## A Lamellar Conducting Polymer by Self-Assembly of an Electropolymerizable Monomer

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Despite the number of studies of electronically conductive polymers,[1] material intractability[2] and the design of anisotropic conductors have only recently been addressed. Attempts to impart directional asymmetry to the structure of conducting polyheterocycles include polymerization in restricted geometries[3] and with bulky counterions,[4] stretch orientation of the polymers,[5] dissolution of the polymers in multilayered films,[6] and polymerization of heterocyclic monomers with high molecular anisotropy.[7] The latter two approaches include studies directed toward the preparation of Langmuir–Blodgett multilayers of conductive polymers. Here we demonstrate that by further increasing the molecular anisotropy (amphiphilicity) of a monomer (**2**) we can rely on molecular self-assembly to afford a highly ordered lamellar polymer which is soluble in chloroform and water.

1, R = H
2, R = $C_{12}H_{25}$
3, R = $C_{18}H_{36}$
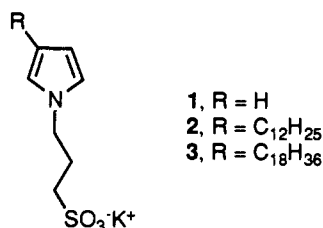
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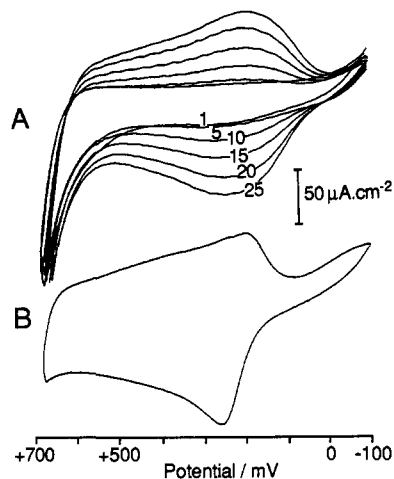
Figure 1. Formation and electrochemical cycling of poly(potassium 3-(3-dodecylpyrrol-1-yl)propanesulfonate): (A) cyclic voltammetry (25 cycles at 100 mV s⁻¹) of 5 mM **2** in 0.1 M aqueous KNO_3 at a gold electrode, versus Ag/AgCl (saturated KCl) reference electrode; (B) cyclic voltammetry (100 mV s⁻¹) of poly(**2**) prepared in part A in 1 M $HClO_4$.

Potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates **1–3** were prepared by the reaction between the potassium salt of 3-alkylpyrrole[8] and 1,3-propanesultone.[9] The critical micellar concentrations (cmc) of these surfactants were determined by the method of Corrin et al., whereby the color of a solution containing pinacyanol chloride turns from pink to blue upon increasing the concentration through the cmc.[10] In deionized water the cmc of **2**[11] is 5×10^{-5} M. Upon addition of potassium nitrate (0.1 M), the value is reduced to 2×10^{-5} M. The higher homologue **3** is not sufficiently soluble to exhibit a cmc. The unsubstituted analogue **1**[9] is freely soluble in water. These potassium sulfonates are soluble in DMSO, only slightly soluble (<1 mM) in acetonitrile and benzonitrile, and insoluble in dichloromethane and THF.

The monomers described here undergo an irreversible electrochemical oxidation to form a nonconductive film on a gold electrode surface if the potential is swept to greater than ca. 1 V (vs Ag/AgCl (saturated KCl)).[9] If the positive potential is limited to +800 mV, polymerization takes place to afford a conducting film. When a 5 mM micellar solution of **2** in 0.1 M KNO_3 is repeatedly cycled between 0 and +700 mV, a smooth red polymer, poly(**2**), is deposited on a gold electrode. The current at the upper potential limit increases during the first 10 cycles, Figure 1A. A reversible wave develops at ca. +200 mV corresponding to redox cycling of poly(**2**), which persists upon transfer to monomer-free electrolyte solution (Figure 1B). The charge beneath the polymer redox wave corresponds to approximately 5% of the charge passed during deposition although this is difficult to determine with certainty because of the change in capacitive charging. Assuming a two-electron oxidative mechanism for the addition of one pyrrole unit to the growing chain, this implies a doping level of ca. 10% (i.e., there is 1 cationic charge/10 repeat units in the oxidized polymer).

In contrast, cyclic voltammetry of 5 mM solutions of pyrrole or *N*-methylpyrrole in 0.1 M KNO_3 failed to deposit a polymer layer, with a conductive polymer being deposited only at higher concentrations (60 mM).[12] The observation of polymer formation

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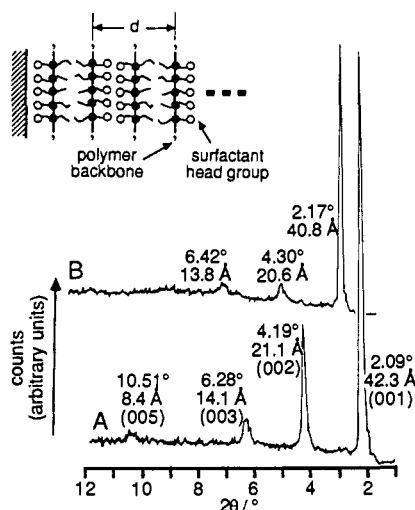
Figure 2. X-ray diffraction (Cu Kα irradiation, λ = 1.5418 Å) patterns of poly(2) before and after ion exchange: (A) as-grown poly(2) (values of 2θ (deg) and *d* (Å) and Miller indices are shown by each reflection peak); (B) after treatment with 1 M aqueous HClO₄, pattern offset by 0.5°. Top: Schematic representation of the head-to-head lamellar structure of poly(2) inferred from X-ray diffraction pattern.

from dilute solutions of **2** is probably a consequence of molecular self-assembly such that, although the bulk concentration of surfactant pyrrole is only 5 mM, the *effective* local concentration around a reactive pyrrole radical cation is much higher. Polymerization then proceeds, in preference to diffusion of the radical cation away from the electrode.

Thicker layers were deposited by potentiostatic polymerization at +650 mV in a gently stirred solution. The electrode was disconnected at a positive potential, and the resulting films were briefly rinsed in water, dried under reduced pressure, and peeled from the electrode to afford free-standing films. Transmission Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were in accord with the proposed polymeric structure and indicated the absence of nitrate (NO_3^-). The infrared spectrum of the polymer has only weak adsorptions in the region for pyrrole C–H out-of-plane bending, which were observed as strong adsorptions in the spectrum of the monomer **2**. The films were completely soluble in chloroform, swollen and partially soluble in water, and insoluble in dimethyl sulfoxide and acetonitrile.

X-ray diffraction of as-grown films on gold or ITO glass gave four reflections, shown in Figure 2A. The spacings indicate a lamellar structure with an interlayer spacing of 42.2 ± 0.2 Å. The diffraction pattern closely resembles that of Langmuir–Blodgett multilayers[13] and is consistent with a head-to-head structure, shown schematically in Figure 2 (inset). These as-grown films are highly resistive. Immersion of the films in 1 M HClO₄ brings about cation exchange of potassium for proton (XPS: no K signal, no ClO_4^- incorporation), with a concomitant contraction of the lamellar spacing to 41.1 ± 0.3 Å (Figure 2B). Preliminary measurements on the ion-exchanged films indicate an anisotropic electrical conductance with a conductivity parallel to the surface ($\sigma_\parallel$) of 10^{-3} $\Omega^{-1}\cdot cm^{-1}$ and a perpendicular conductivity ($\sigma_\perp$) of 10^{-6} $\Omega^{-1}\cdot cm^{-1}$. The conduction mechanism (electronic versus ionic) has not been determined.

The formation of this head-to-head bilayer type assembly by polymerization of pyrrole-containing surfactants from micellar solutions implies that assembly of the monomers, or growing polymer chain, at the electrode (i.e., as a hemimicelle) predominates over the head-first delivery of the surfactant to the electrode by the micelle. The homopolymers assemble into a layered morphology, producing a film which is highly ordered relative to

other poly(heterocycles). This method can be used without the need for an ordered supporting medium, and with the distinct advantage of operational simplicity over the use of the Langmuir–Blodgett technique for the deposition of such materials.

Supplementary Material Available: Characterization (NMR, IR, XPS) of **2**, poly(**2**), and ion-exchanged poly(**2**) (1 page). Ordering information is given on any current masthead page.

Evidence for Monomeric Metaphosphate as an Intermediate in the Hydrolysis of μ-Monothiopyrophosphate

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NMR analysis of the cleavage of μ-monothiopyrophosphate trianion (MTP) by tris(hydroxymethyl)aminomethane (Tris), in competition with water under hydrolytic conditions, shows that Tris competes with water for accepting the phosphoryl group from MTP; however, the kinetics fails to implicate Tris as a nucleophile in the transition state for P–S bond cleavage. The simplest mechanism that is consistent with both the kinetic and trapping results is a preassociation stepwise mechanism, in which metaphosphate monoanion (PO_3^-) is produced from MTP in the rate-limiting step, and PO_3^- is instantly trapped by a nucleophilic species participating in the solvation of MTP. Tris at high concentrations occupies the solvent cage and traps PO_3^- in competition with solvating water.

Monomeric metaphosphate has long been proposed to be an intermediate in phosphoryl group transfer reactions such as the solvolysis of alkyl phosphate monoanions and of aryl and acyl phosphate dianions with very good leaving groups ($pK_a < 7$).[1] Phosphoryl transfer in alcoholic solutions was found to proceed with inversion of configuration at chiral P and failed to give evidence for the existence of diffusible PO_3^-.[2] In poorly solvating organic reaction media, racemization of chiral P in the course of solvolysis has been observed and offered as evidence for the participation of PO_3^- as a discrete, intermediate species.[3] The existence of PO_3^- in organic solvents such as acetonitrile and *tert*-butyl alcohol has also been proposed based on studies of kinetics and product composition.[4] However, kinetic studies in aqueous solutions showed that attacking nucleophiles are partially bonded to P in the transition state for phosphoryl transfer in reactions of acyl phosphates and phosphoramidates.[5]

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