

IN SITU END GROUP MODIFICATION OF REGIOREGULAR POLY(3-ALKYLTHIOPHENES) VIA GRIGNARD METATHESIS (GRIM) POLYMERIZATION.

Malika Jeffries-EL, Geneviève Sauv , Mihaela Iovu and Richard D. McCullough

Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15218

Introduction

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 OLEDs to new specialty plastics.¹⁻⁶ 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),⁷ less attention has been given to the nature and control of the end groups of such polymers.⁸⁻¹² To date, literature procedures to functionalize end groups of conjugated polymers are limited in scope and number. 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.¹³

Previously, our group reported a multistep synthesis of HT-PTs bearing amino- and hydroxyl- groups.¹³ The hydroxylated PTs were further derivatized and used to synthesize e.g. HT-PT-polystyrene diblock and triblock copolymers.⁸ These copolymers self-assemble into nanowires through phase separation, resulting in very high conductivities at low HT-PT percentages. While these materials have very interesting properties, the seven step synthesis limits their usefulness. To fully realize the potential of these materials, new convenient 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.

Experimental

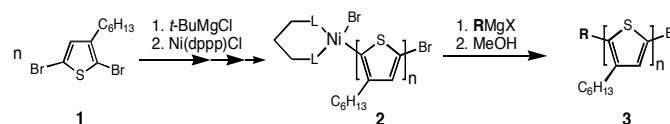
Materials. The monomer 2,5-dibromo-3-hexylthiophene **1** was synthesized according to the literature procedure.¹⁴ All reactions were performed under prepurified nitrogen or argon, using oven-dried glassware. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Ni(dppp)Cl₂, allylmagnesium bromide, butylmagnesium chloride, benzylmagnesium chloride, ethynyl magnesium bromide, methyl magnesium bromide, vinylmagnesium bromide *tert*-butylmagnesium chloride, *p*-tolylmagnesium bromide, phenylmagnesium bromide and 4-(2-tetrahydro-2H-pyranoxyl)phenylmagnesium bromide were purchased from Aldrich Chemical Co. and used without further purification.

Typical Synthesis of end-capped regioregular Poly(3-hexylthiophene) 2,5-dibromo-3-hexylthiophene **1** (1.63g, 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 hours. 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 minutes at room temperature, then a large excess of a Grignard reagent (10-30 mole % of monomer) was added via syringe to the reaction mixture. The mixture was stirred for 2 minutes 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, hexane and chloroform. The polymer was isolated from the chloroform extraction. End-group composition was evaluated with MALDI-TOF MS (Voyager-DE STR BioSpectrometry workstation by Biosystems, terthiophene matrix, sometimes performed before extractions), and confirmed with ¹H NMR (Bruker 300 Mhz instrument).

Results and Discussion

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)¹⁴ method developed by our group. Typical polymerization of 2,5-dibromo-3-hexylthiophene **1**, using the GRIM method, yields a polymer which 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.¹³ Since the polymerization of **1** follows a chain-growth mechanism,³ 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 introduce functionality into the polymer. The reaction is summarized in scheme 1.



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

Using a modification of the published GRIM method,¹⁵ we successfully incorporated a wide variety of R groups at the end of the polymer. 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. In fact it is due to the nature of the capping reagent.¹⁶

The ability to mono-cap HT-PT efficiently using alkenyl Grignard reagents is very important because the alkene-terminated polymers 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 discussed.

	Grignard Reagent	End Group	Di-capped (R = Y)	Mono-capped (R ≠ Y)
Mono-capped	VinylMgBr			X
	AllylMgBr			X
	EthynylMgBr			X
Di-capped	PhenylMgBr		X	
	TolylMgBr		X	
	BenzylMgCl		X	
	<i>p</i> -OTHP-PhenylMgBr ^a		X ^b	
	MethylMgBr		X	
	ButylMgCl		X	
	<i>t</i> -butylMgCl			

Table 1. Summary of reactions.

^a THP= tetrahydropyranyl. ^b Appears to be 100% di-capped polymer.

Conclusions

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.

Acknowledgements. The authors of this paper would like to thank Dr. Tomasz Kowalewski, Elena E. Sheina and Dr. Darin Laird for ongoing discussions about this work, and NSF# CHE0107178 and AFOSR/MURI for financial support of this research.

References

- (1) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741-1744.
- (2) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685-688.
- (3) Kline, J. R.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J.M. *J. Adv. Mat.* **2003**, *15*, 1519-1522.
- (4) Brown, A. R.; Pomp, C. M.; de Leeuw, D. M. *Science* **1995**, *270*, 972-974.
- (5) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 3.
- (6) Huynh, W. U.; Dittmer, J. J.; Alivasatos, P. *Science* **2002**, *295*, 2425-2427.
- (7) McCullough, R. D. *Adv. Mat* **1998**, *10*, 93-116.
- (8) Liu, J. S.; McCullough, R. D. *Macromolecules* **2002**, *35*, 9882-9889.
- (9) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Spiering, A. J. H.; van Dongen, J. L. J.; Vonk, E. C.; Claessens, H. A. *J. Chem Soc. Chem. Comm.* **2000**, *2000*, 81.
- (10) Jayakannan, M.; Dongen, J. L. J. v.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 8.
- (11) Iraqi, A.; Barker, G. W. *J. Mat. Chem.* **1998**, *8*, 25.
- (12) Sauve, G.; Jeffries-El, M.; McCullough, R. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2003**, *44*, 432.
- (13) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 4.
- (14) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mat* **1999**, *11*, 250-258.
- (15) Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324-4333.
- (16) Jeffries-EL, M, Sauve, G. McCullough, R.D. in submission