7-12-2016

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Recommended Citation

Youm, S., Hwang, E., Chavez, C., Li, X., Chatterjee, S., Lusker, K., Lu, L., Strzalka, J., Ankner, J., Losovyj, Y., Garno, J., & Nesterov, E. (2016). Polythiophene thin films by surface-initiated polymerization: Mechanistic and structural studies. *Chemistry of Materials*, 28 (13), 4787-4804. <https://doi.org/10.1021/acs.chemmater.6b01957>

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Polythiophene Thin Films by Surface-Initiated Polymerization: Mechanistic and Structural Studies

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ABSTRACT. The ability to control nanoscale morphology and molecular organization in organic semiconducting polymer thin films is an important prerequisite for enhancing the efficiency of organic thin-film devices including organic light-emitting and photovoltaic devices. The current “top-down” paradigm for making such devices is based on utilizing solution-based processing (e.g. spin-casting) of soluble semiconducting polymers. This approach typically provides only modest control over nanoscale molecular organization and polymer chain alignment. A promising alternative to using solutions of pre-synthesized semiconducting polymers pursues instead a “bottom-up” approach to prepare surface-grafted semiconducting polymer thin films by surface-initiated polymerization of small-molecule

monomers. Herein, we describe development of an efficient method to prepare polythiophene thin films utilizing surface-initiated Kumada catalyst transfer polymerization. In this study, we provided evidence that the surface-initiated polymerization occurs by the highly robust controlled (quasi-“living”) chain-growth mechanism. Further optimization of this method enabled reliable preparation of polythiophene thin films with thickness up to 100 nm. Extensive structural studies of the resulting thin films using X-ray and neutron scattering methods as well as ultraviolet photoemission spectroscopy revealed detailed information on molecular organization and the bulk morphology of the films, and enabled further optimization of the polymerization protocol. One of the remarkable findings was that surface-initiated polymerization delivers polymer thin films showing complex molecular organization, where polythiophene chains assemble into lateral crystalline domains of about 3.2 nm size, with individual polymer chains folded to form in-plane aligned and densely packed oligomeric segments (7-8 thiophene units per each segment) within each domain. Achieving such a complex mesoscale organization is virtually impossible with traditional methods relying on solution processing of pre-synthesized polymers. Another significant advantage of surface-confined polymer thin films is their remarkable stability towards organic solvents and other processing conditions. In addition to controlled bulk morphology, uniform molecular organization and stability, unique feature of the surface-initiated polymerization is that it can be used for the preparation of large-area uniformly nanopatterned polymer thin films. This was demonstrated using combination of particle lithography and surface-initiated polymerization. In general, surface-initiated polymerization is not limited to polythiophene, but can be also expanded towards other classes of semiconducting polymers and copolymers.

Introduction

One of the persistent challenges in designing reliable electronic and optoelectronic devices based on thin films of semiconducting polymers remains the ability to effectively control mesoscale organization and molecular structure of the polymers in the bulk of the films. This control is important

for improving device performance, for example, in enhancing the efficiency of organic polymer solar cells where low carrier mobility due to less than optimal convoluted charge transfer pathways in thin films represents one of the essential bottlenecks to achieving high light to current conversion efficiencies.¹⁻⁶ Similarly, controlling molecular organization in thin films of fluorescent and electroluminescent semiconducting polymers can improve the performance of polymer-based light-emitting and chemosensing devices.⁷⁻¹¹ Currently, almost all successful approaches to prepare thin-film semiconducting polymer devices utilize solution-based processing of soluble polymers, e.g. spin casting. In such processing schemes, some control over molecular organization and phase separation can be achieved indirectly, through the variation of experimental fabrication conditions, post-deposition thermal annealing, using low molecular weight additives, etc. These traditional approaches, however, offer limited options to precisely control over nanoscale molecular organization and alignment of semiconducting polymers in thin layers. Some improvement in controlling the organization and alignment in thin films can be achieved by utilizing the tools of supramolecular chemistry, but this approach is also limited. A viable alternative to using solutions of pre-synthesized semiconducting polymers employs a “grafting from” approach to prepare surface-attached polymer thin films using surface-confined (also often called surface-initiated) polymerization of monomers.¹² This approach allows *in situ* preparation of continuous as well as nanopatterned semiconducting polymer thin films and devices based on them directly from small-molecule monomers. In such a case, the monomers are not required to be functionalized with bulky solubilizing substituents, and this approach affords greater control over mesoscale organization in the films. In addition to better controlled mesoscale organization and molecular composition, the polymer films produced by surface-initiated polymerization benefit from greater mechanical, thermal, and chemical stability, relative to traditional spin-cast thin films. With all of these potential advantages, and despite some recent increase in interest in this area,¹³⁻²² surface-confined *in situ* preparation of semiconducting polymer films remains largely unexplored, still lacking both efficient practical methods and fundamental knowledge of essential details of the

polymerization process as well as detailed information on the structure of the resulting thin films. In this study, we attempted to fill this gap by carrying out an extensive development and optimization of the surface-initiated polymerization process, gaining better understanding of the polymerization mechanism, as well as detailed investigation of the structure and morphology of the produced surface-attached thin films.

Among various classes of semiconducting polymers, polythiophene (PT) and its various derivatives are among the most important organic electronic materials.^{23, 24} These polymers show substantial charge transport efficiency, as well as good thermal stability and photostability. In addition, PT properties can be readily modified through chemical functionalization, and there are numerous synthetic approaches to preparation of polythiophenes and their analogs. One of the most commonly used PT representatives is regioregular poly(3-hexylthiophene) (P3HT).^{25, 26} This solution-processable polymer forms thin films which display good charge mobility and are relatively stable to thermal and photodegradation. Not surprisingly, extensive research efforts have been directed towards improving the molecular organization of P3HT in thin films with the goal of enhancing charge mobility and increasing the efficiency of the resulting devices.²⁷⁻³³ While the majority of these efforts have targeted controlling morphology and organization in thin films of the pre-synthesized polymer, fewer attempts have been made to achieve such control by *in situ* surface-initiated polymerization of a suitable monomer.²⁰⁻²² Such polymerization has a number of advantages, including the possibility to prepare densely packed films of unsubstituted PTs. Functionalizing the PT backbone with bulky solubilizing substituents is required for solution processing as an unsubstituted polymer would be completely insoluble. Whereas it has been shown that interdigitation of solubilizing side groups can improve molecular ordering in thin films, such bulky side groups also disrupt close interchain packing and reduce the molecular organization and co-planarity of the polymer chains in the film, especially if the synthetic chemistry used to prepare the polymer does not afford 100% regioregularity (as the percentage of “head to tail” coupling of thienyl repeating units).³⁴⁻³⁶ The solubilizing side groups may also reduce charge-

transport in polymer thin film materials by effectively “diluting” the π -conjugated backbone. In addition, the α -carbon of the alkyl side chains has been shown to act as a reactive site for initiation of photo- and thermal degradation of semiconducting polymers.³⁷⁻³⁸ Lacking these drawbacks, *in situ* prepared thin films of unsubstituted PT are expected to exhibit improved molecular organization as well as to show better stability than spin-cast films of alkyl-substituted pre-synthesized PTs. In addition to preparation of stable surface-confined polymer films, such polymerization can serve as a convenient method for surface modification with organic semiconducting polymers for optoelectronic, sensing, and biomedical devices.³⁹⁻⁴¹

Many earlier attempts at *in situ* preparation of PT thin films involved electrochemical polymerization.⁴² However, electrochemical method is limited by the availability of the monomers (as not every monomer can be efficiently electropolymerized), and the strong dependence of the properties of the final polymers on subtle variations of experimental conditions (and the related poor reproducibility of the results). In contrast to electrochemical polymerization, using transition metal-catalyzed chemical polymerization to form various derivatives of regioregular PTs is highly versatile. With the availability of various methodologies (of which the most prominent are McCullough’s Grignard metathesis polymerization^{43, 44} and Rieke’s organozinc derivatives coupling⁴⁵) and highly efficient catalytic systems, and with proper choice of protecting groups, chemical polymerization can be carried out with a wide variety of suitably functionalized monomers, and delivers highly reproducible results. With all of these advantages, chemical polymerization appears to be a method of choice for the “grafting from” preparation of surface-confined thin-layer PT films. Surprisingly, until a few years ago this was almost an unexplored area. The groundbreaking discovery simultaneously by McCullough^{46, 47} and Yokozawa^{48, 49} that Ni-catalyzed regiocontrolled Kumada polymerization of 5-bromo-2-thienylmagnesium monomers follows a quasi-“living” chain-growth mechanism, opened up the possibility of surface-confined chemical polymerization. Up to now, a few independent research groups, most notably that of Kiriy, have carried out surface-initiated *in situ* preparation of regioregular poly(3-

alkylthiophene) brushes through Kumada polymerization using surface-immobilized Ni(II) catalytic initiators.⁵⁰⁻⁵² This approach has produced mechanically stable surface-grafted PT thin films, however with an apparently low surface density, and a limited degree of polymerization, possibly due to instability and lower activity of the metal catalytic site and the dominance of side reactions.^{53, 54} Using Kiriya's methodology and a modified Ni catalyst to improve the "living" nature of the polymerization process, Locklin has demonstrated preparation of relatively thick (up to 42 nm) surface-attached poly(3-methylthiophene) films.⁵⁵ Nevertheless, all of the reported systems suffer from low activity and relative instability of the surface-immobilized Ni(II) catalyst, as well as from the complexity of the catalyst preparation; therefore, practical implementation of surface-initiated polymerization still remains a challenge.¹³⁻¹⁵ Even more importantly, very little is known about the molecular organization and bulk morphology of surface-confined PT thin films and the ways that can be used to control these parameters.

Scheme 1. Preparation of Ni(II) external catalytic initiator **1** and its use in preparing regioregular poly(3-alkylthiophene)s by controlled chain-growth Kumada catalyst transfer polymerization.

Recently, we have found that the reaction of aryl bromides or aryl iodides with Ni(0) complex Ni(dppp)_2 (where dppp is 1,3-bis(diphenylphosphino)propane) at moderate temperatures produces a stable Ni (II) complex **1** that can be used as a highly efficient catalytic initiator of Kumada catalyst transfer polymerization (KCTP)^{53, 56} of 5-bromo-2-thienylmagnesium monomers (Scheme 1).⁵⁷ The polymerization efficiently yields highly regioregular (regioregularity, as a fraction of head-to-tail (HT))

coupled 3-alkylthienyl units, is close to 100%) P3HT with the number average molecular weight (M_n) being linearly dependent on the monomer/catalyst **1** ratio. These and other experimental findings have pointed out on the controlled chain-growth mechanism of the polymerization initiated/catalyzed by **1**. In good agreement with this mechanism, each polymer chain was found to be terminated with the aryl group from catalyst **1** at one end, and (somewhat unexpectedly) predominantly with Br at the other end (Scheme 1). The experimental simplicity of preparation of the catalytic initiator **1** and the efficiency of the **1**-catalyzed KCTP prompted us to systematically investigate using this complex for the preparation of surface-attached PT thin films via surface-confined *in situ* polymerization. This paper describes our studies of preparation of the surface-immobilized catalyst, mechanistic details of the polymerization process, and structural characteristics and properties of the resulting surface-confined PT thin films, as well as the use of this method for the preparation of nanopatterned PT films through particle lithography.

Results and Discussion

Preparation and characterization of the surface-immobilized catalytic initiator. For the current study, we selected 2-(triethoxysilyl)-5-iodothiophene **2** as a precursor for the KCTP catalytic initiator (Figure 1). Reacting the triethoxysilyl group with activated inorganic oxide surfaces is a convenient method for the covalent surface immobilization of organic molecules.^{58, 59} Direct, without a flexible aliphatic spacer, attachment of the anchoring silyl group to the thiophene unit was chosen in order to provide a tighter connection between the surface-attached semiconducting polymer brush and the supporting substrate to facilitate charge transfer in the eventual thin-film devices. Furthermore, we expected the short surface linker to help reduce the possibility of a homocoupling (disproportionation) reaction between adjacent surface-immobilized Ni(II) initiator molecules – a catalyst-degradation process which had been previously demonstrated to efficiently occur with flexible long alkyl chain surface-attachment linkers.^{54, 60} First, we studied the solution reaction between the iodothiophenyl precursor **2** and Ni(dppp)₂. The reaction of **2** with 2 equivalents of Ni(dppp)₂ to form catalytic initiator **3** was

carried out in toluene at 45 °C, and monitored by ^{31}P NMR. We chose to use a two-fold excess of $\text{Ni}(\text{dppp})_2$ in order to accelerate conversion of **2** to the active catalytic initiator **3**. Indeed, from a practical standpoint, the presence of unreacted $\text{Ni}(\text{dppp})_2$ when it was taken in excess could not affect the surface immobilization of the catalytic initiator **3**, whereas the presence of unreacted iodothienyl precursor **2** (in case of its incomplete conversion to the catalytic initiator **3**) could undesirably result in incorporating unreactive **2** in the monolayer and therefore diminishing the surface density of catalytic initiator **3**. The main feature in tracking the reaction progress by ^{31}P NMR was a gradual intensity decrease of the singlet at 12.8 ppm corresponding to $\text{Ni}(\text{dppp})_2$. After 24 h reaction time, this signal intensity decreased to 50% of the initial intensity, whereas no new signals could be observed in the ^{31}P NMR spectrum of the reaction mixture, indicating complete conversion of the iodo precursor **2** to the $\text{Ni}(\text{II})$ catalytic initiator **3** (Figure 1, *Direct method*). The lack of observable ^{31}P NMR signals from the $\text{Ni}(\text{II})$ square-planar complex **3** in toluene was in agreement with our previous findings.⁵⁷ When toluene was removed *in vacuo*, and the residual product was redissolved in THF, formation of the square-planar $\text{Ni}(\text{II})$ catalytic initiator **3** was then clearly evidenced by the presence of a pair of broad doublets (at approximately 18.9 and -1.3 ppm) in the ^{31}P NMR spectrum (Figure S1 in the Supporting Information). The as prepared solutions of catalytic initiator **3** were found to be relatively stable with respect to thermal degradation (e.g. they could be stored at -30 °C for up to three months without losing catalytic activity). Therefore, a toluene solution of **3** can be prepared in advance, and used for surface immobilization when needed.

To prepare a surface-attached monolayer of the catalytic initiator, one can use either of two alternative procedures. In a more conventional approach (previously established by Kiriy,⁵⁰⁻⁵² Locklin,⁵⁵ et al.), a substrate with a surface-immobilized monolayer of an aryl halide precursor is converted to an active $\text{Ni}(\text{II})$ catalytic initiator via a suitable chemical reaction on the surface. In our case, this required reacting a substrate-immobilized monolayer of the iodothienyl precursor **2** with $\text{Ni}(\text{dppp})_2$ (Figure 1, *Indirect method*). Alternatively, considering the preparation simplicity and relative

stability in solution of the catalytic initiator **3**, it would be conceivable to prepare a monolayer of catalytic initiator by direct immobilization of **3** to a solid substrate (Figure 1, *Direct method*). Although both procedures are supposed to deliver the same surface-immobilized monolayer of catalytic initiator **3**, it could be possible that the lower efficiency and slow rate of the heterogeneous reaction between surface-bound iodothienyl precursor **2** and Ni(dppp)₂ could hinder the conversion of surface-immobilized iodothienyl precursor **2** to the active initiator **3**, and therefore might result in only partial conversion to **3** in the *Indirect method*. In this sense, *Direct method*, involving solution synthesis of **3**, looked more advantageous as it would offer complete surface coverage with catalytic initiator **3**. Since the latter approach has not been previously investigated, we decided to study both procedures in more detail, and compare their outcomes.

Figure 1. Two alternative methods for the preparation of surface-confined Ni(II) catalytic initiator of controlled chain-growth polymerization, and subsequent surface-initiated Kumada catalyst-transfer polymerization to yield surface-attached polythiophene thin films. In the *Indirect method* (on the left) the surface-immobilized Ni(II) catalytic initiator is prepared by a heterogeneous reaction between the monolayer of iodo-precursor **2** and Ni(dppp)₂. In contrast, the *Direct method* (on the right) relies on direct surface immobilization of the solution-prepared Ni(II) catalytic initiator **3**. The polymer chain alignment normal to the substrate surface is shown only for illustrative purpose, and does not reflect the actual morphology and mesoscale structure of the film.

For this study, the immobilized monolayers of the iodo-precursor **2** and Ni(II) catalytic initiator **3** were prepared on quartz substrates by immersing the freshly activated substrates in solutions of **2** and **3**, respectively, in toluene at 55 °C for 60 h. After monolayer deposition, the substrates were thoroughly rinsed with toluene, and the composition of the monolayers was analyzed using high-resolution X-ray photoelectron spectroscopy (XPS). We found it convenient to look at the iodine signal as it is characterized by two well-resolved peaks in the XPS spectrum, and the peak position is highly sensitive to the chemical state of iodine.^{61, 62} The monolayer of iodothienyl precursor **2** showed two signals at approximately 633 and 622 eV which can be attributed to the I 3d_{5/2} and I 3d_{3/2} peaks (Figure 2A). The monolayer of Ni(II) catalytic initiator **3** (prepared via *Direct method*) displayed similar iodine signals but shifted toward lower binding energies (at approximately 629 and 618 eV). Indeed, one would expect a lower binding energy for the I⁻ anion attached to the Ni(II) center in **3** relative to the iodine covalently connected to an aromatic carbon atom in **2** (similar lower binding energies were found for the ionic salts CsI and NaI⁶³). Within the XPS sensitivity, no signals for the iodothienyl precursor **2** were observed in this monolayer, therefore indicating completeness of the solution conversion of **2** to **3** (as was already evidenced by ³¹P NMR spectroscopy). For the *Indirect method*, chemical conversion of the monolayer of iodothienyl precursor **2** to the catalytic initiator **3** was monitored by XPS and showed that even prolonged (60 h) exposure of a monolayer of **2** to Ni(dppp)₂ solution at 55 °C resulted only in partial conversion to **3**, and approximately 70% of the surface-immobilized iodothienyl precursor **2** remained unreacted, as could be determined from integration of the deconvoluted XPS peaks characteristic of **2** and **3** (Figure 2A). The observed incomplete conversion was in line with the previous observations by Locklin,⁵⁴ and was likely related to steric effects in the densely packed monolayer. Therefore, the monolayer of catalytic initiator prepared by the *Indirect method* would be expected to have a lower surface density of Ni(II) catalytic molecules thus resulting in lower-density polymer films compared to the *Direct method*.

Figure 2. (A) High-resolution I 3d XPS spectra of monolayers of the surface-immobilized Ni(II) catalyst prepared by the *Direct method* (top violet trace) and by the *Indirect method* (middle red trace, deconvolution into two I 3d components is also shown), as well as of a monolayer of iodothiophene precursor **2** (bottom green trace). (B) High resolution Ni 2p XPS spectra for the surface-immobilized Ni(II) catalyst prepared by the *Direct method* (top violet trace) and by the *Indirect method* (bottom red trace). Shirley background (cyan traces) was applied to all spectra. Fitting parameters and deconvolution details are listed in Table S1 in the Supporting Information.

To better understand the chemical nature of the surface-immobilized catalytic initiator **3**, we also analyzed Ni 2p XPS peaks (Figure 2B). Although the structure of the signals in this region was relatively complex, they could be unambiguously attributed to Ni(II). Indeed, in the substrate prepared following the *Indirect method*, the center of gravity of the nickel main ($2p_{3/2}$) peak was found at a binding energy of 856.1 eV, with the second satellite peak positioned at 874.2 eV, which was consistent with values reported for divalent nickel in NiO and Ni(OH)₂.⁶⁴⁻⁶⁶ The first satellite peak at 861.4 eV and the $2p_{1/2}$ peak at 873.9 eV also appeared close to values previously reported for divalent nickel. Overall, the intensity of the XPS signals was significantly higher for the substrates prepared following the *Direct*

method compared to those prepared via *Indirect method*, which was consistent with substantially lower Ni(II) surface coverage in the latter case.

Figure 3. (A) Ferrocene functionalization of ITO surface immobilized Ni(II) catalytic initiator, and (B) cyclic voltammograms of the prepared ferrocene-coated substrates acquired in 0.1 M Bu_4NPF_6 in CH_2Cl_2 , with sweep rate 0.1 V s^{-1} . Dashed trace shows CV data for a substrate prepared following the *Indirect method*, and solid trace – CV data for a substrate prepared by the *Direct method*.

Since XPS experiments could only provide qualitative information on the surface composition, we attempted to quantify the initiator surface coverage, in order to compare with previous results as well as to establish the superiority of the *Direct method* in the preparation of the surface-immobilized polymerization catalyst. Surface coverage by catalytic initiator **3** was quantitatively estimated in electrochemical studies using the approach described by Locklin.⁵⁴ For this purpose, the monolayers of catalytic initiator **3** were prepared following either *Direct method* or *Indirect method* using semiconducting indium tin oxide (ITO) substrates. The substrates were then treated with an excess of the ferrocene-functionalized Grignard reagent **5** to convert active Ni(II) sites into electrochemically

active ferrocene sites (Figure 3A). With an assumption that such a transformation happened quantitatively (which is justified considering the large excess of Grignard reagent **5** relative to the surface-immobilized Ni(II) centers), one could determine ferrocene surface coverage from cyclic voltammetry (CV) studies of the ferrocene-functionalized substrates using the well-defined ferrocene redox wave (Figure 3B). From the CV experiments, we estimated active catalytic initiator **3** surface coverage in the substrates prepared via *Indirect method* as 0.57×10^{13} molecules cm^{-2} , whereas the coverage in the substrates prepared via *Direct method* was 2.42×10^{13} molecules cm^{-2} . These results showing approximately 4 times lower surface coverage in the substrates prepared via *Indirect method* were consistent with the results from XPS studies and showed that direct surface immobilization of the solution-prepared catalytic initiator **3** (*Direct method*) was a superior method to achieve high-density surface coverage by the catalytic initiator. The absolute value of the initiator **3** surface coverage on the ITO substrate was somewhat lower than the number previously reported by Locklin,⁵⁴ which might reflect differences in the measurement conditions or variations in ITO substrates, however we found our value of surface coverage to be quite reproducible and not to vary from sample to sample. Therefore, for the rest of this study we chose the *Direct method* as the procedure to prepare surface-immobilized catalytic initiator for surface-confined polymerization.

Development of surface-initiated polymerization protocol and properties of the resulting PT thin films. Although the surface-immobilized polythiophene thin films are generally intended for use in electronic devices (and therefore should be deposited on conducting surfaces such as indium tin oxide (ITO)), we performed most of our studies on quartz substrates, as this enabled simple monitoring of reaction progress by UV/vis absorption spectroscopy, and the lower surface roughness of quartz substrates would enable measurements of the structural features of polymer films without accounting for the large surface roughness of commercial ITO substrates. After rinsing with a copious amount of toluene, the quartz slides with surface-immobilized Ni(II) catalytic initiator were immersed in a solution of 5-bromothiophen-2-yl magnesium chloride monomer **4** at room temperature to start controlled chain-

growth polymerization yielding surface-attached polythiophene thin films (Figure 1). Monitoring of polymer film growth was performed using UV/vis absorption spectroscopy, and the uniformity of the film surface morphology was confirmed in AFM studies.

Figure 4. UV/vis absorption spectra of a PT thin film prepared by surface-initiated polymerization (red trace) and of a PT thin film prepared by electrochemical polymerization of bithiophene (black trace). Insert shows a photograph of the PT sample prepared by surface-initiated polymerization.

Carrying out polymerization for 6 h afforded a uniform PT film of approximately 20 nm thickness (determined by stylus profilometry). The UV/vis absorption spectrum of the PT film showed a vibronically structured broad band with a maximum at around 500 nm (Figure 4). The presence of pronounced vibronic features in the absorption spectra of conjugated polymer films typically indicates better molecular organization and the presence of a certain level of molecular uniformity in the polymer chains alignment.⁶⁷⁻⁶⁹ To highlight the advantage of our protocol, we also prepared a PT thin film using electrochemical polymerization of bithiophene on an ITO substrate. This approach is known to produce amorphous PT films with a low degree of molecular organization.^{70, 71} Indeed, the UV/vis absorption spectrum of the electropolymerized PT thin film exhibited an absorption band with no vibronic features (Figure 4). Another striking difference between the chemically polymerized surface-confined and electropolymerized PT films was the remarkable stability of the former in the presence of organic solvents. Indeed, ultrasonicated slides modified with surface-confined PT films placed in various

organic solvents (such as chloroform, toluene, etc.) for extended periods (up to 6 h) resulted in no noticeable film degradation or delamination. This behavior becomes even more striking when one compares chemically polymerized surface-confined PT films with their spin-cast analogues (e.g. spin-cast P3HT films) as the latter can be completely washed off by organic solvents (even without ultrasonication). This particularly high solvent stability of the surface-confined thin films would be highly advantageous for the preparation of complex multilayer architectures as the next polymer layer can be solution-deposited over the surface-confined film without any solvent-related damage to the underlying layer; this property also would make surface-confined polymerization particularly suitable for surface modification of inorganic electrodes with organic semiconducting polymers.

Figure 5. Morphology of a PT film prepared by surface-initiated polymerization on a quartz substrate viewed with contact mode AFM images. (A) Wide view topography ($6 \times 6 \mu\text{m}^2$); (B) a simultaneously acquired lateral force image; (C) close-up topography view ($2 \times 2 \mu\text{m}^2$); (D) corresponding lateral force image.

An AFM study revealed uniform coverage of the polythiophene thin films with low surface roughness (RMS roughness 1.4 nm). Representative AFM images are shown in Figure 5. The uniformity of the film surface was highly reproducible throughout the various samples prepared in this

study. The film surface consisted of a few large circular domains of approximately 65 nm in diameter surrounded by smaller (about 40 nm) circular-shaped domains. We observed formation of a similar surface domain morphology throughout all surface-confined PT samples, and therefore infer that circular domain formation is related to the structure and mesoscale organization of the surface-confined polymer in the bulk thin films. More detailed studies of the structure and morphology of the polymer films are discussed below.

Figure 6. (A) Cyclic voltammogram of the PT film prepared by surface-initiated polymerization for 6 h. Data were acquired in 0.1 M Bu₄NPF₆ in CH₂Cl₂, with sweep rate 0.1 V s⁻¹. (B) Spectroelectrochemical studies of the PT film in A. The potentials were referenced to Fc/Fc⁺ reference electrode.

Cyclic voltammetry (CV) data on the PT film prepared by surface-initiated polymerization on an ITO substrate is shown in Figure 6A. The surface-confined PT film was found to be

electrochemically stable and did not experience noticeable changes upon successive CV scanning. As expected for a covalently attached electroactive film, the peak current exhibited a linear dependence on the scan rate. The film showed a quasi-reversible anodic oxidation wave at $E_p^a \sim 0.6$ V (vs. Fc/Fc⁺ reference electrode), and a corresponding main cathodic wave at $E_p^c \sim -0.15$ V. These two waves were centered at $E_{1/2} \sim 0.38$ V – a value similar to that reported for electropolymerized PT films (~ 0.35 V vs. Fc/Fc⁺ reference electrode⁷²), however, two features in the CV data were quite unusual. First, unlike electropolymerized PT films which typically show broad redox peaks, surface-confined PT film displayed rather narrow and sharp peaks. This could be explained by a much more uniform distribution of conjugation lengths in the surface-confined film. Second, the electrochemical data displayed large hysteresis – a separation between forward anodic and backward cathodic peaks. Hysteresis is normally observed in crystalline electroactive films and reflects strong attractive interactions between the crystal-packed molecules which oppose counterion ingress into the bulk structure.⁷³ For electropolymerized PT films, hysteresis is normally not observed, in agreement with their amorphous nature. Further analysis of the CV curve in Figure 6A revealed that it looked quite similar to the CV data previously reported for thin films of thiophene oligomers (in particular, octamer and decamer) which also displayed significant hysteresis between sharp narrow anodic and cathodic waves.⁷⁴ As a preliminary conclusion, the electrochemical data of the surface-confined PT film were consistent with substantial crystallinity, with crystalline domains formed by packing polymer chain segments with 8 to 10 thienyl repeating units. Further structural evidence in favor of this hypothesis is provided later in this paper.

In spectroelectrochemical studies, absorption spectra of the surface-confined PT film were first obtained in the fully reduced (undoped) state of the polymer, and then were recorded as the potential was gradually stepped up toward oxidized (polaron and bipolaron) states (Figure 6B). In the electrochemically undoped, insulating state, the polymer film showed a vibronically structured π - π^* transition in the range of 350–650 nm, with the optical bandgap determined from the onset of absorption estimated at 2.0 eV. As the potential was stepped up, the π - π^* transition band of the neutral state was

observed to gradually decrease, and was replaced with a broad band centered around 750 nm corresponding to a polaronic transition, as well as with an intense bipolaronic band positioned in the near-IR region (maximum at around 1400 nm). Although the bandgap value and spectroelectrochemical behavior of the surface-confined PT film were consistent with those of typical conventionally prepared PT thin films,⁷² the surface-confined film did not show complete transition between neutral (undoped) and oxidized (polaronic/bipolaronic) states. Even at high positive potential, there was still a significant presence of the short-wavelength electronic band corresponding to the neutral state. This resistance of the surface-confined PT film to complete oxidation might again reflect its high crystallinity, and was consistent with the unusual features observed in the CV experiments (*vide supra*).

Experimental evidence of the controlled chain-growth mechanism of surface-initiated polymerization. Although AFM studies revealed the relatively uniform surface morphology of the PT thin films, the advantages of surface-initiated polymerization could be fully implemented only if it indeed followed the controlled chain-growth mechanism. Although we previously showed strong evidence for such a mechanism when **1**-initiated KCTP was carried out in homogeneous solution (Scheme 1), it was important to demonstrate that the robust controlled chain-growth mechanism remains operational in the case of heterogeneous surface-confined polymerization. This confirmation required monitoring both the rate of polymerization and the polymer structure and molecular weight distribution (polydispersity) in the surface-confined thin film. Due to complete insolubility of unsubstituted PT, we could not analyze structure, molecular weight, and polydispersity of the polymer upon its detachment from solid substrate, and thus could only rely upon studies of pristine films. A number of methods could be used for studies of organic thin films, however we specifically chose neutron scattering. Neutron scattering is an attractive tool for the structural characterization of soft organic materials due to the high neutron scattering cross section for light elements and the ability to tune contrast through isotopic labeling. Hydrogen and deuterium have differing scattering cross sections for neutrons so that site-selective deuteration can make some parts of the materials more visible than others without greatly

altering other physical properties. Neutron reflectometry (NR) is a particularly suitable tool to study organic thin films.⁷⁵⁻⁷⁹ The unique sensitivity of NR to the distribution of the deuterated material across the film could be used both to assess the kinetics of polymerization and the controlled (i.e. quasi-“living”) character of the polymerization mechanism.

Figure 7. (A) Preparation of a stratified deuterated PT thin film on a quartz substrate by carrying out polymerization in a solution of fully deuterated monomer **4-D₂** followed by polymerization in a non-deuterated monomer **4**. (B) Neutron reflectivity data for the resulting film (red circles) and the best fit to the data (blue solid line). (C) Scattering length density (SLD) profile based on the best-fit data presented in B shows the sharp interface between deuterated (PDT) and non-deuterated (PT) laterally stratified sublayers in the film.

To evaluate both features, we prepared a PT thin-film sample consisting of stratified sublayers of deuterated PT (polydeuteriothiophene, PDT) and “regular”, non-deuterated PT. To prepare such a

sample, we first immersed a quartz substrate with a surface-immobilized monolayer of catalytic initiator **3** in a solution of fully deuterated Grignard monomer **4** (i.e. **4-D₂**) and carried out surface-confined polymerization for 1 h. Then, in oxygen- and moisture-free conditions, we transferred the active substrate with an initially formed PDT film to a solution of non-deuterated Grignard monomer **4** and kept it there for 6 h to allow for the PT outer layer to form (Figure 7A). The film was then treated with methanol to quench the active Ni(II) catalytic sites, and dried in nitrogen.

The NR studies of the resulting partially deuterated thin film produced a reflectivity pattern which was modeled using a two-layer slab model fitting approach to achieve the best fit of the experimental data (Figure 7B). Fitting the reflectivity vs. wavevector transfer data to a model calculated from the scattering length density (SLD) profile delivered an accurate distribution of the deuterated monomer/polymer as a function of film depth (Figure 7C). In agreement with the controlled chain-growth (quasi-“living”) mechanism of surface-confined polymerization, the thin-film sample showed highly stratified distribution of the deuterated PDT and non-deuterated PT parts of the film. The PDT sublayer was clearly visible in the SLD profile due to the higher neutron scattering cross section of deuterium. The thickness of the PDT sublayer was about 6 nm (which corresponded to a growth rate of 6 nm h⁻¹), and it sharply transitioned to a non-deuterated PT sublayer of approximately 24 nm thickness. The almost constant SLD values within each constituent sublayer indicated uniform mass density of the polymer across the film thus revealing the persistence and high catalytic activity of reactive Ni(II) centers during polymerization. Even more important was the observation of a sharp interface between the deuterated PDT and non-deuterated PT sublayers. This indicated the robustness of controlled chain-growth polymerization in the surface-confined film as transferring the substrate from fully deuterated Grignard monomer **4-D₂** to non-deuterated monomer **4** kept the initially formed active polymer chains alive and able to continue further polymerization – an important characteristic feature of truly quasi-“living” polymerization. It also indicated that polymerization front generally propagated in the direction normal to the quartz substrate. Although limited sensitivity of NR experiments could not guarantee that

100% of surface-confined polymer chains followed quasi-“living” polymerization, it is obvious, that any severe deviation from the sharp interface between the deuterated and non-deuterated sublayers would have indicated that different individual surface-attached polymer chains had grown at different kinetic rates throughout the film, and that further growth of some chains had terminated prematurely by the time of substrate transfer (either due to degradation of the Ni(II) active sites or due to chain transfer to the monomer solution) – thus indicating a less robust, or even not quasi-“living” polymerization mechanism. Similarly diffuse interface would have resulted from random orientation (lack of uniform alignment) of growing polymer chains during surface-initiated polymerization. Therefore, within the sensitivity of NR experiments, our finding both of a sharp interface between sublayers, and a constant, non-changing SLD (and therefore constant polymer mass density) across each sublayer emphasized the controlled (quasi-“living”) chain-growth character of the surface-initiated polymerization, as well as uniform orientation of the polymer chains in the film.

Development of surface-initiated polymerization – catalyst regeneration strategy for the preparation of PT films with larger thickness. The controlled chain-growth mechanism of surface-initiated polymerization allows one to manipulate the thickness of the resulting PT films simply by varying polymerization time. We found that immersing a slide with surface-immobilized Ni(II) initiator in a 50 mM solution of 5-bromothiophen-2-yl magnesium chloride monomer **4** at room temperature for 6 h produced films with an approximately 20 nm thickness. Carrying out polymerization for 12 h afforded PT films with approximately 50 nm thickness. The roughly linear dependence of PT film thickness on the polymerization time reflected the quasi-“living” chain-growth character of the surface-confined polymerization. However, extending polymerization time for a period of longer than 12 h did not result in a further substantial increase in the film thickness, possibly due to eventual degradation of the active surface-bound Ni(II) catalytic sites. This degradation may involve Ni(II) center transfer to Grignard monomer **4** in solution (depicted as chain transfer degradation in Figure 8). Such an active center transfer would terminate further growth of a surface-immobilized polymer chain, and result in

starting a new polymer chain in solution. An alternative degradation pathway could involve disproportionation between two adjacent PT chains as also shown in Figure 8. The disproportionation pathway requires significant torsional bending of the surface-attached chains, and was shown by Locklin to be essential in the case of initiation with Ni(II) active catalyst attached to the surface via flexible alkyl linkages where such bending can be better accommodated.⁵⁴ The disproportionation releases the Ni(dppp)Br₂ catalytic species into solution, where it can initiate solution polymerization of a new PT chain. Although using rigid linkers in our case should diminish this pathway at early stages of surface-confined polymerization, it cannot be completely ruled out. Degradation of surface-bound Ni(II) catalytic initiator was supported by our observation of the formation of a noticeable amount of insoluble PT precipitate in solution upon extended polymerization times, although it would not be possible to determine which way (Ni(II) transfer to Grignard monomer, disproportionation, or both) this degradation has occurred.

Figure 8. Schematic illustration of active surface catalyst degradation through chain transfer and disproportionation, as well as regeneration of the active Ni(II) catalytic initiator for the preparation of thicker polythiophene (PT) films by surface-initiated polymerization. The PT chain alignment normal to the substrate is shown only for illustrative purpose and does not describe the actual complex morphology in the film.

In order to further improve the versatility of surface-confined *in situ* polymerization for preparation of PT films of greater than 50 nm thickness, we have developed a protocol involving intermediate regeneration of the Ni(II) active catalytic center during surface-initiated polymerization. Indeed, if we assume that premature termination of surface-initiated polymerization predominantly occurs by Ni(II) transfer to monomer **4** in solution (chain transfer degradation, as discussed above), this process should terminate the affected surface-attached PT chains with a Br end group from the monomer (Figure 8). In such a case, the Ni(II) active catalytic site could be regenerated by reaction of the surface-confined film with a fresh solution of Ni(dppp)₂ as used in the *Indirect method* (Figure 8). Obviously, such “reactivation” cannot happen at sites that underwent degradation through a disproportionation mechanism. This “reactivated” polymer thin film can be subsequently exposed to Grignard monomer **4** to continue the surface-initiated polymerization. Since such polymerization should mainly happen at the sites on the film surface formed due to the premature termination of polymerization, the overall process is expected to result in a more uniform surface (and bulk) morphology of the resulting PT film.⁸⁰ Based on results from the optimization experiments, we developed a general protocol to achieve the best quality (and high thickness) of PT films produced by surface-initiated *in situ* polymerization. The protocol includes initial surface immobilization of Ni(II) catalytic initiator **3** followed by controlled chain-growth polymerization combined with periodic regeneration of the Ni(II) active catalytic center (by immersing the intermediate polymer film in a solution of Ni(dppp)₂ at 40 °C for 20 h). This protocol allowed us to prepare uniform PT thin films with up to 100 nm thickness (Figure 9). A very important finding was that an increase in the film thickness (tracked by an increase of optical absorbance in the UV/vis spectra) was not accompanied by a hypsochromic shift of the absorption band or a loss of vibronic fine structure of the band, which indicated that initial molecular order and uniform chain orientation remained preserved even in the thicker films.

Figure 9. UV/vis absorption spectra of PT thin films prepared by surface-initiated polymerization on quartz substrates using intermediate regeneration of active surface catalytic initiator. Black trace corresponds to a PT film prepared by polymerization for 12 h without intermediate regeneration (film thickness ~ 30 nm), red trace corresponds to a PT film prepared by polymerization for 6 h followed by catalytic initiator regeneration (for 20 h), and with subsequent polymerization for another 6 h (film thickness ~ 50 nm). Blue trace corresponds to a PT film prepared with three intermediate regenerations (film thickness ~ 100 nm).

Studies of molecular organization and morphology in surface-confined PT thin films.

Although efforts to use surface-confined polymerization have resulted in substantial improvement of the efficiency of the polymerization as well as the surface density and thickness of the resulting thin films, little was known about bulk mesoscale structure and organization of the polymer in such films. In order to gain a deeper understanding of the possible anisotropic organization and chain alignment of polymer molecules in surface-confined thin films, as well as the influence of polymerization conditions on this organization, we carried out detailed structural investigation of the PT thin films using a variety of techniques. First, we carried out polarization-dependent ultraviolet photoemission spectroscopy (UPS) with linearly polarized light from a synchrotron source. In order to increase the probing depth, photons with increased energy (85 eV) were used in this study, which allowed probing the layer of about 3 nm deep from the film surface.

Figure 10. Polarization-dependent UPS studies of PT thin-film samples 1 and 2. (A) UPS data for sample 1 (from left to right): UPS spectra acquired at different light polarizations; angular-dependent UPS spectra collected for (s+p)-polarized incident light (beam energy 85 eV, the emission angle α was changed in 5° increments from 0 to 45°); and integrated intensity of the PT polymer valence band maximum (at ~7 eV binding energy) vs. emission angle α (the area was determined by integration of the valence band peak between Fermi level and 14 eV, with Shirley background subtraction). (B) Data with the same as in (A) experimental setup collected for sample 2.

For the UPS studies, two samples of PT thin films were prepared on semiconducting indium tin oxide (ITO) substrates. Sample 1 (approximately 20 nm thick based on the stylus profilometry measurements) was prepared using a 6 h polymerization time, and sample 2 (thickness approximately 40 nm) was polymerized for 72 h; in both cases, in order to simplify the data analysis, no surface Ni(II) catalytic initiator regeneration (as described above) was used. In the UPS experiments, the incidence angle of the synchrotron light was changed while the emission was collected normal to the surface (Figure S2A in the Supporting Information). In sample 1, the intensity enhancement of the PT valence band (maximum at ~7 eV) in the p-polarized light was indicative of anisotropic orientation of the polymer's transition dipole which coincides with the direction of the PT conjugated backbone (Figure

10A, left graph). Considering the high anisotropy of the stretched polymer molecule, the observed intensity enhancement in the p-polarized light revealed some degree of alignment of the surface-immobilized PT brushes. To determine the preferred orientation angle of the anisotropically aligned polymer chains, we studied the dependence of the intensity of the PT valence band on the emission angle α upon irradiation with (s+p)-polarized light (Figure S2B shows a schematic experimental setup, and central graph in Figure 10A shows actual experimental data). A plot of the intensity of the valence band maximum *vs.* α showed a broad maximum between 10° and 20° , and a peak at 30° (Figure 10A, right graph). Considering the significant contribution of the PT valence band orbitals into the averaged photoemission intensities (the photoemission direction coincides with the molecule's transition dipole), the presence of a signal between α 10° and 20° indicated that the film contained some fraction of the stretched PT chain segments with a tilt angle between 10° and 20° to the surface normal, i.e. very close to the upright orientation. However, presence of the additional peak at higher value of the angle α clearly indicated that a significant fraction of the PT chain segments was tilted further away from the upright position, closer to the in-plane orientation. The technical limitation of the UPS setup precluded us from looking at the values of the angle α above 45° , but one could not exclude possibility of the presence of even more tilted conjugated segments, especially considering overall large upward slope of the plot of photoemission intensity *vs.* α . It is important to keep in mind that the photon beam in UPS experiments could only probe relatively low depth near the film surface (about 3 nm), and thus contribution of the deeper layers positioned further away from the film surface to the observed signal would be much smaller. From the initial analysis of these UPS data, it appears that in the sample 1 thin film, some fraction of the PT chain segments showed close to upright orientation (in agreement with the strong signals at α 10 - 20°), but, at the same time, a large fraction of the chain segments was gradually bending and tilting away from the upright orientation.

In agreement with this structural picture, the thicker sample 2 (thickness approximately 40 nm by stylus profilometry) exhibited a smaller polarization dependence with the p-polarized light (Figure

10B). The signal at lower values of angle α (corresponding to the near-upright orientation of the polymer segments) was much weaker compared to sample 1; instead, an intense peak was found between 20 and 45°. As UPS data predominantly reflected the structure and composition of the near-surface layer of the film, it appears that a large fraction of the π -conjugated polymer segments near the surface of the thicker film were oriented along the direction at approximately 40° to the surface normal. Furthermore, considering high-angle limitation of the UPS experimental setup, it is possible that some polymer segments were oriented at even larger angles, closer to the in-plane alignment. Taking into account low probing depth of UPS, and comparing data for the samples 1 and 2, it appears likely that a relatively small fraction of the PT chain segments showed predominantly upright orientation, however, majority of the polymer chains experienced significant tilting and deviation from the upright orientation, with predominant orientation closer to in-plane direction. As UPS could not probe the entire cross-section of the films, it was impossible to determine if there was any uniformity in the alignment of surface-confined polymer chains (i.e. formation of crystalline domains) or the polymer chains in the bulk of the film were completely randomly oriented, forming a disordered amorphous film.

In the previous experiments on revealing quasi-“living” character of surface-confined polymerization using neutron reflectometry (NR) on selectively deuterated PT film, we concluded that those data supported both the general propagation of the growing polymer chains in the direction normal to the film surface, and uniformity of the resulting polymer chains alignment (*vide supra*). Thus, we decided to carry out additional NR measurements as it can deliver across-the-film profile and thus perfectly supplement UPS studies. A surface-confined PT thin film with an approximate thickness of 50 nm was prepared on a quartz substrate by polymerization of non-deuterated Grignard monomer **4** for 24 h without intermediate Ni(II) surface catalyst regeneration, and the neutron reflectivity data were acquired upon reflecting neutron beam from the polymer/air interface. Figure 11A shows the experimental neutron reflectivity curve along with the theoretical model curve which gave the best fit. The scattering length density (SLD) profile based on the fitting model is shown in Figure 11B.

Remarkably, we found that the film was characterized by constant scattering length density (SLD) of approximately $2.2 \times 10^{-6} \text{ \AA}^{-2}$ across almost the entire film thickness, spanning from quartz substrate to approximately 70% of the film thickness. The mass density of this high-density part of the film calculated from this SLD value was 1.35 g cm^{-3} , which was higher than the density reported for bulk PT prepared by chemical oxidation of thiophene (1.18 g cm^{-3}),⁸¹ but lower than the density obtained from single-crystal X-ray data of octhithiophene (1.58 g cm^{-3}).⁸² Since it is expected that mass density of “crystalline” polymer would always be lower than the density of the corresponding small-molecule crystal, one can safely assume that the bulk of the surface-confined PT film showed uniform morphology and was predominantly formed by closely packed PT chains forming crystalline domains with uniform alignment of the polymer chain segments within each individual domain. NR experiments could not provide information on predominant orientation of these crystalline domains; however, based on the results of the polarized UPS experiments, the polymer chains in the bulk of the film were apparently predominantly oriented along the direction with the tilt angle of at least 40° with respect to the surface normal. In contrast, the outermost layer of the film (approximately 15 nm thick) was characterized by SLD gradually decreasing towards the film surface, with a diffuse film-air interface. Lower SLD values reflected decreasing mass density in this part of the film, possibly due to the less tight packing of the PT domains and increasing amorphous character near the film surface.

Figure 11. Neutron reflectometry study of a 50 nm thick PT film prepared by surface-initiated polymerization on a quartz substrate. (A) Reflectivity data for the film (red circles) and best fit to the data (blue solid line). (B) Scattering length density (SLD) profile based on the best-fit data (single-layer model) presented in A shows two-sublayer stratification in the PT film.

Grazing incidence wide-angle and small-angle X-ray scattering (GIWAXS and GISAXS, respectively) are powerful techniques to study the structure and morphology of thin films of semiconducting polymers, and have been widely used in research of P3HT and related polymers and their blends for photovoltaic applications.⁸³ The GIWAXS data in Figure 12A were acquired using an approximately 40 nm thick PT film prepared on a quartz substrate by surface-initiated polymerization for 72 h without intermediate Ni(II) surface catalytic initiator regeneration (similar to PT sample 2 in the UPS studies, and the sample used in the NR studies described above). The sample showed three distinct arcs at $q_z = 1.41 \text{ \AA}^{-1}$ ($d = 4.47 \text{ \AA}$), $q_z = 1.61 \text{ \AA}^{-1}$ ($d = 3.90 \text{ \AA}$), and $q_z = 1.94 \text{ \AA}^{-1}$ ($d = 3.24 \text{ \AA}$) (Figure 12B). The intensity of the arcs maximized in the $q_y = 0$ plane which clearly indicated the anisotropic nature of the film. The observed GIWAXS pattern was very similar to the previously reported X-ray diffraction pattern of crystalline PT^{84, 85} as well as of unsubstituted thiophene

oligomers,⁸⁶⁻⁸⁹ and indicated a highly planar, predominantly extended conformation of the tightly packed surface-confined PT chains. In particular, the observed d -spacing pattern was almost identical to the pattern reported by Lahav et al. for β -polymorph of crystalline sexithiophene in Langmuir film (q_{xy} 1.38, 1.63, and 1.97 $\text{\AA}^{-1}$).⁸⁹ In Lahav's work, using Langmuir technique resulted in uniform alignment of the sexithiophene long molecular axes along the direction normal to the film surface. Similar upright alignment of PT chains in our case would produce Bragg diffraction rods extending along the q_z direction, however experimentally we observed diffraction arcs with a maximum in intensity near the q_z axis (i.e. with the maximum at $q_y = 0$). The only way to explain this observation was to suggest that the PT chains in the film were packed in the same way as in the β -phase of crystalline sexithiophene, but aligned predominantly parallel to the film surface with herringbone (face-to-edge) packing of the neighboring planarized PT chains within individual crystalline domains. The herringbone molecular packing of unsubstituted PT stays in stark contrast to 3-alkyl-substituted PTs where the alkyl substituents induce face-to-face π -stacking of the conjugated chains⁹⁰ but is rather common for unsubstituted oligomeric thiophenes.

The predominantly in-plane alignment of the PT chain segments in GIWAXS experiments was in agreement with the conclusions from UPS experiment. Whereas, due to technical limitations of the UPS experimental setup, we could not observe features originating from the in-plane polymer chain orientation (i.e. tilt angle about 90° to the surface normal), we did observe in those experiments significant deviation of the polymer chains from the out-of-plane (i.e. normal to surface) orientation, especially in the thicker sample similar to the one studied in the X-ray scattering experiments. Importantly, the broad intensity distribution along the diffraction arcs in GIWAXS experiments indicated that, despite some predominance of the in-plane orientation, the overall pattern was consistent with presence of a full spectrum of crystalline orientations, ranging from out-of-plane to in-plane. This distribution of orientations appeared the same throughout the thickness of the film, and did not change with the angle of incidence. We acquired GIWAXS data at various incidence angles (ranging from

0.16° to 0.22°, both below and above the critical angle for PT) which allowed tunable depth analysis across the film (Figure S3 in the Supporting Information). We found that incidence angle variation changed only total intensity of the diffraction profile, but produced no significant variation in the position and relative intensity of the individual diffraction peaks. Therefore, it was reasonable to conclude that the film showed relatively uniform mesostructure and polymer chain packing across almost the entirety of its thickness, in agreement with the constant density across the film revealed in the NR studies.

Figure 12. (A) Two-dimensional GIWAXS image of a 40 nm thick PT film prepared by surface-initiated polymerization on a quartz substrate. (B) Vertical linecut of the GIWAXS data of the film in A. (C) GISAXS horizontal line trace for the 40 nm thick PT film in (A) (red circles) and fitting these data using a modified Guinier-Porod model (blue trace). (D) Tapping-mode AFM images for the PT film in (A) (left image – topography, right image – phase), scale bars correspond to 100 nm.

Further information on the structure and morphology of the surface-confined PT film was obtained from GISAXS studies. The horizontal linecut showed a “Guinier knee”⁹¹ feature indicating formation of lateral nanoscale domains within the film (Figure 12C). Fitting the scattering data using a

combined Porod plus Guinier model (this model assumes that the Porod region extending from the larger-size domains overlaps with the Guinier region of the smaller-size domains,⁹² whereas the corresponding Guinier region corresponding to the large domains could not be observed due to the low q -range limitation of the GISAXS instrumental setup), allowed us to estimate the diameter of small-size lateral domains as approximately 3.2 nm. This value was much smaller than the average size of lateral surface features (40-60 nm) observed upon subsequent AFM studies carried out on the same film (Figure 12D). On the other hand, AFM provides information on size and morphology of the surface features of the film whereas the GISAXS study is characteristic of the average size of the well-defined high-density crystalline segments within the bulk of the film. Therefore, GISAXS data likely reflected the average size of individual lateral crystalline domains within the bulk of the film whereas AFM imaging showed surface features resulting from combination of these multiple crystalline domains into larger surface domains.

Combining together the experimental data and conclusions discussed in this section, we propose a working hypothesis on the structure of thin PT films prepared by surface-initiated polymerization. The polymerization occurs as a controlled chain-growth process, with overall propagation of the front of the growing polymer film in the direction normal to the surface, as was demonstrated using polymerization of the deuterium-labeled Grignard monomer discussed above. Although the requirement to accommodate multiple simultaneously growing surface-attached polymer chains might invoke the chain alignment in the direction normal to the surface (as, for example, schematically shown in Figures 1 and 8), the results of our experiments completely disagree with this conjecture. Instead, surface-confined polymer chains form densely packed crystalline domains with predominant chain orientation close to the in-plane direction, and in addition showing a continuum of different orientations ranging between in-plane and normal to the surface. Although, at first glance, it may appear impossible to combine both experimentally observed controlled quasi-“living” mechanism of surface-initiated polymerization, and the predominant in-plane alignment of the resulting polymer chains, they could be

accommodated if one assumes that the polymer chains start initial growing in the in-plane direction. Indeed, relatively low Ni(II) catalytic initiator surface density (with each molecule of surface-immobilized initiator **3** occupying an area of about 400 Å²) makes it unfavorable for the polymer chains to align in the normal, out-of-plane direction as they would not be able to achieve close interchain packing. Instead, the attractive van der Waals interactions between the surface-confined polymer chains promote chain tilting which allows to achieve close crystalline packing in the in-plane direction and form a high-density polymer film. However, the clusters cannot grow indefinitely in the initial in-plane direction as they will necessarily start interfering with other neighboring surface-growing clusters. Thus, all of the in-plane growing clusters on the surface can only be mutually accommodated if, at some point, the ensembles of polymer chains gradually twist, eventually forming folded loops allowing to continue the in-plane growth in the opposite direction, without interfering with neighboring growing clusters. The schematic structure of the surface-confined PT film according to this model is illustrated in Figure 13. As the result of in-plane growth and polymer chain folding, the polymer film is composed of laterally packed crystalline clusters with an average size of 3.2 nm (as was found in the GISAXS experiments) which protrude through the entire cross-section of the film. Each cluster is formed from a few folded polymer chains which show predominant in-plane “herringbone” (edge-to-face) packing of the chain segments between the folds. Indeed, considering the lateral size of such clusters at 3.2 nm, the average polymer segment between two folds must consist of about 7-8 thiophene repeating units. This explains why crystal structure of the polymer found in GIWAXS experiments strongly resembled that of β -phase of sexithiophene. Furthermore, such a structure would be consistent with the electrochemical data on the surface-confined PT film. Indeed, due to sufficient disruption of π -electron conjugation at the sites where an individual polymer chain twists and folds, folding of the polymer chain every 7-8 repeating units would create electronically isolated crystalline packed “oligothiophene” segments (7 or 8 thiophene units each) – which was actually observed in the cyclic voltammetry (CV) studies (where the CV data of PT film resembled that of thin-film thiophene octamer with a large

hysteresis, *vide supra*). The formation of folded packed structure also explains the broad range of other orientations found in GIWAXS data, as the wide range of orientations was produced by the out-of-plane fragments of the polymer chains within the folds.

Figure 13. Schematic illustration of the proposed PT thin film structure as based on the experimental evidence in this paper. Surface-confined PT chains bundle together to form folded in-plane packed crystalline domains about 3.2 nm in lateral size. The film consists of these primary domains protruding through the film thickness and densely packed side-by-side. The elements in the image are not up to scale.

The reason for the PT chain to pack in segments of 7-8 repeating units is not clear at this time. It can be simply related to solubility of oligothiophene in the polymerization solvent (THF) as, once the growing chain fragment reaches this critical length, its solubility becomes so low that it has to “crystallize” out of solution. More studies are required to definitely explain this. Overall, this structural model is consistent with controlled, quasi-“living” mechanism of the surface-initiated polymerization, and the relatively smooth surface morphology of the resulting thin films; this is also consistent with finding a sharp deuterated PDT – PT interface in the NR experiments with selectively deuterated films (*vide supra*). On the larger scale, the primary lateral clusters group in larger size circular domains (40-60 nm in size), which were the typical characteristic of the surface morphology found in AFM experiments (Figure 5 and 12D). Considering predominantly close to in-plane orientation of PT molecules in this model, the surface-initiated polymerization has to be highly robust and efficient. Indeed, routine preparation of a 40 nm thick PT film would require producing polymer chains in a

controlled chain-growth fashion with a degree of polymerization corresponding to a few thousand of thiophene repeating unit – a difficult to accomplish task even for a homogeneous solution polymerization. It may be possible, however, that carrying out externally initiated KCTP in surface-confined fashion somehow increases robustness and controlled character of the polymerization relative to solution polymerization. Clarifying this issue will certainly require additional studies.

Although this working model reasonably explains many of the experimental findings, it remains less certain if formation of the lower-density (and seemingly more amorphous) outermost layer found in the NR experiments happens during surface-initiated polymerization as a result of sufficient lengthening of polymer chains (so the increased entropic contribution can overcome attractive interchain interactions resulting in polymer folding), and thus would be dependent on the total film thickness, or it happens after completion of the polymerization, as a result of stabilizing polymer-solvent interactions. In the latter case, the surface-confined polymer film should always possess a lower-density outer sublayer, whereas in the former case one would expect that lower-thickness surface-confined polymer films would consist of only a single higher-density crystalline layer. Our preliminary GIWAXS and NR studies pointed on the formation of the outer lower-density layer even in thinner films, thus indicating the solvent-affected post-polymerization formation of the outer layer. Also, at this point the success of the strategy involving combination of surface-initiated polymerization with intermediate regeneration of the Ni(II) surface catalytic initiator in obtaining thicker PT films (*vide supra*) seems to point on this mechanism as well. It appears (at least from the UV/vis absorption spectroscopy data in Figure 9) that using a repeated “regeneration” approach can furnish thin films with up to 100 nm thickness which still preserve vibronic features typical for a highly organized polymer film. Additional studies are required to further refine the proposed bulk structural model, and to provide better understanding of the polymerization process and its relation to thin-film structure, as well as to determine other ways to improve control over surface morphology and molecular organization in surface-confined PT thin films.

Preparation of nanopatterned PT thin films by surface-initiated polymerization. A unique advantage of surface-initiated polymerization is that it allows preparation of nanopatterned surface-immobilized semiconducting polymer thin films. Preparation of uniformly nanopatterned polymer thin films is virtually impossible with current “top-down” paradigm relying on solution processing of pre-synthesized polymers. On the other hand, preparation of such nanopatterned thin films should be relatively straightforward using our surface-initiated *in situ* polymerization approach combined with an appropriate protocol to prepare nanopatterned monolayer of polymerization catalytic initiator **3**. In a proof-of-concept study, we selected particle lithography as a convenient method to prepare such a monolayer. Particle lithography⁹³ has previously been applied to pattern metals, inorganic materials, alkanethiol self-assembled monolayers (SAMs), organosilane films and polymers.⁹⁴⁻¹⁰⁰ Millions of nanostructures can be prepared on surfaces with relatively few defects and high reproducibility to enable patterning large surfaces with well-defined nanostructures.¹⁰¹⁻¹⁰³ Our approach is illustrated in Figure 14. First, a close-packed periodic hexagonal array of monodisperse latex mesoparticles (300 nm diameter) was prepared on the atomically flat Si(111) surface using solution-based assembly. The mesoparticle array served as a surface mask, and the uncovered areas on silicone surface were functionalized with octadecyltrichlorosilane (OTS) using PDMS stamping transfer followed by washing out the latex particles. An example of nanopores produced by particle lithography is shown in Figure S4 in the Supporting Information. Although the local roughness of mechanically polished silicon wafers prevented us from distinguishing the pore structures in AFM topography views, the simultaneously acquired lateral force images clearly resolved the circular shapes and hexagonal arrangement of the nanopores.

Figure 14. Schematic outline of the optimized approach to prepare hexagonally nanopatterned PT thin films via combination of particle lithography and surface-initiated *in situ* polymerization.

Figure 15. Arrays of PT nanocolumns on Si(111) produced by combination of particle lithography and surface-initiated *in situ* polymerization. (A) AFM topography image of the PT surface patterns. (B) Corresponding lateral force image. (C) Two-dimensional FFT spectrum generated from the topograph in A. (D) Zoom-in view ($3 \times 3 \mu\text{m}^2$) topograph. (E) Corresponding lateral force image for D. (F) Cursor plot for the line in D. (G) High-resolution topograph ($1 \times 1 \mu\text{m}^2$). (H) Lateral force image for G. (I) Height profile for the line in G.

Covalent immobilization of the Ni(II) catalytic initiator **3** in the uncovered with OTS areas produced nanopatterned catalytic surface which was used for surface-initiated polymerization of Grignard monomer **4** for 24 h total time to yield hexagonal arrays of PT nanopillars (Figure 15). The long-range order of the PT nanopillars (bright dots in Figure 15A) is shown with a representative $8 \times 8 \mu\text{m}^2$ topograph and lateral force image (Figure 15B). The regular arrays of PT nanostructures were evident throughout areas of the entire surface, indicating the high-throughput capabilities of particle lithography. The ability to produce large-area PT nanopatterns was also evident from the SEM images of this sample (Figure S5 in the Supporting Information). A plot acquired from two-dimensional fast Fourier transform (FFT) analysis of the $8 \times 8 \mu\text{m}^2$ AFM topography image displayed the reciprocal space and periodicity of the nanostructures (Figure 15C). The symmetric arrangement of the PT patterns can be viewed more clearly in the successive zoom-in views ($3 \times 3 \mu\text{m}^2$) of topography and simultaneously acquired lateral force images shown in Figures 15D and E, respectively. A line profile (Figure 15F) across ten PT nanostructures showed heights ranging from 16 to 38 nm. The center-to-center spacing between nanopatterns measured 289 ± 3 nm, closely matching the periodicity of the initial latex mesoparticle mask. To obtain perfect nanoscale geometries would require an absolutely flat surface at the atomic level and perfectly symmetric monodisperse latex spheres. In a real situation there are few surfaces that are atomically flat, and the variation in the sizes of latex spheres ranges from 1 to 5%. These small imperfections lead to different pore sizes, which produced the observed variations in height for the nanopillars. Due to the covalent immobilization on the Si surface, the nanopatterned films demonstrated unique stability towards organic solvents. Thus, prolonged ultrasonication of the patterned PT films in commonly used organic solvents such as chloroform and chlorobenzene did not result in any degradation of the nanostructures. This remarkable solvent stability would be particular suitable for further processing of the nanopatterned films, e.g. for spin-casting using solutions of other polymers to make more complex organic devices. This example demonstrated the principle capacity of the combination of particle lithography with efficient surface-initiated polymerization to produce large-

area periodically patterned stable PT nanostructures. Further studies on the possibility to control the size of the nanostructures in the surface-confined PT thin films are currently underway.

Conclusions

Controlled Kumada catalyst transfer polymerization occurring by the chain-growth mechanism became an established method for the synthesis of a wide variety of semiconducting polymers in solution. A possibility to carry out this reaction in heterogeneous fashion on surfaces could make it a valuable tool for the preparation of surface-confined semiconducting polymer films directly from small-molecule monomers. We developed and described a simple and efficient approach to the preparation of surface-immobilized monolayer of catalytic Ni(II) initiator, and demonstrated using it for efficient surface-initiated polymerization to form covalently attached PT thin films with thicknesses up to 100 nm. Our demonstration that this reaction occurs by controlled (quasi-“living”) chain-growth mechanism can, in principle, open venues toward controlled preparation of various copolymer and block copolymer thin films with precisely defined molecular composition. The surface-initiated polymerization is also not limited to polythiophenes but can be used to prepare surface-attached thin films of other important semiconducting polymers. We are currently studying using this method to prepare a broader variety of semiconducting polymer and block copolymer films. What makes the surface-confined polymerization truly unique is that it allows preparation of thin films with ordered morphology and uniform alignment of the polymer chains in the bulk of the crystalline polymer film – a property which may result in performance improvement of electronic and optoelectronic devices based on these films. Our extensive structural studies utilizing polarized UPS and X-ray and neutron scattering techniques revealed complex structure and organization of the surface-confined PT thin films; further experiments are still needed to gain better understanding of the film structure, as well as its dependence on various experimental factors. Finally, we demonstrated how the efficient surface-initiated polymerization, combined with nanoscale surface lithography, can be used in the preparation of large-area uniformly nanopatterned PT thin films.

Overall, this initial study will help in further development of surface-confined controlled chain-growth polymerization as a unique synthetic tool for engineering of new electronic and optoelectronic materials based on thin films of semiconducting polymers.

Supporting Information Available. Detailed synthetic and experimental procedures, and additional data and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

Acknowledgements. This research was supported by the U.S. Department of Energy under EPSCoR Grant No. DE-SC0012432 with additional support from the Louisiana Board of Regents. The initial experimental studies were supported by the National Science Foundation (grant DMR-1006336). C.A.C. was supported by the NSF Graduate Research Fellowship Program (DGE-127192). Access to XPS at Nanoscale Characterization Facility of Indiana University Nanoscience Center was provided by NSF award DMR MRI-1126394.

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