Conductivity Shift of Polyethylenedioxythiophenes in Aqueous Solutions from Side-Chain Charge Perturbation

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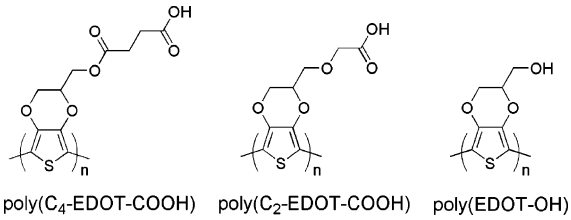
Conductivity-based sensory devices built on electrically conducting polymers (ECPs) offer great promise for the detection of a wide variety of analytes because they provide larger current output compared to the amperometry-based devices.[1,2] To apply these materials as biosensors, it is critical to design and synthesize ECPs that are stable and functionalized in aqueous solution, conjugate the bioprobes through functional groups, and examine the mechanism of perturbing the polymer conductivity from side-chain recognition. Among ECPs, polyethylenedioxythiophene (PEDOT) is of particular interest due to its high stability in aqueous solutions, flexibility of nanostructure assembly, high conductivity, and versatility for side-chain functionalization and bioconjugation.[3−5]

In devices consisting of electrode junctions covered with receptor-incorporated ECPs, amperometric output was increased or reduced upon analyte binding from a variety of molecular mechanisms, including charge localization,[6] analyte-induced reduction in conjugation length,[7] and segmental energy matching/mismatching from adjacent redox-active sites.[8] In these cases, intrinsic conductivity (σ_{max}) of the designed ECP was either enhanced or quenched. Herein, we report the first example of conductometric response from shifting the conductivity curve of functionalized ECPs, poly(C_4-EDOT-COOH) and poly(C_2-EDOT-COOH), upon oxidative doping. Increased negative charge density surrounding the polymer backbone raises disfavored existence and migration of positive charge carriers. Hence, it is necessary to apply a higher potential to increase the density of charge carriers, thereby overcoming the conductive barrier. Notably, this phenomenon was observed and identified in aqueous solutions, and the conductivity maximum remained identical under these conditions.

EDOTs functionalized with carboxylic acid groups (EDOT-COOHs) (Scheme 1) were synthesized from the known hydroxymethyl-EDOT (EDOT-OH),[9] incorporating either an ester (C_4-EDOT-COOH)[10] or an ether (C_2-EDOT-COOH)[11,12] spacer. Electropolymerization of all three monomers were performed in CH_3CN solution containing 10 mM of the respective monomer and 0.1 M of tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$) as supporting electrolyte by repeated cycling between −0.8 and 0.9 V at a scan rate of 100 mV/s.[13] The oxidation current onset after the initial scan displayed an anodic shift, and a new broad redox wave grew in subsequent scans, indicating polymer growth on the electrode surface. All three side-chain functionalized polymers displayed similar intrinsic conductivities as the electropolymerized PEDOT (~10^2 S/cm)[3a] in PBS buffer when the polymer films are electrochemically doped.[14] The three EDOT derivatives formed very stable and electroactive polymer films in aqueous media, and their conductivity and electrochemical properties remained unchanged after over 100 cycles.

Scheme 1. Structures of Functionalized PEDOTs



A horizontal shift of ~200 mV was noticed when we superimposed the conductivity profiles of poly(C_4-EDOT-COOH) and poly(EDOT-OH). We hypothesized that this phenomenon was due to the increased negative charge density from COO^- in PBS buffer (pH 7.4). This observation prompted us to conduct a thorough study of the pH effect on the polymer conductivity of poly(EDOT-COOH)s. For these studies, we switched the main electrolyte to $LiClO_4$ so the ionic strength at different pH buffer was constant. Applying an offset of 100 mV between two sets of working electrodes, the drain current that passed through poly(C_4-EDOT-COOH)-covered interdigitated electrode junctions started to increase when the potential applied was greater than −0.86 V in pH 4 buffer (see Figure 1). This indicated that the polymer became conductive upon oxidative doping. The current reached a plateau at −0.41 V. To better describe the features of the conductivity curves, we defined the onset potential (E_{onset}) as the potential where the first derivative of the drain current curve reached the maximum. Based on this definition, the E_{onset} values of both poly(C_4-EDOT-COOH) and poly(EDOT-OH) were determined to be −0.69 V, and the E_{onset} of poly(C_2-EDOT-COOH) was found to be −0.71 V in pH 4 buffer. Upon exposure to the electrolyte solution at pH 7, E_{onset} of poly(C_4-EDOT-COOH) dramatically shifted to a more positive potential of −0.46 V, while the E_{onset} of poly(EDOT-OH) remained unchanged. When dipped into pH 10 electrolyte solution, E_{onset} of poly(C_4-EDOT-COOH) shifted further to −0.44 V, while E_{onset} of poly(EDOT-OH) remained

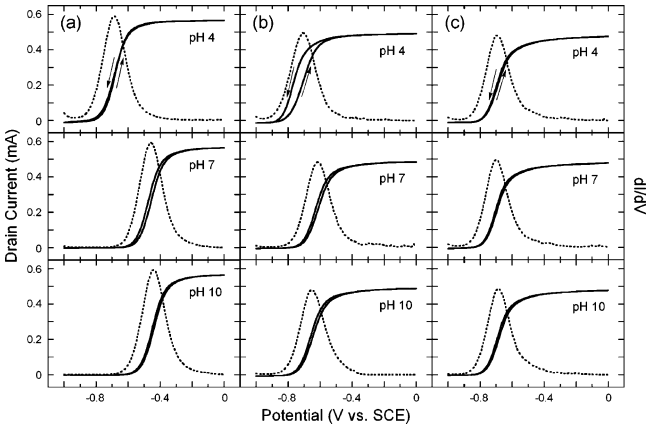


Figure 1. Drain current measurement of (a) poly(C_4-EDOT-COOH), (b) poly(C_2-EDOT-COOH), and (c) poly(EDOT-OH) on 5 μm interdigitated microelectrodes in 10 mM of pH 4, pH 7, and pH 10 buffer solutions with 0.1 M of $LiClO_4$ as the supporting electrolyte. The scan rate is 10 mV/s with a 100 mV offset between the two sets of interdigitated microelectrodes. The dotted lines (···) represent the first derivative of the oxidation sweep.

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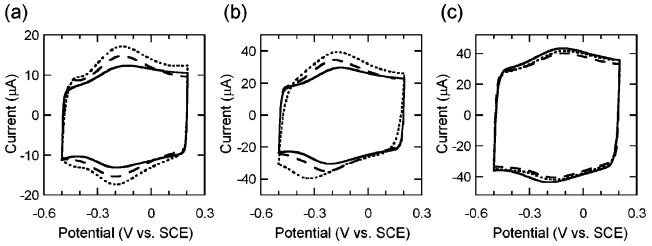

Figure 2. Cyclic voltammograms of (a) poly(C_4-EDOT-COOH), (b) poly(C_2-EDOT-COOH), and (c) poly(EDOT-OH) on Pt button electrode in 10 mM of pH 4 (—), pH 7 (---), and pH 10 (···) buffer solutions, with 0.1 M of $LiClO_4$ as the supporting electrolyte at a scan rate of 50 mV/s.

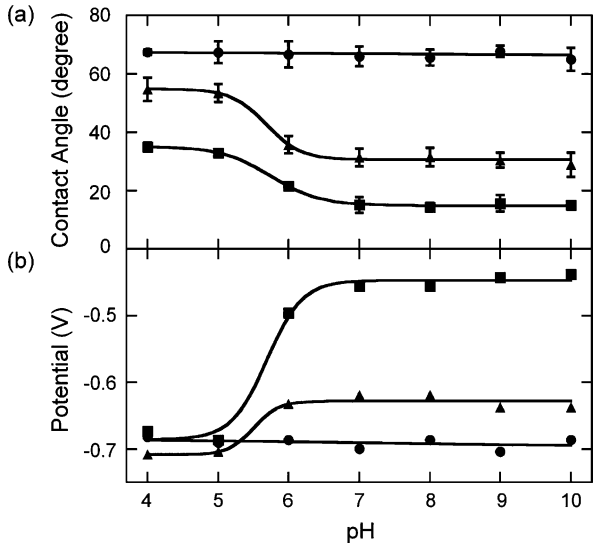

Figure 3. (a) Contact angle measurements and (b) onset potential of (■) poly(C_4-EDOT-COOH), (▲) poly(C_2-EDOT-COOH), and (●) poly-(EDOT-OH) at different pH's.

at −0.69 V. The E_{onset} of poly(C_4-EDOT-COOH) shifted back to the original value with an identical current profile upon reexposure to an aqueous medium of pH 4; this reversible phenomenon was observed repeatedly for over 10 cycles. Poly-(C_2-EDOT-COOH) film showed a similar trend with a smaller shift in E_{onset} from −0.71 V at pH 4 to −0.62 V at pH 7. The E_{onset} then slightly shifted back to a more negative potential of −0.64 V at pH 10. This might be attributed to the stronger $\pi-\pi$ interaction between neighboring poly(C_2-EDOT-COOH) chains.[15] Because of this, oxidation at a slightly higher potential was required to overcome this stabilization at the transition pH of 5−6. This rationale was supported by the greater hysteresis of the conductivity profile of poly(C_2-EDOT-COOH) at pH 4 compared to that of poly(C_4-EDOT-COOH). It was noteworthy that the drain current profiles always reached a plateau at the same value. This showed that the maximum conductivity (σ_{max}) of polymer films remained identical in buffers of different pH's.

Identical shift in conductivity profile was observed on six different interdigitated devices and devices with 3 μm gaps instead of the 5 μm gaps that we used for earlier studies. This confirmed that the pH response of the conductivity curve was not due to the interdigitated device structure. Our proton-controlled conductivity responses were different from those of polyanilines,[16] polypyrroles,[17] and polythiophenes.[18] Deprotonation of these conducting polymer backbone/segment resulted in reduced resonance stabilization of the charge carriers, decreasing the maximum conductivity of the polymers. In contrast, deprotonation of poly(EDOT-COOH) side chains only increased the negative charge density in the polymer matrix

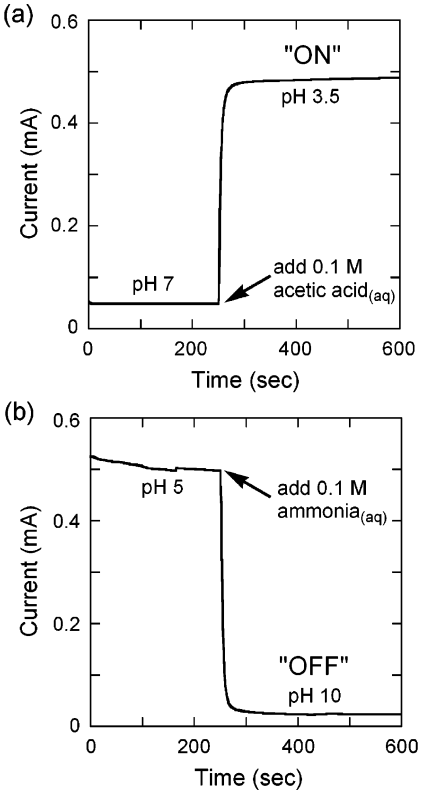

Figure 4. Dynamic current measurement of poly(C_4-EDOT-COOH) on 5 μm interdigitated microelectrodes in an aqueous electrolyte solution with a 100 mV offset between the interdigitated electrodes. Applied potentials are (a) −0.60 V and (b) −0.65 V.

surrounding the polymer backbone, without altering the resonance stabilization structure. As a result, the positive charge carriers (radical cations and dications)[19] in PEDOT matrix were either compensated or restrained upon oxidation. Their migration became less energetically favorable. This was similar to the self-doping of sulfonated and carboxylated polythiophenes reported previously.[20,21] Thus, the same σ_{max} should still be achieved by increasing the mobile charge carrier density with the application of a more positive potential. This was why we observed only a shift without decreasing the maximum drain current of the conductivity curves. Cyclic voltammograms of the poly(EDOT-COOH) films (Figure 2) provided more evidence for the proposed mechanism. Increased peak current and larger difference between anodic and cathodic peak potentials at higher pH suggested more localized and kinetically restrained charge carriers. Poly(EDOT-OH) displayed no conductivity shift at different pH's, further supporting that the pH-induced shift in conductivity profile was compositional, and not morphological, in nature. Optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) showed that the polymer films electropolymerized on top of the interdigitated electrode were amorphous; therefore, the phenomenon was unlikely due to morphological factors. In measuring the contact angles of poly(C_4-EDOT-COOH),[22] we observed a dramatic hydrophilicity enhancement of the polymer film (Figure 3a) at a pH of 5−6. This indicated that the carboxylic acid deprotonated to form carboxylate at a pH of 5−6. This matched perfectly with the shift of the onset potential (Figure 3b), thereby supporting our rationale. In contrast, poly(EDOT-OH) displayed no surface-switch at various pH's, which explained why there was no shift in its E_{onset}. The larger shift in E_{onset} of poly(C_4-EDOT-COOH) could be attributed to the extended side chain from C_4-EDOT-COOH, leading to better charge overlay with the PEDOT backbone.

Upon fixing the applying voltage of interdigitated electrodes at the transitional stages, these poly(C_4-EDOT-COOH)-coated electrode junctions were utilized as resistive sensors with their charge perturbation behavior. In Figure 4a, the polymer film was placed in a pH 7 solution by applying −0.6 V with a 100 mV offset. We observed a current increase of more than 9-fold within 10 s upon the addition of acetic acid. The solution became more acidic (pH 3.5), and the film became conductive due to the E_{onset} shift to a lower potential. In contrast, the current passing though electrodes by applying a potential of −0.65 V was reduced by over 90% within 10 s when the pH of the immersed solution changed from 5 to 10 with the addition of aqueous ammonia solution (Figure 4b).

In summary, we have demonstrated an example of shifting the ECP's conductivity profile in aqueous buffers by modulating the negative charge density in the polymer matrix through side-chain functional groups. PEDOT's stability in aqueous buffers and this novel mechanism pave the way for future biosensing applications.

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Supporting Information Available: Experimental details for the synthesis and characterization of C_4-EDOT-COOH and C_2-EDOT-COOH, film electropolymerization, and AFM studies. This material is available free of charge via the Internet at https://pubs.acs.org.

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