Electrochemical Polymerization of Pyrrole-Containing Self-Assembled Alkanethiol Monolayers on Au

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Received July 14, 1994

We report here the first electrochemical polymerization of a monomer monolayer formed by self-assembly[1,2] of a pyrrolyl-alkanethiol on Au. Voltammetric waves characteristic of poly-(*N*-alkylpyrrole)[3] are observed after electrochemical oxidation of ω-(*N*-pyrrolyl)alkanethiol monolayers on Au in various nonaqueous electrolytes. Enhanced stability of the polymerized monolayer is observed during competitive adsorption experiments[4] with an electroactive ferrocenylalkanethiol.

Self-assembled monolayers of *n*-alkanethiols offer the ability to position redox-active groups at given distances and orientations with respect to the electrode surface.[4,5] We are unaware of any studies concerned with the successful polymerization of monomer units contained in self-assembled monolayers of alkanethiols,[6] although there have been many reports of polymerization in Langmuir–Blodgett and other amphiphilic films.[7–9] With this in mind, a series of ω-(*N*-pyrrolyl)-alkanethiols **1–3** of various chain length were synthesized.[10] We chose the following short-chain ω-(*N*-pyrrolyl)alkanethiols due to their expected liquid-like monolayer structure, which should enhance the probability of oligomer or polymer formation within the monolayer.

After a freshly electropolished[11] polycrystalline gold electrode is placed in a 1 mM solution of ω-(*N*-pyrrolyl)alkanethiol in EtOH for times greater than 3 h, rinsed with EtOH, and placed in monomer-free 0.1 M Bu₄NClO₄/PC (propylene carbonate) electrolyte, there is no observable voltammetric wave for poly-(*N*-alkylpyrrole)[3] in the potential range of 0 to +0.75 V *vs* SSCE (Figure 1A). The double-layer capacitance is decreased relative
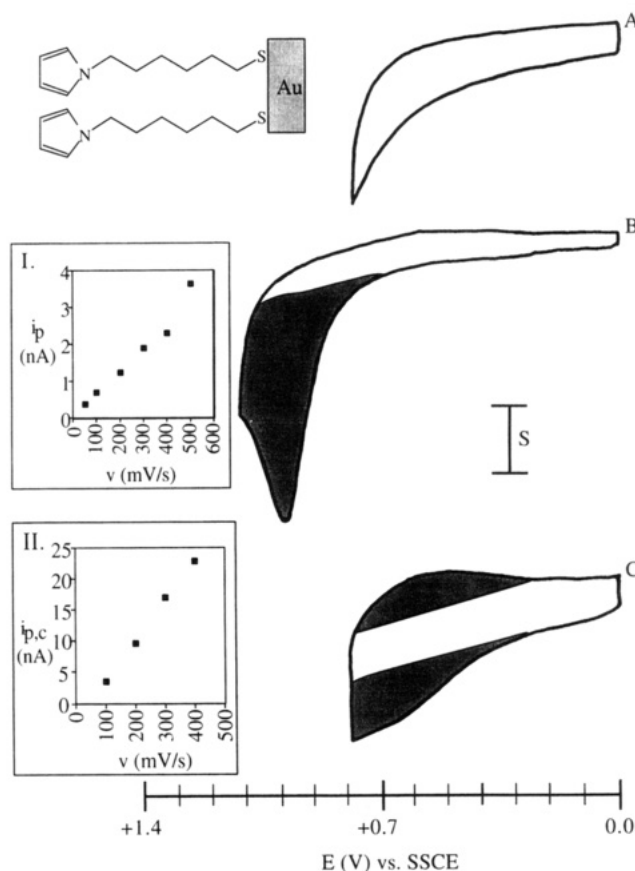
Figure 1. Cyclic voltammetry in 0.1 M Bu₄NClO₄/propylene carbonate electrolyte at (A) **3**/Au electrode surface scanned between 0 and +0.75 V *vs* SSCE; (B) **3**/Au electrode surface scanned between 0 and +1.1 V *vs* SSCE; (C) **3**/Au electrode surface scanned between 0 and +0.75 V *vs* SSCE after the potential excursion in B. $A_{electrode} = 1.96 \times 10^{-3}$ cm², and $v = 0.100$ V s⁻¹. $S = 5$ μA cm⁻² in A and C; $S = 13$ μA cm⁻² in B. A 40 μm diameter Au electrode used for inset I.

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(10) The general synthesis of the ω-(*N*-pyrrolyl)alkanethiols begins with the *N*-alkylation of pyrrole with the appropriate dibromoalkane in DMF. After column chromatography, the pure (bromoalkyl)pyrrole was converted to the corresponding thiol by adding dropwise a DMSO solution of the (bromoalkyl)pyrrole to a saturated NaHS solution in 80%/20% DMSO/H₂O (v/v).

(11) The electrode was cycled between +1.5 and −1.0 V *vs* SSCE in 1 M HClO₄ five times, rinsed with deionized water, and dried in a stream of Ar.
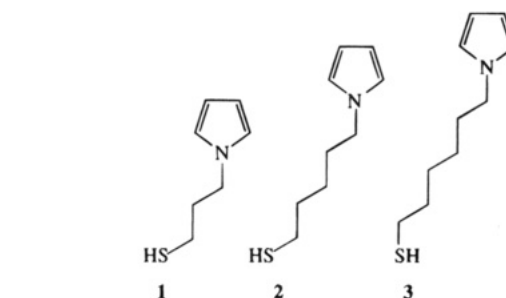
to bare Au, as previously reported for *n*-alkanethiols.[12] If the potential is scanned to more positive values, an irreversible peak, $E_p = +1.0$ V *vs* SSCE, is observed (Figure 1B), which is near that expected for oxidation of *N*-alkylpyrroles in nonaqueous electrolytes.[3] The peak current is directly proportional to scan rate (over the range 25–500 mV s⁻¹), indicative of a surface-confined species, Figure 1, inset I.[13] Subsequent scans over this potential range do not display any voltammetric signal at +1.0 V, but rather a set of waves centered at +0.60 V *vs* SSCE is observed (Figure 1C). The shape and potential of the surface-confined wave at +0.60 V are characteristic of poly(*N*-alkylpyrrole) films formed by the electrochemical polymeriza-

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(13) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1984; Vol. 13. (b) The i_p–scan rate studies were carried out by using a freshly prepared pyrrolylalkanethiol monolayer for each trial.

tion of N-alkylpyrroles in nonaqueous solvents. As expected for a surface-confined electroactive species, peak currents scale linearly with scan rate (over the range 100—400 mV s⁻¹), Figure 1, inset II.[13a] Simple n-hexanethiol-coated Au electrodes do not display any voltammetric peaks in this potential range.[14]

The surface coverage of the wave at +1.0 V (using the shaded area and $n = 2$ electrons equiv⁻¹ for pyrrole polymerization) corrected for electrode surface roughness,[15] Γ_{ecp}, was found to be $(3.9 \pm 0.4) \times 10^{-10}$ mol cm⁻² (10 samples), consistent with a monolayer of electroactive material. A similar value was obtained when using reductive desorption of the monolayer in aqueous NaOH solutions to assess the surface coverage of thiol groups.[16] Integration of the current (either shaded area) associated with the wave at +0.60 V vs SSCE yields a surface coverage (10 samples, $n = 0.25$ electrons equiv⁻¹ for the doping/undoping reaction[3a], Γ_{poly}, of $(4.0 \pm 0.4) \times 10^{-10}$ mol cm⁻². Thus, the observation of $\Gamma_{ecp} = \Gamma_{poly}$ indicates that the pyrrole groups of the monolayer have been *extensively* converted to a conducting polymer or oligomer film on the surface.

The wave at +0.60 V is stable indefinitely when the potential is scanned between 0 and +0.8 V in dry solvents but is unstable (currents slowly decrease) when the potential is scanned to values above +1.2 V. Such behavior is expected for the overoxidation or deactivation of poly(pyrroles).[3,17] Reductive desorption experiments after monolayer oxidation indicate no substantial loss of bound thiol.[16,18] When water or pyridine is added to the Bu₄NClO₄/PC electrolyte, potential excursions through the monomer peak at +1.0 V result in no observable surface wave at +0.60 V. Nucleophiles are known to inhibit poly(pyrrole) formation by attacking the pyrrole cation radical.[3c] Contact angle measurements (sessile H₂O drop[19]) for the unoxidized monolayer on freshly evaporated Au films (58 ± 4°) were found to decrease (49 ± 2°) after being electrochemically oxidized, indicating a more hydrophilic surface, as expected for a monolayer that contains charged sites. We note no changes in the wettability of hexanethiol monolayers treated in a similar manner, but the structure of the pyrrole thiol monolayers may change upon polymerization and cause the contact angle to decrease.

Polymerized monolayers of 1—3 display a higher affinity for Au than the corresponding monolayers prior to electrochemical oxidation. Competitive adsorption experiments[4] with an electroactive ferrocenylalkanethiol indicate that the electrochemically oxidized ω-(N-pyrrolyl)alkanethiol monolayers are not readily displaced.[14] Unoxidized ω-(N-pyrrolyl)alkanethiol monolayers, in marked contrast, are almost completely displaced (>95%) by the competing ferrocene thiol within 90 min. The increase in stability can be attributed to the formation of a large structure (a "knitted monolayer") tethered to the Au surface

through many thiol bonds. Displacing the knitted monolayer from the surface by the competing adsorbate will be energetically unfavorable. This increased stability has also been observed in reductive desorption experiments;[16] the reduction potential of the thiol is shifted negative by several hundred millivolts after monolayer oxidation. *Thus, we conclude that monolayers of ω-(N-pyrrolyl)alkanethiols on Au undergo electrochemical polymerization to yield poly(N-alkylpyrroles) without desorption of the thiol moiety from the Au surface.*

At this point, we can only suggest possible structures for the polymer or oligomer formed.[20] Molecular models indicate that the pyrrole rings can be connected through the 2 and 5 positions without serious strain in the alkane chains bound to the Au surface, yielding a single polymer strand, as in **4**. A similar

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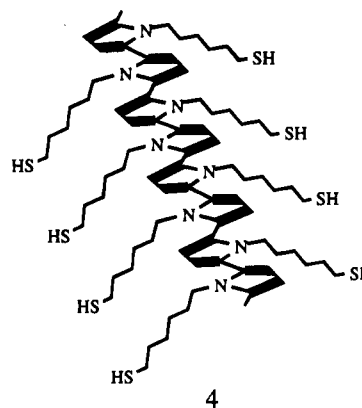
structure has been suggested for Langmuir—Blodgett films of an amphiphilic poly(thiophene).[9] The degree of polymerization (number of pyrrole units in one polymer chain), however, is currently unavailable. Our future plans include careful infrared characterization of monolayers derived from 1—3 in order to obtain information regarding polymer length.[21] In addition, we are currently synthesizing longer chain ω-(N-pyrrolyl)alkanethiols whose monolayers should be more densely packed and have large regions of crystalline-like order, in comparison to the relatively disordered monolayers used in this study. Such structural differences in the monolayers may hinder coupling of pyrrole groups in the monolayer.

Supplementary Material Available: Details of exchange experiments, n-hexanethiol monolayer voltammetry, and surface coverage calculations with figures (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) See supplementary material.

(15) (a) We used the oxidative desorption of iodine[15b] to determine the roughness of the polished electrode. The roughness factor was found to be 2. (b) Rodriguez, J. F.; Mebrahtu, T.; Soriaga, M. P. *J. Electroanal. Chem.* **1987**, *233*, 283.

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(17) Although our solvents were purified using traditional methods, there will still be water present at a level (~0.001%) sufficient to cause damage to the oxidized polymer.

(18) A ferrocene-tailed alkanethiol with an eight carbon spacer is not desorbed in this potential range after scanning for periods of minutes. In addition, preliminary reflectance IR data show no loss of the monolayers, as noted by the presence of the alkane CH₂ stretch.

(19) The 6 μL drop was allowed to equilibrate with the surface for 1 min before measurements were made.

(20) Preliminary attempts to observe the infrared-active C—H out-of-plane bending mode[8] at the 2 and 5 positions in the pyrrole ring (780 cm⁻¹) or any change in this vibration after electrochemical oxidation have not been possible due to spectral limitations of the MCT detector.

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