

## Resonance Effects in Electroactive Poly(3-hexylthiophene) Films

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The convenience and effectiveness with which electrode properties may be modified by an electroactive polymer overlayer has made this one of the largest areas of electrochemical research over the past decade.<sup>1</sup> One of the most important and versatile classes of materials used for this purpose is that of electronically conducting polymers based on polyheterocycles.<sup>2</sup> Here we report a novel observation related to one such material, poly(3-hexylthiophene) (PHT), whose optical and electronic properties have recently attracted interest for exploitation in field effect transistors,<sup>3</sup> color sensors for imagers,<sup>4</sup> and rechargeable batteries.<sup>5</sup>

Rational interfacial design requires understanding the relationship between structure, function, and dynamics of the modifying polymer film, exemplified specifically for PHT by a recent electropolymerization optimization study.<sup>6</sup> More generally, understanding of polymer-modified electrodes has benefitted from innumerable spectroscopic and physical characterization techniques.<sup>1,2</sup> One technique that has contributed to this effort is the electrochemical quartz crystal microbalance (EQCM).<sup>7–9</sup> In the simplest case of a rigidly coupled film, the EQCM can be used as a gravimetric probe of mobile species exchange between the film and its bathing electrolyte. However, when the polymer is viscoelastic, the EQCM response is a function of film rheology. Here we report a special case of this situation, *film resonance*, which arises from acoustic interference effects within the film.

Thickness shear mode resonators utilize the electromechanical coupling properties of a piezoelectric substrate material (here AT-cut quartz) to launch an acoustic wave into the contacting medium. When this medium is a thin, rigid, solid overlayer, its deformation is minimal, and the shift in oscillator resonant frequency is proportional to film mass.<sup>10</sup> This has allowed exploration of redox-driven ion, solvent and small molecule dynamics at electroactive films.<sup>7–9</sup> When the overlayer is *not* rigid, the resonator response is a function of *polymer*, rather than mobile species, dynamics.<sup>11</sup> Although it is generally appreciated that polymer dynamics have

a pivotal role to play in applications of electroactive polymer films, this topic has only recently begun to receive attention.<sup>12,13</sup>

Film viscoelastic properties are described by the complex shear modulus,  $\mathbf{G} = G' + jG''$ . The real component ( $G'$ ) is associated with energy storage, here due to polymer chain deformation, and the imaginary component ( $G''$ ), with energy loss, here due to polymer chain flow. Shear wave deformation across the film can be represented by the acoustic phase shift,  $\phi$ , which is related to the angular frequency ( $\omega = 2\pi f$ ), and the film density ( $\rho_f$ ), thickness ( $h_f$ ) and shear modulus by<sup>11</sup>

$$\phi = \omega h_f \operatorname{Re}(\rho_f \mathbf{G})^{1/2} = (\omega h_f / G') [1/2 \rho_f (|\mathbf{G}| + G')]^{1/2} \quad (1)$$

where Re indicates the real part of the quantity in parentheses. A special case, termed “film resonance”, is predicted when the acoustic phase shift across the film reaches  $\pi/2$ .<sup>14</sup> Here, interference between the acoustic waves launched by the crystal and reflected at the outer film boundary results in maximal motional resistance. This resonance effect has been reported for a few electroinactive polymers exposed to air or vapor,<sup>15–17</sup> by manipulating the acoustic phase shift through the polymer shear modulus.

In the electrochemical context, exposure of the polymer to an electrolyte solution means that the acoustic reflection coefficient at the outer film boundary is unknown, variable, and undoubtedly smaller than that in the vapor phase case. Whether film resonance will then occur at all is an open question. To our knowledge, the only report of film resonance in a liquid environment involved temperature-dependent swelling of an electroinactive polymer brush.<sup>18</sup> We now unequivocally show, through the example of PHT films, that film resonance does indeed occur for electroactive films maintained under electrochemical control.

PHT films were deposited potentiodynamically (0.4–1.9 V in cycle 1, 0.4–1.6 V thereafter; scan rate 20 mV s<sup>-1</sup>) onto the exposed Au electrode of 10 MHz AT-cut quartz crystals (piezoelectric and electrochemically active electrode areas 0.21 cm<sup>2</sup> and 0.23 cm<sup>2</sup>, respectively). Polished crystals were employed to minimize surface roughness effects.<sup>12</sup> The deposition solution contained 3.7 mmol dm<sup>-3</sup> HT (Aldrich) and 0.1 mole dm<sup>-3</sup> tetraethylammonium hexafluorophosphate (Aldrich, >99%) in propylene carbonate. The counter electrode was a Pt gauze. The reference electrode was Ag<sup>+</sup>(0.01 mol dm<sup>-3</sup>)/Ag; for comparison purposes, potentials are reported with respect to SCE. After each polymerization cycle, the potential was held at 0.4 V until the current decayed to zero. Crystal impedance measurements were then recorded at the first and third harmonics, using a Hewlett-Packard HP8751A network analyzer connected via a 50  $\Omega$  coaxial cable to a HP8512A transmission/reflection unit.<sup>12</sup> Together with the doping level ( $n = 0.35$ ), the integral ( $Q_{\text{red}}$ ) of the current response for PHT film reduction in each polymerization cycle provided a dynamic coulometric assay of polymer coverage. Measurements were made at room temperature ( $20 \pm 2$  °C).

Figures 1 and 2, respectively, show representative crystal impedance spectra for the first (10 MHz) and third (30 MHz) harmonics as functions of  $Q_{\text{red}}$ , representing polymer coverage.

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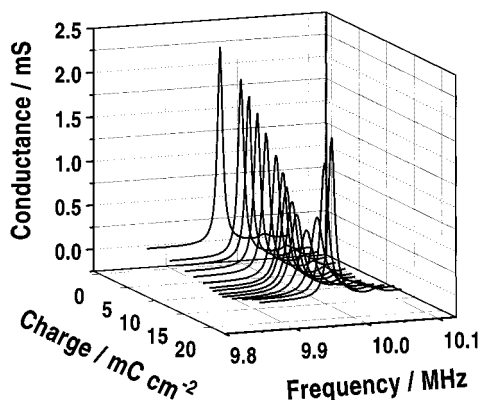
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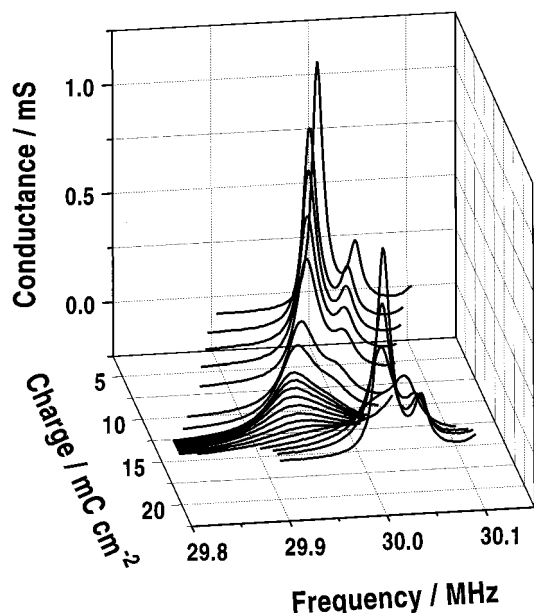
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**Figure 1.** First harmonic crystal impedance spectra as a function of film charge during PHT film deposition. Experimental details as in main text.



**Figure 2.** Third harmonic crystal impedance spectra acquired during the experiment of Figure 1.

From the outset and for the majority of the experiment, the responses are typical of those commonly reported for viscoelastic films: for  $Q_{\text{red}} < 16 \text{ mC cm}^{-2}$ , the peak admittance and resonant frequency systematically decrease. However, this does not continue: the trend in frequency shift is reversed, and then the peak admittance reaches a minimum at  $Q_{\text{red}} \approx 20.0 \text{ mC cm}^{-2}$  (at both 10 MHz and 30 MHz). Finally, at higher  $Q_{\text{red}}$ , the peak conductance and resonant frequency both increase, to the extent that by  $Q_{\text{red}} \approx 22.4 \text{ mC cm}^{-2}$  the resonant frequency returns almost to the value for the uncoated device exposed to the polymerization solution. This latter behavior is clearly not consistent with simple models of a viscoelastic film.<sup>11–13</sup>

Resonator responses can be modeled using Butterworth–Van Dyke and transmission-line equivalent circuits,<sup>11–13</sup> in which resistive ( $R$ ) and inductive ( $L$ ) elements represent energy loss and inertial mass, respectively. The electrical impedance,  $Z_e$ , contributed by the film and contacting electrolyte is related to the mechanical impedance,  $Z_s$ , at the sensing surface of the quartz resonator. We have simulated resonator responses as a function of film thickness using a three-layer model. This model describes  $Z_s$  in terms of an ideal mass layer, a finite homogeneous viscoelastic layer, and a semi-infinite Newtonian fluid.<sup>12</sup> The ideal mass layer is required to account for rigidly coupled material

entrapped within electrode surface features, of vertical dimension  $h_s$ . The fluid is characterized by the liquid viscosity–density product ( $\eta_l \rho_l$ ). Measurements on the bare electrode in the polymerization solution prior to PHT deposition gave  $h_s = 30 \text{ nm}$  and  $\eta_l \rho_l = 0.0307 \text{ g}^2 \text{ cm}^4 \text{ s}^{-1}$ ; these estimates differed by 9% and 2%, respectively, when determined separately at the two operating frequencies. The literature values of the fluid parameters for the pure solvent are  $\eta_l = 0.0247 \text{ g cm}^{-1} \text{ s}^{-1}$  and  $\rho_l = 1.19 \text{ g cm}^{-3}$ , yielding  $\eta_l \rho_l = 0.0294 \text{ g}^2 \text{ cm}^4 \text{ s}^{-1}$ . The slightly higher experimental value (ca. 4% for the product) is almost certainly the result of adding the solute.

Using these parameters, we were able to fit the polymer surface mechanical impedance and thereby obtain its complex shear modulus as a function of coverage during deposition. We find qualitatively similar, but quantitatively *dissimilar*, behavior at the first and third harmonic frequencies. In both cases,  $G' \gg G''$ ,  $G'$  increases during the initial stages of deposition, and then ( $Q_{\text{red}} > 6 \text{ mC cm}^{-2}$ )  $G'$  achieves limiting values characteristic of a rubbery polymer. The separately fitted values of  $h_f$  agree within 20%, as indeed they must. The significant difference at the two harmonic frequencies is the value of  $G'$ :  $6 \times 10^7 \text{ dynes cm}^{-2}$  at 10 MHz and  $1.2 \times 10^8 \text{ dynes cm}^{-2}$  at 30 MHz. This is consistent with the general behavior of polymers in the transition region between a rubbery and a glassy material.<sup>19</sup>

The qualitative claim (based on the evidence of Figures 1 and 2) that we have observed film resonance must be quantitatively supported by eq 1 using the fitted shear moduli. The resonant condition ( $h_f = h_f^*$ ) is that  $\phi = \pi/2$ . Using the fitted shear moduli prior to resonance, application of eq 1 under resonant conditions yields  $h_f^* = 1.9 \mu\text{m}$  at 10 MHz and  $h_f^* = 0.87 \mu\text{m}$  at 30 MHz; the presence of a frequency dependence is a consequence of the form of eq 1. We then have two independent estimates of  $h_f^*$ . First, the film reduction charge at the point of minimum admittance,  $Q_{\text{red}}^*$  from Figures 1 and 2, together with the monomer density and molar mass, yields  $h_f^* = 0.92 \mu\text{m}$ . Second, the fitted  $h_f$  values, which experimentally are linear with  $Q_{\text{red}}$ , prior to resonance can be extrapolated to  $Q_{\text{red}}^*$ , yielding  $h_f^* = 1.1 \mu\text{m}$  (10 MHz) and  $0.80 \mu\text{m}$  (30 MHz).

This level of agreement supports the notion that we have observed film resonance. We attribute the minor discrepancies to our assumption that the film is spatially homogeneous. Neutron reflectivity studies<sup>20</sup> of electroactive polymer films show that solvent penetration is a function of depth within the film, which might result in spatially variant  $G$ . Parametric plots of  $R$  vs  $\omega L$  from Figures 1 and 2 and calculated for model homogeneous films of systematically varied  $G$  support this hypothesis. This added sophistication will be addressed in more detail in a subsequent paper.

In conclusion, we have demonstrated that acoustic resonance effects can occur in electroactive polymer films exposed to a liquid-contacting medium. These are manifested by dramatic changes in the resonator electrical response when the film thickness approaches  $1/4$  of the acoustic wavelength. In particular, trends in the peak conductance and resonant frequency shift are reversed. Future discussion of viscoelastic electroactive films must take this phenomenon into account, and allow for the possibility of structural inhomogeneity and thus spatially variant shear moduli.

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