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Masterarbeit

Synthesis and Characterization of Poly(azanorbornene)s via Ring-Opening Metathesis Polymerization using Ruthenium-based Initiators

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Abstract

A novel class of monomers for ring-opening metathesis polymerization (ROMP), namely azanorbornenes, was examined. It was shown that facile and easy procedures can be applied to synthesize azanorbornenes carrying diverse functional groups attached to the aza position of the unsaturated bicyclic structure. The reaction setup is straightforward and renders products in high yields.

As a model monomer, benzyl-2-azabicyclo[2.2.1]hept-5-ene was intensely investigated. It was polymerized using several ruthenium based initiators and it was shown that latest metathesis initiators such as Umicore's M31 can deal with the presence of the nitrogen atom in the bicyclic structure. The polymerization process itself was looked at closely, showing that this monomer undergoes ROMP in a controlled way. Thus, this particular monomer class is a valuable addition to the "ROMP-toolbox" broadening the spectrum of available monomers.

Furthermore, the biocidal properties of poly(benzyl-2-azabicyclo[2.2.1]hept-5-ene) were evaluated and the scope of protonation and alkylation of the parent monomer was investigated in this context.

Kurzfassung

Die vorliegende Arbeit untersucht eine neue Monomerklasse für die Ring öffnende Metathesepolymerisation (ROMP), die Azanorbornene. Es konnte gezeigt werden dass, Azanorbornene mit unterschiedlichen Substituenten an der aza Position des ungesättigten bizyklischen Systems einfach und in hohen Ausbeuten dargestellt werden können.

Als Modell-Monomer wurde 2-Benzyl-2-azabicyclo[2.2.1]hept-5-en herangezogen und intensiv untersucht. Die Verbindung wurde mittels verschiedener Ruthenium-basierter Initiatoren polymerisiert und es wurde gezeigt, dass neueste Metatheseinitiatoren, wie beispielsweise M31 der Firma *Umicore* die Gegenwart des Stickstoffatoms im bizyklischen System tolerieren. Der Polymerisationsverlauf selbst wurde genau dokumentiert und so konnte gezeigt werden, dass 2-Benzyl-2-azabicyclo[2.2.1]hept-5-en in kontrollierter Weise polymerisiert werden kann. Azanorbornene stellen somit eine wertvolle Ergänzung der „ROMP Toolbox“ dar, da sie das Spektrum der verfügbaren Monomere für diese vielseitige Polymerisationsart erweitern.

Weiters wurden die bioziden Eigenschaften von Poly(2-benzyl-2-azabicyclo[2.2.1]hept-5-en) ermittelt. In diesem Zusammenhang wurde außerdem die Auswirkung von Protonierung und Alkylierung des ursprünglichen Monomers untersucht.

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1. Introduction

Since the discovery and first research on olefin metathesis more than 50 years ago, this scientific field has captured a lot of attention[1,3,4,13]. Achievements in the development of metathesis reactions have been rewarded with the Nobel Prize in 2005[2], thus stressing the enormous potential lying within this topic.

There are various metathesis reactions[3]. One of them is the ring-opening metathesis polymerization (ROMP). ROMP is a very versatile method for generating carbon-carbon bonds. Essential components are a initiator that is able to mediate synthesis of an ever growing polymer chain and a monomer that bears an unsaturated cyclic structure. Since development of novel initiators has taken a leap and nowadays highly active, stable initiators are available, ROMP has become a strong tool for synthesizing novel polymers, carrying diverse functionalities. However there is always a strong demand for undiscovered monomer classes for the use in ROMP, which might show higher activity, easier synthesis or give the possibility to introduce more versatile functional groups.

The goal of the herein presented work was to assess the scope and potential of azanorbornenes as a novel monomer class for ring-opening metathesis polymerization.

Generally, novel ROMP initiators have overcome many of the issues of early day initiators, such as tungsten or titanium multicomponent systems. Functional group tolerance has been increased significantly[1,3,12]. However amine and nitrile functional groups still remain a challenge but it has been shown that tertiary amines are tolerated by Grubbs' third generation type initiators[9,14]. So, issues arising from the aza functionality should not be of concern if these initiators are applied.

Another important consideration, when designing novel monomers for ROMP regards the polymerization mechanism itself. Living or at least controlled polymerization is favored. Living polymerization implies that the mechanism is highly controlled, showing fast propagation and even faster initiation, keeping side reactions such as chain transfer and back-biting low and thereby rendering a precisely designed polymer, having a polydispersity index approaching 1[5,13]. This allows a rather exact design of polymers, primarily controlled by the applied monomer to initiator ratio that affects the polymer length. It thereby also makes block-co-polymer synthesis possible. Of course temperature, solvent, concentration of the monomer in the reaction solution and other parameters influence the polymerization as well. All of these facts make evident that monomers that undergo a controlled or living polymerization are of great research interest.

Furthermore the idea was to create an easy way to introduce functionalities.

Herein an easy and facile way to synthesize azanorbornenes is presented. The procedure is fast, gives high yields and allows generating versatile azanorbornenes carrying required functionalities.

Therefore possible synthetic pathways were investigated closely to select the most appropriate strategy.

Furthermore polymerization mechanisms were assessed, showing that 2-benzyl-2-azabicyclo[2.2.1]hept-5-ene is an ideal model compound to illustrate the potential of this class of monomers.

However investigations also showed that still research has to be conducted on this class of monomers. Attempts to polymerize 2-(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene illustrated that this monomer is not polymerized as easily and that the second amine functionality interferes with the reaction, thus hindering conversion.

Another topic of the assessment was the studying of biocidal activity. Polymers show a lot of potential for the use as antimicrobial agents. Their high molar mass is advantageous towards low molecular agents, which can show toxicity and may be degraded by the microorganisms more easily. For a distinct biocidal activity the polymer must meet certain, essential requirements. Amphiphilicity is an important factor since the polymer needs to have hydrophobic and hydrophilic parts to optimally interact with the cell membrane of the microorganism[17]. Therefore co-polymers are ideal candidates. Another important aspect regards protonation. At least partial protonation is required and was tried to be achieved[17]. However, this issue needs further research since it is a rather complex matter to fine-tune the settings to perfectly meet the requirements. It has to be pointed out that of course different microorganisms react to antimicrobial agents in different ways, thus rendering the approach even more challenging.

2. Theoretical Background

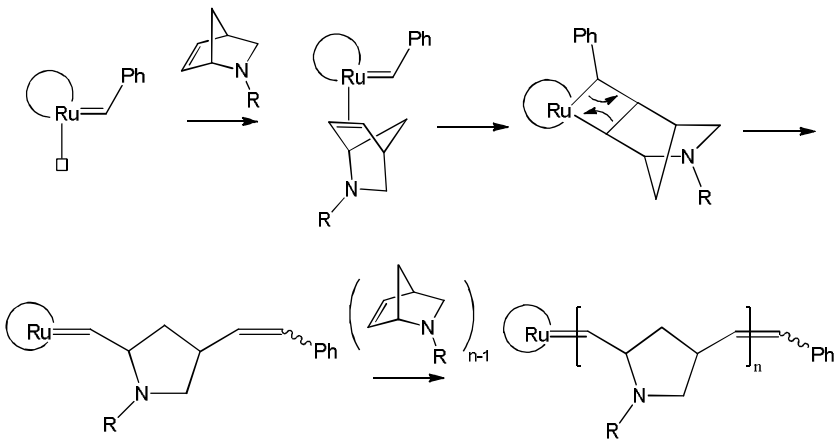
2.1. Ring-opening Metathesis Polymerization (ROMP)

2.1.1. General Aspects

Olefin metathesis in general, and subsequently ring-opening metathesis polymerization, was discovered while examining the polymerization of olefins[4]. Since then a lot of research has been conducted in this field. In 2005 Yves Chauvin, Robert H. Grubbs and Richard R. Schrock have been awarded the Nobel Prize of Chemistry "for the development of the metathesis method in organic synthesis[2]", thus stressing the tremendous potential lying within this scientific field. Metathesis includes many different, nowadays very important techniques and subjects, amongst them cross metathesis (CM), ring-opening metathesis (ROM), ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) and ring-opening metathesis polymerization (ROMP). ROMP will be discussed in the following paragraphs.

In 1971 Chauvin proposed a mechanism for this type of polymerization. In Scheme 1 the mechanism is shown in a modified way. The driving force of the reaction is the high ring strain of the cyclic structure and the initiators aim to acquire a more stable 18 electron configuration.

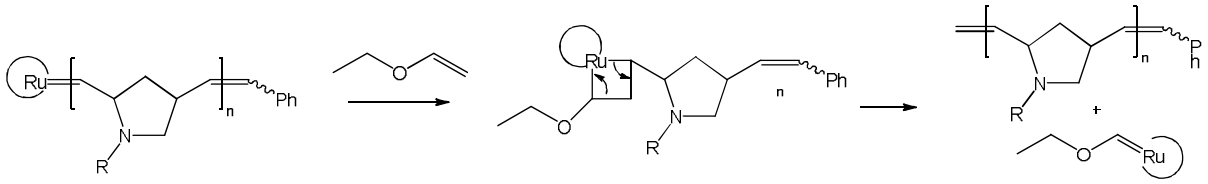
First the initiation takes place. The initiator, nowadays most commonly a transition metal alkylidene complex coordinates to the cyclic olefin, in this case an azanorbornene. In syntheses described in this work ruthenium indenylidene complexes were used, which show similar characteristics. A transition state, a metallacyclobutane structure is formed via a [2+2]-cycloaddition[3]. A rearrangement takes place resulting in a cycloreversion. This general process is repeated in the propagation step where one monomer is added after the other.



Scheme 1: ROMP initiation mechanism

ROMP is a living polymerization method. The term 'living polymerization' was coined by Swarzc in 1956[4]. For a reaction to be living four main aspects have been defined and are dealt with in the following paragraph[3]. Living polymerizations are characterized by fast propagation and even faster initiation. This setting ensures that all chains are initiated at the same time and can therefore grow evenly. Furthermore fast propagation reduces side reactions such as chain transfer and back-biting. A very strong implication if the polymerization is living is given by a narrow molecular weight distribution given by the PDI value of the polymer. Polydispersity indices should be approaching 1 but have to be below 1.5[5]. So, living polymerizations can be regarded as perfectly controlled. This indicates that tailor-made polymers are accessible via this means of reaction by tuning features via addition of a second or third monomer, temperature, solvent, concentration and most importantly initial monomer to initiator ratio.

If not terminated the initiator stays active and attached to the polymer chain. Living polymerizations are normally quenched by reagents that remove the initiator from the polymer chain. Thereby polymerization is finally stopped and a defined functional end group is attached to the polymer chain, following the mechanism stated in Scheme 2. Most commonly vinyl compounds are applied; in the case of the example below ethylvinylether is used. The double bond stays integrated in the polymer structure and the initiator is split of, rendering an electronically deactivated carbene structure.



Scheme 2: ROMP termination by a vinyl compound

Different parameters strongly influence the polymerization reaction, these are the initiator itself, the presence of functional groups and heteroatoms, temperature, solvent and concentration.

ROMP can be very advantageous as it allows the direct introduction of functional groups from the monomer by leaving the backbone unsaturated. The backbone can be functionalized in a succeeding step as well.

2.1.2. Heteroatoms

As already mentioned above diverse parameters have a strong influence on the success and general path of the polymerization. This has to be taken into account, when choosing the right settings and especially the initiator.

Of course designing novel polymers implies also introducing specific functionalities often including heteroatoms. However diverse issues can arise in connection with heteroatoms and in general functional groups. The functional group can compete for the active site and by binding to it, even deactivate the initiator. Another possibility is that the functionality reacts with the initiator and thereby destroys it, making it useless[7].

So, the initiator must meet very specific requirements. It has to be stable towards moisture, air and heteroatoms, show fast initiation, should easily be stopped by termination reagents and not cause side reactions[6].

Early initiators have been difficult to work with. They were ill-defined, consisted of multicomponent systems and required the addition of strong Lewis acids. Initiators were highly vulnerable towards oxygen and moisture. Suitable monomers were limited since heteroatoms were not tolerated. This mainly refers to first titanium and tungsten initiators, which is illustrated in Table 1.

Table 1: Functional group tolerance of various metathesis initiators;
redrawn from: C.W. Bielawski, R.H. Grubbs, *Prog. Polym. Sci*. 2007, 32, pg 21 [3]

Ti / Ta	W	Mo	Ru
acids	acids	acids	**olefins**
alcohols	alcohols	alcohols	acids
aldehydes	aldehydes	aldehydes	alcohols
ketones	ketones	**olefins**	aldehydes
esters/amides	**olefins**	ketones	ketones
olefins	esters/amides	esters/amides	esters/amides

increasing reactivity

Finally, after molybdenum had already been proven to be a much better initiator in many respects, being more stable towards moisture and oxygen and also tolerating a higher amount of functionalities than the previously initiators, the high potential of ruthenium was discovered. It showed that ruthenium initiators have a very low oxophilicity and high reactivity towards olefins, thus making them ideal candidates. Then R.H. Grubbs developed the famous initiators that seemed to include most of the features required, paving the way for

totally new monomer classes and novel possibilities to control the reaction[7,8]. Derivatives of these initiators have been synthesized that show similar activity[9], carrying indenylidene ligands. With these novel initiators heteroatom tolerance has been improved tremendously.

However, as Orton and co-workers point out, spacers between functionalities and the unsaturated cyclic structure are essential for guarantying a successful metathesis, otherwise degenerate processes might occur[10].

2.1.2.1. Amines as functional groups for ROMP

What might have leapt to the eye is that in Table 1 amines or other nitrogen functionalities, except for amides, are not included at all. Early initiators were not able to perform polymerizations in the presence of amines or nitriles. This was also believed to be true for late initiators of the Grubbs' first to third generations type[7,11]. It was assumed that these initiators are not compatible with basic functional groups. However it has been shown by Slugovc et al. that Grubbs' initiators of the third generation do successfully polymerize in the presence of these functional groups, especially tertiary amines[12,13,14]. It is further explained that these functional groups enhance initiation efficiency and slow done the subsequent polymerization by competing with the monomers for the active sites[12]. The reduction of the propagation rate also suppresses side reactions as for instance back-biting and chain transfer. This affects molecular weight and subsequently the polydispersity index. Not only do third generation initiators tolerate amine and nitrile functional groups, these functional groups can even be used as a further tuning method for ROM polymerizations. However it has to be pointed out that a desired smooth polymerization or even an enhancement of the catalytic performance can only be achieved by applying tertiary amines, thus decorating primary or secondary amines with suitable side chains, as for instance methyl groups, does solve this problem in an easy and facile way[12,14].

2.2. Azanorbornenes in ROMP

2.2.1. General Aspects

A common monomer used for ROMP is norbornene (bicyclo[2.2.1]hept-2-ene). The high ring strain of the bicyclic structure facilitates easy ring opening and a fast reaction. Naturally, derivatives of norbornenes should as well be suitable monomers for ROMP.

Azanorbornenes, bearing a nitrogen atom on position two are a novel approach towards opening ROMP to a new and very promising class of monomers. Since it has been shown that latest Grubbs' third generation type initiators tolerate amines, the way should be cleared for this monomer class[12,14]. Exactly this amine functionality would facilitate the synthesis of unsaturated bicyclic structures carrying specific, required side chains.

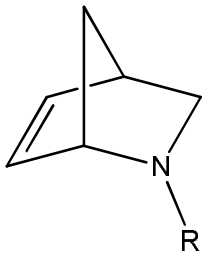


Figure 1: General structure of an azanorbornenes compound

One of the first studies on aza-Diels-Alder reactions and the resulting monomers, amongst them azanorbornenes, was published by Larsen and Grieco in 1984[15]. Although azanorbornenes hold an enormous potential, they have long been neglected. However, the aza functionality is an easy means to insert side chains and create new monomers for this polymerization technique. Since ROMP has undergone a fast revolution, novel, very efficient initiators are available. Initiation as well as propagation rate and heteroatom tolerance have been improved dramatically, thus paving the way for monomers bearing heteroatoms in their structure.

The high potential lies in the facile synthesis that opens up a new class of monomers for ROMP.

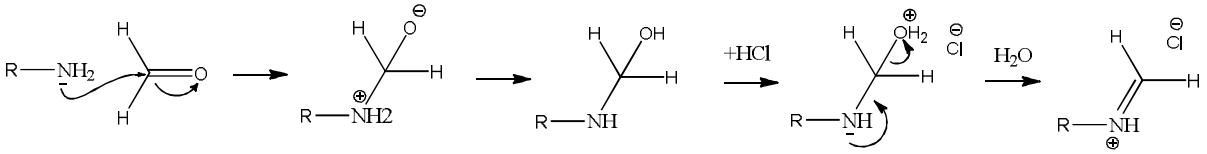
Watkins et al. have already examined azanorbornenes for ROMP[16]. They applied WCl_6-Bu^tPhenol/$AlEt_3$, one of the early tungsten initiators and a monomer to initiator ratio of 1:200.

2.2.2. Synthesis

A very promising approach was, as already mentioned, published by Larsen and Grieco[15]. This topic is enlarged on in the next paragraphs.

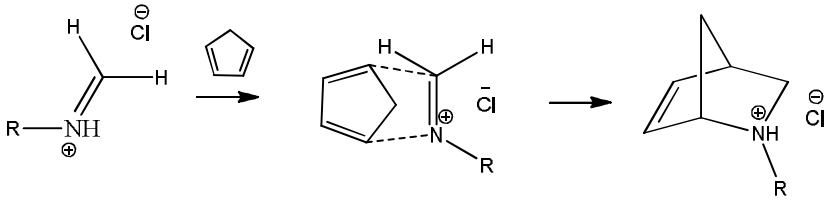
Compared to the all-carbon Diels-Alder reaction, the imino variation has received only scant attention15.

The reaction mechanism includes the in situ generation of a simple unactivated iminium salt. The formation of the iminium salt corresponds to the first step of the Mannich reaction and is illustrated in Scheme 3.



Scheme 3: Generation of an iminium salt species

The iminium salt then reacts with a diene via an aza-Diels-Alder [2+4] cycloaddition that is shown in Scheme 4. In order to obtain an azanorbornene species the diene has to be cyclopentadiene.



Scheme 4: Aza-Diels-Alder reaction mechanism

Since first publications of azanorbornene syntheses since 1984 by Larsen and Grieco15, scientists have stressed advantageous aspects, such as the ‘green’ concept, of this type of synthesis[22]. Reaction conditions are exceptionally mild. The synthesis is performed in aqueous medium at room temperature and is finished after three to four hours. However purification by extraction necessitates the use of a significant amount of solvents. Pure products in high yields can be obtained very fast without any considerable effort.

Another approach towards azanorbornenes was conducted by Schitter et al.[19]. They synthesized an azanorbornene using phenylehthylamine as the amine source and introduced a second functionality, at position three of the bicyclic system. The product has to be purified by means of column chromatography. This synthesis is time-consuming, including tedious

laboratory work by constant cooling of the reaction solution to -50 °C. It only gives moderate yields of 45 %[19].

This approach should only be followed if a second functionality at position three is particularly required. Otherwise the previously discussed approach is the method of choice for the synthesis of azanorbornenes.

2.2.3. Towards Polymers

To my knowledge Orton and co-workers published the only paper on the polymerization of azanorbornenes based on the monomer synthesis strategy by Larsen and Grieco[16].

They examined different cyclic alkenes containing heteroatoms synthesized by an iminium salt formation and subsequent performance of an aza-Diels-Alder reaction. They concluded that unsaturated cyclic structures bearing sufficient spacer groups are inevitable for a successful polymerization. They went over to examining norbornenes carrying side chains with other heteroatoms than nitrogen. Their finding was that azanorbornenes did not polymerize or in the case of benzyl-2-azabicyclo[2.2.1]hept-5-ene only poorly. The synthesis of benzyl-2-azabicyclo[2.2.1]hept-5-ene provided a yield of 11 %. They attributed the weak performance to inactivation of the initiators active site by binding to it or by reacting with the initiator in another form[10]. This is a consistent conclusion since the initiator used was a WCl_6-Bu^tPhenol/$AlEt_3$, one of the early tungsten initiators. This type of initiator is characterized by the need of drastic reaction conditions and above all nearly no functional group tolerance at all. Moreover it is hard to perfectly tune parameters to obtain good results when using these initiators.

However, as already explained in the section on ROMP and heteroatoms in ROMP, novel initiators are available that show much more promising characteristics. Especially initiators of the Grubbs' third generation type tolerate most functional groups among them tertiary amines and work under mild conditions, tolerating oxygen and moisture, thus making strict oxygen free conditions unnecessary. So, azanorbornenes can be regarded as a perfect choice for ROMP, thereby opening a novel class of monomers to this polymerization technique.

2.3. Biocidal Polymers

2.3.1. General Aspects

Microorganisms, including bacteria and fungi, can be the cause of diverse and sometimes very severe diseases. So, the development of new biocidal materials is of great interest, especially for the food industry, water purification and biocorrosion, to name but a few. Requirements for such substance are vast[18,17].

- No toxicity for living beings and nature
- Stability (pH, temperature, decomposition,…)
- Broad spectrum of action
- High penetration
- Low decrease of effect in presence of inactive substances
- Cheap and easy synthesis

In general there are different ways biocides can act against microorganisms. Heavy metals and derivatives block S-H groups, while alcohols act by protein denaturation. Aldehydes and oxidants react with proteins and nucleic acids and surfactants damage the cell membrane. Furthermore phenols, acids and bases, isothiazolinones and biguanides have been used as biocides[18].

Many of the groups mentioned above might show very good activity but have health and ecological risks. Especially biocidal agents with low molecular weights show high toxicities and are easy to be degraded by microorganisms, also leading to the development of resistances.

2.3.2. Specific Requirements

Many of the problems mentioned above can be avoided or at least reduced by introducing biocidal functional groups into polymers.

It is much harder for microorganisms to degrade polymers due to their huge molecular weight. This makes biocidal polymers interesting agents for long-term applications.

Furthermore high charge densities can be achieved by protonizing the polymers and thereby giving them a polycationic character[17]. This is a very important feature since polymers act biocidally by destroying the cell membrane. It has been shown that biocidal agents have to be charged to optimally interact with and bind to the negatively charged

phosphoglycerolipids in the membrane. This leads to a phase separation of charged and uncharged domains inside the membrane, drastically changing the membrane permeability. Transport through the membrane is not regulated anymore. Consequently the cell dies[18].

It has been shown that for a polymer to exhibit biocidal activity the following key factors are important[18].

- Molecular weight -important for the penetration through the cell wall, toxicity aspects and degradability
- Protonation –it is assumed that polycations are more easily adsorbed to the anionic bacterial cell membrane than monomeric cations. For a biocidal compound it is considered essential to at least show partial protonation.
- Amphiphilicity –because of the functionalization the polymer has a very high hydrophilic character. For a successful membrane – polymer interaction also lipophilic side chains are necessary, which can interact with membrane lipids. Furthermore water solubility is an important aspect that can be tuned by this balance.

3. Results and Discussion

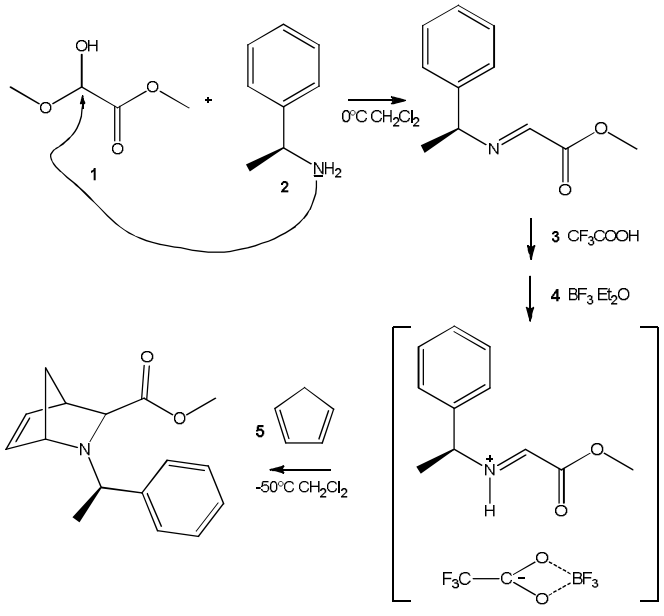
3.1. Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate and derivatives

3.1.1. Introduction

The monomer (methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate) was chosen for synthesis, following an existing procedure. Synthesis of this monomer had already been realized by Schitter et al. before[19]. They utilized this monomer as a basis for ROMP. However their goal was to extensively explore the polymer regarding its stereochemistry and the effect of chain transfer agents. Since the study was conducted in 1997 a molybdenum alkylidene complex was the initiator of choice. Our approach was to show that novel Grubbs' third generation type initiators catalyze the polymerization in a very fast and convenient way. Furthermore the idea behind choosing the monomer was to examine azanorbornenes for ROMP via novel initiators and subsequently optimize reaction procedures and open the field for introducing new azanorbornenes for ROMP.

3.1.2. Monomer

3.1.2.1. Synthesis



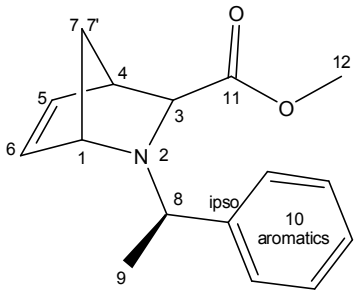
Scheme 5: Reaction mechanism of m*ethyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

The synthesis followed the approach by Schitter et al.[19]. Methylglyoxylatehemiacetale (**1**) was dissolved in CH_2Cl_2, stirred and cooled to 0 °C. The reaction was kept under nitrogen atmosphere, R-(+)-phenylethylamine (**2**) was added. The solution was cooled to -50 °C and trifluoroacetic acid (**3**) and boron trifluoride etherate (**4**) were added. After 10 min freshly cracked cyclopentadiene (**5**) was added and the reaction solution was kept at 0 °C. After 6 hours the product was extracted. The product was dried and later purified by column chromatography.

The reaction mechanism includes a nucleophilic attack followed by the formation of an iminium species and subsequently is finished by a Diels-Alder reaction. Components **1**, **2** and **5** were applied in excess. After purification a perfectly pure product, a white powder, was received. In reference to Schitter et al.[19] yield was poor (4 %; Schitter et al. 45 %). This may be explained by a slightly shorter reaction time of 6 hours instead of 7 hours. Furthermore the reaction was kept at 0 °C after the addition of cyclopentadiene, instead of at -50°C. However, the major part may be attributed to the purification process. It was necessary to run two columns because separation of the different species and thereby purification of the product was not reached after the first column chromatography attempt due to the use of a wrong solvent ratio. A complete extraction of the product from the silica gel of the first column may not have been reached, thus obtaining a high loss of product.

3.1.2.2. Characterization

NMR



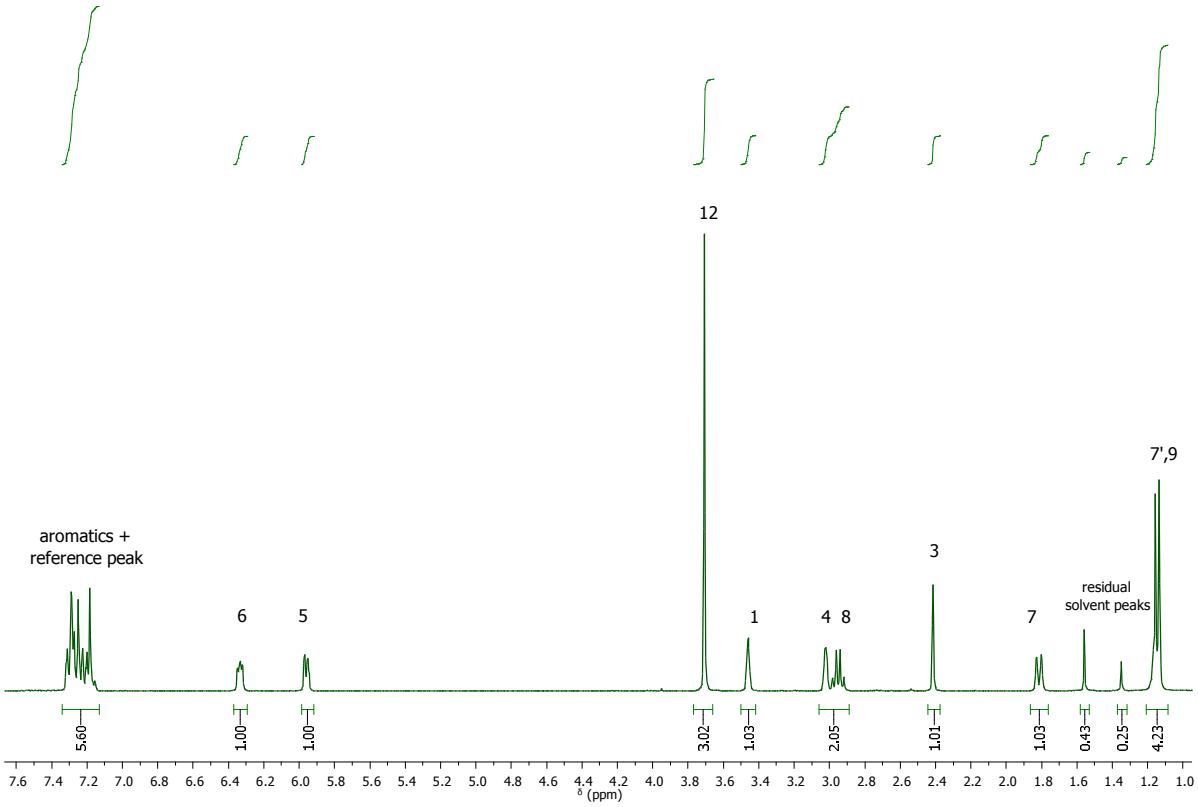


Figure 2: NMR spectrum of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

This ^{1}H NMR spectrum was recorded in $CDCl_3$. A detailed assignment of the corresponding peaks can be found in the experimental section. Peaks **6** and **5** exhibiting a chemical shift of 6.35 ppm and 5.99 ppm, respectively, confirm the presence of an unsaturated bicyclic structure. Peaks at 7.35 ppm, 3.71 ppm and 1.15 ppm correspond to the phenyl ring, OCH_3 and $CHCH_3$, respectively. Additionally all other peaks have been assigned as shown in the figure above.

The monomer's ^{13}C NMR spectrum and assigned peaks can be found in the appendix and the experimental section.

Further, extensive NMR analyses, including COSY and HSQC, have shown that the functional group, attached to the aza position is rotating flexibly and is not rigid at all. Furthermore HSQC analysis has verified that positions **7** and **7'** can be distinguished.

FT-IR

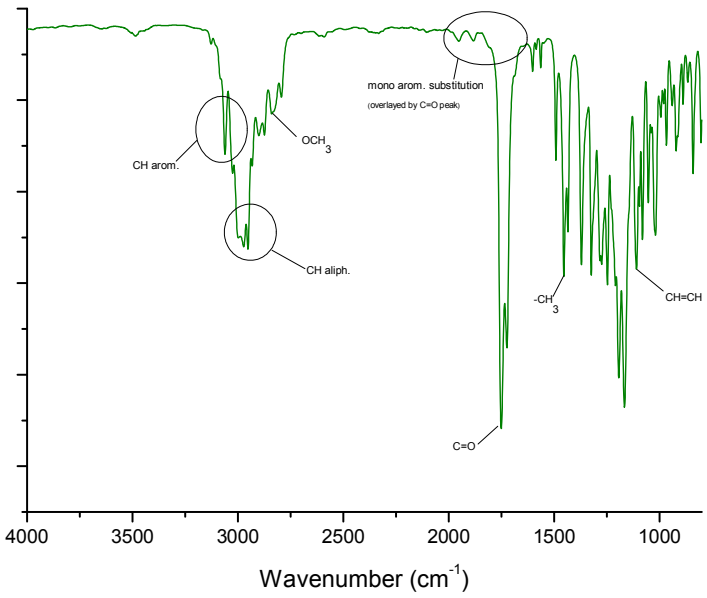


Figure 3: FT-IR spectrum of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

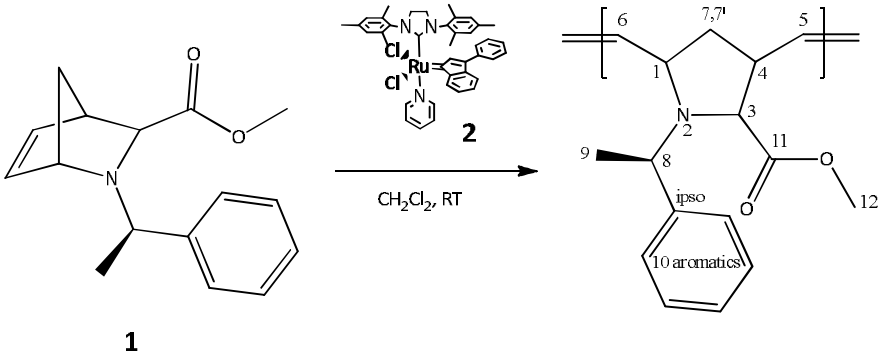
The FT-IR spectrum in Figure 3 shows absorption bands at 3050 – 2800 cm^{-1} corresponding to aromatic and aliphatic C-H vibrations. An O-CH_3 vibration can be observed at 2850 – 2810 cm^{-1}. Vibrations at 2000 – 1700 cm^{-1} correspond to a mono-substituted phenyl ring (although they are partially overlayed and normally consist of 4 signals). C=O and –CH_3 vibrations can be found at 1750 cm^{-1} and 1450 cm^{-1}, respectively. A characteristic vibration at around 1108 cm^{-1} can be assigned to CH=CH vibrations of the unsaturated bicyclic structure. Note that it is rather difficult to assign IR peaks precisely since the high ring strain in the azanorbornene bicyclic system shifts most signals to higher frequencies compared to standard alkanes and alkenes22.

3.1.2.3. Conclusion

According to the above stated results and the comparison to already existing data by Schitter et al.[19], one can assume that synthesis of this monomer was successful and the product is pure.

3.1.3. Polymer

3.1.3.1. Synthesis



Scheme 6: Synthesis of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

The reaction is a Ring-opening metathesis polymerization (ROMP) reaction. It was carried out under nitrogen atmosphere, using a *Umicore* initiator, M31, resembling Grubbs' initiators of the 3rd generation. A 0.1 M concentration of the monomer in the reaction solution was realized. Reaction progress was monitored by thin layer chromatography and stopped after 1.3 hours by adding an excess of ethylvinylether. The product was purified by precipitation in cold ethanol. Yield was 73 % of a brown solid.

3.1.3.2. Characterization

NMR

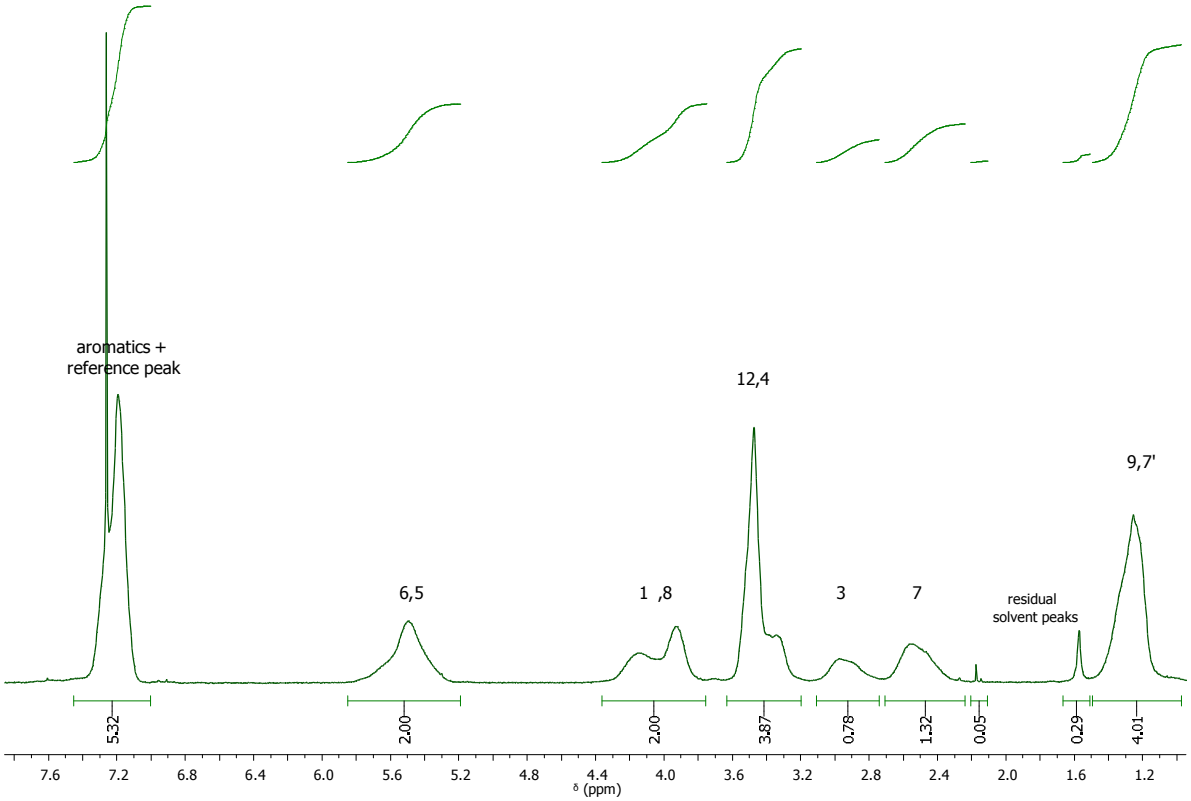


Figure 4: NMR spectrum of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)*

In reference to the previously discussed ^{1}H NMR spectrum of the monomer this spectrum shows peak broadening. This is due to the high number of monomer repeat units in the polymer. Furthermore an important characteristic of the polymer spectrum is that the peaks assigned to **6** and **5**, corresponding to CH=CH have shifted and can now be found at 5.84-5.20 ppm. The absence of peaks at 6.35 ppm and 5.99 ppm proves a total conversion. A detailed assignment of the peaks can be found in the experimental section.

FT-IR

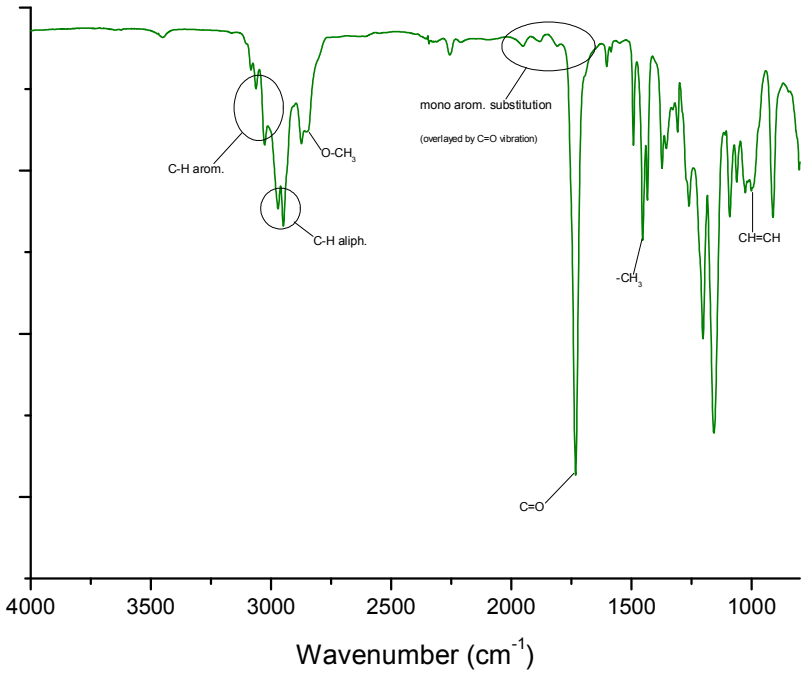


Figure 5: FT-IR spectrum of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)*

Peaks corresponding to aliphatic and aromatic C-H vibrations can be assigned at 3050 – 2800 cm^{-1}. A medium vibration at 2840 cm^{-1} can be related to an O-CH_3 vibration. Vibrations at 1750 cm^{-1} and 1455 cm^{-1} refer to C=O and –CH_3, respectively. The most important characteristic of the polymer FT-IR spectrum is that the signal corresponding to the CH=CH vibration of the unsaturated bicyclic structure has shifted from 1108 cm^{-1} in the monomer spectrum to around 988 cm^{-1}. Exact assignment can be found in the experimental section.

Further Characterizations

GPC was recorded in a solvent mixture ($CHCl_3$/Et_3N/i-Prop, 94:4:2) relative to poly(styrene) standards. The polydispersity index was determined to be 1.3 at a number average molecular mass of 31500 g/mol. T_g was determined to be 89.3 °C by DSC analysis. Furthermore STA analysis showed that mass loss of 5 % is reached at 310.0 °C, which allows the polymer to be compounded in other polymer matrices without major structural degradation.

An antimicrobial analysis was conducted by TTZ Bremerhaven. Biocidal activity was

tested using four different bacterial strains, *Staphylococcus aureus, Escherichia coli, Pseudomonas fluorescens* and *Listeria Monocytogenes*. As shown in the graphs below, the polymer causes death of 86 % of *Staphylococcus aureus* and 99 % of *Pseudomonas fluorescens* bacterial strains. However *Escherichia Coli* and *Listeria Monocytogenes* are not affected negatively by the polymer film, they even show proliferation in this case. These results show that a general biocidal activity is not indicated.

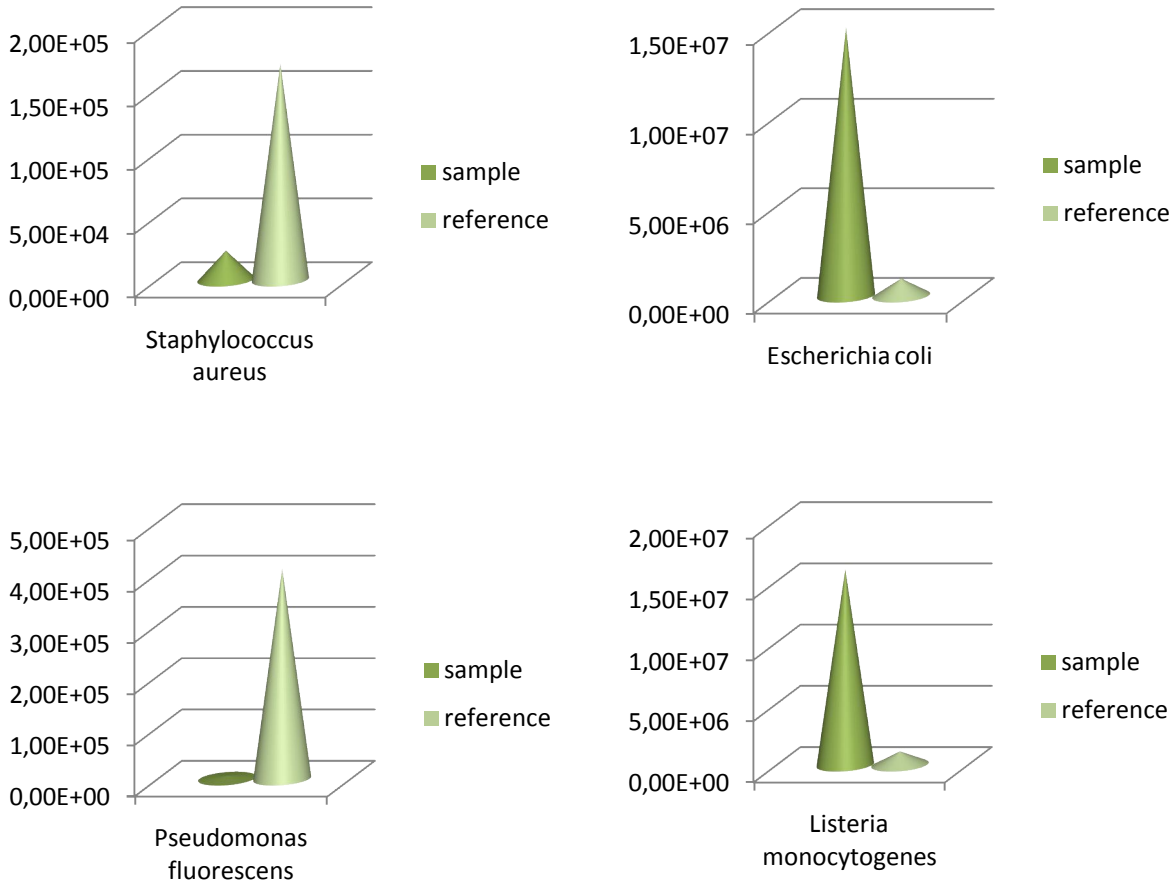


Figure 6: Antimicrobial analysis results of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)*

Table 2: Analytical results of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)*

PDI	**1.3***
T_g *[°C]*	**89.3**
mass loss (5 %) [°C]	**310.0**
antimicrobial activity	**NO**

* monomer to initiator ratio: 100:1

3.1.4. Conclusion

It has to be pointed out that the synthesis of the monomer is very time consuming and constant cooling to temperatures around -50 °C has to be guaranteed. Therefore this procedure might not be considered as a potential general approach towards the fast and easy synthesis of azanorbornene monomers for the application in ROMP.

The reaction time for the polymerization was 1.3 hours, which is moderately fast. Different characterization methods proved a successful synthesis and showed that Grubbs' third generation Ruthenium type initiators can be used for this cause. The polydispersity index however was 1.3, which is a moderate figure. Antimicrobial analysis did not show a sufficient biocidal acitivity. However, as stated under 2.3.2 at least partial protonation of the polymer seems to be necessary for an antimicrobial effect.

It was tried to achieve protonation of the polymer to potentially enhance the biocidal acitivity. Methyl iodide was added to a solution of the polymer in chloroform/acetonitrile and kept under reflux for 48 hours. This attempt did not work out as desired and protonation was not achieved. A possible reason could be the steric hindrance since the attached substituents are space consuming and might not allow a further reaction at the aza position.

These findings do not render these compounds ideal potential candidates for further analysis regarding the establishment of azanorbornenes as an additional monomer class for ROMP.

3.2. 2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene and derivatives

3.2.1. Introduction

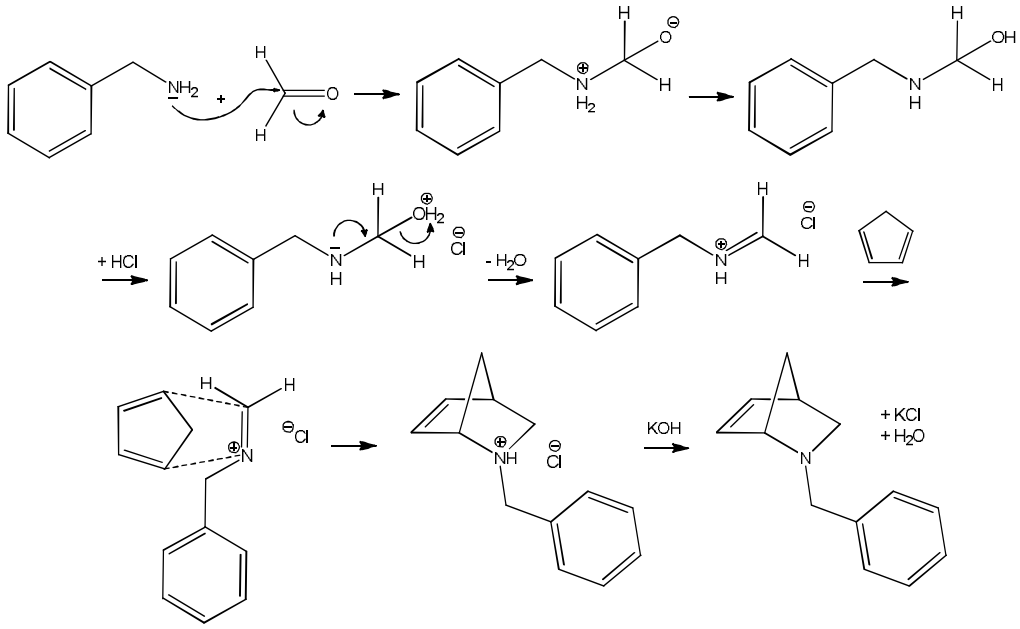
Studies on the monomer and its derivatives were conducted since the synthetic procedure is straightforward, does not afford a lot of time nor a complex setting[21,22]. Thus, this approach could be an easy and facile way of generating azanorbornenes with diverse functionalities. In connection with novel initiators, that show a high tolerance towards heteroatoms, fast initiation and propagation rates and allow handling in mild conditions, these monomers could be ideal candidates for ROMP.

Therefore also the polymer was characterized extensively in order to get a more exact idea of the potential of this class of monomers.

Furthermore a possible biocidal activity was investigated.

3.2.2. Monomer

3.2.2.1. Synthesis



Scheme 7: Reaction mechanism of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*[22]

The synthesis followed an approach by Grieco et al.21. The reaction was performed in deionized H_2O. Benzylamine hydrochloride was dissolved and 37 % aqueous formaldehyde solution and freshly cracked cyclopentadiene were added. Tight sealing of the flask is essential to minimize reagent loss, in particular cyclopentadiene, by evaporation. It was stirred for 4 hours. The product was extracted and dried. Yield was 85 % of a yellow oil.

The reaction mechanism is shown in Scheme 7. In a first step an iminium species is formed by a mechanism referring to the first step of the Mannich reaction. The iminium salt then undergoes an aza-Diels-Alder reaction with cyclopentadiene rendering an azanorbornene compound.

3.2.2.2. Characterization

NMR

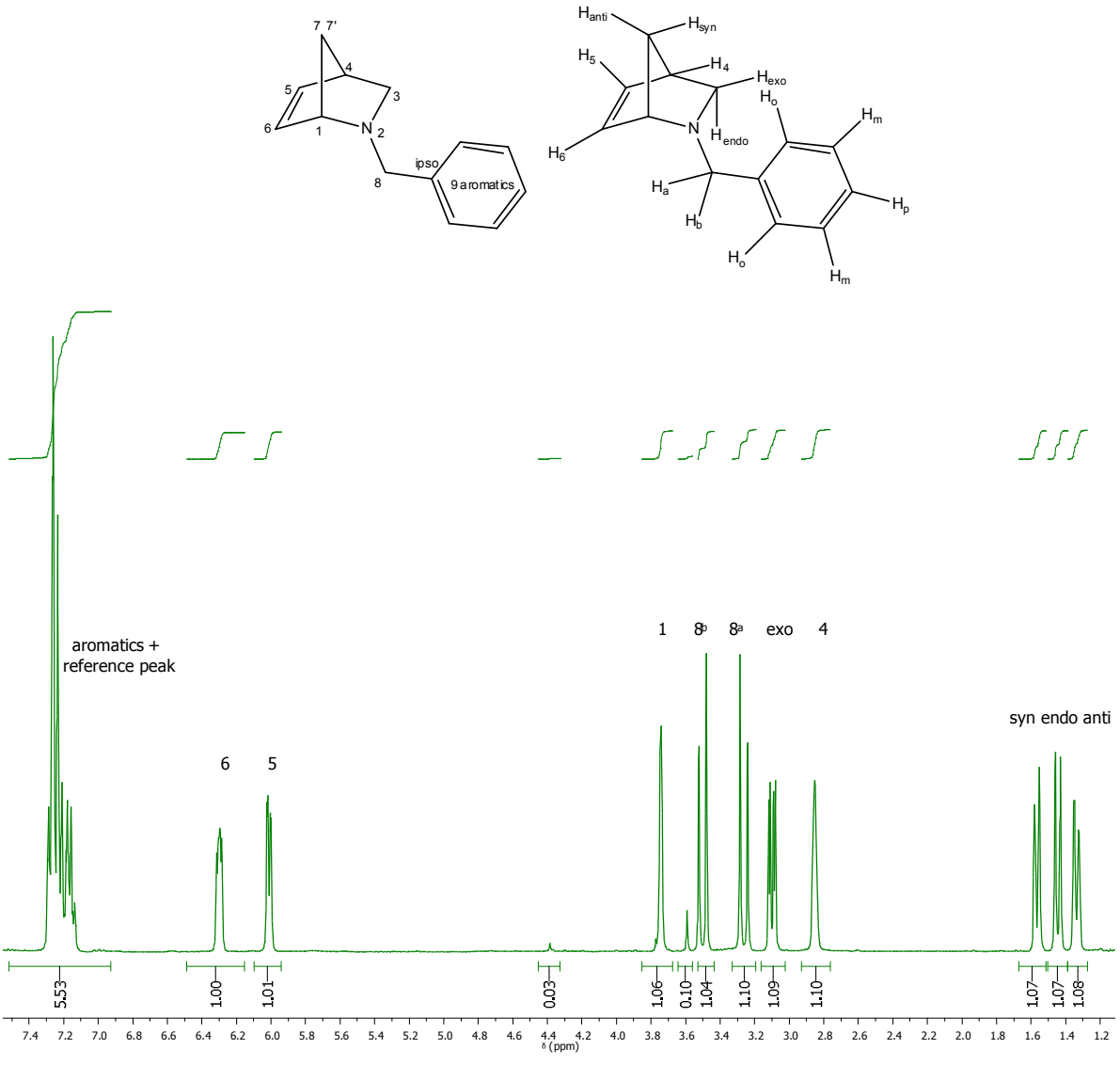


Figure 7: NMR spectrum of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

The peak at 7.2 ppm integrates for five protons. It can be assigned to the five phenyl ring hydrogen atoms. Peaks **6** and **5** indicate the successful synthesis of an unsaturated bicyclic structure since they correspond to CH=CH. Furthermore, due to the rigid structure of the

compound all hydrogen atoms are split up perfectly, show a well defined fine structure and can be assigned to specific positions. Positions **3**, **7**, **8** carry two hydrogen atoms; these are split up and render 6 signals. Having a closer look at the spectrum one can see that signals of the corresponding positions **3**, **7**, **8** have a strong shape resemblance and can thereby by identified to belong to the same position. This is in perfect agreement with data reported in the literature[21,22]. See the experimental section for a detailed list. It has to be pointed out that a minor peak at 3.5 ppm indicates the presence of benzylamine. However this did not interfere with succeeding syntheses.

FT-IR

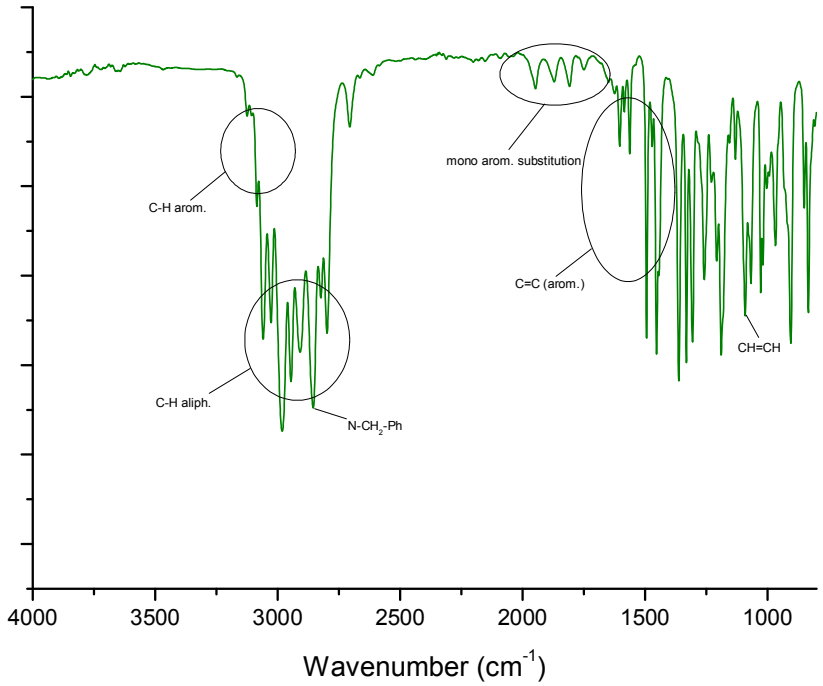


Figure 8: FT-IR spectrum of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

The peaks in the FT-IR spectrum indicate a successful monomer synthesis. The two strong vibrations at 1495 cm^{-1} and 1454 cm^{-1} are assigned to the phenyl ring in reference to the benzylamine hydrochloride spectrum. Special emphasis is laid on the small but defined peaks at 1948 cm^{-1} – 1751 cm^{-1}; those indicate a mono-substituted aromatic compound and are substantial. A very strong signal at 2855 cm^{-1} can be assigned to N-CH_2-Ph. The signal at 1093 cm^{-1} refers to CH=CH of the azanorbornenes bicyclic structure.

Further Characterizations

STA analysis showed that mass loss of 5 % is reached at 115.7 °C, which is a rather critical figure that needs to be taken into account for further syntheses with this compound.

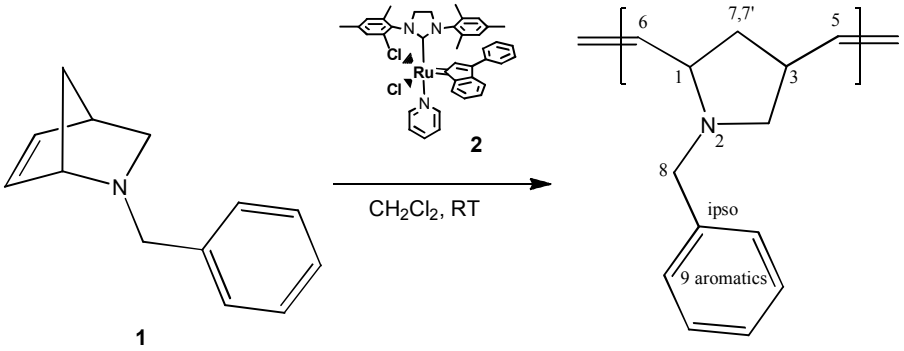
Elementary analysis produced values that did not perfectly match the theoretical ones. These results have to be evaluated with caution. The analyses stated above confirmed a successful synthesis. Furthermore STA analysis showed good results, not revealing any solvent residues, which could have otherwise been an explanation for the obtained data. Therefore one cannot draw any conclusions from these results.

Table 3: Elementary analysis results of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

	measurement	theoretical
%N	8,24	*7,56*
%C	78,82	*84,28*
%H	7,56	*8,16*

3.2.3. Polymer

3.2.3.1. Synthesis



Scheme 8: Synthesis of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

Comments on the general polymer synthesis can be found under paragraph 3.1.3.1 and can be applied to this compound as well. A more specific description is presented in the experimental section.

3.2.3.2. Characterization

NMR

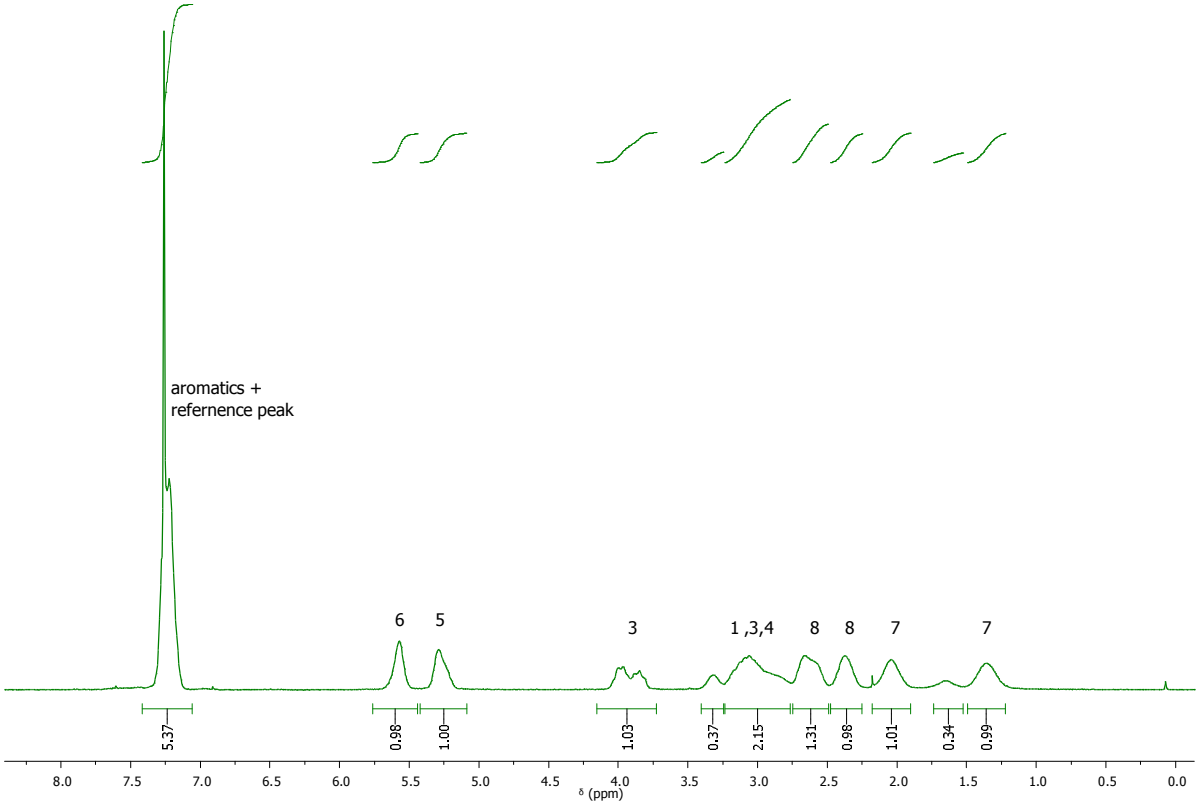


Figure 9: NMR spectrum of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

The spectrum in Figure 9 is in agreement with a spectrum reported in the literature[16]. The peak at 7.4 – 7.1 ppm has an integral of 5 and indicates the presence of the phenyl group. Peaks at 5.7 – 5.1 ppm refer to CH=CH; these have shifted from 6.3 – 6.1 ppm. This indicates the successful polymer synthesis. Furthermore the absence of any residuals at 6.3 – 6.1 ppm shows that the conversion was complete. Differentiation between peaks in the region 4.1 – 1.2 ppm is not an easy task. The peak assignment was accomplished by COSY and HSQC NMR measurements. These don't allow distinction between hydrogen atoms attached to the same carbon atom. NOESY measurement would produce more detailed results.

FT-IR

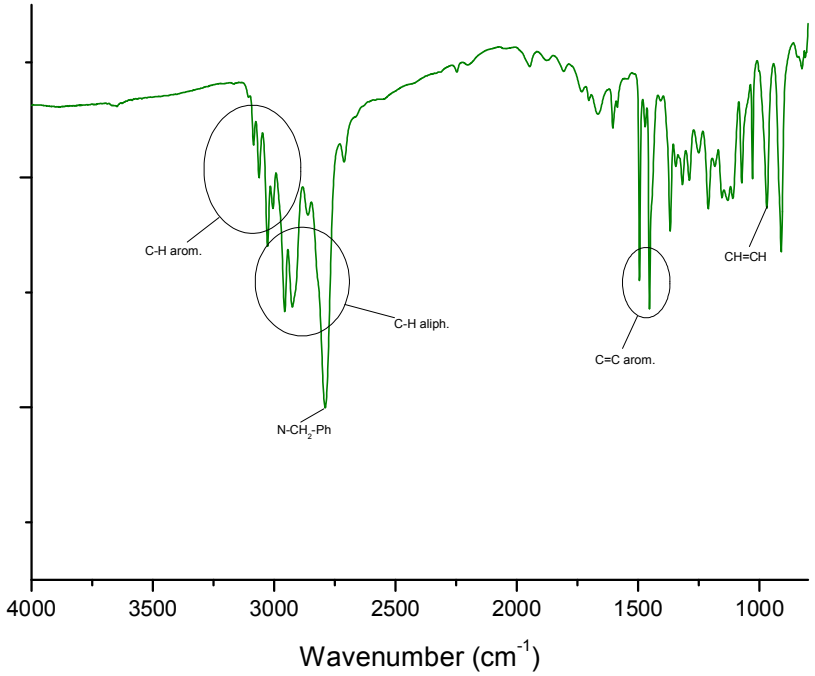


Figure 10: FT-IR spectrum of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

The FT-IR spectrum shows signals at 3050 – 2800 cm^{-1} that refer to aromatic and aliphatic C-H vibrations. A very strong signal at 2790 cm^{-1} indicates N-CH2-Ph. Signals at 1497 cm^{-1} and 1454 cm^{-1} refer to the phenyl ring. Most importantly the signal referring to the CH=CH vibration of the azanorbornene has shifted from 1093 cm^{-1} in the monomer spectrum to 972 cm^{-1} in this spectrum, which is a common characteristic for a successful polymerization.

Further Characterizations

STA analysis gave 283.0 °C (for a polymer with a chain length of 100 repeat units). This was determined to be the temperature at which weight loss was 5 %. This ensures that the polymer stays intact and does not degrade if it is integrated into another polymer matrix.

As mentioned, elementary analysis is difficult to interpret. If measured values don't perfectly fit the theoretical predictions it is hard to give profound explanations. As also indicated by STA analysis of the same sample, there have still been solvent residues.

Furthermore there might as well have been some benzylamine left. No substantiated solution can be drawn out of these results.

Table 4: Elementary analysis results of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

	measurement	theoretical
%N	7,17	*7,56*
%C	82,72	*84,28*
%H	7,90	*8,16*

Antimicrobial analysis indicated a weak biocidal activity. *Staphylococcus aureus, Escherichia coli* and *Pseudomonas fluorescens* bacterial strains were reduced by 90 %, 99.7 % and 99.3 %, respectively. However *Listeria monocytogenes* seemed to show proliferation due to contact with the polymer film. Overall biocidal activity was not proven by all four bacterial strains applied but in regard to the results for three of them a weak activity seems to be present.

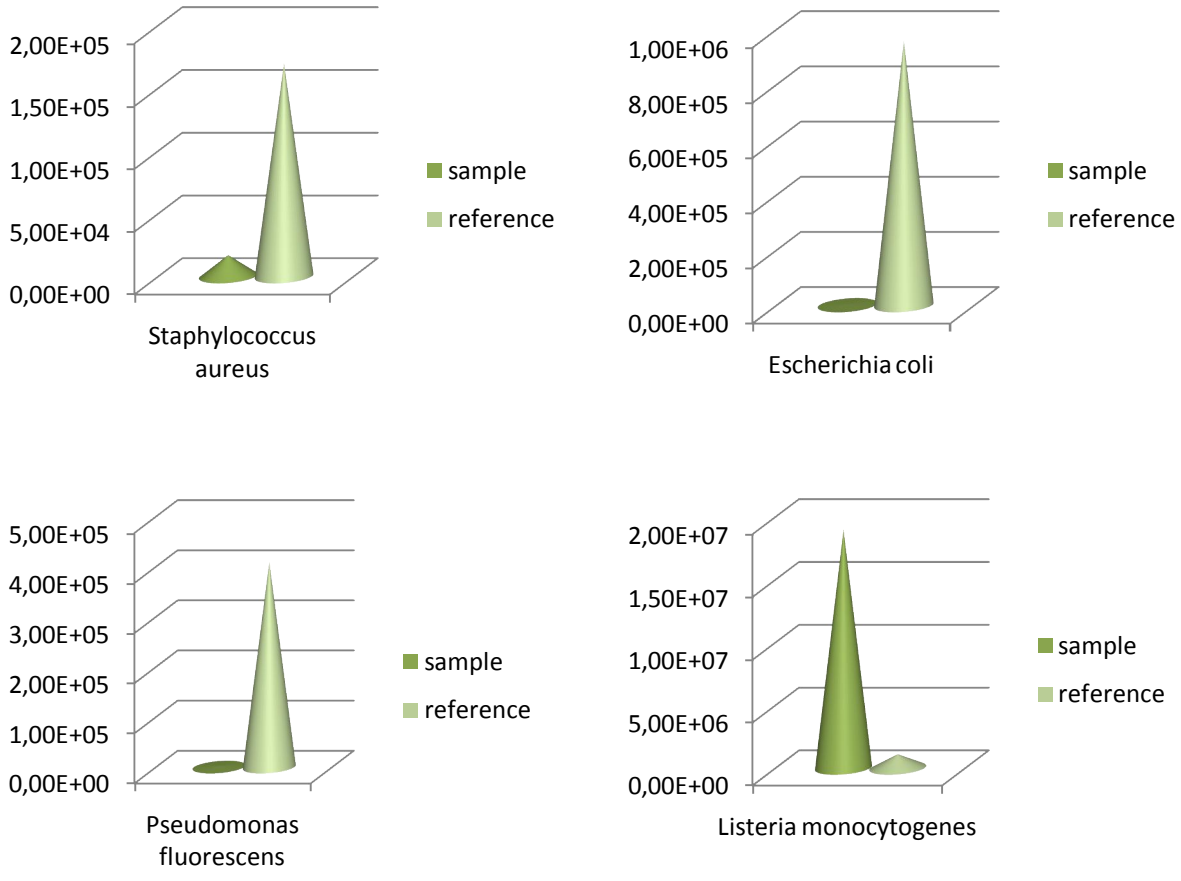


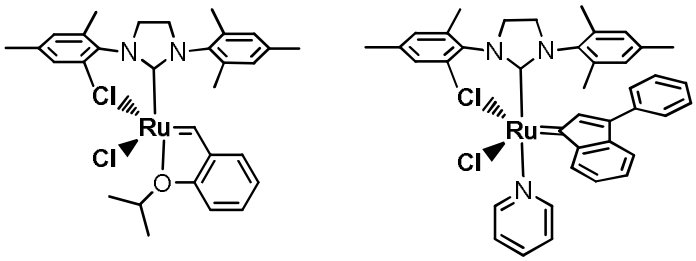
Figure 11: Antimicrobial analysis results of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

Studies on the possibly controlled character of the polymerization

I.

Three polymerization series were conducted to shed light on the polymerization mechanism. The syntheses of each series were conducted simultaneously to ensure equal conditions. For the reactions monomer to initiator ratios of 1: 50, 100, 150, 200, 250, 300, 500, 1000 were applied following the standard polymerization procedure described under 3.1.3.1 and the experimental section.

Two different initiator were utilized, *Umicore*'s *M31* and *Hoveyda*. Initiator *M31* is the initiator used in all polymerization reactions described in this piece of work. Initiator *Hoveyda* was chosen for comparison.



1 **2**

Figure 12: initiators Hoveyda (1) and M31 (2)

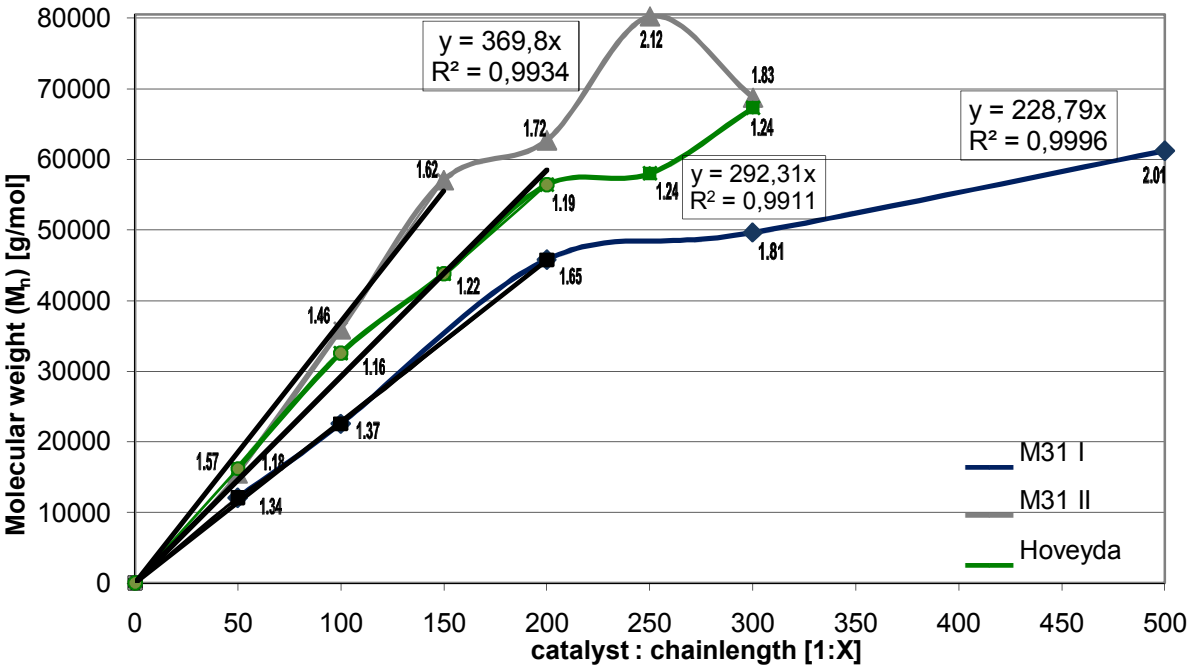


Figure 13: Analysis of the polymerization mechanism of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

The graph shows three polymerization series, grey and blue with initiator *M31* and green with initiator *Hoveyda*. All of them show an almost linear development until initiator to monomer ratios of about 1:200. The blue curve shows the best results due to its slower incline. PDIs, which are displayed at the values, are moderate. On the other hand the green curve, using initiator *Hoveyda*, shows better PDI values but again is too steep, which refers to a less controlled polymerization, since propagation is too fast, producing polymer chains of a higher length difference than the others. The exact same conditions were applied to the grey and the blue polymerization series. The difference between these curves shows that already small differences in conditions and amounts give deviating results.

II.

Furthermore an NMR assisted polymerization conversion recording was conducted.

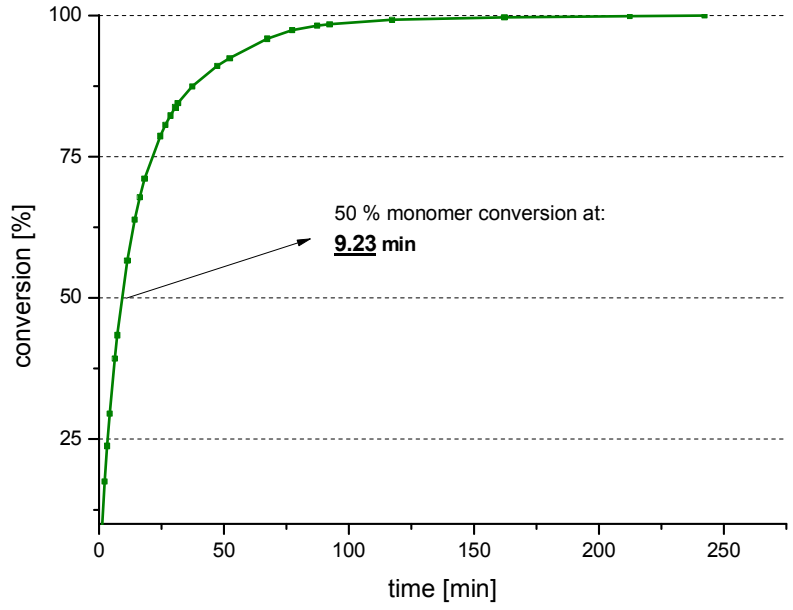


Figure 14: Determination of the polymerization half-life of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

As shown in the graph, a polymerization of the monomer was conducted, that was constantly being monitored by NMR spectrometry. A monomer to initiator ratio of 1:70 was applied. In general the polymerization recording showed a favorable progress, showing fast initiation and propagation. This is also indicated by a half life of 9.2 min, which was derived from the plot. The half life, the point in time, when conversion is 50 % is a characteristic figure. However it can be seen that reaction slowed down at about 75 % of conversion. Total conversion is reached after four hours.

3.2.3.3. Conclusion

In summary this polymer has been investigated extensively. Investigations showed that the polymerization mechanism can be regarded as controlled, though it cannot be considered a living polymerization in the narrowest sense of the term. This means that it ought to have a PDI approaching 1[7]. Polydispersity indices calculated for polymers in the series reach up to 1.6 in the significant range of the plot. (The reaction series using initiator *Hoveyda* is hereby excluded.) Polymerization half life has been calculated to be 9.23 min, compared to the literature this figure ranks in the range of published values for similar polymerizations[9].

Since different reaction series have been conducted, a mean yield and the best achieved PDI of polymerizations with initiator *M31* are provided in the table below. Precise values can be found in the experimental section. Results obtained with initiator *Hoveyda* were slightly better and are not included in the table; average yield was ~ 78 %, while the best reachable PDI was 1.2.

Table 5: Analytical results of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

Polymerization mechanism	**controlled**
Half life	**9.23***
reachable PDI	**1.3****
average yield [%]	**~ 70**
mass loss (5 %) [°C]	**283.0*****
antimicrobial activity	***possibly but weak***

** monomer / initiator (m/c) ratio 70:1, ** best PDI obtained with initiator M31, m/c ratio 50:1, *** m/c ratio 100:1*

A weak antimicrobial activity was assumed to be present. However this was not a satisfying result, so it was tried to protonate the polymer with methyl iodide. An at least partial protonation seems to be essential for biocidal activity (see 2.3.2 for a detailed explanation). This approach has not yet been successful.

It was also tried to protonate the monomer with methyl iodide. This did not work out either. For the monomer a mass loss of 5 % was calculated at 115.7 °C. This finding and an NMR analysis showed that the reaction temperature of ~ 90 °C was too high. The monomer underwent a retro-Diels-Alder reaction. Benzaldehyde was formed, which was detected by the NMR analysis. Additionally the typical smell of this compound was noticeable.

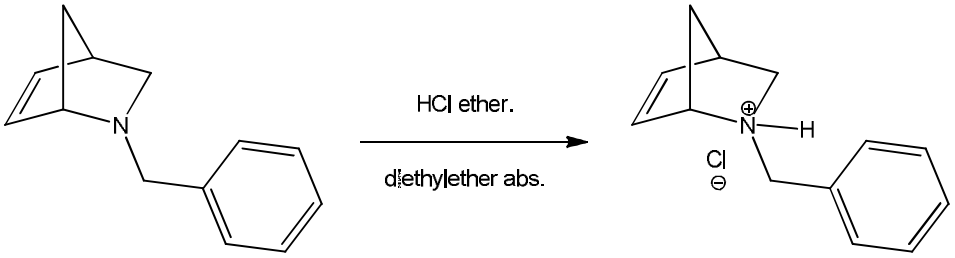
Another attempt was to synthesis 2-benzyl-2-aza-7-oxabicyclo[2.2.1]hept-5-ene. This was not successful because of the weak diene but rather aromatic character of the furan.

3.2.4. Monomer hydrochloride

3.2.4.1. Introduction

As mentioned under 0, to ensure a protonation of the polymer and thereby potentially enhancing biocidal activity was not successful. So a different approach was taken by first protonating the monomer with hydrochloric acid and afterwards polymerizing it.

3.2.4.2. Synthesis



Scheme 9: Synthesis of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride*

This synthesis was performed under inert conditions. The monomer was dissolved in absolutized diethylether under an argon atmosphere. Slowly ethereal hydrochloric acid was added to the solution. The product, benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride, precipitated as a white powder with a yield of 84 %.

3.2.4.3. Discussion

NMR analysis

NMR analysis showed that due to the ionic nature of the monomer conformational changes have occurred. At 7.0 – 6.4 ppm the two characteristic peaks are found that are assigned to CH=CH of the bicyclic structure. However, additionally two less intense peaks can be found in this region, which resemble the peaks mentioned. This is also true for the phenyl hydrogen atoms, which can be found at 7.8 – 7.5 ppm. Here a second species is present as well.

These findings indicate that two defined structures, *endo* and *exo*, are now present, attributed to the protonation at the aza position. Additional peaks appeared at 12.0 – 11.0

ppm indicating the creation of aldehyde species.

Since no polymer was obtained from this approach it was refrained from assigning the monomer peaks exactly. The spectrum can be found in the appendix.

Further Characterizations

STA analysis showed that mass loss of 5 % is reached at 208.9 °C, which is considerably higher than the value for benzyl-2-azabicyclo[2.2.1]hept-5-ene. The analysis also showed that in an initial step hydrochloric acid is eliminated, indicated by a mass loss of ~ 17 %, which has been calculated to be the percentage of HCl in the original compound.

Elementary analysis showed very good results that fit the theoretical estimation. The value for carbon however is not in the tolerance range. As already mentioned, interpretation is not an easy task. Variations may be due to residual solvents.

Table 6: Elementary analysis results of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride*

	measurement	theoretical
%N	6,41	*6,32*
%C	69,06	*70,42*
%H	7,19	*7,27*

Polymerization attempt

Polymerization procedure was conducted using standard Schlenk techniques as described under 3.1.3.1 and the experimental section. As a solvent a mixture of methanol and dichloromethane (9:1) was used.

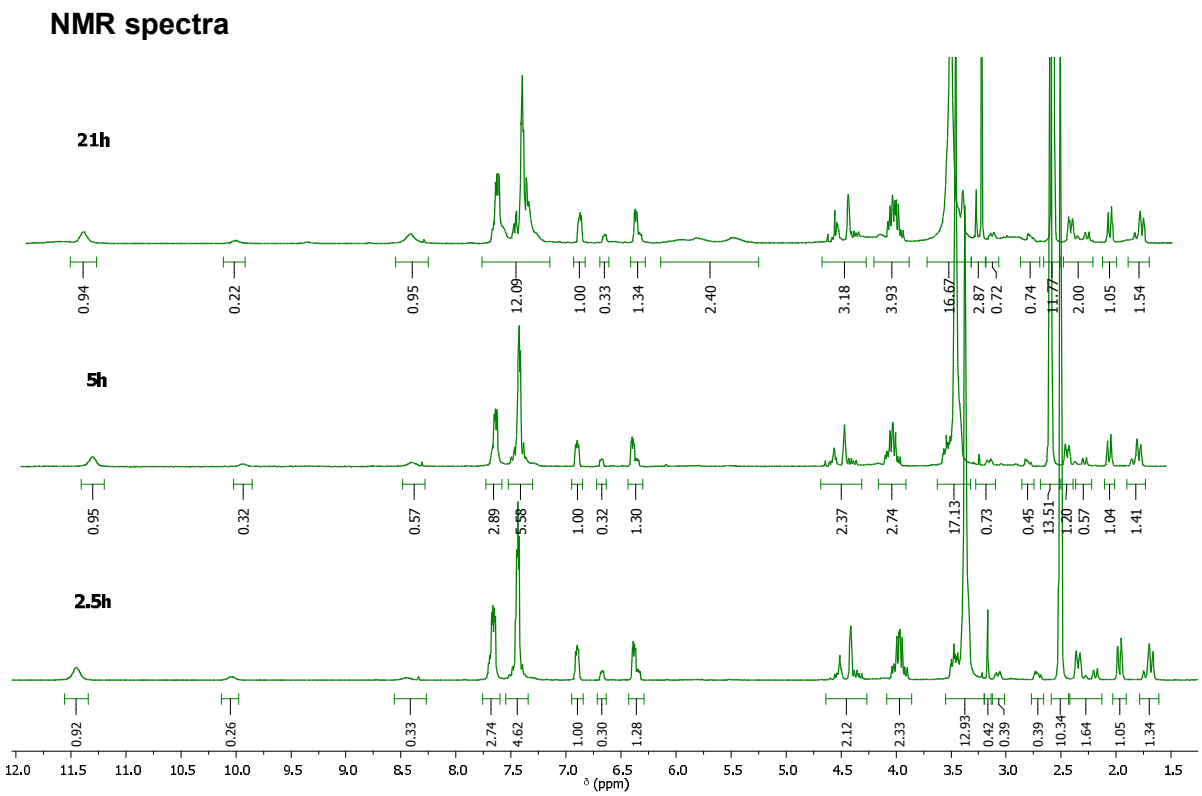


Figure 15: NMR spectra of the polymerization attempt of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride*

As shown in the comparison of the three NMR spectra after 2.5 h, 5 h and 21 h reaction time, only a small part of the monomer is polymerized. Although this result was not expected[20], it seems that the ionic character of the monomer influences the polymerization mechanism negatively but this needs a closer investigation.

3.2.4.4. Conclusion

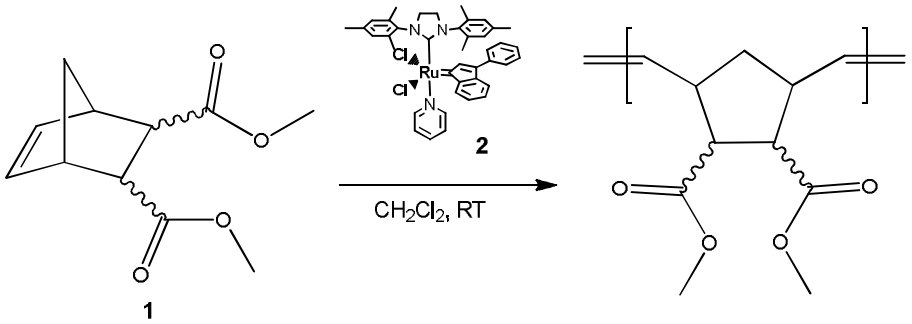
The monomer hydrochloride was synthesized by a straightforward procedure. While this gave a satisfying result, the polymerization of the monomer hydrochloride failed. Synthesis was repeated and reconfirmed the results. It seems as if the ionic character of the monomer hydrochloride has a strongly negative effect and thus renders the polymerization impossible. The rationale has to be investigated more closely.

3.3. Poly-(dimethyl-bicyclo[2.2.1]hept-5ene-2,3-dicarboxylate)

3.3.1. Introduction

This polymer was synthesized to act as a reference for the antimicrobial analyses of poly(Benzyl-2-azabicyclo[2.2.1]hept-5-ene) and poly(methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate, since it is proven to not have any biocidal activity.

3.3.2. Synthesis



Scheme 10: Synthesis of poly-(*dimethyl-bicyclo[2.2.1]hept-5ene-2,3-dicarboxylate*)

The reaction was conducted using standard Schlenk techniques and is dealt with more closely under 3.1.3.1 and the experimental section.

NMR data can be found in the experimental section.

3.4. Co-Polymers

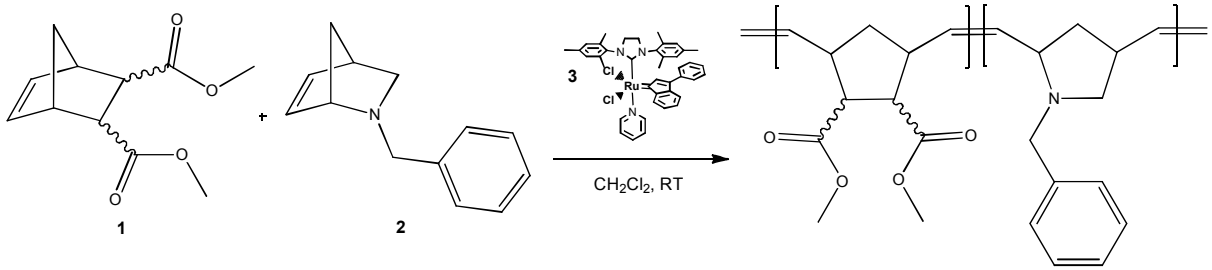
3.4.1. Introduction

The characteristic features of living polymerizations allow co-polymers to be synthesized. The initiator remains active after consumption of the first monomer and polymerization continues if a second monomer is added.

So it was attempted to synthesize co-polymers consisting of the previously discussed monomer, benzyl-2-azabicyclo[2.2.1]hept-5-ene and dimethyl-bicyclo[2.2.1]hept-5ene-2,3-dicarboxylate, a monomer commonly used for investigations of initiators by our group.

Furthermore co-polymerization is a potent tool to vary the amphiphilic balance of a polymer. As stated under 2.3.2 this balance is an important factor for biocidal activity, more specifically the polymer – membrane interaction. By introducing a monomer of higher polarity the amphiphilic balance can be equalized.

3.4.2. Synthesis



Scheme 11: Synthesis of random co-polymers consisting of *dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate* and *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

Standard Schlenk techniques were applied (for more detailed information see 3.1.3.1 and the experimental section).

Block-co-polymer **1** was synthesized by first starting the polymerization with dimethyl-bicyclo[2.2.1]-hept-5ene-2,3-dicarboxylate (**1**). After this monomer had fully reacted benzyl-2-azabicyclo[2.2.1]hept-5-ene (**2**) was added to the reaction solution. It took 20 min for the first monomer to fully react and 5 hours for the second monomer.

Block-co-polymer **2** was synthesized by first adding monomer **2**, after 5.5 hours this synthesis was finished and monomer **1** was added.

Random-co-polymer **3** was synthesized by adding monomers **1** and **2** at the same time.

3.4.3. Characterization

NMR

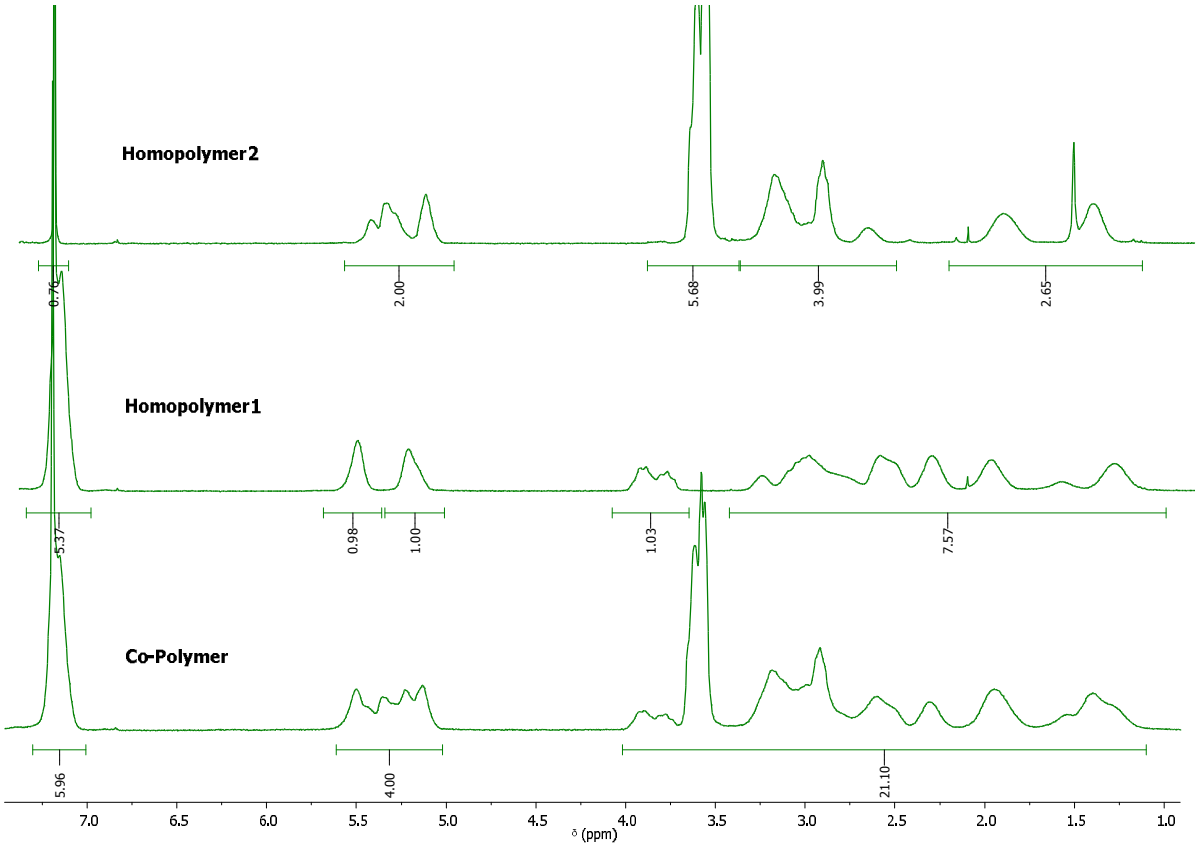


Figure 16: NMR spectra of poly(*dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate), poly(2-benzyl-2-azabicyclo[2.2.1]hept-5-ene) and the random co-polymer*

NMR spectra in Figure 16 clearly illustrate that spectra of Homopolymer 1 (poly-(Benzyl-2-azabicyclo[2.2.1]hept-5-ene)) and Homopolymer 2 (poly-(dimethyl-bicyclo[2.2.1]-hept-5ene-2,3-dicarboxylate)) can be added to give the Co-Polymer spectrum (exemplarily the spectrum for the statistical co-polymer is displayed here) and thus indicating a successful synthesis.

Further Characterizations

The co-polymers were further analyzed by STA, GPC and elementary analysis. Results are shown in the table below.

Table 7: Results of the analysis of the three co-polymers

	Ratio of monomers [%]*	GPC			STA	Elementary analysis		
		M_n	M_p	PDI		N [%]	C [%]	H [%]
Co-Polymer **1** *block*	52 / 48	39800	65000	1.5	306.2	3.34	71.99	7.28
Co-Polymer **2** *block*	52 / 49	55700	100000	1.8	311.7	3.26	72.02	7.29
Co-Polymer **3** *random*	51 / 49	56100	67000	1.4	305.0	3.41	72.14	7.30
theoretical	*50 / 50*	-	-	-	-	*3.54*	*72.89*	*7.39*

*calculated from elementary analysis data; benzyl-2-azabicyclo[2.2.1]hept-5-ene / dimethyl-bicyclo[2.2.1]-hept-5ene-2,3-dicarboxylate

As far as elementary analysis values are considered they are very close to those theoretically predicted and can be regarded as significant. However values for carbon are not in the acceptable ±0.3 % range, although close.

The two monomers have been applied in a 1 to 1 ratio. The actual ratio after polymerization has been calculated from elementary analysis results. Results are displayed in Table 7 and show that the initial monomer to monomer ratio applies for the polymer as well.

STA analysis gave very good results. All co-polymers reside in the same range and can be compounded into polymer matrices without degradation.

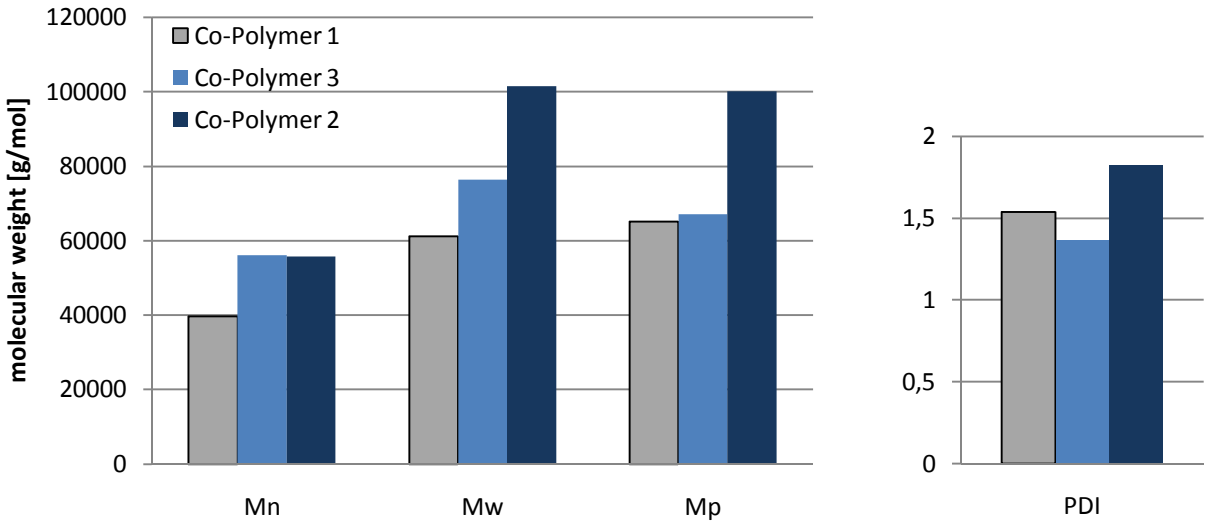


Figure 17: M_n, M_w, M_p and PDI of the co-polymers

A comparison of the GPC results is shown in Figure 17. Values are similar. Co-Polymer **2** varies from the two others. For Co-Polymer **2** the monomer that polymerizes more slowly (benzyl-2-azabicyclo[2.2.1]hept-5-ene) was applied first and later the other one was added. This naturally leads to a broadening of the GPC curve because a slow polymerization can be regarded as less controlled, meaning that more side reactions occur. Different chain lengths are generated, which is illustrated by generally higher values. Since the slower monomer is added first, a starting situation that is far from ideal is created for the faster second monomer.

3.4.4. Conclusion

The co-polymer synthesis was successful. This is another proof for the controlled character of the polymerization of benzyl-2-azabicyclo[2.2.1]hept-5-ene. However, PDI values were rather high (>1.4). Co-polymer **2** produced comparatively worse data but this was expected since the slower monomer was added first.

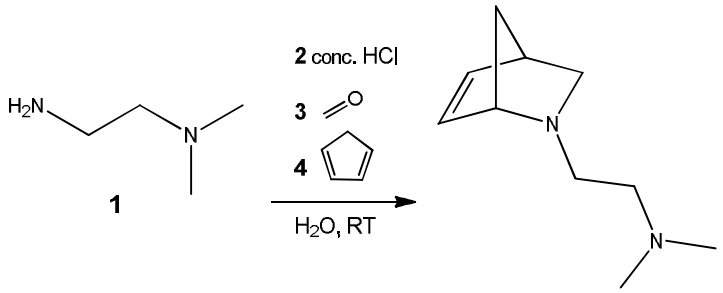
3.5. (N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene

3.5.1. Introduction

After it had been shown that azanorbornenes synthesis was quite simple and facile by investigations on benzyl-2-azabicyclo[2.2.1]hept-5-ene, we searched for a different amine that would have a more polar character. This would be an interesting feature if we think about the previously mentioned co-polymers and equalization of the amphiphilic balance, necessary for biocidal activity. So, N,N-dimethylethylene-diamine was considered to be a good candidate for further studies. Additionally, the double nitrogen functionality might be advantageous, regarding protonation and subsequently biocidal activity.

3.5.2. Monomer

3.5.2.1. Synthesis



Scheme 12: Synthesis of *(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*

It was tried to synthesis this monomer following the approach for benzyl-2-azabicyclo[2.2.1]hept-5-ene. The reaction was performed in deionized H_2O. N,N-dimethylethylene-diamine (**1**) was dissolved. Since **1** is not available in its hydrochloride form, hydrochloric acid had to be added to protonate the nitrogen atoms. 37 % aqueous formaldehyde solution and freshly cracked cyclopentadiene were added. It was stirred for 4 hours. The product was extracted and dried. Yield was 38 % of a brown oil.

Yield was poor, considering the high yield of 85 % for benzyl-2-azabicyclo[2.2.1]hept-5-ene. Additionally impurities were detected on the NMR spectrum. These indicate side reactions.

It was tried to minimize these impurities by adjusting parameters, as for instance ph value, reaction time, applied amounts, temperature. However a reduction of side reactions was not achieved.

3.5.2.2. Characterization

NMR

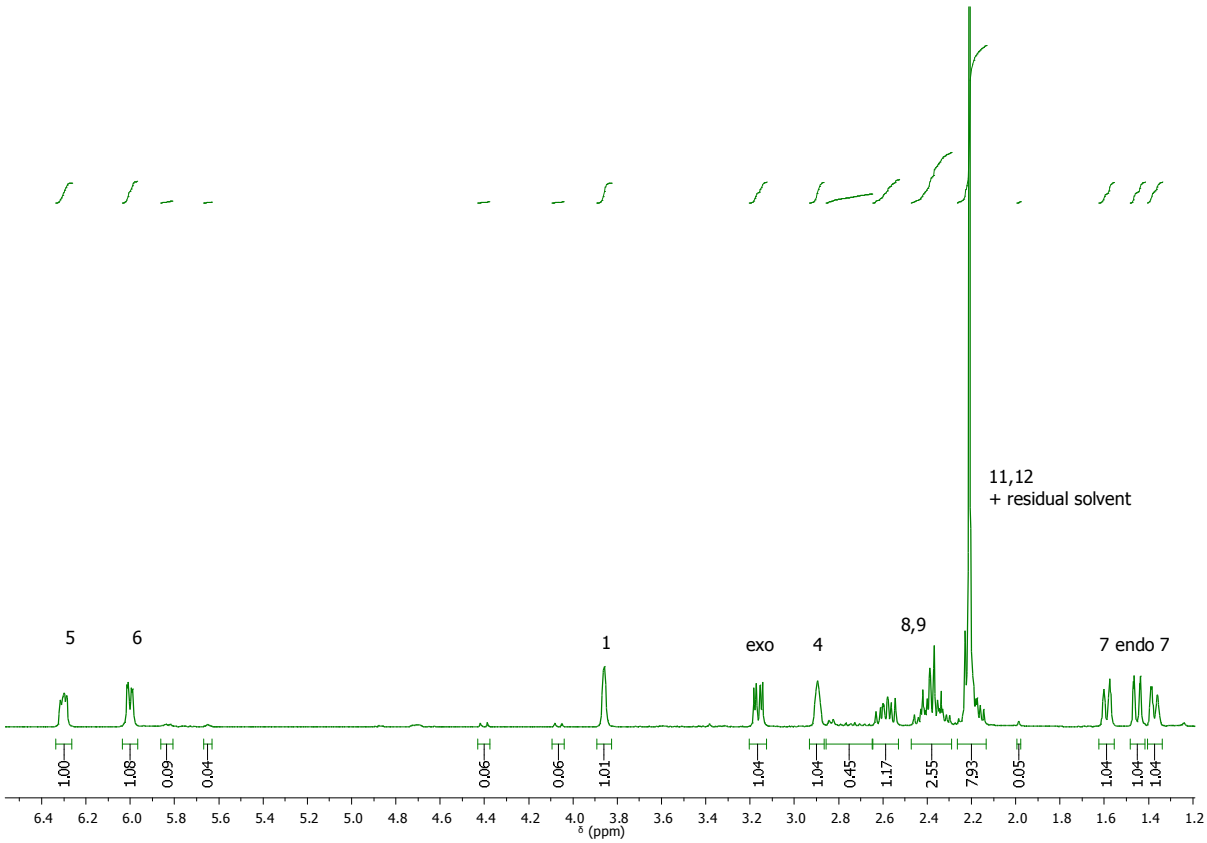


Figure 18: NMR spectrum of *N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*

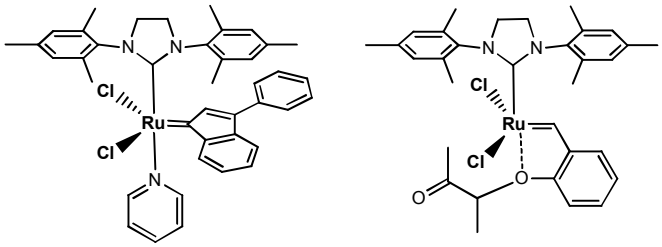
The NMR spectrum shows impurities. Peaks at 5.90 – 5.60 ppm indicate dimerization of cyclopentadiene, forming dicyclopentadiene. Peaks at 4.95 – 4.00 ppm refer to the formation of other amines. However the spectrum is pure at 1.65 - 1.32 ppm, which indicates that no other azanorbornenes have been formed. The other peaks indicate that monomer synthesis was successful.

Investigations on the reaction mechanism of the intended polymerization

The polymerization of the above mentioned monomer did not succeed. This issue was investigated closely and is dealt with in the next paragraph. Therefore, two different initiators, *M31* and *M51*, were used. Monomer and initiator were prepared in a 1 to 1 ratio. Analyses were performed by NMR recording.

NMR

Two different initiators were applied, *Umicore*'s *M31* and *M51*. Initiator *M31* possesses a Fischer carben. Initiator *M51* was chosen because it carries a Schrock carben, bearing a hydrogen atom at the double bond that can easily be detected by ^{1}H NMR spectroscopy and gives a quick and easy possibility to detect the presence of the initiator in the NMR spectrum.



1 2

Figure 19: initiators M31 (1) and M51 (2)

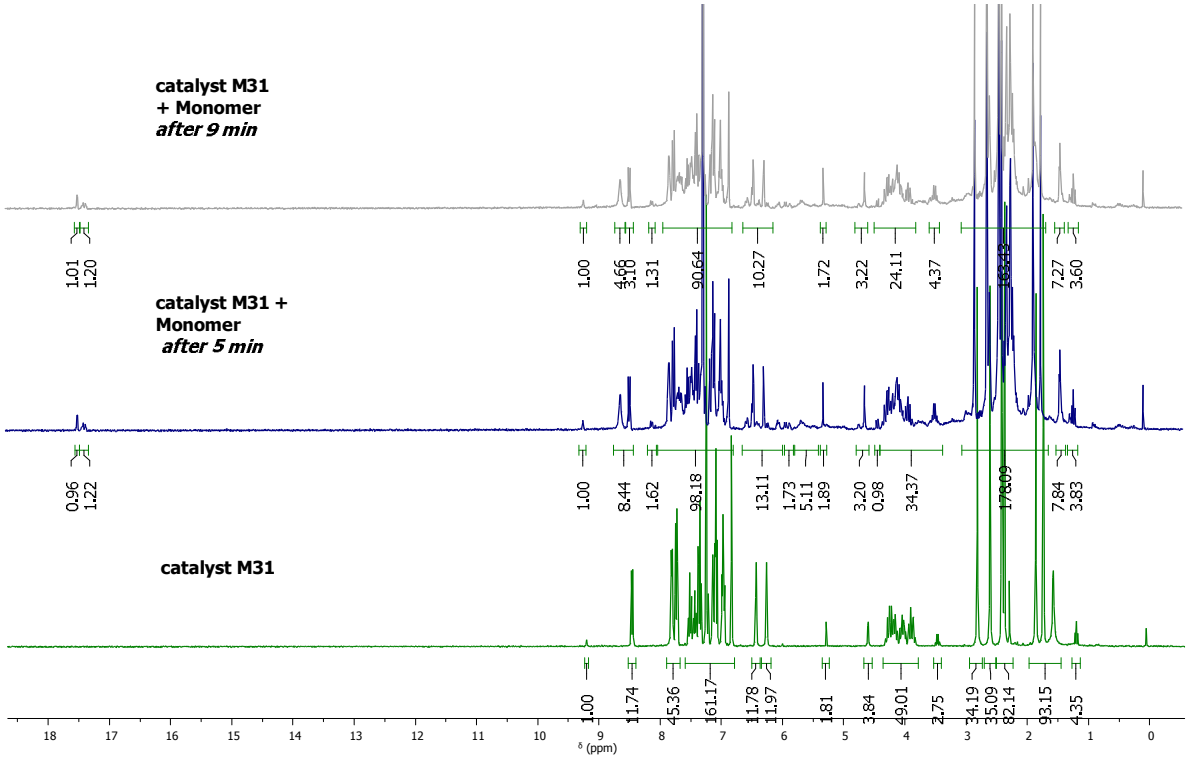


Figure 20: NMR spectra of mechanistic investigations of *(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene* with initiator M31 (I)

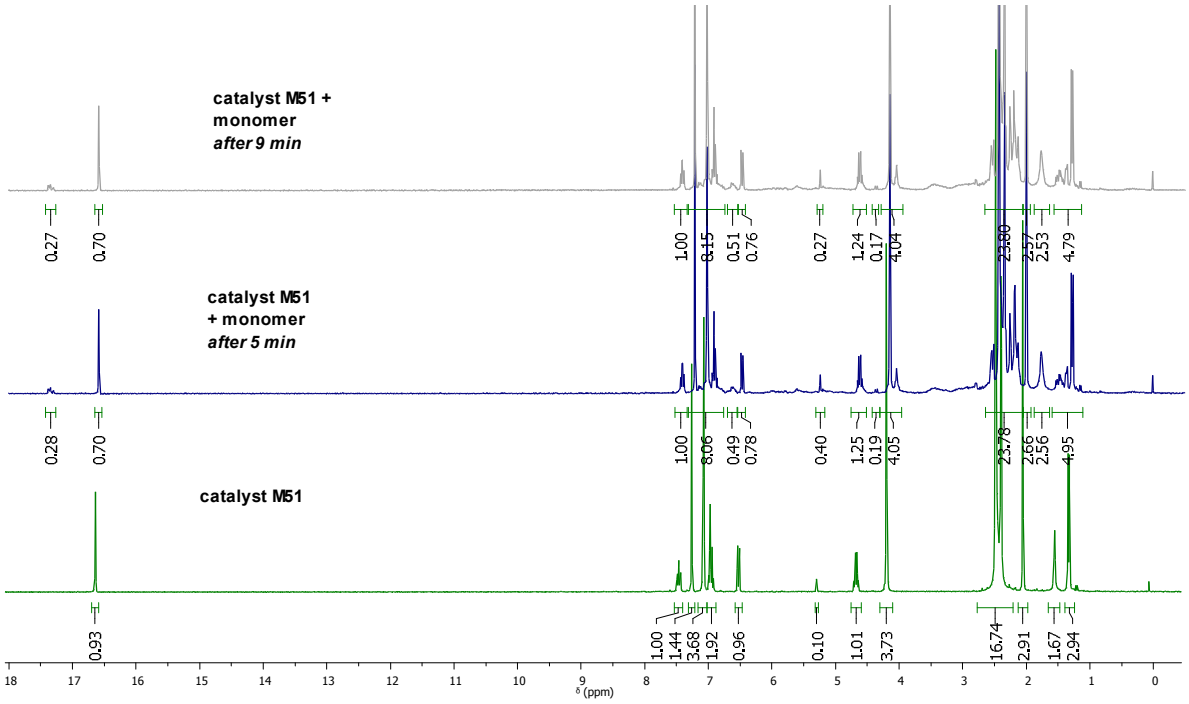


Figure 21: NMR spectra of mechanistic investigations of *(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene* with initiator M51 (I)

The spectra in Figure 20 and Figure 21 show that the monomer attaches to the initiators. The spectrum of initiator *M51* shows a characteristic peak at 16.7 ppm. After the monomer is added to the reaction solution another peak at 17.5 ppm appears. This indicates the binding of the monomer to the initiator. Oligomer formation can be assumed by a close investigation of the spectrum. The spectra of initiator *M31* indicate the same findings. Here two species appear at 17.5 and 17.75 ppm after the monomer has been added.

After 3 hours 10 eq of the monomer were again added to the test tube and a spectrum was recorded. Another spectrum was recorded after 19 hours.

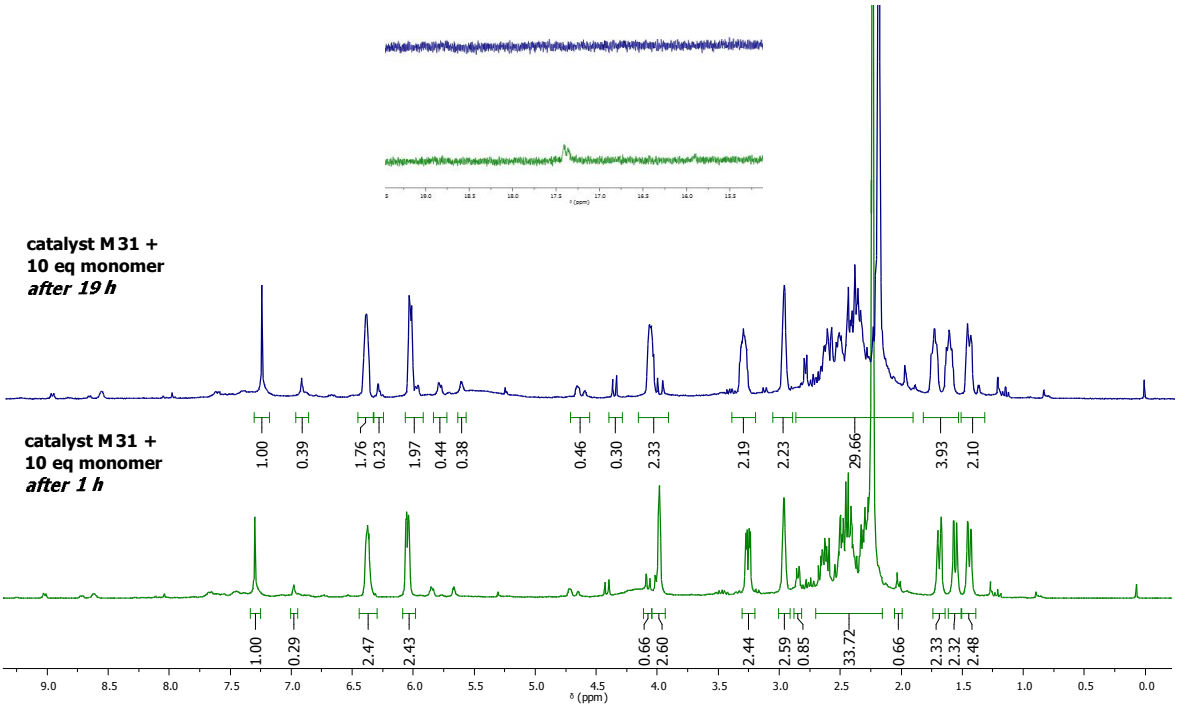


Figure 22: NMR spectra of mechanistic investigations of *(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene* with initiator M31 (II)

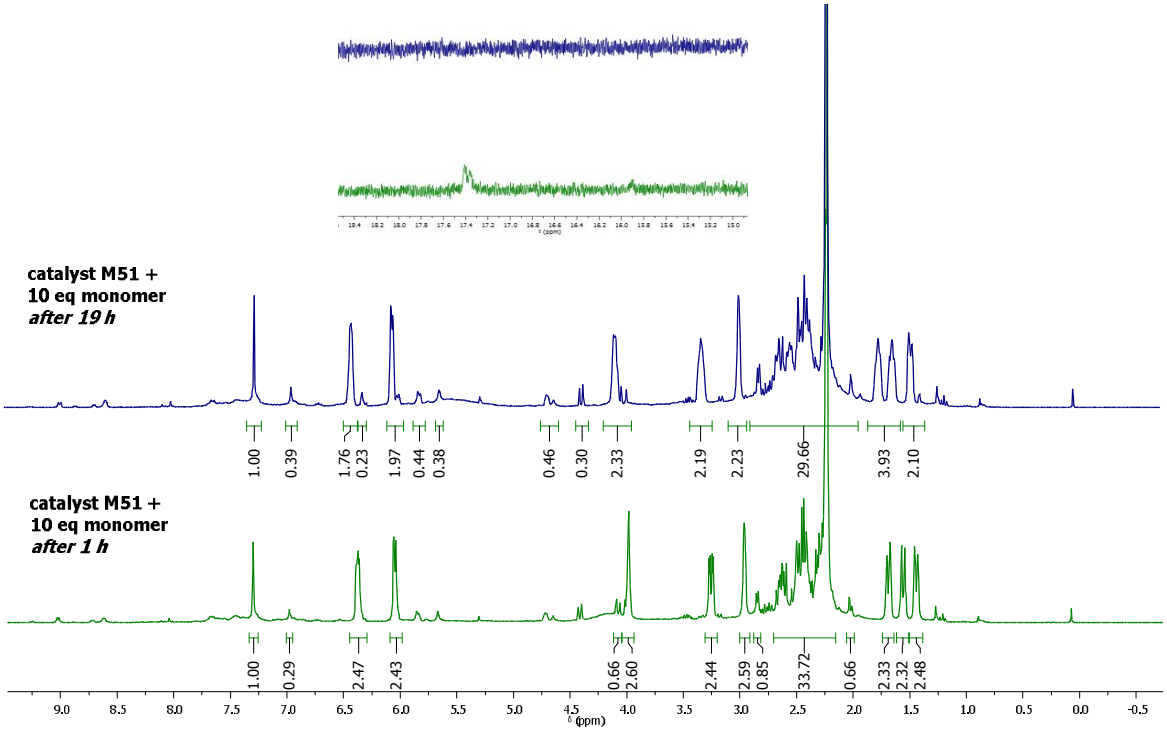


Figure 23: NMR spectra of mechanistic investigations of *(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene* with initiator M51 (II)

The second monomer addition, this time in excess, showed that the initiators cannot cope with the monomer excess. While measurements after 1 hour still showed weak,

characteristic peaks at the high ppm region, these peaks were gone after 19 hours. This indicates that monomers are not attached to the initiators anymore.

3.5.3. Conclusion

Synthesis of and studies on 2-(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene were a complex task. Monomer synthesis was more challenging than expected. It showed that the aliphatic diamine had to be handled differently from the before utilized benzylamine. Although difficulties were not totally overcome it was tried to polymerize the monomer. Extensive studies suggested that the initiator binds to the monomer. A closer look at the NMR spectra showed hints of evolving broad peaks. However, by increasing the monomer concentration in ratio to the initiator concentration, the initiator was deactivated. After these results had been gathered, it was assumed that applying a higher temperature would aid polymerization and accelerate the process. It was tried to polymerize again, keeping the reaction solution on reflux and using toluene as a solvent following the idea that the monomer polymerizes but very slowly. So keeping the reaction on reflux would accelerate the conversion. This did not succeed.

So, it was finally concluded that this amine functionality does not allow a ROM polymerization with the latest, available initiators.

4. Conclusion and Outlook

It has been shown that azanorbornenes are a potent candidate class of monomers, which is worth giving a closer look.
They represent a class that is potentially easy to synthesize, gives good yields and additionally holds a high potential for the fast integration of further functional groups that could still push the boundaries of ROMP. In the mean time the work group has succeeded in synthesis of further azanorbornenes, thus giving further support of these statements.
Poly(azanorbornenes)s also hold a potential for applications as contact biocides. They carry an amine functionality, which could be protonized to enhance biocidal activity, besides the tuning of other features as for instance the amphiphilic character of co-polymers.

Two different ways of azanorbornene synthesis have been assessed.
The approach by Schitter et al.[19] was also successful by using novel initiators. However, it was evaluated to be too time-consuming. Furthermore this approach also introduces a second functionality, which is not necessary for our purpose.
In particular, it was shown that azanorbornenes are easily accessible via the creation of an iminium salt structure and subsequent aza-Diels-Alder reaction as published by Larsen and Grieco[21].
As a model monomer, 2-benzyl-2-azabicyclo[2.2.1]hept-5-ene was characterized extensively. It was shown that its polymerization occurs in a highly controlled way. This finding makes this monomer a good candidate for co-polymerization with other potential monomers.
It was shown that the purification and subsequent polymerization of 2-(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene, although a desirable monomer to access ROMP, have not been achieved.
For the current state regarding initiator development, this finding sets borders to functional group tolerance.

Future work will include studies on how to achieve protonation of polymers and polymerize already protonated monomers to possibly obtain biocidally active polymers. Further fine-tuning into this direction has to be conducted as well.
Of course, further azanorbornenes have to be assessed regarding their applicability for ROMP.

Ongoing research on this topic will reveal its true potential and maybe establish azanorbornenes synthesis and polymerization as a powerful technique for ROMP.

5. Experimental Section

5.1. Materials and Instruments

All reagents used were purchased from commercial sources and used without further purification, unless stated otherwise.

Cyclopentadiene had to be cracked freshly, when required for a reaction. Therefore dicycopentadiene was destilled to give cyclopentadiene by undergoing a retro-Diels-Alder reaction.

For polymerization reactions dichloromethane was degassed. The volume used was set to give a 0.1 M concentration of the monomer in the reaction solution.

Thin layer chromatography was carried out using sheets from *Merck* (silica gel 60 on aluminium).

Nuclear magnetic resonance experiments were carried out on a *Bruker Avance III 300 MHz* spectrometer, referenced to TMS and deuterated solvents ($CDCl_3$, CD_3OD, DMSO-d_6). Measurements regarding studies on polymerization half-life were conducted on a *Varian Inova 500 MHz* spectrometer, referenced to TMS and deuterated solvents. All deuterated solvents were purchased from *Cambridge Isotope Laboratories Inc*. Peaks were characterized as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), b (broad), bs (broad singlet).

IR measurements were performed on a *Perkin Elmer Spectrum One* spectrophotometer with a DTGS detector, operating in transmission mode. Thin films of the sample were solvent cast on CaF_2 plates. Corresponding bands were characterized as very strong (vs), strong (s), medium (m), and weak (w).

Elemental analysis of the elements carbon, hydrogen and nitrogen was carried out on a *Universal Elemental Analyzer*.

Thermal characterization involved DSC and STA measurements. DSC data was collected with a *Perkin Elmer Pyris Diamond*. Samples were heated to 250°C and quenched under nitrogen atmosphere at a rate of 20°C/min. Reported T_g values were taken from the second heat run. STA was done on a *Netzsch 449C* apparatus, using helium as purge gas. Thermogravimetric losses were monitored up to a temperature of 550°C applying a heating rate of 10°C/min.

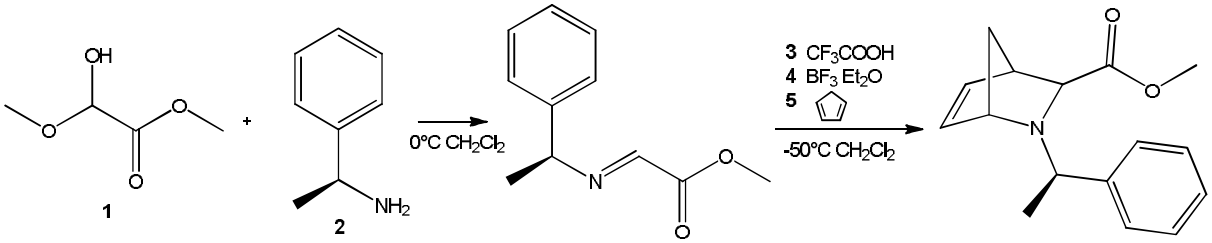
Gel permeation chromatography (GPC) was performed with a *Merck Hitachi L-6000A pump* and detected via a refractive index detector *Waters 410*. As an eluant chloroform/triethylamine/2-propanol (94:4:2) was used. For calibration a polystyrol standard with separation columns consisting of PSS 5 mm with 106 Å, 104 Å and 103 Å was used.

Studies on antimicrobial activity were performed externally by Technologie Transfer *Zentrum TTZ Bremerhaven* according to a modified protocol of the Japanese Industrial Standard *JIS Z2801:2000*.

5.2. Syntheses

5.2.1. Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]-hept-5-ene-3-carboxylate and derivatives

5.2.1.1. Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate



Scheme 13: Synthesis of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

Table 8: Reaction data of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

	1	**2**	**3**	**4**	**5**
MM [g/mol]	120.10	121.18	114.02	141.93	66.10
N [mmol]	55.0	58.0	52.0	52.0	60.0
Eq.	1.06	1.12	1	1	1.15
mass [g]	6.60	7.03	5.93	7.38	3.97

Following the approach by Schitter et al.19 6.60 g of methylglyoxylatehemiacetale (1) and 180 mL of previously degassed dichloromethane were prepared, 50 g of a 4 Å molecular sieve were added and it was stirred vigorously, cooled to 0 °C and set under argon atmosphere. 7.48 ml (7.03 g) of R-(+)-phenylethylamine (**2**) were added through a septum. The reaction solution was stirred for 2.5 h and kept at 0 °C. Then, it was cooled down to -50 °C using an ethanol/liquid nitrogen mixture. 4.01 mL (5.93 g) of trifluoroacetic acid (**3**) and 6.59 mL of boron trifluoride etherate (**4**) were added via the septum. After 10 min 4.96 mL of freshly cracked and pre-cooled cyclopentadiene (**5**) were added. The temperature was kept at 0°C. After 6 h the solution was filtered through a *G3* frit containing a silica gel layer. The product was extracted with saturated sodium hydrogen carbonate solution. The collected organic phase was dried with sodium sulfate and the solvent was removed. 3.68 g of the product that was a yellow oil were collected. The oil was purified by column chromatography.

70 mg of silica gel were prepared with cyclohexane. As a solvent mixture cyclohexane/ethylacetate (20+1) was used. The product was dried under vacuum.

Yield: 611 mg (4 %) of a white powder.

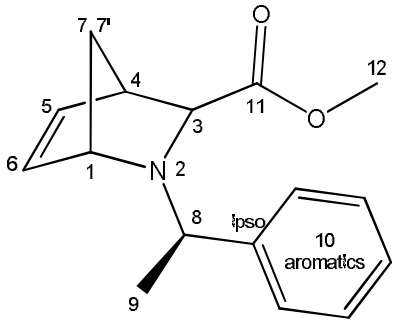


Figure 24: Numbering for *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 7.33-7.14 (5H, m, $H_{aromatics}$), 6.36-6.30 (1H, m, H_6), 5.99-5.93 (1H, dd, H_5), 3.71 (3H, s, H_{12}), 3.46 (1H, s, H_1), 3.02 (1H, s, H_4), 2.99-2.90 (1H, q, H_8), 2.42 (1H, s, H_3), 1.84-1.78 (1H, d, H_7), 1.20-1.10 (4H, d, $H_{7'}$, H_9)

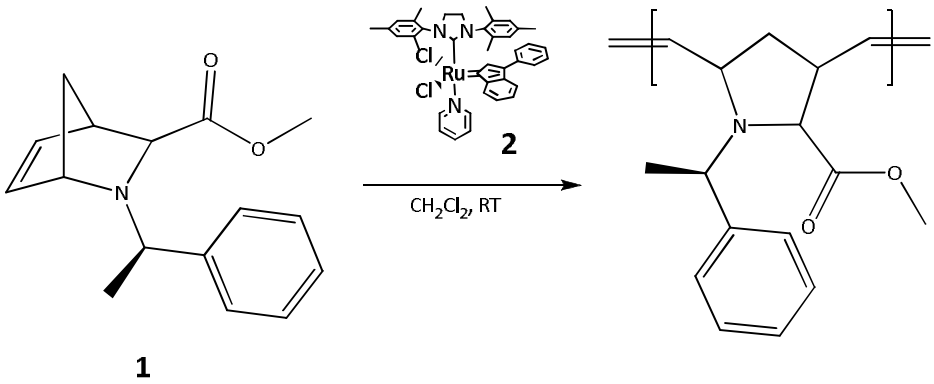
^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$): 175.5 (C_{11}), 145.1 (C_{ipso}), 136.0 (C_6), 134.0 (C_5), 128.5; 127.7 ($C_{ortho,\ meta}$), 127.2 (C_{para}), 64.5 (C_3), 63.7; 63.6 ($C_{8,1}$), 52.2 (C_4), 49.8 (C_{12}), 45.9 (C_7), 23.9 (C_9)

FT-IR (cm^{-1}, film on CaF_2):

Table 9: Characteristic IR vibrations of *methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*

functional group	υ [cm^{-1}]	Intensity
C-H arom.	3050 - 3000	m
C-H aliph.	3000 - 2800	s
O-CH_3	2840	m
C-H arom.	2000 - 1700	w
C=O	1750	vs
-CH_3	1455	s
-CH_3	1373	m
CH=CH azanorb.	1110	s

5.2.1.2. Poly-(methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)



Scheme 14: Synthesis of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*)

Table 10: Reaction data of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate)*

	1	**2**
MM [g/mol]	257.33	747.76
N [mmol]	7.77×10^{-1}	7.77×10^{-3}
Eq.	100	1
Mass [mg]	200	5.86

In a Schlenk tube 200 mg of the monomer (**1**) were dissolved in 6.77 mL of previously degassed dichloromethane. It was stirred and kept under nitrogen atmosphere. Initiator *M31* (**2**) was dissolved in 1 mL of degassed dichloromethane and quickly added to the monomer solution. A colour change of the initiator was observed that proved the immediate start of the reaction. Reaction progress was examined by thin layer chromatography with cyclohexane/ethylacetate (5+1) as a solvent. The reaction was quenched by adding ethylvinylether. Most of the solvent was removed and the product was precipitated in cold ethanol. The product was vacuum dried.

Yield: 146 mg (73 %) of brownish clumps.

^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 7.39-7.04 (5H, $H_{aromatics}$), 5.84-5.20 (2H, $H_{6,5}$), 4.36-3.75 (2H, $H_{1,8}$), 3.62-3.20 (4H, $H_{12,4}$), 3.10-2.74 (1H, H_3), 2.69-2.27 (1H, H_7), 1.50-1.00 (4H, $H_{9,7'}$)

^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$): 147.4 (C_{11}), 145.4 (C_{ipso}), 136.4 (C_6), 130.9 (C_5), 128.1, 127.1, 126.7 ($C_{aromatics}$), 69.2 (C_3), 58.9 (C_8), 57.4 (C_1), 51,0 (C_{12}), 40.2, 39.6 ($C_{4,7}$), 23.3 (C_9)

FT-IR (cm^{-1}, film on CaF_2):

Table 11: Characteristic IR vibrations of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*)

functional group	υ [cm^{-1}]	Intensity
C-H arom.	3050 - 3000	m
C-H aliph.	3000 - 2800	s
O-CH_3	2845	m
C-H arom.	2000 - 1700	w
C=O	1735	vs
-CH_3	1455	s
-CH_3	1370	m
CH=CH azanorb.	994	s

GPC ($CHCl_3$/Et_3N/i-Prop, 94:4:2):

Table 12: GPC results of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*)

M_n	M_w	M_p	PDI
31500	39800	34200	1.3

DSC (T_g): 89.34°C

STA (Δm = 5%): 310.0°C

Antimicrobial analysis: no biocidal activity proven

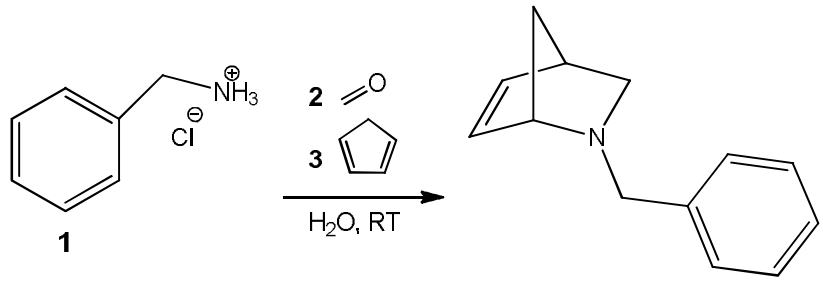
Table 13: Antimicrobial analysis results of poly(*methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate*)

Polymer on glass		Attempt 1	Attempt 2	Average	Comparison with VP at t= 0 h	Comparison with VP at t= 24 h
Staphylococcus aureus	sample	$7,6 \times 10^3$	$3,9 \times 10^4$	$2,3 \times 10^4$	13,50%	-
	Reference at t= 0 h	$1,8 \times 10^5$	$1,5 \times 10^5$	$1,7 \times 10^5$	100%	-
	Reference at t= 24 h	-	-	-	-	100%
Escherichia coli	sample	$2,1 \times 10^6$	$2,9 \times 10^7$	$1,5 \times 10^7$	1563%	5769%
	Reference at t= 0 h	$9,3 \times 10^5$	$9,9 \times 10^5$	$9,6 \times 10^5$	100%	369%
	Reference at t= 24 h	$4,7 \times 10^5$	$5,6 \times 10^4$	$2,6 \times 10^5$	27%	100%
Listeria monocytogenes	sample	$1,6 \times 10^7$	$1,7 \times 10^7$	$1,6 \times 10^7$	1455%	239%
	Reference at t= 0 h	$1,1 \times 10^6$	$1,0 \times 10^6$	$1,1 \times 10^6$	100%	16%
	Reference at t= 24 h	$5,4 \times 10^6$	$8,0 \times 10^6$	$6,7 \times 10^6$	609%	100%
	sample	$3,5 \times 10^6$	$3,2 \times 10^6$	$3,3 \times 10^6$	805%	3300%
	Reference at t= 0 h	$3,7 \times 10^5$	$4,5 \times 10^5$	$4,1 \times 10^5$	100%	410%
	Reference at t= 24 h	$1,5 \times 10^5$	$4,9 \times 10^4$	$1,0 \times 10^5$	24,40%	100%
Pseudomonas fluorescens	sample	$6,9 \times 10^3$	$4,9 \times 10^3$	$5,9 \times 10^3$	1,40%	3,70%
	Reference at t= 0 h	$4,2 \times 10^5$	$3,9 \times 10^5$	$4,1 \times 10^5$	100%	256%
	Reference at t= 24 h	$8,1 \times 10^4$	$2,4 \times 10^5$	$1,6 \times 10^5$	39%	100%

* highlighted values indicate a reduction of the bacteria cell number below the value of the reference (t= 0h, t= 24 h)

5.2.2. 2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene and derivatives

5.2.2.1. 2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene



Scheme 15: Synthesis of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

Table 14: Reaction data of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

	1	2	3
MM [g/mol]	66.10	30.03	143.62
N [mmol]	123	84.6	59.9
Eq.	2.1	1.4	1
mass [g]	8.12	2.54	8.60

In a round-bottomed flask 25 mL of deionized H_2O and 8.6 g of benzylamine hydrochloride were prepared. The reaction was stirred vigorously. 6.3 mL of 37 % aqueous formaldehyde solution and 9.9 mL of freshly cracked cyclopentadiene were added. The flask was stoppered tightly and stirred for 4 h at room temperature. A colour change from colourless to pink and then finally to yellow was observed. After 4 h 50 mL of deionized H_2O were added and the product was washed with hexane/diethylether (1+1). Then the aqueous phase was made basic by addition of potassium hydroxide and the product was extracted with diethylether. The organic phase was dried with sodium sulfate. The solvent was removed, leaving the resulting product, a yellow oil.[21,22]

Yield: 9.43 g, 85 % of a yellow oil.

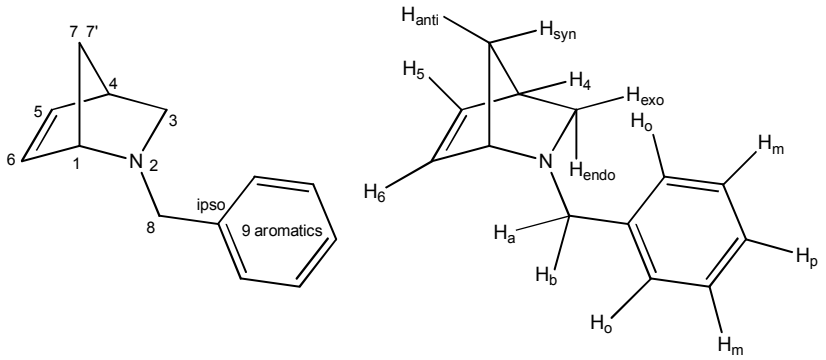


Figure 25: Numbering of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 7.33-7.10 (5H, m, $H_{aromatics}$), 6.33-6.25 (1H, m, H_6), 6.06-5.97 (1H, dd, H_5), 3.76-3.72 (1H, d, H_1), 3.54-3.46 (1H, s, H_{8b}), 3.28-3.24 (1H, d, H_{8a}), 3.14-3.04 (1H, dd, H_{exo}), 2.85 (1H, bs, H_4), 1.60-1.52 (1H, d, H_{syn}), 1.48-1.40 (1H, dd, H_{endo}), 1.38-1.29 (1H, dd, H_{anti})

^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$): 140.2 (C_{ipso}), 136.6 (C_5), 131.2 (C_6), 129.0 (C_o), 128.5 (C_m), 127.0 (C_p), 64.6 (C_1), 59.5 (C_8), 52.8 (C_3), 48.4 (C_7), 44.2 (C_4)

FT-IR (cm^{-1}, film on CaF_2):

Table 15: Characteristic IR vibrations of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

functional group	υ [cm^{-1}]	Intensity
C-H arom.	3050 - 3000	m
C-H aliph.	3000 - 2800	vs
N-CH_2-Ph	2855	vs
C-H arom.	2000 - 1700	w
C=C arom.	1495, 1454	s
C=C azanorb.	1093	s

STA (Δm = 5%): 115.7 °C

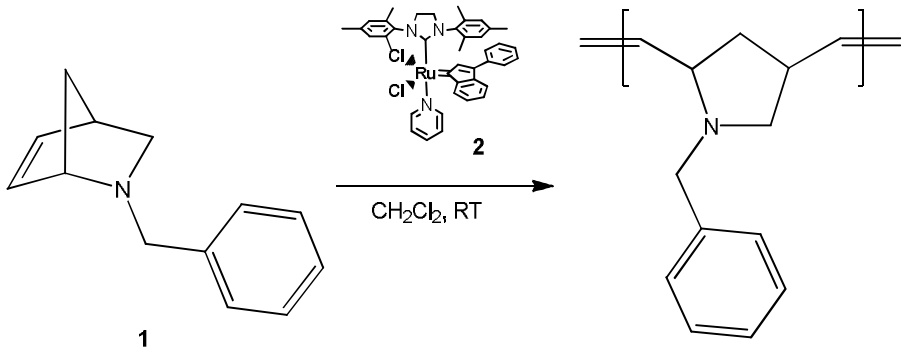
Elementary analysis:

Table 16: Elementary analysis results of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

	measurement	theoretical
%N	8,24	*7,56*
%C	78,82	*84,28*
%H	7,56	*8,16*

5.2.2.2. Poly-(2-benzyl-2-azabicyclo[2.2.1]hept-5-ene)

5.2.2.2.1. Synthesis



Scheme 16: Synthesis of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

Table 17: Reaction data of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

	1	**2**
MM [g/mol]	185.26	747.76
N [mmol]	1.35	1.35×10^{-2}
Eq.	100	1
Mass [mg]	250	10.1

The corresponding amount of monomer **1** was dissolved in 12.5 mL of previously degassed dichloromethane and prepared in a Schlenk tube that was stirred and kept under nitrogen atmosphere. Initiator M31 (**2**) was dissolved in 1 mL of degassed dichloromethane and quickly added to the monomer solution. A colour change of the initiator was observed that proved the immediate start of the reaction. Reaction progress was monitored by thin layer chromatography with n-pentane/diethylether (1+1). The reaction was quenched with ethylvinylether. Most of the solvent was removed and the product was precipitated in cold methanol. The product was vacuum dried.

Yield: 148 mg, 59 % of a greenish, gum-like substance.

^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 7.35-7.10 (5H, $H_{aromatics}$), 5.68-5.48 (1H, H_6), 5.37-5.16

(1H, H_5), 4.07-3.75 (1H, H_3), 3.41-2.70 (3H, $H_{1,2,4}$), 2.70-2.49 (1H, H_8), 2.47-2.26 (1H, H_8), 2.17-1.90 (1H, H_7), 1.49-1.20 (1H, H_7)

FT-IR (cm^{-1}, film on CaF_2):

Table 18: Characteristic IR vibrations of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

functional group	υ [cm^{-1}]	Intensity
C-H arom.	3050 - 3000	m
C-H aliph.	3000 - 2800	vs
N-CH_2-Ph	2790	vs
C-H arom.	2000 - 1700	w
C=C arom.	1497, 1454	s
C=C azanorb.	972	s

GPC ($CHCl_3$/Et_3N/i-Prop, 94:4:2): various reaction series were conducted (see

Table 21 and Table 22t for GPC results)

STA (∆m = 5%): 283.0 °C

Elementary analysis

Table 19: Elementary analysis results of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

	measurement	theoretical
%N	7,17	*7,56*
%C	82,72	*84,28*
%H	7,90	*8,16*

Antimicrobial analysis: no biocidal activity proven, (*weak activity assumed*)

Table 20: Antimicrobial analysis results of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

Polymer on glass		Attempt 1	Attempt 2	Average	Comparison with VP at t= 0 h	Comparison with VP at t= 24 h
Staphylococcus aureus	sample	$1,6 \times 10^4$	$1,8 \times 10^4$	$1,7 \times 10^4$	10%	-
	Reference at t= 0 h	$1,8 \times 10^5$	$1,5 \times 10^5$	$1,7 \times 10^5$	100%	-
	Reference at t= 24 h	-	-	-	-	100%
Escherichia coli	sample	$3,0 \times 10^3$	$2,5 \times 10^3$	$2,7 \times 10^3$	0,30%	1%
	Reference at t= 0 h	$9,3 \times 10^5$	$9,9 \times 10^5$	$9,6 \times 10^5$	100%	369%
	Reference at t= 24 h	$4,7 \times 10^5$	$5,6 \times 10^4$	$2,6 \times 10^5$	27%	100%
Listeria monocytogenes	sample	$1,8 \times 10^7$	$1,9 \times 10^7$	$1,9 \times 10^7$	1727%	284%
	Reference at t= 0 h	$1,1 \times 10^6$	$1,0 \times 10^6$	$1,1 \times 10^6$	100%	16%
	Reference at t= 24 h	$5,4 \times 10^6$	$8,0 \times 10^6$	$6,7 \times 10^6$	609%	100%
	sample	$1,0 \times 10^6$	$1,2 \times 10^6$	$1,1 \times 10^6$	268%	1100%
	Reference at t= 0 h	$3,7 \times 10^5$	$4,5 \times 10^5$	$4,1 \times 10^5$	100%	410%
	Reference at t= 24 h	$1,5 \times 10^5$	$4,9 \times 10^4$	$1,0 \times 10^5$	24,40%	100%
Pseudomonas fluorescens	sample	$3,1 \times 10^3$	$2,5 \times 10^3$	$2,8 \times 10^3$	0,70%	1,80%
	Reference at t= 0 h	$4,2 \times 10^5$	$3,9 \times 10^5$	$4,1 \times 10^5$	100%	256%
	Reference at t= 24 h	$8,1 \times 10^4$	$2,4 \times 10^5$	$1,6 \times 10^5$	39%	100%

* highlighted values indicate a reduction of the bacteria cell number below the value of the reference (t= 0h, t= 24 h)

5.2.2.2.2. Investigations on the polymerization mechanism

I.

According to the above mentioned synthesis further reaction series were conducted. Parameters and results are shown in Table 21 and Table 22.

Table 21: Reaction data of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*) series 1, initiator M31

	1 [mg]	2 [mg]	Ratio [1:X]	Reaction time [h]	Yield [%]	PDI
A	150	12	50	1	38	1.3
B	150	6	100	2	53	1.4
C	150	3	200	20	75	1.7
D	150	2	300	23	71	1.8
E	150	1.2	500	x	*75*	2.0
F	150	0.6	1000	x	*23*	2.1

Table 22: Reaction data of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*) series 2, initiator M31

	1 [mg]	2 [mg]	Ratio [1:X]	Reaction time [h]	Yield [%]	PDI
A	150	12	50	3	77	1.6
B	150	6	100	6	97	1.5
C	150	4	150	25	86	1.6
D	150	3	200	25	85	1.7
E	150	2.4	250	27	81	2.1
F	150	2	300	33	80	1.8

II.

According to the above mentioned synthesis another reaction series was conducted using a different initiator, *Hoveyda* (Figure 26). Parameters and results are shown in Table 24.

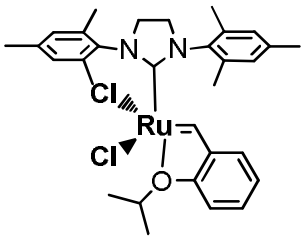


Figure 26: initiator *Hoveyda*

Table 23: molecular weight of initiator Hoveyda

	Hoveyda
MM [g/mol]	627.63

Table 24: Reaction data of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*) series 3, initiator *Hoveyda*

	1 [mg]	2 [mg]	Ratio [1:X]	Reaction time [h]	Yield [%]	PDI
A	150	10.17	50	4	71	1.2
B	150	5.08	100	4	68	1.2
C	150	3.39	150	6.5	77	1.2
D	150	2.54	200	8	82	1.2
E	150	2.03	250	8	77	1.2
F	150	1.69	300	24	95	1.2

5.2.2.2.3. Determination of the polymerization half-life

An NMR assisted recording of the polymerization of Poly-(2-benzyl-2-azabicyclo[2.2.1]hept-5-ene) was performed.

Table 25: Rection data of the NMR assisted recording of the polymerization of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*

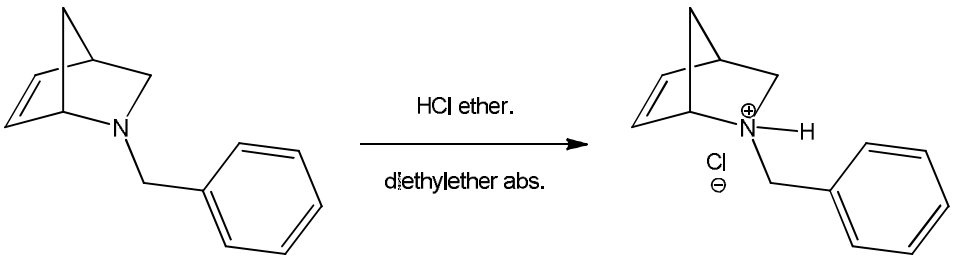
	1	**2**
MM [g/mol]	185.26	747.76
N [mmol]	7.99×10^{-2}	1.14×10^{-3}
Eq.	70	1
Mass [mg]	14.8	0.85

An NMR tube with 14.8 mg of monomer **1** dissolved in 0.4 mL of degassed deuterated chloroform was prepared. The initiator (**2**) was dissolved in 0.4 mL of the solvent and quickly added to the NMR tube, which was rapidly placed into the already preadjusted NMR machine.

Table 26: Half-life of poly(*2-benzyl-2-azabicyclo[2.2.1]hept-5-ene*)

Half life [min]
9.3

5.2.2.3. 2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride



Scheme 17: Synthesis of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride*

For this synthesis common shielding gas techniques were used.

320 mg of the monomer were prepared in a Schlenk tube that was kept under argon atmosphere. With a pipette 10 mL of absolutized diethylether were added to the monomer.

The solution was stirred. Ethereal hydrochloric acid was slowly added to the solution. Immediately a white powder precipitated. This was continued until there wasn't any new precipitate observed anymore. The product was filtered and dried.

Yield: 321 mg, 84 % of a white powder.

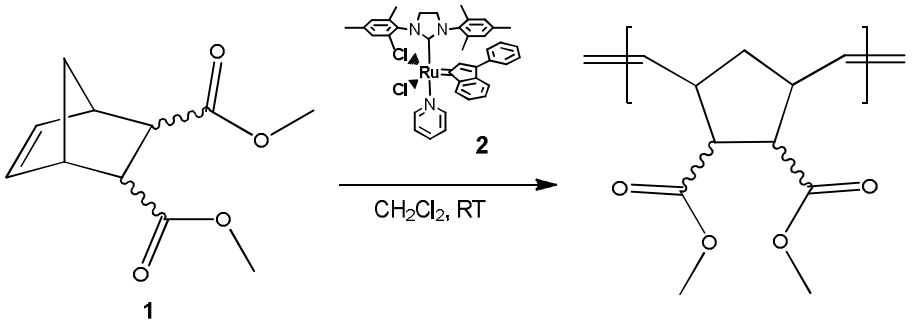
STA (∆m = 5%): 208.9 °C

Elementary analysis:

Table 27: Elementary analysis results of *2-benzyl-2-azabicyclo[2.2.1]hept-5-ene hydrochloride*

	measurement	theoretical
%N	6,41	*6,32*
%C	69,06	*70,42*
%H	7,19	*7,27*

5.2.3. Poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)



Scheme 18: Synthesis of poly-*(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*)

Table 28: Reaction data of poly-*(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*)

	1	**2**
MM [g/mol]	210.23	747.76
N [mmol]	1.90	1.90×10^{-2}
Eq.	100	1
Mass [mg]	400	14.2

400 mg of monomer **1** were dissolved in 18 mL of previously degassed dichloromethane and preprared in a Schlenk tube that was stirred and kept under nitrogen atmosphere. Initiator M31 (**2**) was dissolved in 1 mL of degassed dichloromethane and quickly added to the monomer solution. A colour change of the initiator was observed that proved the immediate start of the reaction. Reaction progress was monitored by thin layer chromatography with cyclohexane/ethyl acetate (5+1) as a solvent. The reaction was quenched with ethylvinylether. Most of the solvent was removed and the product was precipitated in cold methanol. The product was vacuum dried.

Yield: 371 mg, 93 % of a greenish, gum-like substance.

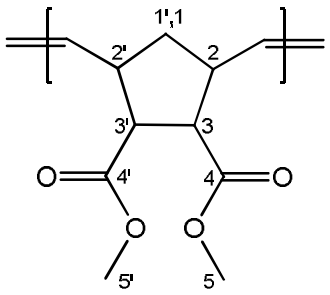


Figure 27: Numbering of poly-(*dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*)

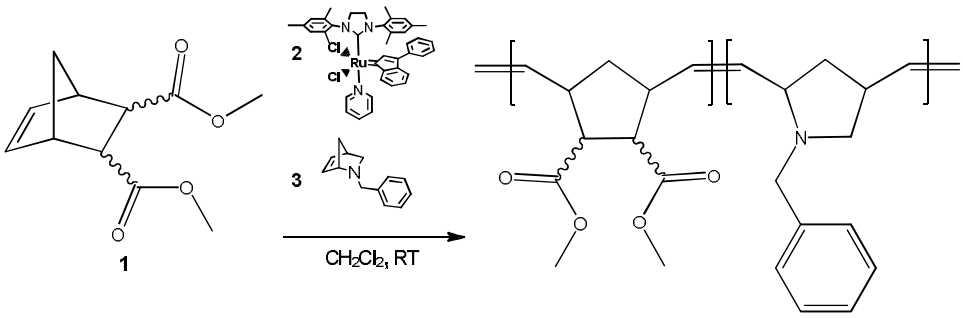
^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 5.59-5.10 (2H, CH=CH), 3.76-3.56 (6H, $H_{5,5'}$), 3.38-2.88 (2H, d, $H_{2,2',3,3'}$), 2.10-1.81; 1.55-1.36 (2H, $H_{1,1'}$)

^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$): 174.3 (2C, $C_{4,4'}$), 130.5 (2C, CH=CH), 52.0 (2C, $C_{5,5'}$), 51.7; 51.6 (4C, $C_{2,2',3,3'}$), 39.8 (1C, C_1).

Antimicrobial analysis: no biocidal activity proven (used as a reference for the analyses mentioned above)

5.2.4. Copolymers

5.2.4.1. Poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-block-Poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)



Scheme 19: Synthesis of the block co-polymers

Table 29: Reaction data of the block co-polymers

	1	2	3
MM [g/mol]	210.23	747.76	185.26
N [mmol]	4.76×10^{-1}	4.76×10^{-3}	4.76×10^{-1}
Eq.	100	1	100
Mass [mg]	100	3.56	88.12

I.

Monomer **1** was dissolved in 3.76 mL of previously degassed dichloromethane and prepared in a Schlenk tube that was kept under nitrogen atmosphere. The solution was stirred. Initiator M31 (**2**) was dissolved in 1 mL of degassed dichloromethane and quickly added to the monomer solution. A colour change of the initiator was observed that proved the immediate start of the reaction. Reaction progress was monitored by thin layer chromatography with cyclohexane/ethyl acetate (5+1). After 15 min this reaction was finished and monomer **3** was dissolved in 4.76 mL of previously degassed dichloromethane and quickly added to the reaction solution. Reaction progress was monitored by thin layer chromatography with n-pentane/diethylether (1+1). After 5 h the reaction was finished and quenched with ethylvinylether. Most of the solvent was removed and the product was precipitated in cold methanol. The product was vacuum dried.

Yield: 144 mg, 72 % of a greenish, gum-like substance.

GPC ($CHCl_3$/Et_3N/i-Prop, 94:4:2):

Table 30: GPC analysis results of *poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-block-poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

M_n	M_w	M_p	PDI
39800	61200	65000	1.5

STA (Δm = 5%): 306.2 °C

Elementary analysis:

Table 31: Elementary analysis results of *poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-block-poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

	measurement	theoretical
%N	3,34	*3,54*
%C	71,99	*72,89*
%H	7,28	*7,39*

II.

This reaction was also carried out following the exact same procedure first adding monomer **3** and afterwards monomer **1**. Reaction with monomer **2** was finished after 5.7 h.

GPC ($CHCl_3$/Et_3N/i-Prop, 94:4:2):

Table 32: GPC analysis results of *poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)-block-poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)*

M_n	M_w	M_p	PDI
55700	101000	100000	1.5

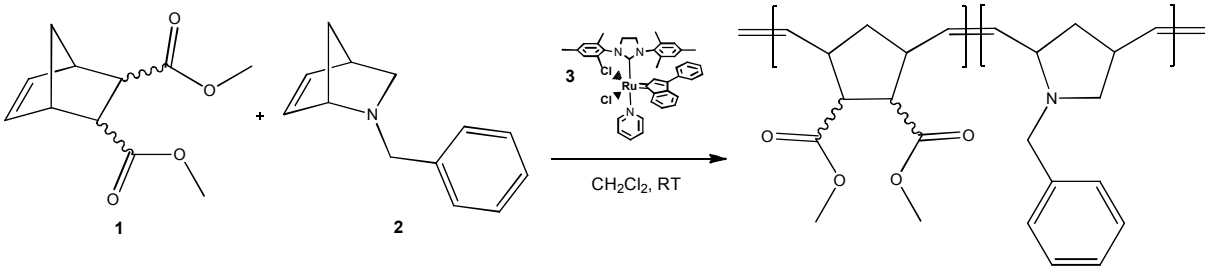
STA (Δm = 5%): 311.7 °C

Elementary analysis:

Table 33: Elementary analysis results of *poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)-block-poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)*

	measurement	theoretical
%N	3,26	*3,54*
%C	72,02	*72,89*
%H	7,29	*7,39*

5.2.4.2. Poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate-stat-2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)



Scheme 20: Synthesis of the statistical co-polymer

Table 34: Reaction data of the statistical co-polymer

	1	**2**	**3**
MM [g/mol]	210.23	185.26	747.76
N [mmol]	4.76×10^{-1}	4.76×10^{-1}	4.76×10^{-3}
Eq.	100	100	1
Mass [mg]	100	88.10	3.56

Monomer **1** as well as monomer **2** were dissolved in 2 mL of previously degassed dichloromethane respectively and prepared in a Schlenk tube that was kept under nitrogen atmosphere. The solution was stirred. Initiator M31 (**3**) was dissolved in 0.76 mL of degassed dichloromethane and quickly added to the solution of the two monomers. A colour change of the initiator was observed that proved the immediate start of the reaction. Reaction progress

was monitored by thin layer chromatography with cyclohexane/ethyl acetate (5+1) and n-pentane/diethylether (1+1) for the conversion of monomer **1** and monomer **2**, respectively. After 22 h the reaction was finished and quenched with ethylvinylether. Most of the solvent was removed and the product was precipitated in cold methanol. The product was vacuum dried.

Yield: 160 mg, 85 % of a greenish, gum-like substance.

GPC ($CHCl_3$/Et_3N/i-Prop, 94:4:2):

Table 35: GPC analysis results of *poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-stat-poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

M_n	M_w	M_p	PDI
561009	76400	67100	1.4

STA (Δm = 5%): 305.0 °C

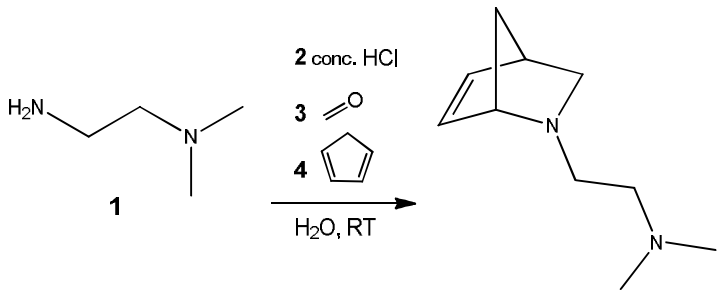
Elementary analysis:

Table 36: Elementary analysis results of *poly-(dimethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-stat-poly-(2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene)*

	measurement	theoretical
%N	3,41	*3,54*
%C	72,14	*72,89*
%H	7,30	*7,39*

5.2.5. 2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene and derivatives

5.2.5.1. 2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene



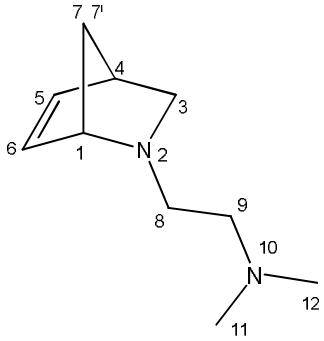
Scheme 21: Synthesis of *2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*

Table 37: Reaction data of *2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*

	1	2	3	4
MM [g/mol]	88.15	36.46	30.03	66.10
N [mmol]	59.6	119	84.6	124
Eq.	1	2	1.4	2.1
mass [g]	5.25	4.29	2.54	8.20

In a round-bottomed flask 25 mL of deionized H_2O and 6.5 mL (5.25 g) of N,N-dimethylethylene-diamine (**1**) were prepared. The pH value was tested to be 12. The pH value was brought to 1 by adding 9.4 mL of conc. HCl (**2**). The reaction was stirred vigorously. 6.3 mL (2.54 g) of 37 % aqueous formaldehyde solution (**3**) and 10.0 mL (8.20 g) of freshly cracked cyclopentadiene (**4**) were added. The flask was stoppered tightly and stirred for 4 h at room temperature. A colour change from colourless to clouded, yellow was observed. After 4 h 50 mL of deionized H_2O was added and the product was washed with hexane/diethylether (1+1). Then the aqueous phase was made basic by addition of sodium hydroxide and the product was extracted with diethylether. The organic phase was dried with magnesium sulfate. The solvent was removed, leaving the resulting product, a yellow oil [21,22].

Yield: 3.75 g, 38 % of a brown oil.

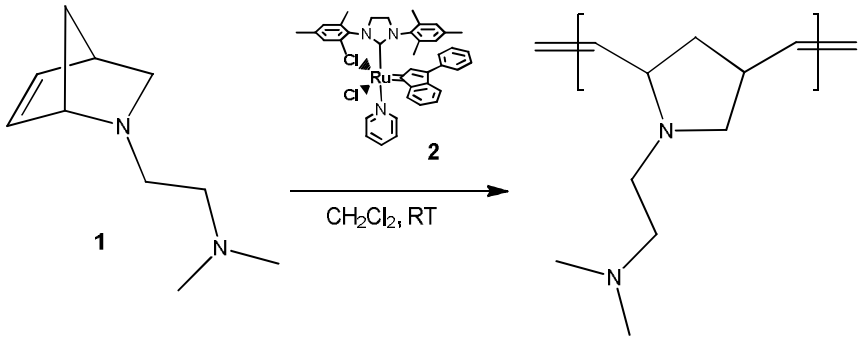


^{1}H NMR (δ, 20°C, 300 MHz, $CDCl_3$): 6.33-6.25 (1H, m, H_5), 6.04-5.95 (1H, dd, H_6), 3.85 (1H, s, H_1), 3.19-3.11 (1H, dd, H_{3exo}), 2.89 (1H, s, H_4), 2.65-2.30 (4H, m, $H_{8,9}$), 2.27-2.14 (6H, m, $H_{11,12}$), 1.62-1.54 (1H, d, H_7), 1.48-1.40 (1H, dd, H_{3endo}), 1.40-1.32 (1H, dd, H_7)

^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$): 136.3 (C_5), 131.7 (C_6), 65.1 (C_1), 58.9; 52.9 ($C_{9,8}$), 52.3 (C_3), 48.2 (C_7), 46.0;45.9 ($C_{11,12}$), 43.8 (C_4)

5.2.5.2. Poly-(2-(N,N-dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene)

5.2.5.2.1. Synthesis



Scheme 22: Synthesis of poly(*2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*)

Table 38: Reaction data of poly(*2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene)*

	1	**2**
MM [g/mol]	166.26	747.76
N [mmol]	6.02×10^{-1}	6.02×10^{-3}
Eq.	100	1
Mass [mg]	100	4.50

I.

100 mg of monomer **1** were dissolved in 5.02 mL of previously degassed dichloromethane and preprared in a Schlenk tube that was stirred and kept under nitrogen atmosphere. Initiator M31 (**2**) was dissolved in 1 mL of degassed dichloromethane and quickly added to the monomer solution. A colour change could not be detected.

II.

The exact same procedure, stated above, was performed using toluene as a solvent and keeping the reaction on reflux.

5.2.5.2.2. Investigations on the reaction step mechanism

Initiators M31 (**2**) and M51 (**3**) were dissolved in 0.6 mL of previously degassed $CDCl_3$ in an NMR tube, respectively. 1.2 eq of Monomer **1** were dissolved in 0.25 mL of previously degassed $CDCl_3$ and quickly added to each tube. Reaction progress was monitored by NMR measurements.

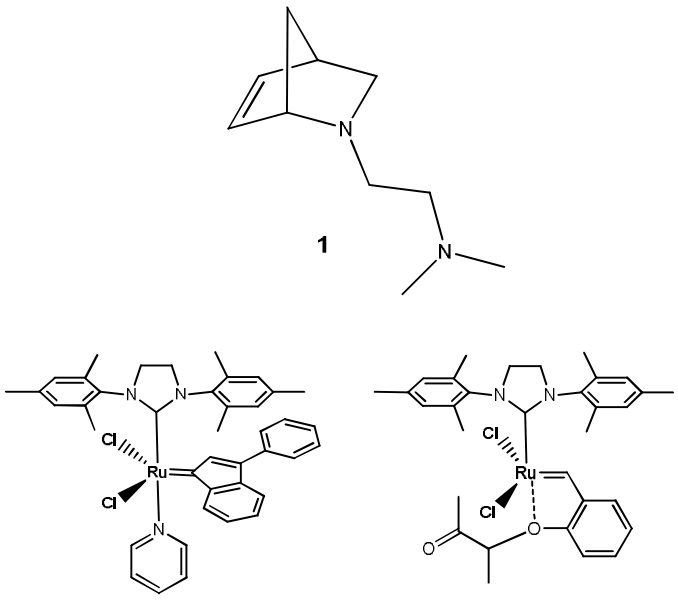


Figure 28: ***2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*** **(1) and initiators M31 (2), M51 (3)**

Table 39: Reaction data of the reaction mechanism investigation of poly(*2-(N,N-Dimethylethylene-amine)-2-azabicyclo[2.2.1]hept-5-ene*)

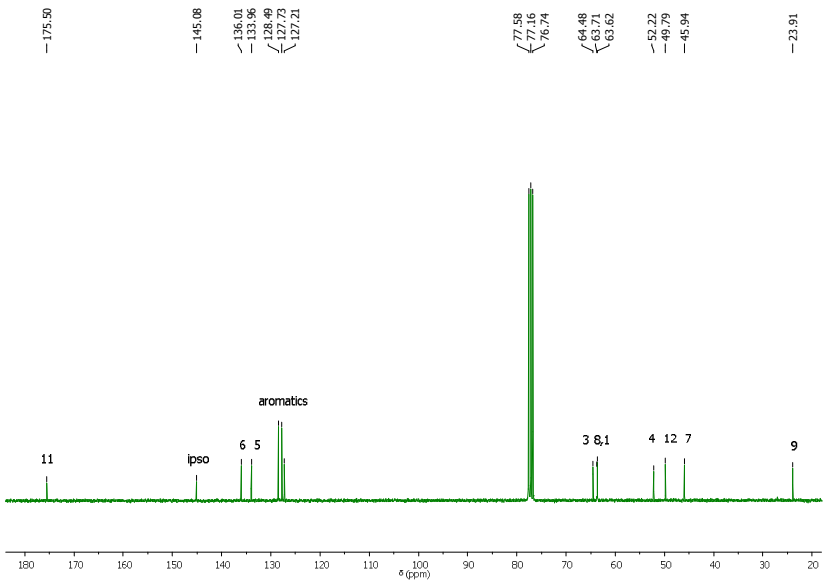
	1	**2**	**3**
MM [g/mol]	166.26	747.76	655.64
N [mmol]	1.60×10^{-2}	1.34×10^{-2}	1.34×10^{-2}
Eq.	1.2	1	1
Mass [mg]	2.66	10	8.76

6. Appendix

6.1. Additional Data

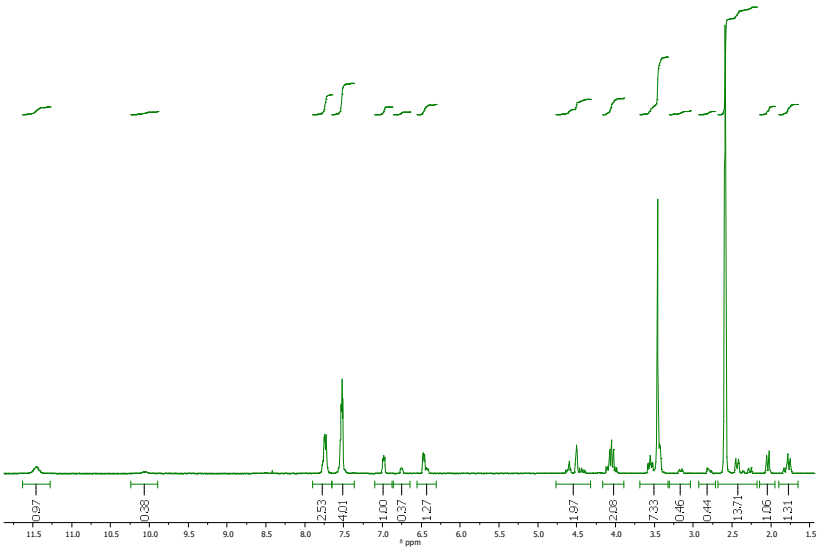
Ad 3.1.2.2

^{13}C NMR (δ, 20°C, 75 MHz, $CDCl_3$)



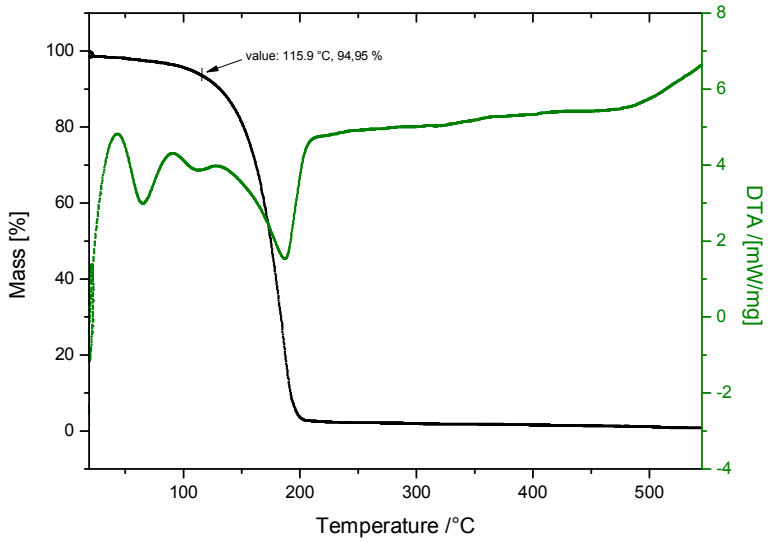
Ad 3.2.4.3

^{1}H NMR (δ, 20°C, 300 MHz, d-DMSO)



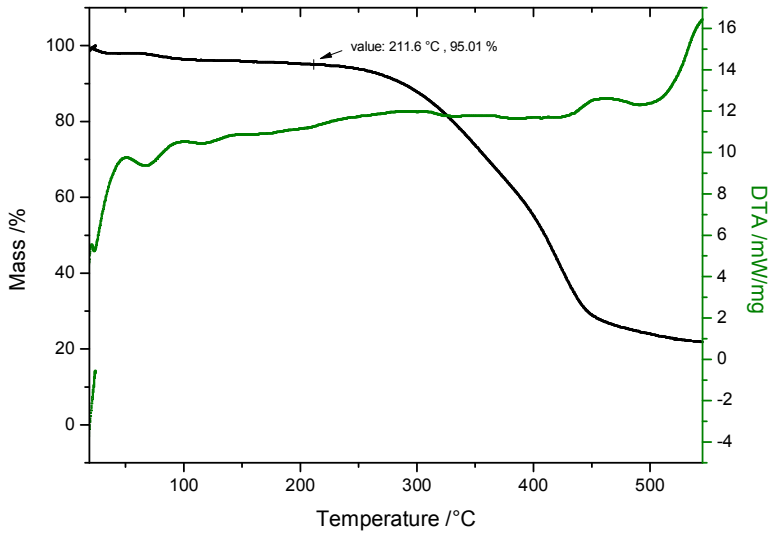
Ad 3.2.2.2

STA analysis plot



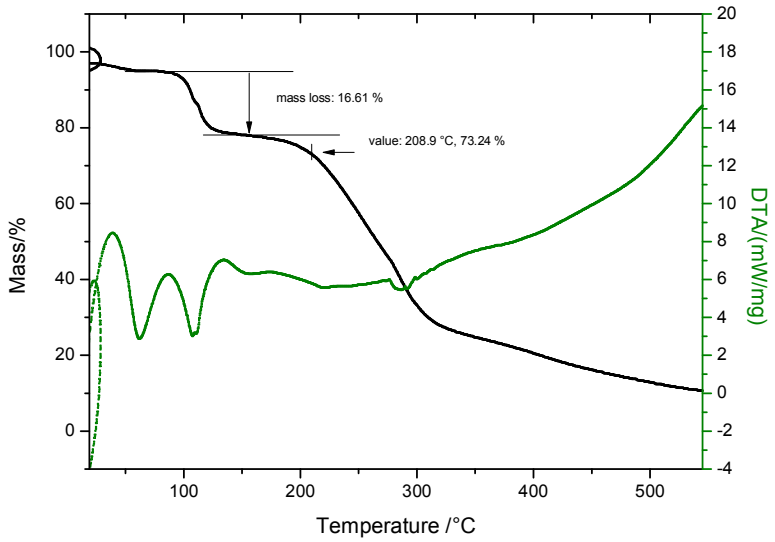
Ad 0

STA analysis plot



Ad 3.2.4.3

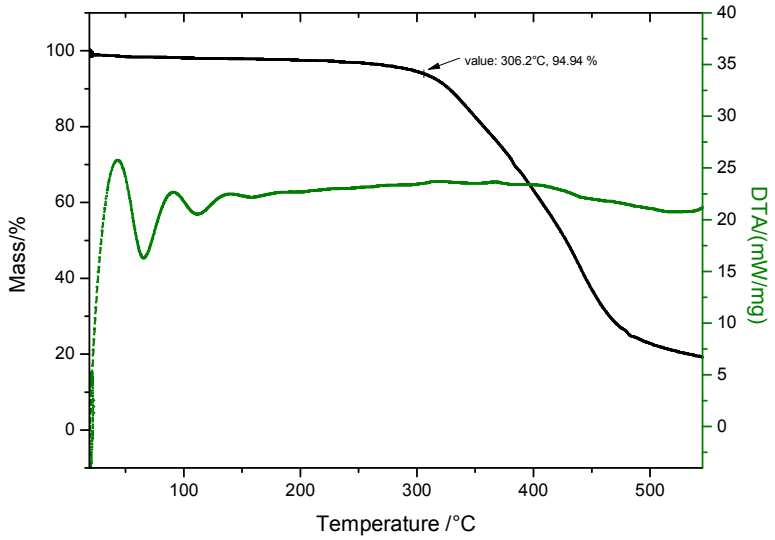
STA analysis plot



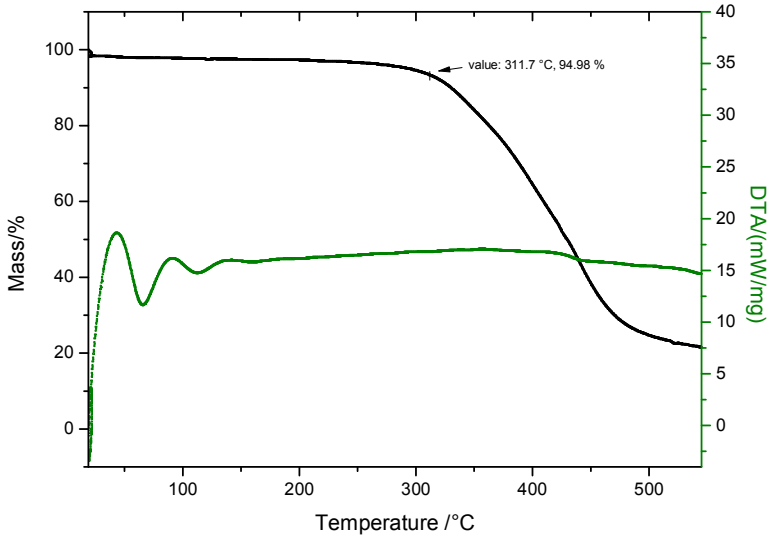
Ad 3.4.3

STA analysis plots

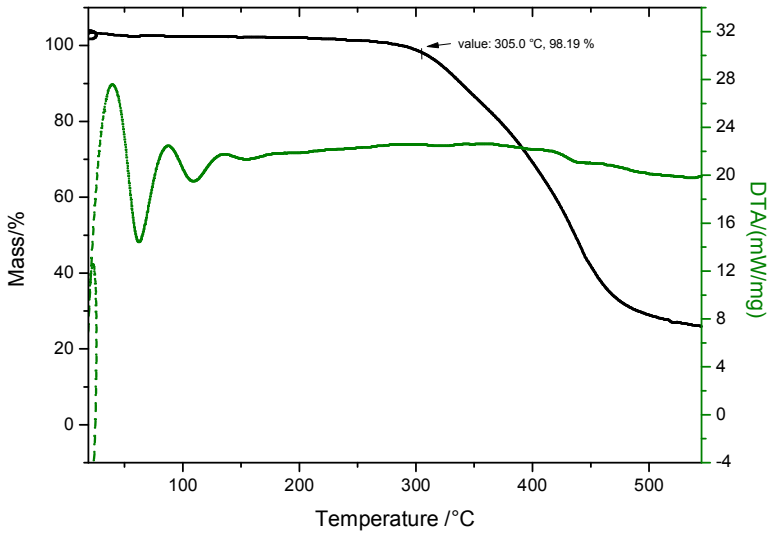
Co-polymer 1



Co-polymer 2



Co-polymer 3



6.2. Abbreviations

(in alphabetical order)

abs.	absolutized
aliph.	aliphatic
arom.	aromatic
$CHCl_3$	chloroform
$CDCl_3$	deuterated chloroform
CD_3OD	deuterated methanol
conc.	concentrated
COSY	correlation spectroscopy
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
eq.	equivalent
Et_3N	triethylamine
ether.	ethereal
FT-IR	Fourier transform – infrared spectroscopy
GPC	gel permeation chromatography
h	hours
HCl	hydrochloric acid
HSQC	heteronuclear single quantum coherence
IR	infrared spectroscopy
i-Prop	2-propanol
min	minutes
MM	molar mass
M	molar concentration
M_n	number average molar mass
M_w	weight average molar mass
M_p	molar mass at the peak maximum
MS	mass spectrometry
N	amount of substance
NMR	nuclear magnetic resonance spectroscopy
NOESY	nuclear Overhauser effect spectroscopy
PDI	poyldispersity index
RT	room temperature
STA	simultaneous thermal analysis
TMS	tetramethylsilane
T_g	glass transition temperature
υ	wavenumber

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