

Designing a Conjugated Polymer Consisting of Phenyl-Oxazole Derivatives Using C-H/C-O Coupling

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Abstract:

Organic π -conjugated semiconducting polymers that have good electronic properties are very important in the development of organic solar cells. Traditionally, organometallic reagents are used in order to perform carbon-carbon coupling reactions of monomers to synthesize conjugated polymers. This requires stoichiometric amounts of organometallic compounds and additional synthetic steps compared to C-H activation chemistry in polymer synthesis. C-H activation eliminates the need to pre-functionalize the normally inert C-H bond found in many organic compounds with metals or other harsher reagents. The C-H activation will reduce byproducts, waste, and inorganic materials, which will aid in the development of “green” reactions. Itami, et al., found that easily synthesized phenol derivatives (containing a C-O-R electrophile) could activate the C-H bond in the 5-position of oxazoles to form a C-C bond [1]. Our work was inspired by this, and the goal of this research was to draw from this methodology to design and synthesize a monomer that had both an electrophilic C-O-R group containing a phenyl ring and an oxazole such that it could undergo polymerization via C-H activation to make a donor-acceptor polymer. Future work includes the study of polymerization growth kinetics and its semiconducting properties.

Introduction:

In recent years, semiconductors have changed the course of human technological advancement. Semiconductors are used in solar cells and in all electronic devices. Silicon (Si) is the most widely used semiconductor. However, making Si based devices is expensive where Si must be extremely pure, which requires energy and time. It also utilizes toxic materials during production that adds more inorganic waste to our environment.

Organic semiconductors, specifically π -conjugated polymers, have been attracting interest as an alternative to Si. Devices made out of organic polymers have advantages over Si based devices because they can be made to be semi-transparent, colorful, and flexible, which give them further range of usage such as in photovoltaics and solar cells. In addition, they require a lower cost of production.

Organic polymer synthesis techniques have developed through the years. However, it has a problem, which is the usage of organometallic reagents (Sn, Li). In order to overcome this issue, C-H activation has been presented as an alternative method to use less organometallic reagents during synthesis. C-H activation utilizes C-H/C-X (X is a halogen) that replaces C-M/C-X (M is metal) in traditional C-C coupling. This eliminates excess transition metal usage creating “green” reactions and less waste product.

The target of this work was to synthesize a π -conjugated polymer by first creating the monomer that is made of phenyl-oxazole derivatives, and by utilizing the C-H/C-O coupling method (inspired by Itami, et al. [1]) polymerize the monomer in order to achieve the conjugated organic semiconducting polymers for its usage in solar cells.

Methodology:

The synthetic steps are shown in Figure 1.

Phenyl-oxazole derivatives are synthesized from the starting material, 2,4-dimethoxy benzaldehyde **1**, which is transformed into first phenyl-oxazole derivative by ring closure **2**. Then, the product is dealkylated to yield the next product **3**, and finally by protection using *p*-toluenesulfonyl group followed by an alkylation, product **5** is obtained.

Results and Discussion:

Analysis of hydrogen nuclear magnetic resonance (¹H NMR) data shows that the monomer precursors (phenyl-oxazole derivatives) **2** and **3** were formed (Figure 2). The labeled peaks clearly show that the desired monomer was formed.

In Figure 3, the final monomer synthesis step (protection via *p*-toluenesulfonyl group and alkylation by bromohexane) gave mixed results. ^1H NMR data showed extra peaks that were not identified. There are extra peaks, d, of tosylate in Figure 3. This may be due to mixed protection where the tosylate reacted at the *ortho* position rather than the *para* position. However, the promising signs are the identification of oxazole peaks a, b, and some aromatic peaks labeled c, g, and f of benzene.

Conclusions:

The synthesis of monomer 5, consisting of a phenyl-oxazole derivatives, was attempted. The synthesis of the first two precursors proved successful, but the final monomer was not completely synthesized. Oxazole formation by ring closure using toluenesulfonylmethyl isocyanide was accomplished. Although the synthesis of the monomer initially was promising, further work needs to be done in order to fully obtain the monomer to perform the synthesis of the desired polymer by utilizing C-H/C-O cross coupling reaction.

Future Work:

So far, the only step that failed was the final step required to fully obtain the desired monomer consisting of phenyl-oxazole derivatives. Therefore, changing the tosylate group with triflate group would be an option. In addition, triflate group would be a better reactive C-O functional group for the polymerization step. If proven to be successful, polymerization will be attempted and further investigation will be done to characterize the polymer such as its growth kinetics and its capacity as a semiconductor for solar cell usage.

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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.

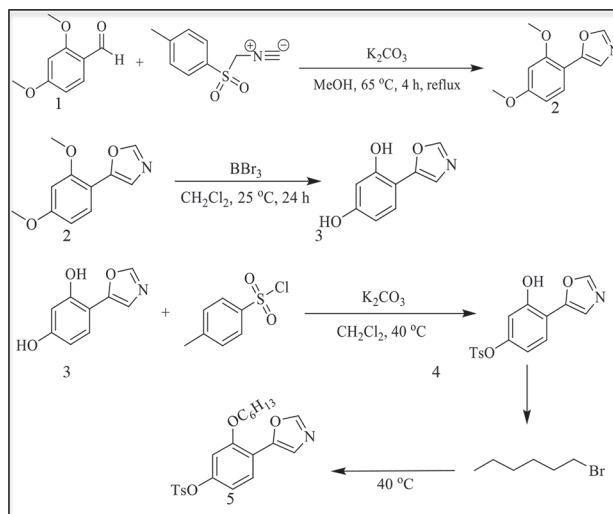


Figure 1: Monomer synthesis scheme in order from top to bottom.

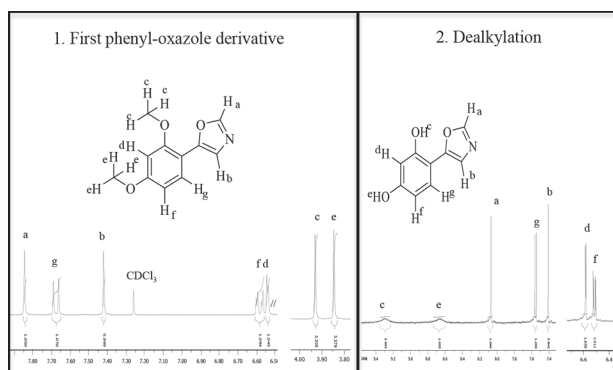


Figure 2: ^1H NMR of molecules 2 and 3.

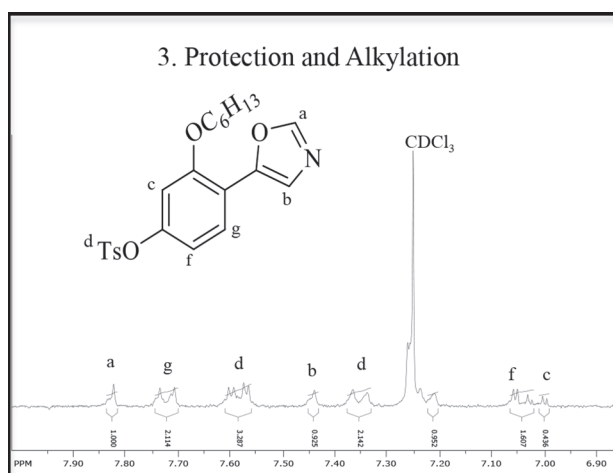


Figure 3: ^1H NMR of product 5 mixture.