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Electroactuation of Alkoxysilane-Functionalized Polyferrocenylsilane Microfibers

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Cross-linked polymer networks that mediate chemical, electronic, optical, and mechanical signals are enticing materials from which to construct manipulators, switches, and sensors. For use in robotics, these materials should ideally exhibit large property changes in response to small stimuli, generate mechanical stress and strain in fast response to electric signals, and be easy to process.[1,2]

We report herein the electroactuation of polymer microfibers made from an ethoxysilane derivative of redox active polyferrocenylmethylvinylsilane[3] (PFMVS) **3,** Scheme 1. Cross-linked fibers of average diameter 2.0 ± 0.4 μm are fabricated by electrospinning high molecular weight polymer solutions of **3** ($0.1 \leq m/n \leq 1.0$) after initiating the acid-catalyzed condensation of ethoxysilane.[4] In cases of low cross-link density, resultant fibers rapidly respond (<100 ms) to electrical stimuli applied either *via* an electrode or by titration with redox active compounds. Videos taken by optical microscope demonstrate that large strains occur within 10 ms when fibers are oxidized electrochemically on an electrode surface submerged in a supporting electrolyte, see Figure 1 and Supporting Information.

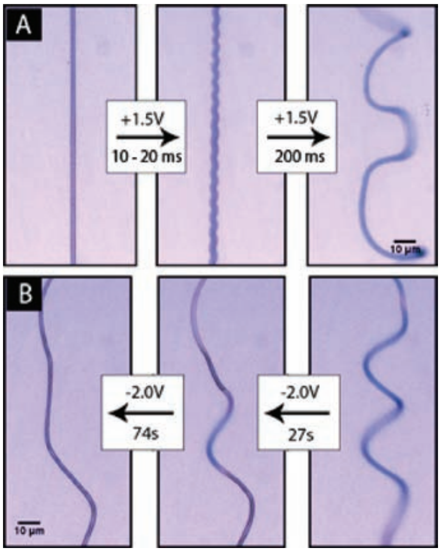
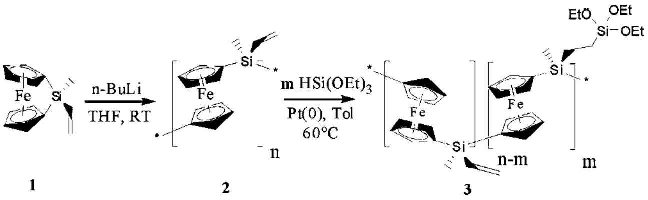


Figure 1. (A) Oxidized electrospun fibers rapidly expand under +1.5 V potential in LiOTf/γ-butyrolactone; (B) cathodic potential decreases roughly 20% of the initial strain within 1 min (scale bar = 10 μm).

For $m/n = 0.1$, we observe a regular buckling of the fiber due to a noncovalent interaction with the substrate as compressive stress along the fiber length reaches a critical limit (discussed later). Lateral and longitudinal strain in the fiber increases toward a maximum of 60 ± 23% and 58 ± 2%, respectively. Localization of the buckling into larger disordered looped segments occurs immediately after the initial deformation. Furthermore, we observe that by applying a reducing potential, much of the strain generated during oxidation is reversible. Cycling between an applied potential of +1.5 to −2.0 V produces a reversible 20% longitudinal strain, Figure 1b. We attribute reduced strain after multiple cycles to decreasing contact with the electrode surface.

In the preparation of actuating fibers, high molecular weight PFMVS **2**[5] ($M_n = 140 \pm 11.6$ kg/mol, PDI = 1.26 ± 0.04) was synthesized by anionic ring-opening polymerization. PFMVS vinyl groups were further functionalized through the Pt-catalyzed hydrosilylation using $HSi(OEt)_3$ to afford PFS **3**.[6,7] Analysis by ^1H NMR of **3** demonstrated the controlled and near quantitative addition of $HSi(OEt)_3$ to 10%, 25%, 50%, and 100% of the vinyl groups.

Scheme 1



The time required for hydrolytic gelation of PFS **3** varied considerably with the loading of alkoxysilane side groups and the amount of catalyst used. *p*-Toluene sulfonic acid hydrate ($PTSA \cdot H_2O$) was used as a catalyst and showed no tendency to oxidize the polymer during the curing process. The average curing time with a catalyst loading of 10 mol % is listed in Table 1. PTSA hydrate also increased the conductivity of electrospinning solutions and improved the uniformity of electrospun fibers by minimizing the amount of bead defects.

Electrospinning solutions were prepared by adding a 20 mM $PTSA \cdot H_2O$/THF solution to a 90 mg/mL (~10 wt %) solution of **3** in THF and thoroughly mixing before loading a syringe and placing it into a syringe pump. For 1 mL of $m/n = 0.1$ hydrosilylated polymer solution, the addition of 16 μL $PTSA \cdot H_2O$ solution allowed 30 min before gelation. During this time, a 5 kV potential was applied between the syringe needle and a conductive indium tin oxide (ITO) or gold substrate. Fibers are produced and collected at an average distance of 10 cm from the needle. Before analysis, fibers were allowed to age for 12 h under ambient conditions so as to maximize the Si−O−Si cross-link density. ITO substrates with collected fibers deposited on them were incorporated into miniature electrochemical cells containing 0.125 M lithium triflate (LiOTf) in γ-butyrolactone as electrolyte and were examined using an optical microscope as shown in Supporting Information.

FT-IR illustrates the effectiveness of PTSA as a gelator and the formation Si−O−Si linkages in a fiber mat. A representative spectrum is shown in the Supporting Information for fibers consisting of $m/n = 1$ hydrosilylated PFMVS and the same polymer cured with 10 mol % of PTSA after 12 h. Peaks at υ 1110, 1088, and 961 cm^{-1} are characteristic Si−OEt absorptions. After the catalyzed condensation

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Table 1. Gelation Time and Mechanical Properties of Crosslinked Dry Films Obtained from (90 mg/mL) Solution of PFS **3** Following the Addition of 10 mol % PTSA·H$_2$O

m/n, fraction hydrosilylation	catalyst loading (mol %)	average curing time (min)	E, elastic modulus (GPa)
0.10	10	33 ± 4	1.7 ± 0.67
0.25	10	15 ± 2	5 ± 2.57
0.50	10	4.0 ± 0.2	8 ± 1.89
1.00	10	2.00 ± 0.04	9.6 ± 0.85

and formation of Si−O−Si cross-links, only a broad absorption peak at 1039 cm^{-1} indicative of Si−O−Si linkages can be detected.

Increased degrees of hydrosilylation afforded higher cross-link densities and allowed the mechanical properties of the fibers to be controlled.[8] The elastic modulii E of polymer thin films were measured by the strain-induced elastic buckling instability for mechanical measurement (SIEBIMM) technique and are summarized in Table 1.[9] It should be noted that the value of 9.60 GPa for $m/n = 1$ is consistent with values obtained for silica thin films and reaffirms our conclusion that the majority of ethoxysilane groups have condensed in the aged films. While SEIBIMM can only be considered to provide a crude approximation to the actual modulus of the same polymer in the form of fibers, a decrease in strain is observed for fibers with largest values of E. Referring to the Supporting Information video, the oxidation of $m/n = 1$ fibers results in fracture and little deformation of fibers.

Our observation that sinusoidal buckling is dependent, at least in part, on the presence of an underlying substrate, was investigated by positioning fibers across micrometer gaps in an etched silicon wafer and oxidizing them using an excess amount of tris(4-bromophenyl)-ammoniumyl hexachloroantimonate in the same solvent electrolyte system used in the electrochemical cells (Figure 2). In regions over a gap, fibers were observed to deform into large randomly oriented loops, whereas fiber segments positioned over silicon were found to buckle regularly in a lateral direction prior to localization of strain in an analogous way to Figure 1a. The sine waveform is indicative of compressive loading of slender columns described by classical mechanics.[10] For the Euler-type buckling to occur, we approximate each microfiber as a beam initially bound electrostatically and/or through hydrogen-bonding to a substrate and prevented from longitudinal displacement. Consequently, oxidation induces an axially compressive force as the fiber volume increases. When the pressure exceeds the stability bifurcation point, the fiber buckles, with the substrate acting as a continuous foundation. The sinusoidal lateral displacement of buckled beams on a foundation has been described by Timoshenko.[11] Railway sun kinks generated by thermal expansion of steel rails supported on closely spaced ties are a macroscopic example of this phenomenon, Figure 2 (inset).

In summary, we have prepared electrospun electroactive microfibers from a gelable PFS derivative possessing cross-linkable alkoxysilane pendant groups. These materials display interesting strain-induced buckling behavior on electroactuation at low voltages (1.5−2.0 V). In contrast to reported methods of making polyaniline (PANI) and polypyrrole (PPy) fibers, there is no need to electrospin PFS as part of a blend[12] with high molecular weight nonconductive polymers or to use nonconductive fibers as polymerization templates.[13] While pH responsive electrospun polyacrylonitrile (PAN) fibers show considerable promise and exhibit longitudinal strains of 40% under basic conditions,[14] PAN is not inherently redox active and such systems require large potentials to actuate electronically via the electrolysis of water. Our future work will concentrate on creating stronger PFS yarns consisting of hundreds of electrospun fibers. Such structures could potentially rival existing bilayer actuators[15] in strength but maintain rapid response times because of significantly larger surface area to volume ratios and smaller ion diffusion lengths.

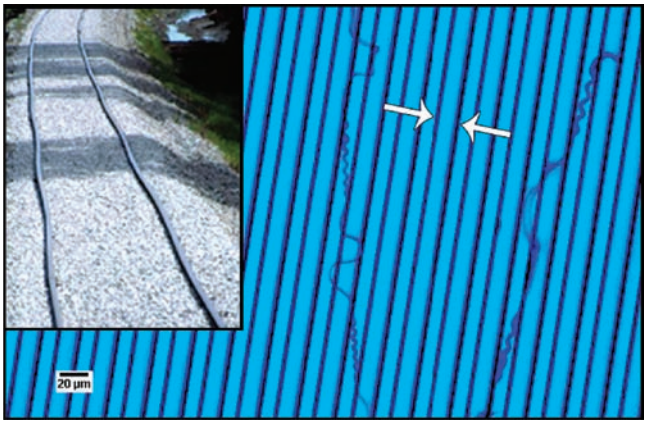

Figure 2. Fibers oxidized chemically on etched silicon grating demonstrate the substrate effect on buckling. Inset is a photograph of a railway sun kink. White arrows indicate a trench 15 μm wide which fibers span periodically (scale bar = 20 μm).

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Supporting Information Available: Details of synthesis and mechanical measurements, real time video demonstrations as well as ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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