Surface Grafting of Functionalized Poly(thiophene)s Using Thiol–Ene Click Chemistry for Thin Film Stabilization

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Supporting Information

ABSTRACT: Regioregular poly[(3-hexylthiophene)-ran-(3-undecenylthiophene)] (pP3HT) and vinyl terminated poly(3-hexylthiophene) (xP3HT) were synthesized by the McCullough method and surface grafted to thiol modified silicon dioxide wafers using thiol–ene click chemistry. Utilizing this method, semiconducting, solvent impervious films were easily generated. Thiol–ene click chemistry is convenient for film stabilization in electronics because it does not produce side products that could be inimical to charge transport in the active layer. It was found through grazing incidence wide-angle X-ray scattering (GIWAXS) that there is no change in microstructure between as-spun films and thiol–ene grafted films, while there was a change after the thiol–ene grafted film was exposed to solvent. Organic field-effect transistors (oFETs) were fabricated from grafted films that had been swelled with chloroform, and these devices had mobilities on the order of 10^-6 cm^2 V^-1 s^-1, which are consistent with poly(thiophene) monolayer devices.

KEYWORDS: conjugated polymers, click-chemistry, polythiophene, surface grafting, microstructure

INTRODUCTION

The emergence of conjugated polymers in the field of electronics has inspired considerable research on their properties and their incorporation into various device structures. As a result of these studies, conjugated polymers can be synthetically tuned to have specific electronic and solubility properties. Presently, constructing thin films of conjugated materials over an assortment of large area substrates is facile and cost-effective and can be accomplished through a variety of methods, including dip-coating, spin-coating, and roll-to-roll processing.

However, conjugated polymer films are susceptible to vapor or solvent vitiation, limiting useable device architectures and device performance. Devices requiring the deposition of multiple layers of polymer films can be difficult to fabricate, as the sequential solutions may disturb the initial film, through swelling, polymer chain reorganization, or by removal of the underlying film. Solvent vapors can change the film morphology, in some cases inducing phase segregation of the two components to such a degree that charge transport is no longer viable.

Grafting conjugated polymers to substrate surfaces presents a unique solution to the above-mentioned thin film instability issues. Grafted polymers are chemically bound to a surface, which enables the films to be solvent resistant and tolerate exposure to solvent vapors without significant swelling. Polymers can be grafted to a surface by functionalizing the polymer and the substrate with complementary chemical moieties, and introducing the polymer to the substrate by either solution or melt processes, and this method is termed “grafting-to”. The ultimate thickness of these grafted films, as measured by ellipsometry or AFM, is dictated by how well the modified polymers diffuse to the surface, where they chemically react with the surface functionalities, and the molecular weight of the polymer. Polymers can also be grafted from a surface. In this case, an initiator is immobilized on the surface and exposed to reactive monomers, allowing the growth of densely packed, uniform polymer chains. In addition to
rendering the film resistant to solvents, grafting allows for precision over the density, orientation, and location of polymers on substrates. This can enable specialized morphologies, different from the spin coated films, which impact charge transport through semiconducting polymer films.

Many different chemistries have been used to create grafted films, including condensation and nitrene insertion reactions, as well as various click chemistry strategies. Click chemistry is particularly advantageous for grafting-to applications because it does not yield byproducts, can be achieved under mild conditions, is nearly quantitative, and has fast reaction times. The most commonly employed click chemistry used for grafting-to applications is the azide−alkyne cycloaddition reaction. Conjugated polymer films grafted through azide−alkyne click chemistry have been shown to be solvent impervious and have charge carrier mobilities comparable to nongrafted devices. Thiol−ene chemistry has also been used for grafting purposes, detailing the photopolymerization of nonconjugated difunctionalized monomers from a functionalized surface, or the anchoring of biocompatible materials to substrates.

We analyze the solid state structure of grafted polymers. In this study, we extend the application of thiol−ene click chemistry to two distinctly functionalized poly(thiophenes). From the moment of the polymerization, the vinyl-Grignard capping was critical to reduce the presence of hydrogenated end groups, formed by magnesium-halogen exchange. The vinyl monocapped P3HT was synthesized using the McCullough method (Figure 1a). It was anticipated that the long undecene chain would be less likely to interact with the Ni(0) catalyst, but after allowing the solution to react for 14 h, 3-undecenylthiophene was only incorporated at 14% (determined by 1H NMR). Mₙ was determined to be about 5460 g/mol via MALDI-TOF, while D was 1.02.

To study the reactivity of chain-end−ene functionalized polymers, vinyl end-capped P3HT (xP3HT) was synthesized using the McCullough method from 2-bromo-5-chlorozinc-3-pentenylthiophene with a nickel catalyst using the McCullough method. The polymerization resulted in a polymer that fluoresced a bluish white color when exposed to UV light, in stark contrast to the bright yellow/orange fluorescence characteristic of low dispersity and high molecular weight poly(thiophene)s. The MALDI-TOF spectrum of P3PNT revealed that the polymer consisted of highly dispersed molecular weights. Mechanistically, it has been hypothesized that the active Ni(0) can coordinate with the pendant alkenes present in the monomer and polymer. This alkene coordination competes with the polymer forming reaction by breaking its complex with the thiophene ring, which limits the effectiveness of the polymerization. Although this polymer was not used for subsequent studies in electronic devices, it was used in thiol−ene click surface reactions (vide infra).

To circumnavigate the polymerization complication, a random copolymer of 3-undecenylthiophene and 3-hexylthiophene (pP3HT), with a molar ratio of 2:3, was synthesized by the McCullough method (Figure 1a). It was anticipated that the long undecene chain would be less likely to interact with the Ni(0) catalyst, but after allowing the solution to react for 14 h, 3-undecenylthiophene was only incorporated at 14% (determined by 1H NMR). Mₙ was determined to be about 5460 g/mol via MALDI-TOF, while D was 1.02.

To study the reactivity of chain-end−ene functionalized polymers, vinyl end-capped P3HT (xP3HT) was synthesized using the McCullough method from 2-bromo-5-chlorozinc-3-pentenylthiophene (Figure 1b). The reactions were set up and allowed to proceed at room temperature for 5 min and then cooled to 0 °C and allowed to react for 10 additional minutes. The growing polymer chains were terminated by adding an excess of vinyl-Grignard reagent. Cooling the reaction before introducing the Grignard reagent was critical to reduce the presence of hydrogenated end groups, formed by magnesium-halogen exchange. The vinyl monocapped P3HT was characterized by ¹H NMR and MALDI-TOF to confirm the success of the vinyl-Grignard capping. Attempts to substitute the bromide end group of the vinyl monocapped P3HT were first made using Kumada coupling. The mono functionalized polymer and Ni(dppp)Cl₂ were cooled to 0 °C, and vinyl-MgCl solution was added dropwise. The MALDI-TOF analysis showed that the resulting polymer was terminated by hydrogen rather than the desired vinyl group. The vinyl substitution was successfully accomplished using Stille coupling to terminate a telechelic vinyl polymer by reacting the monocapped P3HT

![Figure 1](image_url)

**Figure 1.** (a) Synthetic schematic for pP3HT, where R₁ is 7 and R₂ is 3. (b) Synthetic schematic for xP3HT where R₂ is 3.

### RESULTS AND DISCUSSION

**Synthesis of Alkene Functionalized Poly(thiophene).**

Alkene functionalized poly(thiophene)s were synthesized to test the efficacy of thiol−ene click chemistry as a covalent binder between the polymer and a thiol modified silicon dioxide wafer. Poly(3-pentenylthiophene) (P3PNT), a polymer containing terminal alkene moieties on the side chains, was synthesized by polymerizing 2-bromo-5-chlorozinc-3-pentenylthiophene with a nickel catalyst using the McCullough method. The polymerization resulted in a polymer that fluoresced a bluish white color when exposed to UV light, in stark contrast to the bright yellow/orange fluorescence characteristic of low dispersity and high molecular weight poly(thiophene)s. The MALDI-TOF spectrum of P3PNT revealed that the polymer consisted of highly dispersed molecular weights.
with tributyl(vinyl)stannane in toluene at 100 °C for 24 h, using a catalytic amount of Pd[PPh₃]₄. The product was characterized by 1H NMR and MALDI-TOF. The \( M_n \) of the telechelic polymer was found to be 4575 g/mol with a \( D \approx 1.01 \).

**Thiol–Ene Surface Grafting of Polythiophenes.** Heavily doped p-type silicon substrates, with a 200 nm thermally grown silicon dioxide layer, were sequentially sonicated in acetone, ethanol, and isopropanol to remove contaminants, followed by immersion in a piranha cleaning solution (a mixture of 3:1 sulfuric acid to hydrogen peroxide) for 4 h and rinsing with water. This process produced a hydrophilic surface with a nondiscernable water contact angle (WCA) less than 5°. The cleaned silicon wafers were then functionalized with (3-mercaptopropyl)triethoxysilane (MPTS), through vapor phase deposition and concurrent condensation of the MPTS with the native SiO₂ surface. This was accomplished by placing the silicon wafers in a Petri dish overnight at 100 °C next to a shallow glass dish containing 0.1 mL of MPTS on a hot plate. Successful silanation of the surface was probed by measuring the change in WCA. The WCA of the treated surfaces varied between 73° to 87°. The higher contact angles of the MPTS monolayer may be due to less oriented monolayers (Figure S11). The thiol modified wafers were transferred to a glovebox, where 5 mg/mL solutions of functionalized poly(thiophene) in chlorobenzene were spin-coated at 1000 rpm for 60 s. The spin-coated resulting films had WCAs greater than 90°. The wafers were annealed at 150 °C for 5 min and then exposed to 254 nm UV light inside the glovebox for a predetermined amount of time to graft the functionalized poly(thiophene)s to the surface. The grafted samples were introduced to chloroform using one of three procedures (vide infra), to remove any unreacted polymer. They were reheated to 150 °C for 5 min to remove any residual solvent (Figure 2).

Using the procedure described above, P3PNT was grafted in air to a MPTS monolayer, resulting in a film with a WCA of 101°. After immersion soaking in chloroform for 8 h, the film was dried to reveal an essentially unchanged WCA of 103°. The XPS of this surface is shown in Figure S10 and the C 1s peak includes a shoulder which could be deconvoluted into four peaks. The principle integration at 284.71 eV represents 70% of bonds to carbon. An adjacent integration, at 285.94 eV, represents 15% of the bonds to carbon, and is indicative of hydroxyl groups bonded to the \( \alpha \) carbon of the thiophene ring. This position is easily oxidized upon exposure to radical oxygen species. The smallest integrations at 287.25 and 288.93 eV compromise 16% of bonds to carbon and represent carbonyl and carboxyl groups, respectively, signifying further oxidation of P3PNT. A series of control experiments were performed to confirm that a thiol–ene click reaction was the most effective method for the formation of insoluble thin films. These experiments used nonfunctionalized P3HT and P3PNT to show that both the vinyl groups in P3PNT, and the MPTS coated substrate were required for grafting. The UV-initiated grafting reactions were performed in air in order to partially oxidize the P3PNT, as described above. The XPS of oxidized poly(thiophene)s have a distinctive C 1s peak, with the largest integration at 284.75 eV due to the methylene carbons and aromatic bonds between carbon. Three smaller integrated curves protrude like a shoulder from the 284.75 eV peak, which represent various degrees of poly(thiophene) oxidation. This characteristic peak can be used as a label to determine if P3PNT is present on the wafer, which would indicate that thiol–ene click grafting was successful (Figure S7).

The first control experiment involved spin-coating P3PNT onto a clean SiO₂ substrate and exposing it to 254 nm UV light at 150 °C for 1 min. The WCA of the spin-coated film was 93°. The film was immersion soaked in chloroform for 8 h. After drying, the contact angle decreased noticeably to 63°. The C 1s peak for this sample did not possess the oxidation characteristic of oxidized poly(thiophene)s. The small amount of carbon content detected is likely due to residual organic compound contamination either from the chloroform treatment or adsorbed air during handling (Figure S8). This experiment showed that there was not any residual P3PNT on the silicon wafer after the chloroform immersion soak, suggesting that UV exposure and heat are insufficient to induce radical cross-linking or fixing of the polymer to the SiO₂ surface on this time scale.

In the second control experiment, poly(3-hexylthiophene) was spin-coated onto a MPTS modified substrate and received...
the same UV-grafting procedure as described in the first control experiment. The WCA of the resulting film was 98°. The film was then immersion soaked in chloroform for 8 h. After drying, the WCA was observed to decrease to 86°, which is within the range associated with a nonsubstituted MPTS monolayer. The C 1s peak is symmetric and can be deconvoluted into two integrals, one at 284.75 eV and one at 286.10 eV, with the 284.75 eV peak dominating. This spectrum is comparable to reported spectra of MPTS monolayers, representing methylene carbons (284.75 eV), as well as oxygen bonds to carbon from ethoxy groups in the film (286.10 eV; Figure S9).38,42 This control experiment indicated that the MPTS monolayer remained on the wafer, but immersion soaking in chloroform removed all of the poly(3-hexylthiophene).

From the controls it seems evident that both the thiol and vinyl moieties are necessary for insoluble polyiophenes film formation. The XPS and WCA measurements support the claim that thiol–ene click chemistry is the mechanism of insoluble film formation for these conditions, and no other chemistry, namely vinyl cross-linking, is responsible for anchoring P3PNT to the substrate surface. In Figure 3, a bar graph depicts the elemental composition of each sample for the grafted P3PNT film, the first control, the second control, and the rinsed grafted P3PNT film.

**Figure 3.** Bar graph depicting the elemental composition (%) of both controls compared to the grafted film and the grafted and rinsed film, determined by XPS.

**Morphology/Microstructure.** Both xP3HT and pP3HT were grafted to MPTS monolayers in a N2 glovebox for 10 min using the previously described procedure. After grafting, some samples were rinsed with chloroform, which entails dropping 0.3 mL of chloroform on the surface of the grafted film and then immediately spinning it off at 2000 rpm for 60 s, in the glovebox at room temperature. This was done to remove polymer that did not covalently graft to the surface. XPS was performed on spin-coated, grafted, and rinsed samples of xP3HT and pP3HT (Figures S14 and S15).

To investigate the microstructure of these films, grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were performed on the spin-coated, grafted, and rinsed samples of xP3HT and pP3HT (Figure 4). The angle was changed to probe the microstructure throughout the film, and the microstructure was observed to be constant from the interface of the substrate and the graft to the surface of the film. The GIWAXS from the as spun samples show similar orientation for both polymers. The (100) reflection, along with higher-order reflections, is centered at $q = 0.34$ Å$^{-1}$ ($d = 18.5$ Å) along the $q_{\parallel}$-axis. The (010) reflection is present at $q = 1.70$ Å$^{-1}$ ($d = 3.70$ Å) along the $q_{\perp}$-axis. These reflection positions are characteristic of an edge-on orientation with the lamella layer structure oriented normal to the film and the $\pi-\pi$ interchain stacking in the plane of the film. After exposure to UV-light and heat to induce grafting, no morphological differences could be resolved from the scattering. This indicates that the grafting procedure does not effect the microstructure of the poly(thiophene) films. After the films were rinsed, a clear rearrangement could be seen in the structure of the films. The pP3HT samples showed a change in preferred orientation with the (100) reflection present in the plane. Higher-order reflections were absent in this sample, indicating that the film is less ordered after rinsing. xP3HT shows a similar change in orientation, but a more ordered system, as the (100) axis is oriented in the plane and the (010) reflection is present normal to the film. This film also shows a dual texture with the (100)-axis also present normal to the film, but the main reflection positions are representative of a face-on orientation.43

**Film Thicknesses and Grafting Density.** Both xP3HT and pP3HT were grafted to MPTS surfaces with certain procedural variations. The grafting times were varied between 1, 5, and 10 min. Additionally, the grafted films were exposed to chloroform using three different methods to remove residual unreacted polymer. The first method was rinsing, as described above, and the film was only exposed to chloroform for a few seconds. The second method, immersion soaking, required placing the grafted film and 10 mL of chloroform into a scintillation vial, and then setting the vial on a vortex mixer for 24 h. The last method, puddle and rinse, involved dropping 0.3 mL of chloroform onto a grafted film, full wetting the surface, resting on the spin-coater chuck. After 30 s of the chloroform swelling the grafted film, the spin-coater ramped to 1000 rpm over a period of 5 s, and then spun consistently for 60 s, to remove the unreacted polymer that dissolved in the chloroform droplet. These three methods vary the time that the graft was exposed to chloroform. The WCAs of the grafted films were measured after chloroform exposure for each of the grafting times. AFM and profilometry were used to determine the thicknesses of the films. In Figure 5 the thicknesses of the grafted and exposed films are plotted against grafting times for each solvent exposure method. For both pP3HT and xP3HT, rinsing was the least effective method for removing unreacted, interpenetrated polymer, while puddle and rinse was the most effective method. Previous reports describe the calculation of grafting density for both silane monolayers and the polymer grafts.7,13 The MPTS monolayer thickness was around 0.4 nm (Figure S11), corresponding to a grafting density of 1 molecule/nm$^2$. Consequently, it should not be possible for the grafted polymer films to have a grafting density higher than the MPTS density. Grafting densities greater than 1 chain/nm$^2$ are suggestive of residual interpenetrated polymer, or the beginning of a new interphase. As the puddle and rinse method removed the interpenetrated polymer most efficiently for both xP3HT and pP3HT, it seems that the high grafting densities for xP3HT for the 10 min graft times could be a result of secondary vinyl cross-linking reactions. This is likely due to the well-known diradical formation between two styrenic end groups upon exposure to heat. The diradical has an extremely short lifetime, allowing it to quickly ring close. This is one of the possible reactions from the Flory mechanism of styrene thermally initiated autopolymerization. Aliphatic alkenes do not undergo this reaction and are not apt to undergo these kinds of thermally initiated reactions as readily as styrenic materials.
example, a previous report on the thermal cross-linking of poly(3-(5-hexenyl)thiophene), describes needing 2 h of 150 °C heating to create a cross-linked network of this polymer.\textsuperscript{44,45} The high grafting densities from the rinse method are most likely due to interpenetrated polymer.

**Electronic Properties.** Organic field effect transistors (oFETs) were fabricated with a bottom gate, top contact architecture using both grafted pP3HT and xP3HT films as the active layer, and the native SiO\textsubscript{2} as the dielectric. Active layers were grafted for 1, 5, and 10 min, followed by puddle and rinse with chloroform. The hole mobilities were calculated using the slope of $\sqrt{I_D}$ versus $V_{GS}$ line, in the saturation regime (Figures S12 and S13). The channel length of the electrodes was 100 μm, while the width was 2000 μm. The dielectric capacitance of SiO\textsubscript{2} is 1.7 $\times$ 10\textsuperscript{-8} F/cm\textsuperscript{2}.\textsuperscript{46} The devices turned on under negative gate voltages, demonstrating hole transport through the grafted and swelled film. The transfer curves generated for xP3HT and pP3HT based devices are shown in Figure 6. The linear hole mobilities were calculated to be on the order of 10\textsuperscript{-6} cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} for both pP3HT and xP3HT grafted and swelled active layers, for each grafting time. The low mobility for these films could be a result of many factors, including the face-on orientation, the thinness of the films, and high contact resistance. Previous reports indicate that face-on orientation leads to hole mobilities 100x lower than edge-on P3HT films. Charge transport in the direction of the pi-pi stacking is more effective in the architecture of typical oFETs when the film has edge-on orientation.\textsuperscript{47,48} It has also been shown that in monolayers of P3HT, oFET mobilities are typically on the order of 10\textsuperscript{-5}–10\textsuperscript{-4} cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, even for monolayers exhibiting edge-on orientation. In this report, it is explained that ultrathin films may be strained due to their contact with two interfaces (air, substrate) causing them to lose the crystalline order that a bulk film might possess. It is also possible that interfacial defects between the monolayer and the substrate can hinder charge transport entirely, where in a bulk film, the upper layers of polymer would help assist charge transport across such defects.\textsuperscript{48,49}

![Figure 4. Grazing incidence wide-angle X-ray scattering (GIWAXS) where, (top) 2D image maps of spin-coated, grafted, and grafted and rinsed pP3HT films; and (bottom): 2D image maps of spin-coated, grafted, and grafted and rinsed xP3HT films.](image)

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### CONCLUSIONS

This study showed thiol–ene click chemistry effectively grafts functionalized poly(thiophene)s to MPTS modified SiO\textsubscript{2} surfaces. Grafting times between 5 and 10 min were enough to achieve high grafting densities for both end and pendant functionalized poly(thiophene)s. Puddle and rinsing the grafted films with chloroform was the most effective method for removing interpenetrated, nongrafted polymer. The success of the grafting experiments was reliably tested by contact angle and X-ray photoelectron spectroscopy (XPS). Two controls were used to validate that the fabricated films were a result of alkene functionalized poly(thiophenes) grafting to the substrates by thiol–ene click chemistry, as opposed to the alkene functionalities radically cross-linking to create impervious networks. Unexpectedly, the grafting procedure did not effect the microstructure of the film, maintaining an edge-on orientation from the as spun film to the grafted film. The grafts that were rinsed in chloroform showed a significant change in microstructure to a face-on orientation, with the xP3HT graft being more ordered than the pP3HT graft. To our knowledge, this is the first example of an oriented film made by a grafting-to method. Even after swelling with chloroform, these films were electrically active, demonstrating hole transport in field-effect transistors. The mobilities were low for poly-thiophene derivatives, but inline with ultrathin films, which may experience interfacial strain and defects to a greater degree than bulk films do. Thiol–ene click surface grafting offers a simplistic method to fabricate well oriented, solvent resistant, electroactive, ultrathin films.

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### EXPERIMENTAL SECTION

**Materials.** All materials were purchased from Sigma-Aldrich or VWR and used without further purification. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled before using. Silicon substrates (P-doped, 0.01–0.018 ohm-cm, 200 nm thermally grown SiO\textsubscript{2}) were purchased from University Wafers. Gold for metal evaporation was purchased from Kurt Lesker.

**Instrumentation.** All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 500 (500 MHz) spectrometer and internally referenced via residual solvent signal (CHCl\textsubscript{3}; δ H 7.26 ppm).
MALDI-TOF was performed on a MicroFlex LRF MALDI-TOF from Bruker Daltonics (Billerica, MA). Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Center. Dithranol (40 mg/mL in THF) was used as a matrix for both polymers (10 mg/mL in THF). Dithranol solution was mixed with poly(thiophene) solution at a 1:1 ratio and spotted on a target. XPS was performed on a Quantum 2000 Scanning ESCA Microprobe from Physical Electronics. Deconvolutions of Cs1 peaks were made on MultiPak software using a Gaussian Lorentzian mixed function ratio with a Shirley background. fwhm for the integrations ranged between 1.5 and 2. Film thicknesses were measured by a Dektak 150 profilometer or a DI 3000 AFM four in the Scanning Probe Microscopy Facility at University of Massachusetts Amherst.

**Synthesis of 3-Undecenylthiophene.** The procedure for this Kumada coupling is based off of ref 23. A clean multineck round-bottom flask, fitted with rubber septa, a condenser, and an oval shaped stir bar, was dried by alternating pulling vacuum and purging with N2 three times while being heated with a heat gun. While the apparatus was drying, 3-bromothiophene (0.95 equiv), Ni(dppp)Cl_2 (0.0042 equiv), and 11-bromo-1-undecene (1 equiv) were being purged with N2 in separate vials. 1.2 equiv of magnesium turnings were added to the dried round-bottom and the drying procedure was repeated until the magnesium was very shiny and staticky. After the round-bottom cooled, a crystal of iodine was added. Then vacuum was pulled on the apparatus for 10 min. The apparatus was flushed with N2 and 15 equiv of ethyl ether or 2-methyltetrahydrofuran were added, resulting in a dark red solution. (Tetrahydrofuran is not a suitable solvent for this reaction.) The 11-bromo-1-undecene was removed from its vial by a dry syringe and added dropwise over the course of 45 min to the main apparatus at room temperature. As the Grignard forms, the solution consecutively turns orange, yellow, pale yellow, white, then clear and begins to bubble and heat up. This is followed by a slow darkening of the solution to gray. A dark gray solution is a good indicator that the Grignard has formed. After the 11-bromo-1-undecene is added in full, the solution changes to a clear color and begins to bubble and heat up. The Grignard has formed.

**Figure 5.** (top) Thicknesses of grafted films after different solvent exposure methods, the calculated grafting densities and WCAs for pP3HT. The thickness of the spin-coated film was 56 ± 1 nm. (bottom) Thicknesses of grafted films after different solvent exposure methods, the calculated grafting densities, and WCAs for xP3HT. The thickness of the spin-coated film was 57 ± 2 nm.
the reaction is heated to 29 °C for 4 h. 3-bromothiophene was transferred from its vial with a dry syringe and added dropwise to the solution over 30 min at 29 °C. Then while the reaction flask was under positive nitrogen pressure, the septum was removed and Ni(dppp)Cl₂ was added in bulk to the solution. The solution turns redish. The reaction was heated to reflux overnight. After 12 h, the reaction is a red/black color. If the reaction is run in ethyl ether, it is easy for the solvent to evaporate off during the reflux, which may lead to a greasy sludge after 12 h. The round-bottom is placed in an ice bath and 12 M HCl (1:1 ratio of total reaction moles to HCl) is added to the solution. The solution is extracted three times with ether, followed by three washes with water. The organic phase is dried over MgSO₄, filtered, and condensed through rotary evaporation. Thin layer chromatography shows two spots before purification, the topmost spot is the product, while the bottom spot is bisthiophene. The product is purified on a silica column with hexanes. The final product is a clear oil. The best yield achieved was 52%.¹H NMR (CDCl₃, 500 MHz) Reference 7.26 ppm: 7.23 (m, 1H), 6.93 (d,1H), 6.91 (m, 1H), 5.83 (m, 1H), 4.96 (m, 2H), 2.63 (t, 2H), 2.03 (m, 2H), 1.60 (m, 4H), 1.29 (m, 14H) 7.26 ppm: 6.98 (s, 1H), 5.79 (m, 1H), 4.93 (d, 2H), 2.80 (t, 2H), 2.01 (m, 22H), 1.69 (m, 2H), 1.34 (m, 8H), 0.89 (t, 3H) ⁷8°C ³Synthesis of Poly(3-hexylthiophene-ran-3-undecenyli thiophene). This procedure for the McCullough method is based off of ref 23. In a dry scintillation vial, 1.66 eq. of 2-bromo-3-hexylthiophene and 1 eq. of 2-bromo-3-undecenyli thiophene were added and purged with N₂. The total amount of moles for this mixture was set as 1 eq. for the following polymerization. In a multi neck round-bottom flask, that was dried as previously reported, 11 eq. of dry THF were added. The reaction vessel was cooled to -78 °C. One eq. of disopropylamine (DIPA) was added to the cold reaction vessel. The solution was light yellow. The DIPA was never purged before addition to the reaction vessel, but it would not hurt to do that. Following the DIPA, 1 eq. of n-butyl lithium was added with a dry syringe. The reaction was stirred for 1 h at -78 °C. Then the thiophene mixture (1 equiv) was added to the reaction vessel droppwise over the course of 30 min and stirred for 1 h at -78 °C. The solution turned dark yellow. 1.3 eq. of dried zinc chloride dissolved in a minimal amount of dry THF was added dropwise to the reaction vessel over the course of 15 min and reacted at -78 °C for 1 h. The solution turned bright orange. The reaction vessel was warmed to room temperature and 0.009 eq. of Ni(dppp)Cl₂ was added to the reaction vessel. The solution turned red. As the reaction ran, the solution turned dark red, almost looking black. The reaction was run for 14 h at room temperature while covered in aluminum foil, and then precipitated into cooled methanol. The product was filtered and purified by Soxhlet extraction using methanol, hexanes, and chloroform. Each solvent was run for 8 h, while heating at 100 °C. The final product appears to be golden/purple flakes in the solid state. When dissolved, the polymer fluoresces bright yellow.¹H NMR (CDCl₃, 500 MHz) Reference 7.26 ppm: 6.98 (s, 1H), 5.79 (m, 1H), 4.93 (d, 2H), 2.80 (t, 2H), 2.01 (m, 22H), 1.69 (m, 2H), 1.34 (m, 8H), 0.89 (t, 3H) ⁷8°C ³Synthesis of Vinyl Monocapped P3HT. The synthesis for the vinyl capped P3HT is the same as the synthesis for poly(3-hexylthiophene-ran-3-undecenyli thiophene) with the substitution of 2-bromo-3-hexylthiophene as the sole monomer and has similar color changes. After Ni(dppp)Cl₂ was added to the reaction vessel, the reaction proceeded for 5 min before being placed in an ice bath for 10 min. The amount of vinyl magnesium chloride that was added was calculated from a 30:1 ratio to the moles of nickel catalyst. Vinyl magnesium chloride was added quickly to the reaction vessel by syringe, and then the entire solution was immediately poured into an ice bath for 10 min. The solution was a light orange/yellow color. One eq of diisopropylamine (DIPA) was added to the cold reaction vessel. The solution was light yellow. The DIPA was never purged before addition to the reaction vessel, but it would not hurt to do that. Following the DIPA, 1 eq. of n-butyl lithium was added with a dry syringe. The reaction was stirred for 1 h at -78 °C. Then the thiophene mixture (1 equiv) was added to the reaction vessel droppwise over the course of 30 min and stirred for 1 h at -78 °C. The solution turned dark yellow. 1.3 eq. of dried zinc chloride dissolved in a minimal amount of dry THF was added dropwise to the reaction vessel over the course of 15 min and reacted at -78 °C for 1 h. The solution turned bright orange. The reaction vessel was warmed to room temperature and 0.009 eq. of Ni(dppp)Cl₂ was added to the reaction vessel. The solution turned red. As the reaction ran, the solution turned dark red, almost looking black. The reaction was run for 14 h at room temperature while covered in aluminum foil, and then precipitated into cooled methanol. The product was filtered and purified by Soxhlet extraction using methanol, hexanes, and chloroform. Each solvent was run for 8 h, while heating at 100 °C. The final product appears to be golden/purple flakes in the solid state. When dissolved, the polymer fluoresces bright yellow.¹H NMR (CDCl₃, 500 MHz) Reference 7.26 ppm: 6.98 (s, 1H), 5.79 (m, 1H), 4.93 (d, 2H), 2.80 (t, 2H), 2.01 (m, 22H), 1.69 (m, 2H), 1.34 (m, 8H), 0.89 (t, 3H) ⁷8°C ³Synthesis of telechelic vinyl dicapped P3HT. The monocapped P3HT (1 equiv) was dried and placed in a scintillation vial with a septum and a small stir bar. It was moved into a glovebox where the reaction ran, the solution turned dark red. As the reaction ran, the solution turned dark red, almost looking black. The reaction was run for 14 h at room temperature while covered in aluminum foil, and then precipitated into cooled methanol. The product was filtered and purified by Soxhlet extraction using methanol, hexanes, and chloroform. Each solvent was run for 8 h, while heating at 100 °C. The final product appears to be golden/purple flakes in the solid state. When dissolved, the polymer fluoresces bright yellow.¹H NMR (CDCl₃, 500 MHz) Reference 7.26 ppm: 6.97 (s, 1H), 5.49 (d, 1H), 5.12 (d, 2H), 2.81 (t, 2H), 1.69 (m, 2H), 1.44 (m, 2H), 1.33 (d, 4H), 0.90 (t, 3H) ⁷8°C ³Synthesis of telechelic vinyl dicapped P3HT. The monocapped P3HT (1 equiv) was dried and placed in a scintillation vial with a septum and a small stir bar. It was moved into a glovebox where the reaction ran, the solution turned dark red. As the reaction ran, the solution turned dark red, almost looking black. The reaction was run for 14 h at room temperature while covered in aluminum foil, and then precipitated into cooled methanol. The product was filtered and purified by Soxhlet extraction using methanol, hexanes, and chloroform. Each solvent was run for 8 h, while heating at 100 °C. The final product appears to be golden/purple flakes in the solid state. When dissolved, the polymer fluoresces bright yellow.¹H NMR (CDCl₃, 500 MHz) Reference 7.26 ppm: 6.97 (s, 1H), 5.49 (d, 1H), 5.12 (d, 2H), 2.81 (t, 2H), 1.69 (m, 2H), 1.44 (m, 2H), 1.33 (d, 4H), 0.90 (t, 3H) ⁷8°C ³
malleable. The solution was precipitated into methanol and purified in the same way as poly(3-hexylthiophene-ran-3-undecenythiophene). MALDI-TOF indicates the polymer is terminated by vinyl groups. 

$^1$H NMR (CDCl$_3$, 500 MHz) Reference 7.26 ppm: 6.98 (s, 1H), 6.44 (q, 1H), 6.14 (dd, 1H), 5.66 (dd, 1H), 2.81 (t, 2H), 1.71 (m, 2H), 1.43 (m, 2H), 1.34 (d, 4H), 0.91 (t, 3H).

Organic Field Effect Transistor Fabrication. Si/SiO$_2$ (200 nm) substrates were cleaned by sonication for 10 min in a series of solvents, which included acetone, ethanol, and isopropanol alcohol (IPA). IPA is the cleanest solvent and therefore should always be used last. The substrates were dried with a stream of N$_2$ and those being used for the glovebox. Five mg samples of functionalized poly(thiophene) were made and moved to the glovebox. Solutions of 5 mg/mL of functionalized poly(thiophene) was made with dry, glovebox quality water. These solutions stirred at 55°C overnight, covered in aluminum foil. The solutions were spun onto the substrates through a 0.45 µm PTFE syringe filter at 1000 rpm for 60 s. The substrates were annealed and then graphed as described above. Then the substrates were exposed to chloroform and then dried for 5 min at 150°C. A source drain were thermally evaporated through a shadow mask (W/L = 16). The devices were measured in ambient environment outside the glovebox.

**ASSOCIATED CONTENT**

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b08667.

$^1$H NMR spectra, MALDI-TOF mass spectra, XPS spectra (DOCX)

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**Author Contributions**

This manuscript was written through contributions of all authors. All authors have given approval of the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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