

Steric Effects of the Initiator Substituent Position on the Externally Initiated Polymerization of 2-Bromo-5-iodo-3-hexylthiophene

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ABSTRACT: Externally initiated polymerization of 2-bromo-3-hexyl-5-iodothiophene was attempted from four aryl and thiophene based small molecule initiators functionalized with a phosphonate moiety. Initiated poly(3-hexylthiophene) product was obtained in various yields depending on the nature of the initiating molecule. Reaction intermediates for the oxidative addition and the ligand exchange steps were analyzed utilizing both experimental and theoretical methods. It was observed that an *ortho* substituent plays a crucial role in the outcome of the polymerization mechanism and that aryl based initiators are generally more stable than thiophene based initiators. Density functional theory (DFT) calculations revealed the importance of the steric effects on the success of the externally initiated chain growth polymerization mechanism.

Introduction

Conjugated polymers, among these polythiophenes, are an important class of materials in current research field of organic electronics and photovoltaics. Poly(3-hexylthiophene) (P3HT) in particular has attracted much interest in photovoltaic applications due to its desirable electronic and physical properties such as high thermal and environmental stability, high charge-carrier mobility, low optical gap and high solubility.^{1–12} Regiocon-trolled synthesis of poly(3-alkylthiophenes) was first developed by McCullough^{13–15} and Rieke.^{16–18} Yokozawa^{19,20} and McCullough²¹ later pioneered the Kumada catalyst transfer polymerization (KCTP) and the Grignard metathesis (GRIM) technique respectively, which yields highly regioregular polymers with controlled molecular weights, narrow polydispersity index and uniform end groups. The catalytic cycle of the KCTP mechanism begins with the bithiophene initiator which is generated through the transmetalation reaction between two molecules of the grignard functionalized thiophene monomer and Ni^{II}(dppp)Cl₂ catalyst.^{19,21} The polymerization control is thought to originate from either intramolecular transfer of the Ni catalyst or an associated pair formed by the growing polymer chain and the Ni catalyst. There has been substantial evidence for the propensity of the Ni catalyst to undergo selective intramolecular "ring walking" along conjugated and nonconjugated systems that leads to the desired "one-by-one" addition of monomers to a growing end of the polymer chain.^{22–25} The KCTP technique has also been applied to the synthesis of other polymers such as polythiophene-containing block copolymers^{26–33} as well as poly(*p*-phenylenes) and polypyrroles.^{34–36} A few research groups including ours have succeeded in synthesizing poly(3-hexyl)thiophene (P3HT) directly from external aryl halide initiators both in solution and on the surface.³⁷⁻⁴³ Senkovskyy et al. have successfully managed to externally initiate a P3HT polymerization from both small molecules and polymeric supports with the use of a Ni(PPh₃)₄

catalyst.⁴⁴ Our work, as well as by others mentioned above, indicates that oxidative addition of the arvl halide bond of the initiator to the Ni(0) catalyst (or catalyst precursor) is strongly dependent on the position and the type of functionality on the aryl group. In our previously published work, we observed that the presence of another substituent on the aryl halide initiator dramatically influenced the percent headgroup incorporation of the polymerization. The initiation decreases by at least 50% if such a substituent is an electron-withdrawing group and falls to almost 0% when the functionality is electron donating.39 We hypothesized that this effect could be attributed to the para position of the substituent which renders the Ni initiator/catalyst complex less stable than its unsubstituted counterpart. Work published by Uchida et al.45 indicated that in formation of aryl-Ni(II) complexes, ortho-substitution of the aromatic ligand resulted in a dramatic increase in the stability of the Ni complex. It is believed that the interactions of the ortho-substituent with the Ni atom increases the stability of the complex by lowering the energy of the highest occupied molecular orbital (HOMO) through bonding of the d_{xy} -orbitals of Ni with π -orbitals of the aromatic ring. We observed that while the initiation of orthochlorotoluene proceeds in almost quantitative manner, its parasubstituted isomer fails to initiate at all, which provides support for this hypothesis.⁴⁰ Further experiments performed in our laboratory have indicated that the stabilization of the propagating Ni(II) catalyst-capped polymer by alkyl chains located *ortho* to the terminal Br is a factor in promoting chain-growth polymerization character.⁴⁶ Most of the studies on the external initiator performed by our group as well as others, have focused on the thermodynamic effect of the ortho-stabilization, however the investigation of the kinetic effects as a result of steric hindrance has not been well-documented. It has been shown that a methyl substituent ortho to the halide group on the aryl initiator stabilizes the complex, however the effect of other bulkier substituents in that same position has not been investigated. In fact, much about the intermediate Ni catalyst/initiator complex remains

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Figure 1. Molecular structures of the initiators, their Ni complexes with PPh₃ and dppp ligands, and the final polymer products.





speculative as many have not been isolated and thoroughly studied due to their air-sensitive nature. We synthesized several initiators (Figure 1, Scheme 1) in order to study the electronic vs steric interactions and their effect on the chain-growth polymerization mechanism.

The phosphonate functionality on the initiator was chosen for its many potential applications such as the ability to be utilized in Horner-Wadsworth-Emmons reactions and the possibility of deprotection to the phosphonic acid moiety known to form robust monolayers on metal oxides which could possibly be utilized as an anchoring layer for polymer brush synthesis.⁴ Therefore, we sought to verify whether we could incorporate such a functionality at the beginning of the polymer chain. It is worthwhile noting that when we have previously attempted P3HT synthesis from an aryl halide inititator with the phosphonate group para to the halide, we observed complete degradation of the Ni catalyst/initiator complex and it remained to be investigated whether or not the ortho substituent would provide sufficient stabilization to change the polymerization outcome. In order to fully understand which effects are significant in the formation of the nickel catalyst/initiator complex, it is important to know the geometry of this transiently formed complex. Since these materials are air-sensitive and thus difficult to structurally characterize experimentally, DFT modeling was utilized to get

insight on the geometry of the intermediate complexes. Geometrical optimizations of the two starting initiators (Scheme 1), **In1** and **In2** and their corresponding nickel catalyst/initiator complexes were performed using Gaussian 09 program. Additionally, the relative energies of the starting initiator (**In1** and **In2**) to their oxidative addition product (**In1PPh₃** and **In2PPh₃**) were calculated. These theoretical studies combined with experimental results allowed us to elucidate main factors determining the initiator efficiency in the chain-growth polymerization reaction.

Experimental Section

Instrumentation and Materials. ¹H NMR spectra were obtained on Bruker AV300, Varian Mercuries Vx 300 and 400, and AV-500 spectrometers using CDCl₃ as a solvent (peak position δ^{1} H = 7.27 ppm) and internal standard of ¹H NMR spectra was tetramethylsilane (0.00 ppm). ³¹P NMR spectra were obtained on Bruker AV300, Varian Mercury Vx400, and AV499 spectrometers with phosphoric acid as the standard. MALDI spectra were recorded on Bruker Autoflex II spectrometer using terthiophene as the sample matrix. Samples were prepared by dissolving 0.5 mg in 100 µL of matrix solution in chloroform and approximately 1.5 µL of this solution was deposited on the plate. The MALDI experiments were performed in the reflecton mode. The % headgroup incorporation was calculated by analyzing the MALDI–TOF and the NMR spectra. The area under the peaks on the MALDI spectra corresponding to the mass of the polymer with the attached initiator group were divided by the area under all the polymer peaks present and multiplied by 100 to obtain % headgroup incorporation. Molecular weights of polymers were determined using a Waters-1515 gel permeation chromatography (GPC) coupled with UV and RI detectors, in reference of polystyrene standards with THF as the eluent with a flow rate equal to 1 mL/min. GC-MS analyses were performed using a 60 m, 0.32 mm ID, 1.0 μ m HP-1 column or a 30 m, 0.32 mm ID, 0.25 μ m HP-5MS column, programmed at 70 °C for 2 min, to 300 or 340 at 15 °C/min holding for 20 min. All elemental analyses were done at Atlantic Microlab (Norcross, GA).

All chemicals were purchased from Aldrich, Alfa-Aesar, or TCI and used as received unless otherwise stated. Tetrahydrofuran (THF) and toluene were dried using a solvent drying system from Innovative Technologies. All polymerizations were performed under N_2 .

Synthesis of Diethyl 4-Chloro-3-methylbenzylphosphonate (In1). The starting carboxylic acid was reduced to the alcohol by a procedure reported for a similar compound.⁴⁸ A mixture of 4-chloro-3-methylbenzoic acid in distilled THF was stirred at 0 °C under N₂ atmosphere. A solution of 1 M borane in THF (1.3 equiv) was added dropwise via an addition funnel and the mixture stirred for 4.5 h. The excess hydride was quenched by addition of water/THF (1:1) mixture, and basification with carbonate/bicarbonate followed. After extraction, 1b was recovered as orange-colored crystals from toluene (19%). Conversion to 1c was done by mixing 1b in dry toluene with phosphorus tribromide under nitrogen at 40 °C, followed by heating to 100 °C for 10 min, then letting cool to room temperature (80% yield). After extraction, conversion to phosphonate proceeded through neat reaction of 1c with triethyl phosphite at 150 °C under nitrogen (quantitative crude yield). Pure product was obtained in 73% yield after purification through silica plug with ethyl acetate as the eluent. ¹H NMR (300 MHz, CDCl₃) δ 7.21 (d, J = 8.2 Hz, 1H), 7.12 (dd, J = 2.4, 2.2 Hz, 1H), 7.01 (ddd, J = 8.2, 2.4, 2.2, 1H), 3.98 (dq, $J_{H-P} = 8.4, J_{H-H} = 7.1$ Hz, 4H), 3.03 (d, $J_{H-P} = 21.6$ Hz, 2H), 2.30 (s, 3H), 1.21 (t, J = 1.07.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 136.3, 133.2, 132.5, 130.3, 129.3, 128.6, 62.4, 33.2 (d, $J_{C-P} = 138.6$ Hz), 20.2, 16.6. ³¹P NMR (162 MHz, CDCl₃): δ 26.6. HRMS: calculated, 276.0682; found, 276.0686. Anal. Calcd: C, 52.09; H, 6.56; Cl, 12.81. Found: C, 51.85; H, 6.67; Cl, 12.58.

Synthesis of Diethyl 2-Chlorobenzylphosphonate (In2). Neat reaction of bromide 2a with triethyl phosphite (3 equiv) at 150 °C under nitrogen atmosphere overnight was followed by pump off at 60 °C under reduced pressure which resulted in In2, a colorless oil in 96% yield which did not require further purification.⁴⁹ ¹H NMR (300 MHz, CDCl₃) δ 7.46–7.38 (m, 1H), 7.37–7.32 (m, 1H), 7.24–7.12 (m, 2H), 4.02 (dq, J_{H-P} = 8.0, J_{H-H} = 7.1 Hz, 4H), 3.34 (d, J_{H-P} = 22.0 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 134.4, 131.9, 130.1, 129.8, 128.5, 127.0, 62.4, 30.9 (d, J_{C-P} = 133 Hz), 16.6. ³¹P NMR (162 MHz, CDCl₃): δ 26.3. HRMS: calculated, 262.0526; found, 262.0518. Anal. Calcd: C, 50.30; H, 6.14; Cl, 13.50. Found: C, 50.16; H, 6.41; Cl, 13.23.

Synthesis of (5-Bromo-4-hexylthiophen-2-yl)methylphosphonate (In3) and (5-Bromothiophen-2-yl)methylphosphonate (In4). The procedure was based on previous reports for the synthesis of In4.^{50,51} Pure product of In4 was obtained as lightly yellow colored oil. ¹H NMR (400 MHz, CDCl₃): δ 6.85 (d, J = 3.7 Hz, 1H), 6.69 (ddt, J = 3.7, 3.7, 0.9 Hz, 1H), 4.05 (dq, J = 7.1, 7.1Hz, 4H), 3.23 (dd, $J_{H-P} = 20.7, J_{H-H} = 0.8$ Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H).

Similar conditions were used to obtain **In3** (not previously reported in the literature). The crude phosphonate (a dark brown oil, 58% pure product by GC–MS) was subjected to silica column chromatography with 2% ethanol in DCM, followed by a subsequent column with 1:1 hexane:ethyl acetate as the

eluent to afford **In3** as deep orange oil. ¹H NMR (300 MHz, CDCl₃) δ 6.63 (d, J = 3.6, 1H), 4.10–3.98 (m, 4H), 3.18 (dd, $J_{H-P} = 21.7$, $J_{H-H} = 0.8$ Hz, 2H), 2.45 (t, J = 7.6 Hz, 2H), 1.55–1.43 (m, 2H), 1.29–1.21 (m, 12H), 0.84 (t, J = 6.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 142.2, 132.3, 128.7, 122.4, 62.7, 30.8 (d, $J_{C-P} = 150$ Hz), 29.6, 29.5, 29.0, 27.7, 22.8, 16.6, 14.3. ³¹P NMR (162 MHz, CDCl₃): δ 24.6. HRMS: calculated, 396.0524; found, 396.0507. Anal. Calcd: C, 45.35; H, 6.60; Br, 20.11; S, 8.07. Found: C, 45.52; H, 6.77; Br, 20.19; S, 8.33.

Synthesis of Nickel Catalyst/Initiator Complexes. Phosphonate initiators (15 equiv) were allowed to react with Ni(PPh₃)₄ (1 equiv) in 1 mL of toluene overnight in a glovebox environment to form In1-PPh₃ (100%), In2-PPh₃ (39%), In3-PPh₃ (31%) (Figure 1). This step was followed by ligand exchange with dppp (1.5 equiv) for 2–3 h without purification to form In1-dppp (100%), In2-dppp (21%), In3-dppp (26%) also done in the glovebox environment. The complex yields were obtained by analyzing the ¹H NMR spectra of the crude reaction mixture. Upon reaction of In4 with Ni(PPh₃)₄ and subsequent ligand exchange with dppp, the Ni/initiator complex underwent rapid decomposition, thus the reaction yields could not be obtained. After the reaction, the complex mixtures were transferred into sealed round-bottom flasks and taken out of the glovebox.

General Polymerization Protocol. The monomer, 2-bromo-3-hexyl-5-iodothiophene, was synthesized according to previously published procedures.⁸ Addition of reagents into the reaction flask was carried out via a syringe under a stream of nitrogen. Polymerization was initiated by addition of the crude complex mixture to a solution of 2-bromo-5-chloromagnesio-3-hexyl-thiophene (30 equiv) which was prepared by the reaction of 2-bromo-3-hexyl-5-iodothiophene with 0.95 equiv of ^{*i*}PrMgCl at 0 °C in THF for 1 h. After the addition of the complexes, the reaction mixtures were allowed to polymerize for 1 h. After quenching, the solutions were precipitated into methanol and poly(3-hexyl)thiophene products, **polyIn1** (90%), **polyIn2** (78%), and **polyIn3** (69%) were collected via vacuum filtration and analyzed without further purification.

DFT Calculations. Density functional theory (DFT; B3LYP) calculations on the two chosen initiators, **In1** and **In2** as well as two initiator/catalyst complexes **In1-PPh₃** and **In2-PPh₃** were performed using the Gaussian 09 program.⁵² The standard 6-31G* basis set was used for all the atoms except Cl, and Ni, for which 6-31G** and Ahlrichs' valence triple- ζ (VTZ) basis sets were chosen, respectively.⁵³ Geometry optimization was carried out using tight convergence criteria and an ultrafine integration grid. All calculations were performed assuming a singlet ground state. The optimized structures were verified to be true minima by frequency calculations. The nickel-catalyst binding energies to initiator complexes, $\Delta E_{\text{Ni-initiator}}$, were calculated via

$$\Delta E_{\rm Ni-initiator} = E_{\rm Ni-initiator\ complex} - (E_{\rm initiator} + E_{\rm Ni\ catalyst})$$

where $E_{\text{Ni-initiator complex}}$ is the energy of the catalyst/initiator complex, $E_{\text{initiator}}$ is the energy of the initiator compound, and $E_{\text{Ni}\ \text{catalyst}}$ is the energy of Ni(II) diphosphine catalyst. To facilitate the calculations, the ethyl substituents on the phosphonate groups were replaced by methyl groups.

Results and Discussion

KCTP Reaction Pathway. If the reaction proceeds via a chain-growth polymerization mechanism, the P3HT product will have one set of terminal groups, a low PDI, a molecular weight that can easily be tuned by manipulating catalyst/ monomer feed ratio and almost exclusively head to tail regioregularity (~98%).⁵⁴ During the "ideal" catalyst transfer polymerization, where one Ni catalyst molecule propagates through one polymer chain with addition of monomer one at a time, after the reaction is quenched with acid, only initiator/H end groups are observed (Scheme 2). However,

Scheme 2. Polymerization Reaction Pathway



undesired chain termination or chain-transfer reactions lead to a variety of end groups such as initiator/Br if the catalyst reductively eliminates from the polymer chain before complete conversion of the monomer is reached or H/Br, H/H, and Br/Br groups which result from the step-growth polymerization catalyzed by the various Ni species in the solution.³⁸ The externally initiated P3HT synthesis pathway begins with the oxidative addition of the aryl halide initiator to the Ni(PPh₃)₄ catalyst where the halide group is either chlorine or bromine. The oxidative addition step is followed by a ligand exchange with dppp: we have previously shown this ligand exchange procedure to yield fully regioregular P3HT from an externally added o-chlorotoluene initiator with controlled molecular weights and extremely narrow polydispersities (Scheme 2). The final step is the addition of the Grignard-functionalized 2-bromo-3-hexylthiophene monomer that initiates the polymerization.

³¹P NMR Studies. The intermediates in the KCTP reaction of the four initiators were monitored via $^{31}\mathrm{P}$ NMR spectroscopy. After the addition of Ni(PPh₃)₄, the ³¹P NMR spectrum (Figure 2) shows a sharp peak at 19 ppm, consistent with trans-chloro-(3-methylbenzylphosphonate)bis(triphenylphosphine)nickel(II) complex (In1-PPh₃).⁵⁵ The peak at 24 ppm corresponds to the phosphonate group on the starting In1 which was present in a 15 equivalent excess in the reaction mixture. The remaining peak at 26 ppm is attributed to the phosphonate group in In1-PPh₃ complex. Addition of 1.5 equivalents of dppp resulted in rapid ligand subsitution to form the thermodynamically favored cis-chloro(3-methylbenzylphosphonate)(dppp)nickel(II)complex, (In1-dppp). The formation and the geometry of this complex were confirmed by the appearance of two sets of doublets at 18 ppm and -6ppm (which is obscured by the peak of liberated PPh₃). A peak corresponding to Ni(dppp)₂ was also observed at 11 ppm. The ¹H NMR spectra of In1-PPh₃ and In1-dppp show that the oxidative addition and ligand exchange reactions proceed to completion resulting in 100% yield of desired complexes.

The ³¹P NMR spectrum of **In2-PPh₃** (Figure S2, Supporting Information), also confirms the successful formation of the *trans*-chloro(diethylbenzylphosphonate)nickel(II) complex via the presence of the PPh₃ peak which is slightly shifted possibly due to the coordination of the nickel with the nearby oxygen atom. The phosphonate groups of **In2-PPh₃** and of excess **In2** are present at 26 and 24 ppm respectively. After the addition of dppp, the two sets of doublets corresponding to the *cis* complex **In2-dppp** are observed at +19 and -7 ppm. The PPh₃ peak of **In2-PPh₃** is still present, which indicates that the ligand reaction did not reach completion in the allotted reaction time frame. The peak for Ni(dppp)₂ is also larger suggesting partial dissociation of the Ni catalyst from initiator/catalyst complex and its subsequent chelation by



Figure 2. ³¹P spectra of nickel(II) complexes in toluene: (top) In1-dppp; (bottom) In1-PPh₃.

dppp. Analysis of the ¹H NMR spectrum of In2-PPh₃ reveals that the oxidative addition reaction did not proceed to completion as seen by two sets of peaks corresponding to the protons nearest to the reaction center. The yield of the oxidative addition adduct, which is obtained through integration of both peaks, is calculated to be 39%. After the addition of dppp, ¹H NMR data confirms only partial ligand exchange as evidenced by a set of three peaks. The analysis of the final mixture after oxidative addition and ligand exchange steps reveals the following species containing the initiator molecule: In2 (58%), In2-PPh₃ (21%), and In2-dppp (21%). Ni(dppp)₂ is present as well, however it is difficult to quantify with ¹H NMR. The ³¹P NMR spectrum of In3-PPh₃ (Figure S3, Supporting Information) indicates the presence of the transbromo(4-hexylthiophen-2-yl methyl phosphonate)nickel(II) complex. The phosphine peak of the complex appears in the region of 19 ppm while the phosphonate groups of In3-PPh₃ and In3 are present at 25 and 23 ppm respectively. An additional peak is observed at 21 ppm that could correlate to the phosphine peak where the thiophene ring is coordinating to the Ni complex. After the addition of dppp, the characteristic set of doublets can be seen at +16 and -5 ppm. Additional peaks are present between the phosphonate groups of In3 and In3-PPh₃ (22-24 ppm) that are attributed to the nickel species where the thiophene ring is coordinating to the metal center. ¹H NMR spectra reveals incomplete conversion of the original initiator into the desired oxidative adduct with the complex yield of In3-**PPh₃** determined to be 31%. However, the ligand exchange goes almost to completion evidenced by the lack of In3-**PPh₃** peak. The **In3-dppp** complex yield was calculated to be 26% over the two steps. In4 has proved to be the least

Table 1. Overview of Results from the Polymerization Reactions of polyIn1, polyIn2, and polyIn3

Initiator	End Groups	M _n (Da) ^{GPC} M _n (Da) ^{NMR} (PDI) Yield	% Regioregularity	% Head-group incorporation
(EtO) ₂ OP	Initiator/H (75%) Initiator/ ^{<i>i</i>} Pr (9%) H/H (13%) Others (3%)	5200 4900 (1.2) 90%	94	84
(EtO) ₂ OP	Initiator/H (37%) Initiator/ ^{<i>i</i>} Pr (8%) H/H (47%) Others (8%)	3900 3600 (1.6) 78%	92	45
(EtO) ₂ OP	Initiator/H (18%) Initiator/Br (9%) H/Br (65%) H/H (8%)	2900 2000 (2.6) 69%	89	27

stable of the initiators. Upon addition of the Ni(PPh₃)₄ to the initiator, a white precipitate, likely being a mixture of Ni(II) halide salts and other decomposition products, was observed in the reaction mixture after a short period of time. The ³¹P NMR analysis revealed the presence of only the starting material **In4** which was in excess. Since the desired **In4-PPh₃** and **In4-dppp** initiating complexes and consequently **polyIn4** are not formed with this thiophene molecule, this initiator was not included in further studies. The disproportionation reaction likely arises from the lack of a substituent in the *ortho* position. Since the aromatic stabilization of thiophene is already weak (less than half of benzene),⁵⁶ we speculate that in the absence of favorable interactions between the thiophene π system and the nickel d-orbitals the reacting species decompose rapidly.

Polymerization Results. The results of varying initiators on the polymer end groups and molecular weight are summarized in Table 1.

The use of **In1** has afforded a polymer with a good % headgroup incorporation, a molecular weight that is close to the calculated $M_{\rm n}$ and narrow PDI all of which indicate the predominance of a chain growth polymerization mechanism. Various end groups are observed such as initiator/H, initiator/^{*i*}Pr, and H/H. Other extremely small peaks in the MALDI-TOF spectrum could not be identified and are likely polymers with a fragmented initiator group. The initiator/ⁱPr groups are likely to arise from a minor mismatch between the relative amounts of m1 and 'PrMgCl solution because of difficulties in precisely measuring very small volumes of ^{*i*}PrMgCl solution and its high sensitivity to the moisture and air. Despite a reaction time of only 1 h in order to avoid precipitation of P3HT at high conversion, the molecular weight determined by SEC (5200 Da) is very close to the calculated molecular weight (5224 Da) of the 30 unit 3-hexyl thiophene chain. The molecular weight calculated via NMR agrees quite well with the molecular weight determined by SEC showing a polymer with 30 monomer repeat units is indeed obtained in such a short reaction time. The PDI value of 1.2 is much lower than the PDI values for initiated P3HT using other ligands,³⁹ which shows the more controlled polymerization mechanism with the dppp ligand. As previously mentioned, ealier attempts of initiating a polymerization from a *para*-substituted benzylphosphonate molecule have failed and were attributed to the destabilization of the Ni catalyst by the phosphonate moiety. These polymerization results illustrate both the importance of the ortho-substituent and the possibility of introducing a phosphonate functionality with numerous potential applications onto the polymer chain. In agreement to the expected trend based on the ³¹P NMR and ¹H NMR spectra as well as calculated complex



Figure 3. MALDI-TOF spectra of polyIn1 (top) and polyIn2 (bottom).

yields, polyIn2 shows higher % headgroup incorporation than polyIn3 (45% vs 27%). The end group distribution of **polyIn2** is similar to those for **polyIn1** albeit with a higher percentage of H/H (Figure 3). As previously mentioned, the final mixture composition before the monomer addition contained In2, In2-PPh₃, and In2-dppp with the total percentage of catalytically active species equal to 41%. Both In2-**PPh₃** and **In2-dppp** are able to initiate the polymerization, however the major difference between the two species is how long the Ni catalyst can propagate through the polymer chain. As evidenced in our previous work, Ni with PPh₃ ligand tends to reductively eliminate much faster than the catalyst with the dppp ligand.³⁸⁻⁴⁰ Once the Ni catalyst leaves the polymer chain, it begins linking monomer units in a random step growth fashion, without the intramolecular reinsertion into the same polymer chain that is inherent to the KCTP mechanism, which results in the H/H terminated P3HT product. Thus, the % headgroup incorporation is very similar to the total amount of complexed initiator/catalyst species (45% vs 41%), however, the tendency of $Ni(PPh_3)_2$ species to quickly undergo reductive elimination results in a higher fraction of H/H polymer.

The major end groups of **polyIn3** such as H/Br and H/H indicate significant occurrence of chain-termination and chain-transfer processes that are common to a non-initiated step-growth polymerization mechanism. Lower molecular weights (3900 and 2900 Da) as well as higher PDIs (1.6 and 2.6) reflect the decreasing chain-growth character and increasing step-growth character of the polymerizations from **In2** and **In3**. The lowest % headgroup incorporation

from In3 is supported by ¹H NMR data which reveals a low yield of the desired catalytic complex (26%). Thiophene is known to bond to metals in several different configura-tions in organometallic complexes.^{57,58} It can bond through the aromatic π -system of the thiophene ring (η^5 configuration) or through the S atom as a weak Lewis base. Alternatively, the thiophene ring may pucker and the bonding can occur through the four carbon atoms (η^4 configuration) with the sulfur out of plane of the C₄ system. It was also previously demonstrated that thiophene initially coordinates to a platinium bisalkylphosphine fragment through the C–C double bond (η^2 configuration) through the π -backbonding from the metal d_{xy} -orbital to a thiophene C–C π^* -orbital.⁵⁹ Other d⁸ metals such as nickel and palladium are known to form thiophene metallocycle complexes which exist in equilibrium with thiophenic bridged dinuclear complexes and free thiophene.⁶⁰ In that case, the bonding interactions result from the donation of electron density from the HOMO of the Ni(dmpe) fragment into the LUMO of the thiophene fragment and back-donation from the HOMO of the thiophene into the LUMO of the metal fragment. Since donation of electron density from the metal to the thiophene ligand is the main factor in this coordination mechanism, it is reasonable to speculate that the strongly electron-withdrawing phosphonate group leaves the thiophene π -system electron deficient thus promoting the formation of the coordinated complex. We believe that the coordination of the nickel to the thiophene ring prevents the formation of In3-PPh₃, which decreases headgroup incorporation into the polymer chain.

Molecular Modeling and Binding Energies. In order to investigate the effects that may have played a role in the decrease in the initiation of In2 as compared to In1, the geometries of both compounds as well as their corresponding oxidative adducts In1-PPh₃ and In2-PPh₃ were modeled with the Gaussian 09 program. Initially, the potential energies of the optimized structures of In1-PPh₃ and In2-PPh₃ were calculated and compared (for this purpose, a methyl substituent was added to the *para* position of In2-PPh₃ in order to keep the equivalent number of atoms). It is interesting to note that changing the substituent at the ortho position of the initiator from a methyl group to the phosphonate group has no effect on the potential energy value of the molecule leading to the conclusion that both substituents offer similar degree of electronic stability to the nickel(II) complex. Therefore, it is likely that kinetic effects are responsible for the decrease in initiation. To test this hypothesis, the energies for the formation of In1-PPh₃ and In2-PPh₃ from the starting reaction components of In1 and In2 and $Ni(PPh_3)_2$ were calculated. If electronic effects played a determining role in the reaction mechanism, the binding energy of the complex with the more favorable substituent would be more exothermic. The energy of complexation of In1 with Ni(PPh₃)₂, ΔE_1 was calculated to be -36.27 kcal/ mol while the energy of the complexation of In2 with the Ni catalyst, ΔE_2 afforded a very similar value with a negligible difference of less than 1 kcal. These values are similar to other reported values for the energy of formation for nickel complexes.⁶¹ This shows that both reactions are equally spontaneous in agreement with the hypothesis that the effects on the decreased % headgroup incorporation are more likely due to kinetic effects rather than electronic effects. Optimized molecular structures of the starting compounds and the complexes are shown in Figures 4 and 5, respectively. Selected bond distances and angles are given in Tables 2 and 3. Compounds In1 and In2 have very similar C_1 -Cl bond distances of *ca.* 1.763 Å. The bond angles are



Figure 4. DFT-optimized structures and atom labeling for In1 (left) and In2 (right). Mulliken charges for the selected atoms are indicated in blue.

rather similar as well. Both catalyst-initiator complexes In1-PPh₃ and In2-PPh₃ have slightly distorted square planar geometries especially for In2-PPh₃ where the angles slightly deviate from the expected 90°. In terms of bond length, the Ni(II) coordination site is also similar in both complexes. However, in In2-PPh₃, the oxygen atom of the *ortho*-phosphonate functionality on the aryl ligand comes to close proximity to the Ni(II) fifth coordination site. This structural feature might play a determining role in polymerization outcome, as outlined below.

There are at least two possible explanations how steric effects could inhibit the % headgroup incorporation for In2-**PPh₃**, one of which is the possible coordination of the oxygen atom of the phosphonate group to the Ni metal center, inhibiting reaction with an incoming ligand. There have been numerous reports of the P=O group coordinating to the metal center via the oxygen $atom^{62-75}$ particularly when the two are in close proximity to each other such as the case with In2-PPh₃ where the Ni \cdots O distance is 3.443 Å. Such binding would inhibit the dppp ligand exhange reaction as was observed in the ³¹P NMR and ¹H NMR, where there was significant amount of In2-PPh3 remaining after the addition of 1.5 equiv of dppp. Since the dppp and PPh₃ ligand exchange occurs via an associative mechanism, as do a vast majority of ligand exchanges for the d¹⁰ metals,^{76,77} a fivecoordinate Ni complex would lack an available site that would facilitate the ligand exchange. Thus, a significant fraction of In2-PPh₃ complex remains behind leading to a higher yield of step-growth polymer. It should be noted, however, that the DFT modeling of the In2-PPh₃ complex showed that the phosphonate functionality can accept different orientations around the C_3-P_1 bond. The geometry optimization initiated with different starting geometries for the In2-PPh₃ complex, led to stable structures with different phosphonate group orientations, where the oxygen atom was either in close proximity to the Ni center as shown in Figure 5, or turned away from the Ni. These structures were found to be less than 0.5 kcal/mol from each other. Thus, it is plausible that in solution, an average ensemble of these conformations exist allowing ligand exchange to take place, which was observed experimentally.

A second possible explanation is that a bulky phosphonate group *ortho* to the initiation site may affect the kinetics of the oxidative addition reaction. Kochi and others have shown that the mechanism of oxidative addition reaction of nickel-(0) complexes with aromatic halides is quite complex and can involve multiple Ni(I) and Ni(II) species depending on the nature of the aryl halide and it was found that the mechanism involves several steps.^{78,79} The first step is the equilibrium formation of the coordinatively unsaturated NiL₃ from NiL₄ (eq 1), with the ligand studied in this case being L = PEt₃.



Figure 5. Top-view of the DFT-optimized structures of In1-PPh₃ (left) and In2-PPh₃ (right) showing Ni(II) coordination site (hydrogen atoms have been omitted for clarity). Mulliken charges for the selected atoms are indicated in blue.

Table 2. Selected Bond Lengths, Atom Distances, and Bond Angles for In1 and In2

	bond length/atom distance (Å)				
bond of interest	In1	In2			
C ₁ -Cl	1.764	1.763			
$C_2 - C_3$	1.508	1.510			
P-O ₁	1.487	1.485			
$C_3 \cdots Cl$	3.094	3.139			
$O_1 \cdots Cl$	8.513	3.943			
	bond a	ngles (deg)			
angle of interest	In1	In2			
$\angle ClC_1C_2$	119.8	120.7			
$\angle C_1 C_2 C_3$	122.3	123.1			

This step is followed by the slow rate-limiting electron transfer in eq 2 to afford an ion pair indicated in brackets. Cage collapse affords oxidative adduct in eq 3.

$$\operatorname{NiL}_4 \leftrightarrows \operatorname{NiL}_3 + \mathcal{L} \quad (K_1)$$
 (1)

$$Ni^{0}L_{3} + ArX \rightarrow [Ni^{I}L_{3}ArX^{-}] \quad (k_{2})$$
⁽²⁾

$$[\mathrm{Ni}^{\mathrm{I}}\mathrm{L}_{3}\mathrm{ArX}^{-}] \rightarrow \mathrm{ArNi}^{\mathrm{II}}\mathrm{XL}_{2} + \mathrm{L}$$
(3)

They showed that the triphenylphosphine ligand is more highly dissociated and is less readily oxidized than the triethylphosphine ligand. Thus under comparable conditions, the reaction of aryl halides with $Ni(PPh_3)_3$ is significantly slower than that with $Ni(PEt_3)_3$.⁸⁰ Also, Kochi et al. have carried out a study of the steric effects from ortho-methyl substitution on the reaction of nickel(0) with bromobenzene in toluene solution and found that addional steric bulk from the substituents results in the decrease of the rate constant for the rate determining step (RDS).⁷⁹ Taking all of the above information into the account, it is reasonable to draw a conclusion that the phosphonate substituent in such close proximity to the reaction site, decreases the rate of the reaction. Since the two complexes are allowed to react for exactly the same time, the decreased rate constant for the In2-PPh3 reaction results in lower yield of the oxidative addition product as evidenced by ¹H NMR which would result in decreased % headgroup incorporation.

Conclusions

In this work, poly(3-hexylthiophene) was externally initiated from aryl and thiophene halide molecules with an attached

Table 3. Selected Bond Lengths, Atom Distances, and Bond Angles for the Ni(II) Complexes In1-PPh₃ and In2-PPh₃

bond length/atom distance (Å)		
In1-PPh ₃	In2-PPh ₃	
2.278	2.279	
1.895	1.897	
2.296	2.283	
2.294	2.342	
1.512	1.519	
1.488	1.492	
3.295	3.395	
8.738	3.443	
bond a	angles (deg)	
In1-PPh ₃	In2-PPh ₃	
170.1	172.9	
179.6	174.1	
176.3	164.6	
	bond length/ato In1-PPh ₃ 2.278 1.895 2.296 2.294 1.512 1.488 3.295 8.738 bond a In1-PPh ₃ 170.1 179.6 176.3	

phosphonate functional group with varying % headgroup incorporation. Attempts of polymerization from a para-phosphonate substituted aryl halide initiator were made in our previous work and proved unsuccessful.³⁹ These current findings further emphasize the importance of a stabilizing ortho-substituent on the success of the initiation of a KCTP reaction. Thiophene based initiator, In4, lacking a hexyl chain in the 3-position failed to form the desired oxidative adduct upon its reaction with the nickel catalyst, suggesting rapid decomposition of the reactant likely due to its weak aromatic stabilization and the lack of a stabilizing group. ³¹P NMR studies of initiators In1-In3 showed peaks attributed to desired products of oxidative addition and ligand exchange steps in addition to a few side product peaks. In1 provided the best results, with the highest % headgroup incorporation of 84%, a molecular weight close to the calculated $M_{\rm n}$ and a narrow PDI which all pointed to a chain-growth mechanism and is considered the most promising initiator in this study. In2 and In3 resulted in a mixture of chain-growth and stepgrowth polymerization products. In2 performed better than In3 with % incorporation of 45% and 27% respectively. The poor yield of initiated polymer from the In3 initiator was attributed to the nickel metal center coordinating to the thiophene ring and inhibiting its ability to undergo the crucial intermolecular transfer step. The difference in initiation efficiencies between In1 and In2 was suggested to originate primarily from the steric effects. The proximity of the phosphonate group to the oxidative addition site was speculated to promote oxygen atom coordination to the nickel preventing it from undergoing the dppp ligand exchange and also to slow down kinetics of the reaction both contributing to decreased % headgroup incorporation.

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Supporting Information Available: MALDI-TOF spectra of polyIn1, polyIn2, and polyIn3, ³¹P NMR spectra of In1-PPh₃, In2-PPh₃, In3-PPh₃, In1-dppp, In2-dppp, and In3-dppp, and Cartesian coordinates of the DFT models. This material is available free of charge via the Internet at http://pubs.acs.org

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