# A Structural Investigation of Polypyrrole as a Function of Oxidation State

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## ABSTRACT

Polypyrrole exhibits actuation under electrochemical doping and undoping of the polymer matrix. Active strain and x-ray diffraction measurements are performed in order to correlate the microscopic and macroscopic structural changes occurring during actuation. Under galvanostatic reduction, the film shows first a linear contraction with oxidation state due to expulsion of small anions. At 50% of the as-grown doping level, the film reverses direction and begins to expand due to incorporation of the larger cations. X-ray diffraction, however, does not show a linear contraction in the crystalline portions of the polymer. The polymer crystallites go through a sudden contraction in one dimension of approximately 14%, and otherwise remain constant. The contraction in the polypyrrole crystals occurs at the 50% doping level, and appears to be correlated with the reversal of macroscopic actuation.

## INTRODUCTION

Conducting polymers are known to experience volume changes as they are electrochemically doped and undoped under low voltages. This effect has made these materials good candidates for application as light-weight linear actuators, or artificial muscles. Polypyrrole has been the most studied conducting polymer for this application due to its chemical stability, high conductivity and ease of manufacture. Polypyrrole actuators exhibit peak stresses one hundred times that of mammalian muscle, but fall short of real muscle when it comes to strain and strain rate. Strains of 2-5% are typical, and actuation usually occurs at rates of 1 Hz or less [1,2].

Despite much progress in the design of conducting polymer actuators, the mechanisms of actuation are still not well understood. While the volume changes can almost certainly be attributed to the flux of ions during redox cycling [3], the full electromechanical response depends on a complex interconnection of the chemical, electrical and mechanical properties. The one common factor affecting all of these properties is the structure of the polymer matrix [4-9]. The evolution of the microscopic structure during actuation is unknown.

In this study, x-ray diffraction is used to investigate the structural changes in the polypyrrole matrix as it is electrochemically doped and undoped. The active strain occurring under the same electrochemical conditions is also measured in order to understand the relationship between the microscopic structural changes and the macroscopic actuation.

## EXPERIMENT

Polypyrrole is polymerized through electrochemical oxidation of the pyrrole monomer using the method of Yamaura [8]. The electrolytic solution is composed of 0.06M distilled pyrrole, 0.05M tetraethylammonium hexafluorophosphate ($TEA \cdot PF_6$) and 1%vol water in propylene carbonate (reagents from Sigma-Aldrich). The solution is deoxygenated by bubbling with nitrogen before growth. A polished, glassy carbon crucible is used as the working electrode and the counter electrode is a copper foil. The reaction occurs at constant current of 0.125mA/cm$^2$ at a temperature of -40°C for 8 hours to obtain a thickness of approximately 25μm. Polypyrrole is grown in the doped or oxidized state. The doping level in as-grown polypyrrole is one charge per three monomers [4]. The conductivity of the film in the oxidized state is approximately 300 S/cm.

After the deposition, the film is left on the crucible and cycled from fully oxidized (as-grown doping level) to fully reduced with a galvanostatic square wave of magnitude 0.125 mA/cm$^2$ until a steady state is reached. The electrolytic solution is 0.05M TEA·$PF_6$ in deoxygenated propylene carbonate. A sheet of carbon fiber paper (TGP-H, Toray Industries Inc.) is used as the counter electrode in order to maximize the surface area and an $Ag/Ag^+$ reference electrode is used to monitor the potential at the working electrode.

Full reduction is observed by a sharp increase in the magnitude of the working electrode potential and a complete termination of the strain. Further reduction causes the film to degrade and therefore the period of the current square wave is chosen to bring the film just short of this point. After cycling, a 1cm × 4cm piece of film is removed to measure the actuation, and the rest of the film is galvanostatically reduced to the desired doping levels for x-ray diffraction.

The actuation is measured using an Aurora Scientific Muscle Lever 300B-LR. It uses a sensitive rotary motor to apply a constant stress of 1MPa, and a capacitive displacement meter to measure the strain. The actuation is performed under the same conditions as the electrochemical cycling above.

Wide angle x-ray scattering (WAXS) patterns are obtained with a Bruker AXS – D8 Advance diffractometer with a Sol-X SiLi EDX detector. The source is Cu Kα radiation with wavelengths of 1.5406Å and 1.5444Å. 10-20 films are stacked together in transmission mode to maximize the diffracted signal. The sample is placed in a vacuum chamber with Kapton windows at a pressure of ~100mTorr to eliminate unwanted low angle scattering from air. The amplitude of noise with the sample chamber under vacuum is negligible. X-ray diffraction is done on samples at varying oxidation states from overoxidized with respect to the as-grown film to fully reduced. These films are air dried for several days before measurement. The films undergo a contraction of 15% from wet to dry; therefore, these results do not exactly represent the structure of the polymer during actuation in propylene carbonate. To investigate the effect of solvent, the reduced sample is also scanned after being soaked in pure propylene carbonate.

## RESULTS AND DISCUSSION

### Actuation

In Figure 1 we see the results of galvanostatic cycling. At point A the film is fully oxidized. The film experiences a roughly linear contraction from A to B as the $PF_6^-$ ions are expelled from the film at constant current. At B, the film begins to expand. At this point there is also an inflection point in the plot of the working potential, Figure 1(b). These effects are mirrored in the oxidative cycle. Polypyrrole has been found to undergo an active strain proportional to the volume of ions displaced in the polymer matrix [10]. It is usually assumed that only the $PF_6^-$ ions participate in the actuation as they are four times smaller than the $TEA^+$ ion; however, it is possible that at this threshold potential the $TEA^+$ ions begin to penetrate the polymer. Ions can experience an activation potential to moving inside the polymer matrix resulting from the

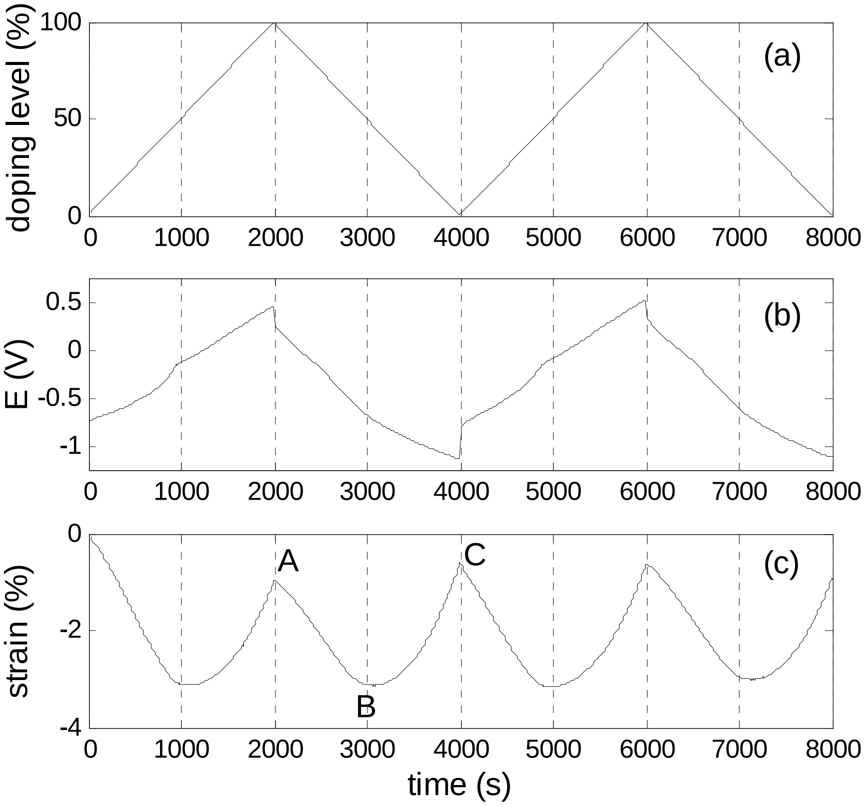

**Figure 1:** The actuation of a polypyrrole film: (a) doping level, (b) working electrode potential, and (c) strain as a function of time. In (c) the film contracts from A to B as $PF_6^-$ is expelled from the polymer and expands from B to C possibly due to $TEA^+$ incorporation.

mechanical energy required to move the polymer chains aside [11]. The current is most likely still carried in part by the more mobile $PF_6^-$ ions. This may explain why the strain rate of the expansion from B to C is less than 1.5 times that of the contraction instead of 4 times as predicted based on swelling due to $TEA^+$ ions alone. Also, neither x-ray photoelectron spectroscopy nor NMR detects any $PF_6^-$ in the fully reduced polymer.

## X-ray diffraction

The x-ray diffraction pattern of a cycled sample in the oxidized state is shown in Figure 2. The large amount of disorder inherent in the polypyrrole matrix means the x-ray peaks are broad and the higher order peaks are severely damped. According to Nogami [12], these peaks represent a monoclinic unit cell with lattice spacings a, b, and c equal to 3.4Å, 4.5Å, and 21Å respectively. The polypyrrole chains are closely stacked in the face to face direction at an angle of 65° to minimize ring-ring repulsion. The ions are believed to occupy spaces between chains in the c direction. If the ions are expelled from the polymer crystals, we expect this peak to broaden as some of the crystals contract, and the peak position to move to smaller d-values. Peak A corresponds to an intermolecular distance of 7Å and has been found to be completely amorphous, even under stretching. This peak has been attributed to the amorphous regions of the polymer [12].

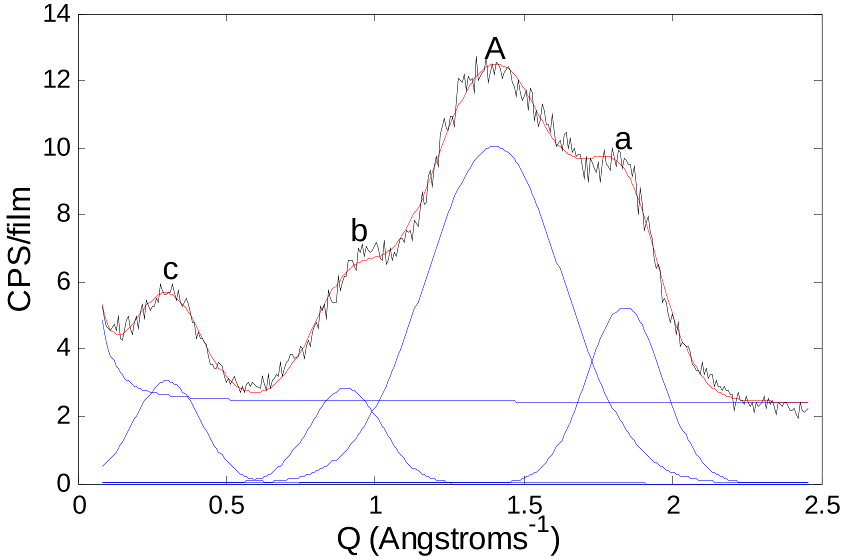

**Figure 2:** X-ray diffraction pattern of cycled polypyrrole in the oxidized state. The pattern is fit to four Gaussians and a background function. Peaks a, b, and c are from the polymer crystal and Peak A is amorphous.

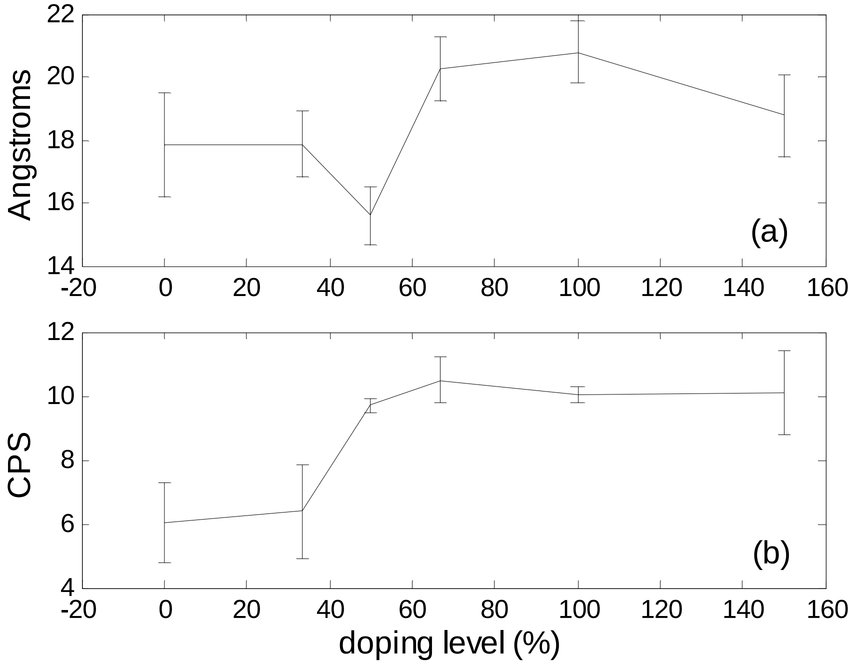

**Figure 3:** Fit parameters from the polypyrrole x-ray patterns as a function of oxidation state: (a) is the c spacing, and (b) is the amplitude of Peak A, the amorphous peak. The other parameters did not exhibit a statistically significant change with oxidation state. Error bars represent a 95% confidence interval.

The x-ray diffraction patterns of the cycled films at various oxidation states are fit to four Gaussian peaks and a background as shown in Figure 2. The background model consists of a constant diffuse portion plus a multiple of the Lorentz-Polarization (LP) factor:

$$LP = \frac{1+\cos^2 2\theta}{\sin^2 2\theta \cos\theta}. \tag{1}$$

The LP factor fits the small angle scattering of the background and generally results from uncorrelated low density scatterers. The source of the small angle scattering is still unknown. It does not appear in the as-grown film, and does not seem to be correlated with the doping level, so it may be related to the initial relaxation of the film. Density variations resulting from small crystalline and amorphous regions could also produce such scattering.

The fit parameters for the length of the c axis and the amplitude of A as a function of doping level are shown in Figure 3; these are the only parameters that show a statistically significant change. The crystal experiences a sudden contraction from 21Å to 18Å at a doping level of about ½, and is constant otherwise within experimental error. Assuming an isotropic film, this would correspond to a sudden strain of (5 ± 3)% from fully oxidized to fully reduced. The linear macroscopic actuation is not reflected in a similar linear contraction in the polymer crystallites. It seems that WAXS is not giving us the complete microscopic picture we are looking for. Future work is required to see if the amorphous regions of the polymer may offer an explanation.

The amplitude of Peak A also sees a rapid change at the level of 50% doping. The changes in microscopic structure occur at the same doping level as the change in actuation from contraction to expansion in Figure 1. The exact relationship between these effects could possibly be determined with experiments using a larger positive counter ion as a larger activation potential would result.

In Figure 4, diffraction patterns of the reduced sample in the dry state and after soaking in pure propylene carbonate show a large increase in the amplitude of Peak A. X-ray diffraction of the solvent alone confirms that bulk propylene carbonate has one strong peak at a spacing of 7Å. This is strong evidence that Peak A is due to trapped solvent in the polymer, and not amorphous regions of polymer as proposed by Nogami [12]. From Figure 3 then, it seems that the

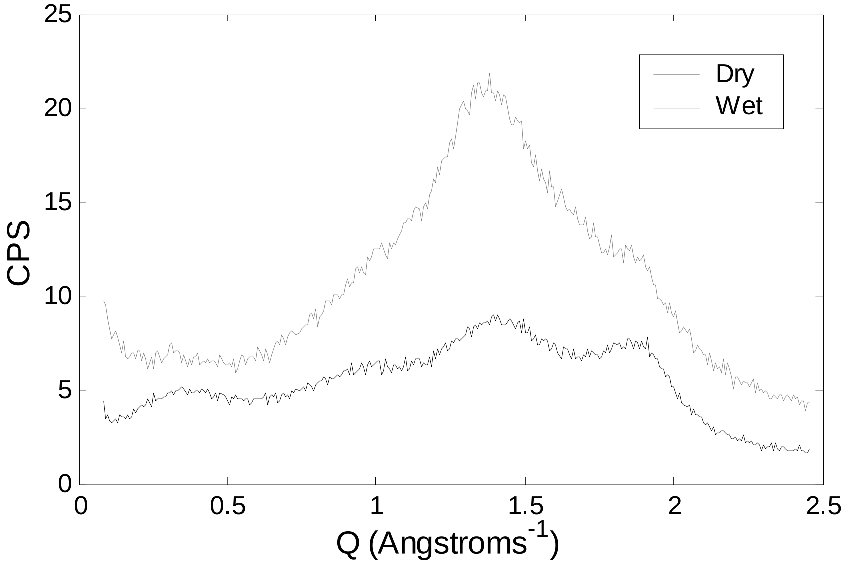

**Figure 4:** X-ray diffraction patterns from the fully reduced sample after air drying for 3 days (black) and after soaking in pure propylene carbonate (gray).

contraction in c is accompanied by a removal of trapped solvent, or a decrease in solvation. This solvent could be associated with ions expelled from the polypyrrole crystals, or it could be indicative of a chemical change in the polymer. Conducting polymers may experience a change in solvent affinity related to the charge on the backbone [13]. There did not appear to be any change in the crystal peaks upon wetting the film, although errors in the fit are large in the wet state due to the larger solvent peak.

## CONCLUSIONS

Wide angle x-ray scattering measurements of polypyrrole as a function of oxidation state are performed in an attempt to correlate the microscopic and macroscopic structural changes occurring during electrochemical actuation. Actuation measurements show the polypyrrole film contracts linearly under galvanostatic reduction and then reverses direction at a doping level of approximately 50%, possibly due to the incorporation of $TEA^+$ ions. At the same doping level, the polypyrrole crystal experiences a rapid contraction, and the solvation of the polymer decreases. The microscopic picture from x-ray diffraction does not explain the linear actuation observed. It is likely that amorphous regions of the polymer that are not visible by x-ray diffraction have a role to play in the actuation.

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