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Synthesis and Characterization of 3-Trifluoromethylstyrene Copolymers

Research Summary

5/6/15

Kyle Dubiak

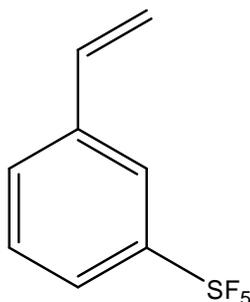
Advisor: Dr. Robert Kopitzke

Introduction

Fluoropolymers are of great interest because of their unique combination of outstanding properties such as chemical inertness (to acids, bases, solvents, and petroleum), low dielectric constants and dissipation factors, low water absorptivity, excellent weather ability, and interesting surface properties¹. All of these properties are due to fluorine, which is a very electronegative element that can handle and stabilize a lot of charge. With the unique characteristics that fluorine gives, these polymers are used in aeronautics, micro-electronics, engineering, chemical membranes, automotive industries, optics, textile finishing, and military use².

In our initial proposal, we wished to study sulfur pentafluoride (SF_5) substituted styrene, due its novel and relatively unstudied characteristics in polymers² (Figure 1).

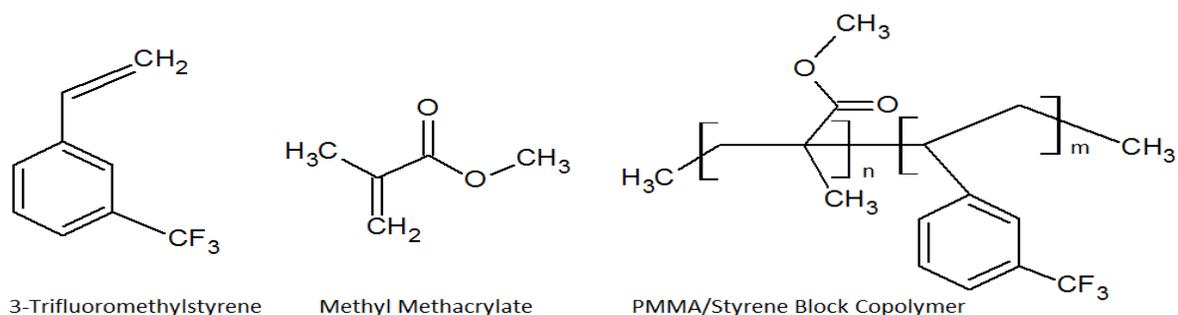
Figure 1: SF_5 Substituted Styrene Monomer



However, due to the cost and safety hazards of shipping the SF_5 gas precursor, this project could not be completed. Instead, we decided to continue studying the properties of a styrene monomer using a trifluoromethyl group (CF_3) in its place. Though it is less electrophilic and unique, the CF_3 may still give interesting characteristics to a variety of polymers.

In order to give even more properties to our styrene, we wanted to also make block copolymers with another monomer. Copolymers are of interest because each individual monomer can affect the overall properties of the whole. In our case, methyl methacrylate was chosen as our second monomer since it was readily available in the lab. Figure 2 below shows both individual monomers and the copolymer that they would create.

Figure 2: CF₃ Styrene, Methyl Methacrylate, PMMA/Styrene Block Copolymer



The styrene monomer will be made using a two-step synthesis, followed by a radically induced polymerization with MMA.

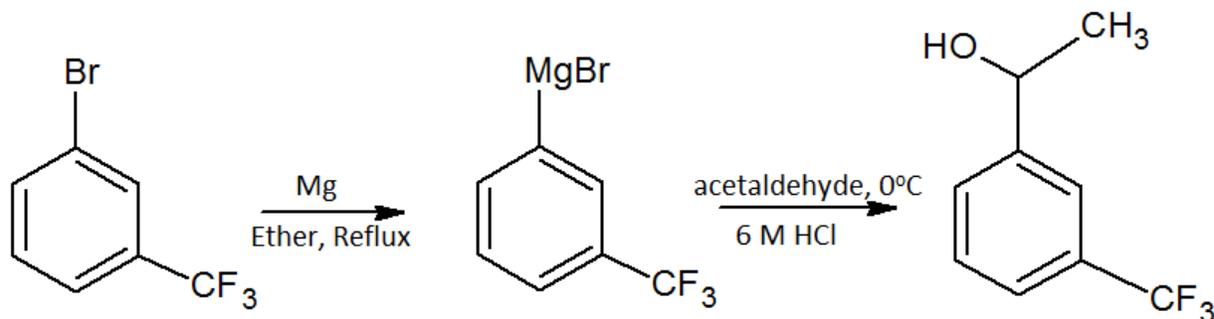
Experimental

All reagents were supplied by Sigma-Aldrich and were used as received. Glassware was oven dried before use.

1-PhenylEthanol Derivative

For the first of two steps in this synthesis, a Grignard reaction followed by the addition of acetaldehyde created our 1-phenylethanol derivative (Figure 3).

Figure 3: First Step of Synthesis to 1-phenylethanol



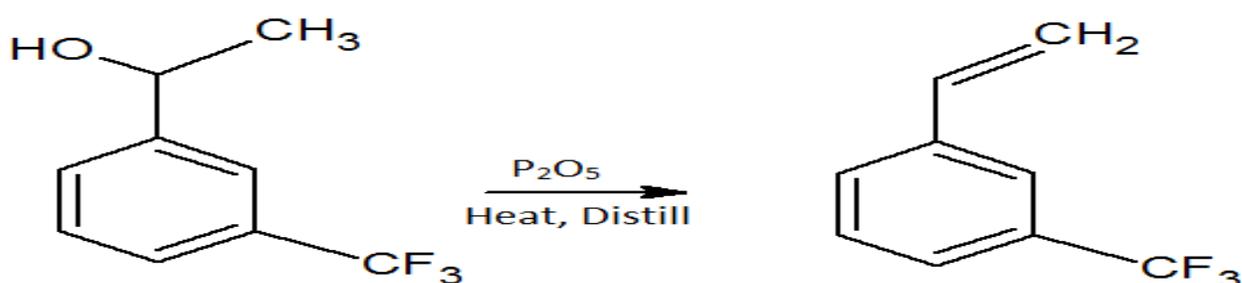
Each step of this synthesis was carried out several times over the course of this research. The first part of the monomer synthesis was completed as follows. 0.59 g (0.025 mol) of Magnesium was weighed and added to an oven dried, 100 mL triple necked round bottom flask. A rubber septum, condenser, and a 25 mL addition funnel was added on top. In the addition funnel, 3.1 mLs of 3-bromobenzotrifluoride (5.00 g, 0.0222 mol) was placed in the funnel along with 20 mLs diethyl ether. The solution was added dropwise until signs of reaction began (cloudy,

boiling). Rest of solution added, stirred and refluxed for an additional 30 mins. Taken off heat, cooled flask in an ice water bath while continuing to stir. Once brought down to temp, 3 mLs of acetaldehyde was added to the funnel and topped off with ether. Solution was added dropwise while cooled in the ice bath. Product was then quenched with 25 mLs of 6M HCl. The organic layer was extracted twice with ether, and dried with Na₂SO₄. Product was a dark yellow/brown colored liquid, with yields typically >95%.

1-phenylethanol Derivative Dehydration

The second step of the synthesis, formation of the styrene, was completed as follows (Figure 4).

Figure 4: Second Step of Synthesis to Styrene



5.00 g of the 1-phenylethanol intermediate was added to a dried 100 mL round bottom flask, along with 1.87 g of P₂O₅ and 20 mLs of benzene. Solution was stirred and refluxed for 4 hours³. Once complete, solution was vacuum filtered leaving a thick, sticky slime behind and a black liquid. Distillation was then attempted on the liquid portion in order to separate out the styrene.

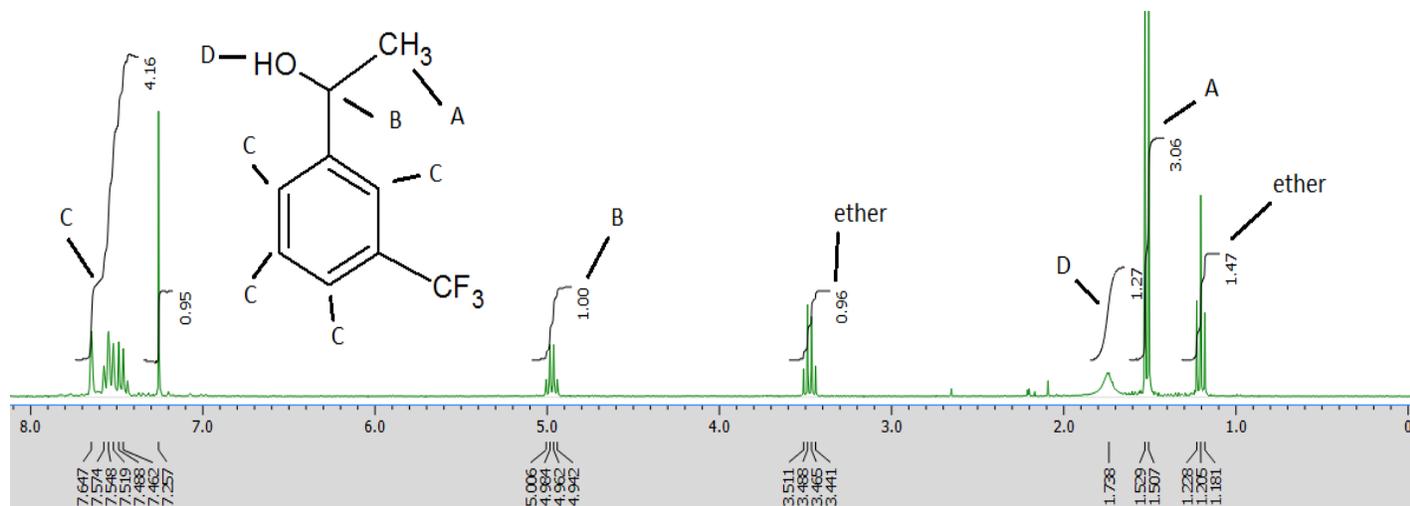
A slightly different method for the dehydration reaction was also attempted⁴. 5.00 g of the 1-phenylethanol was added to a dried 25 mL round bottom flask, along with 1.87 g of P₂O₅ and 0.200 g of hydroquinone. This was placed in an oil bath with a mini vacuum distillation adapter attached on top, so that the styrene could be collected as it's made.

Due to difficulties with the P₂O₅, three different dehydration methods are attempted. The first used molecular sieves (4Å) and 5.00 g of the phenylethanol, stirring and heating this solution at 100°C for 2 hours. The second method used an acid catalyzed resin⁵. 5.00 g of the phenylethanol and 0.100 g of Amberlyst-15 were placed in a 25 mL RBF and using the mini vacuum distillation adapter was stirred and heated at 90°C for 1 hour. Lastly, dehydration was attempted using a standard sulfuric acid dehydration. 5.00 g of phenylethanol and 5 mLs of toluene was placed in a 25 mL RBF and 3 drops of concentrated H₂SO₄ was then added. Solution was stirred and heated using a Dean Stark apparatus for 2 hours.

Results & Discussion

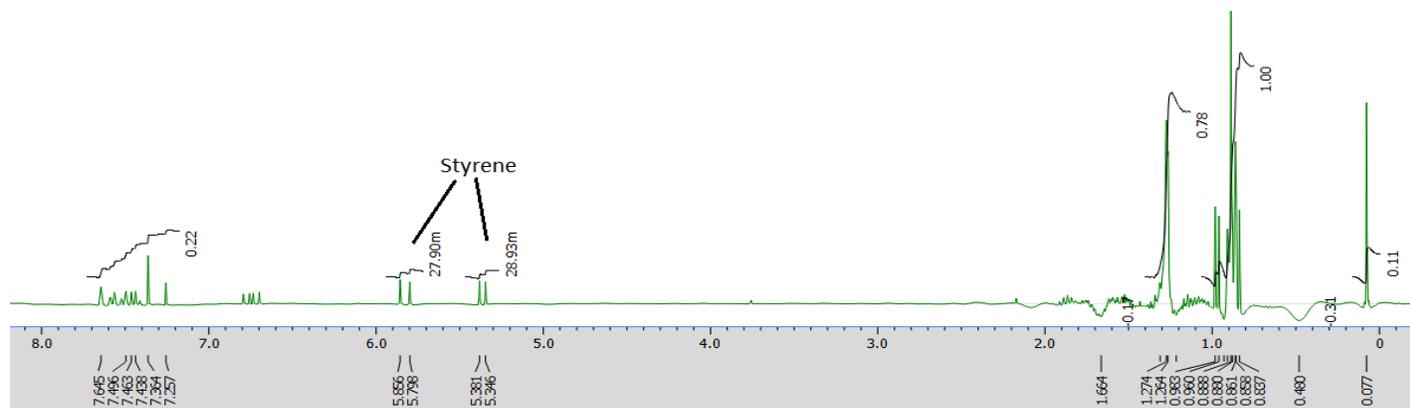
The first step of the synthesis was well understood and gave great yields. A sample ^1H NMR is shown below of a purified 1-phenylethanol derivative.

Graph 1: ^1H NMR of 1-phenylethanol derivative



The trouble and where the project has stalled is on the second part of the synthesis. Most literature sources cite using phosphorus pentoxide as the dehydrating agent of choice for styrene formation. But once the P_2O_5 is added to the solution, it begins to violently heat and boil and form a thick black sludge. A sample NMR below shows the presence of styrene in one of the P_2O_5 dehydrations.

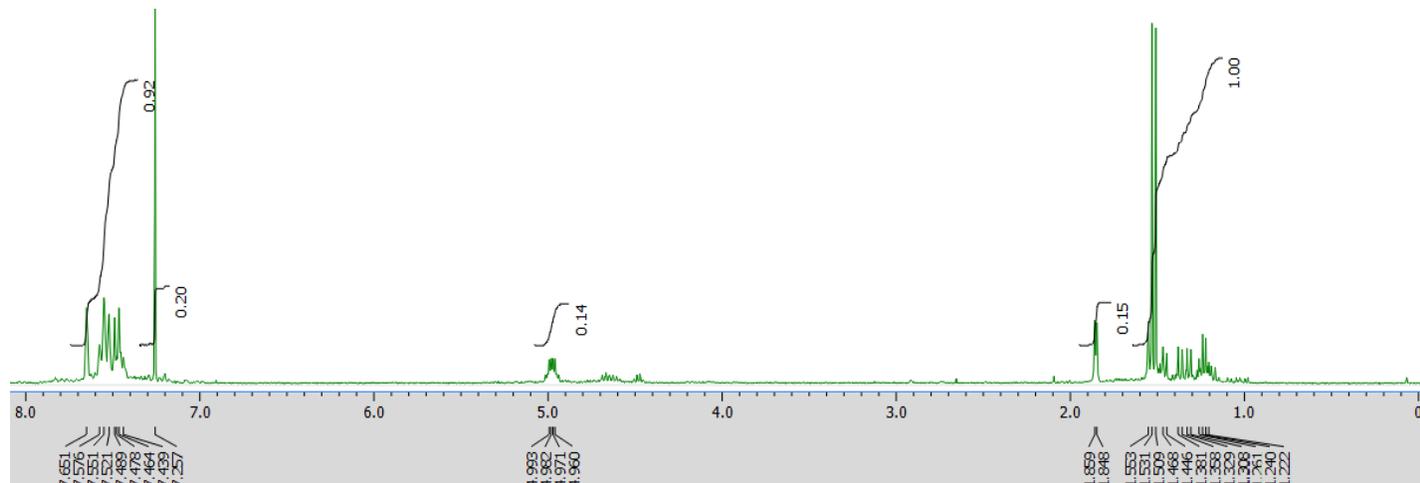
Graph 2: ^1H NMR of P_2O_5 Dehydration Reaction



The problem that occurs is that it is extremely difficult to distill out the styrene from the black sludge. Multiple different attempts were performed, such as varying the amount of P_2O_5 , changing the amount of vacuum applied, purifying the starting material, and using an oil bath to control the temperature.

Late into the project, new dehydration were attempted due to disappointing results using the phosphorus pentoxide. The first new method used molecular sieves and the NMR of the reaction is show below.

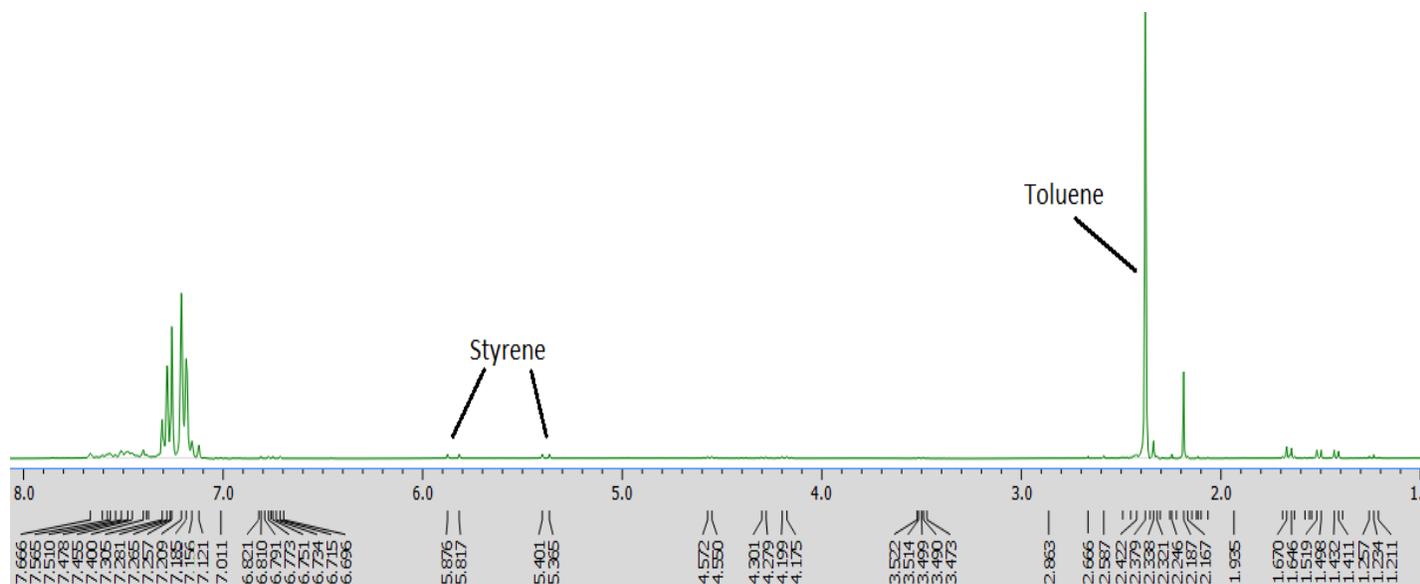
Graph 3: ^1H NMR of Molecular Sieve Dehydration Reaction



Comparing to graph 2, it can be seen that the sieves produced no styrene. Therefore no more trials were attempted using the sieves.

With the second new method, a standard H_2SO_4 dehydration is attempted using a Dean Stark apparatus and toluene as a solvent. The graph below shows the products formed after the reaction.

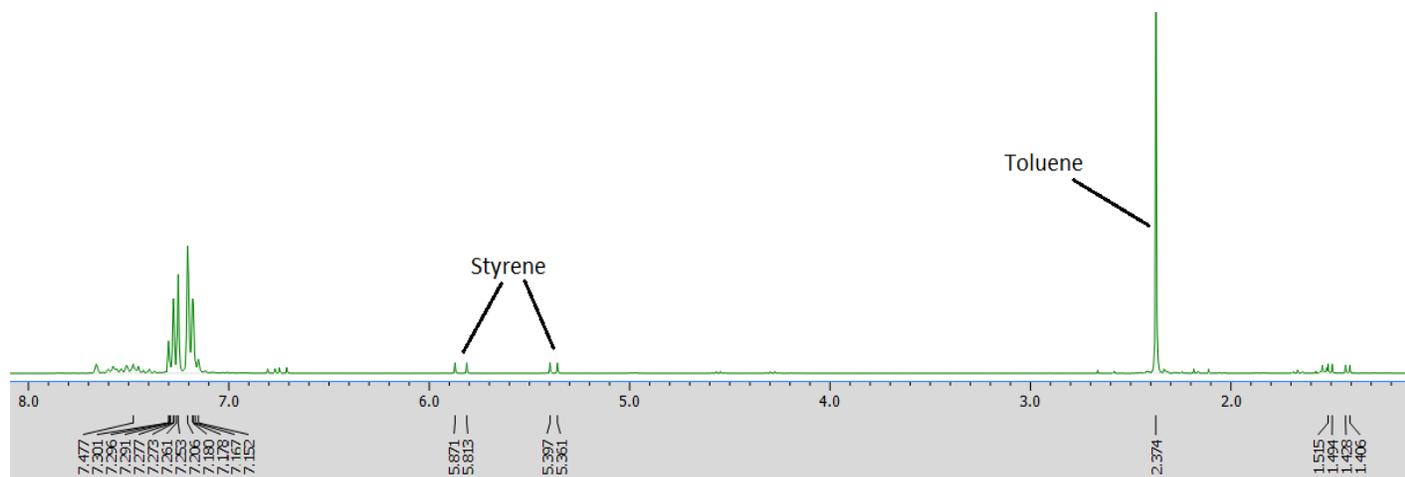
Graph 4: ^1H NMR of H_2SO_4 Dehydration Reaction



As noticed in the graph, it is predominately dominated by the toluene solvent but there are small styrene peaks noticeable in the spectrum. But upon trying to isolate any styrene that was made, it was proven difficult to separate from the toluene.

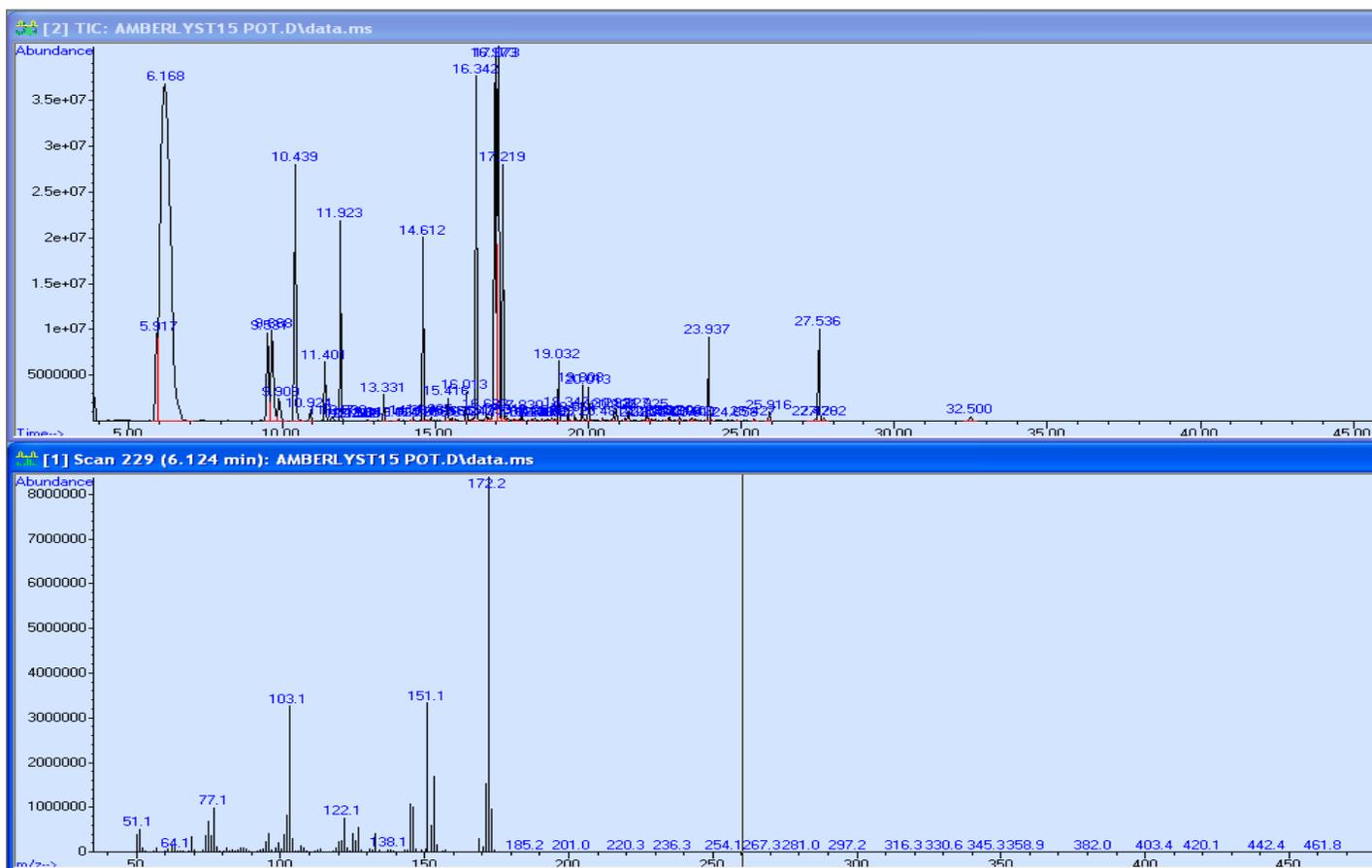
Lastly, the acid catalyzed resin, Amberlyst-15, was attempted to dehydrate the phenyl ethanol. A NMR graph of the reaction is shown below.

Graph 5: ^1H NMR of Amberlyst-15 Dehydration Reaction



Similar to graph 4, the spectrum is dominated by toluene but also shows two distinct styrene peaks which are labeled. It also shows a lack of the 1-phenylethanol reactant, which could mean that there is 100% conversion to styrene. Isolation proved once again unsuccessful due to the high boiling point of toluene. But a GC-MS was performed on this sample to determine the percent content of CF_3 styrene. Below shows the results and mass spec of the large peak at 6.1 minutes.

Graph 6: GC-MS of Amberlyst-15 Dehydration Products



After integration, it is shown that the styrene peak at the beginning yields around 48%, meaning that there was a decent success in the dehydration using the Amberlyst-15. However, it was difficult to separate out from the toluene.

Conclusion

Fluorinated polymers are of special interest due to the unique characteristics that they can display. Although our initial SF₅ group didn't work out, we focused our studies on a CF₃ substituted styrene and potential copolymers that they may create. The styrene monomer was proposed in a two-step synthesis. The first step proved successful and was performed many times, but trouble came up during the second. Due to the difficult nature of P₂O₅ different dehydration reactions are attempted. Of three new procedures tested, the Amberlyst-15 reaction shows the most promise of dehydration (48% yield). From here, more work will need to be done to further test this dehydration method and to hopefully one day perform these syntheses on sulfur pentafluoride styrene.

References

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- (3) C. S. Marvel; C. G. Overberger; R. E. Allen; J. H. Saunders. **1946**, *68*, 736–738.
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- (5) Nazmul Abedin Khan, J.-S. H. *Bull. Korean Chem. Soc.* **2011**, *32* (4).

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Faculty Sponsor:	<input type="text" value="Dr. Robert Kopitzke"/>	Faculty Sponsor Email:	<input type="text" value="rkopitzke@winona.edu"/>
Title of Project:	<input type="text" value="Synthesis and Characterization of 3-Trifluoromethylstyrene Copolymers"/>		

Project Abstract:

Fluorinated polymers are of great interest due to their unique combination of properties such as chemical inertness to acids and bases, low dissipation factors, and excellent weather resistance. Similarly, copolymers exhibit interesting properties due to different characteristics that each individual monomer contributes to the whole. The 3-trifluoromethylstyrene monomer was synthesized in two steps. 3-bromobenzotrifluoride was converted into a Grignard reagent and reacted with acetaldehyde to make the 1-phenylethanol derivative. This was then dehydrated to make 3-trifluoromethylstyrene using phosphorus pentoxide. In this second dehydration step, the project was stalled due to complications with the dehydrating agent. Thanks to this, polymerization was unable to occur during my research endeavors. However, three new dehydration methods were attempted and by using an acid catalyzed resin called Amberlyst-15 there is hope that it can be used to prepare further styrene monomers that can be used in future students' upcoming research.

The student-authored final report **MUST** include each of the following (check boxes to verify inclusion of each component):

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