

Fabrication of Patterned, Electrically Conducting Polypyrrole Using a Self-Assembled Monolayer: A Route to All-Organic Circuits

Christopher B. Gorman, Hans A. Biebuyck, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received September 9, 1994[§]

This paper describes the use of patterned self-assembled monolayers to fabricate small, two-dimensional patterns of electrically functional polypyrrole on a gold electrode. These patterns can be transferred to an insulating polydimethylsiloxane substrate. Thin (10–100 μm) polypyrrole wires retain their electrical conductivity over millimeter length scales. Interdigitated fingers of polypyrrole spaced 50 μm apart are electrically insulated from one another. Polypyrrole can be electrochemically polymerized on patterns with size features of 2 μm into films that are 200–400 nm thick.

Introduction

Polypyrrole is potentially useful as an electrical conductor. It (and other organic conductors) are difficult to process, particularly in features typical of circuits: they are generally insoluble and decompose upon melting. Soluble or melt-processable derivatives of conjugated polymers exist^{1–4} but often display reduced conductivities compared to their parent polymers. Thus, templating the shape of a conjugated polymer during synthesis (e.g., oxidative electropolymerization) may prove useful. Templating environments such as glass capillaries⁵ and membrane pores⁶ have been used to form thin conducting wires of these polymers. We sought to generalize this templating scheme to form arbitrary patterns on a surface.

Recently, we have developed several techniques for the patterning of a SAM on a gold surface,^{7–12} of which the most generally useful (especially for complex patterns) is contact printing on microscales. A number of groups have established that SAMs of an appropriate thickness (e.g., > 10 carbons in length) essentially block interfacial electron transfer.^{13–17} Conjugated polymers such as polypyrrole, polythiophene and polyaniline are

conveniently synthesized via oxidative polymerization of the monomer. By carrying out the oxidative polymerization using a patterned SAM as the electrode, these monomers can be electropolymerized only in selected regions of a gold electrode; this type of process generates the polymer in a well-defined pattern.¹⁸ Once the patterned material has been formed, it can be transferred to another substrate so that its conducting properties can be exploited. Polypyrrole adheres to gold strongly enough so that it can be patterned; this adhesion is, however, also sufficiently weak that the polypyrrole can be stripped from gold and transferred to another surface by contact adhesion. In this paper, we demonstrate this technique and establish that it can be used to generate electrically continuous features on the micron scale.

Results

Patterned Electrodeposition of Polypyrrole Perchlorate. Pyrrole was oxidatively electropolymerized from an aqueous sodium perchlorate electrolyte and formed a black film on a gold electrode. X-ray photoelectron spectroscopy binding energies for the N(1s), C(1s), and Cl(2p) were similar to literature values for polypyrrole perchlorate.^{19,20} When a patterned SAM of hexadecanethiol was present on the surface of the electrode, deposition of polypyrrole perchlorate avoided these regions (Figure 1).²¹ In this regard, the SAM acts as a monolayer-thick electrical resist.²² Regions that

[§] Abstract published in *Advance ACS Abstracts*, December 15, 1994.

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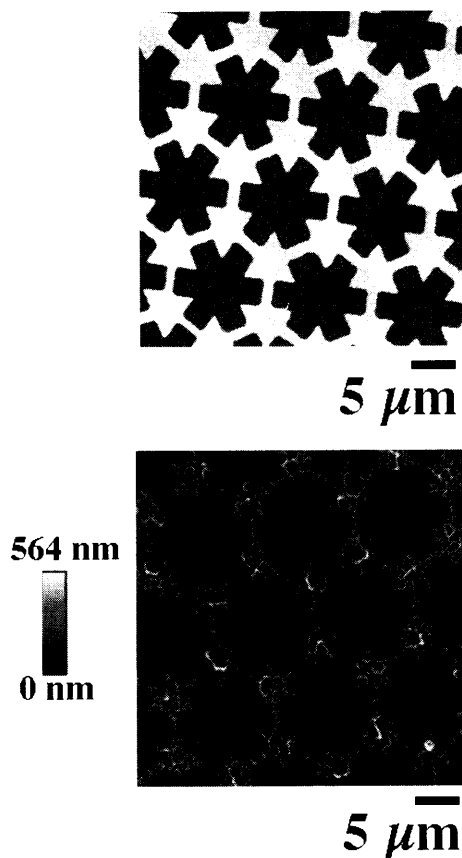


Figure 1. Top: lateral force microscopy image of the patterned SAM used to template electrodeposition of polypyrrole. The dark regions are a SAM composed of hexadecanethiol. The lighter regions are bare in the electrodeposition experiment and are washed with 5 mM ethanolic solution of 11-mercaptoundecanoic acid ($\text{HS}(\text{CH}_2)_{10}\text{COOH}$) to form a carboxylic acid terminated SAM with higher contrast for this image.²⁷ Bottom: atomic force micrograph of a similar pattern after electrodepositing polypyrrole.

had been exposed to a solution of a shorter thiol, 2,2,2-trifluoroethanethiol, did not hinder oxidative polymerization but did permit contact transfer of the pattern to a nonconducting substrate (see below). The ability of a hexadecanethiol SAM to prevent electropolymerization is limited: electropolymerization is selective for,

(21) Although the rippled morphology observed in the lines connecting the triangles is common to electropolymerized polypyrrole (Ko, J. M.; Rhee, H. W.; Park, S.-M.; Kim, C. Y. *J. Electrochem. Soc.* **1990**, *137*, 905–909. Tokito, S.; Tsutsui, T.; Saito, S. *Chem. Lett.* **1985**, 531–534), the larger, craterlike features in the triangles are not observed when pyrrole is electropolymerized on unpatterned electrodes. Detachment at the sharp corners found in this triangular pattern may give rise to this morphology. This result suggests that the shape of the electrode may permit control of the morphology, particularly the surface area of the polypyrrole produced. Such control may be useful in the design of amperometric sensors that employ polypyrrole as a matrix. (Lyons, M. E. G.; Lyons, C. H.; Fitzgerald, C.; Bannon, T. *Analyst* **1993**, *118*, 361–369.)

(22) Preferential deposition should initially occur because the SAM acts as a barrier to electron transfer and can presumably prevent nucleation and growth of polymer by preventing electropolymerization in SAM-covered regions. Once the polymer has begun to grow (and the polymer is effectively the electrode) the reduced conductivity of the polymer compared to the bare gold electrode may limit this contrast. The somewhat hydrophobic nature of polypyrrole may also play a role. The lateral growth of polypyrrole nitrate between two microelectrodes has been promoted by a hydrophobic pretreatment of the region of glass that spanned the electrodes (Nishizawa, M.; Shibuya, M.; Sawaguchi, T.; Matsue, T.; Uchida, I. *J. Phys. Chem.* **1991**, *95*, 9042–9044). In our investigations, selective deposition did not occur when pyrrole was electropolymerized using sodium *p*-toluene sulfonate as the electrolyte. Polypyrrole perchlorate could, however, be deposited selectively.

but not limited to, the regions not covered by a SAM. For patterns containing features with lateral dimensions of 50–100 μm , films of polypyrrole perchlorate that are 0.5–1.0 μm thick²³ could be grown before polypyrrole perchlorate clearly covered the regions containing the hexadecanethiol SAM. In the case of 10–50 μm features, layers of 0.25–0.5 μm thickness could be fabricated. SAM resists have advantages not found in conventional polymeric resists, however. Once the elastomeric stamp has been fashioned, the SAM pattern can be printed on the electrode in a few seconds. Use of conventional resists would require spin-coating, UV exposure, developing and perhaps other postprocessing steps to achieve the same effect. Also, SAM resists continue to adhere to the electrode. After removal of the polypyrrole perchlorate layer (see below), the patterned SAM remains and can be used repeatedly²⁴ to generate the same pattern.

Transfer of Polypyrrole Perchlorate to a Nonconducting Substrate. The next step in demonstrating electrically functional patterns requires that the polypyrrole perchlorate be on an insulating substrate. When the patterned polymer on the gold substrate was pressed (firm finger pressure) against Scotch tape or polydimethylsiloxane elastomer, the polypyrrole transferred from the gold to this new support via contact adhesion. To reduce the adhesion between the polymer and the gold, the underivatized regions upon which the polymer grew were briefly (1–2 s) exposed to a 1 μM ethanolic solution of 2,2,2-trifluoroethanethiol. This thiol should produce a more hydrophobic surface yet should be short enough^{16,17} to permit the passage of current required for oxidative polymerization. In practice, this procedure resulted in patterns with no significant loss of contrast. Control over the surface composition in the region in which the polypyrrole formed resulted in more reproducible depositions than did electropolymerization on “bare” gold.²⁵ Patterns of polypyrrole formed on a SAM of trifluoroethanethiol reliably contact transferred to the second substrate, and this transfer permitted the demonstration of electrical conductivity.

Conductivity and Control of Electrical Connectivity. Using microcontact printing and contact transfer, patterns of polypyrrole perchlorate were fabricated that are appropriate for conducting polymer-based circuitry. The polypyrrole, after transfer, shows continuous electrical conductivity. Moreover, closely spaced but noncontacting regions of the polymer are electrically insulating. Figure 2 shows the patterns employed and a representative pattern of polypyrrole.

Lines of polypyrrole perchlorate (Figure 2a) that were 2 mm long and $0.25 \pm 0.1 \mu\text{m}$ thick (as measured by atomic force microscopy) were fabricated and their conductivity was measured using two-point probes (Table 1). The resistivity of the lines was sufficiently high that contact resistance ($<10^3 \Omega$) was negligible. Resistivities did not increase over the course of at least a week under ambient temperature and atmosphere.

(23) Thicknesses were measured by profilometry or atomic force microscopy, range reflects sample to sample variations.

(24) The polypyrrole pattern was regenerated >10 times from the patterned SAM with no evidence of degradation in the patterned, transferred polypyrrole.

(25) So-called “bare” gold always had adsorbed impurities because it has a high surface solid–vapor interfacial free energy.

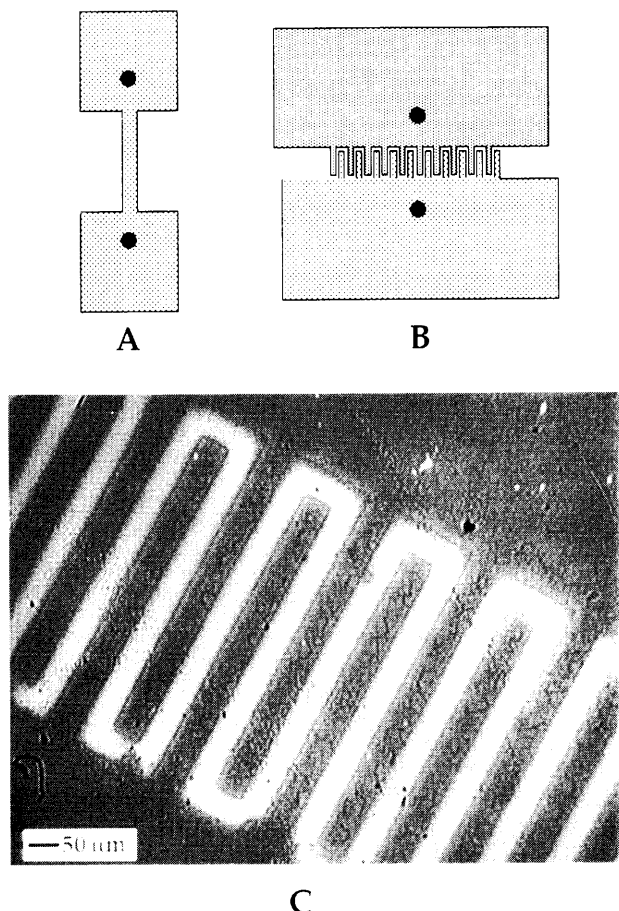


Figure 2. Patterns used to illustrate requirements for conducting polymer-based circuitry. Dots indicate placement of the probe wires for conductivity measurements. (a) Patterned lines of polypyrrole perchlorate. Contact pads are 2 mm \times 2 mm. Lines are 2 mm long and 10–100 μ m wide. (b) Closely spaced interdigitated regions of polypyrrole perchlorate. Contact pads are 2 mm wide and 3 mm long. Teeth are 500 μ m long and either 20 or 50 μ m wide. Spacing between teeth is equal to the width of the teeth. (c) An optical micrograph of this interdigitated pattern after contact transfer to PDMS. Inherent limitations in the SAM are presumably responsible for the defects observed.

Table 1. Resistivities of Polypyrrole Perchlorate Lines^a

line width (mm)	resistivity (M Ω) ^b	calcd conductivity (S/cm)
100	0.80 \pm 0.10	1.5 \pm 0.8
50	1.05 \pm 0.05	2.3 \pm 1.2
20	1.67 \pm 0.02	3.6 \pm 1.8
10	2.55 \pm 0.10	4.7 \pm 2.4

^a For patterns on PDMS under argon flush. ^b The pattern upon which this resistivity was measured is shown in Figure 2.

Measurements were the same within experimental error when taken in laboratory atmosphere and under dry argon atmosphere, indicating that conductivity of any surface adsorbates do not make a contribution. Moreover, resistivities remained constant over time (ca. 10 min) and over at least three decades of applied voltage, indicating that ionic conduction within the sample does not play a role. Using the above geometries (including the thickness of the wire in Table 1), wire conductivities were calculated and found to be in the range 1–5 S/cm; this range of values is expected for polypyrrole.²⁶

An interdigitated array containing two isolated regions of polypyrrole was fabricated. The resistivity across this array was measured in the same manner as before. Despite the close spacing, a resistivity of >1000 M Ω was measured. This value is at least 3 orders of magnitude higher than that in either continuous region, indicating that closely spaced, conductive circuit patterns of polypyrrole perchlorate are electrically isolated at this length scale.

Conclusions

Using this electrodeposition/transfer method, all-organic electrical circuitry can be fabricated and demonstrated to have electrical conductivities comparable to those found in bulk samples of a conducting polymer. Since highly conducting organic polymers are almost all intractable, a method such as this is a necessary first step to use such polymers in more elaborate electrical devices. In addition, this method illustrates the utility of patterned SAMs in the fabrication of such elements. The method is reproducible and convenient: fabrication requires two steps, each of which can be accomplished in a few seconds.

Experimental Section

Materials. Pyrrole (Fluka) was passed through activated, neutral alumina (removing water and colored impurities) and was then distilled and stored under argon. For oxidative electropolymerization, an aqueous solution (0.1 M) of pyrrole containing sodium perchlorate (Aesar, 0.8 M) electrolyte/counterion was employed. Working and counter electrodes were 1000 Å of gold and 50 Å of titanium (to promote adhesion) electron beam evaporated on silicon (Silicon Sense, Nashua NH) of resistivity 1–5 Ω /cm.

Sample Preparation. The working electrode was patterned by microcontact printing using hexadecanethiol as described previously.⁷ The electrode was then briefly (1 s) immersed in a 1 μ M ethanolic solution of 2,2,2-trifluoroethanethiol to promote contact adhesion of the polymer after synthesis. The electrode was then immersed in the solution described above and held at 0.8 V (versus a saturated calomel reference) for 1 s using a Princeton Applied Research Model 371 potentiostat. Longer deposition times could be employed but did not reliably produce a pattern devoid of polypyrrole perchlorate in the hexadecanethiol-covered areas. A black pattern of polypyrrole perchlorate appeared on the electrode. The electrode was removed from the solution, washed with distilled water and ethanol and dried under a stream of argon. The electrode was then pressed against a piece of poly-(dimethylsiloxane) (PDMS, Dow Sylgard 184) or tape (Scotch double-sided tape) using firm finger pressure. After a few seconds, the PDMS or tape was peeled off of the electrode removing the polypyrrole perchlorate pattern. Use of tape resulted in clean removal of the polymer from the electrode. PDMS worked somewhat less reliably. This sample was mounted on a glass slide and used directly in resistivity measurements.

Sample Characterization. Before removal of the polypyrrole perchlorate, a sample of the polymer on the gold electrode was characterized by X-ray photoelectron spectroscopy. XPS spectra were collected on a Surface Science SSX-100 spectrometer using a monochromatized Al K α source ($h\nu = 1486.6$ eV). The binding energies for the elements were referenced to the C(1s) peak in a hexadecanethiol monolayer on gold for which the binding energy was fixed at 284.6 eV. The range of C(1s), N(1s), and Cl(2p) binding energies were similar to those reported in the literature for polypyrrole

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perchlorate. A patterned sample (Figure 1) was also characterized using a JEOL JSM-6400 scanning electron microscope using secondary electron detection and using a Topometrix TMS 2010 atomic force microscope. Thickness measurements were performed on the sample on both the gold electrode and PDMS using either the atomic force microscope or a Tencor Instruments Alpha-step 2000 scanning profilometer (Mountain View, CA).

Resistivity measurements were performed using a Princeton Applied Research Model 273 potentiostat in galvanostatic mode using applied currents of 1 mA to 100 nA (10 V maximum applied potential). Resistance was determined by taking the ratio of measured voltage to applied current. From the sample dimensions and thickness determined as above, the conductivity (σ , S/cm) was calculated using the expression

$$\sigma = \frac{I d}{V l w}$$

where I is the current applied, V is the voltage measured, d is the sample thickness, l is the spacing between the probes, and w is the width of the line (all expressed in centimeters). In the case of the interdigitated array, resistance was greater than that obtainable using this instrument ($>1000 \text{ M}\Omega$).

Acknowledgment. This research was supported, in part, by the ONR and by ARPA.

CM940424Q