SYNTHESIS OF REGIOSPECIFIC POLY(3-SUBSTITUTED-THIOPHENES) USING Ni[II]-α-DIIMINE-INITIATED CROSS-COUPLING REACTION

Elena. E. Sheina, Mihaela C. Iovu, and Richard D. McCullough*

Chemistry Department
Carnegie Mellon University
Pittsburgh, PA 15213

Introduction

Polythiophenes (PTs) continue to be one of the most versatile and extensively studied conjugated polymer systems due to their exceptional spectroscopic and electronic properties, and the ease of synthesis of PTs derivatives. Practical and potential applications of PT derivatives include rechargeable battery,[1a] electrochromic devices (ECDs) (*e.g.*, poly(alkylenedioxythiophene) [PXDOT]),[1b-d] chemical and optical sensors,[1e] light-emitting diodes (LEDs),[1f] field-effect transistors (FETs).[1g] Structurally regioregular PTs can be obtained by several methods[2-4] that utilize a metal-initiated cross-coupling reaction that proceeds by a chain-growth mechanism.[5] The choice of the metal and the ligands used in polymerization is crucial to achieving a high degree of regioregularity in the product PT.[6] After comparing Ni *vs.* Pd with different ligands (*e.g.*, monodentate (PPh₃) or bidentate (Ph₂PCH₂CH₂PPh₂; dppe), it has been observed that cross-coupling selectivity was a function of the steric environment of the metal, where the most sterically hindered Ni(dppe)Cl₂ produced regioregular PT and the least hindered Pd(Ph₃)₄ produced regiorandom PT.

Here we report synthesis of regioregular poly(3-alkyl/alkoxy-substituted-thiophenes) *via* the Grignard Metathesis (GRIM) method[4] employing a Ni[II]-α-diimine catalyst [(ArN=C(An)-C(An)=NAr)NiBr₂ with Ar = 2-*t*-BuC₆H₄)] (see Figure 1, **2**) that has a great tolerance to different functional groups and is mainly used for living polymerization of α-olefines.[7] Utilizing this catalyst leads to regioregular polymers in good yield with narrow polydispersities (PDIs)[8] (*e.g.*, PDI=1.25 for poly(3-hexylthiophene) (**1a**)) with similar electrical and spectroscopic properties previously reported for PT synthesized by the well-established methods.[1f] Furthermore, the synthesis of the catalyst and employing the GRIM method provide a quick, easy and cost effective procedure for the synthesis of regiospecific PT derivatives on an industrial level.

Experimental

Reagents. All polymerization reactions were performed under prepurified nitrogen, using either flame-dried or oven-dried glassware. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. All solvents were freshly distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium/potassium benzophenone ketyl. Titration of the Grignard reagents was performed following the procedure described by Love.[9]

Instrumentation. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz and 500 MHz spectrometer. All NMR spectra were recorded in deuteriochloroform (CDCl₃) as solvent containing 0.003% TMS as an internal reference. The amount of head-to-tail coupling was determined by NMR integration of the small peaks near 7.0 ppm using the Sato and Morii analysis and the peaks near 2.5 ppm using the method of Elsenbaumer *et al.*[10] All UV/Vis spectra were taken on either polymer solutions in chloroform or polymer thin films cast onto cover glass 22 mm sq. using a Perkin-Elmer Lambda 900 UV/Vis NIR spectrometer and are reported in λ in nm. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. Gel Permeation Chromatography (GPC) spectra for poly(3-alkylthiophenes) were recorded on a Waters 2690 Separations Module apparatus and a Waters 2487 Dual λ Absorbance Detector with chloroform as the eluent (flow rate 1.0 mL/min, 35 ºC, λ=254 nm) with a series of three Styragel columns (10⁵, 10³, 100 Å; Polymer Standard Services). GPC spectra for poly(3-alkoxythiophenes) were recorded on a Waters 6000 A apparatus and a Waters R410 differential refractometer with DMF/LiBr (0.05 M) as the eluent (flow rate 1.0 mL/min, 50 ºC). Toluene was used as an internal standard, and calibration based on polystyrene standards was applied for determination of molecular weights for both types of polymers.

Synthesis of (ArN=C(An)-C(An)=NAr)NiBr₂ (Ar = 2-*t*-BuC₆H₄). The Ni[II]-α-diimine catalyst was synthesized according to the procedure described by Killian *et al.*[11]

Synthesis of Poly(3-Alkyl or Alkoxy-Substituted-Thiophene). All polymers were synthesized according to the procedure described by Loewe *et al.*[4a] Polymerizations were allowed to proceed for 12 hours at reflux.

Results and Discussion

Polymer **3** was synthesized *via* the Grignard Metathesis (GRIM)[4a] method as depicted in **Figure 1**. This method involves treatment of aryl dibromide species (**1**) with a Grignard reagent R′MgBr in THF in order to generate a mixture of Grignard intermediates (*e.g.*, 2-bromo-5-bromomagnesio-3-alkyl/alkoxy-thiophene and 2-bromomagnesio-5-bromo-3-alkyl/alkoxy-thiophene), followed by addition of the nickel initiator **2** to produce HT-coupled regioregular polymers. This methodology was expanded to include 3-substituted thiophene derivatives such as 3-hexyloxythiophene, 3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}thiophene, which resulted in a series of poly(3-alkoxy-substituted-thiophenes) (see Figure 1, **1b** and **1c**). The molecular weights, corresponding PDIs, and UV-Vis data for the synthesized polymers are listed in **Table 1**.
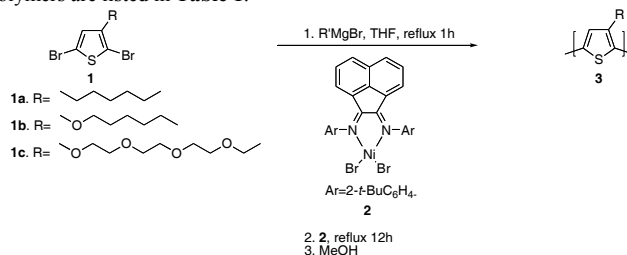

Figure 1. Polymer Synthesis.

Table 1. Optical data and Corresponding Molecular Weights of poly(3-alkyl/alkoxy-thiophene) Synthesized by (ArN=C(An)-C(An)=NAr)NiBr₂ (Ar = 2-*t*-BuC₆H₄).

| Resulting Polymer	M_n(PDI) [GPC]	λ_max (nm) in solution	λ_max (nm) solid state
3a	7650(1.25)	446	514
3b	4530(1.75)	576	607
3c	23820(1.86)	561	589

As expected, only one aromatic resonance can be observed in the ¹H NMR spectra of regioregular poly(3-hexylthiophene) (**3a**) (Figure 2). The chemical shift of this peak is around δ = 6.98 ppm, which is typical of a head-tail sequence (HT-HT). Since relatively low molecular weight was obtained for **3a**, ¹H NMR resonances for the end-group thiophene residues and the α-methylene protons of the 3-substituent may be readily observed in the spectrum at around δ = 6.9 ppm and δ = 2.54 ppm, respectively. The spectroscopic data for solution and solid state UV/Vis obtained for **3a** are comparable to regioregular HT PT samples with identical substituents (*e.g.*, 98-99% HT-HT PHT prepared by the original McCullough method exhibits a λ_max of 442 nm in solution[2b] and λ_max of 550 nm[2c]).

Incorporation of an alkoxy group on the 3 position of a thiophene ring (*e.g.*, **3b**) results in the polymer being more stable in the oxidized state and less soluble in common organic solvents due to a phenomenon called S-O "through bond" interaction (TBI).[12] An electron rich oxygen in the alkoxy group acts as a charge donor and electronegative sulfur attracts electrons resulting in partial double bond character, which leads to a rigid polymer backbone and thus a lower solubility. Utilizing a Ni[II]-α-diimine catalyst **2** in the synthesis of **3b** affords a polymer, which is completely soluble in chloroform. In addition, incorporation of several oxygen atoms in a polymer backbone (*e.g.*, **3c**) leads to polymers that are soluble in common organic solvents, such as acetone, methylene chloride, DMF, THF, and possess excellent film-forming abilities.
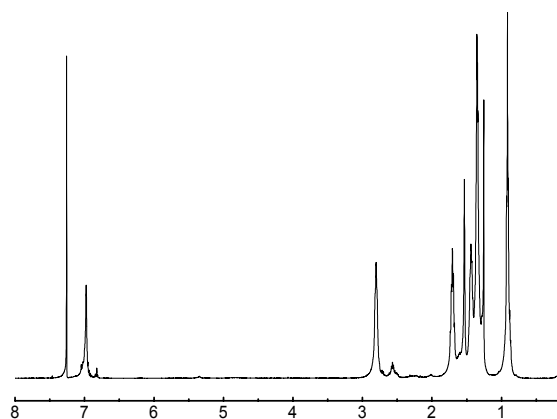
Figure 2. NMR spectra of poly(3-hexylthiophene) prepared by utilizing (ArN=C(An)-C(An)=NAr)NiBr$_2$ (Ar = 2-t-BuC$_6$H$_4$) catalyst.

Furthermore, due to its high solubility in methanol, the remaining catalyst can be easily removed from the final PTs during a simple Soxhlet extraction with methanol producing polymers that are free of organometallic impurities, which can be readily observed in the MALDI spectra (Figure 3).
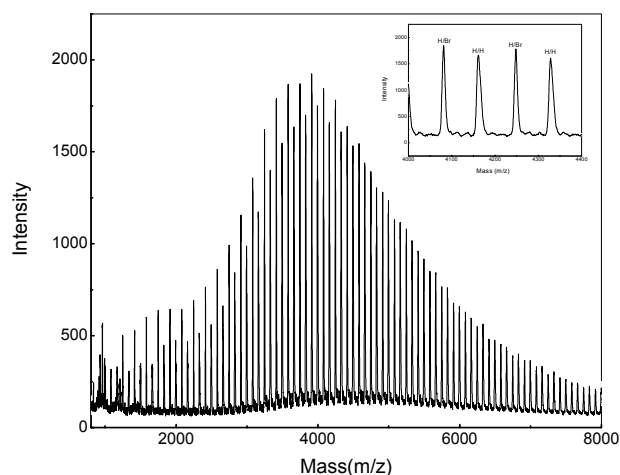
Figure 3. MALDI-TOF MS poly(3-hexylthiophene) prepared by (ArN=C(An)-C(An)=NAr)NiBr$_2$ (Ar = 2-t-BuC$_6$H$_4$) [M_n = 4180; PDI = 1.18].

Conclusions

We have demonstrated a regiocontrolled synthesis of poly(3-alkyl/alkoxy-substituted-thiophenes) mediated by a Ni^{II}-α-diimine catalyst [(ArN=C(An)-C(An)=NAr)NiBr$_2$ with Ar = 2-t-BuC$_6$H$_4$)]. Furthermore, due to its high solubility in methanol, the remaining catalyst can be easily removed from the final PTs during a Soxhlet extraction yielding polymers that are free of organometallic impurities leading to improved physical properties, formation of better films with improved microstructures resulting in higher mobility/conductivity. In addition, this work has been extended to utilizing different ligands at the Ni center in order to optimize the reaction conditions (*e.g.*, obtaining higher molecular weight polymers, shorten reaction times). The GRIM method and the catalyst combined provide a quick and cost effective procedure for the synthesis of regiospecific PT derivatives on an industrial scale.

References

(1) (a) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, **1986**. (b) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater*. **2002**, *12*, 89. (c) De Paoli, M. A.; Nogueira, A. F.; Machado, D. A.; Longo, C. *Electrochim. Acta*, **2001**, *46*, 4243. (d) Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J.R. *Adv. Mater*. **2003**, *15*, 855. (e) Scrosati, B. *Applications of Electroactive Polymers*; Chapman & Hall: London, **1994**. (f) Skotheim, T. A.; Reynolds, J. R.; Elsenbaumer, R. L. *Handbook of Conducting Polymers*; Marcel Dekker: New York, **1998**. (g) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc*. **1993**, *115*, 8716.

(2) (a) McCullough, R. D.; Lowe, R. D. J. *Chem. Soc. Chem. Commun*. **1992**, 70. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem*. **1993**, *58*, 904. (c) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc*. **1993**, *115*, 4910.

(3) Chen, T. A.; Rieke, R. *J. Am. Chem. Soc*. **1992**, *114*, 10087.

(4) (a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater*. **1999**, *11*, 250. (b) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.

(5) (a) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526. (b) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.

(6) Chen, T. A.; Wu, X.; Rieke, R. *J. Am. Chem. Soc*. **1995**, *117*, 233.

(7) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev*. **2000**, *100*, 1169.

(8) The polymers were precipitated in methanol, filtered and Soxhlet extracted in sequence with methanol, hexanes, and chloroform. PDIs are reported for the chloroform fraction. The % yields obtained ranged from 50% to 70%.

(9) Love, B. E.; Jones, E. G. *J. Org. Chem*. **1999**, *64*, 3755.

(10) Elsenbaumer, R. L.; Jen, K. Y.; Miller, G. G.; Eckhardt, H.; Shacklette, L. W.; Jow, R. *Electronic Properties of Conjugated Polymers*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer Series in Solid State Sciences **1987**, *76*, 400.

(11) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc*. **1996**, *118*, 11664.

(12) Villa, E.; Agosti, E.; Castiglioni, C.; Galazzi, M. C.; Zerbi, G. *J. Chem. Phys*. **1996**, *105*, 9461.