Microstructured Photopolymer Films of a Ruthenium(II) Polypyridine Complex. Fabrication of an Electrochemically Switchable Phase Grating

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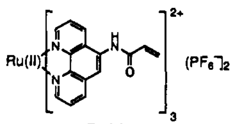
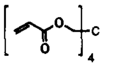
Fabrication of thin polymeric films composed of redox-active monomers via electropolymerization is an established technology.[1,2] Although electropolymerization is a versatile method for preparation of films containing multiple chemical sites or multilayer films in which each layer comprises chemically distinct monomer units,[3,4] the method does not afford a direct means to create films that are patterned within the plane of the substrate.[1c] By contrast, photolithography provides a means to fabricate thin polymer films that are structured in 2-D patterns with micron and submicron spatial resolution.[5] Photolithography is most often used to prepare microstructured films composed of monomers that are not interesting from an electrochemical standpoint;[5] however, in principle the method can be applied to any species that can be photopolymerized, including electroactive monomers.[6–8]

Herein we report a unique application of photolithography to fabricate microstructured electroactive polymer films that are adsorbed to an optically transparent, conducting substrate. This study has focused on microstructured films composed largely of a polypyridyl-Ru(II) monomer, a system which has featured in many studies of electropolymerized films.[1b,3,9,10] These microstructured photopolymer films display interesting and potentially useful electrochemical and optical properties; the present report describes application of this new technology to the fabrication of an optical diffraction grating that can be electrochemically modulated.

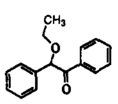
The lithographically-defined photopolymer films that are the heart of this investigation are composed largely of the monomeric triacrylate complex RuAAP.[11] This complex was selected for the investigation because the Ru–phenanthroline chromophore exhibits electrochemical and photochemical properties typical of polypyridine–Ru(II) complexes[12] and because acrylamides undergo rapid free radical polymerization.[13] In a typical film preparation, a concentrated DMF solution of RuAAP, pentaerythritol tetraacrylate (PETA4), and benzoin ethyl ether (BEE) (molar ratio 1.0:1.6:0.1 Ru/PETA4/BEE, respectively) is spin-coated onto Pyrex or In-SnO$_2$ (ITO)-coated glass. After a 1-h drying period, the film-coated substrate is placed into contact with a chrome-on-glass reticle that has a Ronchi grating pattern with a spatial frequency of 100 lines/mm (e.g., alternating 5-μm lines and gaps). The substrate–grating pair is then exposed to Pyrex-filtered light from a medium pressure Hg arc lamp (60 mW/cm^2) for 30–60 min. Following exposure, the film is developed by immersion in MeOH followed by CH$_2$Cl$_2$.



RuAAP



PETA4



BEE

Figure 1 illustrates an optical microscope image of a typical grating-patterned RuAAP/PETA4 film on a borosilicate glass substrate. The RuAAP/PETA4 film is present only in regions that were exposed to light, consistent with the hypothesis that near-UV irradiation produces a free-radical initiator (via Norrish type I cleavage of BEE) which induces polymerization of the acryloyl monomers.[14] This hypothesis is supported by the fact that a polymer film which is stable to solvent development is *not* formed if (1) BEE is not present in the spin-coat mixture and (2) the film is exposed only to visible light ($\lambda > 400$ nm). Although the best photopolymer films are obtained using BEE, acceptable films are produced using other free radical (co-)initiator systems such as 1-hydroxycyclohexyl phenyl ketone, tetrabutylammonium triphenylbenzyl borate, or triethanolamine.[14] Close inspection of Figure 1 reveals that the line widths of the RuAAP/PETA4 photopolymer film are only slightly (e.g., ≈ 1 μm) broader than the 5-μm line width of the reticle; this degree of resolution is typical for negative-tone photolithography.[5] Scanning electron microscope images of freeze-fractured samples indicate that the median thickness of the photopolymer films is 0.4–1.0 μm.

All of the available evidence indicates that the light-initiated reaction in the RuAAP/PETA4 films involves free radical chain polymerization of the acryloyl groups.[14] Because each monomer features three or more acryloyl groups, even a low degree of polymerization is expected to produce a highly cross-linked (and therefore insoluble) matrix. Experiments carried out with varying levels of PETA4 in the spin-coat mixture indicate that this component stabilizes the photopolymer films so that they are insoluble in strong solvents (e.g., CH$_3$CN or CH$_2$Cl$_2$). This result suggests that the degree of polymerization is higher when PETA4 is present in the films, possibly because propagation of the free radical chain proceeds more readily in the RuAAP/PETA4 mixture, which is less viscous compared to a "dry" film that contains only RuAAP.[15]

RuAAP/PETA4 photopolymer films that are adsorbed onto ITO-coated glass are electroactive. A reversible wave for the Ru(II/III) couple is observed at $E_{1/2} = +1.38$ V vs SSCE in an anodic cyclic voltammogram of a grating-patterned RuAAP/

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(11) RuAAP was prepared by acryloyl chloride treatment of [Ru^{II}(5-aminophenanthroline)$_3$$^{2+}$][PF$_6^-$]$_2$, which was obtained by Sn/HCl reduction of [Ru^{II}(5-nitrophenanthroline)$_3$$^{2+}$][PF$_6^-$]$_2$. RuAAP was purified by chromatography on alumina eluting with CH$_3$CN/CH$_2$Cl$_2$ (1:1 v/v); purified samples exhibit the expected ^{1}H and ^{13}C NMR spectra. Anal. Calcd for C$_{45}$H$_{33}$N$_9$O$_3$P$_2$F$_{12}$Ru·2H$_2$O: C, 46.01; H, 3.17; N, 10.73. Found: C, 45.96; H, 3.02; N, 10.59.

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(15) PETA4 is a viscous liquid. Therefore, the spin-coated film of RuAAP/PETA4 is essentially a viscous, concentrated solution of RuAAP dissolved in PETA4.

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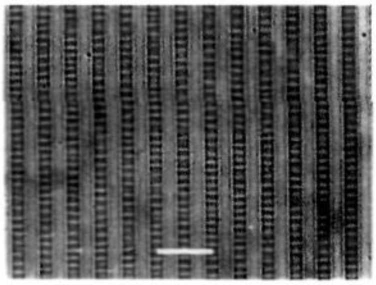

Figure 1. Optical microscope image of a grating-patterned RuAAP/PETA4 photopolymer film (magnification ≈1000×). The horizontal white bar corresponds to a distance of 20 μm. Photopolymer lines are aligned along the vertical axis in the image. Irregularly-spaced, alternating light/dark areas within polymer lines may be due to phase separation of RuAAP and PETA4. Experiments in progress are exploring this possibility.

PETA4 film on an ITO electrode (area = 0.079 cm^2) immersed in CH_2Cl_2/0.1M tetrabutylammonium hexafluorophosphate (TBAH).[16] At a sweep rate of 10 mV/s the Ru(II/III) wave is very symmetrical, however, the peak-to-peak separation between the anodic and cathodic waves (ΔE_p = 120 mV) is greater than expected for a surface-immobilized species.[1a] This deviation is likely due to poor redox conductivity and/or slow ion transport within the photopolymer film.[17] Integration of the anodic current waves for 10 representative ITO electrodes coated with a grating-patterned RuAAP/PETA4 film reveals an average surface coverage over the electrode of $\Gamma = 3.5 \times 10^{-9}$ mol/cm^{-2} of RuAAP sites. Since the RuAAP/PETA4 film is present as a grating pattern (e.g., 50% electrode coverage), an average film coverage of $\Gamma = 7.0 \times 10^{-9}$ mol/cm^{-2} is implied. This coverage is consistent with that expected on the basis of the film thicknesses observed in freeze-fracture SEM measurements.

Owing to the narrow line spacing of the grating-patterned RuAAP/PETA4 photopolymer, a film-coated substrate operates as a diffraction grating.[18] The diffraction properties of film-coated substrates were explored using a CW He–Ne laser (633 nm, 0.5 mW). Since the RuAAP/PETA4 films are optically transparent at 633 nm, diffraction arises because the microstructured film produces a regularly spaced modulation in the refractive index ($\Delta\eta$) in the plane of the substrate (e.g., the film-coated substrates are phase gratings).[19] When a He–Ne laser beam impinges on a film-coated substrate, the first-order diffracted beam is observed at $\theta = 3.6°$ relative to the axis defined by the incident beam, which is the angle expected on the basis of the grating equation ($\theta = \sin^{-1}(\lambda/d)$, where λ = 633 nm and d = 10 μm).[18b] For a typical RuAAP/PETA substrate, the intensity of the first-order diffracted beam is approximately 10% relative to that of the undiffracted beam (e.g., the diffraction efficiency, DE ≈ 10%).

A remarkable feature is that the DE of the RuAAP/PETA4 phase gratings can be electrochemically modulated.[20] Figure 2 summarizes the results of an experiment which demonstrates this effect. A RuAAP/PETA4 film-coated ITO electrode was immersed in a CH_2Cl_2/TBAH solution. The potential of the electrode was controlled with a potentiostat while the intensities of the first-order diffracted and the undiffracted beams from a He–Ne laser were monitored with photodiodes. The potential of the electrode was swept from 0 to +1.80 to 0 V (triangular wave) at a rate of 10 mV/s. Figure 2a shows the electrode potential and the current response (*i–t* plot) of the electrode, and Figure 2b illustrates the relative intensity of the first-order diffracted laser beam. On the first sweep, the relative DE remains constant until the electrode reaches +1.30 V, at which point the DE rapidly drops to 71% of the initial DE (DE_0). The DE remains low until the electrode potential reaches +1.50 V on the return scan, at which point it rapidly increases again, settling at >90% of DE_0. On the second sweep the same pattern is observed with the DE switching from ca. 90% to 71% to 90%. Additional sweeps were performed, and it was observed that the DE could be reversibly switched at least 10 times, with a slight but noticeable decrease in the modulation depth with each succeeding sweep. A concomitant slight decrease in the current response is also evident with each succeeding sweep.

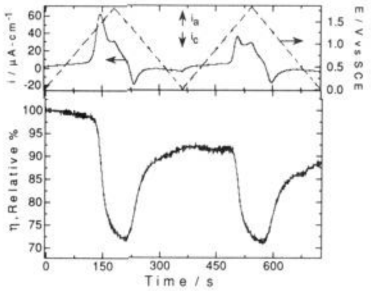

Figure 2. Plots of applied potential, current response, and relative diffracted laser beam intensity for the electrochemically-modulated phase grating experiment (see text for details). (a, top) Dashed line: applied potential, scale on right axis. Solid line: current response, scale on left axis. (b, bottom) Relative intensity of first-order diffracted beam.

The modulation in DE is clearly associated with the Ru(II/III) oxidation, as evidenced by the correspondence between the DE changes and the cathodic and anodic waves in the *i–t* plot. Furthermore, the magnitude of the change in DE correlates with the amount of charge transferred due to the Faradaic process. For example, the first anodic wave in the *i–t* plot is larger than the subsequent cathodic and anodic waves, while the first excursion in DE (a 29% change) is larger than subsequent excursions (≈20% changes). This initial burst in charge is frequently observed in the electrochemistry of redox polymers and is ascribed to charge trapping within the film.[21]

The origin of the electrochemically-induced modulation in the DE of the grating-patterned RuAAP/PETA4 film is likely due to a change in the refractive index (η) of the film which is coupled with the Ru(II/III) oxidation/reduction.[22] One possible explanation for the electrochemically-induced change in η is that when the Ru(II/III) oxidation occurs, there is an influx of counterions (PF_6^-) into the film. The influx of counterions may increase the effective η of the film, leading to a net *decrease* in $\Delta\eta$ created by the grating-patterned film, which results in a decrease in DE.[23] Experiments in progress seek to further explore and optimize the electrochemically-modulated change in DE for grating-patterned photopolymer films containing RuAAP and other photoactive and redox-active monomers such as viologens, diimides, and porphyrins.

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[16] Reductive scans (0 → −1.50 V) of the RuAAP/PETA4 films induce an irreversible cathodic wave ($E_p \approx -1.4$ V) which triggers a virtually complete loss of electroactivity upon subsequent anodic or cathodic scans. Experiments in progress seek to elucidate the origin of this effect.

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[22] The change in DE is not due to a change in transmittance of the film, since little or no change in the intensity of the undiffracted beam is observed concomitant to the Ru(II/III) oxidation/reduction.

[23] Since η of CH_2Cl_2 is likely larger than that of the RuAAP/PETA4 film, an increase of η for the film leads to a *decrease* in $\Delta\eta$. Because DE is proportional to $\Delta\eta$, the DE will decrease in this case.