

MECHANISM AND KINETICS OF THE NICKEL-ASSISTED CROSS-COUPLING POLYMERIZATIONS OF REGIOREGULAR 3-ALKYL-FUNCTIONALIZED POLYTHIOPHENES

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Introduction

Polythiophenes (PTs) continue to be one of the most versatile and extensively studied conjugated polymer systems due to their exceptional spectroscopic and electronic properties. The straightforward synthesis of PT derivatives yields soluble and processable polymers with a wide range of practical and potential applications.^{1,2,3} Regioselective syntheses of poly(3-alkylthiophenes) (PATs)^{4,5,6} that contain almost exclusively head-to-tail (HT) couplings result in enhanced electrical conductivities and a greater effective conjugation length of HT-PATs over their regiorandom analogues.⁷

All of the aforementioned polymerizations are nickel-promoted cross-couplings.⁸ The generally accepted mechanism of these metal-assisted cross-coupling (MAC) polymerizations, which involves a catalytic cycle of three consecutive steps: oxidative addition, transmetalation, and reductive elimination, is an extension of metal-catalyzed cross-coupling condensation reactions of organometallic compounds and organic halides.⁸ While this mechanism has been widely investigated, there still remains some controversy over the intervening steps from the arylnickel(II) to the diarylnickel intermediates and the oxidation state of the latter.⁹

Recently, it has been proposed that the nickel-promoted cross-coupling polymerization proceeds *via* a chain growth mechanism rather than the generally accepted step growth mechanism.^{10,11,12} It has also been suggested that the nature of polymerization mechanism is reminiscent of a living system. Herein we report kinetic studies of the modified McCullough and GRIM methods that utilize Grignard cross-coupling methodology for the synthesis of HT-PATs. The results that follow provide new insight on the nature of the MAC polymerizations.

Experimental

Materials. All reactions were conducted under prepurified nitrogen or argon, using either flame-dried or oven-dried glassware. Commercial chemicals, 3-bromothiophene, [1,3-bis(diphenylphosphino)propane] dichloronickel(II) (Ni(dppp)Cl₂), zinc chloride (ZnCl₂) (anhydrous beads, ~10 mesh), 2,2'-bithiophene, were purchased from Aldrich Chemical Co., Inc. and used without further purification. *N*-Bromosuccinimide (NBS) was recrystallized from acetic acid. Prior to use, tetrahydrofuran (THF) and diisopropylamine were dried over and distilled from sodium benzophenone ketyl and calcium hydride, respectively. Titration of the Grignard/organolithium reagents was performed following the procedure described by Love.¹³

Instrumentation. GC/MS was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n , of polymer samples with respect to polystyrene standards. The system configuration has been described previously.¹² ¹H and ¹³C NMR spectra were recorded on a Bruker Avance AV-300 (operating at 300.13 MHz in ¹H and 75.47 MHz in ¹³C) and Bruker Avance DMX-500 (operating at 500.13 MHz in ¹H and 125.76 in ¹³C) spectrometers. All NMR spectra were recorded in deuterated chloroform (CDCl₃) as solvent containing 0.003% TMS as an internal reference unless noted otherwise.

Synthesis of HT-Poly(3-Hexylthiophene). In a typical polymerization experiment, a dry 100-mL three-neck flask was flushed with N₂ and was charged with diisopropylamine (0.50 mL, 3.5 mmol) and THF (30 mL), in which both were added *via* syringe. The reaction flask was cooled to 0°C and *n*-butyllithium (2.0 mL, 3 mmol) was added dropwise *via* syringe. After 20 minutes of stirring at 0°C, the solution was chilled to -76°C (acetone/dry ice bath) and stirring continued for 5 minutes. 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 hour at -76°C. Anhydrous ZnCl₂ (0.50 g, 3.6 mmol) was added in one portion and completely dissolved after 30 minutes of stirring. The cooling bath was removed and the reaction mixture was allowed to warm to ambient temperature, 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)Cl₂ (29 mg, 0.053 mmol) was added in one portion. Aliquots (1 mL) were taken at different time intervals (e.g., 1, 3, 5, 8 minutes etc. and the final aliquot was taken at 12 hours) and each was precipitated in methanol (5 mL). For each aliquot, a GC sample was prepared in diethyl ether (Et₂O) (2 mL) and was subjected to GC-MS analysis. After filtration through PTFE filters (0.45 μm), the molecular weight of the polymer samples was measured by GPC.

Results and Discussion

Parallel kinetic experiments were performed for both the McCullough and GRIM methods. The results obtained were nearly identical and reproducible, indicating that the two methods proceed *via* the analogous nickel-assisted cross-coupling chain growth polymerization mechanism. Small variations in reaction rates between the two methods were anticipated due to the differences between the organometallic isomers (e.g., bromomagnesium species versus chlorozincio intermediates) and/or possible side reactions (e.g., formation of lithium chloride (LiCl) in the McCullough method).¹⁴ However, the differences were indistinguishable; therefore, the two methods are evaluated in conjunction with each other. As shown in **Figure 1**, the McCullough and the Grignard (GRIM) methodologies employ nickel-promoted polymerization of organometallic reagents (in which the metal can be either zinc or magnesium) derived from bromo- or dibromo-alkylthiophenes, respectively.^{4,6}

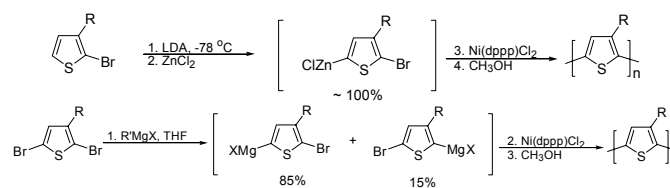


Figure 1. The synthesis of regioregular alkyl functionalized polythiophenes by the McCullough method (top) and Grignard Metathesis (GRIM) method (bottom).

Despite the differences in the starting materials, reaction conditions, and intermediates, the aforementioned methods proceed *via* the analogous nickel-assisted cross-coupling chain growth polycondensation mechanism.¹²

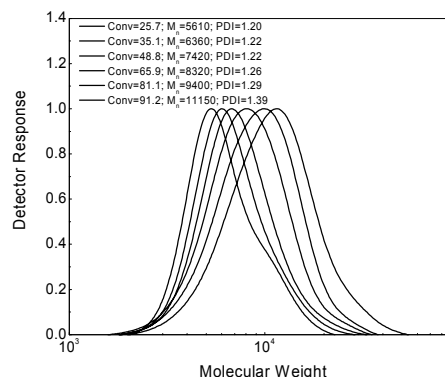


Figure 2. GPC traces for 2-bromo-5-chlorozincio-3-hexylthiophene polymerization (23-25°C); $[M]_0 = 0.075$ mol/L; $[M]_0 : [Ni(dppp)Cl_2] = 57:1$ (McCullough)

In **Figure 2**, the GPC traces show the increase of the molecular weight with the conversion, which supports the proposed chain growth mechanism. However, the tailing observed at the low molecular weight region is indicative either of a slow initiation or the presence of termination reactions. On

average, polymers with relatively narrow polydispersities ($M_w/M_n \sim 1.2$) were obtained at high concentrations of Ni(dppp)Cl_2 . The optimum ratios of monomer to initiator concentrations, which showed good agreement between theoretical and observed molecular weights, were found to lie below 70:1. In fact, higher molecular weight polymers with narrow molecular weight distributions can be generated if the aforementioned stoichiometric conditions are considered with respect to monomer concentration in the reaction medium.

The rate of polymerizations displayed a value of ~ 1.2 with respect to the Ni(dppp)Cl_2 concentrations. The deviation from the expected value of 1 may be attributed to an experimental error. As depicted in **Figure 3**, the reaction order for both methods was obtained from the slope of the logarithmic plot of the initial rate of polymerization versus the logarithm of the Ni(dppp)Cl_2 concentration.

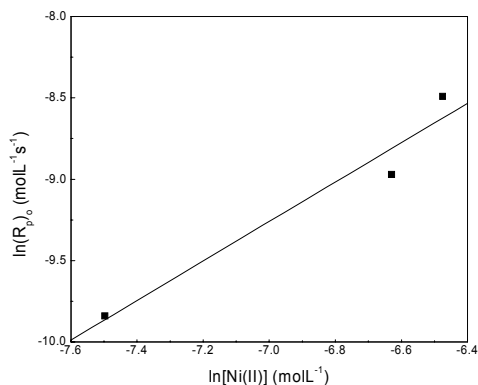


Figure 3. Plot of the logarithm of the initial rate of polymerization versus the logarithm of the Ni(dppp)Cl_2 concentration (McCullough).

Conclusions

The kinetic studies of nickel-assisted cross-coupling polymerization of regioregular 3-alkyl functionalized polythiophenes (HT-PATs) utilizing either the modified McCullough or Grignard metathesis (GRIM) methods revealed that the polymerization proceeds *via* a chain growth mechanism. In both instances, conjugated polymers with well-defined molecular weights and narrow molecular weight distributions were synthesized. The nickel-assisted cross-coupling polymerizations exhibited an increase in molecular weight which is directly proportional to the molar ratio of monomer to Ni(dppp)Cl_2 . Additionally, they exhibited internal first-order kinetics with respect to both the monomer and the Ni(dppp)Cl_2 concentrations. Furthermore, the molecular weight of PATs can be predetermined by the molar ratio of monomer to Ni(dppp)Cl_2 which is incorporated at the end of the polymer chain and, thus acts as an initiator rather than a catalyst. These results represent the experimental evidence for the pseudo-*living* nature of the metal-assisted cross-coupling (MAC) polymerizations of HT-PATs utilizing the aforementioned methods.

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