Aqueous Processing for Printed Organic Electronics: Conjugated Polymers with Multistage Cleavable Side Chains

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Supporting Information

ABSTRACT: The ability to process conjugated polymers via aqueous solution is highly advantageous for reducing the costs and environmental hazards of large scale roll-to-roll processing of organic electronics. However, maintaining competitive electronic properties while achieving aqueous solubility is difficult for several reasons: (1) Materials with polar functional groups that provide aqueous solubility can be difficult to purify and characterize, (2) many traditional coupling and polymerization reactions cannot be performed in aqueous solution, and (3) ionic groups, though useful for obtaining aqueous solubility, can lead to a loss of solid-state order, as well as a screening of any applied bias. As an alternative, we report a multistage cleavable side chain method that combines desirable aqueous processing attributes without sacrificing semiconducting capabilities. Through the attachment of cleavable side chains, conjugated polymers have for the first time been synthesized, characterized, and purified in organic solvents, converted to a water-soluble form for aqueous processing, and brought through a final treatment to cleave the polymer side chains and leave behind the desired electronic material as a solvent-resistant film. Specifically, we demonstrate an organic soluble polythiophene that is converted to an aqueous soluble polyelectrolyte via hydrolysis. After blade coating from an aqueous solution, UV irradiation is used to cleave the polymer’s side chains, resulting in a solvent-resistant, electroactive polymer thin film. In application, this process results in aqueous printed materials with utility for solid-state charge transport in organic field effect transistors (OFETs), along with red to colorless electrochromism in ionic media for color changing displays, demonstrating its potential as a universal method for aqueous printing in organic electronics.

INTRODUCTION

From self-driving cars to robotics to home temperature control, the “Internet of Things” vision of seamless integration between the physical world and the digital world is rapidly becoming a reality. To fully achieve this vision, electronic components including transistors, sensors, displays, and batteries must be made both commoditized and customizable. Currently, the printed electronics industry aims to provide these inexpensive, versatile electronic components by transitioning away from rigid, silicon based semiconductor chips and toward organic electronic devices that can be printed from solution onto a variety of substrates (e.g., plastics, paper, glass).1−3 While printed electronics are beginning to meet performance metrics for select applications, the solvents used in the printing process are typically aromatic or chlorinated, which carry risks associated with toxicity, volatility, and flammability. Not only are these solvents a risk to employees and the surrounding environment, but their use also carries financial burdens associated with their regulation and disposal.

To avoid these safety issues and costs, the conjugated polymers (CPs) in electronic inks can be designed for aqueous printing, providing a safer and more sustainable method for printed electronic components. Estimates show that, with current printing processes for organic photovoltaic (OPV) devices, 16 million liters of chlorobenzene (over 6 Olympic swimming pools) would be needed to print 1GWp of solar panels.4 Industries will not adopt this technology if large quantities of halogenated solvents are required as the carrier solvent; so many have focused their attention on using xylene derivatives, which have led to photovoltaic and field-effect transistor performance comparable to that of chlorobenzene.5−8 However, these solvents are only slightly preferred over their...
chlorinated counterparts, and aqueous inks still represent the safest, and likely the most sustainable, option for large scale printing of electronics.

While the motivation to print from water is clear, the methods for doing so are still in early development. There are 3 predominant approaches to processing electroactive polymers from aqueous solutions: (1) pendant ionic side chains (sulfonates, carboxylates, ammoniums), (2) polar nonionic side chains (glycols, alcohols), and (3) dispersion of polymer colloids using surfactants. Polymers with pendant ionic side chains have been widely studied and are commonly used in electrode modification and solution based redox applications, but have limitations in solid-state semiconductors due to their inherent conductivity and the ability of ions to screen a voltage bias.9,10 Use of polar, nonionic side chains, such as oligoethers, remedies the effects of pendant ions, and this approach has been used to achieve water-soluble polythiophenes for OFETs with mobility values on the order of 10−5 cm2 V−1 s−1.11 However, many oligoether functionalized CPs suffer from poor solubility in both organic and aqueous solvents, and while they can be coated from dispersions, they often cannot be characterized by common methods like gel permeation chromatography (GPC).12 Polymer dispersions in aqueous solutions have led to the most promising results as they make use of polymers that are already known to attain high mobility. Using a polymer with an OFET hole mobility of ~5 cm2 V−1 s−1 when processed from chlorobenzene, the Chung group was able to process from water to yield materials with ~10−3 cm2 V−1 s−1 using SDS as a surfactant, and up to 2.5 cm2 V−1 s−1 when using nonionic surfactants.13 While this method has led to promising transport properties, the deposition methods discussed are limited to drop casting.

Considering these presently employed methods, they attempt to work within the processing framework designed for organic soluble polymers with fixed, solubilizing chains. As an alternative, materials can be redesigned with both electronic functionality and processing functionality. Examples can be found within the Frechet group, where thermocleavable ester side chains were incorporated into CPs as a route to postprocessing functionality.14,15 These polymers could be cast from chlorobenzene and then heated to ~200 °C to cleave ester side chains, resulting in solvent resistant CPs with pendant carboxylic acids that exhibited up to a 0.5 eV decrease in bandgap compared to their noncleaved counterparts. In an alternate approach to esters, Reeves et al. synthesized CPs with heptanoate side chains that were aerosol spray coated from toluene and subsequently saponified by submersion into KOH in methanol.16 After methanolysis, the alcohol functionalized CP films became solvent resistant and retained their electrochromic properties. In these systems, long aliphatic side chains were utilized for their solubilizing properties, but the ester linkage provided processing functionality that allows for their removal after deposition.

CPs with ester side chains have also been saponified in bulk, providing access to aqueous soluble CPs via carboxylate side chains.17,18 These conjugated polyelectrolytes were spray cast from water and converted to solvent resistant films by acidification of carboxylates to carboxylic acids, providing an environmentally benign method for producing robust CP films for electrochromic and supercapacitor applications. These systems make use of aliphatic side chains to achieve organic solubility for conventional polymerizations, characterization, and purification, while the ester linkage provides the processing functionality to bring aqueous solubility to the materials. In all of these examples, ester side chains can provide the processing functionality for a postdeposition cleavage or a predeposition solubility transition, depending on the orientation of the ester. Both functionalities are desirable for printed electronics processing, but in these systems the ester side chains can provide only one or the other.

In this work, we present design guidelines for integrating two orthogonal processing functionalities into CPs, enabling new routes for aqueous processing of organic electronic materials. The general concept is outlined in Figure 1. Multistage cleavable side chains are designed to provide CPs with three processing stages, with each being removed to transition to the following stage. In stage 1 the polymer is soluble in organic solvents, allowing for the use of traditional polymerization methods (Stille, Suzuki, direct arylation), Soxhlet purifications, and characterization in organic solvents. It should be noted that, in application, this stage would be carried out by a chemical manufacturer in typical polymer production facilities. After production, the first responsive functional group can be triggered to transition into stage 2. In this processing stage the polymer is soluble in aqueous solutions and can be printed onto substrates without the use of surfactants. Here, the processing may be done in a myriad of printing and coating facilities where the water solubility will limit toxic exposure. After printing, the second responsive functionality can be triggered to remove the cleavable side chains and transition to the Core polymer. The Core is primarily made up of the conjugated backbone alone, providing an insoluble electroactive film ready for application in an electronic device. As such, the final material will be composed as much as possible of electroactive, conjugated material. Using this concept, we demonstrate a proof of concept polymer with multistage cleavable side chains that can be processed from an aqueous solution and used as the active material in organic field-effect transistor (OFET) and electrochromic (EC) applications.

A polythiophene bearing multistage cleavable side chains, P(T3-MS)-O, was synthesized to demonstrate the use of this process. Shown in Figure 2, this regiorandom polythiophene contains two reactive functional groups: esters and an o-nitrobenzyl group. The esters provide the ability to transition...
from an organic soluble polymer to an aqueous soluble polyelectrolyte through a postpolymerization reaction in base. Saponification of ester side chains to carboxylates has been previously used within the Reynolds group to allow for aqueous processing of conjugated, electrochromic polymers.\textsuperscript{17,18} The o-nitrobenzyl functionality embeds a mechanism for cleaving off the bulk of the side chain through UV induced formation of a radical on the nitro group. o-Nitrobenzyl groups have been commonly used by polymer chemists to create controlled cleavage points,\textsuperscript{19} and have recently been used by the Thomas group to create UV patternable polythiophene photoresists.\textsuperscript{20} In combination, these reactive functionalities provide the organic soluble P(T3-MS)-O with the ability to transition to an aqueous soluble polyelectrolyte, P(T3-MS)-PE, and then transition to an insoluble polymer P(T3-MS)-I following UV irradiation.

**Multistage Polymer Synthesis, Saponification, and Cleavage.** P(T3-MS)-O was synthesized via a traditional Stille polymerization in toluene from a distannyl bithiophene with a dibromothiophene bearing the multistage cleavable side chain. The complete synthesis is described in Methods S1. Following Soxhlet purification, a red polymer with $M_n$ 11 kDa ($D = 1.9$) was yielded in 68\% from the chloroform fraction. A portion of the polymer was stirred overnight in a solution of potassium hydroxide and methanol, yielding an aqueous soluble polyelectrolyte P(T3-MS)-PE. The transition from stage 1 to stage 2 was affirmed by the shift in solubility from organic soluble to aqueous soluble, a change in water contact angle on thin films from 70$^\circ$ to 50$^\circ$ as seen in Figure S4, and the observed loss of ethyl groups via $^1$H NMR in Figure S1.

To test the effectiveness of the UV cleavable o-nitrobenzyl functionality, films of both P(T3-MS)-O and P(T3-MS)-PE were blade coated onto glass slides from chloroform and 1:1 water/isopropyl alcohol (H\textsubscript{2}O:IPA), respectively, and irradiated in a UV chamber for 150 min at 365 nm and $\sim5$ mW/cm\textsuperscript{2}. For P(T3-MS)-PE, IPA was used as a cosolvent in order to reduce the surface tension of the deposition solution, allowing for enhanced wetting and film formation during blade coating.\textsuperscript{21} UV−vis spectra before and after irradiation are shown in Figure 3. The main feature to be noted in the UV−vis data is the minimal change in the conjugated backbone $\pi$ to $\pi^*$ transition in conjunction with the loss of a peak around 312 nm for both polymer systems, which is characteristic of the transition from an o-nitrobenzyl group to the cleaved nitroso group.\textsuperscript{22} In both cases, irradiation leads to loss of this peak, while subsequent rinsing in the casting solvent leads to a negligible loss in peak absorption.
Figure 4. Grazing-incidence wide-angle X-ray scattering (GIWAXS) plots of P(T3-MS)-PE thin films as-cast (a), irradiated (b), and irradiated and washed with 1:1 H2O:IPA (c). Atomic ratios of N:S (d) and K:S (e) within P(T3-MS)-PE films calculated via XPS. Pristine, irradiated, and irradiated and washed films are shown at varying depths from the surface (relative depth = 0) and through the thickness of the film (relative depth = 1) in comparison to the expected ratio of 0.33 (N:S) and 0.66 (K:S).

absorption, indicating that the polymer has become solvent resistant. Cleavage was also observed by 1H NMR in filtered solutions of both P(T3-MS)-O and P(T3-MS)-PE after UV irradiation. As shown in Figures S2 and S3, irradiated solutions reveal the loss of a benzy1 peak that is converted to a ketone during the cleaving process. Contact angle measurements, shown in Figure S4, also suggest that cleavage from either P(T3-MS)-O or P(T3-MS)-PE leads to the same anticipated polymer structure. P(T3-MS)-O shows a water contact angle of 70° which is reduced to 62° upon conversion to P(T3-MS)-I after irradiation and a chloroform wash. P(T3-MS)-PE films show a contact angle of 50°, which increases to 65° when converted to P(T3-MS)-I after irradiation and a 1:1 H2O:IPA wash. The minimal differences in contact angle between films of P(T3-MS)-I indicate that a similar polymer surface structure is obtained whether the film is initially cast in its organic soluble form or in its polyelectrolyte form.

We next sought to answer whether or not the cleavable side chain was fully removed from the film, and what this removal does to the polymer’s solid-state structure. Because the side chains of P(T3-MS)-PE contained two elements not found in the main polymer backbone, nitrogen (N) and potassium (K), XPS surface and depth profiling experiments on thin films of this polymer were used to quantify the amount of side chain within the film throughout the multistage process. Alongside these results, P(T3-MS)-PE was studied using grazing-incidence wide-angle X-ray scattering (GIWAXS) to monitor structural variations of the polymer throughout the multistage process. The results are summarized in Figure 4. Since sulfur (S) is unique to the polymer backbone, integrated peaks for N 1s and K 2p were normalized to the S 2p peak area and compared to the expected repeat unit atomic ratios. Full XPS spectra and integration details can be found in Methods S4 and Figures S8, S9, and S10. For the N 1s peak, both the pristine and irradiated films show ratios close to the expected N:S ratio of 0.33. Slight deviation in the pristine sample may be caused by surface impurities or prematurely cleaved side chains. The K 2p peaks show similar results, though the K:S ratio never reaches the expected value of 0.66. This difference could be caused by incomplete saponification of the side chains, premature side chain cleavage, and/or a loss of the counterion during the deposition. In the GIWAXS scattering plots shown in Figure 4, irradiation leads to a large change (a → b), notably the formation of discrete crystallite scattering peaks. These peaks, which can be seen as small spots of intensity in Figure 4b, are commonly indicative of the presence of discrete molecular crystallites. The GIWAXS data suggests that side chains are being cleaved after irradiation, but remain in the film as discrete crystalline domains, which agrees with the minimal changes in atomic makeup seen in the XPS data.

Once irradiated and washed, the N:S ratio drops to 0.1, corresponding to a large loss in elemental nitrogen. These results show that, while irradiation cleaves the polymer side chains, about a third of the side chains are either not cleaved or not removed by the aqueous wash. Alternatively, the K 2p peaks show complete removal of K after the aqueous wash. Unlike the nitrogen on the side chain, the potassium exists as the polyelectrolyte’s counterion and therefore has a greater ability to diffuse out of the film in conjunction with ion exchange or weak acid protonation of the carboxylates to carboxylic acids. The complete loss of potassium ions, but not side chains, could also result in the self-doping of the polythiophene backbone by the anionic carboxylates leftover on the side chains. Evidence for this self-doping can be observed in the irradiated and washed P(T3-MS)-PE UV–vis spectrum in Figure 2, where a peak around 1000 nm begins to appear, typically corresponding to polaronic charge carriers in conjugated polymers.

GIWAXS results of the film after the aqueous wash process (Figure 4, b → c) show a disappearance of most of the small crystallite peaks, aligning with the significant removal of side chain mass seen in the XPS atomic ratios. It is also worth noting that the overall (100) and (010) diffraction pattern seen for the polymer remains unchanged, with strong edge-on
Multistage Cleaved Polymer Application Testing. To observe the effects of the multistage process on device applications, P(T3-MS)-O and P(T3-MS)-PE were tested for OFET mobility and electrochromism, representing solid-state applications and solution based redox applications, respectively. Charge carrier properties were investigated through p-type OFET devices with a bottom-gate/bottom-contact architecture. Device fabrication details are provided in Methods S5. OFET transfer curves are shown in Figure 5 with calculated mobility values averaged across 3 P(T3-MS)-O devices and 9 P(T3-MS)-PE devices. The pristine P(T3-MS)-O films cast from chloroform exhibit an average mobility of $8.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, on the same order of magnitude as the mobility observed by the Thomas group’s polythiophene with photocleavable side chains ($2.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$) as well as regiorandom P3HT ($10^{-4}–10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$). After irradiation and washing, the mobility drops to $3.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$.

The pristine P(T3-MS)-PE films cast from 1:1 H2O:IPA obtain an average mobility of $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$. This result was unexpected, as conjugated polyelectrolytes do not typically function well in OFET devices due to the presence of mobile counterions and high OFF currents caused by intrinsic conductivity. At this time, there is no clear explanation for why these conjugated polyelectrolytes show OFET response while most do not. To our knowledge, the only other example reported for a polyelectrolyte OFET material is a n-type polymer from the Bazan group, making P(T3-MS)-PE novel in its ability to function as a polyelectrolyte p-type OFET. After irradiation and washing of this polymer, the mobility drops to $6.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$. For both polymers, an intermediate stage was tested after irradiation but before washing, but neither showed an electrical response. We hypothesize that OFET mobility is disrupted by the presence of mobile side chains that have not yet been removed from the film.

While the mobility of the aqueous processed and cleaved P(T3-MS)-PE is not state-of-the-art for CPs, the results are promising when compared to other regiorandom polythiophenes that achieve similar mobility values. It is possible that higher mobility values will be achieved by applying the multistage concept to a regioregular, highly planar backbone similar to current high mobility polymers. However, the aqueous processed OFETs in this study show high OFF currents, leading to ON/OFF ratios on the order of $10^{8}$. Likely caused by the presence of water and ions within the film, this represents a limitation for the multistage concept that will need to be addressed in future work.

Redox response and red to colorless electrochromism were observed in films of P(T3-MS)-O and P(T3-MS)-PE on ITO/glass before and after irradiation and washing. Broad, reversible oxidation peaks were recorded for both polymers by cyclic voltammetry (CV) and showed negligible changes after irradiation, with the onset of oxidation remaining around $–0.1 \text{ V}$ relative to the ferrocene/ferrocinium redox couple throughout the multistage process. CV and differential pulse voltammetry (DPV) data can be found in Figure S5. The oxidation of these polymers is accompanied by a color change from red in the neutral state to colorless in the oxidized state. Figure 6 shows the spectroelectrochemical series of a P(T3-MS)-PE film on ITO/glass along with photographs of the resulting color change. The electrochromic film demonstrates up to a 47% contrast for the pristine polymer and 40% contrast after irradiation, comparable to the ~50% contrast achievable in P3HT films. Irradiated films show faster switching speeds, reaching 95% contrast in 6 s, while the pristine films take 14 s. Switching speed data can be found in Figure S12. This may be the result of superior ion intercalation throughout the film and faster electronic response due to removed side chain mass. Similar results are seen for the chloroform processed P(T3-MS)-O and can be found in Figure S11. As with the OFET devices, these multistage polymers do not compare to state-of-the-art high contrast electrochromic polymers, but rather demonstrate the ability for aqueous processed multistage polymers to be used in redox applications.

CONCLUSION

We have demonstrated that the use of multistage cleavable side chains is a viable approach for processing conjugated polymers from aqueous solutions, while ultimately providing benefits to both solid-state and redox active applications. This methodology allows for traditional polymer synthesis, purification, and characterization in organic solvents, thin film processing via aqueous solution, and postdeposition side chain cleavage that results in a solvent-resistant electroactive film. In this initial proof of concept study, aqueous soluble CPs exhibit p-type mobility in OFET devices and red to colorless electrochromism. Through this work, we unexpectedly observed p-type mobility in a conjugated polyelectrolyte film in contrast to most conjugated polyelectrolytes, opening up opportunities for future work in semiconducting polyelectrolytes.

While the proof of concept polymer within this paper obtained the desired processing metrics, future work will focus...
on increasing the performance of conjugated polymers with multistage cleavable side chains by translating the concept to current high performance polymer backbones. A major limitation lies within the high OFF currents observed in aqueous processed OFETs, and may be remedied by enhanced UV irradiation conditions for side chain cleavage, optimized washing conditions, and surface treatments prior to thin film deposition.

Overall, the concept of multistage cleavable side chains provides distinct opportunities and advantages in the area of aqueous processing and UV patterning for OFETs, electrochromics, OPVs, and bioelectronic devices. As these technologies continue to mature, it is essential to consider industry adoption by designing materials that can be processed safely and economically on a large scale. Conjugated polymers with multistage cleavable side chains address these requirements by enabling scalable, environmentally benign processing while preserving electronic properties for device applications.

**ASSOCIATED CONTENT**

* Supporting Information
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Procedures, characterizations, materials, and instrumentation details (PDF)

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**Author Contributions**

B.S. designed the concept, synthesized and characterized the polymer, performed the electrochromism study, and coated films for OFET device study. Z.Y. provided OFET substrates, tested the devices, and worked up the transfer curves for mobility values. A.W.L. performed the XPS study and worked up elemental ratio data. J.L.H. was consulted for blade coating of aqueous inks and worked up GIWAXS data. All authors contributed to the manuscript writing and editing.

**Notes**

The authors declare no competing financial interest.

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