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ARTICLE

Evidence of Ni(0) Complex Diffusion during Grignard Metathesis Polymerization of 2,5-Dibromo-3-hexylthiophene

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ABSTRACT: It has been previously reported that the Grignard Metathesis polymerization of 3-alkyl thiophenes proceeds by a quasi-“living” chain growth or “catalyst transfer polycondensation” mechanism. Several publications present data in support of the transition metal species acting as an initiator and specifically maintaining Ni(0) association with a single growing polymer chain. However, our study of 2,5-dibromo-3-hexylthiophene polymerization via GPC, MALDI-TOF, and GC-MS verifies independently and in conjunction with one another that the transition metal is involved in transfer/diffusion from chain to chain during polymerization and presents the possibility of additional mechanistic controlling factors. Kinetic monitoring and characterization studies support transfer of the transition metal through diffusion from chain to chain during polymerization.

Introduction

Since the discovery of conductive polymers in 1977,[1] conjugated polymeric systems have continued to prove more useful and interesting due to their potential in diverse applications. However, controlling the conductivity range of π-conjugated systems is a challenge, as it is a function of structural properties such as regioregularity, molecular weight control, molecular weight polydispersity, control of terminal groups, and morphology. Among conjugated polymers, polythiophenes (PTs) are preferred for many organic electronic applications due to the base polymers' relatively high conductivity, environmental stability, and tunable bandgaps with varying side groups. The first PTs prepared via chemical polymerization of unsubstituted thiophenes through 2,5-coupling were highly conductive, environmentally stable polymers that were insoluble in common solvents.[2,3] Poly(3-alkylthiophene)s (P3ATs) were the first solvent soluble conductive PTs to be synthesized.[4] Subsequent developments led to the synthesis of regioregular (rr) P3ATs that are highly conductive, more easily processed, and environmentally stable systems.[5,6] While many methods have been developed to synthesize soluble PTs, techniques that specifically yield regioregular polymers are more valuable as higher order correlates with better conductivity.[7] Such synthetic techniques include, but are not limited to, the Grignard Metathesis (GRIM),[8] McCullough,[9] and Rieke[10] methods. All three methods proceed through transition metal catalyzed cross-coupling reactions. While the GRIM method allows ambient or reflux temperature processes to produce rrP3ATs, the McCullough and Rieke methods require cryogenic temperatures.[8,11,12] The Rieke method also requires highly reactive “Rieke Zinc” to produce rrP3ATs. Each of these methods seeks optimum control over molecular weight, molecular weight distribution, end group functionality, and regioregularity as a means for improved conjugated polymer utility.

In the generally accepted GRIM mechanism, 2,5-dibromo-3-hexylthiophene is first Grignardized in a 85:15 mixture of the 2 or 5 position (Scheme 1a), where the selectivity of the 5 position is driven by steric hindrance of the alkyl chain. In the second phase, several sources claim that the transition metal species [nickel(0)] is associated with a single chain and maintains this association throughout polymerization.[13,14,16,17] For this reason, the transition metal is thought to be an initiator species rather than a catalyst. The McCullough group suggested that the mechanism proceeds through oxidative addition of monomer followed by reductive elimination to generate a nondiffusive associated pair of a nickel(0) species and bromine terminated polymer chain end (Scheme 1b).[13] However, Yokozawa claims that the mechanism proceeds through intramolecular transfer of the nickel species to the terminal C−Br chain during propagation (Scheme 1c).[14]

In this paper, we report data in support of GRIM polymerization proceeding via nickel(0) diffusion but at high rates of reassociation. The ability to reassociate allows for adequate end-capping reactions, while polymer−polymer aggregation and separation rates in solution act as a molecular weight control mechanism. Further, monomer consumption continues throughout polymerization with the formation of new polymer chains after a maximum molecular weight is reached and is thought to be controlled by molarity. The data contradicts earlier reports of a direct correlation between $[M]_0/[Ni]_0$ and molecular weight. The MALDI-ToF analysis of nonfractionated samples confirmed nickel(0) species diffusion by end group analysis. The combination of continued conversion after a peak molecular weight is achieved and low polydispersities throughout the reaction further suggest that above a molarity controlled threshold, the nickel(0) species is more likely to associate with oligomeric species than higher molecular weight polymer chain ends. Possibly, the results are affected through the relationship between increasing molecular weight, solubility and functional end group access.

Experimental Section

Materials. All materials were used as received unless otherwise noted. 2,5-Dibromo-3-hexylthiophene (99%) was purchased from Waterstone Technologies. Anhydrous, inhibitor-free tetrahydrofuran (THF) and 1,3-*bis*(diphenylphosphino)-propane dichloronickel [Ni(dppp)Cl_2] were purchased from

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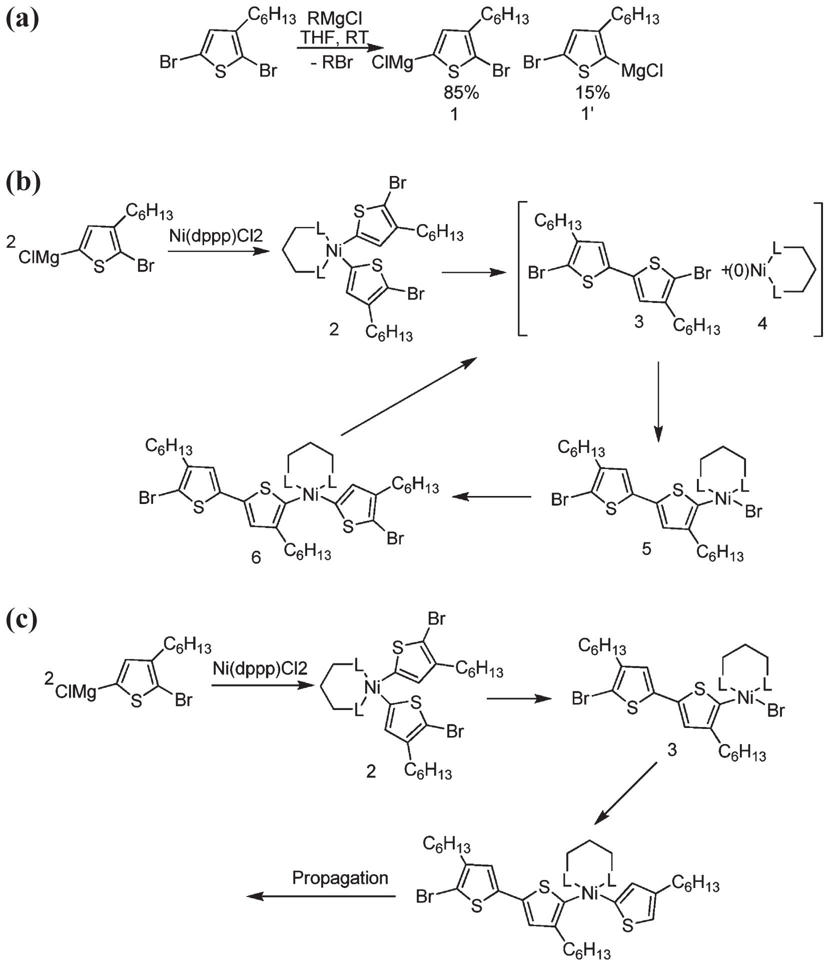
Scheme 1. Accepted Mechanisms of Grignard Metathesis Method for the Synthesis of Regioregular Poly(3-hexylthiophene)[13,14] [a]



[a] (a) Grignardizing 2,5-Dibromo-3-hexylthiophene.[13] (b) GRIM Mechanism by McCullough Group [Ni(0) Species].[13] (c) GRIM Mechanism by Yokozawa Group (Intermolecular Transfer).[14]

Aldrich Chemical Co. *Tert*-butyl magnesium chloride (1.7 M in THF) was purchased from Acros Chemical Co.

Polymerization of 2,5-Dibromo-3-hexylthiophene. The synthesis procedure is exemplified for polymerization at 0.25 M monomer concentration. Common literature monomer concentrations are 0.1 M and the experiments below were performed using each 0.1, 0.25, and 0.5 M for experimental comparison. Each reaction was performed in a nitrogen atmosphere. A dry 100 mL round-bottom flask was charged with 5 g of 2,5-dibromo-3-hexylthiophene (0.015 mol) and anhydrous THF (62 mL). Next, 9 mL of the 1.7 M solution of *tert*-butyl magnesium chloride in THF (0.015 mol) was added to the flask and allowed to react for two hours at ambient temperature. Two volumetrically controlled aliquots for gel permeation chromatography (GPC) and gas chromatography–mass spectrometry (GC-MS) analysis were removed from the system and quenched via methanol and acetone, respectively, and considered as time $t = 0$ for the reaction. At this point, 0.1385 g of Ni(dppp)Cl_2 (2.5×10^{-4} mole) was added to the reaction mixture at a ratio of $[M]_0/[Ni(0)]_0$ of 60:1. Aliquots were taken periodically to quantify monomer conversion (GC-MS) and molecular weight (GPC). After polymerization was complete, the mixture was quenched by precipitating the resulting polymer into methanol and filtered. Consecutive Soxhlet extractions were performed with methanol and hexane to remove residual monomer/salts and oligomeric chains, respectively. A final Soxhlet extraction with chloroform isolated the pure polymer product from the nickel species. To confirm that there was no chain to chain coupling during quenching procedure, replica runs were preformed with all parameters held constant except for the quenching step switched from methanol to 5 M hydrochloric acid.

Analysis. GPC was performed on a Varian PL GPC-50 equipped with dual angle light scattering, differential pressure and refractive index detectors. THF was used as the eluent at a flow rate of 0.8 mL/min at 40 °C and a series of four Polymer Laboratory columns (three Polypore and one 50 Å PLGel column). Toluene was used as an internal standard and GPC data was collected from polystyrene standards using corrected Mark–Houwink constants from literature, that is, K and a values of 2.28 and 0.97, respectively.[15] GC-MS was performed on a Hewlett-Packard Agilent 6890–5972A GC-MS workstation using an Agilent DB-1 high resolution column under the following conditions: carrier gas helium, injector temperature 200 °C, initial temperature 50 °C (3 min hold), initial temperature ramp to 150 °C (1 min hold), 10 °C/min; final temperature ramp to 250 °C (20 min hold); 10 °C/min. The samples for GC-MS and GPC were withdrawn as volumetrically controlled aliquots to ensure that molar concentration was maintained/tracked throughout the synthesis and characterization. This allowed the raw RI curves to correspond directly to polymer concentration and the area under each peak to be directly proportional to P3HT conversion and synthesis, as well as GC-MS data to correspond to previous calibration curves. ^1H NMR spectra were performed in $CDCl_3$ on a Varian Unity 300 MHz spectrometer. Scanning electron microscopy (SEM) was utilized to analyze each fraction via X-ray analysis on an FEI Quanta 200 with Thermo System 7 Energy Dispersive X-ray

Table 1. Number Average Molecular Weight by Comparison of GPC (non-corrected), GPC (corrected), and MALDI-ToF

polymer	$[M]_0/[Ni(0)]_0$	molarity (mol/L)	non-corrected (g/mol)	corrected (g/mol)	MALDI-TOF (g/mol)
4K P3HT	60:1	0.1	7850	4040	4110
10K P3HT	60:1	0.5	17500	7950	8720

(EDX) analyzer utilizing 20.0 kV accelerating voltage. Matrix-assisted laser desorption ionization-time of flight (MALDI-ToF) spectra were obtained using a Bruker Daltonics Microflex equipped with a 337 nm N_2 laser in linear mode with a 20 kV acceleration voltage. Dithranol was employed as the matrix and all samples were prepared at 1 mg/mL in anhydrous THF as described by McCullough and co-workers.[16] Polymer samples were mixed with Dithranol matrix solution (0.1 M in THF) in a 50/50 ratio by volume and 2 μL of each sample were then spotted onto a stainless steel target. An external protein calibration standard (Bruker, protein standard II) was employed for accurate measurements of polymer molecular weight. Over 2000 laser shots on average were taken for each sample and peak molecular weight values were determined by Microflex analysis software.

Results and Discussion

Polymerization Fractions and Components. After filtering the precipitated polymer, the remaining media was concentrated to separate the resulting salts. The salts and filtered raw polymer were analyzed via SEM-EDX. The results verified the Soxhlet extraction process for removal nickel species, as well as the use of acetone for extraction of residual monomer in preceding monomer conversion studies. Results are shown in the Supporting Information.

Polymer Molecular Weight. Molecular weight measurement of poly(3-hexylthiophene) is a key variable in mechanistic considerations. Previously, molecular weight analysis has been performed by GPC analysis based on polystyrene standards, MALDI-ToF, and NMR. Holdcraft performed ebulliometric studies on poly(3-hexylthiophene) samples and showed a drastic overestimation of molecular weights calculated against polystyrene standards.[15] Consequently, molecular weight analysis was performed using a corrected calibration curve utilizing the Mark−Houwink values reported in literature.[15] Also, MALDI-ToF analysis was used to verify the corrected values. The results of MALDI-ToF and the corrected calibration curve were in close agreement when compared with the traditional universal calibration. Table 1 summarizes the number average molecular weights for two model polymers as noncorrected, corrected, and MALDI-ToF data.

Influence of Overall Molarity. Molarity effects were studied in experiments conducted at a constant monomer to nickel species ratio of 60:1. The ratio corresponds to a calculated molecular weight of 9960 g/mol at 100% conversion (plus the molecular weight of the terminal units, i.e., 10 041 g/mol and 10 120 g/mol for monobrominated and dibrominated, respectively). This theoretical maximum molecular weight would present itself if the nickel is associated with only a single chain during polymerization and 100% conversion was reached. However, an increase in the number of actively growing chains should decrease the average molecular weight markedly versus conversion. A decrease in the number of growing chains versus time would be reflected as a trend of increasing molecular weight versus conversion. As the overall system molarity is varied, the number of polymer chains and their molecular weight are expected to remain constant in the absence of factors such as $\pi-\pi$ stacking induced aggregation and a correlating loss of solubility.

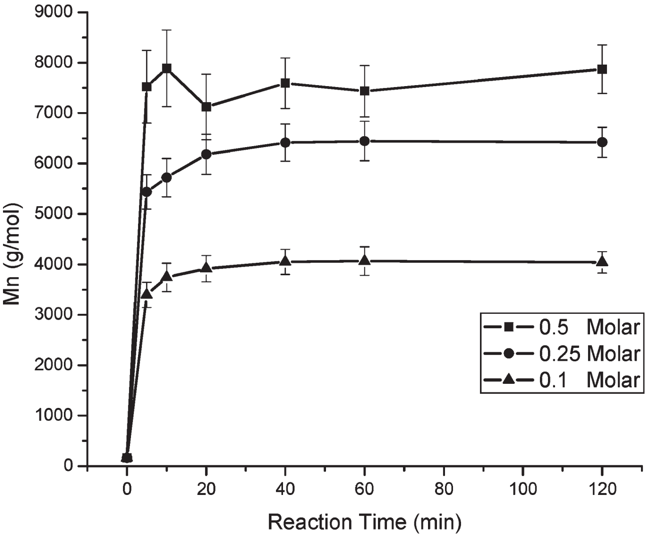


Figure 1. Corrected number average molecular weight via GPC of P3HT throughout reaction period with various initial molar monomer concentrations and constant 60:1 monomer to nickel ratio.

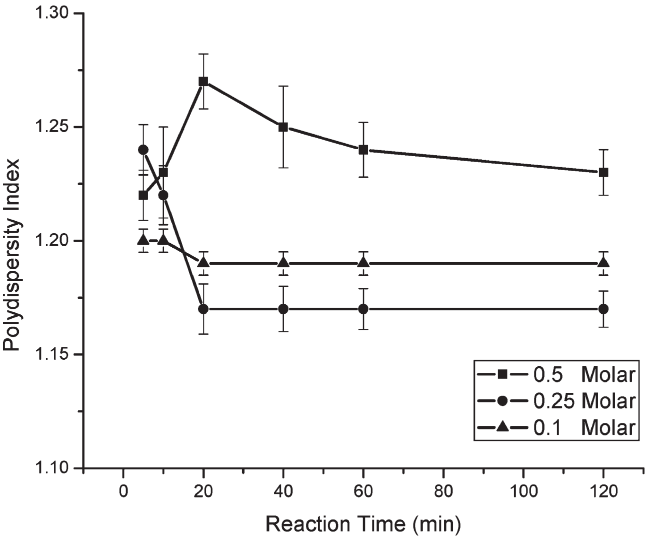


Figure 2. GPC based polydispersity index values for P3HT throughout reaction period with various initial molar monomer concentrations and a constant 60:1 monomer to nickel ratio.

Figure 1 illustrates the number average molecular weight curves of polymers obtained with 0.1, 0.25, and 0.5 M monomer concentrations over a two hour reaction period. The results shown below are averages of three polymerizations with error bars correlating to the standard deviation. The reaction was maintained longer than typically reported in the literature to account for extended monomer conversion in the later stages of the reaction.[13,14] The data demonstrates that increasing the initial monomer molarity results in higher overall molecular weight with limited effect on polydispersity (Figure 2). It is to be noted that after two hours, no formulation has reached the theoretical corrected maximum molecular weight. It is believed that each association of the

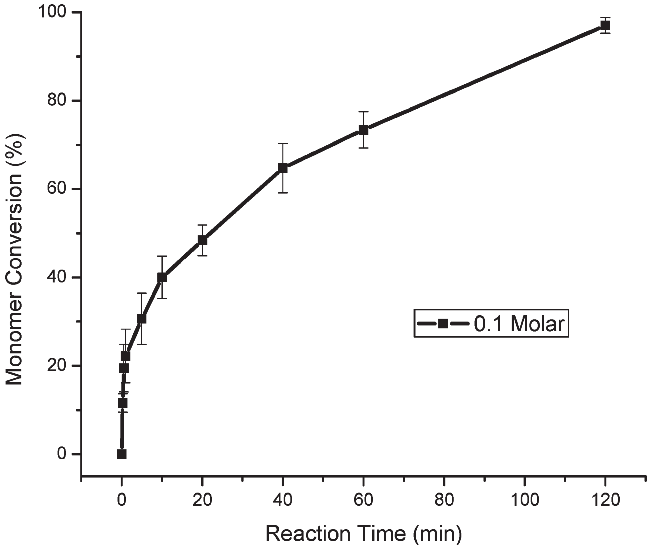


Figure 3. Percent conversion of 0.1 M polymerization of P3HT as monitored by GC-MS.

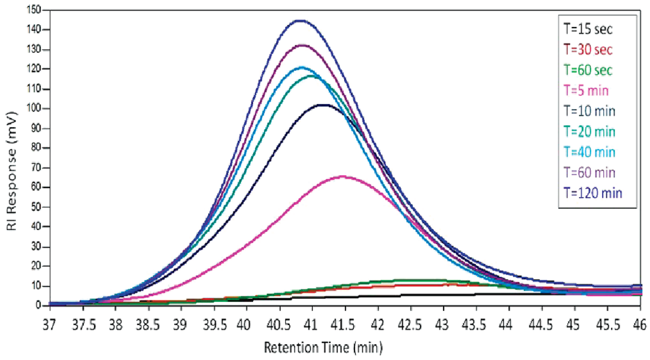


Figure 4. RI trace of 0.1 M polymerization of P3HT showing molecular weight increase and leveling with continual increase of polymer concentration.

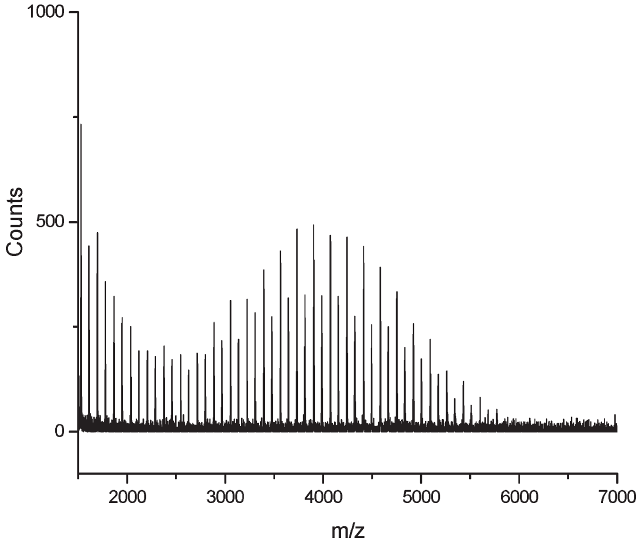


Figure 5. MALDI-TOF of 0.1 molar polymerization of P3HT quenched with MeOH showing both H−Br terminated chains as well as Br−Br terminated chains.

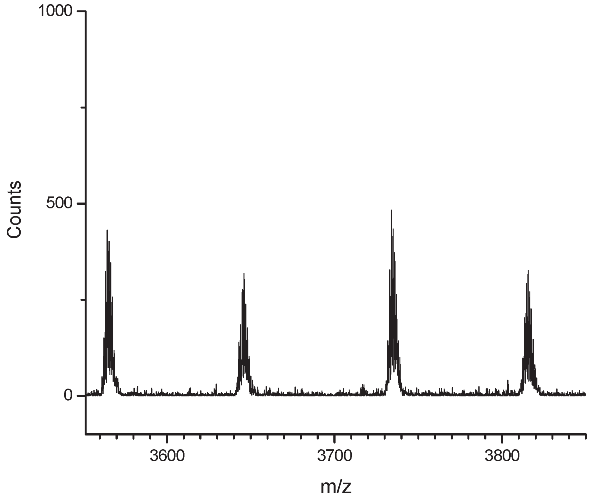


Figure 6. Expanded MALDI-TOF of 0.1 molar polymerization of P3HT quenched with MeOH showing both H−Br terminated chains as well as Br−Br terminated chains.

nickel species adds a predetermined number of monomer units depending on the instantaneous molar concentration and overall solubility limits before it diffuses either to another chain end or to begin a new chain. Polymer and oligomeric chain ends would not be exempt from further association, however, increasing molecular weight will reduce the chances of reassociation. The ability to reassociate with polymer chain ends offers an explanation of literature reports on end-capping of active polymer chains.[17]

Conversion versus Molecular Weight. When the reactions failed to yield the predicted theoretical molecular weight, the monomer conversion was analyzed via GC-MS. Figures 3 and 4 summarize monomer conversion as a function of time determined over a two hour reaction period for an initial monomer concentration of 0.1 M. The polymer molecular weights were confirmed to be constant after 20 min, however, the overall peak intensity continued to increase along with concurrent decrease in monomer concentration. The data confirms the fact that under these conditions, that is, at a given molarity, any new polymer chains that are formed are limited to the same molecular weight by another controlling factor.

Polymer Chain Ends. The discrepancy between molecular weight versus molar ratio of Ni and continued conversion versus time with limited molecular weight were not consistent with prior literature results and required polymer chain end analysis for further understanding. When the nickel species is associated with a chain end and the polymerization is quenched by methanol, the end group should be converted to terminal hydrogen.[16] The opposite and remaining end-group would be bromine. To confirm whether each nickel(0) species was associated with a single chain during polymerization, MALDI-ToF analysis was performed to search for specific and iterative end group effects on molecular weight. Figures 5 and 6 reveal the MALDI-ToF results for a reaction conducted with the same molecular weights and ratios as employed in Figures 3 and 4. The peaks correspond to either $m/z = 166n + 1 + 80$ (monobrominated) or $m/z = 166n + 80 + 80$ (dibrominated), where 166 is the repeat unit molecular weight, n is the number of repeat units, 1 refers to the terminal hydrogen, and 80 is from the terminal bromine group. The reported mechanisms would yield peak locations that match only the monobrominated equation with very low concentration of peaks matching the dibrominated set. The presence of two peak sets at appreciable ratios confirms the absence of nickel on a percentage of chains during quenching. The corresponding molecular weight for a reaction

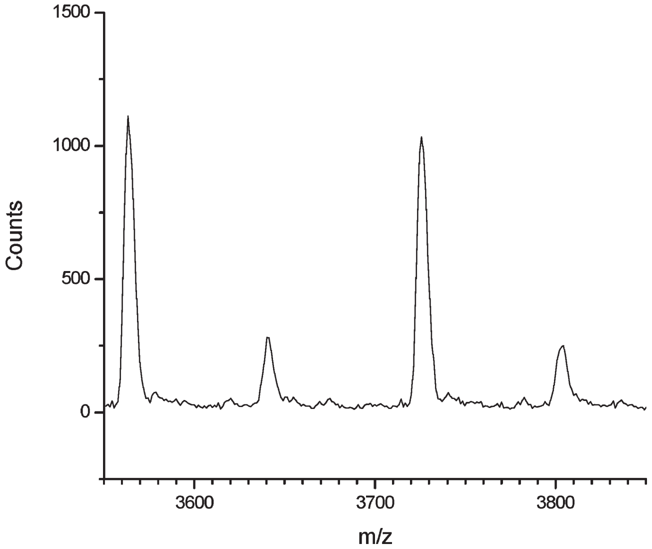


Figure 7. Expanded MALDI-TOF of 0.1 molar polymerization of P3HT quenched with 5 M HCl showing both H−Br terminated chains as well as Br−Br terminated chains.

at 97% conversion (Figures 3 and 4) is much lower than the theoretical molecular weight if nickel were to remain associated to a single chain throughout the polymerization, strongly suggesting diffusion of the nickel species from higher molecular weight chains to both oligomeric species and monomer, and creating additional new chains.

It has been previously reported that quenching growing polymer chains with water will cause chains to couple generating dibrominated chains with higher molecular weight.[18] However, the lack of bimodality and low polydispersity in MALDI-ToF analysis suggest that such coupling does not occur. To confirm that there was no coupling, replica runs were performed with the quenching step changed from methanol to 5 M hydrochloric acid. A detailed examination of the results shown in Figure 7 shows the continued presence of both mono and dibrominated chain ends. Furthermore, the GPC results shown in Figure 4 reiterate the lack of bimodality. Uniform polymers with low polydispersity index (PDI) are observed in spite of a 4 column series, which would increase separation and exaggerate any bimodal properties.

Extended Monomer Reaction for Proof of Continued Monomer Conversion. To further test the Ni diffusion theory, reactions were performed to extend the duration of the monomer addition process. The experimental goal was to distort the polydispersity and molecular weight plateau further from the results of a single monomer addition process and also to allow the procedure to mimic a staged block copolymer synthesis while using the same monomer. If the polymerization was based upon a constant nickel association with a single polymer chain, the extended monomer addition would increase the bulk molecular weight significantly while maintaining polydispersity. The corresponding theoretical molecular weight for a single-chain nickel-association would increase to 17 370 g/mol, a 75% increase. Accordingly, polymerization was initiated at a starting concentration of 0.1 M and allowed to react to 50% conversion. At this point, the polymerization was extended using a secondary batch of monomer formulated to 0.06 M concentration in THF. The monomer was fed continuously into the reaction at a feed rate on the same order of magnitude as the experimentally determined monomer consumption rate at that corresponding point in the reaction. The same, but secondary addition of monomer (0.012 mol), was fed into the reaction over two hours and the mixture was allowed to react for an additional two hours. Aliquots were extracted at predetermined intervals throughout all stages of polymerization. As shown in Figure 8 and Table 2, GPC traces of the resulting polymer confirmed our theory of nickel diffusion and limited return to the original chains based upon a diminished collision frequency at a given molarity. The reduction in the main peak areas is related to dilution effects from the second monomer addition. As shown, the limited peak molecular weight shift, increasing overall PDI, and a small, yet clear shift to higher molecular weight for late adding chains are key points to confirm diffusion. Under these conditions it is clear that the majority of chains are not continuing to grow but are new chains resulting from nickel diffusion for additional chain initiation and propagation. It should be noted that the molecular weight data was collected on a different GPC instrument with two PL-gel columns in series at a flow rate of 1.0 mL/min, and all other parameters including correction from polystyrene standards followed previous conditions. This change in conditions accounts for the variance in retention time.

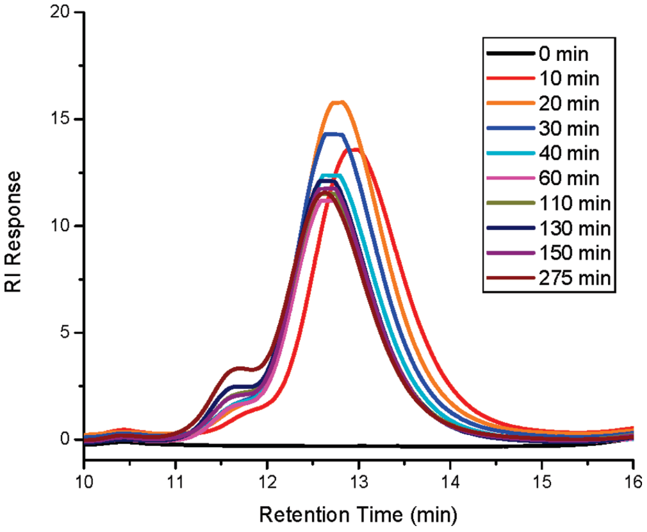


Figure 8. RI traces of 0.1 molar polymerization of P3HT with secondary 0.06 M monomer addition (P3HT).

Table 2. Corrected Number Average Molecular Weight, Polydispersity Indices, and Percent Area of High Molecular Weight Shoulder

reaction time (min)	M_n (g/mol)	PDI	% area shoulder
10	3440	1.20	4.42
20	4030	1.19	5.72
30	4070	1.15	6.97
40	4100	1.15	7.77
60	4220	1.33	8.26
110	4250	1.35	9.50
130	4420	1.34	10.43
150	4590	1.52	11.51
275	4690	1.60	15.44

Conclusions

We investigated the mechanism of Grignard metathesis polymerization and report evidence that the mediating nickel species diffuses from chain to chain throughout the reaction. The diffusion of the nickel species indicates a loss of uniform chain ends, however, it does not correspond to a loss in control. Molecular weight was controlled by monomer to nickel ratio and initial monomer molarity with the latter dominating under these conditions. A combination of polymerization kinetics, molecular weight monitoring, and end-group analysis after methanol and HCl quenching confirm an alternative mechanism of polymerization and offers insight into controlling final molecular weight and achieving greater control over the resulting polymer architecture.

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Supporting Information Available: SEM-EDX of each P3HT fraction during Soxhlet extraction process, NMR, and GC-MS characterization of 2,5-dibromo-3-hexylthiophene indicating purity. This material is available free of charge via the Internet at http://pubs.acs.org.

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