Chain Growth Mechanism for Regioregular Nickel-Initiated Cross-Coupling Polymerizations

Elena E. Sheina, Jinsong Liu, Mihaela Corina Iovu, Darin W. Laird, and Richard D. McCullough*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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Poly(3-alkylthiophenes) are conducting polymers that have good solubility, environmental stability, and processability.[1] The synthesis of regioregular polythiophenes has produced defect-free, structurally homogeneous, head-to-tail coupled poly(alkylthiophenes) (HT-PATs) that have greatly improved electronic and photonic properties over regiorandom analogues.[2,3] Regioregular polythiophenes have led to a multitude of important and novel nano- and microscale electronic materials and devices.[4−7] Very recently, we have developed an end-group functionalization methodology of HT-PATs that allows for the synthesis of a plethora of well-defined block copolymers that form nanowires with high electrical conductivity.[7] Here, we have discovered that the nickel-initiated regioregular polymerization of alkylthiophenes proceeds by a chain growth mechanism and does not occur by the accepted step growth mechanism.[8] We also observed that the degree of polymerization of the synthesized poly(alkylthiophenes) increases with the conversion and can be predicted by the molar ratio of monomer to nickel initiator. On the basis of our experimental results, we predict that nickel-initiated cross-coupling polymerization is essentially a *living* system, giving PATs with low polydispersities (PDIs).

In a cross-coupling step polymerization catalyzed by Ni(dppp)Cl$_2$, one would expect a fast disappearance of the monomer and increase of the polymer molecular weight toward the end of the polymerization.[8−10] On the basis of the experimental results, we observed that relatively high molecular weight polymer forms almost immediately. As a model reaction, we have also found that 2 equiv of a variety of aryl dibromides and 1 equiv of an aryl organometallic (either magnesium or zinc) *always* gives a near quantitative yield of the trimeric aryl and minor amounts (<1%), if any, of the dimer.[11] These results indicate the very strong preference of the Ni(0) (see Scheme 1, intermediate **3**) to form a nondiffusive associated pair, resulting in near 100% formation of the trimer. All of the results indicate that the polymerization proceeds with selective oxidative addition to the growing 2-bromopolythiophene and that these regioregular polymerizations progress by a chain growth mechanism rather than a step growth.

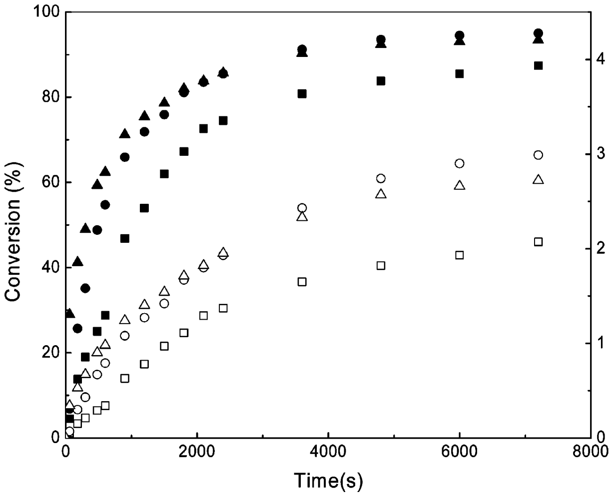

Figure 1. Conversion (filled symbols) and logarithm of monomer concentration (open symbols) vs time plots for 2-bromo-3-hexylthiophene polymerization at different concentration of Ni(dppp)Cl$_2$ initiator (23−25 °C); [M]$_0$ = 0.075 mol/L: (■, □) [M]$_0$:[Ni(dppp)Cl$_2$] = 136:1; (●, ○) [M]$_0$:[Ni(dppp)Cl$_2$] = 57:1; (▲, △) [M]$_0$:[Ni(dppp)Cl$_2$] = 49:1.

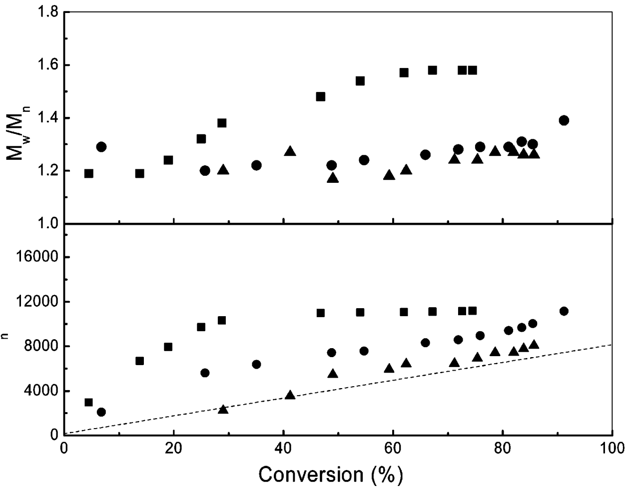

Figure 2. Dependence of molecular weights and polydispersities on conversion for 2-bromo-3-hexylthiophene polymerization at different concentrations of Ni(dppp)Cl$_2$ initiator (23−25 °C); [M]$_0$ = 0.075 mol/L: (■) [M]$_0$:[Ni(dppp)Cl$_2$] = 136:1; (●) [M]$_0$:[Ni(dppp)Cl$_2$] = 57:1; (▲) [M]$_0$:[Ni(dppp)Cl$_2$] = 49:1 (the dashed line shows the theoretical molecular weight).

Poly(3-hexylthiophene) (HT-PHT) was prepared by the original method[2] that provides a high specificity of H−T configuration of the repeating units (>98% H−T coupling).[12] The mechanism of the cross-coupling chain-growth polymerization is outlined in Scheme 1. The first step in the mechanism, where the 2-bromo-5-chlorozinc-3-hexylthiophene monomer (**1**) generated in situ from 2-bromo-3-hexylthiophene reacts with Ni(dppp)Cl$_2$, yielding the organonickel compound (**2**), is as it has been described by others.[9,13] We differ in our mechanism in that reductive elimination of **2** *immediately* forms an associated pair [**3·4**] of the tail-to-tail aryl halide dimer (**4**) and nickel (0) (**3**). The dimer **4** undergoes fast oxidative addition to the nickel center generating **5**, in view of the fact that the formation of the complex **3·4** eliminates potential separation of **4** from **3**. Subsequently, growth of the polymer chain occurs by insertion of one monomer at a time as shown in the reaction cycle (**5** → **6** → [**3·7**] → **5**), where the Ni(dppp) moiety is *always* incorporated into polymer chain as an end group. Addition of various Grignard reagents (R′MgX) at the end of polymerization results in end-capping of HT-

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* Corresponding author: e-mail rm5g@andrew.cmu.edu.

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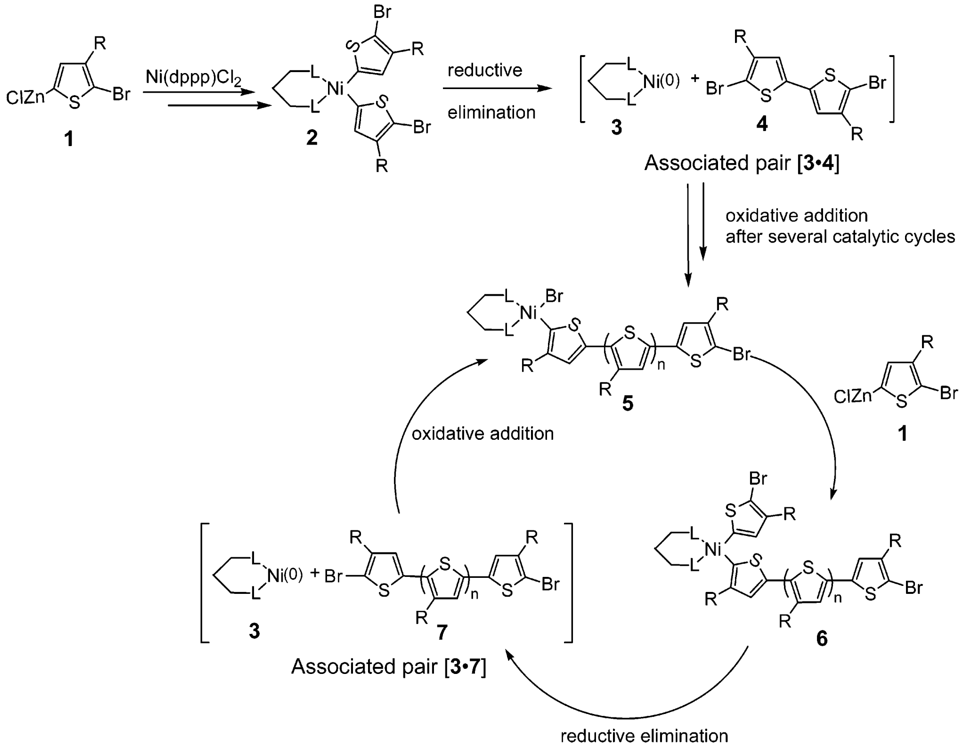
Scheme 1. Proposed Mechanism for the Nickel-Initiated Cross-Coupling Polymerization



PATs with R′ end group,[14] which supports the fact that $Ni(dppp)Cl_2$ acts as an initiator rather than a catalyst. Furthermore, adding organometallic (e.g., magnesium or zinc) thiophene bromides to species **5** results in the formation of block copolymers, providing a strong evidence for the *living* nature of this polymerization.[15]

To support the proposed chain growth mechanism, several experiments were performed at constant monomer concentration and variable $Ni(dppp)Cl_2$ concentration. All the reactions were very fast, reaching almost 90% conversion in less than 2 h, at room temperature. The reaction rates increased with the increase in the $Ni(dppp)Cl_2$ concentration (Figure 1). Linear semilogarithmic kinetic plots were obtained up to 50% conversion (e.g., $[M]_0$:$[Ni(dppp)Cl_2]$ = 49:1). The nonlinearity of semilogarithmic kinetic plots would, however, indicate the presence of termination reactions, which could be due to the formation of large supramolecular aggregates of polymer species mixed with unassociated or very weakly associated polythiophene chains.[16] The nature of the termination reactions is currently under investigation. A reaction order of ~1 with respect to $Ni(dppp)Cl_2$ concentration was obtained from the slope of the plot of the logarithm of the initial rate of polymerization vs the logarithm of the $Ni(dppp)Cl_2$ concentration.[17]

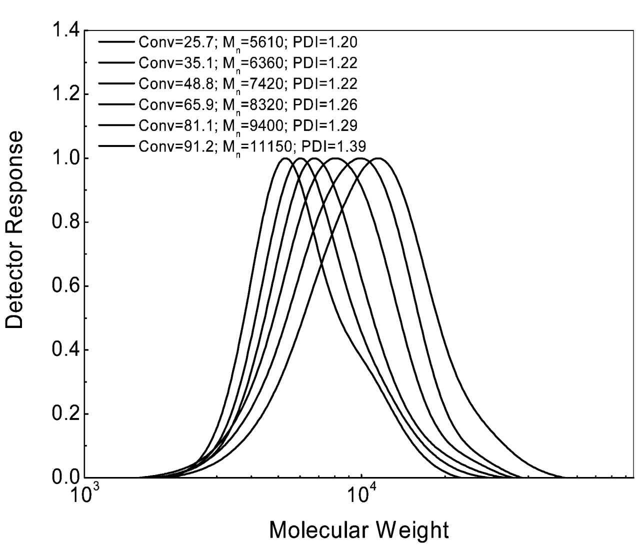


Figure 3. GPC traces for 2-bromo-3-hexylthiophene polymerization (23−25 °C); $[M]_0 = 0.075$ mol/L; $[M]_0$:$[Ni(dppp)Cl_2]$ = 57:1.

The molecular weight vs conversion plot (Figure 2) and the GPC traces (Figure 3) show the increase of molecular weight with conversion, providing a further support for the mechanism of the nickel-initiated cross-coupling polymerization being a chain growth process. Our results indicate that the molecular weight of polymer can be predicted by the molar ratio of monomer to $Ni(dppp)Cl_2$, which means that 1 mol of $Ni(dppp)Cl_2$ initiates one polymer chain. In most of our previous work, we used relatively low concentrations of $Ni(dppp)Cl_2$, which leads to higher molecular weights and broad PDIs as illustrated in Figure 2 (e.g., $[M]_0$:$[Ni(dppp)Cl_2]$ = 136:1; M_w/M_n ranges from 1.2 to 1.6). When a lower ratio of monomer to initiator is employed, however, one finds a good correlation between the theoretical and observed molecular weights, and narrow PDIs are obtained (e.g., $[M]_0$:$[Ni(dppp)Cl_2]$ = 49:1, $M_w/M_n \approx 1.2-1.3$).[18] We have also found that the Grignard metathesis method (GRIM)[19] for the synthesis of regioregular polythiophenes has similar kinetic behavior as shown here, indicating that it is a chain growth mechanism as well.[20]

The power of generating polythiophenes with well-defined molecular weights and narrow PDIs is important in optimizing the electrical properties of conducting polymers. Further work is expected to lead to truly *living* conducting polymers.

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Supporting Information Available: Mechanism for model reactions of aryl dibromides and an aryl organometallic with Ni(dppp)Cl_2; plot of the logarithm of the initial rate of polymerization vs the logarithm of the Ni(dppp)Cl_2 concentration. This material is available free of charge via Internet at http://pubs.acs.org.

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(11) A typical example is when a 0.1 M solution of thiophene (0.42 g, 5 mmol) or 2-methylthiophene (0.49 g, 5 mmol) in anhydrous THF (50 mL) cooled to −40 °C (acetonitrile/dry ice bath) was charged with a dropwise addition of *n*-butyllithium (2 mL, 5 mmol) via a syringe. After stirring the reaction mixture for 40 min at −40 °C, anhydrous $ZnCl_2$ (0.7 g, 5 mmol) was added in one portion, and the stirring continued for another 15 min. The cooling bath was removed, and the reaction mixture was allowed to warm to RT, at which point the reaction mixture was transferred to a different reaction flask charged with 10 mmol an appropriate dibromoaryl compound (e.g., 2,5-dibromo-3-methylthiophene, 2,5-dibromothiophene, or 1,4-dibromobenzene) and 0.05 mmol of [1,3-bis(diphenylphosphino)-propane]dichloronickel(II) (Ni(dppp)Cl_2) via cannula. The reaction was allowed to proceed for 12 h followed by quenching in water. The organic layer was extracted with diethyl ether (Et_2O) and subjected to GC-MS analysis to determine product composition and distribution. The reaction schemes and obtained results are provided in the Supporting Information.

(12) In a typical polymerization experiment, a dry 100 mL three-neck flask was flashed with dinitrogen (N_2) and was charged with diisopropylamine (0.50 mL, 3.5 mmol) and THF (30 mL); both were added via a syringe. The reaction flask was cooled to 0 °C, and *n*-butyllithium (2.0 mL, 3 mmol) was added dropwise via a syringe. After 20 min of stirring at 0 °C, the solution was chilled to −76 °C (acetone/dry ice bath), and stirring continued for 5 min. To this reaction mixture a previously chilled to −76 °C 0.3 M solution of 2-bromo-3-hexylthiophene (0.73 g, 3 mmol) in anhydrous THF (10 mL) was added via cannula. The reaction mixture was stirred for 1 h at −76 °C, at which time anhydrous $ZnCl_2$ (0.50 g, 3.6 mmol) was added in one portion and completely dissolved after 30 min of stirring. The cooling bath was removed, and the reaction mixture was allowed to warm to RT, at which time 2,2′-bithiophene (0.16 g, 1 mmol) was added in one portion and used as an internal standard. To this mixture Ni(dppp)Cl_2 (29 mg, 0.053 mmol) was added in one portion, and the reaction mixture was stirred at RT. Aliquots (1 mL) were taken at different time intervals (e.g., 1, 3, 5, 8 min etc., and the final aliquot was taken at 12 h), and each was precipitated in methanol (5 mL). For each aliquot a GC sample was prepared in Et_2O (2 mL) and was subjected to analytical GC and subjected to GC-MS analysis. After filtration, the molecular weight of the pristine polymer samples was measured by gel permeation chromatography (GPC) on a Waters 2690 separations module apparatus and a Waters 2487 dual λ absorbance detector with chloroform as the eluent (flow rate 1.0 mL/min, 35 °C, $\lambda = 254$ nm) with a series of three Styragel columns (10^4, 500, 100 Å; Polymer Standard Services). Toluene was used as an internal standard, and calibration based on polystyrene standards was applied for determination of molecular weights. GC-MS was performed on an Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethyl siloxane. Helium was the carrier gas (1 mL/min). Unless otherwise noted, the following conditions were used for all GC/MS analyses: injector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 300 °C.

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(17) See Supporting Information for details. In addition, unpublished results in our group showed a value of 1 for the reaction order with respect to monomer for nickel-initiated cross-coupling polymerization.

(18) Molecular weights of the polymers were estimated relative to polystyrene standards.

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