Developing Methodology for Living Polymerization of Functionalized Conjugated Monomers using Nickel Catalysts with Electron-Rich Phosphine Ligands

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Abstract:

The potential applications of polymers in the semiconductor industry have spawned further research into developing their synthetic routes. Organic semiconductors are poised to revolutionize the electronics industry because the devices made using organic semiconductors are inexpensive to fabricate when compared to their traditional silicon counterparts. One difficulty associated with polymer synthesis is molecular weight control. Living polymerization, a form of chain growth polymerization that allows for precise control of molecular weight and dispersities, has been shown to potentially solve this issue. Methods such as the Kumada Ni-Catalyzed Transfer Polymerization allow such control through the adjustment of monomer to catalyst ratios. Also problematic of polymer synthesis is the use of toxic organometallic monomers. This may be solved by involving C-H functionalization, eliminating the need for organometallic monomers, and reducing overall environmental impact. Recent reports [1] of C-H/C-O biaryl coupling of benzoxazoles via Ni(0) with electron-rich phosphine ligands have inspired our approach towards a living polymerization methodology with functionalized conjugated benzoxazole monomers. In this report, the syntheses of monomer precursors are reported.

Introduction:

Semiconductors have revolutionized human technological advancement. Used in electronics and solar energy industries, semiconductor devices made from silicon (Si) are by far the most prevalent. Despite its popularity, Si fabrication is rather expensive. Electronics-grade Si must be extremely high in purity, refined in a process that is expensive and energy intensive, both in man hours and energy used. Si production also utilizes many toxic materials, creating environmental issues that must be dealt with.

Organic semiconductors, such as conjugated polymers, have presented themselves as a viable alternative to silicon. Devices made using organic semiconductors are typically less expensive than their Si counterparts. They also utilize lower production temperatures and may have attractive properties such as transparency and flexibility that expand their range of possible uses.

Current polymer synthesis techniques pose two challenges for organic semiconductor production: molecular weight control and the use of toxic organometallic monomers. The two can be solved by utilizing living polymerization (a form of chain growth polymerization where the growing polymer chain cannot self-terminate) to solve molecular weight issues and C-H functionalization (replacing organometallic aryl
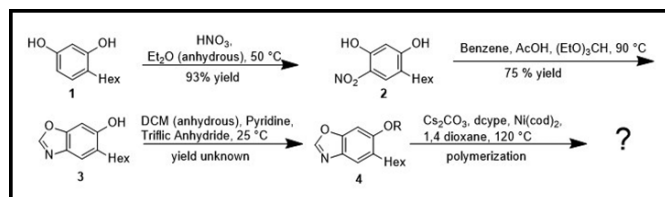

Figure 1: Reaction schemes, reactions progress in order from top to bottom.

nucleophiles/electrophiles in traditional cross-coupling with hydrogen/oxygen) to eliminate the need for organometallic reagents.

The goal of this project is to develop a methodology for the living polymerization of functionalized conjugated benzoxazole monomers using C-H functionalization. Specifically, benzoxazole monomers and monomer precursors were synthesized, and polymerizations were attempted and analyzed.

Methodology:

The synthetic steps used are shown in Figure 1.

Monomer precursors were synthesized from the starting material 4-hexylresorcinol, which was first nitrated to form
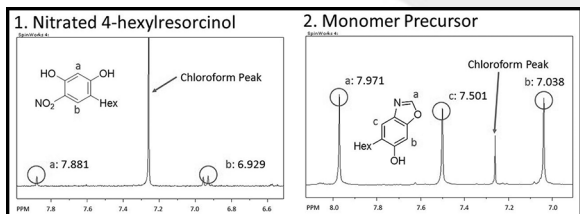
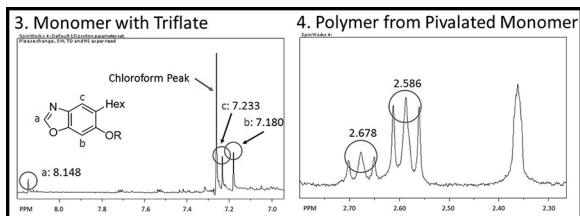Figure 2: ¹H NMR of molecules **2** and **3**.

Figure 3: ¹H NMR of molecule **4** and polymerization mixture.

6-nitro-4-hexyresorcinol. A ring-closing reaction was then performed to produce 5-hydroxyl-6-hexylbenzoxazole. This monomer precursor was functionalized with either a pivalate or trifluoromenthanesulfonate (triflate) to produce the benzoxazole monomer [1]. Living polymerization trials were then performed with benzoxazole monomers with either group [1, 2].

Results and Discussion:

Analysis of ¹H NMR data as well as mass spectrometry data show that the benzoxazole monomer **3** as well as precursor **2** were successfully synthesized (Figure 2). The labeled peaks strongly suggest the presence of the desired products.

In Figure 3, molecule **4** (monomer functionalized with triflate) shows a shift in peaks in comparison to the monomer precursor **3**. Note that multiple peaks have shifted both downfield and upfield. This may indicate that triflation has indeed occurred as the electronegative triflate group deshields the proton furthest away from it while shielding the two closest to it. Yields of the triflate functionalized monomer have yet to be determined. Figure 3 also shows a polymerization attempt of the benzoxazole monomer functionalized with the pivalated monomer. The presence of the two triplets in the hexyl region indicate that a dimer may have formed. This is a promising sign that biaryl coupling may have occurred, indicating that the monomer is reactive, but is not a good indication that living polymerization is successful with this monomer.

Refer to Table 1 for polymerization conditions and results.

Conclusions:

The development of a methodology for the living polymerization of functionalized conjugated benzoxazole monomers using C-H functionalization was attempted. Synthesis of benzoxazole monomers and their precursors proved successful, but successful living polymerizations were not achieved. Benzoxazole monomers functionalized with pivalate groups show promising reactivity, as shown by dimer formation during living polymerization attempts, but further work must be done to achieve living polymerization of benzoxazole monomers. Monomers functionalized with triflate groups did not display reactivity, and further work must be performed to achieve successful polymerizations.

Future Work:

Currently, the only step of the methodology that has failed is the polymerization itself. This may be due to poor monomer quality or an unreactive C-O group. Therefore, refinement of the C-O group is required, as well as refinement of the monomer synthesis reaction. Further living polymerization attempts of the triflate monomer are also to be attempted. If proven successful, adjustments of monomer to catalyst ratios may be attempted to see if polymer chains of varying lengths may be achieved while maintaining low dispersities.

Acknowledgements:

References:

[1] Muto, K.; Yamaguchi, J.; Itami, K. Nickel-Catalyzed C-H/C-O Coupling of Azoles with Phenol Derivatives. Journal of the American Chemical Society. 2012, 134, 169-172.

[2] Housekeeper, J. Laboratory Notebook Book II; University of Washington: Seattle, 2013. p 195.

Polymerization Conditions	Result
Pivalated monomer (1 equiv), $CsCO_3$ (1.5 equiv), dcype (0.2 equiv), $Ni(cod)_2$ (0.1 equiv), 1,4 dioxane (4 mL)	Indication of dimer
Pivalated monomer (1 equiv), $CsCO_3$ (1.5 equiv), dcype (0.2 equiv), $Ni(cod)_2$ (0.1 equiv), 1,4 dioxane (4 mL)	No indication of polymerization
Triflated monomer (1 equiv), $CsCO_3$ (1.5 equiv), dcype (0.2 equiv), $Ni(cod)_2$ (0.05 equiv), 1,4 dioxane (2 mL)	No indication of polymerization

cod = 1,5-cyclooctadiene, dcype = 1,2-bis(dicylohexylphosphino)ethane

Table 1: Polymerization conditions and results.