

Substituted Poly(*p*-phenylene) Thin Films via Surface-Initiated Kumada-Type Catalyst Transfer Polycondensation

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ABSTRACT: Conjugated polymer films of unsubstituted and alkoxy-substituted poly(*p*-phenylene) have been prepared via a Kumada-type catalyst-transfer polycondensation in a grafting-from configuration. A surface-bound external initiator was formed by reacting a Ni(0) complex with a thienyl bromide monolayer, and this surface-bound initiator was used to polymerize several Grignard monomers prepared from the corresponding 1,4-dihalobenzenes resulting in surface-bound, conjugated polymer chains with thickness up to 30 nm. A series of 1,4-diodo monomers with alkoxy side chains ranging from unsubstituted 1,4-diiodobenzene to 1,4-diiodo-2,5-dihexyloxybenzene were polymerized in order to explore the influence of steric bulk on the surface-initiated polymerization process. Within the series of molecules, it was observed that monomers with smaller, less bulky side chains were more easily polymerized from the surface, resulting in smooth, regular films for unsubstituted and methoxy-substituted polyphenylene. Islands of polymer growth were observed with the ethoxy-substituted material and only sparse, irregular growth for the hexyloxy-substituted polymer. The resulting films were characterized by AFM, infrared spectroscopy, ellipsometry, and UV-vis spectroscopy.

Introduction

Conjugated polymers are an important subject of current materials research due to their unique properties and applications in solar cells, polymer light-emitting devices, sensors, and printable circuitry.¹⁻³ Many of the most important applications for this class of material involve the use of a conjugated polymer in thin film device architectures, for either their optical or electronic properties. A distinct advantage of conjugated polymers is the ability to tune their electronic properties through synthetic design. However, synthetic design of conjugated polymers is inherently constrained by the need to confer processability, usually by adding bulky, aliphatic side chains to monomers. Modifying a monomer in this way generally has the effect of lowering the conductivity of the polymer, but use of monomers without such modifications generally leads to intractable polymers with poor solubility and low molecular weight. When solution processing is limited, few techniques for formation of conjugated polymer thin films exist.^{4,5} Among existing techniques, oxidative electropolymerization of an electron-rich monomer onto an electrode surface is the most common: however, this method is only applicable to conducting substrates and suffers from a lack of regiospecificity and morphological control. New routes to conjugated polymer films are highly desirable and can provide access to materials with electronic properties that are not possible with current synthetic methodologies due to the inherent insolubility that limits processability.

Furthermore, the emergence of nanotechnology has led to an interest in the synthesis of nanowires for interfacing species at the nanoscale such as enzymes, molecules, and nanoparticles with macroscale electrodes.⁶ Conjugated polymers are excellent candidates for these applications as long as appropriate methods for connecting the polymers to both the surface and the molecule or

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nanoscale object exist. Such methods, however, have not been forthcoming; few techniques have been developed for controllably forming processable conjugated polymers and even fewer for attaching them at a surface or to a molecular species.^{7–11} Among the techniques that have been reported, the Kumada-type catalyst-transfer chain growth polymerization of McCullough^{12,13} and Yokozawa^{14,15} shows considerable promise, having been used to prepare end-functionalized polymers, ^{16–19} polymers grown through surface-initiated polymerization, ^{20,21} and a variety of conjugated polymers and block copolymers in solution.²² A related technique, Suzuki-type chain growth polycondensation as first reported by Yokozawa et al.,²³ has also been used for the synthesis of several conjugated polymers and in the surface-initiated polymers and in the surface-initiated polymerization of a 9,9-dialkylfluorene monomer.²⁴

Kumada-type catalyst-transfer polycondensations depend on a unique intramolecular reaction that occurs within the catalytic cycle (Scheme 1). In a catalytic cycle similar to that in most metalmediated aryl-aryl coupling reactions, a Ni(0) species undergoes oxidative addition to a carbon-halogen bond to form an organometallic Ni(2+) complex. This complex then undergoes a transmetalation step with a source of nucleophilic carbon, which results in an organometallic species containing two aryl groups bound directly to the nickel center.^{25,26} This unstable intermediate, following a cis-trans isomerization, can reductively eliminate a Ni(0) species with any attendant ligands, forming an aryl-aryl C-C bond as a byproduct. A considerable body of indirect evidence suggests that the eliminated biaryl compound is initially coordinated to the Ni(0) center.^{27,28}

In most applications of Kumada coupling, this initial coordination is unimportant, as the product ring quickly dissociates from the nickel center or is displaced by more powerfully coordinating ligands. However, it has been established that coordination of the aromatic ring to the Ni center is the first irreversible step in oxidative addition of the catalyst to the Ar–X bond.²⁹ Therefore, if the ring is functionalized with an aryl halide

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group of its own, the Ni(0) species will oxidatively add to that Ar-X bond instead of being displaced, and the catalytic cycle will continue. For the polymerization of an X-Ar-MgCl monomer via the Kumada reaction, this intramolecular chain transfer mechanism can lead to a chain-growth polymerization and is a suitable strategy for surface-initiated polymerization if appropriate surface-bound initiators can be made.

In a recent report, we described a surface-initiated polymerization of poly(thiophene) and poly(*p*-phenylene) from a thienyl bromide monolayer on gold via SI-KCTP.²¹ We were interested in further developing this technique, using monomers with a variety of side chains in order to tune the properties of the films formed and exploring the use of different catalyst systems and initiators to achieve greater control of the system by reducing termination reactions. To this end, we attempted the polymerization of several 1,4-dihalo-2,5-dialkoxybenzene monomers using a Kumada-type catalyst-transfer polycondensation from a surface-bound nickel initiator. The preparation of this surfacebound initiator follows a strategy similar to reports of externally initiated polymerizations in solution by Luscombe et al. for nickel-based initiators.²³

Early attempts to prepare surface-grafted conjugated polymer films from 1,4-dihexyloxybenzene monomers in our laboratory only produced films with a nominal thickness of 1-2 nm after polymerization. We attempted several different surface-bound initiator metal/ligand combinations, which all gave similar results. After multiple trials, we speculated that the poor performance of this polymerization reaction from the surface might be due to the steric bulk of the hexyl side chain, attached *ortho* to the halomagnesium moiety on the monomer. To test this hypothesis, we synthesized aryl monomers substituted with smaller alkoxy side chains and found that they were readily polymerized from the initiator-functionalized surface to yield conjugated polymer films.

We believe that this technique enjoys considerable advantages over electrochemical methods for the formation of surface-bound conjugated polymers due to the more controlled nature of chaintransfer coupling polycondensation as opposed to electrochemical oxidation, the ability to form undoped polymers, and the applicability of the technique to the formation of polymer films on nonconducting substrates.

Experimental Section

Materials. 1,4-Diiodo-2,5-dialkoxybenzenes were synthesized according to literature procedures as described below.³¹ Isopropylmagnesium chloride solution (2.0 M in THF), bis-(cyclooctadiene)nickel(0), and periodic acid were obtained from Sigma-Aldrich. 2,5-Dibromothiophene, allyl bromide, ethyl bromide, hexyl bromide, 1,4-dimethoxybenzene, 1,4-diiodobenzene, hydroquinone, KOH, iodine, trichlorosilane, H₂PtCl₆, sulfuric acid, acetic acid, carbon tetrachloride, tetrahydrofuran (THF), toluene, dimethylformamide (DMF), dichloromethane, and glass slides were obtained from VWR. Toluene and THF were distilled from sodium ketyl and degassed by sparging with Ar before use. Quartz substrates were obtained from Technical Glass Products, Inc. (Painesville Township, OH). Unless indicated otherwise, materials were used as received. 1,4-Dibromo-2,5-dimethoxybenzene and 1,4-dibromo-2,5dihexyloxybenzene were synthesized from the corresponding 1,4-dialkoxybenzenes according to literature procedures.³²

Synthetic Methodology. All syntheses were carried out under an inert atmosphere of purified argon or nitrogen, using standard Schlenk techniques or a glovebox (Unilab BP with an MB10 purification system, MBraun, Inc.). NMR spectra were recorded using a Varian Mercury 300 NMR spectrometer working at 300 MHz. Chemical shifts are reported relative to an internal tetramethylsilane standard.

2-Allyl-5-bromothiophene. 2.0 g (0.93 mL, 8.3 mmol) of 2,5dibromothiophene was dissolved in 20 mL of THF and cooled in an ice bath. 5.0 mL (8.3 mmol) of freshly titrated 1.65 M isopropylmagnesium chloride solution in THF was added dropwise from a syringe, and the reaction was stirred 1 h. 0.9 mL (10.4 mmol) of allyl bromide was added dropwise from a syringe, and the reaction was stirred and allowed to come to room temperature overnight. The THF was removed in vacuo, and the resulting oil was extracted with 3×20 mL portions of hexane. The organic phase was washed three times with deionized water and once with brine, dried over anhydrous sodium sulfate, and the solvent removed in vacuo. The resulting yellow oil was purified by column chromatography (hexanes:silica) to yield 0.592 g (35%) of a clear oil. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.86 (d, 2H, J = 3.5 Hz), 6.56 (d, 2H, J = 3.7 Hz), 5.93 (m, 1H), 5.12 (m, 2H), 3.48 (d, 2H, J = 6.6 Hz).

3-(5-Bromothiophen-2-yl)propyltrichlorosilane. 0.59 g (8.3 mmol) of 2-allyl-5-bromothiophene was dissolved in 10 mL of freshly distilled dichloromethane under nitrogen, and 10 equiv (83 mmol, 3 mL) of trichlorosilane was added via syringe through a rubber septum. A match-head-sized portion of chloroplatinic acid hexahydrate was added, and the reaction was stirred overnight. After reaction, the vessel was fitted with a short-path distillation head, and the solvent and excess trichlorosilane were distilled off via heating to 70 °C. The product was subjected to vacuum at 0.5 Torr for 3 h, yielding a yellow oil which was used without further purification. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 6.87 (d, 2H, J = 3.6 Hz), 6.57 (d, 2H, J = 3.6 Hz), 2.86 (t, 2H, J = 7.4 Hz), 1.92 (m, 2H), 1.43 (m, 2H).

General Synthesis of 1.4-Diiodo-2.5-dialkoxybenzenes. 1.4-Diiodo-2,5-dimethoxybenzene (I2DMB), 1,4-diiodo-2,5-diethoxybenzene (I2DEB), and 1,4-diiodo-2,5-dihexyloxybenzene (I2DHB) were synthesized according to the following procedure: 6.63 g of hydroquinone (60.2 mmol) was dissolved in 50 mL of DMF, and 14 g of powdered KOH was added. The reaction was stirred for 1 h, and 180 mmol of alkyl bromide was added in one portion. The reaction was stirred overnight and quenched by pouring over ice. The product was collected by filtration, washed with 1 M NaOH solution and water, and recrystallized from ethanol to give white flakes. (Commercially available 1,4-dimethoxybenzene was used, so this step was not performed in the synthesis of 1,4-diiodo-2,5-dimethoxybenzene.) 36 mmol of 1,4-dialkoxybenzene was dissolved in 36 mL of carbon tetrachloride, and 180 mL of glacial acetic acid was added. 9.05 g of iodine (36 mmol) was added, followed by 6 mL of sulfuric acid and 18 mL of water. 4.04 g (18 mmol) of periodic acid was added in one portion, and the reaction was heated to gentle reflux overnight under nitrogen. The reaction was cooled and diluted with 200 mL of dichloromethane, and the organic layer was collected and washed 3 times with water, 1 time with saturated sodium bicarbonate solution, 2 times with saturated

sodium thiosulfate solution, and 1 time with brine. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The resulting yellow solid was recrystallized from chloroform/methanol. Yield: (I2DMB) 9.0 g, 60% for one step; (I2DEB) 8.5 g, 34% overall; (I2DHB) 7.2 g, 23% overall. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): (I2DHB) 7.17 (s, 2H), 3.93 (t, 4H, J = 6.5 Hz), 1.80 (p, 4H, J = 6.5 Hz), 1.50 (p, 4H, J = 7.4 Hz), 1.35 (m, 8H), 0.91 (t, 6H, 7.0 Hz). (I2DMB) 7.19 (s, 2H), 4.01 (q, 4H, J = 7.1 Hz), 1.43 (t, 6H, 7.0 Hz). (I2DMB) 7.19 (s, 2H), 3.82 (s, 6H).

Preparation of Initiator Wafers. Silicon wafers (Silicon Quest) and glass slides (VWR) were cut into 2 × 3 cm rectangles and subjected to plasma cleaning using argon plasma, using the "high" setting on a plasma cleaner (Harrick Plasma) for 3 min. The substrates were then treated for 15 min in a UV-ozone cleaner and transferred to a nitrogen-filled glovebox. 40 μ L of 3-(5-bromothiophen-2-yl)propyltrichlorosilane was dissolved in 10 mL of toluene, and the solution was poured over the substrates, which were capped and left for 12 h. The substrates were then removed from the solution, sonicated 1 min in toluene, rinsed 3 times with toluene, sonicated 1 min in isopropyl alcohol, rinsed with isopropyl alcohol, sonicated 1 min in chloroform, and rinsed several times with chloroform. The substrates were dried in a stream of nitrogen gas and transferred back inside a glovebox.

Magnesiation of 1,4-Dihalo-2,5-dialkoxybenzene Monomers. 1 mmol of monomer was dissolved in 10 mL of freshly distilled THF in a Schlenk flask under nitrogen, and 0.9 equiv of freshly titrated isopropylmagnesium chloride solution was added dropwise from a syringe at RT. For aryl iodide-based monomers, the reaction was stirred 1 h. For aryl bromides, the reaction was stirred 24 h as per Yokozawa et al.³² After the given reaction time, the Schlenk flask was sealed and transferred to a glovebox. For polymerizations in the presence of LiCl salt, 42 mg (1 equiv) of LiCl was added, and the monomer solution was stirred 10 min before addition of external initiator-functionalized substrates. The efficiency of magnesium-iodine exchange was verified by quenching a portion of Grignard monomer with dimethylchlorosilane. ¹H NMR of the product confirmed complete conversion of the 1,4-diiodo-2,5-dihexyloxybenzene monomer to 1-iodo-4-dimethylsilyl-2,5-dihexyloxybenzene. Alternatively, a commercial solution of isopropylmagnesium chloride lithium chloride complex (Aldrich, 1.3 M in THF) was also used for magnesiation,³² without a noticeable difference in the resulting films.

Formation of Surface-Bound External Initiator and Polymerization. A toluene solution 20 mmol in Ni(COD)₂ and 20 mmol in 1,2-bis(diphenylphosphino)ethane (dppe) was made up by dissolving 55 mg of Ni(COD)₂ and 80 mg of dppe in 10 mL of toluene inside a nitrogen-filled glovebox. Thienyl bromidefunctionalized slides were placed in a glass slide holder, and the bright yellow Ni complex solution was poured over them. The slides were allowed to react for 1 h, then the solution was removed, and the slides were washed three times with fresh toluene. The slides were immediately transferred to a solution of Grignard monomer to begin polymerization. Polymerizations were allowed to proceed overnight, after which time the substrates were removed, washed with acetone, water, acetone, and toluene, and then sonicated in chloroform to remove any physisorbed polymer. After rinsing with chloroform, the films were dried in a stream of nitrogen and characterized.

Thin Film Measurements. Null ellipsometry measurements of thin films were performed on a Multiskop (Optrel GbR) with a 632.8 nm HeNe laser light source at 70°, and film thicknesses were determined using integrated specific software. Film thickness was obtained by fitting ellipsometric data using manufacturer-provided specialized software. At least three spots on each wafer were measured, and the thickness was averaged. To obtain thickness values of the samples, a simple box model was employed and a refractive index of n = 1.5, k = 0 was used

for all polymer layers. AFM imaging was performed in tapping mode on a Multimode Nanoscope IIIa (Digital Instruments/ Veeco Metrology Group) using silicon AFM probes with a nominal spring constant of 40 N/m and a resonant frequency of 300 kHz. The scan rate used was 1 Hz. UV–vis spectra of polymer substrates were taken using a Cary 50 UV–vis spectrophotometer from Varian. Variable angle polarized light UV–vis was performed using a custom-built variable angle sample holder fitted with a rotatable polarizing filter. Infrared spectra of films were acquired using a Thermo-Nicolet Model 6700 spectrometer equipped with a variable angle grazing angle attenuated total reflection (GATR-ATR) accessory (vari-GATR, Harrick Scientific) and processed using OMNIC 8.0 software (ThermoNicolet, Madison, WI).

Results and Discussion

Preliminary experiments on the surface-initiated polymerization of Grignard monomers based on substituted 1,4-halobenzenes indicated that the thickness of the resulting films is strongly influenced by the size of the side chain. In order to systematically examine the effect of side chain bulk on surface-initiated Kumada catalyst transfer polymerization, we used a series of p-diiodobenzene monomers with alkoxy side chains of various lengths as well as the parent compound p-diiodobenzene. The substituted diiodobenzenes were prepared by standard electrophilic iodination of the corresponding *p*-dialkoxybenzene. Aryl iodide-based p-dialkoxy monomers were chosen for this project because of our initial finding that the Grignard monomer based on unsubstituted *p*-diiodobenzene reacted readily to form poly(*p*-phenylene) films with a related catalyst system.²¹ Magnesium-halogen exchange of one iodide substituent to form the Grignard monomer proceeds readily even in the presence of electron-donating alkoxy substituents on the ring. Although Yokozawa et al. report the successful chain-growth polymerization of the related aryl bromide monomer 1,4-dibromo-2,5-dihexyloxybenzene,³² we did not observe polymer growth on the surface with either this monomer or its less hindered relative 1,4-dibromo-2,5-dimethoxybenzene. It is not entirely clear why the aryl bromide monomers fail to form surface-bound polymer, but it may be due to the terminating chain-transfer reaction that can occur in the presence of unreacted isopropylmagnesium chloride. Another possibility is that oxidative addition of the Ni(0) species to the stronger C-Br bond is sufficiently slow that the catalyst reductively eliminates and transfers off the chain rather than performing a catalyst-transfer step.

Design and Synthesis of the Surface-Bound Initiator. The aryl bromide monolayer used to prepare the external initiator in this set of experiments was prepared using a simple two-step synthesis outlined in Scheme 2, consisting of magnesium-halogen exchange on the commercially available 2,5-dibromothiophene followed by alkylation of the aryl Grignard with allyl bromide. The alkylation step has an inherently low yield due to the sluggish activity of Grignard reagents in nucleophilic substitution. Ordinarily, a Cu catalyst is added to such reactions to catalyze alkylation,³³ but in this case this technique results in polymerization of the aryl bromide Grignard intermediate. Hydrosilylation of the alkene produced by the first step using H₂PtCl₆ as a catalyst yields a trichlorosilane bearing an alkyl chain terminated with the reactive thienyl bromide moiety. Formation of monolayers of this product by immersing activated silicon oxide surfaces in a toluene solution of the trichlorosilane results in a surface-bound species from which an external initiator for SI-KCTP can be prepared.

The Ni(0) catalyst solution most likely consists of a Ni(0) center complexed to a single dppe ligand and a single remaining COD ligand,³⁴ although an equilibrium certainly









exists between the different complexed forms of Ni(0) due to the rapid dissociation of ligands, including phosphines, from zerovalent nickel.³⁵ Luscombe et al.³⁶ report that the Ni- $(COD)_2$ + dppe catalyst system fails to react with chlorobenzene to produce an external initiator. We attribute the success of this catalyst system in our experiments to the superior reactivity of 2-bromothiophenes over chlorobenzene toward oxidative addition of the Ni(0) species. Although oxidative addition of Ni(0) to thienyl halides has not been thoroughly studied, it is known that Ni(PPh₃)₄ adds rapidly at room temperature to 2,5-dibromothiophene³⁷ and that a Ni(0) catalyst generated from Ni(COD)₂ and 4 equiv of PPh₃ adds quickly to 2-bromothiophene.²¹ Furthermore, oxidative addition of Ni(0) to aryl halides has been reported by Kochi et al.³⁵ to follow a Hammett correlation such that electron-withdrawing substituents accelerate the rate of reaction. 2-Bromothiophenes are known to react rapidly in reactions such as magnesium-halogen exchange³⁸ which are similarly assisted by electron-withdrawing groups, due in part to the heterocyclic sulfur atom acting as a π -acceptor. Finally, Luscombe et al.³⁶ report that although the Ni- $(COD)_2 + dppe$ system does not oxidatively add to chlorobenzene to produce an external initiator, it does react with the Grignard monomer 2-bromo-5-chloromagnesio-3hexylthiophene to form polymer, implying that this catalyst system is capable of oxidatively adding to 2-bromothiophenes even in the presence of a strong electron donor at the 5-position.

Formation of Polymer Films. We first tested the surfacebound catalyst system by using it to initiate SI-KCTP of 4-chloromagnesio-1-iodobenzene, a Grignard monomer which we have previously shown to react with a surfacebound catalyst prepared from Ni(COD)₂ + 4PPh₃ to form poly(*p*-phenylene) (PPh) films.²¹ The Grignard monomer is formed easily at room temperature on addition of iPrMgCl to *p*-diiodobenzene. Reaction of this monomer with the new

 Table 1. Polyphenylene Film Thicknesses As Determined by Ellipsometry^a

	film thickness (nm)	rms roughness (nm)	$\lambda_{\rm max}$ (nm)	absorbance
monolayer	36+01	0.9	()	
PPh	26.4 ± 0.1	7.9	371	0.4
PDMP	17.0 ± 0.1	3.1	307	0.08
PDEP	12 ± 1	6.0	347	0.04
PDHP	4.8 ± 0.1	2.4	347	0.01

^{*a*} Each value is the average of three or more measurements. The rms roughness was determined by analysis of corresponding AFM topography images. λ_{max} and absorbance values were obtained from UV-vis measurements of polymers grown on quartz.

surface-bound catalyst yielded a 30 nm thick polymer film, as measured by both ellipsometry and surface profiling with AFM. The film displayed the characteristic blue fluorescence of PPh. The new catalyst therefore appeared effective, and we performed polymerizations with a variety of substituted *p*-diiodobenzene monomers in order to investigate the effect of monomer substituents on the surface-initiated polymerization reaction (Scheme 3).

The morphology, thickness, and surface coverage of the polymer film produced by a SI-KCTP reaction depend strongly on the size of the alkoxy substitutent on the aryl monomer, as seen in ellipsometric thickness measurements and AFM micrographs of the resulting films in each case. The unsubstituted and methoxy-substituted monomers appear to add readily to the nickel-functionalized surface. Table 1 shows thickness measurements of the polymer films as determined by ellipsometry. We observed an average value of 26 nm for PPh, 14 nm for PDMP, 8 nm for PDEP, and 1 nm for PDHP, after subtracting the thickness of the monolayer. The surface-initiated polymerization technique applied to PPh in this work overcomes several inherent limitations of existing deposition techniques, directly forming thick PPh films on a nonconducting oxide surface. Article



Figure 1. UV-vis spectra of polymer thin films on quartz.

Spectroscopic and AFM Analysis of Polymer Films. UV-vis spectroscopy of the polymer films (Figure 1) grown on quartz substrates correlates well with the observed thickness of the films grown on silicon as measured by ellipsometry and AFM. The absorbance intensity of the lowestenergy $\lambda_{\rm max}$ follows the trend $A_{\rm PPh} \gg A_{\rm PDMP} > A_{\rm PDEP} \gg$ A_{PDHP} and is shown in Table 1 for films prepared under identical conditions. The PPh film has an absorbance at 371 nm, which is a good match for previous literature reports of the UV-vis spectrum for thin films of this polymer.^{39,40} The appearance of fine structure (shoulder at 425 nm) indicates crystalline structure in the film. The absorption onset at 440 nm (2.82 eV) is also slightly lower than that observed in other cases. $^{41-44}$ The positions of the observed absorptions for the poly(alkoxy)phenylenes are consistent with the known electronic structure of the polymers, which are high-band-gap semiconductors.45 PDEP and PDHP have similar lowestenergy absorption maxima at 347 nm, which is consistent with that reported for PDEP⁴⁶ but lower than that reported for PDHP (373 nm).⁴⁵ The reason for this is probably the very low degree of polymerization that occurs for PDHP using this surface-initiated technique, as evidenced by the low film thickness (2.4 nm) of PDHP. For films of PDMP, a low-energy absorbance maximum of $\lambda = 307$ nm is observed. Electropolymerized PDMP has previously been prepared by Lamy et al.⁴⁷ on a Pt electrode and characterized in situ through spectroelectrochemical techniques. These electropolymerized films show a strong absorption ca. 435 nm, which we do not observe with PDMP films grown by SI-KCTP. The difference in film properties of PDMP may lie with the ability to form PDMP in an entirely undoped form using SI-KCTP, without recourse to the use of Lewis acids or electrochemical oxidative polymerization.

Figures 2 and 3 show the infrared spectrum of unsubstituted and alkoxy-substituted PPh films grown on SiO₂ substrates as measured by GATR-FTIR at a grazing angle of 63°. Unsubstituted PPh (Figure 2) has a C=C asymmetric ring mode at 1480 cm⁻¹, an in-plane C-H bend at 1001 cm⁻¹, and a very strong and distinctive C-H out-of-plane bend at 810 cm⁻¹. An intense, broad absorption at 900 cm⁻¹, and a broad absorption centered at 1100 with a shoulder at 1250 cm⁻¹, are due to the underlying silicon oxide surface. Analysis of the C-H out-of-plane bending region allows for an estimate of the degree of polymerization of the PPh film, based on the ratio *R* of the intensity of the C-H *p*-substituted



Figure 2. GATR-FTIR spectrum of PPh film, with arrows indicating the location of bands corresponding to out-of-plane bending of the main chain and end group.



Figure 3. FTIR spectra of alkoxy-substituted polymer films and monolayer. From top to bottom: PDMP, PDEP, PDHP, and initiator monolayer.

out-of-plane bending peak to the intensity of the lowerfrequency out-of-plane bending modes for the monosubstituted end group.⁴³ The peaks are indicated in Figure 2 by arrows. The DP is then given by DP = 2R + 2. *R* in this case is ~34, giving a DP of 68. Molecular modeling shows that the length of one repeat unit of PPh is ~3.6 Å, which for an extended conformation of the polymer gives a chain length of ~24 nm. This value is a reasonable match for the 26 nm polymer film as measured by ellipsometry (Table 1).

Figure 3 shows the GATR-FTIR spectra of each alkoxysubstituted phenylene used in this study. The spectra are not baseline corrected, as the intensity of each absorbance corresponds directly to the film thickness. The C–H stretching region is magnified $3\times$. The FTIR spectrum of the monolayer is also shown in Figure 3 in order to ascertain the absorbances due to the underlying silicon oxide layer. Broad absorptions at 900 and 800 cm⁻¹, as well as a broad absorption centered at 1100 with a shoulder at 1250 cm⁻¹, are due to the underlying silicon oxide surface. Visible in the C–H region of PDMP is a strong peak at 2995 cm⁻¹ corresponding to an aromatic C–H mode and distinguishable from the alkyl C–H stretching bands at 2955 and 2930 cm⁻¹. Relatively low-frequency C–H vibrations at 2853 and 2831 cm⁻¹ are also distinct from other alkyl vibrations and are attributed to asymmetric C–H modes in the aryl methyl ether. Similar peaks are visible in the C–H region in PDEP. A shoulder is seen near 2995 cm⁻¹ likely due to aromatic C–H stretching, and the peak at 2970 cm⁻¹ is due to a methyl C–H stretching mode. Lower-frequency symmetric and asymmetric methylene vibrations are found at 2927 and 2870 cm⁻¹. Four C=C aromatic ring stretching bands are visible at 1496, 1467, 1444, and 1401 cm⁻¹ in PDMP and 1497, 1475, 1443, and 1397 cm⁻¹ in PDMP and at 1215 cm⁻¹ in PDEP and is barely visible in PDHP as a



Figure 4. AFM topography image $(1 \times 1 \mu m)$ of a 30 nm PPh film.

shoulder at 1215 cm^{-1} . This mode is the only vibration with a sufficiently intense signature to be distinguished from the monolayer in the inefficiently grafted PDHP layer. Around 1060 cm^{-1} in both PDMP and PDEP are several sharp peaks consistent with alkyl C–O stretching modes in aryl ethers. A sharp peak at 805 cm^{-1} in both PDMP and a shoulder at the same frequency in PDEP is attributed to the aromatic C–H out-of-plane bend.

We have investigated the morphology and thickness of the conjugated polymer films formed via SI-KCTP using AFM. The PPh film has a regular but somewhat globular morphology, similar to that observed in PPh and polythiophene films grown from metal substrates using thiol-based aryl bromide initiators.²¹ This globular morphology is uniform over large areas and appears typical of unsubstituted conjugated polymers prepared via SI-KCTP. The rms roughness of the PPh film is 7.9 nm, and the film does not show the ultrasmooth morphology which is indicative of fully stretched polymer chains with high initiation efficiency.

The methoxy-substituted monomer also reacts readily with the surface-bound catalyst, producing a thick polymer film with a remarkably smooth, regular morphology. (Figures 5 and 6, Table 1). The rms roughness of the resulting PDMP film is 3.1 nm. The ethoxy-substituted monomer reacts with the surface-bound catalyst less effectively, producing an unusual surface morphology visible via AFM consisting of isolated islands of complete surface coverage resembling that seen in the methoxy derivative (Figures 5 and 6). Between these areas are regions of lower coverage, containing isolated polymer features 20–30 nm in height. The hexyl-substituted monomer adds even less efficiently, producing only sparsely distributed 20 nm islands of polymer



Figure 5. AFM topography images $(1 \times 1 \,\mu\text{m})$ of thin films of PDMP (left), PDEB (center), and PDHB (right).



Figure 6. Large area topography scan ($5 \times 5 \mu m$) of PDMP film formed in the presence of LiCl salt (left) and without LiCl (right). The film made with added LiCl is substantially smoother and more regular than the film without the additive.

(Figure 5, right), which are nearly undetectable by FTIR and absorb only weakly in the UV.

Effect of LiCl and Halide Type on SI-KCTP Preparation of Polyphenylene Films. In the case of poly(p-alkoxy)phenylenes synthesized in solution using a Ni(2+) catalyst, Yokozawa et al. have found that the addition of lithium chloride to the reaction mixture before magnesium-halogen exchange is beneficial in the synthesis of PDHP from 1,4-dibromo-2,5-dihexyloxybenzene, producing a polymer with higher molecular weight and lower polydispersity.² Lanni and McNeil, on the other hand, have shown that under their reaction conditions the polymerization of this monomer is essentially unaffected by the presence of LiCl.48 The discrepancy between these two reports is attributed to a difference in the initiators used in the two experiments; in the Yokozawa report, a suspension of Ni(dppe)Cl₂ was added directly to the Grignard monomer, while Lanni and McNeil added 5-7 equiv of Grignard monomer to the catalyst solution before beginning the main polymerization. It was suggested that the difference is due to the effect of LiCl on the reaction of the Grignard monomer with Ni(dppe)Cl2.48 Because of the difference in these results, we were interested in determining the effect of LiCl on the surface-initiated polymerization of polyphenylenes.

We investigated the effect of LiCl on the formation of PDMP films by adding LiCl at various points in the experiment. The Grignard monomer solutions were formed three ways: (1) by reacting the diiodobenzene species with commercially available iPrMgCl-LiCl solution, (2) adding LiCl to a solution of Grignard monomer prepared from the corresponding diiodobenzene and iPrMgCl, and (3) Grignard monomer prepared from the diiodobenzene and iPrMgCl without any added LiCl salt. We have found no significant effect of LiCl on the average thickness of the resulting polymer films, obtaining a value of ca. 20 nm from ellipsometry in all cases. However, the film produced from monomer without added LiCl had a considerably rougher surface morphology, with a rms roughness of 7.4 nm compared to 3.1 nm for the film made from monomer with added LiCl (Figure 6). This result is consistent with Yokozawa's report of improved polydispersity on adding LiCl in the solution polymerization of the hexyl-substituted aryl bromide monomer with Ni(dppe)Cl2.32 Lanni and McNeil suggest that the improvement is due to enhanced reactivity of the monomer with the catalyst, demonstrating that the effect disappears when the polymerization is preinitiated with a few equivalents of Grignard monomer.⁴⁸ Our results are reasonable in light of these findings. To initiate surfacedirected polymerization, the Grignard monomer must react with the surface-bound catalyst. Surface-based initiation appears to be a more sterically demanding process than initiation by catalyst in solution based on the dramatic effect of side chain bulk that we observe in this series of experiments. It is well-known that LiCl has the effect of breaking up aggregated Grignard species in solution, thus increasing their reactivity;49 this effect could be responsible for the smoother film formed in the presence of LiCl. The more reactive Grignard monomer may add more readily to the surface, resulting in more uniform initiation and lower polydispersity of the surface-bound polymer chains.

We observed no polymer growth when aryl bromide-based monomers were used regardless of whether LiCl was added, possibly due to chain transfer induced by unreacted isopropylmagnesium chloride. Yokozawa et al. report an 89% yield for the polymerization of the aryl bromide Grignard monomer based on 1,4-dibromo-2,5-dihexyloxybenzene, suggesting that small amounts of magnesiating agent may remain unreacted in solution. In the case of the aryl iodide monomers used in this study, a slight excess of aryl diiodide was added to ensure that no isopropylmagnesium chloride would remain during the polymerization. The presence of excess aryl halide has been shown to have little or no effect on the catalyst-transfer step in Kumada coupling reactions.⁵⁰ It is also possible that slow oxidative addition of the nickel catalyst to the stronger C–Br bond in the aryl bromidebased monomer is leading to reductive elimination of the nickel catalyst competing with intramolecular chain transfer. Further exploration of this issue is underway in order to determine optimal catalyst/monomer systems and polymerization conditions.

Under all polymerization conditions with each monomer, polymer was formed in solution and isolated by precipitation with ethanol after 24 h, suggesting that the nickel catalyst does not remain permanently associated with the surfacebound polymer chain. This finding is consistent with the results of Rawlins and Achord,⁵¹ who observe that the synthesis of P3HT using the GRIM method with Ni-(dppp)Cl₂ as a catalyst does not proceed in a perfectly living fashion, but rather reaches a maximum molecular weight determined by monomer concentration. This result suggests that it may be possible to tune film thickness by varying monomer concentration. We will explore this possibility in future work.

Conclusions

We and others have encountered difficulties in forming films of the versatile conjugated polymer poly(3-hexylthiophene) via SI-KCTP of the Grignard monomer 2-bromo-5-chloromagnesio-3-hexylthiophene from a monolayer.^{20,21,52} Kiriy et al. report the successful surface-initiated Suzuki polymerization of 9,9-dialkylfluorene,²⁴ in which the solubilizing chains are on the 9-position of the fluorene ring, distant from the boronic acid moiety. Luscombe et al.⁵³ have observed a steric effect in the solution synthesis of P3HT; hindered 5-bromo-2-chloromagnesio-3hexylthiophene does not polymerize in the presence of Ni-(dppp)Cl₂ and aryl bromide-based external initiators, while the isomer 2-bromo-5-chloromagnesio-3-hexylthiophene polymerizes readily. In light of these results, it is possible that bulky substituents adjacent to the metal or metalloid group in a surfaceinitiated coupling reaction substantially hinder the reaction. This putative effect of chain bulk would present a fundamental problem in efforts to synthesize surface-bound polymer brushes of conjugated polymers, since attachment of such chains to the conjugated polymer backbone is a ubiquitous strategy for the preparation of soluble derivatives of conjugated polymers. Further experiments to test this hypothesis and prepare surface-grafted conjugated polymers using a variety of polymerization techniques and monomers are underway in our laboratory.

Relatively few techniques exist for the synthesis of surfacebound conjugated polymers. The technique reported here, which relies on simple and inexpensive catalysts and monomers, holds considerable promise for the fabrication of new thin-film architectures and devices. Furthermore, the dramatic dependence observed of the film morphology upon the nature of the solubilizing side chain suggests that SI-KCTP is a sterically demanding reaction strongly affected by the substitution of the monomer. Our results also raise the possibility of tuning the film properties by varying the bulk or length of the side chain. Further investigation into the effect of the monomer side chain in this system is currently under investigation in our laboratory.

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