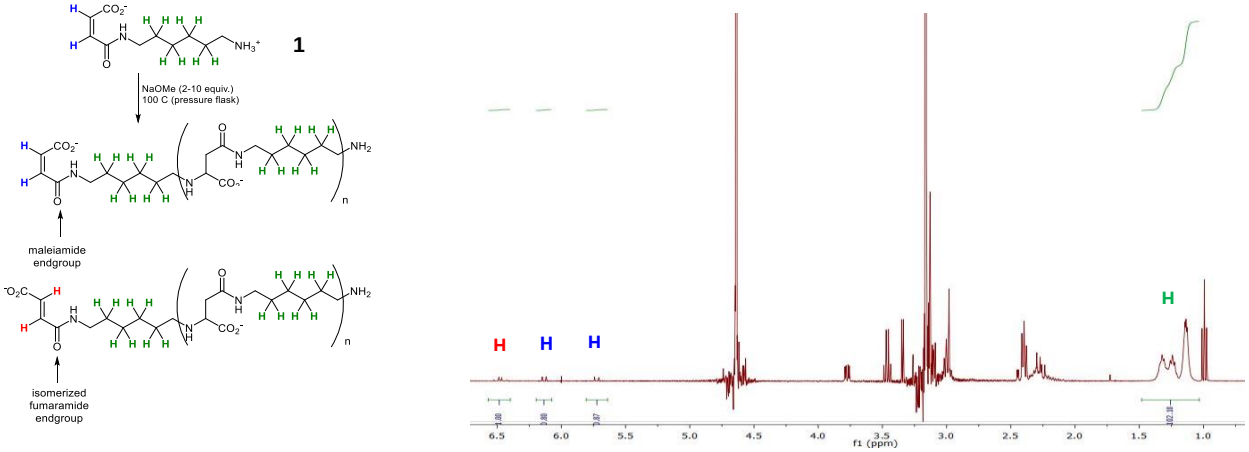
1) ACS PRF# 58478-UR7
2) New Materials via Hydroamination and Hydroamidation
3) Hans-Jörg Schanz, Georgia Southern University
4) No co-PI

Hydromaniation of mixed aminomaleiamide: The synthesis of zwitterion **1** containing the two reactive functional groups was the starting point of our investigations. The treatment with base generated the sodium salt **2** that undergoes hydroamination with itself to produce polymers or macrocycles. The progress of the hydroamination was monitored via NMR. The fastest reaction was observed when a large excess of base (10 equiv. of NaOMe with respect to compound **1**) was used in methanol at a reaction time of 20 h at 100°C in a pressure vessel at maleiimide concentrations of 100 mg/mL. The initial reaction solution is homogeneous but the formation of a precipitate suggest the formation of a polymer. The highest conversion observed was 96% as determined by the conversion of the maleiimide end via ^{1}H NMR spectroscopy (Scheme 1). Interestingly, the presence of a copper catalyst as opposed to our initial hypothesis and in contrast to the very early investigations does not accelerate nor slow the
reaction under these conditions. It is not conclusive that the reaction indeed will exclusively form linear polymers, the possibility of cyclic molecules with low molecular weights is supported by the presence of sharp signals (e.g. for the CH group that has added the nitrogen atom at 3.8 ppm – Scheme 1) in a significant number of experiments. Further complications were observed in the isomerization of the maleiamide into the fumaramide isomer (Scheme 1). The fumaramide still is capable of hydroamination but the reaction is significantly slower. We have not quantified its reactivity yet. In another variation of this reaction, diisopropylethylamine (DIPEA) was used as base. The reaction proceeded but resulted in a low soluble solid, possibly as a result of cross-linking with the secondary amino functionalities.

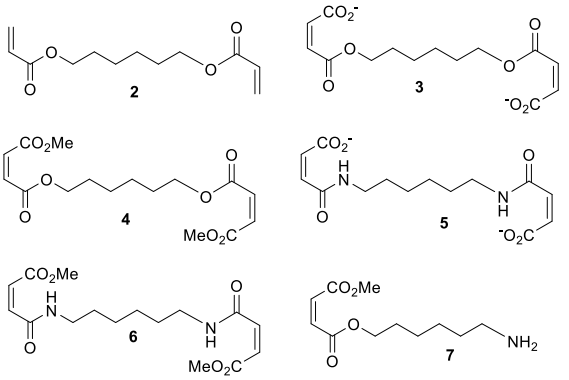


Scheme 1. Polymerization of aminomaleiamide **1** and the ^{1}H NMR spectrum of the reaction solution at 92% conversion

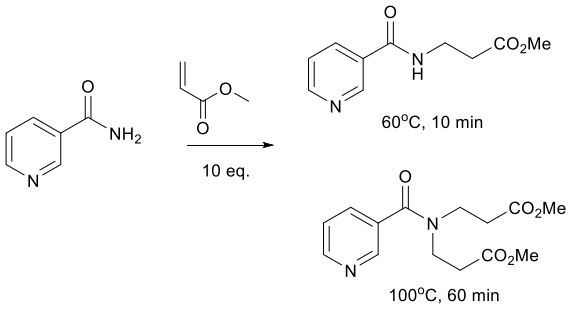
Outlook: At this point, we are trying to develop an end group analysis method based on NMR spectroscopy. Hence, the Schiff base formation with various salicyl aldehydes is currently investigated as potential quantitative reaction converting the primary amino group into a functionality with a characteristic ^{1}H NMR shift. The reaction with deprotonated compound **1** should reflect in a 1:1:1 integral ratio between the maleate and imino functional end groups. Crosslinking should reflect in a relative increase of the imino endgroup integral. Another strategy involves a conversion of the carboxylate functionality of the maleate resulting in a decreased reactivity in the hydroamination. Attempts to esterify with H_3CI failed so far. Finally, the materials formed, cyclic or polymeric, do not exhibit any solubility in thf or other organic solvents suitable for the GPC instrument in house. A collaboration for conducting aqueous SEC is currently sought. Erin Anderson, Alanna McMahan, Micah Spandau and Tytianna Robinson have been or are currently involved on this part of the project.

Difunctional maleates/maleiamides and their reactions with diamines: In this part of the project, novel diacrylates, dimaleates and dimaleiamides **2-6** have been synthesized and their initial reactivities have been evaluated in reaction with 1,6-hexanedimaine. A synthetic strategy for the maleate counterpart **7** to monomer **1** could not be realized. Conversions of the acrylate or maleate end groups as high as 97 % were registered via ^{1}H NMR spectroscopy, with the maleates and mixed maleates/maleiamides exhibiting clear superiority in their reactivity over monomer **1**.

However, in particular, the maleate diesters **2** and **5** exhibited a tendency of ester hydrolysis which adversely affects the ability to accomplish high molecular weights. On the flip side, these polymers exhibit higher solubility in organic solvents and GPC analyses will be performed in the second phase of the project as soon as the instrument is operational again. Initial investigations were also conducted for the reactions of these monomers with other diamines such as ethylene diamine and *S*,*S*-1,2-cyclohexanediamine. The reactions not only performed than with hexandiamine but went to lower conversions as well. Sterics may be a reason but also the reactivity of these diamines with carbon dioxide may signify a complication for the synthetic access to these materials. Simon Schrickel and Anasalea Caroland have been or are currently involved in the project and we are currently looking for a long term research student to continue in this area. The graduate student Hunter Whitetree may also become involved on this end.



Hydroamidation: This is a project we just started several weeks ago. The literature is still void of examples using an electron deficient alkene and a carboxylic acid amide in order to form a secondary or tertiary amide via hydroamidation. Our initial investigations show that the use of base (KOtBu) as catalyst causes a reaction of acrylamide or nictoninamide with methyl acrylate at 60-100ºC. At this stage, we still optimize the protocol to isolate the product of these reactions. Interestingly, using two different conditions for nicotinamide (60ºC, 10 min or 100ºC, 60 min) we were able to identify two different main products of these reactions with 10 equiv. of methyl acrylate). We anticipate the two major products to be the mono and disubstituted products of the hydroamidation as illustrated in Scheme 2, however, isolation and characterization of these compounds is needed to be sure. We will continue to lay the fundament in understanding this reaction, its scope and its selectivities. Then we will attempt to synthesize difunctional molecules, e.g. compound **2**, in order to use the reaction for the formation of polyamides. Hunter Whitetree is currently investigating this reaction and the plan is that this project will become the center of his Master's thesis.



Scheme 2: Proposed hydroamidation of methyl acrylate with nicotinamide under different conditions

Presentations:

1) Erin R. Anderson, Simon Schrickel, Anasalea J. Caroland, Hans J. Schanz: "Hydroamination as Polyaddition Methodology to Access Multifunctional Polymers" 257th Meeting of the American Chemical Society, Orlando, FL, April 1, **2019**.

2) Erin R. Anderson, Simon Schrickel, Hans J. Schanz: "Polymerization via Hydroamination" (Poster), 70th Southeastern Regional Meeting of the American Chemical Society (SERMACS), Augusta, GA, November 2, **2018**.