.; Graham, S.C.; Friend, R.H.; Salaneck, W.R. Low energy electron degradation of poly(p-phenylenevinylene). *Adv. Mater.* **1999**, *11*, 826–832.
23. Ahn, H.; Whitten, J.E. in preparation.
24. Gebauer, W.; Sokolowski, M.; Umbach, E. Optical processes in ultrathin oligothiophene films on well-defined substrates. *Chem. Phys.* **1998**, *227*, 33–48.
25. Schoonveld, W.A.; Stok, R.W.; Weijtmans, J.W.; Vrijmoeth, J.; Wildeman, J.; Klapwijk, T.M. Morphology of quaterthiophene thin films in organic field effect transistor. *Synth. Met.* **1997**, *84*, 583–584.
26. McCord, M.A.; Kern, D.P.; Chang, T.H.P. Direct deposition of 10-nm metallic features with the scanning tunneling microscope. *J. Vac. Sci. Technol. B* **1988**, *6*, 1877–1880.

