CONTROL OF END-GROUPS OF REGIOREGULAR POLY(3-ALKYLTHIOPHENES) USING GRIGNARD METATHESIS.

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

Department of Chemistry
Carnegie Mellon University
4400 Fifth Ave.
Pittsburgh, PA 15213

Introduction

Poly-3-alkylthiophenes (PATs) constitute an important group of conjugated polymers due to their good solubility, environmental stability, and conductivity.[1] They find potential applications in electronic, photonic and sensor materials and devices. Control over the regiochemistry of poly(3-alkylthiophene) has been efficiently achieved by Kumada coupling of either organomagnesium[2-4] or organozinc[5] monomers using Ni(II) catalyst complexes. Such defect-free head-to-tail polyalkylthiophenes (HT-PATs) have improved electronic and photonic properties over regiorandom analogs.[3,4] Using these materials, a multitude of nano- and micro-structured electronic devices and materials have been produced.

Although poly(3-alkylthiophene)s can now be considered as well-studied and easily prepared polymers, less attention has been given to the nature and control of the end groups of such polymers.[6,7] End-group control and functionalization of PATs is of great interest in order to extend the application of this class of conducting polymers. This could lead to the synthesis of novel materials with interesting properties. For example, our group recently prepared novel block-copolymers containing HT-PAT and polystyrene that have improved mechanical properties over the homopolymer.[8] These copolymers self-assemble into nanowires through phase separation, resulting in unexpectedly high conductivities at low HT-PAT loadings.

Literature procedures to functionalize end groups of conjugated polymers are limited in scope and number.[9] Recently, our groups reported the end-group functionalization of PATs using post-polymerization modification methods.[6] However, this method relies on the ability to make HT-PAT with hydrogen termination at one end and bromine termination at the other (H/Br) using the McCullough method,[6] which can be tricky. There is great interest in developing simpler methods to prepare telechetic conjugated polymers. In this paper, we report a way to make H/Br terminated PT using the Grignard metathesis (GRIM) method reproducibly. We then demonstrate an easy and quick way to end-cap the polymer using Grignard reagents.

Experimental

Materials. The monomer 2,5-dibromo-3-hexylthiophene **1** was synthesized according to the literature procedure.[2] 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, *tert*-Butylmagnesium choride, *p*-Tolylmagnesium bromide and Phenylmagnesium bromide were purchased from Aldrich Chemical Co. and used without further purification.

Instrumentation. GPC spectra were recorded using a Waters 2690 Separations Module and a Waters 2487 Dual λ absorbance detector. The eluent was $CHCl_3$ kept at 30°C. The flow rate was 1.0 ml/min. The system was calibrated using polystyrene standards. MALDI/TOF MS was used to analyze the end group composition,[6] and the analysis was performed using a Voyager-DE STR BioSpectrometry workstation by Biosystems.

Synthesis of regioregular Poly(3-hexylthiophene) 2,5-dibromo-3-hexylthiophene **1** (0.65g, 2.0 mmol) was dissolved in THF (13 mL). *tert*-Butylmagnesium chloride (1.0 mL, 2.0 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)Cl_2 (20 mg, 0.037 mmol) was added in one portion. The mixture was stirred for 15 min at room temperature and then poured into methanol to precipitate the polymer. M_n= 10000 g/mol, PDI 1.2 by GPC.

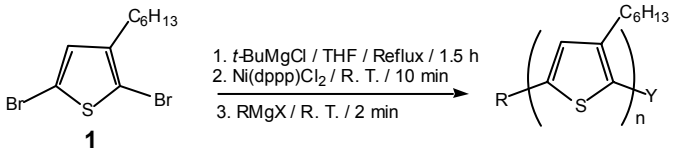
End-capping: The preparation of end-capped polymers was similar to the preparation of Poly(3-hexylthiophene) except that 10 minutes after adding the catalyst Ni(dppp)Cl_2, a large excess of a Grignard reagent (>0.5 mmol) was added via syringe to the reaction mixture. The mixture was then poured into methanol to precipitate the polymer.

Results and Discussion

We have found that HT-PATs that have a high percentage of H/Br end-groups can be easily produced via the GRIM method. The end-group analysis by MALDI/TOF MS shows about 80% H/Br and 20% H/H terminated HT-PATs (by peak height). The H/Br terminated HT-PAT can be used to prepare novel diblock copolymers via post-functionalization of the bromine end-group.

Additionally, we have found that the GRIM method can be modified to yield HT-PATs with a variety of end-groups (Scheme 1). A growing chain of regioregular poly(3-hexylthiophene) was easily capped by adding *p*-Tolylmagnesium bromide 10 to 15 minutes after the addition of the Ni(dppp)Cl_2 catalyst. The resulting polymer consisted of 80% tolyl/tolyl and 20% H/tolyl terminated HT-PATs (by peak height of MALDI/TOF MS). Similar results were observed using Phenylmagnesium bromide. The 80/20 ratio corresponds to the uncapped polymer for H/Br and H/H, respectively. This is consistent with the hypothesis that the *p*-Tolymagnesium bromide added both at the growing end of the polymer and at the bromine end-group. This also indicates that the H end-group is not due to the capping with the Grignard reagent, but happens during the polymerization step. When we followed the end-group composition of the HT_PATs with polymerization time, we found that the 80/20 ratio was set within the first minute of the polymerization. The origin of the H-termination is not yet understood.

The end-capping of HT-PATs by a variety of other Grignard reagents with different functionalized groups is being investigated. We are particularly interested in using this method to prepare a thiol/thiol terminated HT-PAT for use in molecular wire applications. Progress towards understanding the mechanism for the polymerization and end-group control is also in progress and will be discussed. This work has great potential for end-group control of HT-PATs.



Scheme 1. Synthesis of HT-PATs with different end-groups. Y could be H, Br or R.

Conclusions

The GRIM method was successfully used to obtain ~80% H/Br terminated HT-PAT easily and reproducibly. When *p*-Tolylmagnesium bromide or Phenylmagnesium bromide was added towards the end of the polymerization, the polymer was rapidly capped. We are currently exploring a variety of Grignard reagents with different functional groups to cap the polymer. Work is also underway to better understand the mechanism for the polymerization and end-group control. This new end-capping method has great potential for making novel materials.

Acknowledgements. The authors of this paper would like to thank Elena E. Sheina and Dr. Darin Laird for ongoing discussions about this work and NSF for financial support of this research.

References

(1) Skothein, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; 2nd ed.; Marcel Dekker: New York, 1998.
(2) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250-253.
(3) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc. Chem. Commun.* **1992**, 70.
(4) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904-912.
(5) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
(6) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777-5785.
(7) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Spiering, A. J. H.; Dongen, J. L. J.; Vonk, E. C.; Claessens, H. A. *Chem. Commun.* **2000**, 81.
(8) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 329-332.
(9) Marsitzky, D.; Klapper, M.; Mullen, K. *Macromolecules* **1999**, *32*, 8685-8688.