Hydroamination Of Activated Dialkenes As A Novel Way For Polymerizations

Bachelor Thesis

Hydroaminierung aktivierter Dialkene als neuartige Reaktion für Polymerisation

Bachelorarbeit

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Preamble

For Research purposes, the Georgia Southern University has accepted me as a research scholar in their chemistry and biochemistry department. Together with the American students of the self-proclaimed “Forschung Club Schanz”, I was working in the field of material sciences. While I was tasked with the general development of polymeric materials via hydroamination, I had the chance to get insights to other projects, laboratory routine and NMR spectroscopy. Aside from the work place, I experienced the day-to-day life of America and its wonderful people.

With these words I want thank everyone who made this experience possible. Firstly, I would like to thank my professors, Dr. Rödel and Dr. Schanz, who came up with the idea and initiated the cooperation. Secondly, I would like to thank the international offices of either university, mainly Mrs. Lorenz and Dr. Mertz-Weigel as well as the DAAD Promos for financial support. Lastly, I want to thank all the people who have companioned me on this journey, starting with Blythe Schanz for hosting and caring for me over the course of my stay; the Gato family, for always inviting me over to make me feel home; the entire research group, namely Nadia, Alanna, Cole, Thao-Nhi, Arturo, Anasalea, Erin, Michele, Micah, Imani and Haley; And all other faculty/staff members and friends who helped to enjoy my trip on a daily bases.

Abstract

This thesis reviews the research in the field of material sciences which has been conducted during the bachelor internship. The project involves the development of new techniques to access polymeric materials via hydroamination as well as the characterization of their physical and chemical properties.

As the project started from scratch, protocols for the syntheses of different monomers had been developed and optimized, using general laboratory equipment and spectroscopic analysis. Monomers have further been adjusted to fit necessary reaction conditions and were tested for the addition of amines.

Catalyst have been developed as they were deemed to be a necessity for hydroamination. The research revealed the expandability of catalytic systems for activated alkenes in alkaline environments.

Polymers have been synthesized from various monomers and diamines. NMR spectroscopy has been implemented for a preliminary end group analysis but does not allow for an accurate determination of molecular weights and average chain lengths. By the time the research was terminated, solid polymeric materials were produced via hydroamination; however, the complete removal of left-over monomers, solvent, or ancillary compounds and therefore a pure product was not achieved.

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List of abbreviations

AcOEt	-	Ethyl acetate
CO_2	-	Carbon dioxide
CuCl	-	Copper(I)-chloride
$CDCl_3$	-	Deuterated chloroform
Cu_2O	-	Copper(I)-oxide
DCM	-	Methylene chloride
DMF	-	Dimethylformamide
DMSO-d_6	-	Deuterated dimethyl sulfoxide
D_2O	-	Deuterated water
Et_3N	-	Triethylamine
EDA	-	Ethylenediamine
EtOH	-	Ethanol
HCl	-	Hydrochloric acid
HMDA	-	Hexamethylenediamine
H_2SO_4	-	Sulfuric acid
KO^tBu	-	Potassium *tert*-butoxide
LHCl	-	Ligand precursor
LCuCl	-	Catalyst precursor
MA	-	Maleic anhydride
MeI	-	Methyl iodide
MeOH	-	Methanol
$NaBH_4$	-	Sodium tetrahydroborate
$NaHCO_3$	-	Sodium bicarbonate
NaN_3	-	Sodium azide
Na_2SO_4	-	Sodium sulfate
NaOMe	-	Sodium methoxide
NHC	-	N-heterocyclic carbene
NMR	-	Nuclear magnetic resonance
PdC	-	Palladium on activated carbon
SEC	-	Size exclusion chromatography
S_N2	-	Second order nucleophilic substitution

$SiMe_3Cl$	-	Trimethylsilyl chloride
^tBuOH	-	*Tert*-butanol
THF	-	Tetrahydrofuran
MALDI-TOF	-	Matrix-assisted laser desorption/ionization – time of flight

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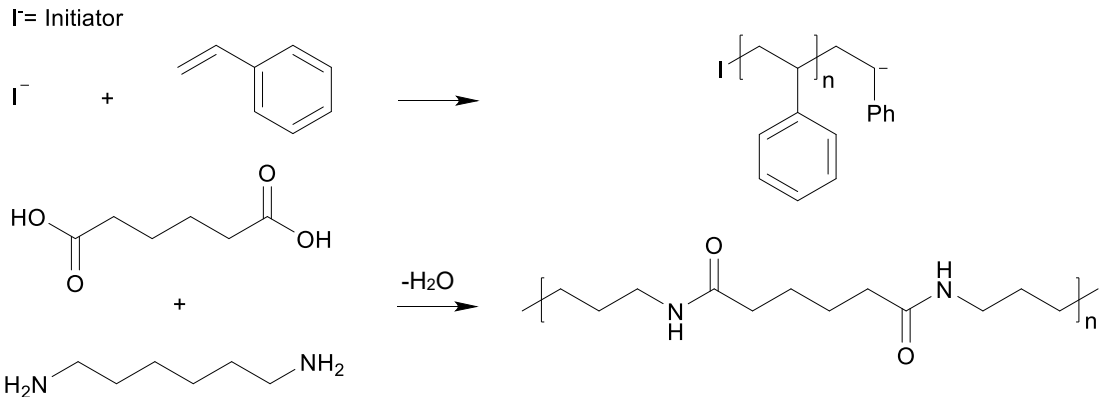
1. Introduction

"[…] Without organic molecules, our society would be sent back to the stone ages.[1]" Although the first manmade polymer was manufactured from casein in the 16th century[2], Maulide's statement holds true. You could not live a day in modern times without these synthetic macromolecules!

Plastics can be compounded from a variety of monomers giving them different physical and chemical properties, which then allows to find the right composition for almost any application. Even more interesting is the fact that polymers from the same monomeric compounds can have deriving properties depending on the way they were produced. Hence giving us reason to explore new reactions and methods for polymerizations.

Polymerization reactions can be divided in two general types, chain-growth and step-growth reactions. Chain-growth polymerization is induced by an initiator of radical, anionic or cationic nature. The initiator poses as the first molecule of the polymeric chain, passing its electronic property to the first monomer allowing it to further react with other monomers. Each addition regenerates the reactive species creating a living chain. This Chain reacts with monomers in its vicinity until the reaction is stopped or the monomer supply ceases.[3]



Scheme 1 *Catinonic polymerization of polystyrene and polycondensation of Nylon6.6*

Step-growth polymerizations require two different functional groups in the monomeric structures, which can react with one another. Step-growth reactions

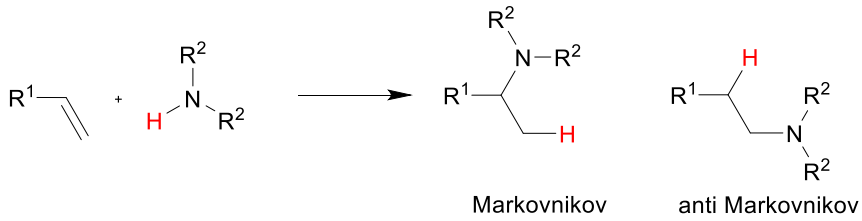
[1] Translated from TV interview, ZIB 24 (ORF), 07.01.**2019.**
[2] http://www.deutsches-kunststoff-museum.de/rund-um-kunststoff/textbeitraege/info/do-it-yourself/rezept-zur-herstellung-von-kunsthorn/, 22.01.**2019.**
[3] Article *Polymerisation* in: Römmp Online. Thieme Medical publisher, 23.03.**2019**

are less coordinated since monomers, oligomers and polymers can randomly bind with other molecules. The connection is performed either by polycondensation or polyaddition. During polycondensations, smaller compounds, most often water, are formed as side products while combining larger molecules to polymers[4]. Whereas polyaddition compares to a regular addition reaction; breaking double or triple bonds to connect molecules [5].

To produce polymers of high molecular weight via step-growth polymerization it is critical that the reagents are present in equal amounts. That is due to the formation of smaller oligomers, which are later combined to large polymeric chains. An imbalance of functional groups leads to the consumption of one reactive species and the premature end of the polymerization.

The conjugated addition to α, β- unsaturated carbonyl compounds is already a valuable and versatile reaction for the synthesis of different compounds by introducing a C-C bond formation[6]. Hence making the addition of amines to electron deficient double bonds a pathway for N-C bond formations[7].

Hydroamination is the conjugate addition of amines across a carbon-carbon π-bond, introducing a wide spectrum of applicable amines and unsaturated hydrocarbons. The addition of secondary amines experienced huge progress over the years. Meanwhile the hydroamination of non-activated olefins received limited attention[8].



Scheme 2 *Possible products of hydroamination*

Since the Markovnikov rule is based on electrophilic addition, the more commonly products for Hydroamination, being a nucleophilic addition, are anti-Markovnikov. The reaction can be inter- or intramolecular, whereby most intermolecular

[4] Article *Polykondensation* in: Römmp Online. Thieme Medical publisher, 23.03.**2019**
[5] Article *Polyaddition* in: Römmp Online. Thieme Medical publisher, 23.03.**2019**
[6] Angew. Chem. **2017**,129, 8075–807.
[7] J. Am. Chem. Soc. **2006**, 128, 5, 1446-1447.
[8] Chemical Society Reviews **2003**, 32(2), 104-114.

hydroaminations require a catalyst[9]. These catalytic systems can be used to shift the product outcome by altering steric hindrance and reaction mechanisms; therefore, allowing controlled stereoselectivity[10]. The possibility to synthesize chiral amino compounds makes it an interesting reaction for natural and pharmaceutical substances. Being an addition reaction with high atom economy, as well as inexpensive and easily accessible substrates, it displays a versatile and desirable pathway for the formation of higher substituted amines[11].

Recently Extensive studies of hydroamination have been conducted, using transition metal-based catalyst with N-heterocyclic carbene (NHC) ligands[12]. In those studies, special substrate dependent catalyst had been prepared for each reaction. Hydroamination can be catalyzed with a scope of electropositive elements, ranging from alkali over transition to rare earth metals, while all of them form an amido transition status to introduce the nucleophilic addition[13].

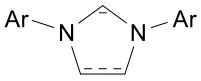
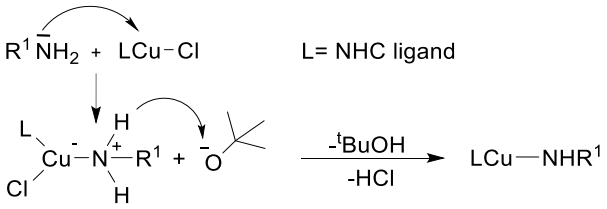


Figure 1 *NHC generic depiction*

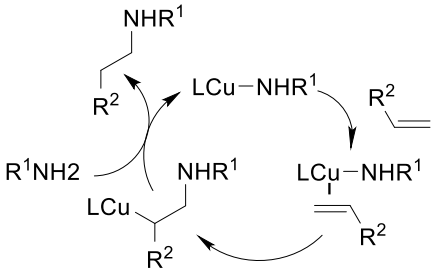


Scheme 3 *Catalyst formation*

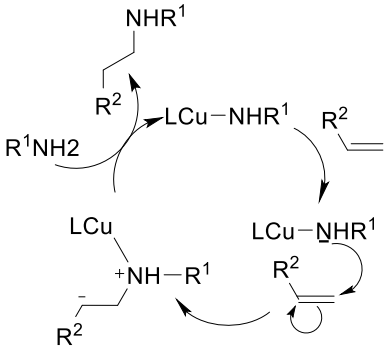
In his studies, Gunnoe showed that copper(I)-amido complexes work sufficiently for the addition of amines to olefins, striving away from expensive elements such as palladium, ruthenium and platin[14]. As ancillary ligands, NHC compounds are more advantageous than other catalyst ligands; such as tertiary phosphines. Although being sensitive, they can be stored as stable complexes without any loss of quality over time. Carbenes are better σ-donors than common ligands, enabling stronger binding to the metal center and therefore reducing ligand dissociation. Also, the implication of different aryl groups allows to tune inductive and steric properties[15].

[9] Org. React. **2015**, 88, 1.
[10] J. Am. Chem. Soc. **2003**, 125, 41, 12584-12605.
[11] Chem. Sci. **2014,** 5**,** 101-106.
[12] J. Am. Chem. Soc. **2006**, 128, 5, 1446-1447.
[13] J. Am. Chem. Soc. **2003**, 125, 41, 12584-12605.
[14] Organometallics **2007**, 26, 1483-1493.
[15] Dalton Trans. **2009**, 1428-1435.

There are two major catalytic cycles that have been proposed. The first one is initiated by pre-coordinating the olefin, followed by a migratory insertion between the copper-amido bond, forming a copper-alkyl complex. The catalyst is then reformed by protonolysis through another equivalent of the amine substrate. The second one is initiated by coordinating the copper to the functional group of the olefin, activating the amine for the nucleophilic attack. It is presumed that the addition leads to an unobserved intermediate zwitterionic compound that quickly decays by transmitting a proton. The catalyst is then reformed by a ligand exchange through another amine.[16]



Scheme 4 *Catalytic cycle 1*



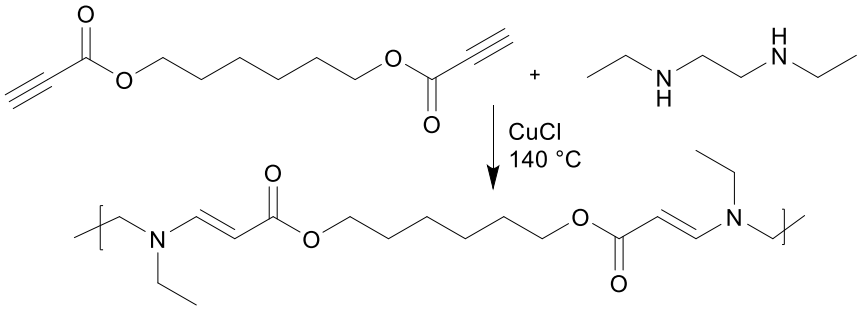
Scheme 5 *Catalytic cycle 2*

The reaction rate of transition metal catalyzed hydroamination depends mostly on three parameters. (a) Electron deficiency of the alkene. The reactivity of the substrate is strongly enhanced by an electron withdrawing groups next to π-bond. Hence, acrylates and maleates are viable candidates. (b) The basicity of the amine as the counterpart to the electron deficiency of the double bond. Therefore, an alkaline environment is mandatory. (c) Steric and electronic parameters of the transition metal catalyst and its ability to facilitate the N-C and C-H bond formation[17].

Further, the addition of alkyl amines to acrylates, using Lewis bases or acids, is a known reaction to form β-alanine derivatives, and even a neat reaction without catalysts has been realized[18]. Therefore, the use of amines, themselves being Lewis bases, might be sufficiently to catalyze the hydroamination, allowing a polymerization even without an actual catalytic system.

[16] Organometallics **2007**, *26,* 1483-1493.
[17] Inorg. Chem. **2006**, 45, 9032-9045.
[18] ARKIVOC **2002**, 7, 76-81.

A click reaction to form a polymeric material from secondary diamines and dialkynes has already been achieved. Copper chloride has been utilized as a catalyst and the reaction was carried out at harsh conditions above 140 °C[19], offering limited usefulness. Given that, it is expected that the polymerization of alkenes and amines would be possible with the application of the right catalytic system.

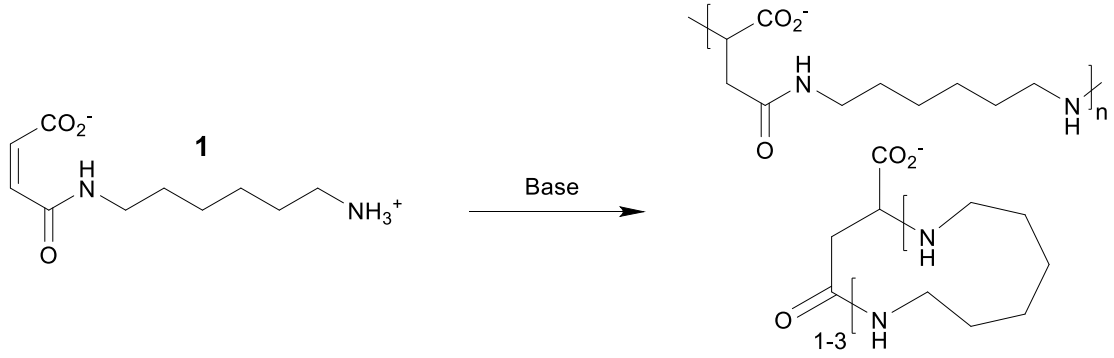


Scheme 6 *Polymerization of secondary amines with diynes*

Given adequate reactivity, the reactions should be run at the lowest possible temperatures and highest possible concentrations; provided that addition reactions are enthalpically favored and entropically disfavored. According to Gibbs-Helmholtz, increasing the temperature will result in a high contribution of entropy to the free energy, hence favoring the side with the larger number of molecules. High temperatures promote dehydroamination and cyclization over polymerization.

$$\boldsymbol{\Delta G = \Delta H - T \cdot \Delta S}$$

Impulse for researching hydroamination as a possible polymerization reaction was an unrelated project. The Schanz group tried to react a monoamide, from



Scheme 7 *Polymerization and oligocyclization of N-(6-aminohexyl) monomaleamide (**1**) under basic conditions*

hexamethylenediamine, and maleic anhydride with chloroacetyl chloride. The aim was to convert the amino group of the N-(6-aminohexyl) monomaleamide (**1**) to

[19] J. Am. Chem. Soc. **2017**, 139, 5437-5443.

a chloroacetamide. In the basic environment, contrary to the expectations, the signals of the maleic backbones double bonds have disappeared from the ^{1}H-NMR spectrum, leading to the assumption that they might have been hydroaminated.

For their project, compound **1** was synthesized on a multigram scale by combining equal amounts of HMDA and MA in ethanol, allowing for essential investigations on the polymerization in methanol. Its reactivity together, with the later introduced IXyCuCl-based catalyst, marked the baseline on which the other monomers would be evaluated.

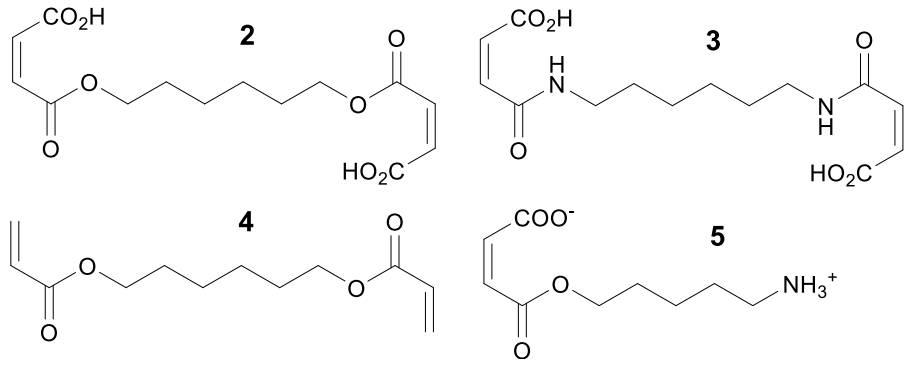


Figure 2 *Possible Monomers*

As a nucleophilic addition, the reaction should perform with any Michael acceptor, meaning unsaturated carbonyl compounds like acrylates, maleates and fumarates. Thus, introducing a vast array of possible monomeric compounds which can then be combined with different diamines, such as shown in **Figure 3**. These combinations could form a variety of polymers, compared to that of polyamides, differing in chain length and the contribution of functional groups.

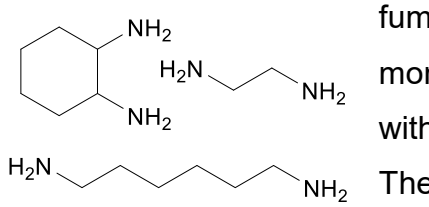
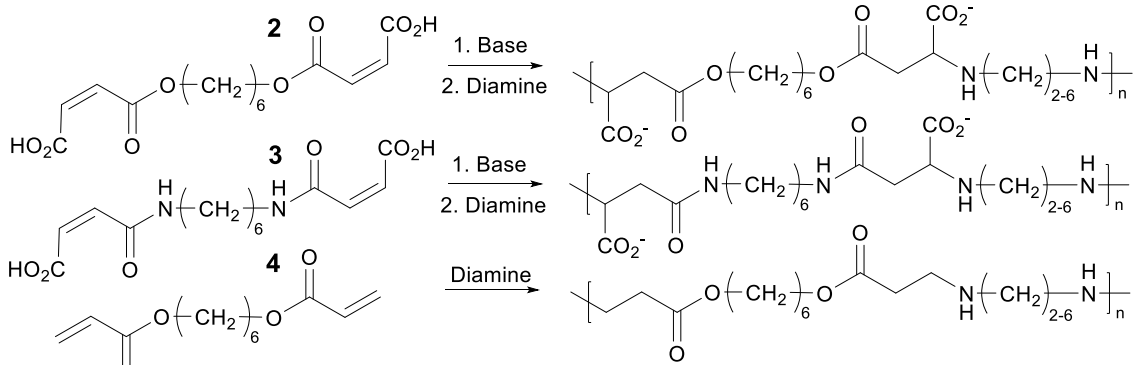


Figure 3 *Possible diamines*



Scheme 8 *Polymerization of the monomers 2...4*

Due to the maleates' carboxyl group and its electron withdrawing effect, they are expected to be highly activated and therefore very reactive. For the same reason, esters should be more reactive then amides, given the stronger electron withdrawing effect of the oxygen over the nitrogen. Compound **1** comes with the significant advantage that it provides opposite functionalities in the same molecule, hence guaranteeing an equimolar ratio which should lead to high molecular weights.

This report reviews the monomer- and catalyst synthesis, explaining why certain modifications were implemented and what problems have appeared; moving on to preliminary investigations on hydroamination and finishing with the polymerization of said monomers. This report focuses on dialkenes, although monomaleates and monomaleamides are introduced to give an insight on different approaches.

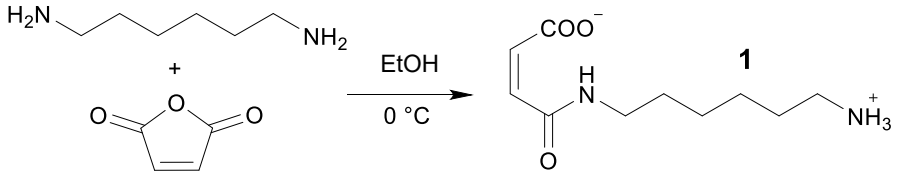
2. Monomer synthesis

Like all monomers performing step growth polymerization, these compounds are required to have two functional groups involved in hydroamination. Opposing functionalities may be present in the same monomer or distributed in between diamines and dialkenes, thus allowing a scope of different compounds to be developed. Starting from compound **1**, modifications have been applied that were expected to be more reactive, and that may lead to a variety of polymeric structures.

The polymeric structures would exhibit a high density of polar groups, which might allow them to exhibit physical strength comparable to known polyamides such as Nylon. Contrary to common polyester—due to hydroamination, polymers made from monosubstituted maleates provide a free carboxylic group which could alter chemical and physical properties through treatment with bases or acids. Using those polymers combined with established fibers could allow a completely new scope of applications.

All monomers were synthesized based on the structure of the original monomer **1** and have been modified as needed. ^{1}H NMR spectroscopy has been employed to determine conversion and to characterize the products of each reaction.

Monomer **1** was synthesized by adding MA to an EtOH solution of HMDA at 0 °C. The product slowly precipitated over the course of a week in the refrigerator and could be filtered to afford a wax like substance.

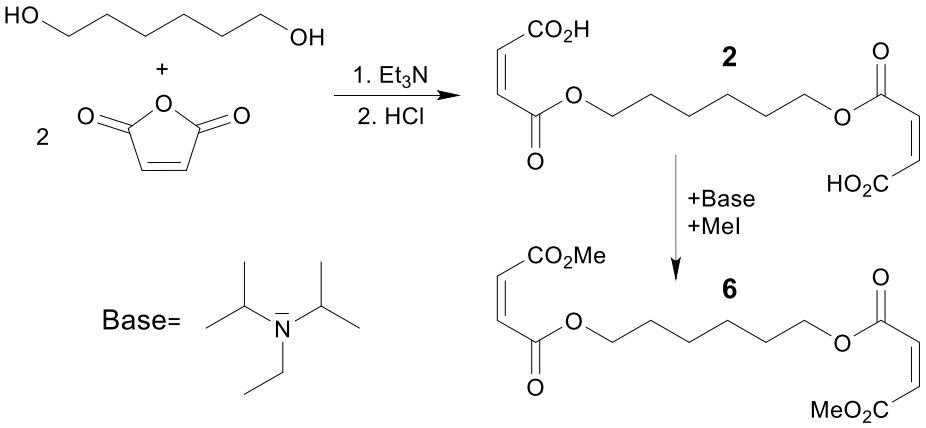


Scheme 9 *Synthesis of N-(6-aminohexyl) monomaleamide (**1**)*

In order to increase the electron deficiency of the alkene and therefore its activity, it was proceeded to synthesize the maleic ester **2**. This was done a by a base catalyzed esterification of MA. In an ice bath, hexanediol was deprotonated with triethylamine as preparation for a nucleophilic attack. Shortly after the addition of

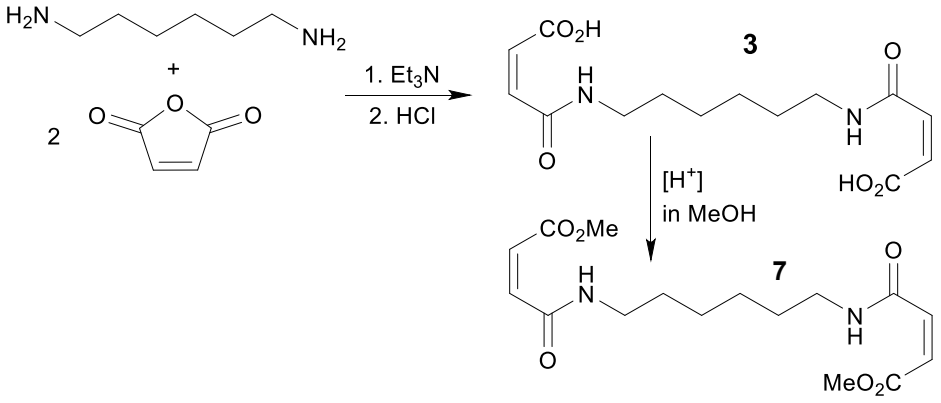
MA the solvent was removed. The residue was treated with HCl and the product was isolated from the aqueous solution via filtration.

In later experiments, solubility issues, due to salt formation between the monomer and the employed base, have been encountered. To circumvent that, a second esterification was performed, taking away the carboxylic groups. Compound **2** was deprotonated at high temperature using Hünig's base (N,N-diisopropylethylamine), allowing it to undergo an S_N2 substitution with methyl iodide. The product (**6**) was isolated via extraction and has proven to be very reactive for hydroamination even at room temperature.



Scheme 10 *Synthesis of hexane-1,6-diyl dimaleate (**2**) and its esterification (**6**)*

Before project relevant monomer synthesis was investigated, another group produced monomer **3** by refluxing the original maleamide (**1**) in the presence of phosphoric acid. Since their protocol could not be reproduced, the procedure of monomer **2** was applied to HMDA respectively. Therefore, a solution of HMDA

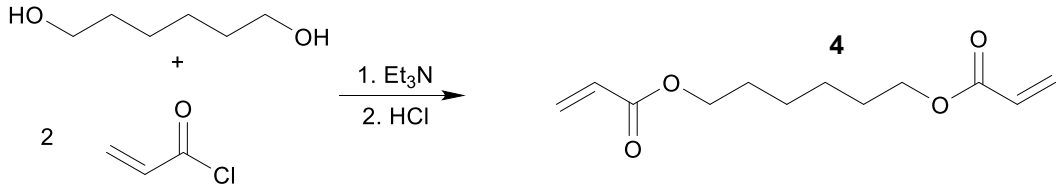


Scheme 11 *Synthesis of hexane-1,6-diyl dimaleamide (**3**) and its esterification (**7**)*

and Et_3N had been prepared and was cooled to 0 °C, before MA was added. After removal of the solvent and later treatment with HCl, the product was isolated via

filtration. With amides being more stable then esters, an additional acid catalyzed esterification was performed. Under vigorous stirring, a MeOH solution of monomer **3** was treated with a few drops of sulfuric acid. Since MeOH was used as a reactant and a solvent, it appeared with virtually infinite concentration, driving the equilibrium to the product side. After 24 hours, the product (**7**) was isolated and purified via extraction. Being a time sensitive reaction, it took several attempts to achieve an adequate conversion and selectivity.

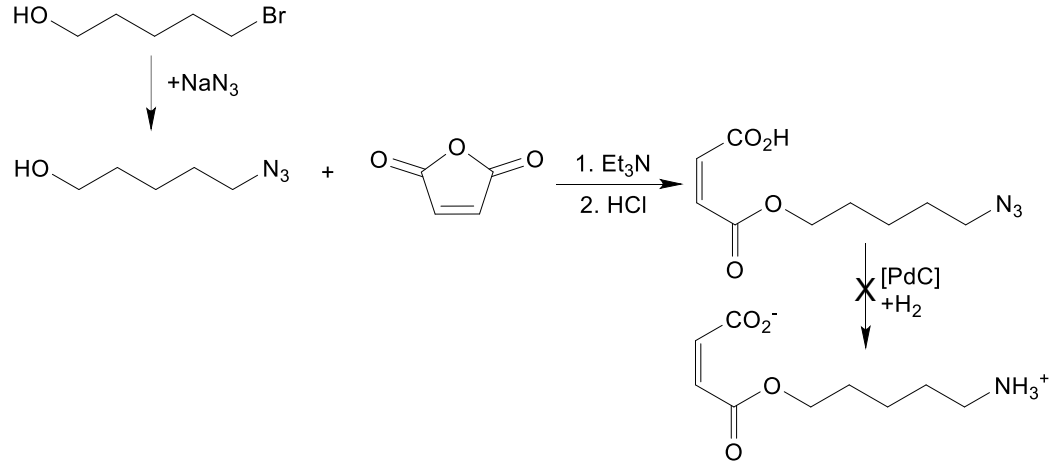
As another way of preventing the monomeric acids from forming salts, acrylates have been employed instead of maleates. At 0 °C, a solution of acryloyl chloride was slowly added to a solution of hexanediol and Et_3N. Evaporating the solvent and treating the residue with diluted HCl allowed to isolate Monomer **4**. This monomer showed excellent solubility and reactivity.



Scheme 12 *Synthesis of hexane-1,6-diyl diacrylate (**4**)*

Further, a respective methacrylate was synthesized which showed no reaction in the presence of amines, even at elevated temperatures.

Lastly, it was attempted to make the highly desirable Monomer **5**, which was expected to combine the elevated reactivity provided by the ester with bifunctionality present in Monomer **1.** In a three-step synthesis, the bromide of 5-



Scheme 13 *Synthesis of N-(5-aminopentyl) monomaleamid*

bromo-pentan-1-ol was exchanged in an S_n2 reaction using sodium azide. The reaction was carried out in DMF, which had to be washed out in an extraction

with water and ethyl acetate, affording 5-azido-pentan-1-ol. Applying the same procedure with Et_3N and MA to the alcohol, allowed the isolation of 5-azido-pentyl maleate. In the last step, the conversion of the azide to an amine was attempted. For the hydrogenation, a solution of 5-azido-pentyl maleate was prepared and palladium on activated carbon was added to it. In another flask, hydrogen was produced from sodium tetrahydroborate and passed through the reaction mixture. Unfortunately, the analysis of the product showed that not only the azide, but also the maleic backbone had been hydrogenated.

3. Synthesis of NHC ligand complexes

Based on the studies conducted by Gunnoe et al. NHC-Cu(I)Cl complexes with the notation of LCuCl (L= IXy; IPr; ITap and IMes {IXy= 1,3-bis(2,6-dimethylphenyl)-imidazol-2-ylidene; IPr= 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; ITap= 1,3-bis(N,N,2,6-tetramethyl-4-aminophenyl)imidazol-2-ylidene; IMes=1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene}) had been synthesized for the research. ITap and IPr were used with an unsaturated backbone (ITapCuCl; IPrCuCl) as well as in their saturated form (H_2ITap; H_2IPr). IXy and H_2IMes were only used in their respective forms, and therefore acted as saturated and unsaturated counterparts.

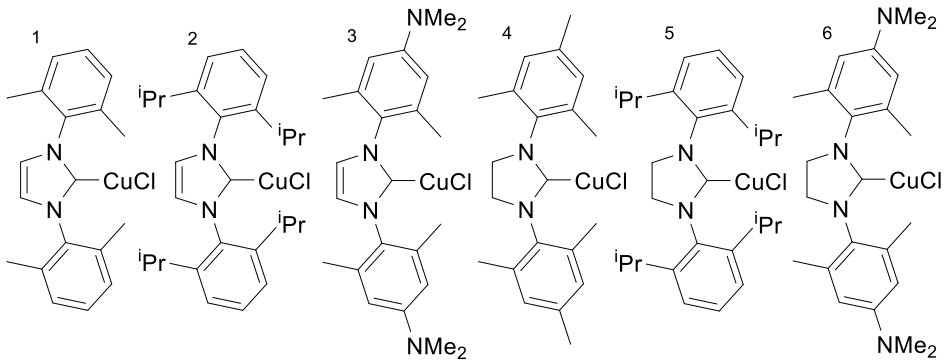
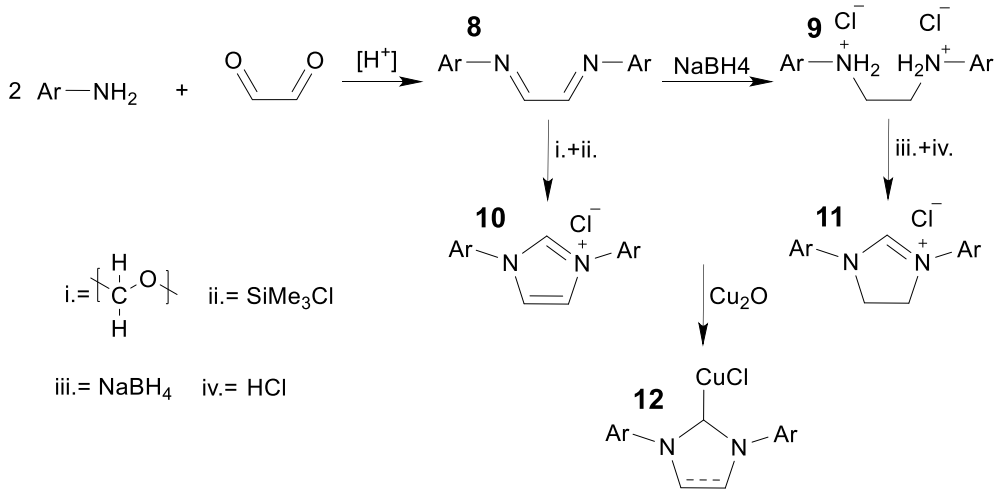


Figure 4 *Synthesized NHC complexes: 1 IXyCuCl; 2 IPrCuCl; 3 ITapCuCl; 4 H_2IMes; 5 H_2IPr; 6 H_2ITap*

These complexes are the precursors for catalysts used in various addition reactions, for which they are converted to a substrate-specific catalyst by exchanging the chloride ligand with the substrate itself. As proven in earlier reactions, the ligand exchange can be performed in situ by adding a strong base, in our case KO^tBu.

While the unsaturated catalyst precursors (LCuCl) can be prepared in a three-step synthesis, the saturated ones need an extra step. The first step is an acid catalyzed condensation of glyoxal with the respective aniline at room temperature, forming a double Schiff base (**8**) with the generic structure of N,N'-(diaryl)-ethylenediimine.



Scheme 14 *General synthesis of the NHC ligands and catalyst precursors*

For the saturated ligands, the double Schiff base (**8**) needs to be hydrogenated. Therefor it is, together with $NaBH_4$ and boric acid (posing as Lewis acid), dissolved in tetrahydrofuran to afford a diamine. After 24 h, upon the addition of HCl, it is isolated as an insoluble diammonium salt (**9**).[20]

Secondly, ring-closing reactions are performed by introducing another carbon atom. In the case of the imine (**8**), this accessible with paraformaldehyde in presence of trimethylsilyl chloride, which is slowly added to the reaction mixture in AcOEt. The imidazolium chloride salt (**10**) precipitates from the solution as an off-white solid, that is pure according to the H^1 NMR data.

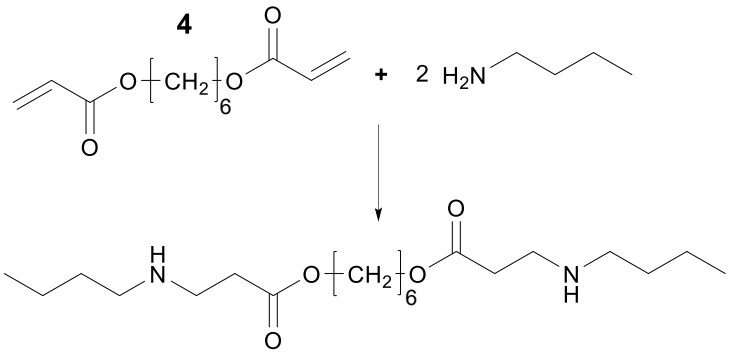
To form the imidazolinium salts, compound **9** is mixed with triethyl orthoformate and heated to 145 °C in a microwave reactor. The Mixture is then suspended in diethyl ether and the product is generally obtained as a white solid (**11**) via filtration.[21] The saturated ligand precursors had already been prepared and were not synthesized during this project.

[20] Org. Synth. **2010**, 87, 77.
[21] Org. Synth. **2010**, 87, 77.

Complexation is the last step for both kinds of ligands. The carbene is formed by deprotonating the imidazol(in)ium cations (**10** and **11)** with basic reacting copper(I) oxide, which are then able to coordinate towards the metal. This reaction is feasible in various solvents and at different temperatures[22]. For us, the reaction in MeOH at 100 °C, using a pressure flask, has shown to be the most efficient so far. The slurry is filtrated to afford a mixture of product and unreacted copper(I) oxide. The product is then dissolved on the filter using methylene chloride, separating it from the other components of the residue. When dried, all LCuCl complexes (**12**) are white crystalline powders.

4. Hydroamination of monomeric compounds

To evaluate reactivity of the synthesized dialkenes for hydroamination, experiments on the addition of primary amines have been conducted before trying for polymerizations. This helped to identify and anticipate issues, such as solubility, hydrolysis, dehydroamination and the resulting isomerization. For these evaluations n-butyl and t-butylamine have been implemented, as they could easily be removed due to their volatility – allowing for an accurate conversion analysis using NMR spectroscopy.



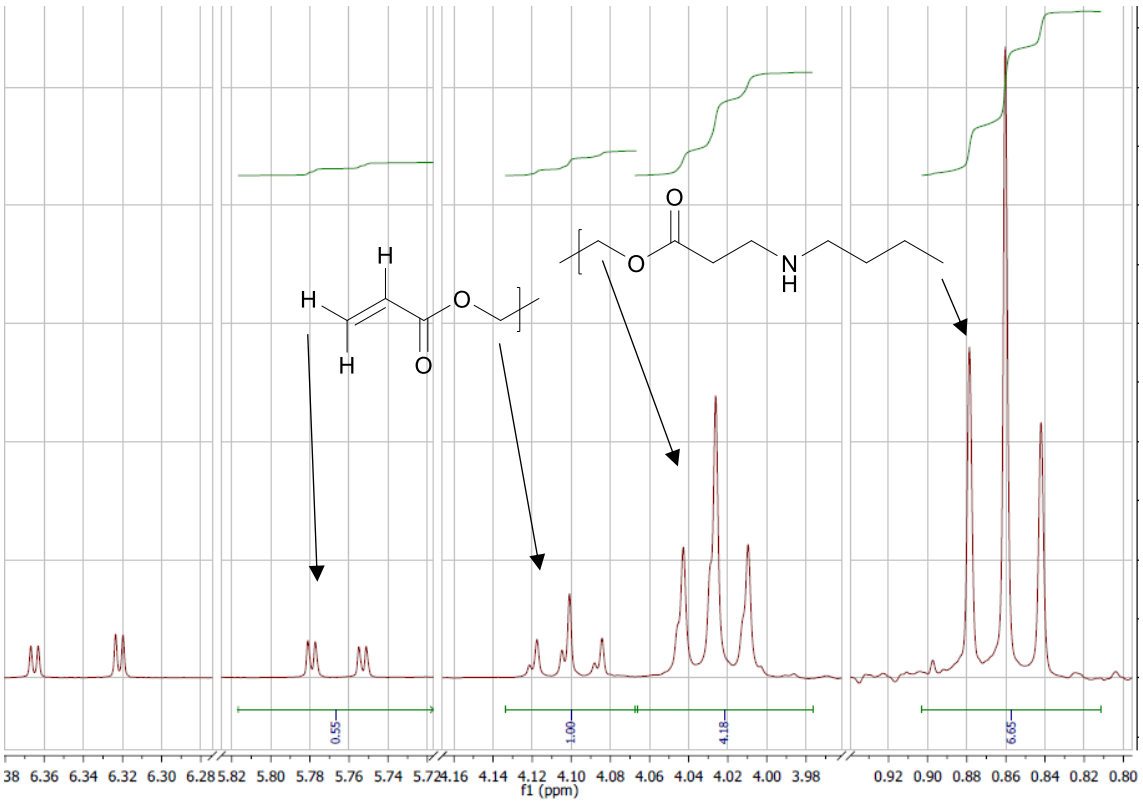
Scheme 15 *Hydroamination of hexane-1,6-diyl diacrylate (**4**) with n-butylamine*

Analog to the hydroamination of acrylate derivatives, the addition to simplest representative, monomer **(4)**, had been performed first. Starting off with a catalyst loading of 5 % and a molar ratio of 2:1 for n-butylamine, full conversion had been achieved after 20 h at 60 °C. The only problem was a high rate of hydrolyses at around 10 %, which has also been apparent for monomer **2**. This issue was

[22] Dalton Trans. **2010**, 39, 4489-4491.

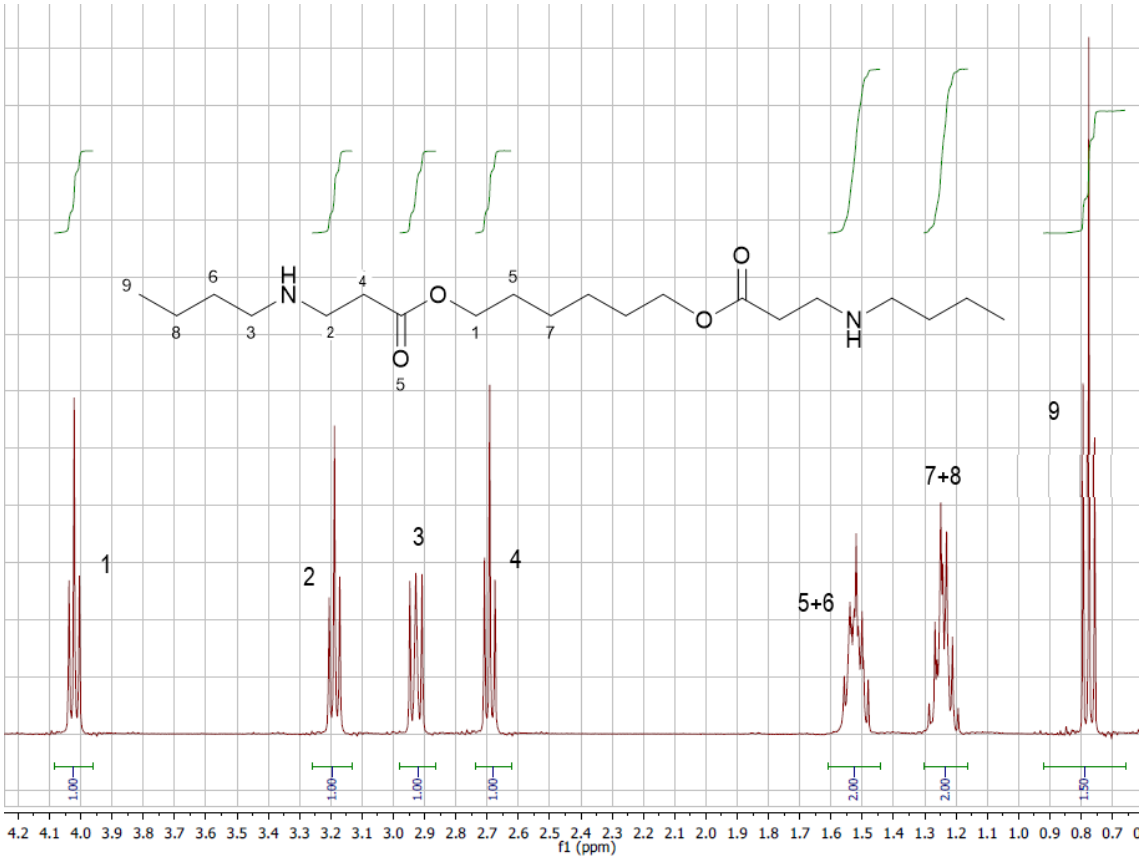
counteracted by employing AcOEt as a solvent, providing a basically unlimited amount of another ester to protect the monomer. Raising the ratio of amine to 10:1, allowing for the assumption of a pseudo first order reaction, lead to full conversion in less than a minute, even at room temperature. The blank showed that neither the catalyst, nor additional base was needed to promote this Michael-like reaction. While most intermolecular hydroaminations require catalysts, this species had been rendered so reactive that catalysts were expendable. The direct addition of 10 equivalents amine to the diacrylate, as a neat reaction, and the immediate removal through evaporation, led to a conversion of 80 % in less than 10 seconds. The conversion was measured by comparing the shifted O-CH_2 signal of the product to the original one and the residual olefin signal. For further validation the shifted signal had to appear in a 2:3 ratio to the -CH_3 (0.86 ppm) of the added amine (2:9 for t-butylamine).

Spectrum 1 was cut down to the significant peaks showing the O-CH_2 triplets of the product (4.02 ppm) and the starter (4.10 ppm) in a ratio of about 4:1 corresponding to 80 % conversion. To validate the peaks the ratios of 2:1 for the starter and 2:3 for the product are present as well.



Spectrum 1 *^{1}H NMR — significant signals for hydroamination*

For product isolation, the solvent, as well as excess amines, had been removed under vacuum before concentrated HCl was added to the residue. Using a mixture of EtOH and toluene, the water was evaporated as they form a low boiling azeotrope. On addition of acetone, the product precipitated and was filtered off as a white powder which was pure according to the H^1 NMR.



Spectrum 2 *^{1}H NMR — n-butyl hydroaminated hexane-1,6-diyl diacrylate (**4**)*

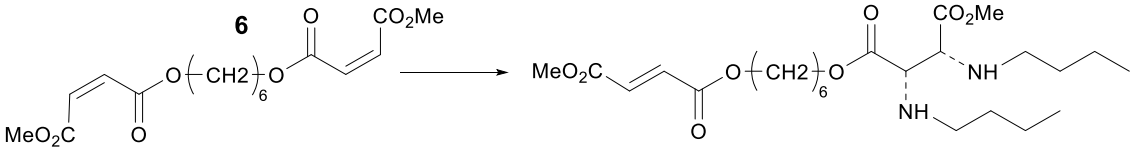
The reaction with t-butylamine was significantly slower but reached full conversion after about 20 h at room temperature. Using the same procedure as before, the isolation of a pure product was not possible and was considered to not be necessary.

To perform the addition to monomer **2** additional base was required. At first KO^{t}Bu and THF were used, but as the monomer formed a salt with the base it precipitated from the solution, stopping the reaction immediately. Using DMF as a more polar solvent, led to a moderate reaction rate above 60 °C; temperatures above 80 °C promoted the reversion of the reaction and enhanced the hydrolyses of the monomer. Knowing that the reaction was feasible, DMF was substituted with acetonitrile and excessive amounts of tertiary amines were used to

deprotonate the monomer. While still precipitating, full conversion was achieved within 2 hours.

As mentioned earlier, the amides are less vulnerable for hydrolyses which allowed us to employ MeOH and NaOMe for the reaction of monomer **3**. With this setup full conversion was achieved within 24 hours. These reactions had been performed by other members of the research group and being short on time, it was decided to move on to polymerizations without further investigations of the hydroamination. Same goes for monomer **7**, which had still been under development by the time the project was concluded.

Monomer **6** presented a reaction kinetic that could not be explained. The experiment was run in AcOEt at room temperature and within 2 hours, 100 %

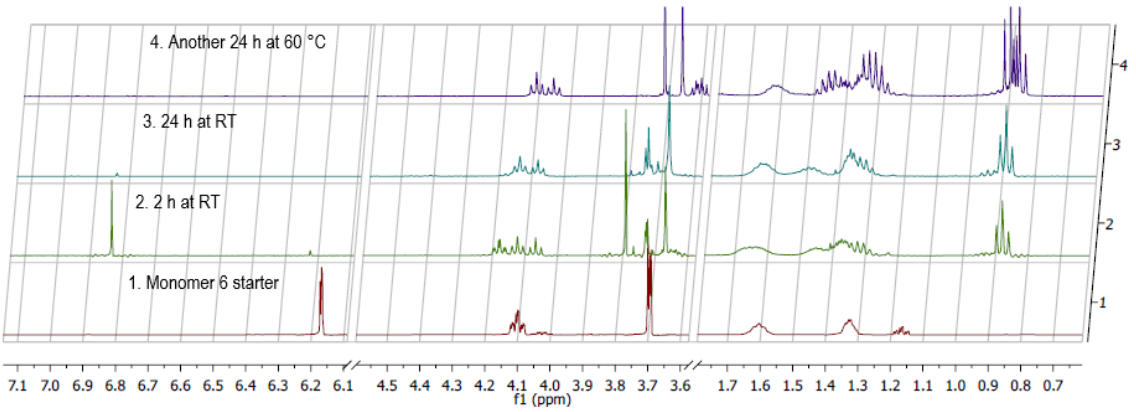


Scheme 16 *Isomerization and hydroamination of monomer* ***6***

conversion had been achieved; but only with 50 % selectivity. At this point half of the starters double bonds had been converted to a mixed α- and β- addition product, while the other half was isomerized to the respective fumerate. The solution was further stirred overnight, converting the fumerate to the mixed product as well. Isomerization was anticipated for more reactive monomers, but from a thermodynamical point of view, it was expected that the equilibrium would shift to the most stable compound, preventing further addition.

Spectrum 3 shows the conversion of monomer **6** in presence of n-butylamine. Within the first 2 h the conversion of the *cis* double bond to the *trans* double bond, lead to a shift of the double bond singlet from 6.18 ppm to 6.83 ppm. With the formation of the fumerate and the mixed product the three different signals are shown for the O-CH_2 triplets and the CO_2Me singlets. The far-left signals of each

group belong to the fumerate as they disappear with the double bond when full product conversion is achieved.

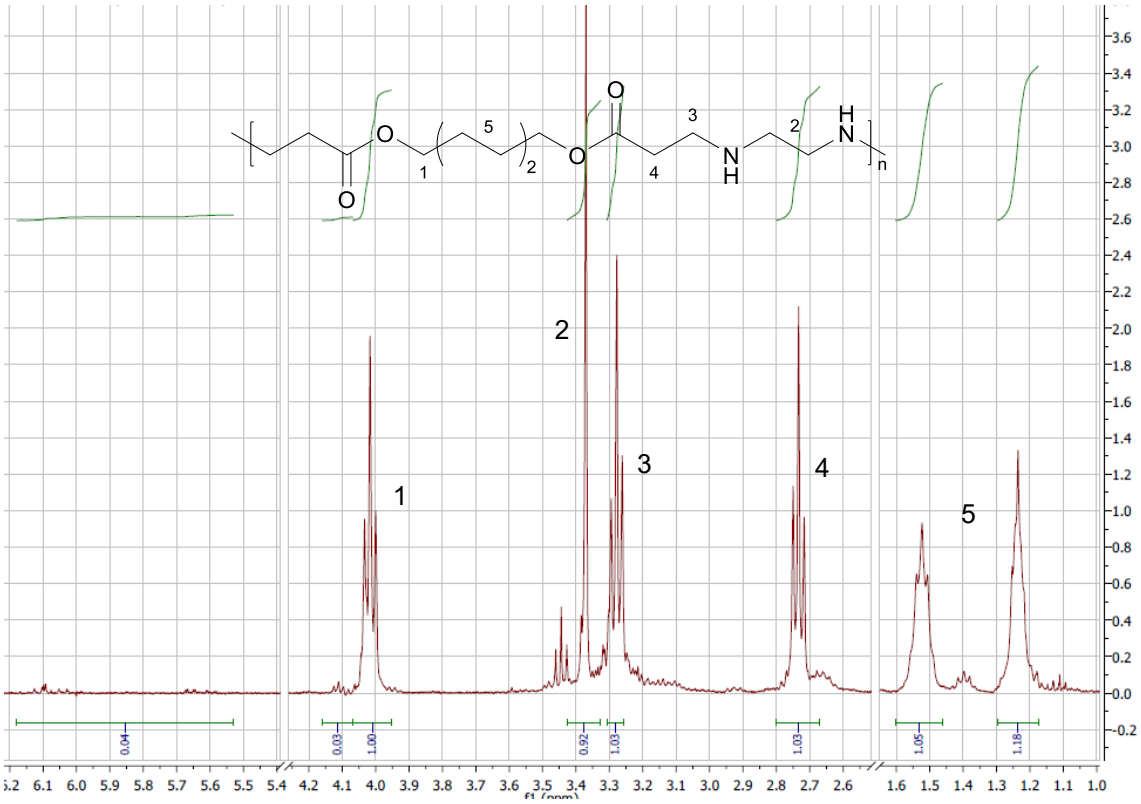


Spectrum 3 *^{1}H NMR — n-butyl hydroamination of monomer* ***6***

It was attempted to force the equilibrium back to the fumerate by increasing the reaction temperature. In this case the temperature did not lead to dehydroamination but enhanced the hydrolysis of the monomer (3.61 ppm).

5. Polymerization through hydroamination

For the polymerization reactions, Monomer **4** was the most investigated starter because it does not require any extra preparations or conditions and does not engage in significant side reactions. Respective to **Scheme 8**, the polymerization of each monomer with either diamine was attempted. Reaction with equal molarity posed to be impossible on the small scale they were carried out, especially for ethylenediamine. Due to its volatility it could not be brought into the glovebox to prevent its quick reaction with CO_2 from the air. Since the catalyst had been abandoned, the use of bases was not required for Monomer **4** and practically any organic solvent could have been used. For both, the HMDA as well the EDA, conversion above 95 % were achieved within 24 h at 60 °C. Although, full conversion of the monomer could not be achieved even with an excess of the amine and run times up to 72 h.



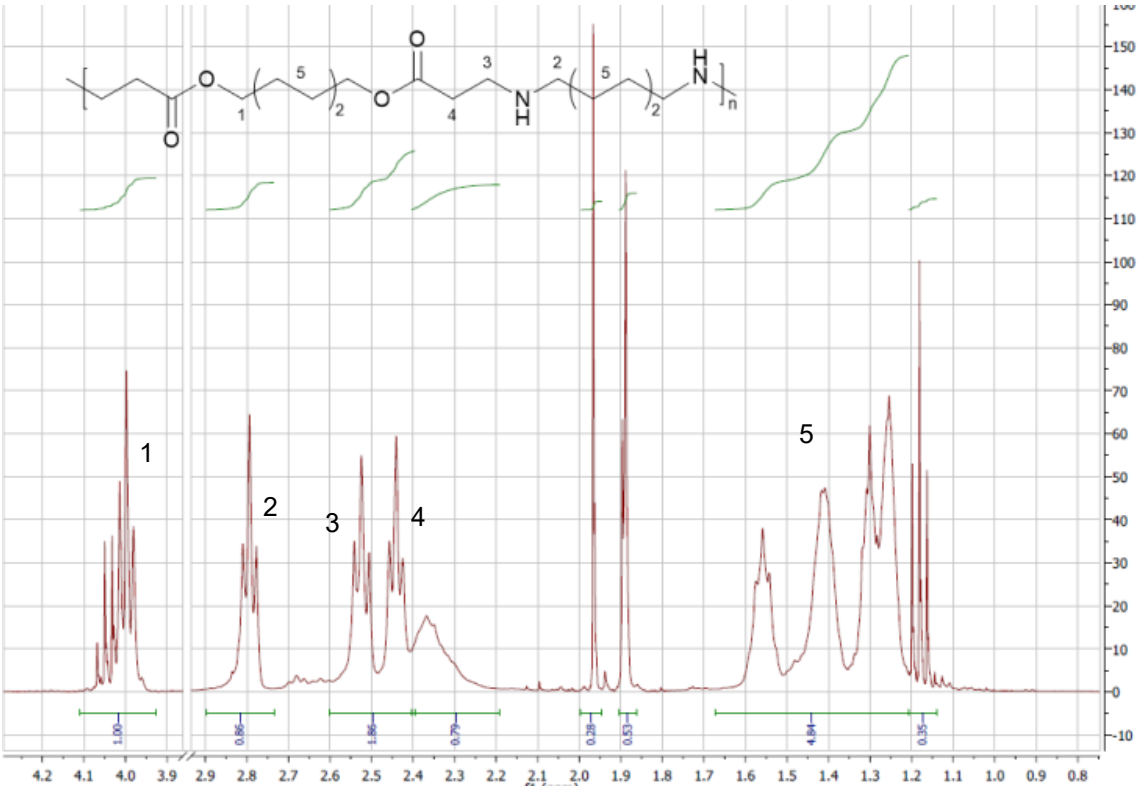
Spectrum 4 *^{1}H NMR — Polymerization of hexane-1,6-diyl diacrylate (**4**) with EDA*

With the assumption, that polymer end groups are represented by the leftover starter; 95 % conversion would only lead to chain lengths of 10 to 20 repeating units. This inaccurate estimation is due to the fact, that the observed end group is presented either once or twice in the spectrum, while the corresponding polymeric group appears twice. Hypothetically, if the conversion ceases because both ends are substituted with the alkene and they are not able to further react, an average chain length of 20 to 30 units could be achieved. At this point, an accurate determination is unnecessary because the average chain length and purity of the product is insufficient for successive investigations.

Full conversion of the double bonds was achieved with HMDA at 100 °C. In this case, a gel like substance formed around the stir bar. The solvents had been removed and the gel was dissolved in concentrated HCl. The solution was dried with toluene and EtOH until a brittle, solid foam was left in the flask. It seemed that this product was hygroscopic, as it formed a gel when left open to the air. Since then, all products have been stored under nitrogen.

In **Spectrum 5**, the quartet of AcOEt covers any residual O-CH_2 peaks and possible amino end groups are covered by other amine signals, preventing an

end group analysis. There is no profound assignment for the peak at 2.36 ppm; all other peaks belong to AcOEt or acetone. For any assertions about the average chain length of fully converted monomers, an aqueous SEC would be needed; and if more than 100 repeating units were present, a MALDI-TOF would be recommended.



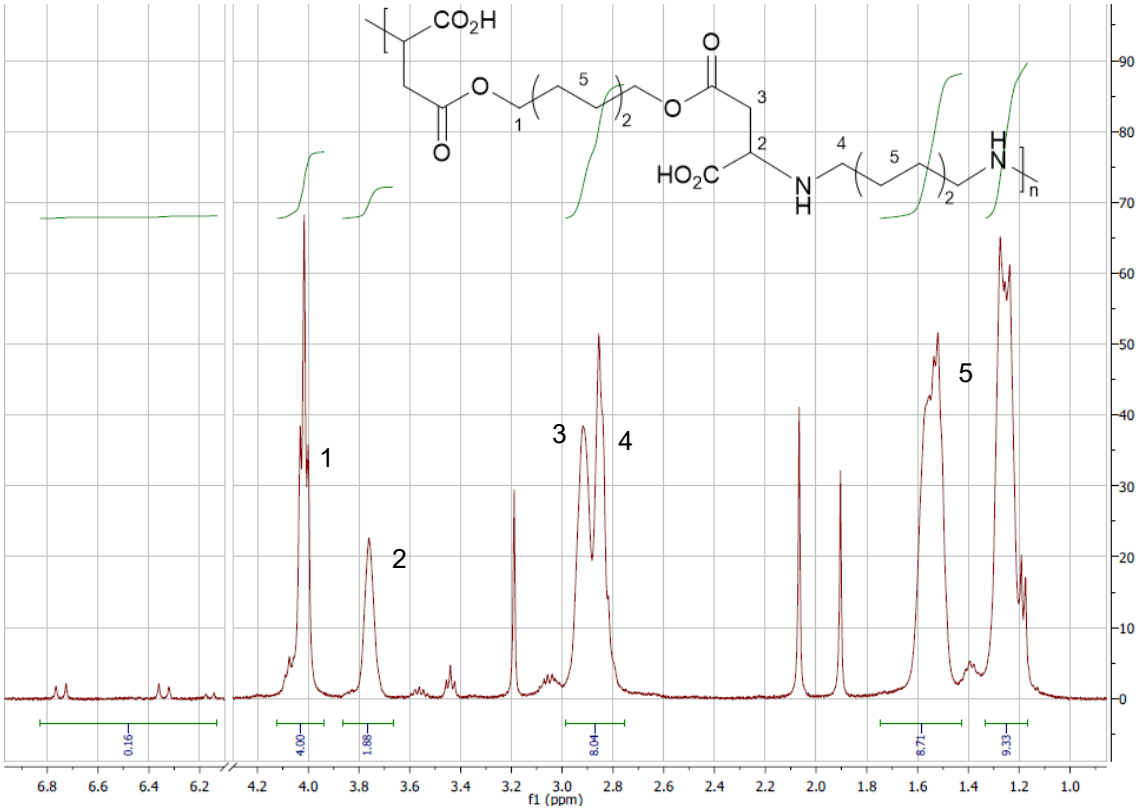
Spectrum 5 *^{1}H NMR — Polymerization of hexane-1,6-diyl diacrylate (**4**) with HDMA*

For polymerizations involving maleate monomers, the conversion rate is slowed down drastically above 95 %. Addition reactions to maleates are being inhibited by fumarate-isomerization. Hence preventing full conversion within adequate reaction times, as other researchers have shown as well[23].

[23] Reac Kinet Mech Cat, **2015**, 115: 431.

Spectrum 6 shows the product of Monomer **2** and HMDA. The polymerization was run in acetonitrile with Hünig's base for 24 h, at 100 °C. The solid product was washed with acetone and MeOH before being protonated with HCl. Even after multiple washings, the base could not be removed as shown by the doublet on the far right. The other peaks are residual solvents from the isolation process; although they should have been removed with the water. The product was dried down to a brittle foam and stored under nitrogen. Since desired chain lengths were not achieved, it was not bothered to further purify the product at the time.

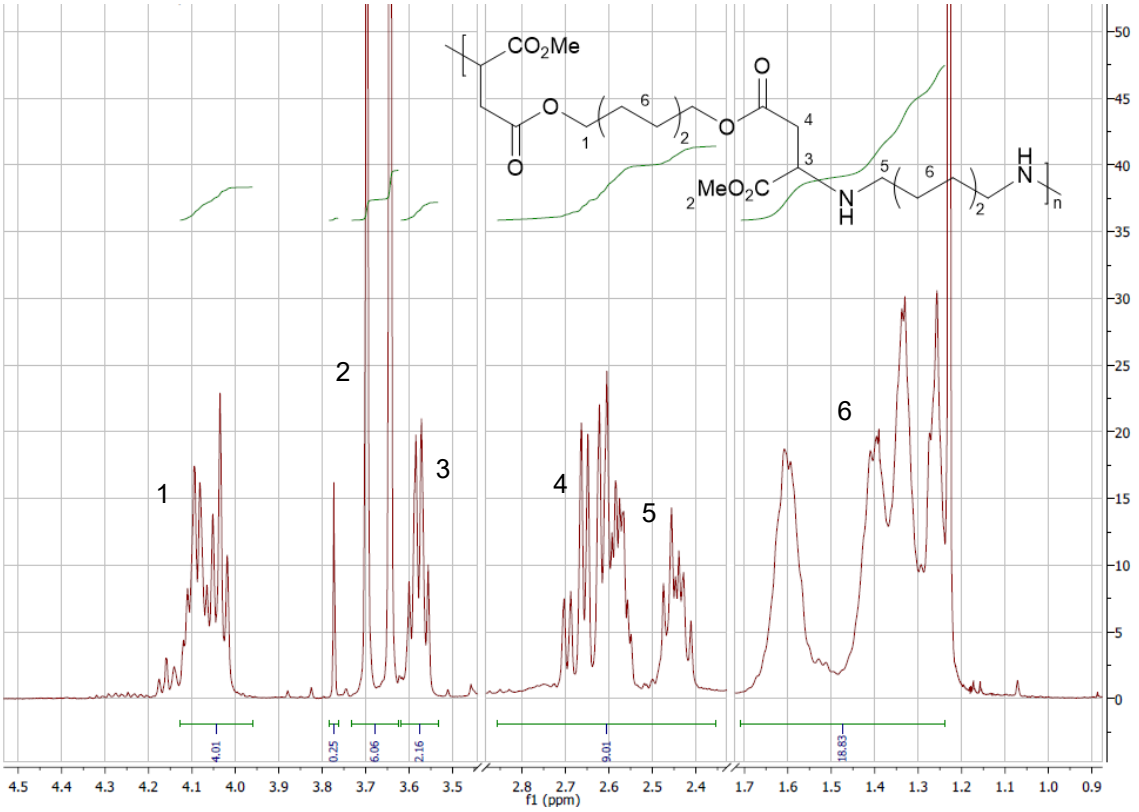
Spectrum 7, of monomer **6** and HMDA, gives a riddle. On one hand, it shows a



Spectrum 6 *^{1}H NMR — Polymerization of hexane-1,6-diyl dimaleate (**2**) with HDMA*

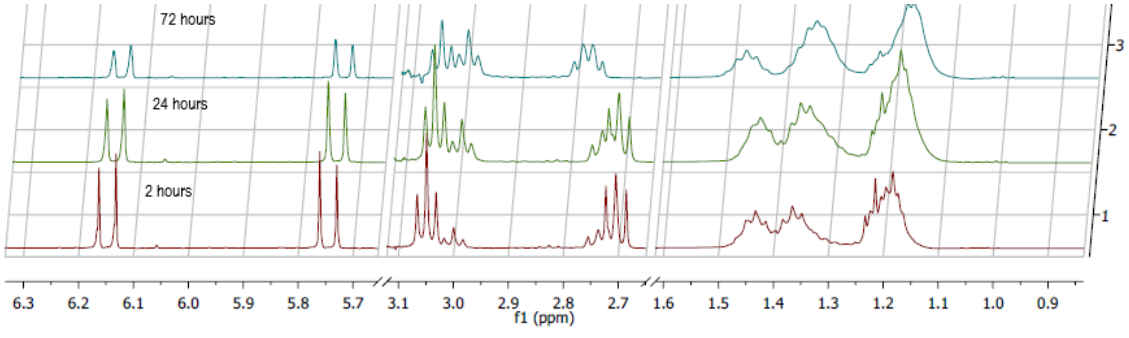
conversion of about 95 %, with the O-CH_2 and O-Me peaks each showing up three times, as predicted through preliminary experiments. On the other hand, the signals for the β- hydrogens (labeled 4) show up three times as well, although their presence is limited to the two different addition products. One possible explanation could be the decomposition of the neighboring ester. In that case, other compounds would show up on the spectrum as well, mainly speaking of hexanediol. Another, and more realistic one, would be the influence of the end group on the opposing site of the monomeric structure. Although, the distance between the hydrogens should not allow for a chemical shift, the ratio the

doublets correspond to the other peaks mentioned earlier. Other speculations would not be profound, and since these peaks appear for different solvents and temperatures, they seem to be part of the polymer.



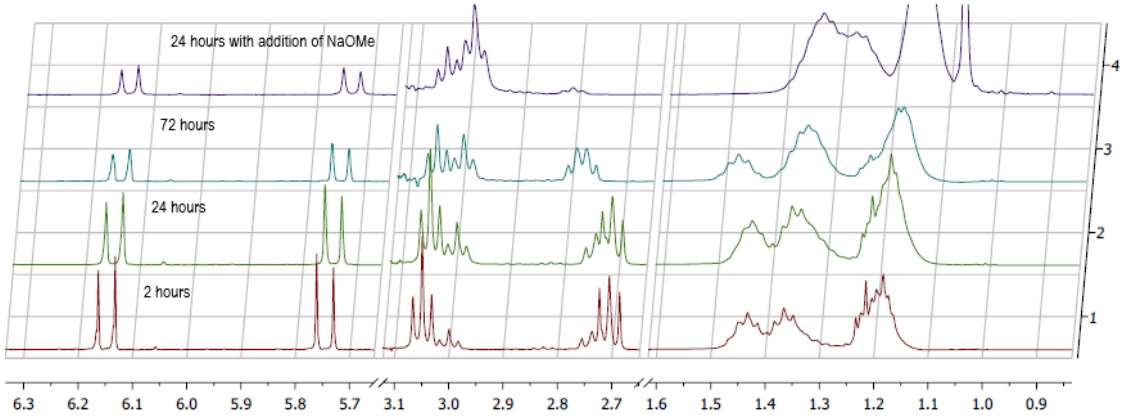
Spectrum 7 *^{1}H NMR — Polymerization of monomer **7** and HDMA*

Lastly, Monomer **3** was polymerized with HMDA and NaOMe, in MeOH at 70 °C. The monomer reacted slowly but steadily over the course of 3 days. At this point the conversion has barely reached 50 %. As shown in **spectrum 8**, the HN-C*H*$_2$ signal shifts from 3.05 ppm to 3.00 ppm, corresponding to the decrease of HC=CH signals of the monomer. Simultaneously the H_2N-C*H*$_2$ triplet of the diamine at 2.71 ppm decreases, while an overlapping quartet of the polymers α-hydrogen increases. Further, the shift of some overlapping signals in the alkyl region on the far-right can be seen.



Spectrum 8 *^{1}H NMR — Polymerization of hexane-1,6-diyl dimaleamide (**3**) with HDMA for 72 h*

If the triplet at 2.71 ppm really *does* reflect the amount of diamine being present, it would have been consumed while only half of the monomer reacted. This is interesting, because the monomer was further converted with the addition of another equivalent NaOMe. This allows to speculate, that free NH groups keep reacting with the alkene, shifting the quartet into a region of minor, unidentified peaks that have been cut out.



Spectrum 9 *^{1}H NMR — Polymerization of hexane-1,6-diyl dimaleamide (**3**) with HDMA for 96 h*

Another reaction with *trans*-cyclohexanediamine had been conducted. There are two possible ways to use the diamine, each comes with its own issues. It can be either added as a liquid, presenting the same problems as EDA; or as a salt, where it needs to be deprotonated with additional base. Using cyclohexanediamine dihydrochloride it is required to add two more equivalents of KO^{t}Bu, increasing the amounts of ancillary compounds. The reaction led mostly to isomerization and side reactions. The reaction required high work effort and material use, but did not provide reliable results; Therefore, it has been abandoned for the time being.

6. Conclusion

With this project we have set the basics for polymerization via hydroamination but there is wide spectrum of things that need to be improved.

We were able to develop protocols for the synthesis of six out of seven monomeric compounds. The scope of reagents allows to further investigate substituent dependent activity of the double bond, and the resulting reactivity of the olefins in correspondence to the amines. Adapting the protocols might allow to synthesize similar monomers with various chain lengths or cyclic components.

Experiments on hydroamination have shown issues that needed to be addressed, which forced us to modify the monomers and make additions to our proposals. Contrary to the assumptions, we have shown that intermolecular, catalyst free hydroamination is possible for activated alkenes, if an alkaline environment is provided.

We were able to produce polymeric compounds using the synthesized monomers and accessible diamines. As we observed reversibility of the hydroamination, thermodynamic considerations (lower temperature; higher concentration) will need to guide future projects to obtain polymeric products of high molecular weights.

Besides the low average chain length, product isolation needs to be addressed. Especially for polymers that require an additional base, protonation is not optimal as other amines are being protonated as well, making everything water soluble or insoluble. In foresight of processing, isolating the product as a salt would be problematic. Given that their melting point is out of reach we would rely on wet spinning. We also need to be cognizant of the fact, that all polymers that have been produced are hygroscopic, as far as we can tell. If that issue persists for pure polymers, new modifications need to be thought off. One possibility would be to further react the amines.

If the average chain length can be increased in the future, we aim to determine molecular weights and thermal properties using thermogravimetric analysis and differential scanning calorimetry.

7. Experimental section

All experiments have been performed inside a fume hood. All chemicals, including NMR solvents, were present in the laboratory or have been bought from chemical vendors. The catalyst precursors ITapHCl, H_2ITapHCl, H_2IPrHCl and H_2IMesHCl were already synthesized and have not been prepared during this project. All numbered compounds and the polymers based on them, have been synthesized for the project. NMR analysis was conducted on an Agilent 400 MHz NMR spectrometer at 24 °C. Hydroamination additions and polymerizations have been conducted with 1 or 2 mol starter in different solvents and at various temperatures. As qualitative experiments, their syntheses are not included because an optimal procedure could not be developed.

7.1. N-(6-aminohexyl) monomaleamide (1)

A 125 mL Erlenmeyer flask was charged with 10.22 g HMDA (60 % aqueous solution, 52.9 mmol) and cooled to 0 °C. While stirring, a solution of 5.06 g (51.6 mmol) MA in 50 mL EtOH was slowly added to the amine, resulting in an exothermic reaction.

After 20 min, the solution was stirred at room temperature for another 30 min, then transferred and kept at +4 °C (refrigerator). After 7 days, the product precipitated and was filtered. The precipitate was dried under vacuum, affording the gel like product in 87 % yield (9.65 g).

^{1}H NMR (D_2O, 400 MHz, 24 ºC) δ (ppm) 6.28 (d, 1 H, ^{3}J [^{1}H ^{1}H] = 12.3 Hz), 5.88 (d, 2H, 3 J [^{1}H ^{1}H] = 12.4 Hz, HC=CH), 3.18 (m, 2 H, CONH-CH_2), 2.95 (m, 2 H, H_2C-NH_2), 1.63 (m, 2 H, CH_2), 1.50 (m, 2 H, CH_2), 1.37 (m, 2 H, CH_2), 1.31 (m, 2 H, CH_2).

7.2. Hexane-1,6-diyl dimaleate (2)

A 250 mL round bottom flask was charged with 5.00 g (42.3 mmol) hexanediol and dissolved in 50 mL DCM. Et_3N (10.70 g, 105.8 mmol) was added and the solution was cooled to 0 °C. Slowly adding 8.71 g (88.9 mmol) MA made the solution turn from colorless to bright yellow.

After 30 min, the solvent was removed under vacuum, leaving a dark brown, viscous residue. Under vigorous stirring, 50 mL HCl (3 M) were added using a dropping funnel. Violent stirring and a slow addition are crucial to the purity of the product, which precipitates due to its water insolubility. The suspension was then filtered, and the filter residue was washed three times with water (20 mL). Spreading the product on an evaporation dish and drying for 48 h afforded a pure, white, crystalline powder in 98 % yield (13.02 g).

^1H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 6.38 (d, 2 H, ^3J [^1H ^1H] = 12.3 Hz), 6.27 (d, 2H, ^3J [^1H ^1H] = 12,3 Hz, 2x HC=CH), 4.26 (t, 4 H, ^3J [^1H ^1H] = 6.00 Hz, 2x O-CH_2), 1.69 (m, 4 H, 2x CH_2), 1,42 (m, 4 H, 2x CH_2).

7.3. Hexane-1,6-diyl dimaleamide (3)

In a 200 mL round bottom flask, 7.90 g HMDA (60 % aqueous solution, 40.9 mmol) and 9.00 g (88.2 mmol) Et_3N were dissolved in 50 mL MeOH. Stirring the solution at 0 °C, 8.8 g (89.8 mmol) MA were slowly added, resulting in an exothermic reaction.

After 2 h, the solvent was removed using a rotary evaporator. The residual brown liquid was dissolved in 50 mL EtOH and concentrated HCl was added dropwise leading to immediate precipitation. The suspension was filtered, and the first product washed twice with 20 mL acetone. The filtrate was reduced and placed in the freezer. The precipitate was then filtered and added to the first residue. Drying the combined product for 48 h afforded a white powder in 64 % yield (8.15 g).

^1H NMR (DMSO-d_6, 400 MHz, 24 ºC) δ (ppm) 9.07 (t, 2 H, ^3J [^1H ^1H] = 7.0 Hz, 2x N-H), 6.37 (d, 2 H, ^3J [^1H ^1H] = 12.6 Hz), 6.20 (d, 2 H, ^3J [^1H ^1H] = 12.6 Hz,

2x HC=CH), 3.14 (td, 4 H, ^{3}J [^{1}H ^{1}H] = 7.0 (N-H), ^{3}J [^{1}H ^{1}H] = 5.7 (CH_2), 2x *H_2*C-NH), 2.47 (s, 2 H, 2x OH), 1.43 (m, 4 H, 2x CH_2), 1.26 (m, 4 H, 2x CH_2).

7.4. Hexane-1,6-diyl diacrylate (4)

A 50 mL round bottom flask was charged with 1.00 g (8.46 mmol) hexanediol and dissolved in 10 mL DCM. To that solution, 2.57 g (25.39 mmol) Et_3N were added and the solution was stirred at 0 °C. Dropwise addition of 1.91 g (21.15 mmol) acryloyl chloride solution in 5 mL DCM over 5 min, made the amine precipitate and the suspension turned yellow.

After 30 min, 30 mL HCl (1 M) were added. Using a separatory funnel, the organic layer was drained, the aqueous layer was extracted with another 15 ml of DCM. The organic layer was then washed with 15 mL of a diluted $NaHCO_3$ solution (0.001 M); and dried with Na_2SO4. After removing the solvent, the residual product afforded a yield of 1.62 g (85 %).

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 6.35 (dd, 2H, ^{3}J [^{1}H ^{1}H] = 17.3 Hz (trans), ^{2}J [^{1}H ^{1}H] = 1.5 Hz, 2x H_2C=CH), 6.08 (dd, 2H, ^{3}J [^{1}H ^{1}H] = 17.3 Hz (trans), ^{3}J [^{1}H ^{1}H] = 10.4 Hz (cis), 2x CH=CH_2), 5.78 (dd, 2H, ^{3}J [^{1}H ^{1}H] = 10.4 Hz 2x (cis), ^{2}J [^{1}H ^{1}H] = 1.5 Hz, 2x H_2C=CH), 4.12 (t, 4 H, ^{3}J [^{1}H ^{1}H] = 6.63 Hz, 2x O-CH_2), 1.65 (m, 4 H, 2x CH_2), 1.38 (m, 4 H, 2x CH_2).

7.5. Dimethyl ester of monomer 2 (6)

A 75 mL pressure flask was charged with 1.00 g (3.18 mmol) of Monomer **3**. Under nitrogen, the monomer was dissolved in 3 mL tetrahydrofuran and 1.00 g (7.75 mmol) Hünig's base was added. Inside the fume hood, 1.36 g (9,55 mmol) MeI were added and the solution was stirred at 100 °C for 24 h.

The solution was cooled to room temperature and the solvent was removed. The residue was dissolved in 30 mL AcOEt and washed twice with 20 ml HCl (0.4 M), and further with 20 mL $NaHCO_3$ solution (0.001 M). The organic layer was dried with Na_2SO_4 and after evaporating the solvent, the product was obtained as a dark yellow liquid affording a yield of 92 % (0.99 g).

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 6.19 (m, 4 H, 2x HC=CH), 4.17 (t, 4 H, ^{3}J [^{1}H ^{1}H] = 6.69 Hz, 2x O-CH_2), 3.77 (s, 6H, 2x O-CH_3) 1.67 (m, 4H, 2x CH_2), 1.39 (m, 4H, 2x CH_2).

7.6. Dimethyl ester of monomer 3 (7)

In a 50 mL round bottom flask, 2.04 g (6.5 mmol) of Monomer **2** were dissolved in 20 mL MeOH. Under vigorous stirring, H_2SO_4 (27.5 mg) was added dropwise.

The MeOH was removed after 24 h, the residue was dissolved in 20 mL DCM, and washed twice with 20 ml $NaHCO_3$ solution (0.001 M). The organic phase was dried over Na_2SO_4 and evaporated, affording 1.74 g (78 %) white crystalline powder. For further purification, the product was recrystallized from toluene leaving 1.00 g (44 %).

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 8.14 (t, 2 H, ^{3}J [^{1}H ^{1}H] = 5.2 Hz, 2x CO-NH), 6.25 (d, 2 H, ^{3}J [^{1}H ^{1}H] = 11.8 Hz), 6.18 (d, 2 H, ^{3}J [^{1}H ^{1}H] = 11.8 Hz, 2x HC=CH), 3.59 (s, 6 H, 2x O-CH_3), 3.04 (m, 4 H, 2x HN-CH_2), 4.24 (m, 4 H, 2x CH_2), 4.47 (m, 4 H, 2x CH_2).

7.7. Catalyst synthesis

7.7.a. Double Schiff Base (8)

In a 1 L Erlenmeyer flask, 20 g (165.0 mmol) 2,6-dimethylaniline were dissolved in 200 mL MeOH and cooled to 0 °C. Under stirring, a mixture of 11.96 g (82.5 mmol) glyoxal (40 % aqueous solution) and another 100 mL MeOH were added, as well as 10 drops HCl. The solution was stirred at 0 °C until a gold/yellow precipitate formed. At this point, the ice bath was taken away and the suspension was further stirred at room temperature for 24 h.

The suspension was filtered, and the residue was washed twice with 50 mL MeOH and once with 50 mL EtOH. The dry precipitate afforded a yellow powder in 58 % yield (12.6 g).

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 8.10 (s, 2 H, 2x HC=N), 7.08 (d, 4 H, ^{3}J [^{1}H ^{1}H] = 7.5 Hz, 4x meta-H), 6.99 (t, 2 H, ^{3}J [^{1}H ^{1}H] = 7.0 Hz, 2x para-H), 2.17 (s, 12 H, 4x ortho-CH_3).

Applying the same procedure to 20 g (113.0 mmol) 2,6-diisopropylaniline with 8.18 g (56.4 mmol) glyoxal solution afforded 31 % yield (7.36 g).

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 8.08 (s, 2H, 2x HC=N), 7.17 (m, 6 H, 4x meta-H; 2x para-H), 2.92 (h, 4 H, ^{3}J [^{1}H ^{1}H] = 6.9 Hz, 4x ^{i}Pr-CH), 1.19 (d, 24 H, ^{3}J [^{1}H ^{1}H] = 6.9 Hz, 8x ^{i}Pr-CH_3).

7.7.b Ligand precursor (10)

In a 250 mL round bottom flask, after dissolving 5.00 g (18.94 mmol) of product a. in 50 mL AcOEt, the solution was stirred in an oil bath and heated to a gentle reflux at 80 °C. At this point, 853 mg (28.41 mmol) paraformaldehyde were added. A solution of 2.13 g (20.16 mmol) $SiMe_3Cl$ in 40 mL AcOEt was added dropwise over the course of 15 min. The solution changed its color to dark brown, while an off-white precipitate was formed. The reaction was further refluxed at 80 °C, and after 2 h removed from the oil bath. After cooling to room temperature, the solution was cooled for 20 h and filtered. The residue was washed twice with 50 mL AcOEt and dried under vacuum. The final product afforded an off-white powder in 91 % yield (5.39 g) of IXyHCl.

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 10.96 (s, 1 H, N-C=N), 7.64 (s, 2 H, HC=CH), 7.32 (m, 2 H, 2x para-H), 7.19 (d, 4 H, ^{3}J [^{1}H ^{1}H] = 7.7 Hz, 4x meta-H), 2.19 (s, 12 H, 3x ortho-CH_3).

In an equivalent procedure, IPrHCl was obtained in 86 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 10.96 (s, 1 H, N-C=N), 7.64 (s, 2 H, HC=CH), 7.32 (m, 2 H, 2x para-H), 7.19 (d, 4 H, ^{3}J [^{1}H ^{1}H] = 7.7 Hz, 4x meta-H), 2.19 (s, 12 H, 3x ortho-CH_3).

7.7.c Catalyst precursor (12)

A pressure flask has been charged with 1.00 g (3.19 mmol) IXyHCl and 297 mg (2.08 mmol) Cu_2O. After the addition of 3 mL MeOH, the suspension was stirred at 100 °C for 24 h. The mixture was cooled to -20 °C for 2 h and later filtered. The filter residue was washed with 3 mL ice-cold MeOH. The residue was taken up in DCM and filtered. The solvent was evaporated, leaving the product as a white crystalline solid in 90 % yield (1.07 g).

In equivalent procedures following complexes were synthesized.

Table 1 *Measurements and yield for the synthesis of different NHC-CuCl complexes*

	LHCl		**Copper(I) oxide**		**LCuCl**
NHC	m [mg]	n [mmol]	m [mg]	n [mmol]	Yields [%]
IPr	1,000	2.35	219	1.51	83
ITap	1,000	2.50	233	1.63	79
H_2IMes	1,000	2.92	271	1.90	70
H_2IPr	500	1.17	109	0.76	69
H_2ITap	500	1.25	116	0.81	72

IXyCuCl: ^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 7.29 (m, 2 H, 2x para-H), 7.19 (m, 4 H, 4x meta-H), 7.08 (s, 2 H, HC=CH), 2.15 (s, 12 H, ortho-CH_3); IPrCuCl: ^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 7.50 (m, 2 H, 2x para-H), 7.29 (d, 4 H, ^{3}J [^{1}H ^{1}H] = 7.6 Hz, 4x meta-H), 7.11(s, 2 H, HC=CH), 2.56 (s, 4 H, 4x ^{i}Pr-CH), 1.24 (m, 24 H, 8x ^{i}Pr-CH_3); ITapCuCl: ^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 6.97(s, 2 H, HC=CH), 6.51(s, 4 H, 4x meta-H), 3.00 (s, 12 H, 4x N-CH_3), 2.09 (s, 12 H, ortho-CH_3); H_2IMes: ^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 6.94 (s, 4 H, 4x meta-H), 3.89 (s, 4 H, H_2C-CH_2), 2.30 (s, 12 H, 4x ortho-CH_3), 2.28 (s, 6 H, 2x para-CH_3); H_2IPrCuCl: ^{1}H NMR ($CDCl_3$, 400 MHz, 24 ºC) δ (ppm) 7.39 (m, 2 H, 2x para-H), 7.24 (d, 4 H, ^{3}J [^{1}H ^{1}H] = 2.3 Hz, 4x meta-H), 3.05 (h, 4 H, ^{3}J [^{1}H ^{1}H] = 6.9 Hz, 4x ^{i}Pr-CH), 4.00 (s, 4 H, H_2C-CH_2), 1.34 (m, 24 H, 8x ^{i}Pr-CH_3).

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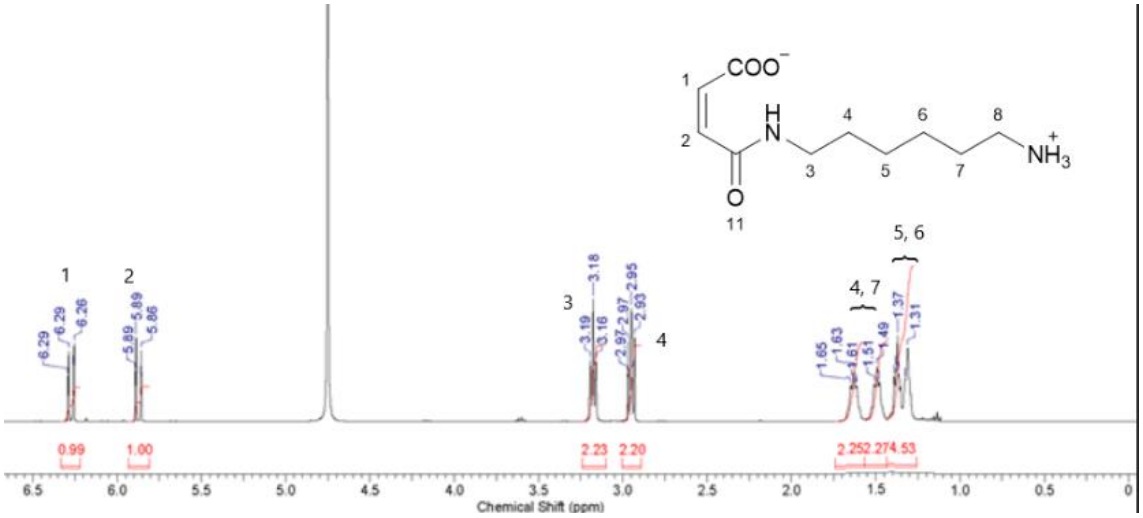
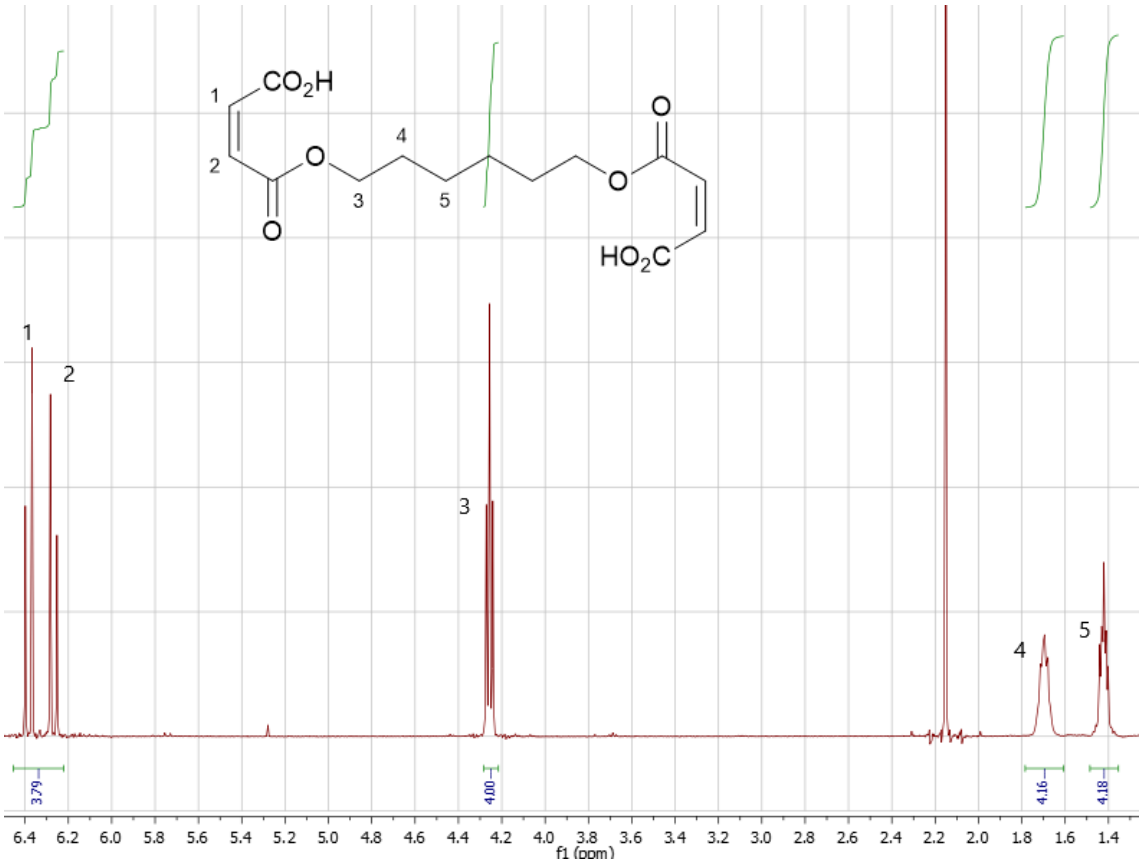
Appendix

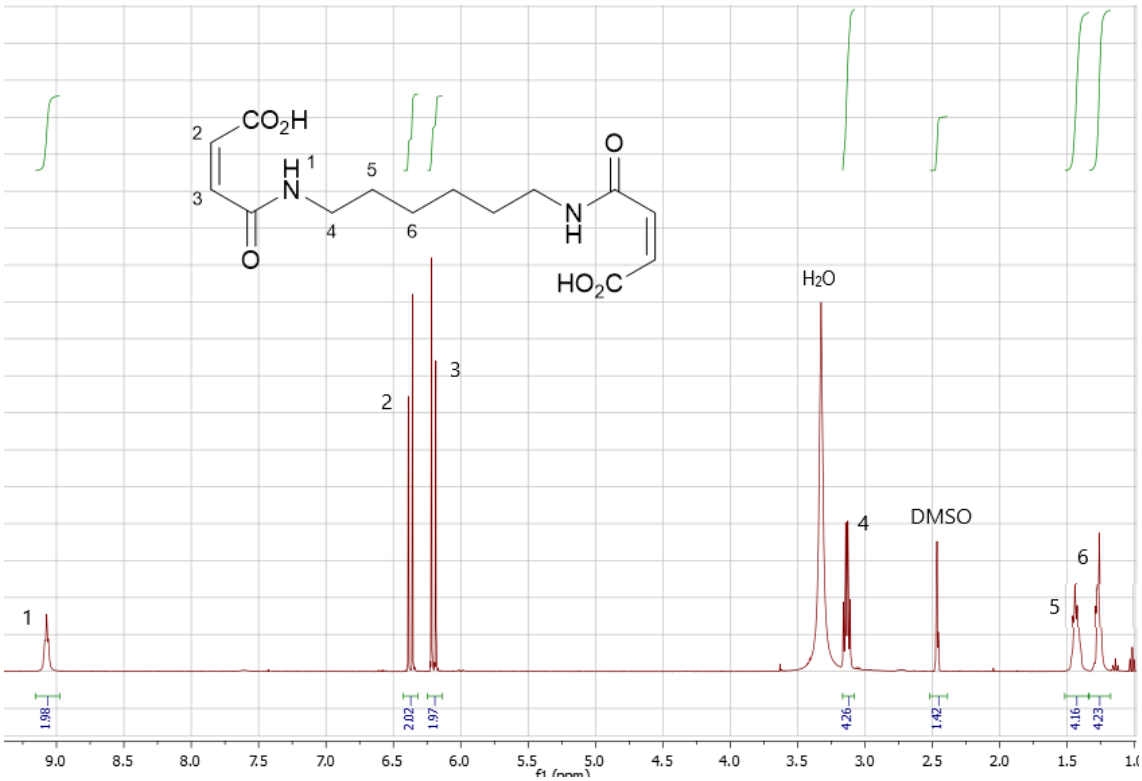
Spectra of the isolated monomers **1…7** are shown, excluding **5** since it has not been made at this point. Spectra regarding the catalyst synthesis have also been excluded, as they are well known compounds.



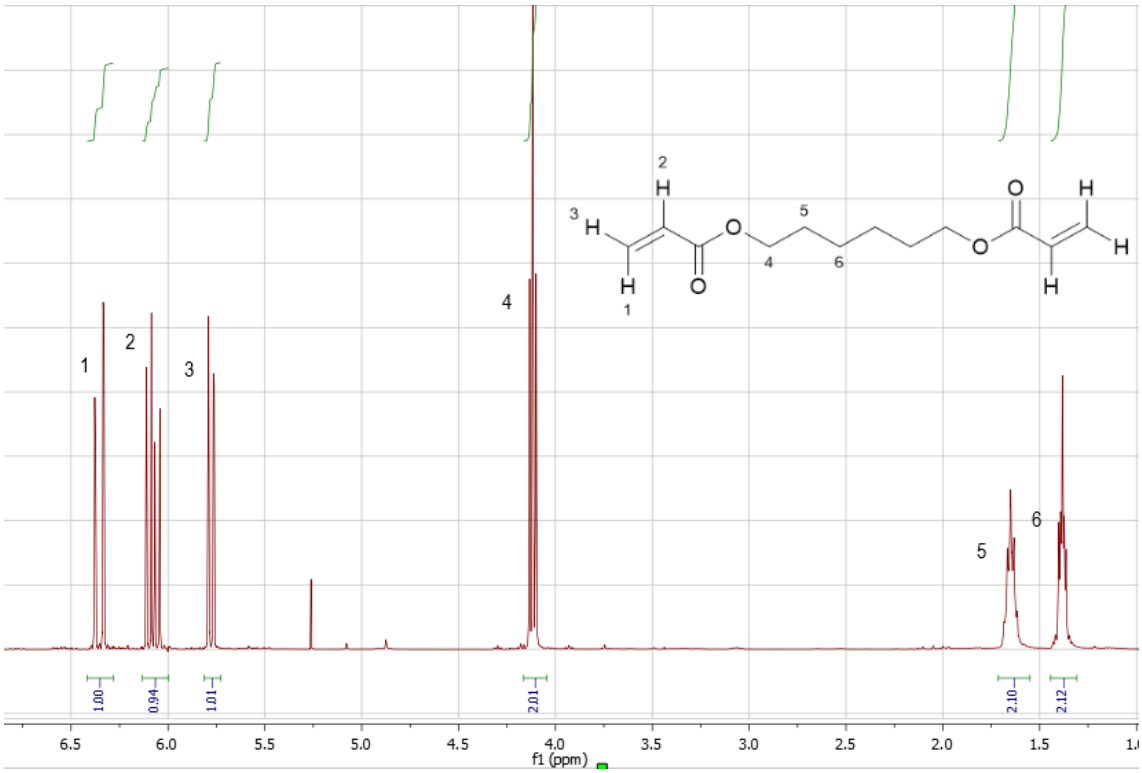
Spectrum 10 *^{1}H NMR — N-(6-aminohexyl) maleamide (**1**)*



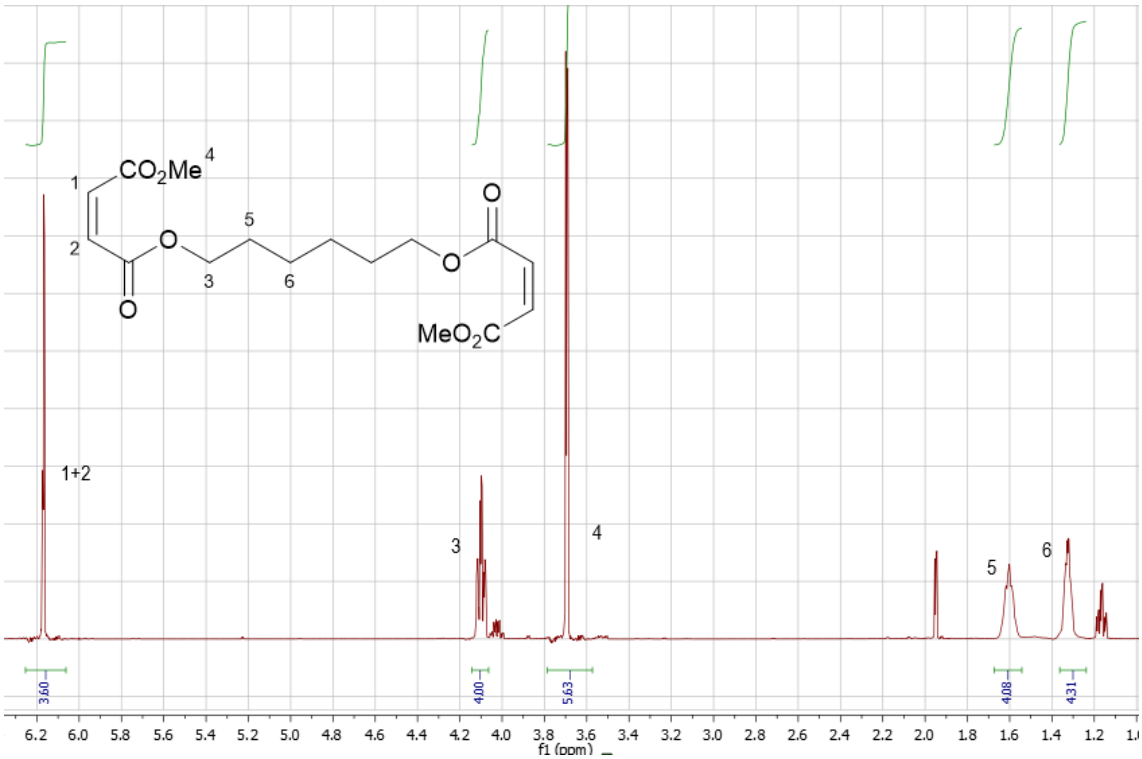
Spectrum 11 *^{1}H NMR — hexane-1,6-diyl dimaleate (**2**)*



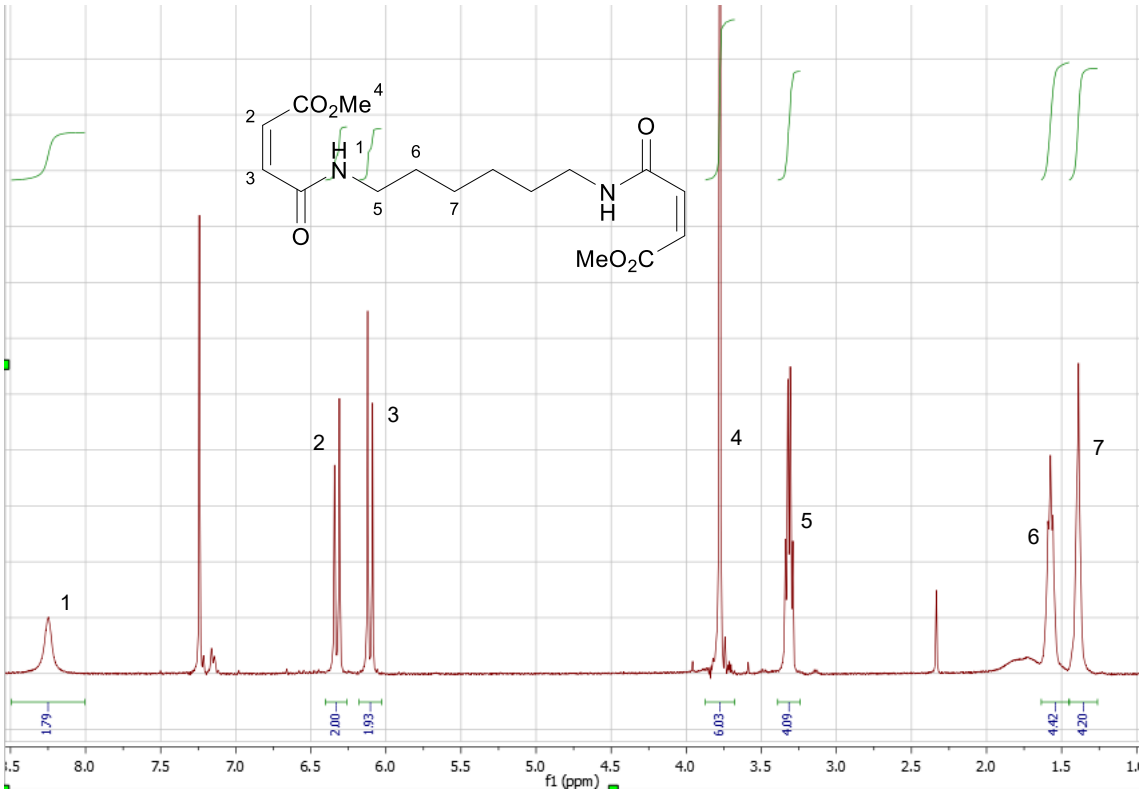
Spectrum 12 *^{1}H NMR — hexane-1,6-diyl dimaleamide (**3**)*



Spectrum 13 *^{1}H NMR — hexane-1,6-diyl diacrylate (**4**)*



Spectrum 14 *^{1}H NMR — dimethylester of hexane-1,6-diyl dimaleate (**6**)*



Spectrum 15 *^{1}H NMR — dimethylester of hexane-1,6-diyl dimaleamide (**7**)*

Declaration of Authorship

Herewith I affirm that the thesis submitted is my own unaided work. All sources used have been acknowledged as references.

I am aware that the use of unauthorized or not referenced sources is deemed plagiarism and therefore leads to an unsuccessful completion of the examination.

City, Date	Author's Signature