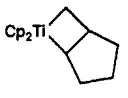
(**9–11**) derived from cyclic olefins leads to the corresponding cyclopropanes, suggesting a new method for end-capping living ring-opening metathesis polymers.[7c] Oxidative cleavage of the numerous Ti and Zr metallacycles in the literature, particularly five-membered-ring systems attainable by cyclizations of alkenes, alkynes, and carbonyl compounds,[17] could provide new routes to hetero- and carbocycles.



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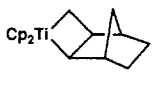

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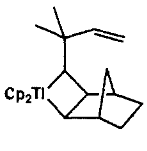

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We are currently investigating the redox chemistry and photochemistry of other organometallic complexes as well as examining the synthetic applications of their oxidation chemistry.

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Supplementary Material Available: Experimental methods including electrochemical details and kinetic analyses (5 pages). Ordering information is given on any current masthead page.

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Morphology Control in Electrochemically Grown Conducting Polymer Films. 1. Precoating the Metal Substrate with an Organic Monolayer

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We report in this communication on a significant increase in the density of an electrochemically grown conducting polymer film obtained by preadsorbing a self-assembling monolayer onto the surface of the electrode substrate.

The properties of electrochemically grown conducting polymer (CP) films have been described recently by many authors. Relatively limited attention has been paid, however, to the mechanism of the film growth process. Park and co-workers have described in a series of recent papers[1] the detection of molecular species (mainly dimers) that serve as intermediates in the film growth process, as well as the products of parallel anodic processes and of film degradation.[1] The results of this last work suggest that the net electrochemical growth rate for a CP film depends on the relative rates of several parallel anodic processes, all of which may be associated with very close onset potentials. To generate the polymer itself from soluble intermediates, the newly formed phase has to (a) nucleate and (b) grow in three dimensions. These are two elementary steps that have been investigated extensively for metal electrodeposition processes, but much less so for the growth of electronically conducting polymers. Important film characteristics that may be strongly affected by the nature of the nucleation-and-growth process are the morphology and the degree of space filling. These may have, in turn, strong effects on the electrical and electrochemical characteristics of the film. Previous in situ investigations by ellipsometry[2-4] have demonstrated the capability of this optical technique to obtain some information on details of the electrochemical growth of conducting polymer films. Other investigations[5,6] have shown that the quartz crystal microbalance (QCM) is an effective tool for measuring charge efficiencies in the process of CP film growth. We have recently reported a system for simultaneous in situ ellipsometry and QCM measurements.[7] This system allows us to measure continuously the film thickness and mass as two independent parameters and thus follow in situ the density of the film during electrochemical growth.

A significant barrier to polymer growth on a metal surface may originate from poor adhesion between the growing phase and the substrate. This could result in inhibited nucleation and growth of the film along the substrate, preventing the formation of films with good space filling. An example of the optical properties of a film formed under such conditions is given in Figure 1A. This curve is the ellipsometric Ψ vs Δ plot for a film of polyaniline (PANI) grown galvanostatically at a gold electrode substrate. Some familiarity with this type of ellipsometric plot allows an immediate qualitative observation: the small radius of curvature of this plot is testimony for a film with a refractive index very close to that of the electrolyte.[8] A quantitative evaluation of the optical properties and thickness of this film has shown that optical parameters vary somewhat during film growth, but this variation is slight and does not amount to a significant change in film characteristics. The refractive index can be expressed in this case as $\hat{n}_{\text{film}} = 1.30 \pm 0.02 + (0.025 \pm 0.015)i$. It is readily seen that this film can be described optically as a "slightly perturbed layer of electrolyte" (the refractive index of the electrolyte at this wavelength is $n = 1.335 + 0i$). Results of a QCM measurement taken simultaneously during the same experiment of galvanostatic growth are shown in Figure 2 (dashed curve). The calculated film density obtained from the division of film mass (QCM) by its thickness (ellipsometry) shows some variations at growth times smaller than 50 min, but for growth times larger than 50 min the evaluated density stabilizes in the range of 1.07–1.08 gr/cm^3. Such a low density agrees well with the conclusion reached above from the optical properties of this film, namely, that this is a CP layer with a high electrolyte content and poor space filling.

Suspecting that a surface wetting problem is an important reason for the poor film morphology, we tried to treat the gold surface so as to increase film/substrate adhesion. To achieve that, we adsorbed on the gold substrate a self-assembled monlayer of *p*-aminothiophenol (PATP)[9] so as to form a uniform monolayer of bound aniline monomers on the electrode. (In general, sulfur–hydrocarbon molecules are adsorbed readily onto gold,[10] and hydrocarbon–thiol self-assembling monolayers were used previously to modify electrode surfaces for other purposes.[11]) Following the coating of the gold surface with this monolayer, we grew on it the film of PANI, using the same galvanostatic growth conditions as in the "bare" gold case. The film that formed now on the gold surface had substantially different properties. The

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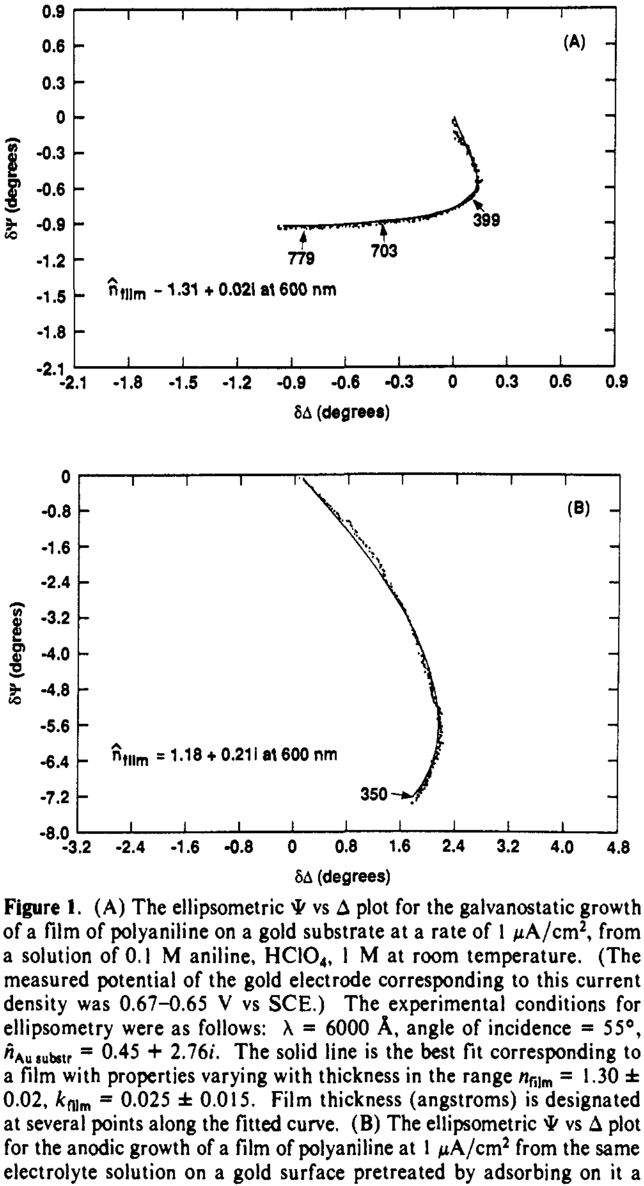

Figure 1. (A) The ellipsometric Ψ vs Δ plot for the galvanostatic growth of a film of polyaniline on a gold substrate at a rate of 1 $\mu A/cm^2$, from a solution of 0.1 M aniline, $HClO_4$, 1 M at room temperature. (The measured potential of the gold electrode corresponding to this current density was 0.67–0.65 V vs SCE.) The experimental conditions for ellipsometry were as follows: λ = 6000 Å, angle of incidence = 55°, $\hat{n}_{\text{Au substr}} = 0.45 + 2.76i$. The solid line is the best fit corresponding to a film with properties varying with thickness in the range $n_{\text{film}} = 1.30 \pm 0.02$, $k_{\text{film}} = 0.025 \pm 0.015$. Film thickness (angstroms) is designated at several points along the fitted curve. (B) The ellipsometric Ψ vs Δ plot for the anodic growth of a film of polyaniline at 1 $\mu A/cm^2$ from the same electrolyte solution on a gold surface pretreated by adsorbing on it a self-assembling monolayer of *p*-aminothiophenol (PATP). The solid line corresponds to the best fit: a film with properties $\hat{n}_{\text{film}} = 1.18 + 0.21i$ (independent of film thickness). Experimental conditions for ellipsometry were the same as in part A. (The gold electrode potential was 0.65–0.64 V.)

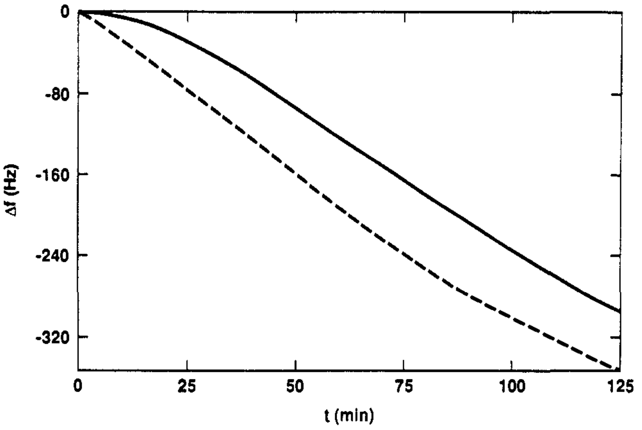

Figure 2. Dashed line: The variation of QCM resonance frequency with time during the growth of the film of polyaniline on the "bare" gold electrode. Solid line: The variation of QCM resonance frequency with time during the growth of the film on gold precovered by a monolayer of PATP. QCM sensitivity = 60 Hz/μg cm^{-2}.

characteristic ellipsometric plot shown for this case in Figure 1B is quite different in nature and is associated with a significantly larger radius of curvature. For this film, the optical properties could be fit, assuming no variation with film thickness. The solved imaginary component of the refractive index is 0.21. This means that the absorption coefficient of this film at λ = 6000 Å is about 8 times higher than the average absorption coefficient found for the film grown on "bare" gold. The real part of the complex refractive index is seen to be smaller in the film grown on the PATP-treated surface (1.18 vs 1.30), and this trend has to do with the interrelationship between the real and imaginary components of $\hat{n}_{\text{film}}$, as discussed in detail elsewhere.[8] QCM readings obtained simultaneously for the PANI film grown on the treated surface (Figure 2, solid curve) show that, although this layer is only ca. 400 Å thick, its mass is almost as large as that of the ca. 800 Å thick film grown on "bare" gold. The density calculated for this thinner film varies in the range 1.8–2.1 gr/cm^3, for growth time greater than 50 min. This is a density somewhat higher than expected for a polymer film of this type, even with very good space filling, and we believe that this is caused in part by the perchlorate anions incorporated. However, we cannot rule out the possibility of a slightly underestimated (10–15%) optical thickness. The latter can be caused by some interplay in the fit between optical properties and film thickness, as well as by some lateral nonuniformity of the film within the area probed by the beam.

In conclusion, we have shown that a substantial increase in CP film density can be achieved for electrochemically grown PANI films by preadsorbing on the gold electrode surface a self-assembled monolayer of PATP. The PATP molecules bind well to the gold substrate, apparently through the sulfur end,[9] and in turn facilitate and regulate the bonding between the modified surface and the growing phase of the PANI. The beneficial effect obtained on film morphology is apparently caused by a more uniform and efficient nucleation-and-growth process on the treated surface, resulting in a film with signficantly improved space filling. Further work in progress addresses questions of the preservation of the effect of this surface treatment in thicker CP films and the nature of the resulting changes in mechanical, electronic, and electrochemical properties of the CP film.

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Unusual Deacylations: The 2-Acetyl-3-methylbenzothiazolium Cation

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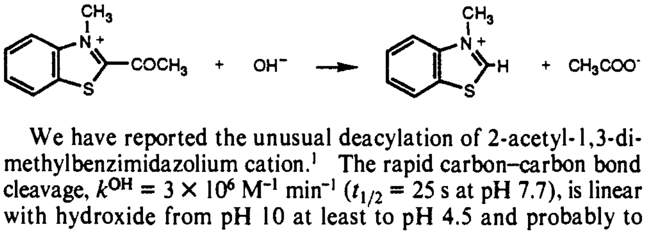
The 2-acetyl-3-methylbenzothiazolium cation undergoes deacylation to acetate and 3-methylbenzothiazolium ions with a second-order rate constant, k^{OH}, close to 10^9 M^{-1} min^{-1}. Despite the reaction being a carbon–carbon bond cleavage, this may be the fastest hydroxide-mediated deacylation yet discovered.



We have reported the unusual deacylation of 2-acetyl-1,3-dimethylbenzimidazolium cation.[1] The rapid carbon–carbon bond cleavage, $k^{OH} = 3 \times 10^6$ M^{-1} min^{-1} ($t_{1/2}$ = 25 s at pH 7.7), is linear with hydroxide from pH 10 at least to pH 4.5 and probably to pH 2. No water reaction is seen. The reaction rate is unaffected,

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