

In-Situ End-Group Functionalization of Regioregular Poly(3-alkylthiophene) Using the Grignard Metathesis Polymerization Method**

By Malika Jeffries-EL, Geneviève Sauvé, and Richard D. McCullough*

Due to their excellent electrical properties, regioregular polythiophenes are rapidly being developed into new commercial products with applications ranging from transistors to hole-transport layers in organic light-emitting diodes (OLEDs) to new specialty plastics.^[1–3] As regioregular polythiophenes grow in importance, so does the development of inexpensive and convenient methods for the synthesis of these polymers. While a great deal of work has been reported for the modification and variation of the side chains of regioregular, head-to-tail coupled polythiophenes (HT-PTs),^[4] less attention has been given to the nature and control of the end groups of such polymers.^[5,6] Procedures published to date to functionalize end groups of conjugated polymers are limited in scope and number.^[5,6] End-group functionalization of HT-PTs would lead to a number of new uses for these polymers including end-group-driven self-assembly onto surfaces and into conducting polymer networks, and their use as building blocks for the synthesis of block copolymers.^[7]

Previously, our group reported a multistep synthesis of HT-PTs bearing amino and hydroxyl groups.^[5] The hydroxylated PTs were further derivatized and used to synthesize, e.g., HT-PT–polystyrene diblock and triblock copolymers.^[7] These copolymers self-assemble into nanowires, resulting in surprisingly high conductivities, even with relatively low percentages of HT-PT in the copolymer. While these materials have very interesting properties, their seven-step synthesis limits their ease of preparation and usefulness. To fully realize the potential of these materials, new convenient synthetic methods must be developed that are simple and highly reproducible. Herein, we report a new protocol for controlling the end-group composition of the polymer. This method is used for the simple synthesis of HT-PTs bearing a wide variety of functional end groups, including critical functionalities that will allow for the synthesis of conducting block copolymers in only three steps.

The main objective of this work was to find a method to systematically functionalize the end groups of HT-PT using the simple Grignard metathesis polymerization (GRIM)^[3] meth-

od developed by our group. Typical polymerization of 2,5-dibromo-3-hexylthiophene **1**, using the GRIM method, yields a polymer that has primarily one end-group composition, namely H/Br. Selective conversion of the Br terminated polymer to yield a functionalized end-capped PT can be accomplished by a post-polymerization functionalization reaction.^[5] Since the polymerization of **1** follows a chain-growth mechanism,^[8] we believed that the simple addition of a Grignard reagent would terminate the polymer growth and give mono-capped HT-PTs. Indeed, we have found that the addition of a Grignard reagent effectively ‘end caps’ the polymer, and provides a simple one-pot method to control the end-group composition of HT-PT and introduces functionality into the polymer. The results are summarized in Scheme 1.

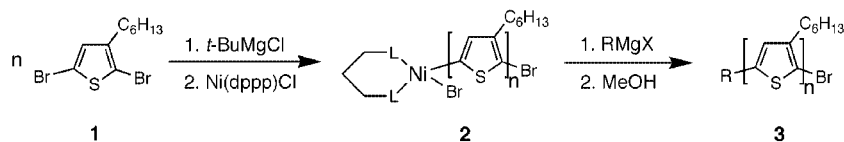
Using a modification of the published GRIM method,^[9] we successfully incorporated a wide variety of R groups at the end of the polymer. This was accomplished by adding a large excess of Grignard reagent RMgX to the polymer reaction mixture after 10–15 min of polymerization time. The mixture was then poured into methanol to precipitate the polymer. The end group composition of the polymer was analyzed by matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS)^[10] and the results are summarized in Table 1. To our surprise, we found that while some Grignard reagents gave mono-capped products, many others gave di-capped products. The only Grignard reagent that did not cap the polymer is the sterically hindered *t*-butylMgCl. Whether we obtained mono- or di-capped polymers was not a function of the concentration of the Grignard reagent, nor of the reaction time with the Grignard reagent.

Upon further examination of the data in Table 1, one notices that the Grignard reagents that have a double or triple bond produced mono-capped polymers, while all the other ones produced di-capped polymers. These results are explained in Scheme 2. First, we grow a polymer starting from a thienyl Grignard **4** and catalytic amounts of the Ni(dppp)Cl₂. After the polymerization is nearly complete, we are left with species **2** in solution. Polymer **2** reacts with RMgX to yield **5**, and a reductive elimination yields the mono-capped polymer **3** and highly reactive Ni⁰dppp. The Ni⁰ forms an associative pair^[8] with **3** followed by oxidative addition with **3** to give **6**, which can then further react with another RMgX to yield the di-capped product **7**. In the case of alkenyl and alkynyl Grignard reagents, the unsaturated group^[11] can react with reactive Ni⁰ to form a stable π -complex,^[12,13] hence preventing any further reaction with the bromine end group of the polymer.

The ability to mono-cap HT-PT efficiently using alkenyl Grignard reagents is very important because the alkene-terminated polymer can easily be used as building blocks in the synthesis of diblock copolymers. We are currently exploring innovative methods of synthesizing diblock copolymers using materials synthesized via this new ‘capping’ method and the results will be published elsewhere. As an example, we have found that diblock copolymers can be efficiently made from polymer **1**.^[14]

[*] Prof. R. D. McCullough, Dr. M. Jeffries-EL, Dr. G. Sauvé
Department of Chemistry, Carnegie Mellon University
4400 Fifth Ave., Pittsburgh, PA 15213 (USA)
E-mail: rm5g@andrew.cmu.edu

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Scheme 1. Mono-capping of the growing polymer chain by adding RMgX.

Table 1. Summary of Reactions

	Grignard reagent	End group	Di-capped [a] (R=Y)	Mono-capped [a] (R≠Y)
Mono-capped	VinylMgBr	1	0%	91%
	AllylMgBr	2	0%	87%
	EthynylMgBr	3	14%	86%
Di-capped	PhenylMgBr	4	76%	24%
	TolylMgBr	5	80%	20%
	BenzylMgCl	6	80%	20%
	<i>p</i> -OTHP-PhenylMgBr [b]	7	75%	12%
	MethylMgBr	8	76%	24%
	ButylMgCl	9	67%	21%
	<i>t</i> -butylMgCl [c]	10	0%	0%

[a] In cases where the sum is not equal to 100% the remainder of the polymer is uncapped. [b] THP=tetrahydropyranyl, polymer was deprotected and analyzed as the phenol. [c] No reaction.

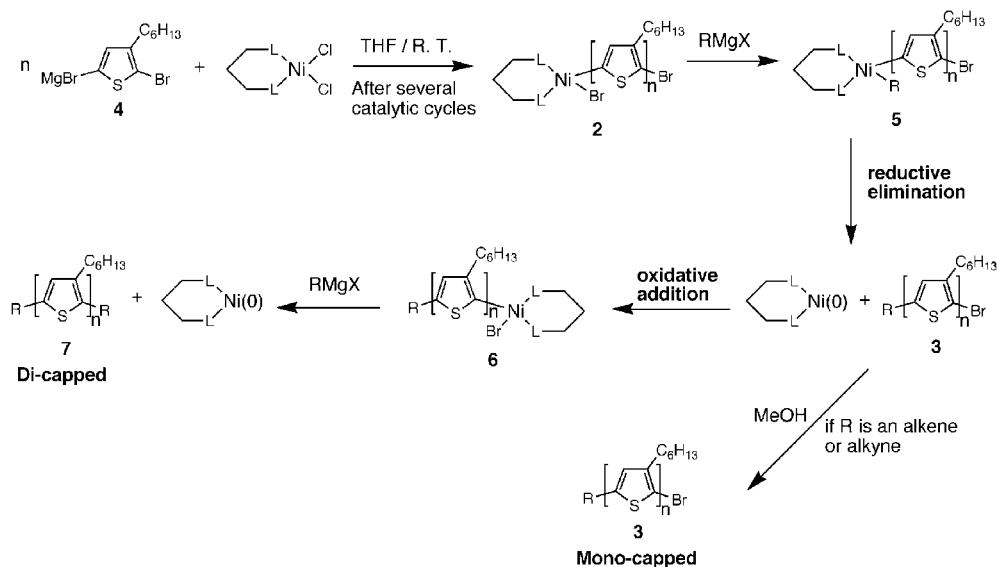
In conclusion, we have demonstrated that a wide variety of HT-PTs bearing a large variety of end groups can be made via a facile one-step procedure. We found that alkenyl and alkynyl Grignard reagents mono-capped the polymer whereas others di-capped the polymer. Strategies developed from this work will allow for the synthesis of a plethora of new materials, via the incorporation of simple and functionalized Grignard reagents.

Furthermore, this simple procedure will allow for the synthesis of a library of capped polymers that can be used to better understand the effect of end-group composition on polymer morphology and self-assembly.

Experimental

Materials: The monomer 2,5-dibromo-3-hexylthiophene **1** was synthesized according to the literature procedure [3]. 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)Cl₂, allylmagnesium bromide, butylmagnesium chloride, benzylmagnesium chloride, ethynyl magnesium bromide, methylmagnesium bromide, vinylmagnesium bromide *tert*-butylmagnesium chloride, *p*-tolylmagnesium bromide, phenylmagnesium bromide and 4-(2-tetrahydro-2*H*-pyranoxy)phenylmagnesium bromide were purchased from Aldrich Chemical Co. and used without further purification.

Typical Synthesis of End-Capped Regioregular Poly(3-hexylthiophene) [15]: 2,5-dibromo-3-hexylthiophene **1** (1.63 g, 5.0 mmol) was dissolved in THF (50 mL). *tert*-Butylmagnesium chloride (2.5 mL, 5.0 mmol) was added via syringe and the mixture was refluxed for 1.5 h. The reaction mixture was then allowed to cool to room temperature and Ni(dppp)Cl₂ (45 mg, 0.08 mmol) was added in one portion. The mixture was stirred for 10 min at room temperature, then the Grignard reagent (10–30 mol-% of monomer) was added via syringe to the reaction mixture. The mixture was stirred for 2 min and then poured into methanol to precipitate the polymer. The polymer was



Scheme 2. Proposed mechanism of end capping.

filtered into an extraction thimble and then washed by Soxhlet extraction with methanol, hexane, and chloroform. The polymer was isolated from the chloroform extracts. End-group composition was evaluated with MALDI-TOF MS (Voyager-DE STR BioSpectrometry workstation by Biosystems, terthiophene matrix, linear mode, sometimes performed before extractions), and the polymer structure was confirmed with ^1H NMR (Bruker 500 MHz instrument).

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- [15] Characterization of (H/Br poly(3-hexylthiophene): ^1H NMR (500 MHz, CDCl_3): δ_H 0.91 (t, $J=7$ Hz, 3H), 1.40 (m, 6H), 1.69 (t, $J=7$ Hz, 2H), 2.80 (t, $J=7$ Hz, 2H), 7.46 (s, 1H); GPC: M_n : 11 364, PDI: 1.2; MALDI-MS: m/z : 6239.4 [M^+] (calcd: 6231.2, DP of 46, H/Br end groups). Characterization of **1**: ^1H NMR (500 MHz, CDCl_3): Hexyl peaks are the same as above with δ_H 5.11 (d, $J=11$ Hz, 1H), 5.49(d, $J=11$ Hz, 1H), 6.20 (m, 1H), 7.14 (s, 55H); GPC: M_n : 11 218, PDI: 1.1; MALDI-MS: m/z : 4927.2 [M^+] (calcd: 4927.7, DP of 29, Br/Vinyl end groups). Characterization of **2**: ^1H NMR (500 MHz, CDCl_3): Hexyl peaks same as above with δ_H 3.49 (d, $J=6.5$ Hz, 2H), 5.12 (d, $J=6.5$ Hz, 2H), 5.98 (m, 1H), 7.14 (s, 44H); GPC: M_n : 6068, PDI: 1.1; MALDI-MS: m/z : 4110.3 [M^+] (calcd: 4111.6, DP of 24, Br/Allyl end groups). Characterization of **10** (uncapped): ^1H NMR (500 MHz, THF d_8): δ_H 0.92 (t, $J=7$ Hz, 3H), 1.37 (m, 6H), 2.85 (t, $J=7$ Hz, 2H), 7.08 (s, 1H), (remaining two protons buried under solvent peak); GPC: M_n : 11 200, PDI: 1.2; MALDI-MS: m/z : 7561.0 [M^+] (calcd: 7561.4, DP of 45, H/Br end groups). Characterization of **3**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks are the same as for **10** with, δ_H 4.12 (s, 1H), 7.05 (s, 39H); GPC: M_n : 8232, PDI: 1.4; MALDI-MS: m/z : 5768.0 [M^+] (calcd: 5758.6, DP of 34, ethynyl/Br end groups). Characterization of **4**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks same as for **10** with, δ_H 7.11 (s, 41H), 7.43 (m, 2H), 7.47 (m, 8H); GPC: M_n : 12 000, PDI: 1.1; MALDI-MS: m/z : 8305.9 [M^+] (calcd: 8302.2, DP of 49, phenyl/phenyl endgroups). Characterization of **5**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks same as for **10** with, δ_H 7.10 (s, 29H), 7.24 (d, $J=8$ Hz, 4H), 7.36(d, $J=8$ Hz, 4H); GPC: M_n : 6700, PDI: 1.1; MALDI-MS: m/z : 4508.6 [M^+] (calcd: 4505.6, DP of 26, tolyl/tolyl). Characterization of **6**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks same as for **10** with, δ_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). Characterization of **7**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks same as for **10** with, δ_H 6.81 (d, $J=8.5$ Hz, 4H), 7.07 (s, 34H), 7.28 (d, $J=8.5$ Hz, 4H); GPC: M_n : 4118, PDI: 1.51; MALDI-MS: m/z : 4348.2 [M^+] (calcd: 4343.2, DP of 25, Ph-OH/Ph-OH). Characterization of **8**: ^1H NMR (500 MHz, CDCl_3): (Hexyl peaks same as for H/Br poly(3-hexylthiophene) with, δ_H 2.37 (s, 6H), 6.98 (s, 43H); GPC: M_n : 8.500, PDI: 1.1; MALDI-MS: m/z : 5185.9 [M^+] (calcd: 5184.8, DP of 31, methyl/methyl). Characterization of **9**: ^1H NMR (500 MHz, THF d_8): (Hexyl peaks same as for **10**, butyl peaks overlap with hexyl); GPC: M_n : 7506, PDI: 1.1; MALDI-MS: m/z : 4508.6 [M^+] (calcd: 4505.6, DP of 26, butyl/butyl).

Hierarchical Structure: Silicon Nanowires Standing on Silica Microwires**

By Changhui Ye,* Lide Zhang, Xiaosheng Fang, Yinhai Wang, Peng Yan, and Jianwei Zhao

Silicon nanowires are attractive building blocks for the next generation of nanoelectronic devices because they can function both as the core of the devices and as the interconnectors between components.^[1] With the ongoing miniaturization of silicon-based electronics, conventional lithography is reaching its limits. Fortunately, the self-assembly of nanoscale building blocks has proven successful in microelectronics and this technique is accessible to many laboratories, since costly fabrication lines are avoided.^[2] However, the fabrication of nanodevices by either a self-assembly or improved Langmuir–Blodgett approach still entails lengthy and elaborate processing, although the new, emerging, so-called hierarchical struc-

*] Dr. C. Ye, Prof. L. Zhang, Dr. X. Fang, Prof. Y. Wang, Dr. P. Yan, Dr. J. Zhao
Key Laboratory of Materials Physics
Institute of Solid State Physics
Chinese Academy of Sciences
Hefei 230031 (P.R. China)
Email: chye@issp.ac.cn

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