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ARTICLE

Effect of Initiators on the Kumada Catalyst-Transfer Polycondensation Reaction

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ABSTRACT: An investigation for the initiation of a chain-growth polymerization, Kumada catalyst-transfer polycondensation, for the synthesis of poly(3-hexylthiophene) is described. A novel method for the generation of an active catalyst/initiator complex was developed utilizing the inexpensive, air stable $Ni(PPh_3)_2Cl_2$ precursor to generate the active $Ni(PPh_3)_4$ catalyst *in situ*. Poly(3-hexylthiophene) polymerization reactions were carried out using aryl halides with various substituents on the phenyl ring as external initiators, and it was found that the type of the functional group present on the initiator plays a crucial role in the polymerization. The new method provided a more efficient way to initiate polymerization yielding polymers with higher regioregularity, larger molecular weight, and lower polydispersity than the previously reported methods.

Introduction

The ability of chemists to design and synthesize π-conjugated organic polymers with precise control over the molecular weight with narrow polydispersities remains the key to technological breakthroughs using polymeric materials in electronic and photonic devices. Being able to synthesize semiconducting polymers with control over the molecular weight with narrow polydispersities will reduce the variability between synthetic runs which can lead to differences in electronic device performances between different research laboratories. Additionally, being able to synthesize well-defined block copolymers, star-shaped polymers, and surface-grafted polymers will expand the structural library of semiconducting polymers, which will allow us to obtain a more in-depth knowledge of the relationship between the structure and electronic properties of semiconducting polymers. In order to realize the goal of controlled polymerization and to be able to create additional polymer architectures, a new polymerization technique must be utilized. Regioregular poly(3-hexylthiophene) (rr-P3HT) has received much attention in photovoltaic application in recent years because of its small band gap, high hole mobility, and good solubility.[1] Regiocontrolled synthesis of poly(3-alkylthiophenes) has been developed by McCullough[2−6] and Rieke,[7−9] and the recent discovery of chain-growth polymerization of rr-P3HT that was reported by McCullough[6] and Yokozawa[10,11] has attracted our attention as a gateway to achieve our goals. Polythiophene containing block copolymers,[12−19] as well as conjugated polymers such as poly(*p*-phenylene)s and polypyrroles have been successfully synthesized by a handful of researchers using the Kumada catalyst-transfer polycondensation (KCTP), also commonly known as the GRIM method.[20−23] The chain-growth polymerization of polyfluorenes, which utilizes a Suzuki coupling, has also been investigated.[24,25]

The mechanism for the KCTP was proposed by McCullough[6] and Yokozawa[10] as shown in Scheme 1. According to the reaction scheme, the 5,5′-dibromo-4,4′-dihexyl-2,2′-bithiophene chain initiator is generated *in situ* via transmetalation of two molecules of **1** at their magnesium ends with $Ni^{II}(dppp)Cl_2$ yielding the symmetrical bis-organonickel compound, which is thought to be the initiator of the polymerization. In the next step, the Ni either intramolecularly transfers to the C−Br bond end of the polymer or reductively eliminates but reinserts into the C−Br bond of the same growing polymer chain without diffusion into the surrounding solution. Thus based on this unexpected ability of Ni catalyst to migrate intramolecularly, polymerization occurs with addition of one monomer unit at a time leading to a chain growth polymerization mechanism. In this mechanism, one Ni molecule forms one polymer chain, so the molecular weight of the polymer is proportional to Ni loading and the polydispersity index is very narrow. Kiriy et al.[26−28] and Locklin et al.[29] have succeeded in applying KCTP in the synthesis of poly(3-hexylthiophene) brushes on the surface. However due to chain-transfer mechanisms, if the polymer is grown from a monolayer, the brush film thickness is low.[29] The goal of this work was to develop an alternative initiation strategy that would provide a polymer with greater initiation efficiency.

Kiriy et al. have utilized a $Ni(PPh_3)_4$ catalyst and an external bromobenzene initiator.[26−28,30] The mechanism of chain growth polymerization for their method is shown in Scheme 2. Unfortunately, $Ni(PPh_3)_4$ is unstable as well as expensive and carcinogenic, and the catalyst/initiator complex requires extensive purification steps, in addition to the need to perform the reactions in the glovebox environment. The complexity involved meant that, in our hands, this initiation scheme proved to provide variable results and could not be used for more complex initiators (see Table 1). Also, in order to make the KCTP technique more widely applicable and to be able to synthesize more complex polymers such as block polymers, brush polymers and star-shaped polymers, alternative initiators besides bromobenzene need to be tested. In this paper, we report a novel, more facile method for the externally initiated growth of rr-P3HT from various aryl halide initiators, which provides rr-P3HT with enhanced initiation efficiencies, greater regioregularity and increased molecular weights. The investigation into the relationship between the type functional group on the initiator and the polymerization mechanism is also presented.

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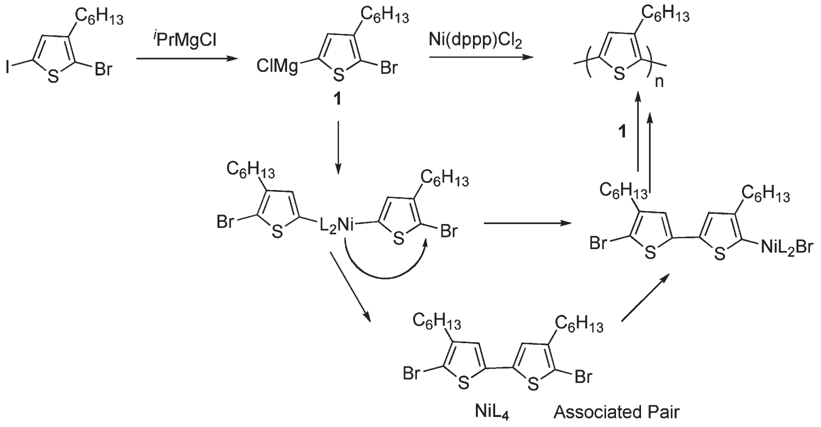
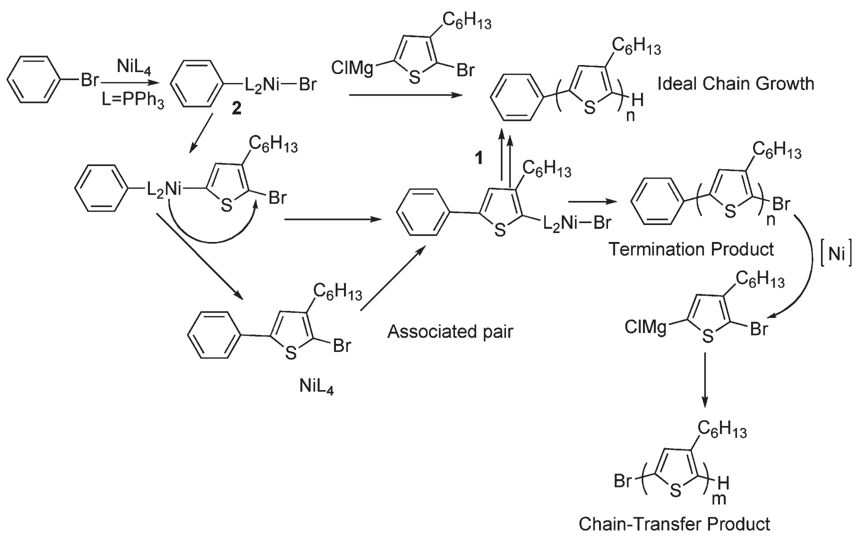
Scheme 1. Polymerization Mechanism According to McCullough[6] and Yokozawa.[10,11]



Scheme 2. Catalyst-Transfer Polymerization from Small Molecule Initiators According to Kiriy et al.[15]



Experimental Section

Instrumentation and Materials. ^{1}H NMR spectra were obtained on Bruker AV-500 spectrometer using $CDCl_3$ as a solvent (peak position $\delta(^1H) = 7.27$ ppm) and internal standard of ^{1}H NMR spectra was tetramethylsilane (0.00 ppm). 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 reflection mode. The % initiation efficiency 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 % initiation efficiency. 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. 2-Bromo-3-hexylthiophene, $Ni(PPh_3)_4$, $Ni(PPh_3)_2Cl_2$, triphenylphosphine, *n*-butyllithium (^{n}BuLi), isopropylmagnesium chloride (^{i}PrMgCl), and all initiators besides methyl 4-bromobenzoate were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) was dried using a solvent drying system from Innovative Technologies. All polymerizations were performed under N_2.

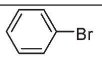
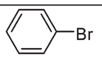
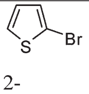
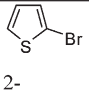
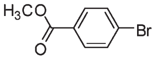
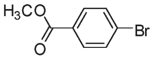
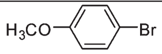
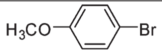
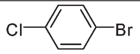
Synthetic Procedures. 2-Bromo-3-hexyl-5-iodothiophene (**1**) was synthesized according to synthetic procedures.[11] All experiments involving $Ni(PPh_3)_4$ were performed according to previously published procedures.[28]

General Procedure for the Generation of Ni(PPh$_3$)$_4$ Catalyst in Situ. All glass apparatuses were dried prior to use. $Ni(PPh_3)_2Cl_2$ (2 mol %) and PPh_3 (4 mol %) were added to the flask and the atmosphere was replaced with nitrogen. Dry THF (5 mL) was added to the mixture and solution was stirred for 20 min. Bromobenzene (20 mol %) was added and the mixture was stirred for 1 h. The amounts of other initiators varied between 20 to 50 mol % however, the amount used did not affect the experimental outcome.

General Procedure for Generation of Organolithium Initiator. All glass apparatuses were dried prior to use. Bromobenzene (2 mol %) and THF (5 mL) were added to the reaction flask and the atmosphere was replaced with Nitrogen. The mixture was cooled to −78 °C with dry ice/acetone bath and ^{n}BuLi (2 mol %) was added to the reaction flask. The mixture was stirred for 1 h at −78 °C. A suspension of $Ni(PPh_3)_2Cl_2$ (2 mol %) in THF (5 mL) was added to the mixture and stirred for 1 h.

General Procedure for the Polymerizations. Addition of reagents into the reaction flask was carried out via a syringe under a stream of nitrogen. 2-bromo-3-hexyl-5-iodothiophene (**1**) (500 mg, 1.34 mmol, 30 equiv) was placed in the flask and atmosphere was replaced with nitrogen. Into the flask was added dry THF (5.0 mL) and the mixture was stirred at 0 °C. Isopropylmagnesium chloride (^{i}PrMgCl: 2.0 M solution in THF, 0.64 mL, 1.28 mmol, 29 equiv) was added dropwise and the mixture was stirred at 0 °C for 1 h. The catalyst/initiator solution (1 equiv with respect to Ni) was then added to the mixture and was allowed to

Table 1. Results of P3HT Polymerization with Various Initiators Using $Ni(PPh_3)_4$ and $Ni(PPh_3)_2Cl_2$[h]

Entry	Initiator	Catalyst	Yield	End Groups[a]	M_n[b] (Da)	PDI[c]	rr[d] (%)	% Initiation[a,d,e]
1	 Bromobenzene	$Ni(PPh_3)_4$	43%	Phe/H (41%) Phe/Br (24%) Br/Br (34%)	5000 (5200)	1.8	89	65%
2	 Bromobenzene	$Ni(PPh_3)_2Cl_2$	62%	Phe/H (60%) Phe/Br (29%) H/H (11%)	8400 (9500)	1.6	92	89%
3	 2-Bromothiophene	$Ni(PPh_3)_4$	45%	Thiophene/Br (60%) Thiophene/H (12%) Br/Br (28%)	5500[f]	1.5	85	72%
4	 2-Bromothiophene	$Ni(PPh_3)_2Cl_2$	51%	Thiophene/Br (56%) Thiophene/H (15%) Br/Br (29%)	6700[f]	1.3	93	71%
5	 Methyl 4-bromo-benzoate	$Ni(PPh_3)_4$	35%	Benz/Br (12%) Benz/H (10%) H/H (9%) Br/Br (21%) H/Br (48%)	6700 (4300)	1.4	93	22%
6	 Methyl 4-bromo-benzoate	$Ni(PPh_3)_2Cl_2$	53%	Benz/Br (33%) Benz/H (9%) H/Br (40%) Br/Br (18%)	6700 (4200)	1.6	91	42%
7	 4-Bromoanisole	$Ni(PPh_3)_4$	40%	H/Br (72%) Br/Br (28%)	4200[g]	2.1	93	0%
8	 4-Bromoanisole	$Ni(PPh_3)_2Cl_2$	41%	Anisol/Br (10%) H/Br (62%) Br/Br (28%)	8400[g]	1.6	95	10%
9	 4-Bromo-chlorobenzene	$Ni(PPh_3)_2Cl_2$	58%	Cl-Phe/Br (27%) Cl-Phe/H (10%) H/Br (36%) Br/Br (27%)	6900 (5600)	1.6	90	37%

[a] Based on MALDI−TOF data. [b] M_n was obtained using both GPC and NMR (number in parentheses corresponds to the value obtained by NMR). [c] Based on GPC data. [d] Obtained by NMR. [e] The initiation efficiency for the purpose of this work was calculated using the distribution of products and we have not taken the yield of the polymerization into account. The reaction mixture at the end of the polymerization contains starting material, initiated as well as noninitiated oligomers, and polymer. We have assumed that the oligomers would have initiated at the same ratio as the polymers; [f] The M_n for the thiophene initiated P3HT is based on GPC alone since the end-capped thiophene peak overlaps with rr-P3HT backbone peak. [g] The initiation efficiency was too low for the end-group to be visible by NMR. [h] All polymerizations were carried out using 30:1 ratio of monomer to Ni ($M_{n,calc}$ = 5000 Da) except for entry 2 which used 50:1 monomer:Ni ratio ($M_{n,calc}$ = 8400 Da).

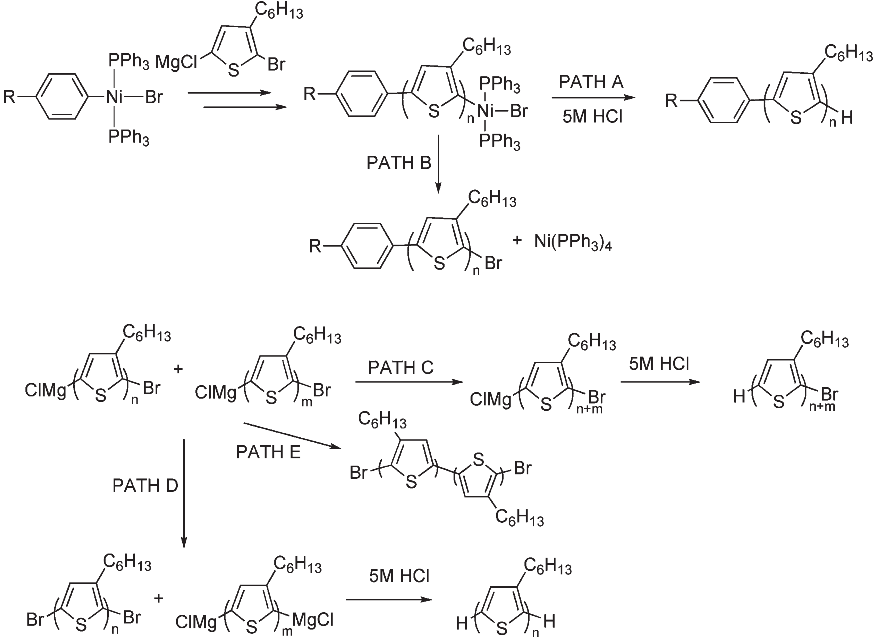
polymerize for 6 h at room temperature. The mixture was then precipitated into MeOH, the polymer was isolated via filtration and washed with hexane to provide initiated poly(3-hexylthiophene) as a purple solid (typical yield varied between 90 and 133 mg, 40−60%); δ_H(500 MHz; $CDCl_3$; Me_4Si) 6.98 (s, 1H), 2.78 (m, 2H), 2.65 (m, 0.3 H), 1.67 (s, 4H), 1.35 (t, 8H) and 0.92 (s, 4H). The small peaks between δ 7.4−8.1 are attributed to the initiator and the magnified spectra are displayed in Figure 1.

Results and Discussion

Chain-Growth vs Step-Growth Polymerization. Chain-growth polymerizations with "living" character are vastly different from the step-growth mechanisms. If the chain-growth polymerization is also a living polymerization, the P3HT product will only have one set of terminal end groups, a PDI approaching 1, the molecular weight that can be easily tuned by manipulating catalyst/monomer feed ratio and almost exclusively head-to-tail regioregularity (~98%).[31,32] However, the majority of chain-growth polymerizations catalyzed by $Ni(PPh_3)_4$ are not "living" due to the high activity of the catalyst which often leads to undesired side chain-termination or chain transfer reactions.[30]

Scheme 3 illustrates all the various pathways that can occur during a poly(3-hexylthiophene) polymerization.

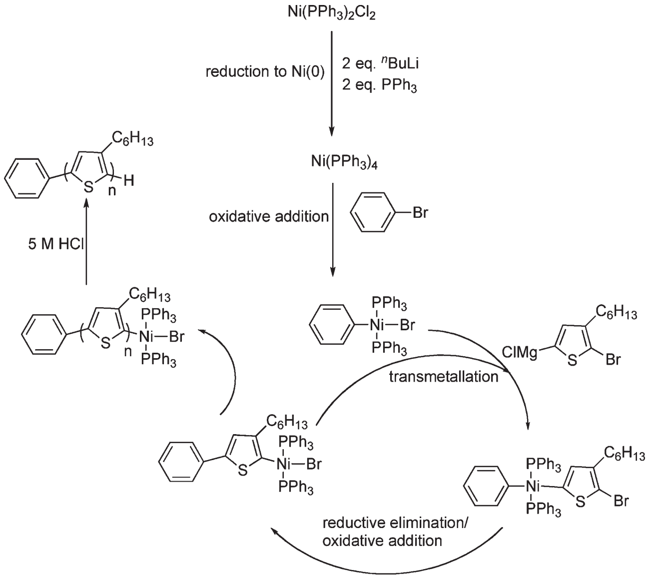
Scheme 3. Various Pathways to Terminal Groups



Path A represents the "ideal" catalyst transfer polymerization, where the one Ni catalyst molecule propagates through one polymer chain with addition of monomer one at a time after which the reaction is quenched with acid and initiator/H end groups are observed. Path B illustrates an early chain termination step, where the polymerization still occurs from the initiator molecule, however the catalyst reductively eliminates from the polymer chain before complete conversion of the monomer is reached leading to Initiator/Br terminal groups. Various end groups in paths C−E result from a step-growth mechanism catalyzed by the escaped Ni(0). Path C shows the end groups corresponding to H/Br result from the protonation of the terminal Grignard reagent upon quenching the reaction with HCl. Bromine−magnesium exchange has been previously observed on thiophene monomers.[33] Similarly, oligomeric and polymeric Grignard species may also undergo metathesis provided that the products are of greater stability. Long polymer chains are likely to undergo metathesis with shorter fragments leading to H/H and Br/Br terminal groups (path D). If the terminal groups are the Ni catalyst and the Grignard moiety, quenching the polymerization reaction will lead to H/H groups. Finally, Br/Br end groups can occur from a homocoupling process between Grignard reagents on different polymer chains (path E). These pathways will be referred to in our paper to explain the polymerization results.

Alternative Initiation Method. Since the prospect of employing $Ni(PPh_3)_4$ catalyst was unappealing we focused our attention on creating a novel procedure for the generation of catalyst/initiator complex. $Ni(PPh_3)_2Cl_2$ is a widely used catalyst which is inexpensive and air stable, and actively used in small molecule syntheses.[34,35] Based on these factors, we chose to use it as a catalyst precursor for the reaction. $Ni(PPh_3)_2Cl_2$ is easily reduced with 2 eq of ^{n}BuLi in the presence PPh_3 ligand to form the highly active Ni(0) catalytic species *in situ*[36] which immediately reacts with the aryl halide initiator present in the solution to yield the catalyst/initiator complex (Scheme 4). The monomer was then added directly to the mixture without further isolating the Ni complex. The catalyst cycle begins with the catalyst/initiator complex undergoing transmetalation reaction with Grignard functionalized thiophene monomer, then inserting into the C−Br bond at the growing polymer chain end.

Scheme 4. Catalytic Cycle of $Ni(PPh_3)_2Cl_2$



In order to test this new initiation method, the polymerization was attempted with 20 mol % of bromobenzene initiator and 2 mol % of $Ni(PPh_3)_2Cl_2$ (target M_n = 8400 Da). As mentioned previously, the molecular weight of the P3HT obtained is proportional to the amount of Ni catalyst used. We deliberately targeted a low molecular weight so that the initiator molecule on the polymer would be clearly visible by NMR. It is interesting to note that, despite using a large excess of the bromobenzene, polymerization proceeds confirming the chain-growth, catalyst transfer polymerization mechanism of rr-P3HT. If the polymerization occurred through primarily a step-growth mechanism, the polymerization would have been terminated. According to MALDI−TOF results as shown in Figure 1b, ~90% of P3HT is terminated by the phenyl group from one side and either hydrogen or bromine atoms on the opposite side (60% Phe/H and 29% Phe/Br). The rest of the peaks correspond to H/H terminated P3HT. Integrating the peaks in the ^{1}H NMR spectra (Figure 1a) provided us with a similar quantitative result. When chlorobenzene was used as the initiator, similar results to bromobenzene were obtained where ~90% of P3HT was initiated from the phenyl group.

The molecular weight of the polymer was determined by GPC and NMR ($M_{n,GPC}$ 8400 Da; $M_{n,NMR}$ 9500 Da; PDI 1.6) providing a molecular weight that was expected. Based on this, we hypothesized that P3HT polymerization with a higher monomer to catalyst ratio would yield a polymer with larger molecular weight. We attempted to test this hypothesis by performing a P3HT polymerization with a 100 equivalent of monomer to a catalyst (target molecular weight: 16 600 Da). However, the GPC results revealed a much lower than expected molecular weight ($M_{n,GPC}$ 8300 Da; $M_{n,NMR}$: 10 100 Da; PDI 1.6) causing us to conclude that the polycondensation is no longer controlled, when using PPh_3 as a ligand, at DPs higher than 50 due to termination and chain-transfer reactions[30] such as paths B−E depicted in Scheme 3. The end group analysis shows the presence of Phe/Br end groups, which are indicative of the catalyst-transfer termination step (Scheme 3, path B). In such a case, the Ni catalyst reductively eliminates from the initiated polymer chain to transform back to Ni(0), and diffuses into the bulk reaction mixture. It then undergoes oxidative addition to another monomer and initiates a new polymerization yielding a polymer chain with H/H end groups after quenching (Scheme 3, path D), which is also present in our polymer according to our MALDI−TOF data. We have attempted to utilize another method where the oxidative addition step is eliminated altogether and the main focus is increasing the reactivity of the initiator. This was accomplished by the generation of a highly active aryl lithium reagent (Scheme 5).

The generation of organolithium reagent has proved to be successful with $Ni(PPh_3)_2Cl_2$ catalyst yielding a polymer, 86% of which had a phenyl initiator group (Phe/H: 64%, Phe/Br: 22% and H/H:14%) (Supporting Information: Figure 2). With both methods, $Ni(PPh_3)_2Cl_2$ provided us with successful results where almost 90% of P3HT polymer was initiated from the phenyl group at room temperature, therefore we have utilized this catalyst for the following study of various initiators.

Polymerization from Various External Small-Molecule Initiators. We began by repeating the experiments performed by Kiriy et al. with the $Ni(PPh_3)_4$ catalyst. The results for polymerization with various initiators utilizing $Ni(PPh_3)_4$ and $Ni(PPh_3)_2Cl_2$ catalyst are summarized in Table 1. While Kiriy's group performed the filtration and purification step to isolate the catalyst/initiator complex **2**, we also investigated the possibility of eliminating these steps and performing a one-pot polymerization. In our hands, the one-pot polymerization procedure yielded better results and so these are shown in Table 1. When using $Ni(PPh_3)_4$, although the thiophene and bromobenzene initiation experiments were successful (Table 1, entries 1 and 3), variable results were obtained for the other initiators especially when filtration steps were involved in the experimental procedure. Polymerization had completely failed when we attempted to use the $Ni(PPh_3)_4$ complex with 4-bromoanisole (Table 1, entry 7) and the purified methyl 4-bromobenzoate/$Ni(PPh_3)_4$ complex. When comparing both methods of initiation, it is worthwhile to note that the polymers synthesized using our method are of better quality. Specifically, initiation using $Ni(PPh_3)_2Cl_2$ generally provides higher polymerization yields, higher molecular weights and lower PDI, better regioregularity and/or improved percent initiation especially for more complex initiators (compare entries 1 vs 2, 3 vs 4, 5 vs 6, and 7 vs 8).

From the results presented in Table 1, it can be clearly seen that as electron-withdrawing groups (EWG) and electron-donating groups (EDG) are introduced onto the phenyl ring, the initiation efficiency changes. Oxidative addition was expected to become the crucial step in the formation of the aryl halide/initiator complex **2** and the initiation efficiency is largely determined by the type of the functional group on the

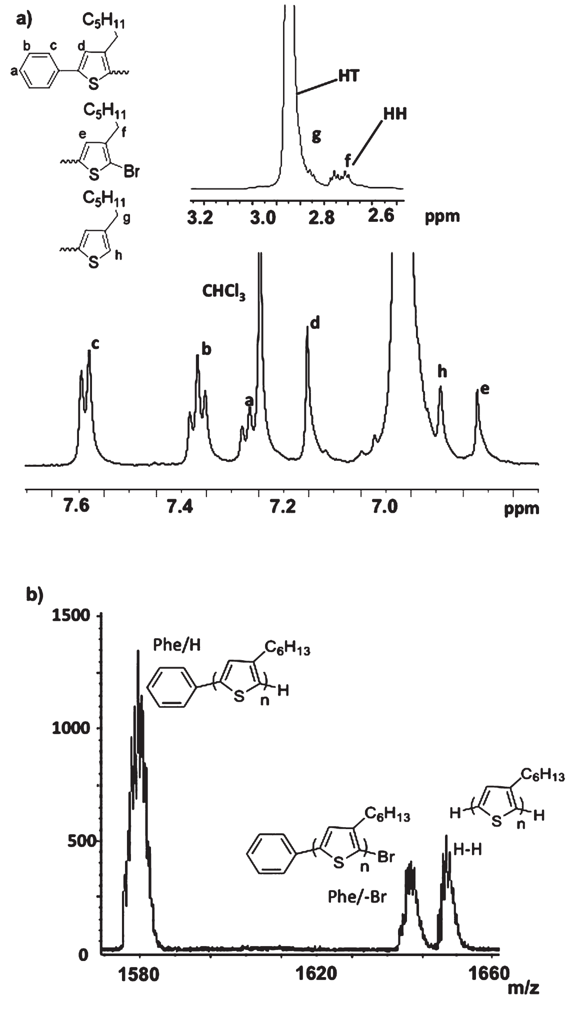
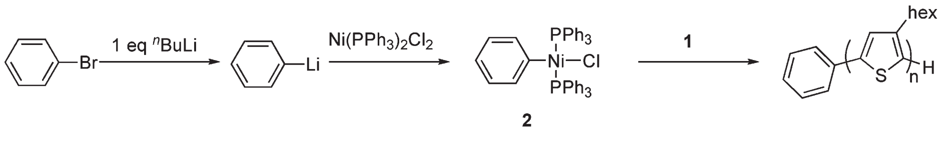


Figure 1. (a) ^{1}H NMR and (b) MALDI−TOF spectra of P3HT obtained upon the polymerization of **1** with $Ni(PPh_3)_2Cl_2$ catalyst and bromobenzene initiator.

Scheme 5. Transmetallation Reaction of Organolithium Reagent with Ni(II) Catalyst



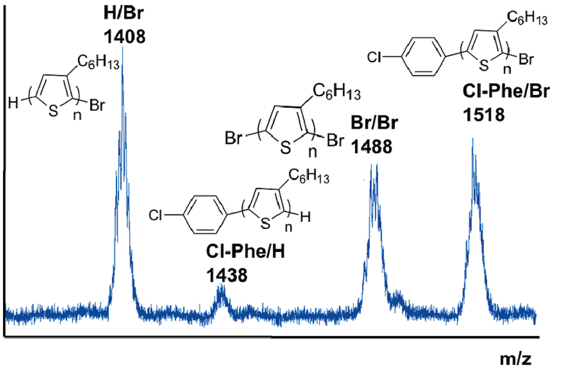


Figure 2. MALDI–TOF spectrum of P3HT polymerization performed with 4-bromochlorobenzene external initiator.

phenyl ring. Oxidative addition occurs faster with EWGs on the phenyl ring and slower with EDGs on the ring, since the electron-rich Ni(0) catalyst would prefer to insert into an R–X bond with minimal electron density.[37] Therefore, we predicted that initiation efficiency would be higher for EWG aryl halides than for EDG initiators.

In addition to this, it was hypothesized that 4-bromochlorobenzene (Table 1, entry 9) would initiate via catalyst insertion into the more reactive C–Br bond. The MALDI–TOF spectrum of P3HT polymerization from 4-bromochlorobenzene initiator (Figure 2) shows that the sample consists of four different polymer fractions.

The four different polymer end groups were calculated to be H/Br (36%), Br/Br (27%), Cl–Phe/Br (27%), and Cl–Phe/H (10%) showing that 37% of the polymer chains had initiated from the aryl halide. Approximately 37% of P3HT molecules had a chlorophenyl initiating group, indicating that, as expected, the C–Br bond is more susceptible toward oxidative addition. It was surprising to see that initiation efficiency was much lower than for nonfunctionalized aryl halide (37% vs 88%). It is unlikely that this difference is due to the oxidative addition step issues, since EWGs such as halides on the phenyl ring should theoretically enhance this reaction. Two probable factors are the stability and reactivity of the formed catalyst/initiator complex. Due to either of the above reasons, the majority of the Ni catalyst disassociates from the phenyl group and initiates the polymerization via step-growth mechanism leading to a variety of terminal groups such as H/Br, Br/Br and H/H depicted by paths C, D, and E in Scheme 3.

Initiators with other EWG were tested to see if the type of the functional group (i.e., halide, ester, or phosphate ester) on the phenyl ring made a difference. Two different polymerization reactions were carried out with methyl 4-bromobenzoate. The reduction of Ni(PPh$_3$)$_2$Cl$_2$ was performed with 2 and 4 equiv of ^{n}BuLi. When 2 equiv of ^{n}BuLi was used to reduce the catalyst which was subsequently employed in the polymerization, the product had the following distribution of terminal groups (Br/Br 34%; H/Br 42%; Benz/Br 24%) with $M_{\mathrm{n,GPC}} = 4100$ Da, $M_{\mathrm{n,NMR}} = 3600$ Da, and PDI = 1.6 (Supporting Information: Figure 3). When 4 equiv of ^{n}BuLi was used, the initiation efficiency increased from 24% to 42% as shown in Table 1, entry 6. The molecular weight increased as well ($\mathrm{M}_{\mathrm{n,\ GPC}}$ 6700 Da; $M_{\mathrm{n,NMR}}$ 4,200 Da; PDI 1.6). The MALDI–TOF spectrum of this polymerization is shown in Figure 3.

Since the initiation efficiency almost doubled when using 4 equiv of ^{n}BuLi, it is believed that exactly 2 equiv of ^{n}BuLi functions purely to reduce the Ni catalyst, while the rest goes on to react with the excess of functionalized aryl halide initiator present in the solution. Since the nickel catalyst tends to reductively eliminate early from the polymer chain, instead of starting a new step growth polymerization, the catalyst reacts with the generated organolithium initiator via transmetalation reaction thereby doubling the initiation rate. Lowering the temperature of polymerization to 0 °C decreased the % initiation to 14%.

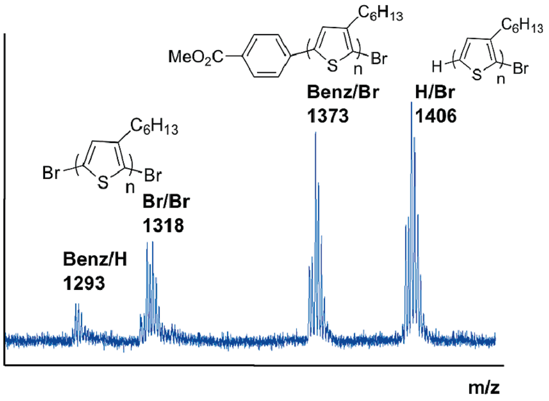


Figure 3. MALDI–TOF spectrum of P3HT polymerization with methyl 4-bromobenzoate.

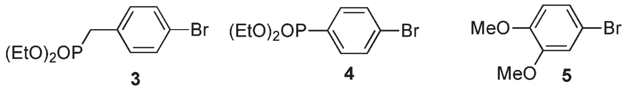


Figure 4

The last two initiators with EWGs on the phenyl ring were 4-bromobenzyl diethyl phosphate ester **3** and 4-bromophenyl diethyl phosphate ester **4** (Figure 4). P3HT polymerization completely failed to initiate from both of these molecules under all experimental conditions. In all attempts, P3HT polymers were obtained with varying percentages of H/Br (65–80%), Br/Br (12–27%), and H/H (12–40%) end groups. The molecular weights of the resulting polymer ranged from 1400 to 5900 Da while the PDIs ranged from 1.6 to 2.4 depending on the reaction conditions. Both NMR and MALDI data show that the esters and phosphate esters do not react with ^{n}BuLi or the Grignard. The complete lack of initiated polymer indicates that the oxidative addition of the catalyst to the initiator does not occur at all perhaps due to unfavorable interactions of nickel with phosphorus, or oxidative addition step proceeds smoothly and the phosphate ester moiety fully destabilizes the initiator/catalyst complex leading to its immediate dissociation in the solution.

The remaining initiators, 4-bromoanisole (Table 1, entry 8) and 4-bromoveratrole (**5**) had one or two electron donating methoxy groups respectively on the phenyl ring. It is known that the rate of oxidative addition is reduced by the presence of electron donating groups, therefore it was not at all surprising when 4-bromoveratrole (**5**) completely failed as the initiator under all experimental conditions. Instead, noninitiated P3HT was obtained with different percentages of end groups (H/H 0–86%, Br/Br 0–55%, and H/Br 13–45%) with M_{n} ranging from 1000 to 4900 Da and varying PDIs. A very small percentage of initiation was observed with 4-bromoanisole (Table 1, entry 8). MALDI–TOF shows that the polymer end groups correspond to H/Br (62%), Br/Br (28%), and Anisol/Br (10%). The M_{n} was 8400 Da with a PDI of 1.6. Thiophene (Table 1, entry 4) had the second best performance as the initiator with 71% of the resulting polymer bearing an initiator group. The chain-termination mechanism (path B) was predominant for this type of the initiator as the majority of the polymer chains had the thiophene/Br terminal groups versus the thiophene/H ends. It is worthy to note that the polymers obtained with our method of reducing $Ni(PPh_3)Cl_2$ catalyst were of superior quality than the polymers produced with $Ni(PPh_3)_4$. The yields and the molecular weights were higher, and the regioregularity was better compared to previously published results.

The Nature of the Catalyst/Initiator Complex 2. Since both the initiation protocols using $Ni(PPh_3)_4$ and $Ni(PPh_3)_2Cl_2$ should result in the formation of the same catalyst/initiator complex **2**, it is somewhat surprising that the two methods produce different results for the polymerization. Locklin et al. have also observed a difference in polymerization when either $Ni(PPh_3)_4$ or $Ni(COD)_2$ with $(PPh_3)_4$ was used for a surface-initiated polymerization of polythiophene, and did not observe polymerization when $Ni(PPh_3)_4$ was used.[29] It is commonly assumed that arylnickel(II) intermediates are formed by the oxidative addition of the Ni into the aryl halide. However, Kochi et al. have shown that the exact nature of the Ni is quite complex, and the Ni can be in a number of different oxidation states (0, +1, +2, or +3) depending on the halide and solvent used.[38] Other researchers have also studied the controversial nature of the Ni catalyst.[39,40] We have attempted to study the nature of the intermediates by following the reaction by NMR as well as GC−MS, but these results confirm the complexity of the Ni species involved and the spectra are very difficult to decipher. We are in the process of isolating the intermediates involved in the polymerization and will discuss these results in another paper.

Conclusion

We have developed a new method for the initiation of rr-P3HT with $Ni(PPh_3)_2Cl_2$ catalyst, and the ability of various aryl halides with different substituents on the phenyl ring to function as the external initiators for P3HT polymerization was studied. The new method provides a more facile method to initiate the polymerization and yields polymers that have improved properties than those synthesized with $Ni(PPh_3)_4$ catalyst. The polymers obtained with our method have higher yields, larger molecular weight, lower PDIs, better regioregularity and higher % initiation from external small molecule initiators. We are currently in the process of isolating intermediates of the polymerization to identify why this is the case and this will be the subject of another paper. Polymerization from nonfunctionalized initiators showed predominantly chain-growth characteristics, while polymerization from initiators with electron donating and electron withdrawing functionalities on the phenyl ring had variable mixture of chain growth and step-growth mechanisms. The % initiation values and the reactivity trend reveal that oxidative addition of the Ni(0) catalyst to the C−Br bond of the initiator is not the crucial step. If that were the case, the reactivity trend would be initiators w/EWG > nonfunctionalized initiators > initiators w/EDG. The mere presence of another functionality on the phenyl ring decreases the initiation rate by a least 50%. This is likely due to the position of the functional group on the initiator. The para position likely lacks the stabilization effects of lowering the energy of the highest filled orbital by bonding the d_{xy} orbitals of Ni with π^* orbitals of the aromatic ring, therefore these type of initiators are more prone to catalyst disproportionation leading to undesired side reactions.[25] These results provide an improved understanding of the initiation/polymerization mechanism of P3HT which is vital for making the catalyst-transfer polymerization process a more general reaction for π-conjugated polymers. Future experiments will focus on improving the catalyst system via utilization of different ligands on the nickel catalyst and the study of intermediates, so that a more controlled polymerization can be achieved.

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Supporting Information Available: Figures showing MALDI−TOF and ^1H NMR spectra and SEC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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