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Externally Initiated Regioregular P3HT with Controlled Molecular Weight and Narrow Polydispersity

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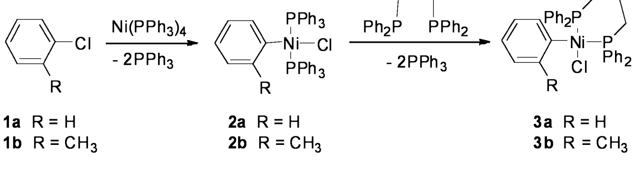
Poly(3-hexylthiophene) (P3HT) remains the most commonly used polymer in organic photovoltaics because of its desirable electronic properties.[1] Both the Yokozawa and McCullough groups have developed methods for the synthesis of highly regioregular P3HT with controlled molecular weights and narrow molecular weight distributions using the 1,3-bis(diphenylphosphino)propanenickel(II) chloride [$NiCl_2$(dppp)]-catalyzed polymerization of Grignard-type monomers.[2,3] The polymerization control is thought to originate from either intramolecular transfer of the Ni catalyst[3] or an associated pair formed by the growing polymer chain and the Ni catalyst.[4] The drawback of this synthetic methodology is that it is not possible to initiate the polymerization from an external moiety, as has been demonstrated for the chain-growth polymerization of polyfluorene.[5] This is necessary for the synthesis of more complex polymer architectures such as brushes and star and block copolymers. There are a small number of examples of externally initiated P3HT,[6,7] including Senkovskyy et al.,[6] who demonstrated chain-growth polymerization of P3HT from both small-molecule and surface initiators. We have also recently investigated methods for the external initiation of P3HT, including the effect of varying the initiating aryl halide.[8] However, these examples all employed the more reactive tetrakis(triphenylphosphine)nickel(0) [$Ni(PPh_3)_4$] catalyst, and while the regioregularity of the synthesized polymer was high, the molecular weight distribution was broad. Furthermore, the polymer end groups were not uniform, which would significantly impair the synthesis of a block copolymer. Consequently, the externally initiated polymerization of P3HT with high regioregularity and narrow polydispersity (PDI) remains a highly desirable goal. We believed that in order to realize this, it would be necessary to employ dppp as the spectrator ligand on the Ni catalyst, as it has been established that its use leads to the greatest degree of polymerization control in nonexternally initiated P3HT synthesis.[3]

Scheme 1



In order to synthesize the desired initiating complexes, $Ni(PPh_3)_4$ was added to neat aryl chlorides **1a** and **1b** at room temperature and left overnight (Scheme 1). Sharp peaks at ~21 ppm were observed in the corresponding ^{31}P NMR spectra (Figure 1a), which indicated the formation of the *trans*-chloro(aryl)bis(triphenylphosphine)nickel(II) complexes **2a** and **2b**.[9] Broad peaks were observed at −6 ppm due to the liberated triphenylphosphine. The broadness indicates exchange processes on the NMR time scale, which can be attributed to residual $Ni(PPh_3)_4$, resulting in rapid ligand exchange with the free triphenylphosphine.

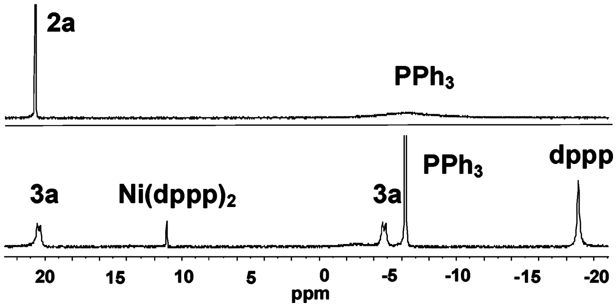


Figure 1. ^{31}P{H} NMR spectra of nickel(II) complexes in chlorobenzene: (top) *trans*-chloro(phenyl)bis(triphenylphosphine)nickel(II) **2a**; (bottom) *cis*-chloro(phenyl)(dppp)nickel(II) **3a**.

Addition of 1.5 equiv of dppp resulted in rapid ligand substitution, which reached completion within 2 h to form the thermodynamically favored *cis*-chloro(aryl)(dppp)nickel(II) complexes **3a** and **3b** (Scheme 1). The cis geometry was confirmed by the appearance of two sets of doublets in the ^{31}P NMR spectra at ~20 and −6 ppm ($J_{P-P} = 44$ Hz) (Figure 1b). The excess dppp was observed at −18 ppm, and the liberated PPh_3 peak became sharp, indicating the absence of exchange reactions. In the case of **3a**, a small amount (~5%) of what is believed to be $Ni(dppp)_2$ was observed; this could be formed by chelation of the residual $Ni(PPh_3)_4$ by dppp.[10] This species was not observed in the synthesis of **3b**.

Polymerization was initiated by addition of the crude complex mixture to a solution of 2-bromo-5-chloromagnesio-3-hexylthiophene in THF at 0 °C followed by stirring at room temperature (Scheme 2). The reaction mixture was quenched with 5 M HCl and precipitated into methanol, after which the polymer was isolated by filtration and washed with methanol and cold hexane.

Addition of complex **3a** (1.43 mol %) to the Grignard-type monomer **4** afforded P3HT with an M_n of 11.2 kDa and a PDI (i.e., M_w/M_n) of 1.1 versus polystyrene standards (Figure 2a). ^{1}H NMR analysis revealed the polymer to be fully regioregular, with the presence of peaks corresponding to the initiating groups [Figures 5 and 6 in the Supporting Information (SI)]. Integration of the initiating peaks with respect to the polymer backbone signals indicated a degree of polymerization of ~63 (conversion = 90%). MALDI-TOF analysis indicated the majority of the peaks to be Ph/H terminated, alongside a small amount of Ph/Br (<5%) and H/H (<1%) termination (Figure 2b and SI Figure 7). The presence of Ph/Br-terminated polymer chains is believed to be due to the partial precipitation of the polymer toward the end of the reaction because of the decreasing solubility of the polymer chain, which subsequently undergoes quenching processes. The H/H-terminated P3HT likely originates from the small amount of $Ni(dppp)_2$ complex that was observed in the crude initiator mixture. Furthermore, as a result of the similarity in the molecular weights of a phenyl group and a bromine atom, it is possible that the major peaks observed

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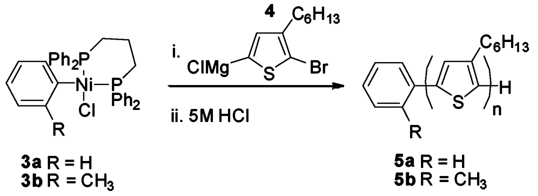
Scheme 2



in the MALDI-TOF spectrum are not exclusively Ph/H-terminated polymer chains but instead a mixture of Ph/H and Br/H end groups. However, on the basis of the good agreement between the M_n value obtained using gel-permeation chromatography (GPC) ($M_n = 11.2$ kDa) and that calculated from the ^{1}H NMR spectrum assuming complete Ph initiation ($M_n = 10.5$ kDa), it is likely that the percentage of Br/H-terminated polymer is very low.

In order to study the polymerization in greater detail, aliquots were taken and analyzed by ^{1}H NMR spectroscopy and GPC. The linear relationship between M_n and % conversion of **4** as well as the narrow polydispersities indicate that the polymerization proceeds through a chain-growth mechanism. Furthermore, there is excellent agreement between the calculated and experimental values (Figure 3).

A polymerization was initiated using 1.43 mol % *cis*-chloro(2-tolyl)(dppp)nickel(II) complex **3b** in order to establish the generality of this synthetic method and, via the methyl substituent on the phenyl ring, to enable facile MALDI-TOF end group analysis of the polymer. The polymerization was quenched after only 1 h in order to avoid precipitation of the P3HT at high conversion, as was observed in the previous experiment. GPC analysis of the polymer again showed a unimodal curve with $M_n = 9.8$ kDa and PDI = 1.2. ^{1}H NMR analysis again revealed that the synthesized P3HT was fully regioregular, and peaks corresponding to the *o*-tolyl group were clearly visible (SI Figures 8 and 9). Integration and comparison of the methyl signal at 2.49 ppm against the signals originating from the alkyl protons on the polymer chain at 2.80 ppm indicated that the polymer consisted of ~55 hexylthiophene repeat units ($M_n = 9.2$ kDa), which is in good agreement with the value obtained by GPC. MALDI-TOF end group analysis revealed only one set of peaks corresponding to Tol/H-terminated P3HT, demonstrating that the polymerization was solely initiated by complex **3a** (Figure 4 and SI Figure 10); this is remarkable, considering that no purification steps were required during the initiator synthesis.

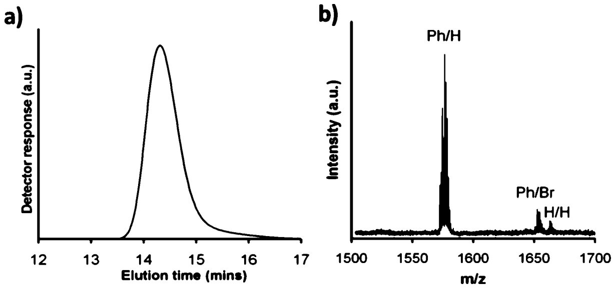


Figure 2. Characterization of P3HT from external initiation using **2a**: (a) GPC chromatogram using THF as eluent; (b) MALDI-TOF mass spectrum using a terthiophene matrix, showing different polymer end groups.

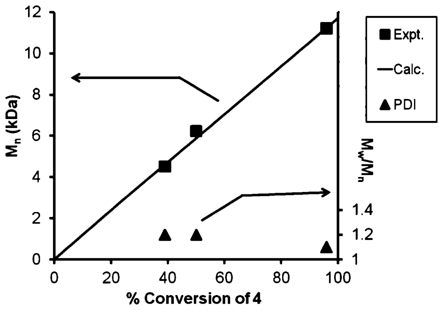


Figure 3. M_n and M_w/M_n (PDI) values for P3HT as functions of monomer conversion. Conversion was determined by ^{1}H NMR analysis; M_n and M_w/M_n were determined using GPC relative to polystyrene standards with THF as the eluent.

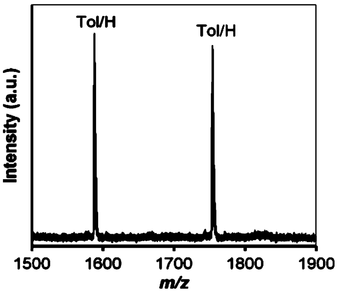


Figure 4. MALDI-TOF mass spectrum (terthiophene matrix) of P3HT possessing only Tolyl/H end groups.

In conclusion, we have successfully initiated the polymerization of **4** from an externally added *cis*-chloro(aryl)(dppp)nickel complex, resulting in fully regioregular P3HT (no peaks corresponding to head−head-coupled thiophenes were observed) with controlled molecular weights and extremely narrow polydispersities. Complete introduction of the initiating aryl group was observed; this should allow the future synthesis of well-defined polymer architectures such as brushes and block copolymers. Isolation of the initiating species and kinetic studies are ongoing.

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Supporting Information Available: ^{31}P NMR spectra for compounds **2a**, **2b**, **3a**, and **3b**; ^{1}H NMR and MALDI spectra for polymers **5a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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