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Steric Stabilization Effects in Nickel-Catalyzed Regioregular Poly(3-hexylthiophene) Synthesis

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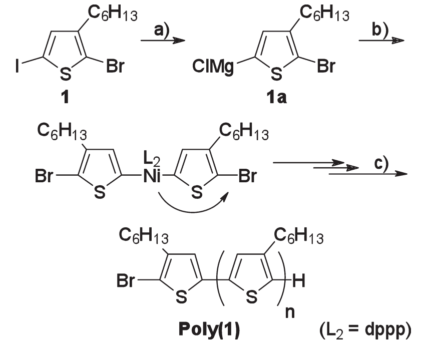
Thiophene-based conjugated polymers have recently received widespread attention for use in organic electronic devices. Poly(3-hexylthiophene) (P3HT) in particular has become the p-type polymer workhorse of the field due to its combination of relative high thermal and environmental stability, high charge mobility, low bandgap, and high solubility.[1−16] Regiocontrolled synthetic techniques have been developed by McCullough[17] and Rieke[18,19] via metal-catalyzed dehalogenation polymerization, and the electronic properties of these highly regioregular P3HT have proven to be superior to those of regiorandom polythiophenes. More recently, Yokozawa et al. have further developed the synthetic procedure, using a Kumada catalyst-transfer chain polymerization, achieving a well-defined polymer with narrow polydispersity, controlled molecular weight, regioregularity, and good control over the end groups of the resulting polymer (Scheme 1).[8,20,21]

Scheme 1. P3HT Polymerization Mechanism[a] According to Yokozawa et al.[8]



[a] Key: (a) ^{i}PrMgCl, THF, 0 °C, 1 h; (b) Ni(dppp)Cl$_2$, THF, RT, 4 h, (c) 5 M HCl.

The development of this controlled chain-growth polymerization method for P3HT is a great advance in the state of the art; however, much about the polymerization mechanism is based on speculation, as intermediates have not yet been isolated. A full understanding of the polymerization is necessary for expansion of these techniques to be able to utilize different monomers in a controlled polymerization, and to be able to synthesize more complex shapes such as star-shaped polymers, hyperbranched polymers, and block copolymers.

Recently published work in our group as well as others,[22−25] in which P3HT was polymerized from various externally added functionalized aryl halide initiators, indicates strongly that oxidative addition of the Ni(0) catalyst into the C−Br bond of the initiator is strongly dependent on the position of the functionality on the aryl group. We found that functionalization of the initiator at the *para* position with any kind of electron-withdrawing group (EWG) or electron-donating group (EDG) resulted in significant decreases in initiation efficiency,[24] while placing a substituent *ortho* to the halogen resulted in a quantitative initiation.[22] This led us to suspect that this *ortho*-stabilization is a major factor in the controlled synthesis of P3HT. Work by Kiriy et al. in which P3HT was synthesized from various mono- and oligothiophenes used as monomers,[26] further supports our theory. In their work, polymers made with oligothiophenes that had alkyl chains *ortho* to the terminal Br exhibited significantly higher percent conversion, average molecular weight, percent initiation, and a narrower polydispersity compared to polymers made from oligothiophenes lacking an *ortho*-substituent.

Work by Uchida et al.[27] indicated that in the formation of aryl−Ni(II) complexes, *ortho*-substitution of the aromatic ligand resulted in a dramatic increase in the stability of the Ni complex. This *ortho*-substituent was considered to hold the aryl ligand perpendicular to the plane of the Ni(II) complex, and in so doing increased the stability by allowing interaction between the aryl π^* and Ni d_{xy} orbitals, as well as steric blocking of other coordination sites. Applied to P3HT polymerizations, the net effect of all this extra stabilization would be to promote adherence of the Ni catalyst on the chain end and reattachment onto the end of the same chain immediately after coupling with a new monomer. In addition, the additional steric blocking of other coordination sites would also assist in preventing head-to-head coupling of monomer units. In work by McCullough et al.,[28] this steric hindrance is the main explanation used to explain the high regioregularity (95−97%) of a polymer with low polydispersity, even when metalation of the monomer yields a 85:15 mix of 5- to 2-Grignard reagent; we would argue that the *o*-alkyl stabilization of the propagating Ni catalyst complex also plays a major role in the high degree of control in observed in the polymerization.

In this communication, we report the synthesis of a new thiophene monomer, in which the 2- and 5-substituted halogen moieties are reversed, and the use of this monomer in initiation studies to further elucidate the mechanism of polymerization of regioregular P3HT by the Ni(dppp)Cl$_2$ catalyst.

Results and Discussion. A reversed thiophene monomer (with I and Br functionalities reversed with relation to the usual monomer used in Kumada catalyst transfer polymerization) was synthesized via a published procedure by lithiation with 1.1 equiv of *n*-butyllithium and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (TMEDA) in diethyl ether, under which condition the lithiation occurs preferentially at the carbon γ to the hexyl chain (Scheme 2).[29] After distillation of the 2-bromo-3-hexylthiophene isomer and 2,5-dibromothiophene side-product from the desired product (resulting in significant losses and overall low product yield), iodination was accomplished via a standard iodination procedure with iodine and iodobenzene diacetate in dichloromethane.

Polymerization Results. Use of the reverse monomer **2** in a polymerization (Scheme 3) performed side-by-side with one using a regular monomer **1** yielded absolutely no polymer at

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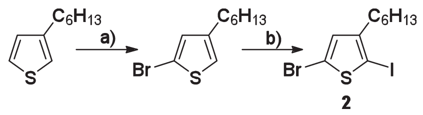
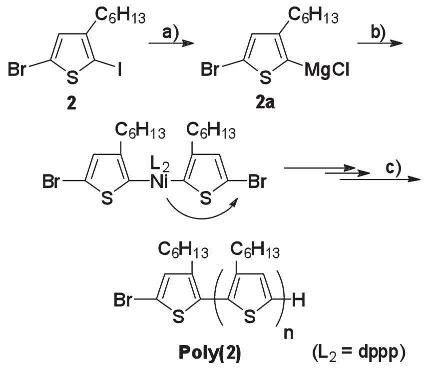
Scheme 2. Synthesis of Reversed Monomer[a]



[a] **Key: (a) (i) *n*-BuLi, TMEDA, Et$_2$O, −78 °C → reflux, 30 min, (ii) CBr$_4$, Et$_2$O, −78 °C, 8 h; (b) I$_2$, PhI(OAc)$_2$, DCM, RT, 4 h.**

Scheme 3. Polymerization of Reverse Monomer[a]

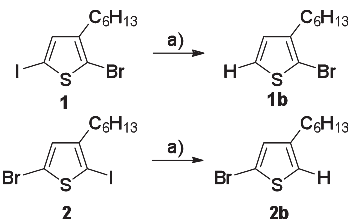


[a] **Key: (a) ^{i}PrMgCl, THF, 0 °C, 1 h; (b) Ni(dppp)Cl$_2$, THF, RT, 4 h; (c) 5 M HCl.**

all, whereas the polymerization using the regular monomer **1**, yielded H−Br and H−H terminated P3HT as expected. The simple failure of the reversed monomer to form a P3HT polymer was informative, but it provided no information on which process failed in the polymerization; for this reason, we investigated the different initiating steps involved in the polymerization (Grignard formation followed by initiating dimer formation) to elucidate where the polymerization was failing.

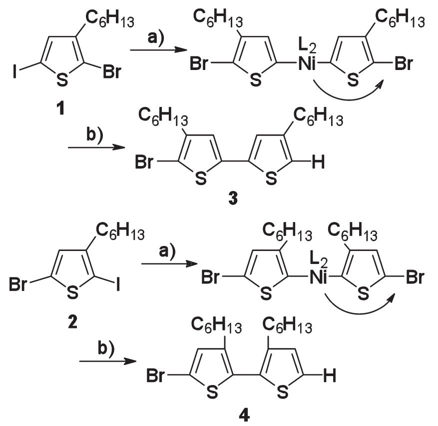
Monomer Quenching Results. Before isolation of the bithiophene initiators, it was first deemed necessary to determine that the Grignard was indeed forming in a good yield, and to determine for certain what the regiochemistry of the activated Grignard thiophene monomer was (Scheme 4). The reaction of ^{i}PrMgCl with monomers **1** and **2** followed by quenching with 5 M HCl resulted in near-complete conversion to quenched monomers **1b** and **2b** (a small amount of 3-hexylthiophene was also observed), as shown by GC−MS and ^{1}H NMR. It was considered possible that although the iodine is more vulnerable to attack by Grignard reagents, steric hindrance of the *ortho*-hexyl chain in **2** could result in a measurable amount of 2-iodo-3-hexylthiophene; however, this was not observed.

Scheme 4. Initiated Monomer Quenching[a]



[a] **(a) (i) ^{i}PrMgCl, 0 °C, 1 h; (ii) 5 M HCl.**

Scheme 5. Bithiophene Initiator Formation[a]

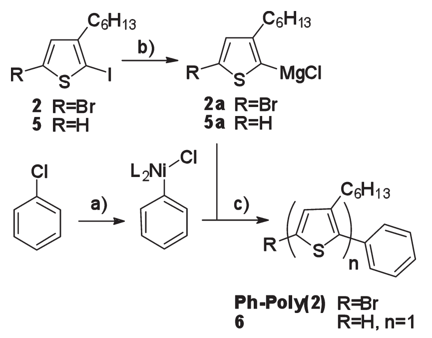


[a] **Key: (a) (i) ^{i}PrMgCl, THF, 0 °C, 1 h, (ii) 0.5 equiv of Ni(dppp)Cl$_2$, THF, 0 °C → RT, 4 h; (b) 5 M HCl.**

Bithiophene Initiator Formation. In order to more closely investigate differences in the initial stages of polymerization of regular and reversed monomers **1** and **2**, the initiating bithiophene species were isolated following a procedure used by Yokozawa et al. (Scheme 5).[8] Grignard-activated monomers **1a** and **2a** (2 equiv) were generated in the usual way by reaction with ^{i}PrMgCl at 0 °C. After 1 h, they were transferred dropwise via cannulae to a suspension of Ni(dppp)Cl$_2$ catalyst (1 equiv) in THF, also stirring at 0 °C, and allowed to react at room temperature for 4 h before quenching with 5 M HCl and extracting with ether. The bithiophene **3** was easily detected as reported in the literature,[8] but bithiophene **4** was not formed in any detectable amount. This is believed to be a result of steric hindrance in the formation of head-to-head coupled bithiophenes. In order to further investigate the failure of dimer formation for the reversed monomer **2**, ^{31}P NMR spectrum (Figure S1, Supporting Information) of the reaction mixture was taken before quenching with 5 M HCl. The NMR shows the presence of 5 different phosphorus containing species, two of which were identified to be Ni(dppp)$_2$ (major peak) and *cis*-chloro(hexylthienyl)bis(dppp)nickel.[22] Because of the difficulty in isolating the intermediates, we have not been able to identify the remaining species. We speculate that the species may be regioisomers of the thiophene−Ni(II)−thiophene complex and/or Ni(0)−arene π complexes.[30] Regardless of the species, the absence of the bithiophene as observed by GC−MS in the quenched mixture, as well as the presence of *cis*-chloro(hexylthienyl)bis(dppp)nickel by ^{31}P NMR, suggests that the bithiophene formation is not observed because the second transmetalation by a thiophene monomer and/or reductive elimination is prevented to a certain extent when a reversed monomer is used.[31−33]

Initiator Formation and Polymerization from Externally Formed Phenyl−Ni(II) Complexes. Difficulty in forming the bithiophene inititator **4** was expected from the large amount of steric hindrance, and gives no information about the subsequent polymerization mechanism. Thus, it was decided to attempt initiation and subsequent polymerization from an externally formed phenyl−Ni(II)−Cl complex because an unsubstituted phenyl ring was considered to present a minimum of steric interaction (Scheme 6) using a procedure developed in our group. First, reverse monomer analogue **5** was coupled to the phenyl-Ni(II) complex to form **6**; analysis by GC−MS showed its presence. Then, polymerization of **2** via the same procedure was attempted, but yielded no polymer. Apart from the phenyl thiophene dimer formation, no other products were observed by GC−MS. ^{31}P NMR analysis (Figure S1; Supporting Information) of the reaction mixture prior to quenching with 5 M HCl showed the presence of free PPh$_3$ and excess dppp as well as free Ni(dppp)$_2$[10,22] showing that Ni(0) reductively eliminates after

Scheme 6. Initiation of Analogous Dimer Formation and Polymerization From Chlorobenzene Initiator[a]



[a] Key: (a) (i) $Ni(PPh_3)_4$, RT, 10 h, (ii) dppp, RT, 3 h; (b) $^{i}PrMgCl$, THF, 0 °C, 1 h; (c) (i) 0 °C → RT, THF, 2−4 h, (ii) 5 M HCl.

dimer formation but does not undergo oxidative addition to any remaining monomer. Use of this method allowed us to separate the sterically hindered formation of **4** from the propagation of the polymer itself. Thus, the inability of **2** to polymerize and form **Ph−Poly(2)** is believed to be due to the lack of *ortho*-stabilization in the propagating Ni complex preventing oxidative addition of the nickel into Ar−Br bond.

In conclusion, we have studied the mechanism of Kumada catalyst transfer polymerization of P3HT with $Ni(dppp)Cl_2$, which yields a highly regioregular polymer even under conditions where different regioisomers of the monomer exist in solution. Up until now, this high degree of control has been explained simply by steric hindrance largely preventing formation of head-to-head bithiophene coupling. By synthesizing and using the reverse monomer **2** instead of the commonly used **1**, we have confirmed that steric hindrance does indeed present difficulties in the formation of the head-to-head bithiophene **4** during initiation as proposed by McCullough. In addition, we have also shown that 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 character. We note that others polymers such as poly(*p*-phenylene)[34] and poly(pyrrole)[35] have been synthesized with a high degree of control, while others such as unsubstituted polythiophenes[36] and polyfluorene[37,38] have been synthesized using Ni as a catalyst but with limited control. We speculate that the origin of the lack of control may partly be due to the presence or absence of an *ortho* substituent, and we believe that this is an important monomer design criterion to consider when trying to achieve a controlled polymerization using Ni catalysts. Isolation of the initiating species and kinetic studies are currently ongoing.

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Supporting Information Available: Text giving monomer, polymer, and initiator synthetic details and a figure showing the ^{31}P NMR spectra for the phenyl-initiated reaction and bithiophene initiator reaction using the reverse monomer. This material is available free of charge via the Internet at http://pubs.acs.org.

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