Narrative Progress Report:

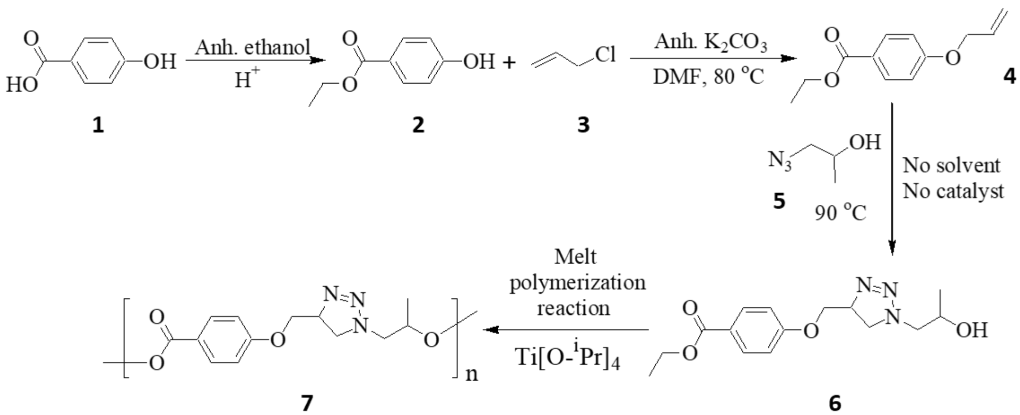
2a) PRF # 56629-UNI7.

2b) Project Title: Development of New, Solvent and Catalyst-Free "Click-ene" Chemistry: One-Step, Green Chemistry Approach for the Low-Cost Synthesis of Petroleum-Based Building Blocks and Polymers for Industrial Applications

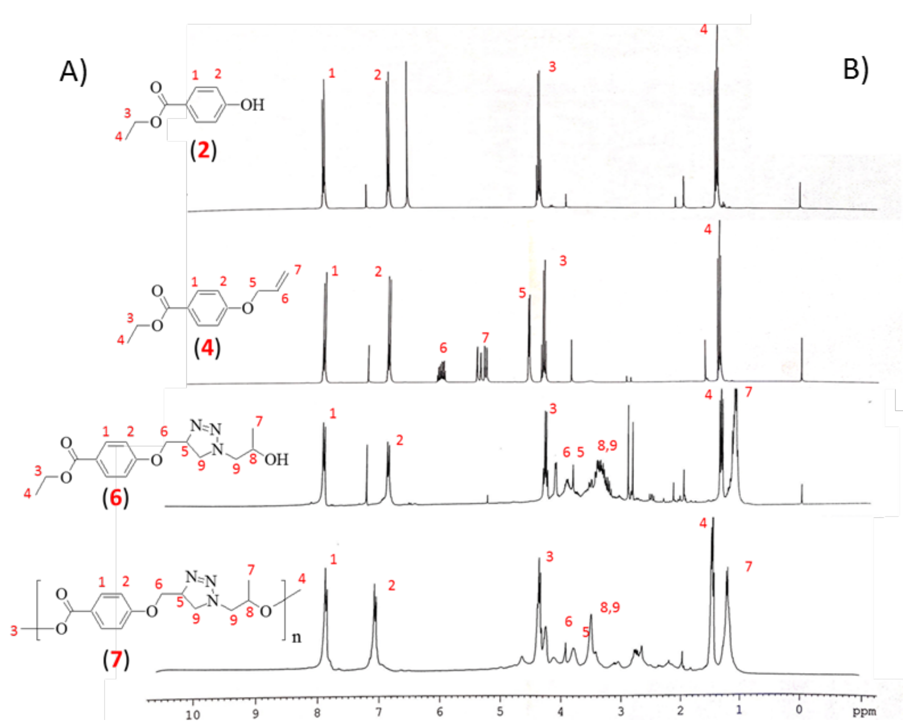
2c) Principle Investigator: Santimukul Santra, PhD. Associate Professor. Chemistry, Pittsburg State University.

The main goal of this project is to establish new, one-step, solvent and catalyst free chemistry between alkyl azides and alkenes. We hypothesized that, the reaction between alkene and azide could be carried out at elevated temperatures or, in the presence of UV radiation or, may be under microwave conditions. This innovative green approach would be a powerful paradigm in the low-cost synthesis of petroleum-based building blocks, catalysts and polymeric materials. This reaction is named by the PI as “click-ene” chemistry.

Prior year, we have synthesized new small molecules by utilizing the proposed “click-ene” chemistry. This year, we took one step ahead to design and synthesize new functional monomers and petroleum-based polymers using this new chemistry. In these reactions, no other reagents including any solvent or catalyst are used other than heat. Towards this end, we have designed a novel AB monomer (**6**) using “click-ene” chemistry, **Scheme 1**. This monomer was characterized before performing the polymerization reaction. The resulting polymer (**7**) was characterized in order to see the thermal stability as containing the click-ene triazole bond in the polymeric backbone. The polymer showed 10% weight loss at 225 °C. The polymerization reaction was performed at 90 °C and continued for 24 h. The expected “click-ene” product (**6**) was found to be 90% pure before purification using flash column chromatography. The formation of the final AB monomer and the polymer were confirmed by ^{1}H NMR and GPC as shown in **Figure 1**.



Scheme 1. Design and synthesis of functional AB monomer (**6**) using “click-ene” chemistry and the production of new petroleum-based polyester polymer (**7**)



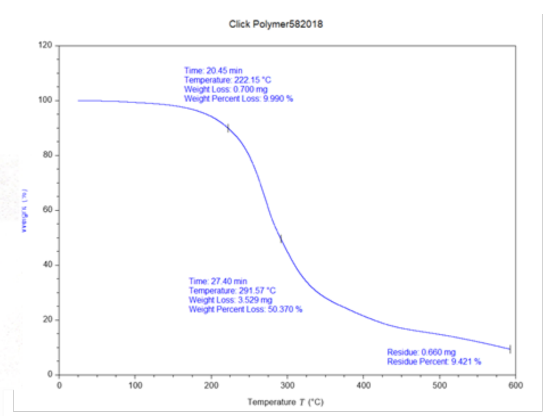
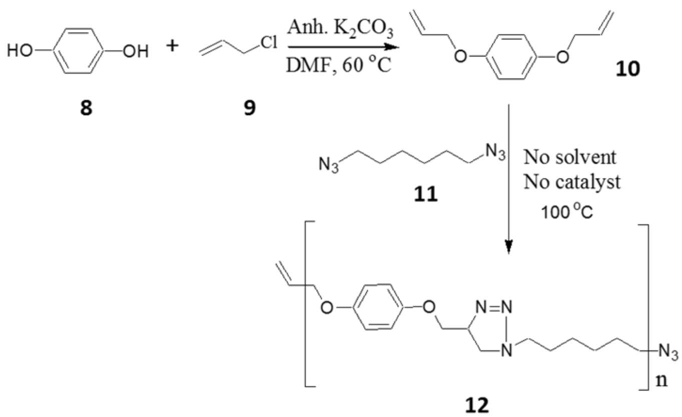


Figure 1. A) NMR spectra of the Monomer and polymer. B) Thermal stability of the polymer (7) by using TGA.



Scheme 2. Design and synthesis of "Click-ene" polymer (**12**)

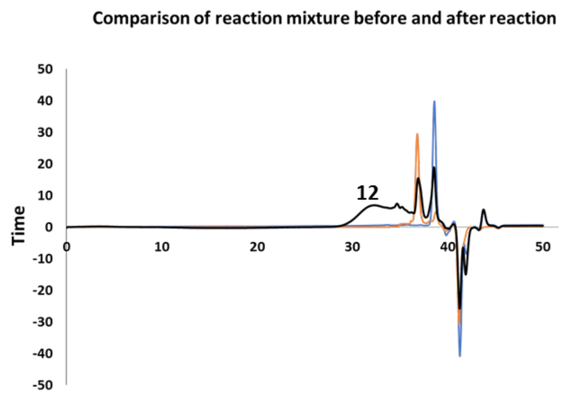


Figure 3. GPC of monomers and polymer (**12**)

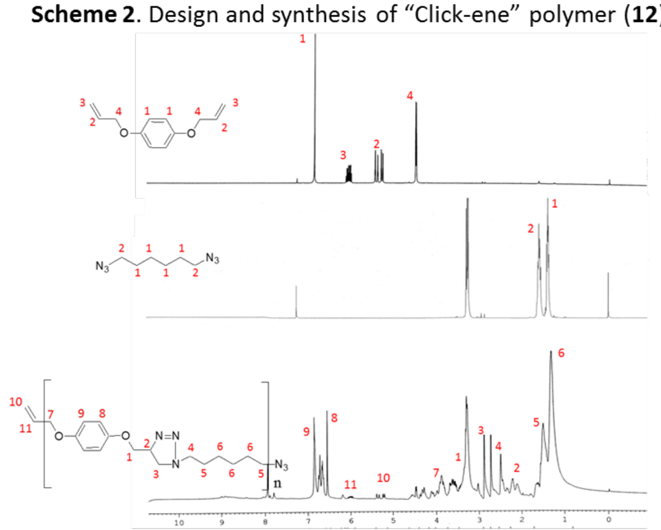


Figure 2. 1H NMR of the monomers (**10, 11**) and polymer (**12**)

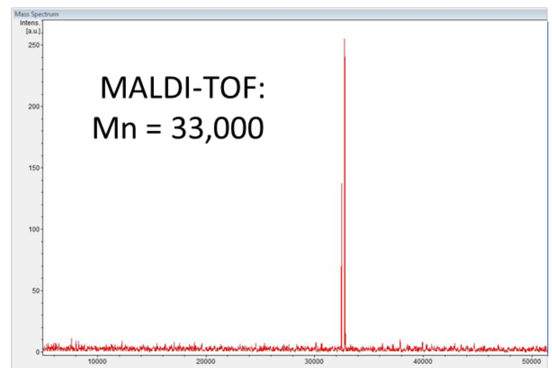
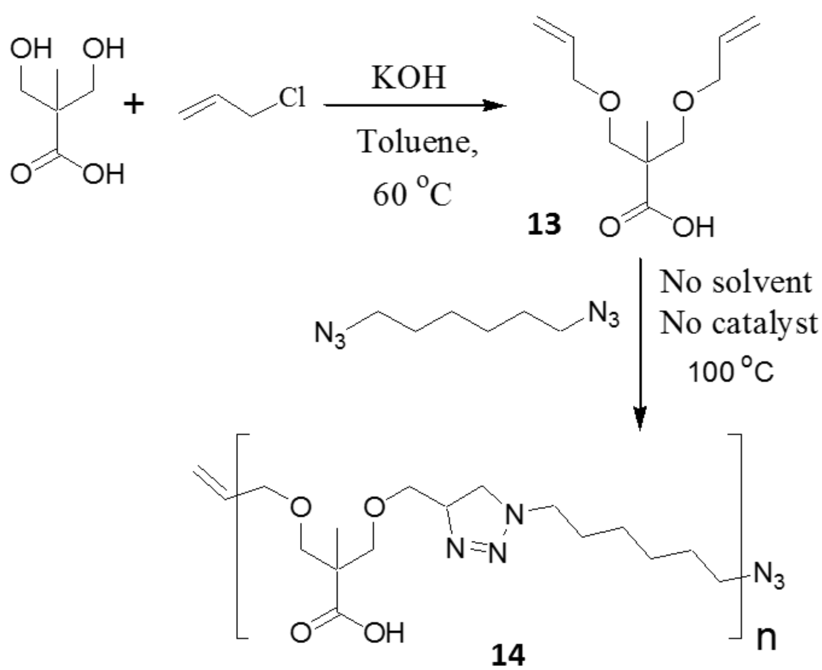


Figure 4. MAL-TOF data of the polymer (**12**)



Next, we have designed A2 + B2 systems to synthesize "Click-ene" polymers. These polymers were synthesized in one-step without using solvent and catalyst. Diallyl benzene (**10**) and hexyldiazide (**11**) were synthesized (**Scheme 2**) and the polymer (**12)** was synthesized in one-step using "click-ene" chemistry. The monomers and the polymer were characterized by ^{1}H NMR (**Figure 2**) and GPC (**Figure 3**). These results indicated that using this novel chemistry, not only petroleum-based functional monomers but one-step polymers also can be synthesized. Next, we wanted to see whether or not this chemistry can useful for the synthesis of functional polymers like **14** (**Scheme 3**). We have used diallyl bis-MPA (**13**) and clicked with hexyl diazides to get the click-ene polymer (**14**) in one-step, without using any solvent or catalyst, characterized by using all spectroscopic and chromatographic methods including MALDI-TOF (**Figure 4**).

Scheme 3. Synthesis of functional "Click-ene" polymer from A2 +B2 monomers.