Synthesis and Properties of PTEMA

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The growing world population is leading to an increasing demand for energy. This demand places responsibilities on us to seek either alternative renewable energy sources or more efficient means of energy usage. The search for more energy-efficient technology has led to research on devices such as thermoelectric generators to recover low-grade waste heat. Specifically, conductive polymers, like polythiophenes, can greatly enhance the feasibility of these devices. Polyalkylthiophenes are widely studied due to their favorable solid-state and optoelectronic properties, well-controlled synthesis, and tunable microstructure. The optoelectronic and solid-state properties can be easily altered by changing the polythiophene microstructure. This allows us to synthesize a wide variety of polythiophenes presenting an opportunity to enhance the performance of solar panels, thermal electric generators, organic photovoltaics, and sensors due to their tunable microstructure.

To better understand how varying microstructure affects the optoelectronic and physical properties of polythiphenes, we synthesized a novel 2-(2-(thiophen-3-yloxy)-ethyl) malonate monomer in order to enable the synthesis of a polythiophene with unique properties. Figure 1 shows the synthesis of this monomer, which involves several steps. One of the main difficulties in synthesizing the monomer was the synthesis of 3-(2-bromo)-ethyloxythiophene from 3-methoxythiophene. These two intermediate monomers have very similar structures, making their separation difficult. Upon analysis of 3-(2-bromo) ethyloxythiophene via 1H NMR spectroscopy, 3-methoxythiophene peaks were noticed, and it was determined that the 3-methoxythiophene should be removed via vacuum distillation or through further reaction. The 3-(2-bromo) ethyloxythiophene was successfully separated via vacuum distillation and the successive steps of the monomer synthesis were performed without interruption.

In future work, this monomer will be polymerized using Grignard Metathesis polymerization to yield poly(2-(2-thiophen-3-yloxy)-ethyl) malonate. Grignard Metathesis polymerization along with the base work up will transform the malonate group to malonic acid. The final product will be poly(2-(2-thiophen-3-yloxy)-ethyl) malonic acid (PTEMA). Since this polymer has not yet been successfully synthesized, intense characterization including UV-Vis spectroscopy, 1H NMR spectroscopy, FTIR spectroscopy, gel-permeation chromatography, differential scanning calorimetry, and X-Ray Diffraction will be performed following synthesis. This polymer is expected to possess halochromic behavior, as demonstrated by a chemically similar polythiophene. The functionalization of the polythiophene with malonic acid will allow the polymer to change color with a change in pH, and potentially alter other optoelectronic properties. This derivative of polythiophene presents a possible route for the fabrication of a polymeric pH sensor that indicates a change in pH through optical and electronic means.

Statement of Research Advisor:

Jihyuk successfully navigated a difficult series of reactions and found a successful means for purifying his target molecule, 2-(2-(thiophen-3-yloxy)-ethyl) malonate. His work lays the foundation for further synthetic efforts for the synthesis of a multifunctional polymer that would combine the semiconducting properties of polythiophenes with the pH-responsiveness of malonic acid.

—Bryan S. Beckingham, Chemical Engineering

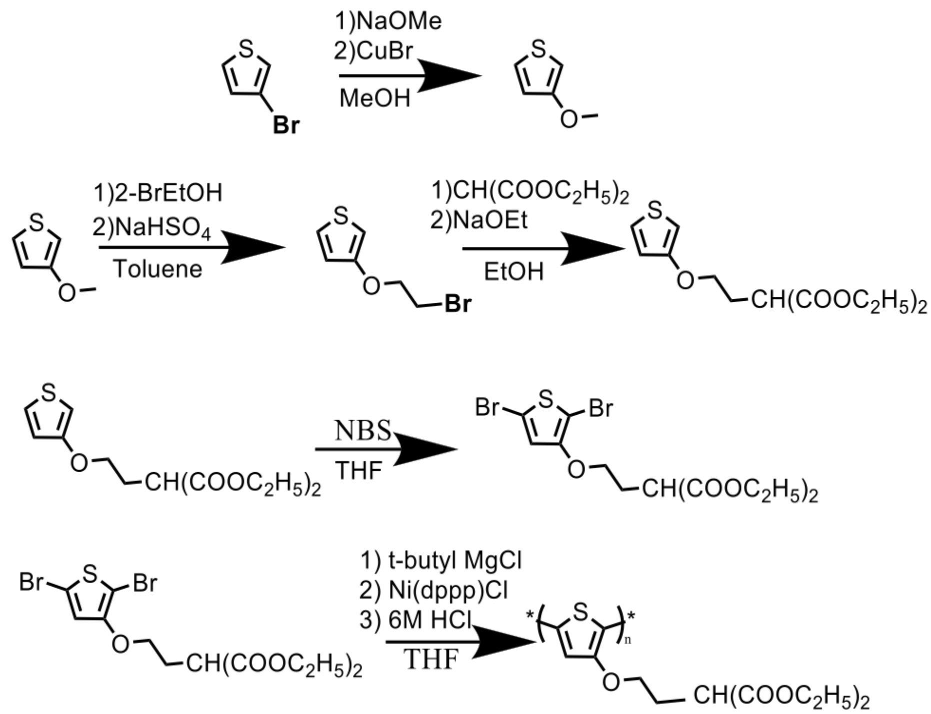

Figure 1: Schematic diagram of PTEMA Synthesis