# Articles

## Facile Synthesis of End-Functionalized Regioregular Poly(3-alkylthiophene)s via Modified Grignard Metathesis Reaction

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ABSTRACT: A simple method for the synthesis of end-functionalized regioregular poly(3-alkylthiophene)s is presented. Using a modified Grignard metathesis (GRIM) reaction, a series of polymers have been synthesized bearing functional groups on one or both ends of the polymer. This method has been demonstrated to work with a variety of different types of Grignard reagents (i.e., aryl, alkyl, allyl, vinyl, etc.). The reactivity of these depends on their nature, where allyl, ethynyl, and vinyl groups produced monofunctionalized polymers, and all others yielded difunctionalized polymers. The end group composition of the polymers was monitored by a combination of MALDI-TOF and $^1$H NMR and approaches 100% in most cases. By utilizing the proper protecting groups −OH, −CHO, and $-NH_2$ groups have been incorporated onto the polymer ends. The main advantage of this method is that it allows for the in situ functionalization of regioregular polythiophene, generating a variety of end-capped polymers in one step. This approach is advantageous in comparison to previously reported methods because it is not only reliable but also highly versatile and highly efficient.

Regioregular poly(3-alkylthiophene)s (rr-P3ATs) are among the most widely studied conducting polymers. Potential and practical applications include chemical and optical sensors,[1] electrochromic devices,[2] field effect transistors,[3] and solar cells.[4,5] The regioregular synthesis of rr-P3ATs can be achieved by a variety of well-established methods,[6−8] creating polymers with higher mobilities[9] and conductivities[10] than their regiorandom analogues. Moreover, it has also been established that modification of the substituent at the 3-position not only improves the solubility of the polymer but also serves as a method to tune the electronic properties of the polymer. Thus, a large number of papers on the synthesis of rr-P3ATs bearing a variety of side chains have been published. More recently, it has been determined that polymer morphology also plays a key role in the electronic properties of the material.[4] As such, the development of new methods to control polymer morphology has tremendous potential.

While side-chain functionalization has been demonstrated to be an effective way to alter the physical and electronic properties of rr-P3ATs, another approach is end group modification. Limited research has been done in this area, namely the in situ synthesis of trimethylsilyl-terminated rr-P3ATs and a multistep synthesis of rr-P3ATs bearing amino and hydroxyl groups.[11,12] Each study had practical limitations. The former study was applicable to only trimethylsilyl groups whereas the latter involved a multistep synthesis, which limits the broad-scale utility of this method. The multistep synthesis did yield interesting materials; for example, the hydroxylated PTs could be further derivatized to produce rr-P3AT−polystyrene diblock and triblock copolymers.[13] These interesting copolymers self-assemble into nanowires through phase separation, resulting in very high conductivities at low rr-P3AT percentages. To date, the use of these materials has been limited because the existing synthetic methods are not for a large scale.

Because of the importance of end group functionalization in the synthesis of diblock copolymers and in other applications such as end group driven self-assembly, we set out to develop a method for controlling the end group composition of regioregular polythiophenes. We wanted a method that would work with yielding a variety of different types of end groups, would produce functionalized regioregular polymer in high yield, and would be easily reproducible. Recent work by our group and by others showed that Ni (dppp)$Cl_2$ was capable of catalyzing cross-coupling polymerizations via a chain growth mechanism, rather than a step growth mechanism as previously thought.[14] Thus, we anticipated that we could find the proper reaction conditions to "cap" or terminate the reaction, yielding an end-functionalized rr-P3AT. Past attempts at in situ end-functionalization were based on halogen-containing reagents. However, we have determined that capping reagents must be organometallic. Herein we report an efficient, versatile, and reliable method to functionalize the ends of rr-P3AT.

### Experimental Section

**Materials.** All reactions were performed under prepurified nitrogen or argon, using oven-dried glassware. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Ni(dppp)$Cl_2$, allylmagnesium bromide, benzylmagnesium chloride, 3-(bis[trimethylsilyl]amino)phenylmagnesium chloride, *tert*-butylmagnesium chloride, ethynylmagnesium

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bromide, methylmagnesium bromide, phenylmagnesium bromide, 4-(2-tetrahydro-2*H*-pyranoxy)phenylmagnesium bromide, *p*-tolylmagnesium bromide, and vinylmagnesium bromide were purchased from Aldrich Chemical Co. and used without further purification. 4-(1,3-Dioxan-2-ylphenyl)magnesium bromide was purchased from Rieke Metals Inc. 2,5-Dibromo-3-hexylthiophene (**1**)[8] was synthesized according to the literature procedures from 3-hexylthiophene.[15]

**Instrumentation.** $^1$H NMR spectra were recorded using a Bruker 500 MHz instrument. A MALDI-TOF MS (Voyager-DE STR BioSpectrometry) workstation by Biosystems was used to record spectra in linear mode, in which samples were irradiated under high vacuum using a nitrogen laser (wavelength 337 nm, 2 ns pulse). The accelerating voltage was 20 kV, and the grid voltage and low mass gate were 92.0% and 1000.0 Da, respectively. The matrix used for all samples was 2,2′:5,2″-terthiophene (Aldrich). GPC measurements were carried out on a Waters 2690 separation module equipped with three 5 $\mu$m Phenogel columns connected in series (guard, $10^5$, 1000, and 100 Å) and a Waters 2487 dual $\lambda$ absorbance UV detector. Analyses were performed at 30 °C using chloroform as the eluent, and the flow rate was 1.0 $\mu$L/min. Calibration was based on polystyrene standards obtained from Polymer Standards Service.

**Typical End-Capping Reaction.** In a three-neck round-bottom flask 2,5-dibromo-3-hexylthiophene **1** (1.63 g, 5.0 mmol) was dissolved in THF (10 mL) and stirred under $N_2$. *tert*-Butylmagnesium chloride (2.5 mL, 5.0 mmol) was added via syringe, and the mixture was stirred at room temperature for 2 h. The reaction mixture was then diluted to 50 mL with THF, and Ni(dppp)$Cl_2$ (1.75−2.25 mol %) was added in one portion. The mixture was stirred for 10 min at room temperature, and the Grignard reagent (20−30 mol % of monomer) was added via syringe to the reaction mixture. The mixture was stirred for an additional 2 min and then poured into methanol to precipitate the polymer. The polymer was filtered into an extraction thimble and then washed by Soxhlet extraction with methanol, hexanes, and chloroform. The polymer was isolated from the chloroform extraction. All polymers had a $\lambda_{max}$ of 450 nm in solution and 552 nm in the solid state, e.g., **7g** and **7i**.

Characterization of **2a** (allyl-terminated). $^1$H NMR (500 MHz, $CDCl_3$): $\partial_H$ 0.913 (t, $J$ = 7 Hz, 3H), 1.40 (m, 6H), 1.69 (t, $J$ = 7 Hz, 2H), 2.80 (t, $j$ = 7 Hz, 2H), 5.12 (d, $J$ = 6.5 Hz, 2H), 5.95 (d, 2H), 6.90 (m, 1H), 6.98 (s, 34H); GPC: $M_n$: 6900, PDI: 1.19; MALDI-MS: *m/z*: 4105.85 [M$^+$] (calcd: 4110.50, DP of 24, Br/Allyl end groups).

Characterization of **2b** (ethynyl-terminated). $^1$H NMR (500 MHz, $CDCl_3$): (hexyl peaks are the same as for **2a** with $\partial_H$ 3.14 (s, 1H), 6.98 (s, 68H); GPC: $M_n$: 12 041, PDI: 1.2; MALDI-MS: *m/z*: 7252.15 [M$^+$] (calcd: 7252.89, DP of 43, ethynyl/Br end groups).

Characterization of **2c** (vinyl-terminated). $^1$H NMR (500 MHz, $CDCl_3$): hexyl peaks are the same as for **2a** with $\partial_H$ 5.12 (d, $J$ = 11 Hz, 1H), 5.51 (d, $J$ = 11 Hz, 1H), 6.83 (m, 1H), 7.26 (s, 28H); GPC: $M_n$: 6987, PDI: 1.17; MALDI-MS: *m/z*: 4106.38 [M$^+$] (calcd: 4101.51, DP of 24, Br/vinyl end groups).

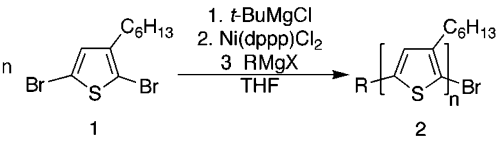
Characterization **2d** (aminophenyl-terminated): $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 7.08 (s, 40H), 7.13 (m, 4H); GPC: $M_n$: 15 532, PDI: 1.24; MALDI-MS: *m/z*: 8080.88 [M+] (calcd: 8070.52, DP of 48, Ph−$NH_2$/H).

Characterization of **7a** (phenyl-terminated). $^1$H NMR (500 MHz, THF-$d_8$): $\partial_H$ 0.926 (t, $J$ = 7 Hz, 3H), 1.37 (m, 6H), 2.85 (t, $J$ = 7 Hz, 2H), 7.10 (s, 43H), 7.43 (m,2H), 7.47 (m, 8H); (remaining two protons buried under solvent peak). GPC: $M_n$: 10 900, PDI: 1.12; MALDI-MS: *m/z*: 6317.21 [M$^+$] (calcd: 6308.05, DP of 37, phenyl/phenyl end groups).

Characterization of **7b** (tolyl-terminated). $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 7.08 (s, 37H), 7.24 (d, $J$ = 8 Hz, 4H), 7.36 (d, $J$ = 8H, 4H); GPC: $M_n$: 9300 PDI: 1.1; MALDI-MS: *m/z*: 5845.42 [M$^+$] (calcd: 5837.54, DP of 34, tolyl/tolyl).

Characterization of **7c** (benzyl-terminated): $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for with $\partial_H$ 4.13 (s, 2H), 7.10 (s, 41H), 7.26 (m, 10H); GPC: $M_n$: 13,700, PDI: 1.2; MALDI-MS: *m/z*: 8002.1 [M$^+$] (calcd: 7997.6, DP of 47, benzyl/benzyl).

**Scheme 1. General Scheme for the Synthesis of End-Capped Polymers**




Characterization of **7d** (1,3-dioxan-2-ylphenyl)-terminated): $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 3.97 (t, 3H), 4.19 (t, 3H), 5.51 (s, 2H), 7.08 (s, 49H), 7.33 (d, $J$ = 9 Hz, 4H), 7.49 (d, $j$ = 9 Hz, 4H); GPC: $M_n$: 11 648, PDI: 1.27; MALDI-MS: *m/z*: 7001.45 [M$^+$] (calcd: 6999.60, DP of 40, dioxolane/dioxolane).

Deprotection of aldehyde. In a round-bottom flask the dioxanyl-terminated polymer **7d** (1.00 g) was dissolved in 100 mL of THF. The reaction was heated to reflux, and then pyridinium *p*-toluenesulfonate (PTS) (50 mg) in 10 mL of (80% acetone(aq)) was added. The reaction was heated overnight and then precipitated into a beaker of methanol. The crude polymer was filtered, dried, and recovered in quantitative yield. Characterization of **7e** (benzaldehyde-terminated): $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 7.09 (s, 55H), 7.69 (d, $J$ = 8 Hz, 4H), 7.95 (d, $j$ = 8 Hz, 4H); GPC: $M_n$: 12 034, PDI: 1.09; MALDI-MS: *m/z*: 7045.81 [M$^+$] (calcd: 7053.60, DP of 41, Ph−CHO/Ph−CHO).

Characterization of **7f** (phenyltetrahydropyranyl-terminated): $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 7.08 (s, 30H), 7.11 (d, $J$ = 8.5 Hz, 4H), 7.36 (d, $j$ = 8.5 Hz, 4H); GPC: $M_n$: 9362, PDI: 1.17; MALDI-MS: *m/z*: 4509.03 [M$^+$] (calcd: 4509.75, DP of 25, Ph−OTHP/Ph−OTHP).

Deprotection of Phenol. In a round-bottom flask the tetrahydropyranyl ether-terminated polymer **7f** (2.00 g) was dissolved in 50 mL of THF. The reaction was heated to reflux, and then 5 drops of 6 M HCl were added. The reaction was heated overnight and then precipitated into a beaker of methanol. The crude polymer was filtered, dried, and recovered in quantitative yield. Characterization of **7h** (phenol-terminated) $^1$H NMR (500 MHz, THF-$d_8$): (hexyl peaks same as for **7a** with $\partial_H$ 6.81 (d, $J$ = 8.5 Hz, 4H), 7.07 (s, 36H), 7.28 (d, $j$ = 8.5 Hz, 4H); MALDI-MS: *m/z*: 4348.2 [M$^+$] (calcd: 4343.2, DP of 25, Ph−OH/Ph−OH).

Characterization of **7i**: $^1$H NMR (500 MHz, $CDCl_3$): (hexyl peaks same as for **7a** with $\partial_H$ 2.37 (s, 6H), 6.98 (s, 43H); GPC: $M_n$: 8500, PDI: 1.1; MALDI-MS: *m/z*: 5185.9 [M$^+$] (calcd: 5184.8, DP of 31, methyl/methyl).

## Results and Discussion

The general approach for the synthesis of end-functionalized HT-PATs is shown in Scheme 1. This straightforward approach utilizes the Grignard metathesis reaction of 2,5-dibromo-3-hexylthiophene (**1**) with *tert*-butylmagnesium chloride, to yield 2-bromo-5-magnesiobromo-3-hexylthiophene (**3**) as a major product.[7,16] The addition of the nickel catalyst to the reaction mixture resulted in the formation of a "living chain" of the HT-PAT **(4)** (Scheme 2). While the polymer is still in solution a second Grignard reagent was introduced. Since the polymerization followed a chain growth mechanism,[14] this termination reaction stopped the polymerization and results in the formation of an end-functionalized polymer. During our investigation we examined a variety of different types of Grignard reagents (allyl, alkyl, aryl, benzyl, vinyl, etc.) The end group composition of these polymers was examined by MALDI-TOF MS, and the results are summarized in Table 1.

**Scheme 2. Proposed Mechanism for the End-Capping Reaction**

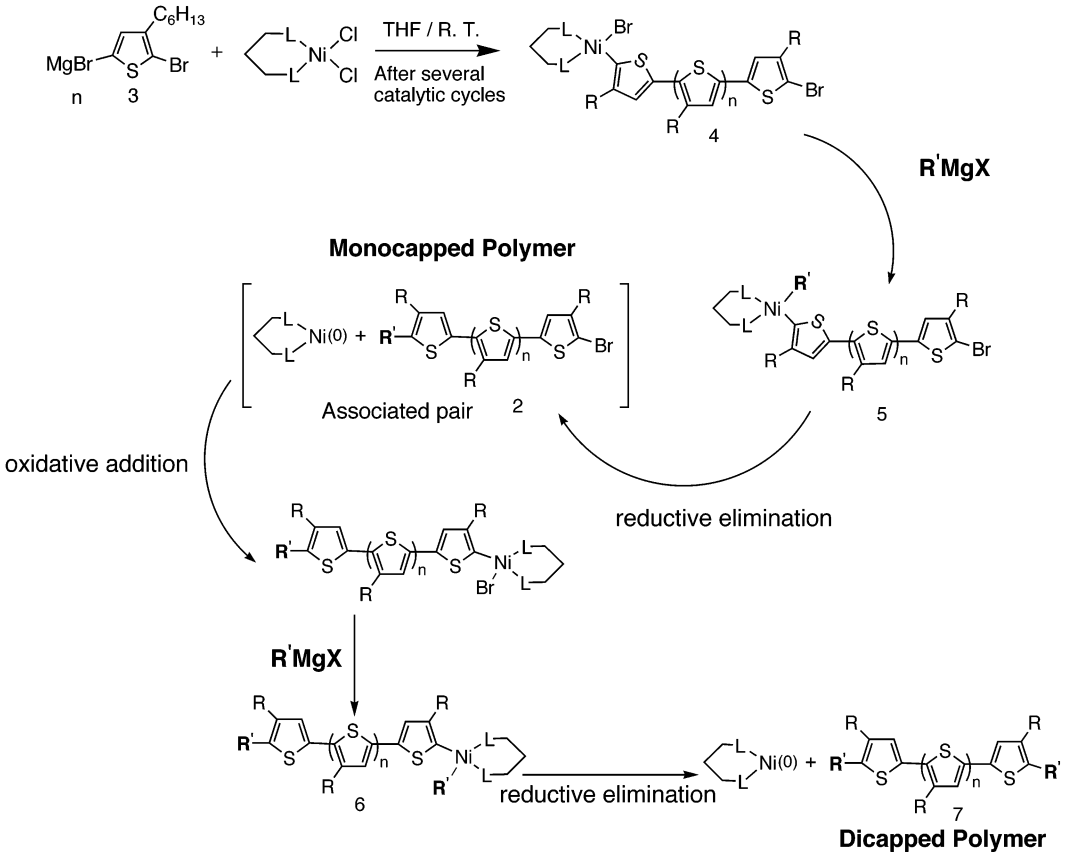
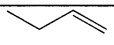
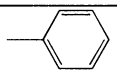
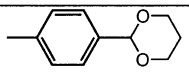
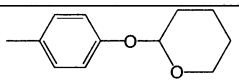
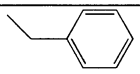
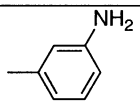



**Table 1. End Groups Synthesized and Resulting Polymers**

| 2 Monocapped | | 7 Dicapped | | | |
|---|---|---|---|---|---|
| **2a** |  | **7a** |  | **7d** |  |
| **2b**[a] |  | **7b** |  | **7f** |  |
| **2c** |  | **7c** |  | **7i** | — |
| **2d** |  | | | | |

[a] Polymer contains 15% of dicapped product.

Initially, we expected that the Grignard reagents would couple to our living chains to produce monofunctionalized polymers. To our surprise, we found that while some Grignard reagents gave monofunctionalized products, many others gave difunctionalized products. The only Grignard reagent that did not cap the polymer was the sterically hindered *tert*-butylmagnesium chloride. Whether we obtained mono- or difunctionalized polymers was not a function of the concentration of the Grignard reagent, nor of the reaction time with the Grignard reagent. Rather, we found that it was due to the nature of the Grignard reagent. This result can be explained by the proposed mechanism as shown in Scheme 2. First, we grew a polymer starting from a thienyl Grignard **3** and catalytic amounts of the Ni(dppp)$Cl_2$. After the polymerization was nearly complete, we were left with species **4** in solution. Polymer **4** reacted with RMgX to yield **5**, and a reductive elimination yielded the monocapped polymer **2**, which formed an associative pair with the highly reactive dppp

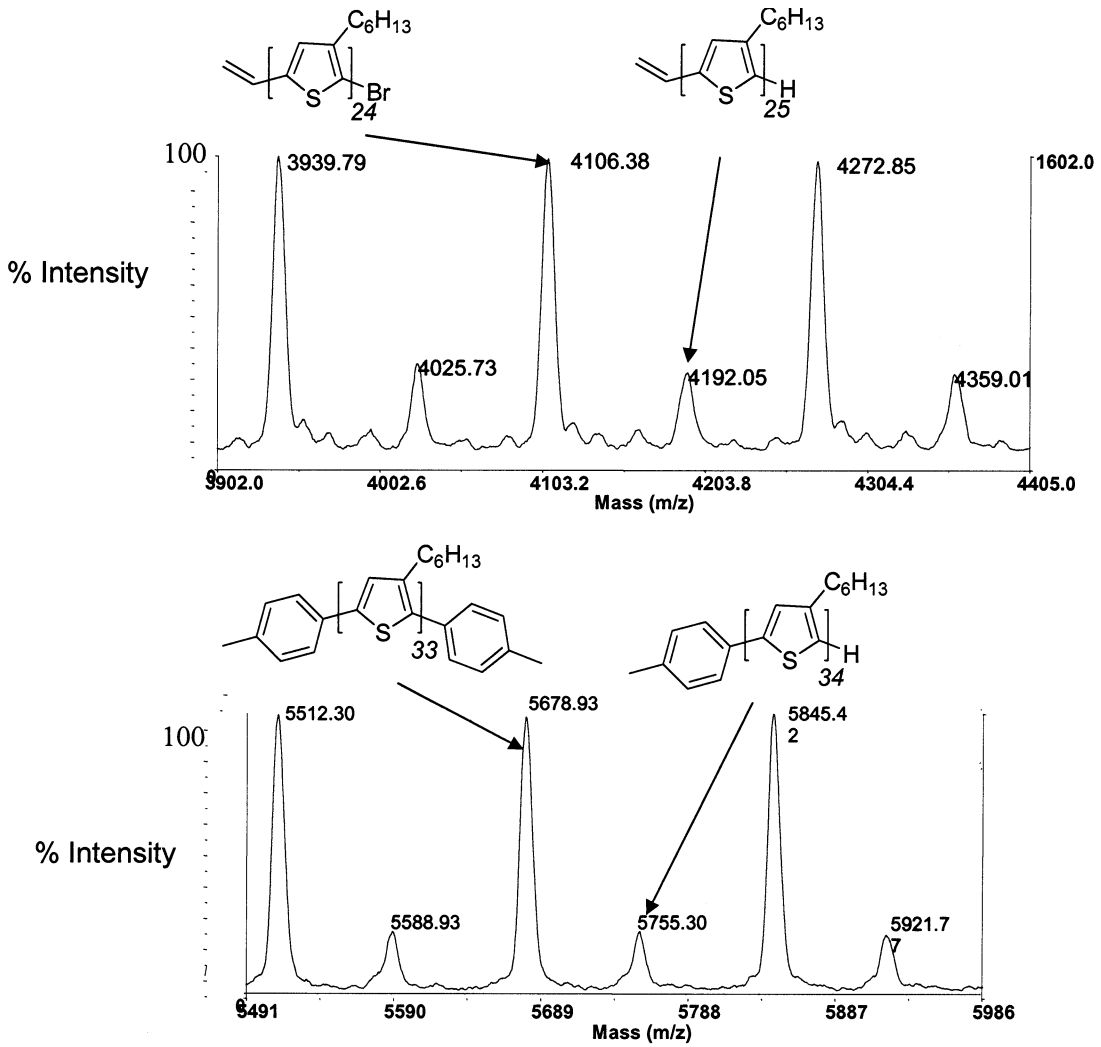



**Figure 1.** MALDI-TOF spectra of vinyl (top) and tolyl (bottom) terminated polymers.

Ni(0). The Ni(0) species reacted quickly with the Br end of polymer **2** to give **6**, which then further reacted with another RMgX to yield the dicapped product **7**.

As seen in Table 1, one notices that the Grignard reagents that produced monocapped polymers have a double or triple bond, while all others produced dicapped polymers. In the case of alkenyl and alkynyl Grignard reagents, the unsaturated group reacted with reactive Ni(0) to form a stable $\pi$-complex,[17] hence preventing any further reaction with the bromine end group of the polymer. While the alkene on the polymer end may play a role, the excess Grignard in solution reacting may also play a role. At this point it is unclear whether it is either one or a combination of both.

**Polymer Characterization. MALDI-TOF Mass Spectroscopy.** Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was employed to determine the end group composition of the end-capped P3ATs. This method was used because of its ability to ionize and analyze macromolecules with minimal fragmentation in the mass spectrometer. It has been established previously that terthiophene is the best matrix for use with P3ATs.[12] Sample preparation is critical. The best results are obtained when a solution of the matrix (75 mg/mL) in THF and a solution of the polymer (5 mg/mL) in THF are mixed 10:1 and then spotted on the sample well. Using this method, we were able to obtain spectra for all samples with molecular weights ranging from 4000 to 14 000.

The MALDI-TOF spectra of the end-capped P3ATs typically contain two populations, one major and one minor (Figure 1). In the case of the monocapped polymers, such as the vinyl-terminated polymer, the major peak corresponds to vinyl/Br and the minor peak to vinyl/H. In the case of the dicapped polymers, such as the tolyl-terminated polymer, the major peak corresponds to tolyl/tolyl and the minor peak to tolyl/H. In both cases the end group composition can be determined by $(166)n + 2(\mathrm{EG})$, $(166)n + 1 + \mathrm{EG}$, or $(166)n + 80 + \mathrm{EG}$ depending on the reactivity of the capping agent, where EG is the molecular weight of the end group and $n$ is the number of repeat units. This technique allows for identification of the peaks within $\pm 5$ Da, which is the expected error due to isotope effects.[18]

The MALDI-TOF spectra of the polymers bearing protected functional groups were slightly more difficult to analyze. In some cases (amines, aldehydes, and phenols) peaks are present that correspond to the unprotected species, suggesting some partial cleavage. For example, the MALDI-TOF spectra of the OTHP protected polymer shows two peaks corresponding to OTHP/OTHP and OH/OTHP. When compared to the $^1$H NMR spectrum, which shows only one species present, we surmised that cleavage is occurring within the mass spectrometer. The best spectra were obtained from the unprotected functional groups.

**$^1$H NMR Spectroscopy.** To further elucidate the structures of the end-terminated polymers, $^1$H NMR

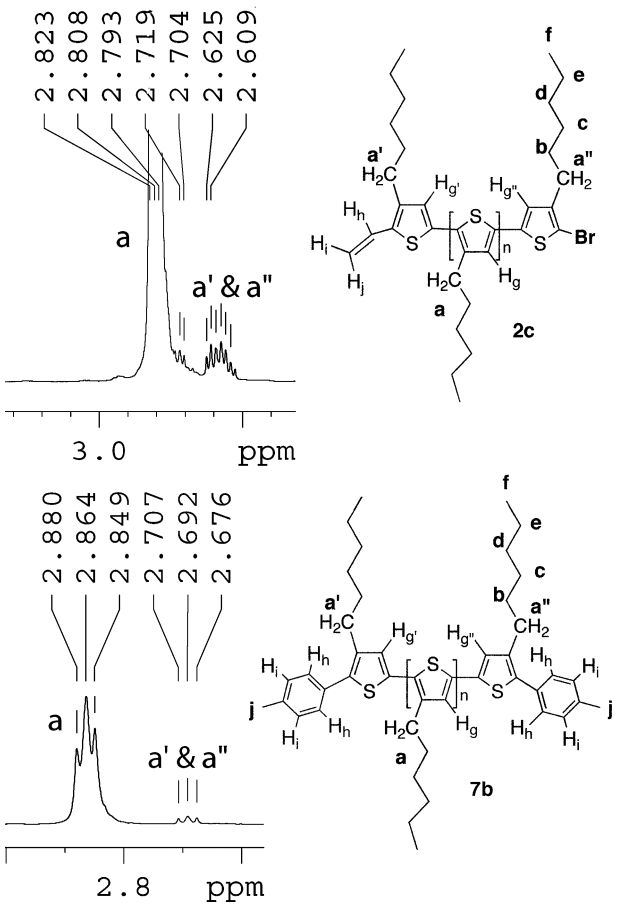



**Figure 2.** $^1$H NMR spectra of vinyl (top) and tolyl (bottom) terminated polymers.

spectroscopy was employed. For this study two different solvents were used: chloroform for most samples and THF for polymers with aromatic end groups. In all cases the end groups were identified by their chemical shifts and splitting patterns. Additionally, the integration of the end group protons to the thiophene proton was in agreement with the predicted structures. For example, the vinyl-terminated polymer shows three peaks: two doublets at 5.12 and 5.51 ppm corresponding to the geminal protons *i* and *j* with coupling constants of 11 and 17 Hz, respectively (Figure 2). The remaining vinyl proton is a multiplet at 6.48 ppm that partially overlaps the aromatic region. All of these protons integrate for a value of 1, giving a value of 28 for the thiophene proton. The latter value is consistent with the number-averaged degree of polymerization. Similarly, the spectra of the tolyl-terminated polymer has two doublets at 7.24 and 7.36 ppm, each with a coupling constant of 8 Hz, as is consistent with an AB system. These protons each integrate for a value of 4 giving a $DP_n$ of 41 for the polymer, as is consistent with the degree of polymerization for the molecular weight of the polymer by MALDI.

Additional information can be obtained from the aliphatic region of the spectra. Previous research has shown that the first step in the polymerization is the homocoupling of two monomers via the organometallic portion of the molecule. As a result, a tail-to-tail dimer is formed and every polymer chain contains one bad coupling at the end. The composition of the end-cap polymers can best be represented by the structure shown in Figure 3. The differences in the protons can

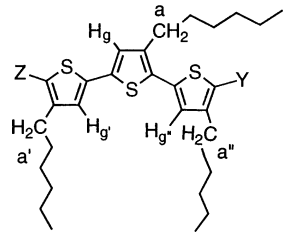
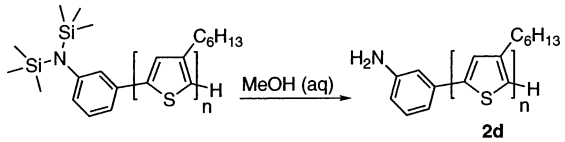


**Figure 3.** Detailed structure of polymer showing signifigant protons for NMR characterization.

**Scheme 3. Deprotection of Amine Polymer**




be seen in the aromatic and aliphatic regions of the $^1$H NMR spectra. In the latter a small multiplet is seen adjacent to proton a, corresponding to protons a′ and a″. In the case of monofunctionalized polymers, like the vinyl-terminated polymer, a′ and a″ are not equivalent, and as a result these peaks are two triplets which may appear as a multiplet. In the case of difunctionalized polymers, like the tolyl-terminated polymer protons, a′ and a″ are equivalent, and as a result the minor peak is a clear triplet. Previously, we estimated the end group composition of the dicapped polymers to be ~80% via MALDI.[19] However, it appears that end group determination by MALDI is diminished due to fragmentation. It is evident from the lack of a multiplet in the aliphatic region suggests that this percentage of end group functionality approaches 100% as we see no evidence of monocapped polymer in the NMR spectra.

**Masked Functional Groups.** To generate a more diverse group of end-capped polymers, the synthesis of Grignard reagents bearing masked protecting groups was investigated. It was believed that such a strategy would allow for the incorporation of a variety of different functional groups if suitable protecting groups could be found. Groups of interest included aldehydes, amines, phenols, and thiols. An amine group was successfully incorporated using the masked Grignard 3-[bis(trimethylsilyl)amino]phenylmagnesium chloride. This protecting group is very labile and is hydrolyzed during the workup yielding the amino-terminated polymer (Scheme 3). The MALDI-TOF and $^1$H NMR spectroscopy show that this polymer is monoterminated. This is most likely due to deactivation of the catalyst by the electron-rich trimethylsilyl groups. Aldehyde groups were introduced onto the polymer by using the masked Grignard (1,3-dioxan-2yl)phenylmagnesium bromide. The incorporation of the dioxan-2yl end groups onto the polymer was unclear by MALDI due to the similarity between the molecular weight of the end group 163.08 and the polymer repeating unit 166.23. However $^1$H NMR showed the incorporation of the masked aldehyde onto both ends of the polymer. Treatment of a solution of the dioxan−polymer in THF with pyridinium *p*-toluenesulfonate (PTS) yielded the aldehyde-terminated polymer in quantitative yield (Figure 4). The deprotection was monitored by MALDI-TOF MS and $^1$H NMR. The MALDI spectra of the dioxane polymer showed one set of peaks corresponding to both dioxane/dioxane (calcd 5643.81) and dioxane/H (calcd 5652.01), for example when $n = 32$ for the former and $n = 34$ for the latter. However, the MALDI-TOF spectra of the aldehyde

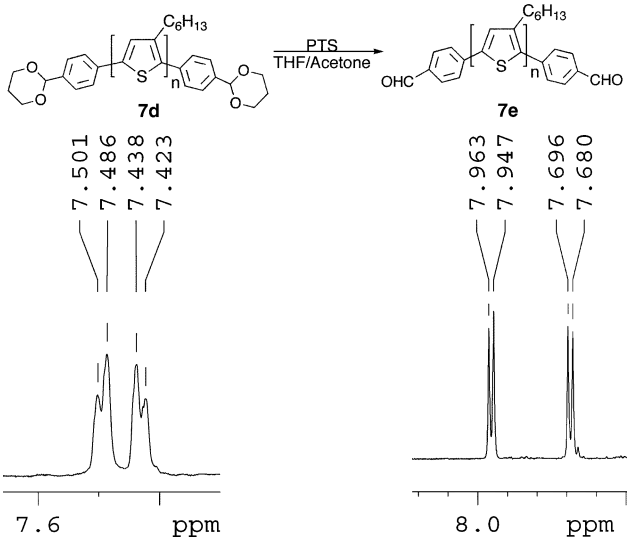



**Figure 4.** Aromatic region of $^1$H NMR spectra of phenyldioxolane and benzaldehyde terminated polymer.

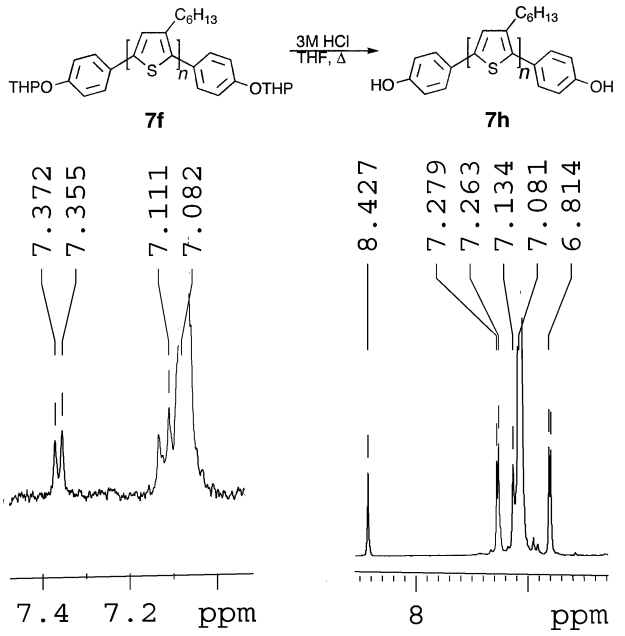



**Figure 5.** Aromatic region of $^1$H NMR spectra of tetrahydropyranyl and phenol terminated polymer.

polymer shows narrow peaks at 5537.66 and 5570.67, corresponding to Ph−CHO/Ph−CHO (5527.72) and Ph−CHO/H (calcd 5589.86) for $n = 34$ and 35, respectively. The $^1$H NMR spectrum shows peaks at 7.43 and 7.49 for the dioxane polymer. These peaks disappear from the spectra of the deprotected polymer, and two new peaks appear at 7.69 and 7.96 ppm. Additionally, a small aldehyde peak can be seen at 10.15 ppm.

In a similar fashion using 4-(2-tetrahydro-2*H*-pyranoxy)phenylmagnesium bromide, a masked phenol was introduced onto the polymer. Treatment of a solution of the OTHP polymer in THF with 6 M HCl yielded the phenol-terminated polymer in quantitative yield (Scheme 3). The MALDI spectrum of the OTHP polymer has peaks at 4427.08 and 4509.03, corresponding to OTHP/OH (calcd 4425.88), due to partial deprotection and OTHP/OTHP (calcd 4508.61) for $n = 25$. However, the MALDI-TOF spectrum of the phenol polymer shows narrow peaks at 4417.36 and 4511.17, corresponding to OH/H (calcd 4416.06) and OH/OH (calcd 4509.1) for $n = 26$. Although the masses for the peaks before and after the deprotection reaction are similar, unambiguous assignment of these peaks is aided by the $^1$H NMR spectrum, which shows peaks at 7.11 and 7.36 ppm for the OTHP polymer. These peaks disappear from the spectra of the deprotected polymer and two new peaks appear at 6.80 and 7.27 ppm. Additionally, a small phenol peak can be seen at 8.43 ppm.

The examples presented herein demonstrate the efficiency and versatility of the modified Grignard metathesis reaction to generate P3ATs bearing a variety of different end groups in situ. This method is also very reliable and consistently produces polymers with high percentages (80−99%) of end group functionality. This reaction also works well on the large scale. Experiments performed in our labs with 16 g of monomer yielded 5.5 g of P3HT with >90% end group functionalized, showing no decrease in functionality as the reaction is scaled up. This opens the door to the possibility of synthesizing these materials on large scale and using these materials in a variety of applications.

## Conclusions

The modified Grignard metathesis reaction can be used to functionalize HT-poly(3-hexylthiophenes) at one chain end or at both chain ends. We have demonstrated that a wide variety of HT-PTs bearing a large variety of end groups can be made via this facile one-step procedure. We found that unsaturated Grignard reagents yielded monofunctionalized polymers whereas others produced difunctionalized polymers. Strategies developed from this work will allow for the synthesis of a plethora of new materials via the incorporation of simple and functionalized Grignard reagents. End group functionalization of rr-P3ATs will allow for the control of polymer morphology via end group driven self-assembly onto surfaces. Additionally, these polymers can be used as building blocks for the synthesis of rod−coil and coil−rod−coil polymers, allowing for fine-tuning of the supramolecular architecture of the polymer.

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**Supporting Information Available:** Representative NMR of polymers **2a**, **2b**, **7a**, **7b**, **7f**, **7g**, and **7h** and MALDI-TOF MS of **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, **7g**, and **7h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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