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Communications

Anisotropy of Electroactive Strain in Highly Stretched Polypyrrole Actuators

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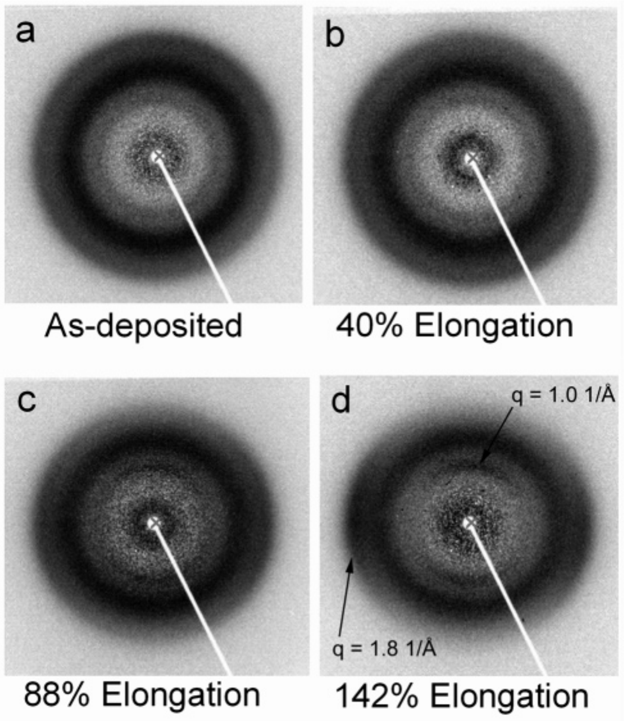

Figure 1. X-ray diffraction of stretched polypyrrole samples. Images taken at Brookhaven National Laboratories. Air scattering background is subtracted from each image. As the degree of elongation is increased, the isotropic rings observable in the first image separate into arcs that are perpendicular or parallel to the direction of stretch. In these images, the incident X-ray beam was normal to the film surface and the stretch direction is vertical. Slight misorientation of arcs from perfectly vertical and horizontal in Figure 1d is a result of a slight misalignment of the film in the beamline.

Conducting polymers such as polypyrrole (PPy) provide a particularly attractive platform for designing electroactive materials because they have a high power density (150 W/kg) and operate at low voltage (1−3 V) while providing high active stresses (10−30 MPa) and moderate active strains (2%).[1] However, for muscle-like applications in robotics and biomimetic devices, strains of 20% and strain rates of 100%/s are necessary. Polypyrrole has been extensively studied as an electroactive material,[2−11] but these studies have provided little insight as to the detailed influence that morphology has on the nanoscale actuation mechanisms. Polypyrrole has a conjugated backbone and in its conductive state is supported by an ionic dopant (in our case, hexafluorophosphate). It is actuated by electrochemically changing the oxidation state

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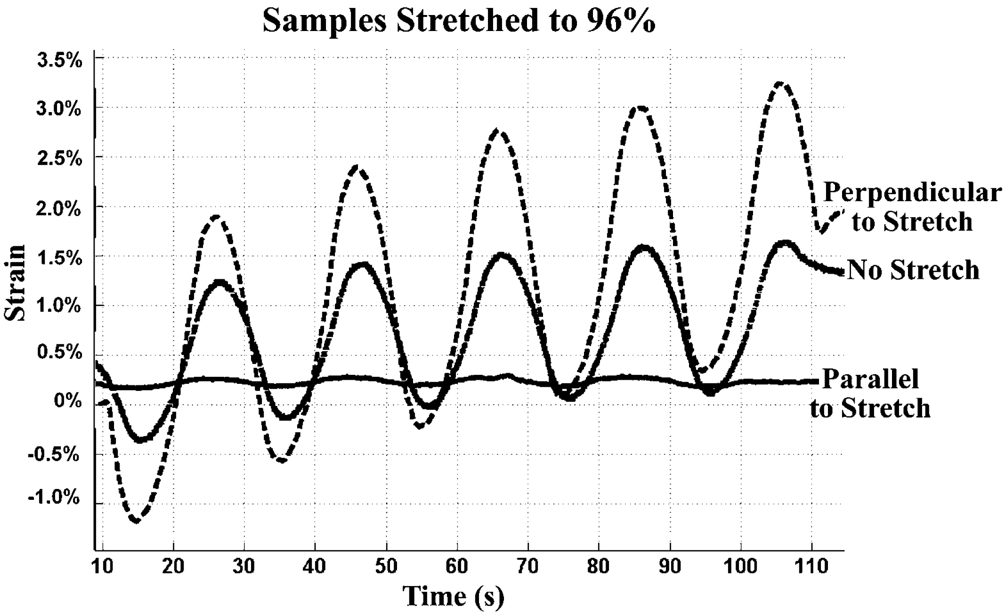

Figure 2. Anisotropic active strain response from stretched films. The film cut perpendicular to stretch shows the largest active strain, while the film cut parallel to stretch shows very little active strain. For these tests, a ±1.5 V triangular waveform was applied with a frequency of 0.05 Hz.

of the polymer backbone, causing ions to enter or leave the polymer matrix to balance the charge of the system leading to a bulk volume change or "active strain". By discovering and exploiting the connection between nanoscale transport events and macroscale active strain, we hope to learn how to process polypyrrole and other conducting polymers for improved electroactive device performance. In this communication we show that, by controlling polymer chain configuration and packing, a polypyrrole actuator can be engineered that shows a significantly larger macroscopic electroactive response for a given set of driving conditions.

Anisotropy in electroactive strain due to chain alignment has previously been observed in polyaniline (PA),[12] with a ratio of active strain (ϵ) perpendicular to the chain axis to that parallel to the chain axis of $(\epsilon_{\perp}/\epsilon_{\|})_{\mathrm{PA}} = 3.5$. Anisotropy in electroactive strain has not been previously reported for polypyrrole, and in this study we demonstrate a factor of approximately 10 times greater anisotropy ($(\epsilon_{\perp}/\epsilon_{\|})_{\mathrm{PPy}} = 38$). Polyaniline is an interesting actuator candidate because it is more processable than polypyrrole[12,13] but is used in acidic environments where the pH is below 4.[14] Polypyrrole provides a conducting polymer actuator platform that regularly achieves comparable active strains to polyaniline (around 2%)[15] and can be actuated in a variety of less severe environments.[1,6,7,14]

We electrochemically deposit films and then uniaxially deform them to induce chain alignment. Structural anisotropy induced by stretching is observable in the two-dimensional wide-angle X-ray diffraction patterns. The as-deposited film (Figure 1a) is isotropic in the plane parallel to the film surface, while the diffraction pattern of the film stretched 140% (Figure 1d) shows clear meridian and equatorial arcs. The location and orientation of the meridian arc at $q = 1$ Å^{-1} and the equatorial arc at $q = 1.8$ Å^{-1} indicate chain axis orientation parallel to the direction of stretch, as has been discussed previously.[16−18]

Chain alignment in the stretched polypyrrole film is further evidenced by observed anisotropy in both the conductivity and the electroactive strain. In films stretched 96%, the conductivity observed parallel to stretch was 7.5×10^4 S/m while that in the orthogonal direction was 1.7×10^4 S/m, resulting in a conductivity ratio $\sigma_{\|}/\sigma_{\perp} = 4.4$. The ratio of the conductivity of films stretched 96% to the conductivity of unstretched films was $\sigma_{\|}/\sigma_{\mathrm{unstretched}} = 2.75$, in good agreement with previous studies of stretched polypyrrole doped with hexafluorophosphate.[16]

While other researchers have produced highly oriented polypyrrole films,[16−18] the consequence of this orientation on actuation behavior has not previously been investigated. Figure 2 compares the electroactive strain response for films loaded parallel and perpendicular to the stretching direction with that of an unstretched film. The "active strain" was measured as the difference between the maximum peak strain and the following minimum strain of each voltage cycle. This corresponds to the contractile strain in the polymer. There is often a larger expansion (dip to peak) than contraction (peak to dip) as the polymer sample exhibits irreversible creep during testing. While creep during electrochemical cycling of a conducting polymer has been observed previously,[12] an in-depth study of polymer creep during actuation has not yet been conducted. To minimize its effects in this

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case only the contractile strain was considered as "active strain". An alternate approach, where the creep is modeled as a linear expansion with time, is considered in Supporting Information.

Under the conditions employed for the data in Figure 2, an unstretched sample of polypyrrole exhibits an active strain of approximately 1.45%. A film stretched 96% and tested parallel to stretch presents an active strain of only 0.07%, while a film tested perpendicular to the stretch axis exhibits an active strain of approximately 2.65%. One should note that the conditions used in this study were not optimized to give maximum absolute electroactive strain, and larger electroactive strains have been reported in several locations.[12,19,20] This study demonstrates for the first time the ratio of perpendicular to parallel active strain $(\epsilon_{\perp}/\epsilon_{||})_{\mathrm{PPy}}$ which was found to be approximately 38:1. Our results suggest that when the films are oxidized, counterions migrate to locations between the oriented polymer chains so that the directions of high active strain are perpendicular to the chain axis. In this mechanism there is no possibility for active strain along the chain axis, so the small active strain observed parallel to the direction of stretch in our samples is likely due to imperfect chain alignment.

In summary, the linear active strain produced by polypyrrole films can be controlled by inducing chain orientation via stretching. Stretching will be a valuable processing technique toward achieving large strains for linear actuator applications, as long as the modestly lower conductivity and higher polymer creep that occur in the direction of high active strain are not limiting. Knowledge of the anisotropic actuation mechanism in this material will help us intelligently process polypyrrole in the future, as well as design polypyrrole-driven devices that harness this mechanism to realize higher electroactive strains.

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Supporting Information Available: Polymer preparation and measurement methods, one-dimensional X-ray diffraction data, and creep-subtracted electroactive strain data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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