Balancing Ionic and Electronic Conduction for High-Performance Organic Electrochemical Transistors

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Abstract

Conjugated polymers that support mixed (electronic and ionic) conduction are in demand for applications spanning from bioelectronics to energy harvesting and storage. To design polymer mixed conductors for high-performance electrochemical devices, relationships between the chemical structure, charge transport and morphology must be established. We synthesized a polymer series bearing the same p-type conjugated backbone with increasing percentage of hydrophilic, ethylene glycol side chains, and studied their performance in organic electrochemical transistors (OECTs) in an aqueous electrolyte. By using device physics principles and electrochemical analyses, we find a direct relationship between the OECT performance and the balanced mixed conduction. While hydrophilic side chains are required to facilitate ion transport – thus enabling OECT operation – swelling of the polymer is not de facto beneficial for balancing mixed conduction. We show that heterogeneous water uptake disrupts the electronic conductivity of the film, leading to OECTs with lower transconductance and slower response times. The combination of in situ electrochemical and structural techniques shown here contributes to the establishment of the structure-property relations necessary to improve the performance of polymer mixed conductors and subsequently of OECTs.
1. Introduction

Conjugated polymers with delocalized π-molecular orbitals exhibit electronic conduction along and between their chains. This feature has encouraged the development of solid-state organic electronic devices over the last few decades.\(^1\)\(^-\)\(^3\) More recently, another property of conjugated polymers is attracting significant interest: the simultaneous transport of ionic and electronic charges when electrically addressed in aqueous electrolytes. Efficient mixed (electronic and ionic) conduction allows for electrochemical oxidation and reduction reactions within a conjugated polymer film that involve ions migrating from an aqueous electrolyte into the bulk of the polymer to compensate for electronic charges. Mixed conduction is the basis of a number of organic electrochemical devices, such as batteries,\(^4\) supercapacitors\(^5\) and electrochromic devices.\(^6\) Together with their soft and biocompatible nature, the mixed conductivity of conjugated polymer thin films has led to the development of many organic bioelectronic devices, including neural probes,\(^7\) organic electronic ion pumps,\(^8\) soft actuators\(^9\) and organic electrochemical transistors (OECTs).\(^1\)\(^0\)

An OECT is an electrochemical device that shows great technological potential for sensing biochemical molecules,\(^1\)\(^1\) monitoring or stimulating cell activity,\(^1\)\(^2\)\(^-\)\(^1\)\(^0\) and also for use as a building block in neuromorphic devices.\(^1\)\(^3\) OECTs are three-terminal devices in which a conjugated polymer thin-film channel is patterned between two metal electrodes (drain and source) (Figure 1a). The channel is in contact with an electrolyte in which an electrode (gate) is immersed.\(^1\)\(^4\) A voltage in the gate \((V_G)\) controls the doping state of the channel material, while the conductance of the channel is probed by measuring the drain current \((I_D)\) when applying a bias between the drain and source \((V_D)\). The OECT performance is governed by the mixed conductivity of the polymer film in the channel, with high transconductance being a
desirable OECT characteristic. The majority of OECTs reported to date use the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) as the channel material. PEDOT:PSS allows the simultaneous transport of hydrated cations through the hydrophilic PSS phase and of holes through the hydrophobic PEDOT backbone.\cite{16}

Due to its widespread use, our current understanding of what makes a material an efficient mixed conductor is mostly built upon studies of PEDOT:PSS. These studies suggest that ion-to-electron coupling depends on the polymer thin-film microstructure and morphology, and the arrangement of these two phases in the solid state.\cite{15,16,17}

Recently, conjugated polymers comprised of conjugated backbones functionalized with hydrophilic side chains have emerged as promising OECT materials.\cite{18-21} Unlike PEDOT:PSS, these materials exhibit synthetic flexibility, which furnishes them with specific properties that promise broader applications of OECTs, e.g., functionalization of the material for selective sensing of biomarkers\cite{22} or promoting interactions with target cells.\cite{23} Moreover, while PEDOT:PSS is a conducting material, these materials are poorly conducting in their pristine state. During the OECT operation, hydrated ions penetrate the film in the channel through the hydrophilic side chains to compensate for polaron formation on the backbone during electrochemical charging (i.e., accumulation mode operation). This volumetric coupling of ions and electrons inside the channel leads to high-gain OECTs and a simultaneous increase in both the capacitance and the electron mobility of the film.\cite{24} Previous studies have shown that exchanging the hydrophobic, aliphatic side chains of a conjugated backbone with hydrophilic, ethylene glycol (EG) side chains improves the OECT performance.\cite{19,25,26,27} Giovannitti et al reported a series of n-type random copolymers comprising various EG side chain percentages with respect to alkyl side chains and observed that the reduction potential of the copolymers depends on the percentage of EG side chains where glycol chain percentages of $\geq 50\%$ are required to operate the copolymer in n-type OECTs.\cite{19} This result was attributed to facile ion
uptake in the channel due to enhanced swelling of copolymers with high percentage of glycol side chains in aqueous electrolytes.\cite{18,19,25,26} Currently, the top accumulation mode OECT performer (beyond depletion mode OECTs based on PEDOT:PSS derivatives\cite{17}) is the p-type, hydrophilic conjugated polymer poly(2- (3,3′- bis(2- (2- methoxyethoxy)ethoxy)ethoxy)- [2,2′- bithiophen]- 5- yl)thieno [3,2- b] thiophene) p(g2T-TT), which shows significantly higher transconductance than its analogue with aliphatic chains (p(a2T-TT)).\cite{27} While p(g2T-TT) performed better than p(a2T-TT), it is unclear whether the performance of p-type polymers in OECTs scales with the amount of EG side chains. Moreover, if EG side chain functionalization is the rule-of-thumb design principle for OECT materials, it is tempting to develop a more hydrophilic polymer based on the same backbone - which would have the potential to exceed the performance of previous materials.

On the other hand, recent studies have shown that the electrochemical properties of such polymer films strongly depend on their nano- and microstructures.\cite{28-30} Importantly, the film microstructure changes dynamically upon the doping/de-doping events in the channel. When dopant ions migrate from the electrolyte into the polymer bulk, the film experiences a large degree of deformation.\cite{31-32} The volumetric expansion/deformation depends on the size and hydration shell of the dopant ion,\cite{33} as well as on the water molecules that follow the injected ions due to osmotic forces.\cite{32} Although a hydrated channel is important for unobstructed ion conduction, we have recently reported that it also negatively influences the electron transport and, consequently, the performance of OECTs.\cite{32} In that study, we gradually changed the hydration shell of the dopant anion which led to differences in the amount of water that the polymer uptakes, hence its degree of swelling. Flag et al. reported a similar observation, showing that swelling of a p-type mixed conductor hinders the electronic connectivity of the crystalline regions, which leads to low hole mobility in OECTs.\cite{30} To decrease the swelling percentage of their polymer, the authors annealed the films. These studies highlight the importance of maintaining a balance between the transport of the electronic charges and the
hydrated ions to maximize the electrochemical behavior of the polymer films and, as a result, the OECT performance. These initial findings regarding the relationship between the polymer hydration and OECT performance can be regarded as a design rule if verified with different polymers, which requires new synthetic efforts where the chemical structure is systematically altered to control degree of hydration. Thus, establishing the electronic and ionic transport-structure relationships as well as understanding the impact of chemical structure on in operando hydration and thereof the device performance become crucial for the rational design of materials for OECTs and other electrochemical devices.

Here, we study the OECT performance and the electrochemical redox-reactions of a p-type polymer series with varying amounts of EG side chains attached to a dialkoxybithiophene-co-thienothiophene (2T-TT) backbone (i.e., p(g2T-TT) analogues) in aqueous electrolytes. By controlling the amount of attached hydrophilic side chains in the polymer structure, we aimed to understand how the hydration of the polymer films affects the OECT performance. We found that the OECT performance scales with the EG side chain fraction of this p-type series, however, maximum transconductance values were recorded for the aforementioned p(g2T-TT) rather than for the most hydrophilic polymer of the series. The top OECT performer of this polymer series, p(g2T-TT), exhibited the optimum balance of hole and anion conduction, as well as the largest modulation of the absorption spectra upon doping, indicative of efficient ion-to-electron coupling. By using a combination of in situ electrochemical measurements, we found that the most hydrophilic polymer of the series had lower volumetric capacitance and hole mobility values than p(g2T-TT) despite having better ion conduction associated with its superior hydration both before and during electrochemical doping. Strikingly, this polymer accommodated more water yet less of the dopant anions compared to the less hydrophilic p(g2T-TT). Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements showed that all the dry polymer films had a similar texture and \( \pi-\pi \) stacking distances, while the lamellar
spacing is controlled by the side chains. Importantly, in situ atomic force microscopy (AFM) measurements showed that the polymers, particularly those with a high EG content, exhibited a dynamic expansion of their surface upon doping. We suggest that this structural deformation interrupts hole transport pathways, hindering hole mobility, volumetric capacitance and, consequently, the performance of the OECTs operated in aqueous electrolytes. While the degree of electrochemical charging increases, to a large extent, with the hydrophilic side chain content in the polymer structure, limited in-operando hydration is a desired film characteristic as channel hydration can be detrimental to OECT performance.

2. Results and discussion

The synthesis of the polymers is reported in the Supporting Information and their chemical structure is shown in Figure 1b. Whilst maintaining the same conjugated backbone, the polymers in this series differed by a fractionated exchange of the linear alkyl side chains for linear triethylene glycol side chains, and are referred to hereafter as follows: “g-0%” for the fully alkylated homo-copolymer poly(2-(3,3’-bis(tetradecyloxy)-[2,2’-bithiophen]-5-yl)thieno[3,2-b]thiophene) known also as p(a2T-TT),[27] “g-100%” for the fully glycolated homopolymer (p(g2T-TT)),[27] “g-50%” and “g-75%” for the random copolymers with glycol:alkyl (p(g2T-TT):p(a2T-TT)) ratios of 50:50 and 75:25, respectively, and “2g” for the homopolymer with longer EG side chains (i.e., hexakis EG). Therefore, from g-0% to g-100%, the glycol side chain percentage increases from 0 to 100 with respect to the alkyl side chains, while 2g is the most hydrophilic polymer with twice the length of EG side chains of g-100% (hexakis and triethylene glycol respectively).

We started our analysis by measuring the OECT steady-state and transient characteristics of the polymer series in 0.1 M NaCl(aq.). Output and transfer characteristics are shown in Figure S1-S2. An important metric for efficient ionic-to-electronic signal conversion
is the transconductance \((g_m)\) of the OECTs, which scales with the product of volumetric capacitance \((C^*)\), hole mobility \((\mu_{h-OECT})\) and overdrive voltage \((V_G - V_{TH})\) according to \(g_m = \frac{W}{L} d \mu C^* (V_{TH} - V_G)\).[24]

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**Figure 1**: a) Schematic representation of an OECT operated in the common source configuration, where an Ag/AgCl electrode is used as the gate, immersed in NaCl(aq.) 0.1 M. Channel dimensions were \(W = 100 \mu m, L = 10 \mu m\) and \(d \sim 55 \text{ nm}\). b) Chemical structure of the polymer series with increasing contents of EG side chains: g-0% is the fully alkylated homopolymer (p(a2T-TT)), g-50% and g-75% are random copolymers with glycol:alkyl (p(g2T-TT):p(a2T-TT)) ratios of 50:50 and 75:25, respectively, g-100% is the fully glycolated homopolymer (p(g2T-TT)), and 2g is the homopolymer with longest EG side chains. c) the transconductance \((g_m)\), d) the product of hole mobility \((\mu)\) and volumetric capacitance \((C^*)\), e) the threshold voltage \((V_{TH})\), and f) the response time of the OECTs \((\tau_{OECT})\). The OECT data shown here were recorded at \(V_G = V_D = -0.5 \text{ V}\). The output characteristics were recorded at a \(V_D\) sweep rate of 5 V/s.

OECTs containing the fully alkylated homopolymer g-0% exhibited the lowest transconductance \((g_m \sim 10^{-5} \text{ mS})\, \text{ Figure 1c}\) due to the combined effects of a low \(\mu C^*\) (Figure 1d) and a large threshold voltage \((V_{TH} = -0.3 \text{ V})\, \text{ Figure 1e}\). Giovannitti et al. have previously shown that this is due to low degree of swelling and ionic conduction, which increases the voltage required to oxidize the polymer.[27] Poor ionic conduction is most possibly the reason
for the hysteresis behavior in the current-voltage characteristics as shown in Figure S1 and S2a for the polymers with low EG percentage. When the alkyl side chains were exchanged for EG side chains in g-50%, g-75% and g-100%, the transconductance increased by five orders of magnitude due to the improvement in the $\mu . C^*$ product as well as a decrease in $V_{TH}$. Substituting the alkyl side chains with longer EG side chains in 2g, however, resulted in a lower $\mu . C^*$ product and decreased transconductance compared to g-100%, its shorter EG side chain analogue. We characterized the transient OECT behavior by extracting the response time ($\tau_{OECT}$, Figure 1f) from a single exponential fit to the drain current when applying a 5 ms long, square-shaped voltage pulse at the gate electrode (Figure S3). OECTs based on g-0%, g-50% and g-75% switched relatively slowly with $\tau_{OECT} > 1$ ms, while the OECTs based on g-100% switched one order of magnitude faster ($\tau_{OECT} = 116$ $\mu$s). OECTs based on 2g were slower than the g-100% devices but faster than the g-0%, g-50% and g-75% devices ($\tau_{OECT} = 166$ $\mu$s). This trend was verified by calculating the cut-off frequencies of transconductance-frequency plots (Figure S3a). The steady-state and transient metrics for OECT polymers are summarized in supporting Table S1.

In OECTs, both the transient and steady-state characteristics rely on the efficient transport of electronic and ionic charge carriers through the polymer films in the channel.$^{[34]}$ Therefore, understanding the electrochemical redox-reactions is of great importance. To this end, we first recorded the cyclic voltammetry curves of the polymer films in NaCl$_{(aq)}$ 0.1 M. Figure S4 shows that an increase in the EG content caused the oxidation potential to shift towards zero and more current to be generated, as also observed previously.$^{[27]}$ The oxidation potential shift was directly correlated with the lower $V_{TH}$ (Figure 1f), while the change in current was in line with the trend in $C^*$ (Table S1). Importantly, while the ionization potential of the polymers with glycol side chains did not show a significant variation, the ionization potential of the g-0 % polymer was slightly higher (4.74 eV for g-0% and ~4.50 eV for all the other
polymers). As such, the energetics were unlikely to affect the hole injection from the source electrode into the polymer valence band and, therefore, were unlikely to cause the differences observed in the electrochemical behavior of the polymers with glycol side chains.

To investigate the swelling behavior upon doping, we used electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D). EQCM-D allows for recording in situ changes in the mass of a polymer film coated onto a piezoelectric crystal as it is electrochemically addressed in an electrolyte. The mass (anions and water) injected into the polymer during doping is reflected as a change in frequency \( f \) and dissipation of energy \( D \) of the oscillating crystal, which we calculated by fitting these variables with a viscoelastic model as described in the experimental section. We then expressed the mass changes as the swelling percentage of the polymer films (Figures S5-S7). We also performed electrochemical impedance spectroscopy measurements (EIS – Figure S8). EIS and swelling studies (QCM-D) were conducted first in the absence of applied potential at \( V = 0 \text{ V vs } V_{OC} \) (open circuit potential) and then upon doping at \( V = 0.5 \text{ V vs } V_{OC} \). The results are summarized in Figure 2a and b.

**Figure 2.** Swelling percentage of the polymer films (right axis, dashed line) determined from QCM-D and the capacitance (left axis, solid line) determined from the electrochemical impedance spectra recorded at a) \( V = 0 \text{ V vs } V_{OC} \) and b) \( V = 0.5 \text{ V vs } V_{OC} \). c) The relative changes in the intensity of the absorption peaks recorded at \( V = 0.5 \text{ V vs } V_{OC} \) and d) the corresponding charge generated in each system. All the data presented here were collected in \( \text{NaCl(aq.)} \ 0.1 \text{ M} \) using the polymer coated EQCM-D sensors for a and b and polymer coated ITO electrodes for c and d. In all measurements, the electrodes had the same electrochemical area (i.e., 0.785 cm²) and the polymer films had similar thicknesses between 50 nm and 60 nm.
The $V_{OC}$ was 0.17 V, 0.16 V, 0.15 V, 0.12 V, and 0.13 V for g-0%, g-50%, g-75%, g-100%, and 2g, respectively.

In agreement with previous studies,$^{[19]}$ we found that increasing the EG content caused the polymers to swell more when immersed in NaCl$_{aq.}$ 0.1 M (Figure 2a, right axis). The alkylated homopolymer g-0% remained the least hydrated (2% swelling), while g-50%, g-75% and g-100% swelled gradually up to 12%, and 2g swelled significantly (50%). The swelling of the polymers resulted from the diffusion of ions and water, which migrated from the electrolyte into the films until the systems reached equilibrium (i.e., flat QCM-D signals in Figure S5 and a stable $V_{OC}$ value). After each system reached equilibrium, we recorded the electrochemical impedance spectra at $V = 0$ V vs $V_{OC}$ and extracted the frequency-dependent capacitance of the polymers from these spectra at 0.1 Hz (Figure S8). The capacitance values show to what extent each polymer film is charged. As shown in Figure 2a (left axis), the capacitance of the polymers at low frequencies scaled with their EG content and degree of swelling. The 2g polymer exhibited a capacitance higher by two orders of magnitude than the g-0%, suggesting that ions may have already diffused into and charged the 2g film in the absence of applied voltage. To further investigate this, we recorded the cyclic voltammetry curves of the polymer films in NaCl$_{aq.}$ 0.1 M to determine their oxidation potentials (Figure S4). The onset of oxidation potential is approaching to 0 V vs Ag/AgCl for the polymers with high EG content, indicating that these polymers are already oxidized in the absence of an applied bias. Cendra et al showed that due to its low ionization potential, g-100% can become oxidized by side reactions in ambient conditions.$^{[33]}$ It might be also possible that the longer EG hydrophilic chains present in the 2g polymer, chelate ions, contributing to the capacitance in the unbiased condition.

Next, we performed the same analysis, this time upon doping at $V = 0.5$ V vs $V_{OC}$ (see Figure S6 for the real time changes in QCM-D signals and Figure S7 for the corresponding
changes in mass and current). As shown in Figure 2b, the polymers swelled more upon doping (due to the increased uptake of anions and water) and the extent of the swelling increased with the content of EG side chains (right axis). The capacitance measured at low frequencies also followed this trend (Figure 2b, left axis). Note that given the higher oxidation onset of polymers with less EG content (Figure S4), it is reasonable to consider that their capacitance might increase further with an increase in scanning potential above 0.5 V. We chose this potential to compare the doped state of films because 1) for $V_G$ values above -0.5 V, there is negligible increase (most cases, a decrease) in the OECT transconductance (Figure S2b), and 2) it is not practical to use higher voltages as even though the low EG content-polymers can theoretically store as many charges as the high EG content-polymers, the operation voltages to achieve such state are too high and detrimental for film stability. Importantly, although during doping, more mass was loaded onto the 2g film compared with g-100% (110 % vs 86 % swelling), the capacitance of the 2g polymer in its doped state was lower than that of g-100%.

To further investigate the electrochemical behavior of the polymer films, we monitored in situ changes in their UV-VIS spectra upon application of doping potentials (Figure S9), and recorded the amount of charge produced by each system during these measurements (Figure S10). As shown in Figure 2c, upon application of a doping pulse, the absorption spectra of all the films underwent changes at two particular wavelengths with complementary behavior. The absorption peak at 900 nm (related to the absorption of polaronic species) increased while the absorption peak at ca. 593 nm ($\pi$-$\pi^*$ absorption peak) was quenched. In line with our EQCM-D analysis, g-100% exhibited the largest spectral modulation and highest amount of charge injected at 0.5 V, whereas 2g showed limited charge injection despite swelling substantially more than g-100% (Figure 2c and d).

A swollen film is known to facilitate ion motion,$^{[35,36]}$ but, as shown in Figure 2, this is not a requirement for high capacitance or swelling is not de facto beneficial for OECT
performance. The volumetric capacitance might decrease due to the increased film volume,\textsuperscript{[37]} and increased fraction of EG side chains which dilutes the electronic content. Moreover, Proctor et al describes capacitance in terms of “sites” in which ions injected from the electrolyte compensate for the electronic charges that are injected to the film by a metal contact.\textsuperscript{[38]}

According to this picture, the film contains a certain number of sites consisting of anion/hole pairs and the volumetric capacitance decreases as the distance between these sites increases. As the side chains get longer, the polymer swells further, and this may lead to a longer distance between the possible-to-pair polarons and anions. Overall, the increased volume fraction of side chains is expected to contribute towards an unchanged or decreased capacitance in 2-g compared to g-100%. Taken together, the mixed-conduction performance of the 2g polymer, which exhibited the largest mass uptake upon doping, was worse than that of g-100%. Next, we decoupled the anion and water uptake by quantifying the number of Cl\textsuperscript{-} ions and water molecules injected into the polymer films during doping, using the same methodology described in our previous study.\textsuperscript{[32]} During the application of a doping pulse, the films (especially the ones with high EG content) gain a significant amount of mass and accumulate electronic charge (i.e., oxidation). If each Cl\textsuperscript{-} anion compensates for one hole, the amount of charge we measure corresponds to the number of doping anions in the film. However, since each anion enters the film hydrated, water uptake is also to be expected.\textsuperscript{[31]} Therefore, the mass calculated by modelling the EQCM-D data (Figures S5-S7) contains the mass of anions as well as of water. As a matter of fact, if all this mass were to be converted to the number of anions, the amount calculated is higher than the values suggested by the current profiles. This discrepancy stems from the presence of water dragged in the film along with the anions. Note, however, that in these calculations, we do not consider any possible contribution of counterions (i.e., Na\textsuperscript{+}) or faradaic side reactions (e.g., oxygen reduction reactions) on the mass changes that the films undergo or on the charge recorded. As such, we calculate the amount of mass that the films uptake during doping and decouple the amount of water and Cl\textsuperscript{-} molecules per unit volume.
Figure 3a shows that while the concentration of anions injected into the film upon doping was maximized for g-100%, the 2g film uptakes almost twice as many water molecules as g-100% (35 x 10^{21} vs 18 x 10^{21} H_2O molecules/cm^3).

To understand how the water transferred into the films during doping influence the electronic and ionic transport properties, we extracted i) the hole mobility from OECT hole transit-time measurements and ii) the ion diffusion coefficient from chronoamperometry measurements (based on the Cottrell equation as described in the experimental section), and analyzed their relation to the water concentration in the film (Figure 3b). Our results suggest that although a lower concentration of anions migrated into the 2g film compared with the g-100%, these ions were more mobile (Figure 3b, right axis). The enhanced ion diffusivity in this polymer is due to the increased water content therein, suggesting that polymer hydration facilitates ion transport in accordance with previous reports. [35, 36] Nevertheless, the excessive hydration impacts the electronic hole transport (Figure 3b, left axis). While EG side chains facilitate the transport of hydrated ions, our results suggest that, in the case of 2g, the excessive hydration associated with its high EG content reduced its charging ability (i.e. reduced C*) and hole mobility. A smaller value of \( \mu C^* \) explains the low \( g_m \) obtained for this polymer. On the other hand, given that 2g polymer has lower C* measured at 0.5 V vs \( V_{oc} \) (and presumably improved ion transport properties) than g-100%, we expect the 2g devices to switch on faster compared to g-100%. These OECTs, however, switch on slower, suggesting a hole mobility-dependent transient behavior. Overall, from this polymer series, g-100% exhibited the optimal balance between ionic and electronic transport, which is reflected in its high steady-state and transient OECT performance.
Figure 3: a) Concentration of anions (Cl\(^-\)) and water molecules taken up by the films during \textit{in situ} doping in NaCl\(_{aq.}\) 0.1 M at \(V = 0.5\) V vs \(V_{OC}\). b) Hole mobility calculated from hole transit time measurements in OECTs and ion diffusion coefficient extracted from the chronoamperometry measurements as a function of the amount of water taken up by the polymers upon doping at 0.5 V vs \(V_{OC}\).

Understanding the structural and morphological features that lead to extensive swelling is important. To analyze differences in the microstructure, we first collected grazing incidence wide angle X-ray scattering (GIWAXS) 2D patterns of the films in their dry, as-cast condition (Figure S11, Figure S12). The predominant lattice spacings were extracted from the peak center positions of the scattering peaks (Figure 4b). The films present a predominantly edge-on texture and very similar \(\pi\)-stacking distances (3.88-3.95 Å), whereas the lamellar spacing (100) depends on the length and nature of the side chains. The lamellar spacing was reduced when triethylene glycol side chains replaced the alkyl tetradodecyloxy side chains (e.g., 18.2 Å for \(g\)-0% and 14.0 Å for \(g\)-100%). As expected, \(2g\) showed the largest lamellar spacing (21.1 Å) due to its longer linear hexakis EG side chains.

Next, we sought to understand the correlation between the EG content and the morphology of the polymer films, and how the film morphology was affected by the injection of ions and water. Since the polymers with a relatively high EG content (\(2g\), \(g\)-100% and \(g\)-75%) took in large concentrations of ions and water molecules during doping, we expected significant doping-induced distortions in their morphology. We used \textit{in situ} atomic force
microscopy (AFM) to investigate the surface morphologies of the polymers upon doping and de-doping (Figure 4).

**Figure 4:** a) Atomic force microscopy (AFM) topography measurements of all the polymers under study. The rows from top to bottom show the measurements of g-0%, g-50%, g-75%, g-100% and 2g films, respectively, performed in air and in NaCl(aq.) 0.1 M before, during, and after doping. All films have the same roughness in the range of 0-15 nm. b) 3D analysis of the AFM data for the films under doping at 0.5 V vs Ag/AgCl in NaCl(aq.) 0.1 M. The scale bars in both panels are 500 nm.

There were differences among the surface topographies of the polymers in their dry, as-cast condition. The polymers with a low EG content, g-0% and g-50%, showed an aggregated surface topography due to the low solubility of these polymers in organic solvents, whereas the surfaces of g-75%, g-100%, and 2g were smoother. It is worth mentioning that g-0% was cast from a warm chlorobenzene solution since the polymer was insoluble in chloroform while all the other polymers were cast from chloroform. Once the films were immersed in NaCl(aq.) 0.1 M, the surface topographies of g-0% and g-50% remained almost unaltered from their dry, as-cast conditions. However, the polymers with higher EG contents (g-75%, g-100%, and 2g) showed significant changes in their morphology as they swelled. In particular, the surface of the 2g film exhibited distinctive patterns of smoother and rougher regions. Once the films were
electrochemically doped, the surface topographies of g-0% and g-50% barely changed, while the g-75%, g-100% and 2g surface topographies appeared significantly expanded. Overall, the polymers with a high EG content appeared smoother when immersed in the electrolyte (i.e., darker images in Figure 4c-bottom rows), indicative of a film swollen by anions and water. When the potential was switched from -0.5 V to 0 V vs Ag/AgCl (i.e., discharging), the surface of the films became more compact and rougher than in the doped state, indicative of a repolarization due to the Cl\(^-\) ions moving out of the polymer into the electrolyte towards the counter electrode. To further analyze the \textit{in situ} changes on the polymer films topography, we re-plotted the non-relative 2D and 3D topographies taken from the polymers under doping and extracted the cross-section lineouts (Figure 4b and Figure S13). The results suggest that the polymers with high EG contents expanded their structure as a result of anion penetration, forming distinct regions with different height profiles. These regions were significantly more pronounced for the g-75%, g-100% and 2g films than the g-0% or g-50% films.

Our results demonstrate that conjugated polymers operating in aqueous electrolytes experience significant changes in their structure and morphology during electrochemical doping. Previous work with p(g2T-TT), i.e., g-100%, evidenced that during doping, anions cause a lamellar expansion in the crystallites as they infiltrate the crystallites and accumulate between the hydrophilic side chains.\(^{32,33}\) The majority of water uptake, on the other hand, occurs in the amorphous regions of the film.\(^{21}\) Semi-crystalline conjugated polymers have a complex microstructure comprised of crystalline regions embedded in an amorphous matrix. The amorphous parts of the film are thus the regions that are most affected by the doping induced hydration and, as such, they should show the largest volumetric expansion. This results in a heterogeneously swollen morphology. We observe this morphology change that the films undergo from the AFM measurements taken during electrochemical charging (Figure 4c). The 2g takes in significantly more water, with respect to the amount of injected Cl\(^-\), and undergoes
large and uneven changes in its morphology upon doping. The film surface exhibits distinct regions of different height profiles, indicative of “localized” ion and water penetration and swelling of only these particular regions. While this swollen network is advantageous for ionic conduction, it also lowers the OECT hole mobility. The heterogeneous volumetric expansion of the 2g film likely leads to disconnections for inter-crystallite hole transport. The 2g film, therefore, suffers from the large amount of water molecules in its matrix. As a consequence, with the most hydrophilic polymer, the OECTs have a low gain and slow response. Figure 5 shows a schematic illustration of the structural changes that such a hydrophilic semiconducting film undergoes upon doping with Cl\(^-\) ions.

Figure 5: Illustration of the coupling between anions and holes, and the uneven swelling of a p-type conjugated polymer film during electrochemical doping in an aqueous electrolyte. The polymer-film morphology in the dry state, swollen state (no bias) and swollen state upon doping is depicted in the left, middle and right panels, respectively. The polymer swells with ions/water and the extent of swelling increases with doping. The amorphous regions are depicted as areas between the islands of ordered chains - which are drawn here at an exaggerated scale to highlight their difference. The amorphous regions swell excessively leading to a heterogeneously swollen global morphology. The heterogeneous swelling disrupts the connection between the ordered chains that are responsible for hole transport, resulting in reduced hole mobility.

3. Conclusion

In summary, we have shown that the electrochemical performance of a p-type polymeric mixed conductor can be tuned by controlling its degree of hydration which has a severe impact
on the OECT performance. In the polymer series investigated in this work, incorporating EG side chains caused the $g_m$ of the OECTs to increase by five orders of magnitude due to both the combined improvement of $C^*$ and $\mu_{h,OECT}$ and a shift in $V_{TH}$ towards 0 V. The increased EG content also improved the transient characteristics by making the switching speeds 10 times faster. However, further increasing the hydrophilicity and water-uptake properties of the polymer did not improve performance. Although the polymer with hexakis EG side chains (i.e., 2g) absorbed a high quantity of ions that could easily travel across the hydrated polymer film, the $g_m$ was lower and the devices switched on slower than those with triethylene glycol side chains (i.e., g-100%). This was a result of the uneven volumetric expansion of the 2g film’s microstructure, triggered by excessive water uptake. We suggest that during the expansion of its amorphous domains, the crystalline regions of 2g became separated, reducing the inter-crystalline hole conduction in the microscale OECT channels. Therefore, while a certain level of hydration is necessary for facile ion transport in the film, water uptake can also hinder the electronic charge transport. Overall, in this polymer series, g-100% was the system with the optimal balance of ionic and electronic conduction leading to high OECT performance. We conclude that EG side chain engineering is a valuable strategy to control the swelling and associated ion transport, but the effect of doping-induced hydration on the polymer morphology must be taken into account when designing new OECT materials for operation in aqueous environments. The fundamental knowledge provided by this study paves the way for designing efficient organic mixed conductors for high-performance OECTs as well as other electrochemical devices.

4. Experimental Section
The experimental section is available in the supporting information of the manuscript.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.
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References

Organic electrochemical transistors (OECTs) rely on conjugated polymers that support ionic and electronic conduction. While swelling of the polymer film is required to promote the transport of electrolyte ions, extreme hydration can hinder electronic charge transport, lowering the OECT performance. Fine-tuning of the hydrophilicity of the polymer balances the ionic and electronic conduction necessary to build high performance devices.

**Keywords:** Bioelectronics, Doping, Electrochromic Polymers/Materials, Structure-Property Relationships, Transistors


Balancing Ionic and Electronic Conduction for High-Performance Organic Electrochemical Transistors