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Bifunctional monomers for radical polymerisation and postfunctionalisation via metathesis

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Zusammenfassung

Diese Arbeit beschäftigt sich mit der Synthese zweier bifunktionaler Monomere, die mittels Atom Transfer Radikalischer Polymerisation (ATRP) polymerisiert und mittels Kreuzmetathese funktionalisiert wurden. Die ATRP soll eine enge molekulare Gewichtsverteilung sowie kontrollierte radikalische Polymerisation hervorrufen. Die Metathese wiederum soll die Eigenschaften des Polymers verbessern.

Das erste Monomer (2-(methacryloyloxy)ethyl norborn-5-en-2-carboxylat) wurde mittels Veresterung und Diels-Alder-Reaktion hergestellt, während das zweite Monomer (*endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornen-2,3-dicarboximid) vom Norbornen Anhydrid mit Ethylendiamin und Maleimid umgesetzt wurde. Anschließend wurden die beiden Monomere mittels ATRP copolymerisiert (Monomer 1 mit Methylmetacrylat und Styrol, Monomer 2 mit Styrol), nachdem zuvor an Testmonomeren (Methylmetacrylat, Styrol und Ethylacrylat) die Erfahrungen auf dem Stand der Technik gesammelt und der Stand der Technik verbessert wurde. Die Copolymerisation mit Styrol war mit beiden Monomeren erfolgreich.

Gleichzeitig wurde versucht die Monomere zu funktionalisieren (Monomer 1 mit Ethylacrylat und Styrol, Monomer 2 mit Styrol). Die Funktionalisierung war nur partiell erfolgreich, da nicht, wie gewünscht, nur funktionalisierte Monomere entstanden, sondern die Monomere oligomerisierten.

Die Produkte wurden mittels NMR-Technik sowie Gelpermeationschromatographie (GPC) und Infrarotspektroskopie (FTIR) charakterisiert.

Abstract

The recent work describes the synthesis of two bifunctional monomers, which are polymerised by atom transfer radical polymerisation (ATRP) and functionalised by cross metathesis on one hand. A narrow molecular weight distribution as well as controlled radical polymerisation shall be obtained by ATRP. On the other hand the cross metathesis shall develop better properties of the polymers.

The first monomer (2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate) was synthesised by esterfication and a Diels-Alder reaction, while the second monomer (*endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide) was synthesised based on the carbic anhydride with ethylene diamin and maleimide. Afterwards both monomers were copolymerised by ATRP (monomer 1 with methyl metacrylate and styrene, monomer 2 with styrene). Several polymerisation trials (of methyl metacrylate, styrene and ethyl acrylate) were done based on the state of art which was optimised in a second step. The copolymerisation with styrene was in both cases successful.

In the mean time the monomers were functionalised (monomer 1 with ethyl acrylate and styrene, monomer 2 with styrene). The functionalisations were partially successful. The monomers have oligomerised and the ends have functionalised, although it was desired to get monomers functionalised.

The characterisation of the products was done by NMR-spectroscopy, gel permeation chromatography (GPC) and infrared spectroscopy (FTIR).

Acknowledgements

First and foremost I want to express my gratitude to my supervisor Assoc. Prof. Dr. Christian Slugovc for the opportunity to write my diploma thesis as part of his group and for his guidance and advices during the course of my work.

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Next, I would like to thank all members of the ICTM group for the wonderful working atmosphere and their valuable support. I want to give a special thank you to my dear office 'roomies' who cheered me up with all those long, sophisticated and very deep conversations always on a steady standard. Thank you, Katie, Katrin, Sascha and David!

All the scientific research would be needless without characterisation and the right chemicals. Therefore I want to give my thanks to Dipl.-Ing. Dr.techn. Petra Kaschnitz for her help in NMR spectroscopy, Amtsrätin Ing. Josefine Hobisch for the endless measurements of GPC and Birgit Ehmann for the support each and everywhere!

My deepest thanks I give to my family. They gave me their everlasting support and pushed me always over the limits. They supported me with their trust and helped me to find my own way in troubles and doubts. Thank you for staying understanding!

Last but not least, I would like to thank my friends - new and old ones. We shared a lot together, either by living together or by sharing the same hobbies as well as travelling together. Thank you for your understanding, your encouragement and making me laugh all the time. There is no way to express my happiness of having you guys!

Contents

1. Introduction

Polymerisation techniques which have the aim to improve the chain-growth based on cationic, anionic and conventional free radical processes were developed and performed in the last decades. The commodity polymers, like polyvinyl chloride, polyethylene, polypropylene, polystyrene etc., which are formed have a wide range of molecular weight distribution which gives uplift to diverse and important physical and mechanical properties. Often this is needed for several applications, but some need precisely controlled polymers. Living radical polymerisation enables the control over the architecture of the polymer. This includes the composition of the polymer as well as its molecular weight, the polydispersity and the functionality[1]; therefore it can be used to prepare organic/inorganic composites, surface-tethered copolymers as well as bioconjugates.[2]

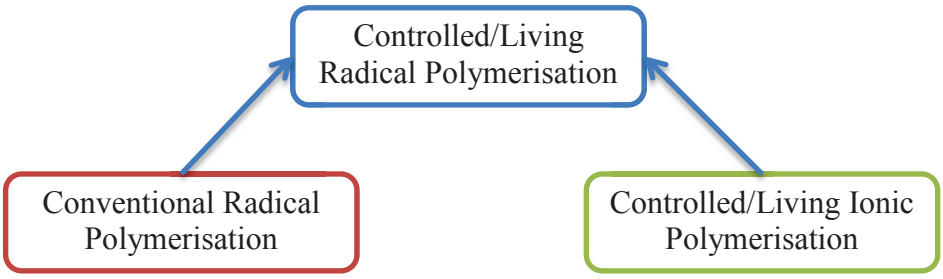


Figure 1: Development of controlled/living radical polymerisation.

The polymer science was changed due to the discovery of living anionic polymerisation by Michael Szwarc.[3,4] He developed techniques to have living species in polymerisations, which were applied onto conventional radical polymerisation (RP). The fundamental principles behind radical polymerisations include slow initiation and chains, which are essentially dead at any instant. But controlled/living radical polymerisation (CRP) includes fast initiation as well as absence of termination, which was developed not only in anionic, but also in cationic, ring-opening and coordination polymerisations. The lifetime of the growing chains is another difference between the conventional and the controlled polymerisation. While RP has a lifetime of about one Second, the lifetime of CRP is extended to more than one hour because

1 Grajales, S.; *Sigma-Aldrich*, **Controlled Radical Polymerization Guide**, *Preface*.

[2] Matyjaszweski, K.; & Spanswick, J.; *materialstoday*, **2005**, Controlled/living radical polymerization, p. 26-33.

[3] Szwarc, M.; *Nature*, **1956**, *vol. 176*, p. 1168-1169.

[4] Szwarc, M.; Levy, M.; & Milkovich, R.; *J.Am. Chem. Soc.*, **1956**, *vol. 78*, p. 2656-2657.

of the intermittent reversible activation and the participation of dormant species. Finally the termination is another difference between the two polymerisation techniques. In RP termination usually occurs between long chains and new ones are generated constantly. By comparison CRP has short chains at the beginning and these become longer progressively.[5] Dormant species, which is the inactive part of the reaction, are remaining chains, which are capable of chain extension, reactivation as well as functionalisation. Due to this fact, CRP behaves like a 'living' system.[6,7]

For example, a possible living radical polymerisation of styrene was observed and developed for emulsion polymerisation, in 1957.[8]

All controlled/living radical polymerisations have in common that an establishment of a dynamic equilibrium between various dormant species and propagating radicals is central to them.[6,7] To achieve the desired polydispersity, the wished molecular weight and the chain architecture, the system uses the fast exchange between the dormant and the active species.

Three fundamental techniques have developed out of controlled radical polymerisation, which are atom transfer radical polymerisation (ATRP), reversible addition/fragmentation chain transfer (RAFT) and nitroxide-mediated polymerisation (NMP).1

Every procedure has its benefits and limitations. While ATRP is versatile and the catalysts meet specific needs, it has to use transition metals and its characteristics are affected by many variables[1], including temperature, solvent, monomer, catalyst and initiator.[9,10] RAFT is versatile as well, but does not need, opposite to ATRP, any transition metals. The primary limitation is that it has a high potential for odour and discolouration.[1] Finally NMP is the least versatile technique, but has a low potential for odour and discolouration and it also does not need any transition metals.[1] Still, ATRP is the most cited technique of the three. Furthermore, it is one of the most powerful synthetic method for polymers, because of the ability to control

[5] Braunecker, W. A.; & Matyjaszewski, K.; *Prog. Polym. Sci.,* **2007**, *vol. 32*, p.93-146.

[6] Greszta, D.; Mardare, D.; & Matyjaszewski, K.; *Macromolecules*, **1994**, *vol. 27*, p. 638-644.

[7] Goto, A.; & Fukuda, T.; *Prog. Polym. Sci.*, **2004**, *vol. 29*, p. 329-385.

[8] Bianchi, J. P.; Price, F. P.; & Zimm. B. H.; *J. Polym. Sci.*, **1957**, *vol. 25*, p. 27-38.

[9] Matyjaszewski, K.; *Chem. Rev.*, **2001**, *vol. 101*, p. 2921.

[10] Nanda, A. K.; & Matyjaszewski, K.; *Macromolecules*, **2003**, *vol. 36*, p. 1487-1493.

the molecular weight of the polymer as well as to achieve a narrow distribution of the molecular weight.[11]

ATRP has a broad area of application. According to Matyjaszewski et al.[12] polymers achieved by ATRP can be used as drug delivery systems, thermoplastic elastomers, porous membranes, photonics, particle dispersants, carbon nanofibres and many more. Next to the variaties of possible applications, there are many variations in the composition (homopolymer, periodic polymers, block polymers, gradient polymers, statistical polymers), architecture (hybrid particles, side chain block copolymer brush, multifunctional star), topology (linear, cyclic, star, grafted, network, branched and hyper branched) and functionality (end-functional, telechelic, macromonomer, side functional, multi-functional).

Due to the oxygen-sensitivity of the catalyst several variations of ATRP was developed, including reverse, Activators ReGenerated by Electron Transfer (ARGET), Activators Generated by Electron Transfer (AGET) and Initiators for Continuous Activator Regeneration (ICAR) ATRP. The advantage of normal ATRP is that it is very versatile, but its biggest limitation is the high copper content (which is problematic for biomedical and food packaging applications) and the unstable catalyst precursor. This disadvantage is lowered in the variations mentioned above. They all have a low copper content of copper. Besides this the catalyst precursors are more stable. Limitations in the new variants compared to the common ATRP are:

- high tin content (AGET and ARGET),
- AIBN, which causes side reactions (ICAR), and
- limited end group functionality (reverse ATRP).

It depends upon the needs of the application which variant of ATRP is the most appropriate one. Is it more important to minimize copper concentrations? Or is a narrow distribution of chain lengths the desired priority?[13] The ligand, which was chosen for the synthesis done in the recent study, was *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), which balances between activity and control.[14]

[11] Coca, S.; & Woodworth, B. E.; *Polym. Mat. Sci. Eng.*, **2004**, *vol. 90*, p. 182-184.

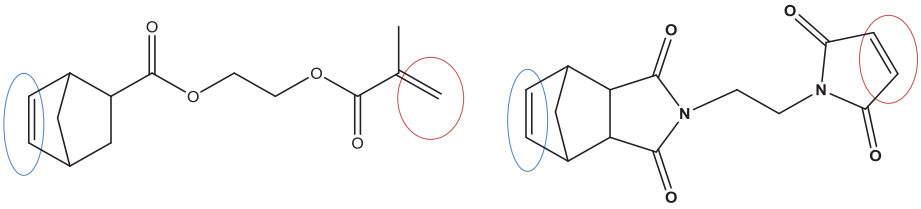
[12] Matyjaszewski, K.; & Tsarevsky, N. V.; *J. Am. Chem. Soc.*, **2014**, *vol. 136*, p. 6513-6533.

[13] Grajales, S.; *Sigma-Aldrich*, **Controlled Radical Polymerization Guide**, *Tools for Performing ATRP.*

[14] Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; & Matyjaszewski, K. J.; *J. Am. Chem. Soc.*, **2008**, *vol. 130*, p. 10702-10713.

2. Research objectives

The aim of this thesis was to synthesise two bifunctional monomers. On one hand it should be possible to functionalise the norbornene group of the monomer with acrylates or styrene by cross metathesis. On the other hand another functional group should be used in the so-called atom transfer radical polymerisation (ATRP). ATRP was chosen due to the fact that the polymer's molecular weight is controlled as well as the achievement of narrow molecular weight distribution (chapter 1).



Monomer 1 **Monomer 2**

Figure 2: Monomer 1= HEMA-Nbe; Monomer 2= DCI-Et-MI-Nbe.

Monomer 1 and monomer 2 were chosen as target substances because of the two functional groups, which are marked red and blue (Figure 2). The blue marker indicates the functional group in the norbornene moiety. It can be functionalised by olefin metathesis (Figure 3).

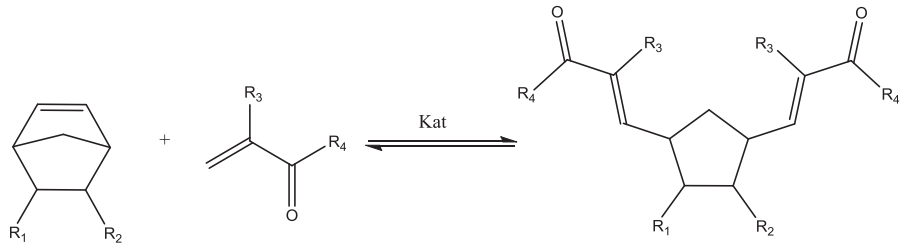


Figure 3: Cross metathesis of the norbornene moiety.

The red marked moiety can be polymerised. This happens by ATRP (Figure 4). The advantage of this polymerisation is that these reactions are very robust and tolerant of many moieties like vinyl, allyl, epoxy, hydroxyl and amino groups in either initator or monomer.[15]

[15] Cowie, J. M. G.; & Arrighi, V.; *In Polymers: Chemistry and Physics of Modern Materials*; CRC Press Taylor and Francis Group: Boca Raton, Fl, **2008**; *3rd Ed*., pp. 82–84.

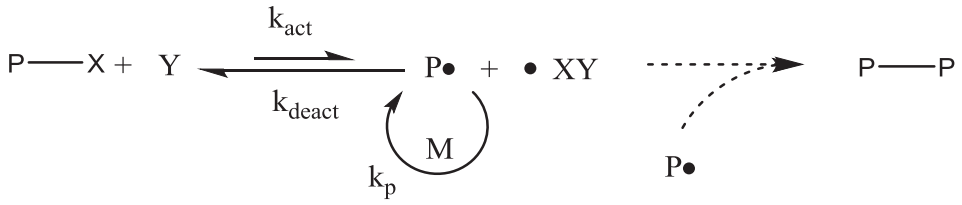


Figure 4: ATRP equilibrium equation (P* active species; Y transition metal complex; X halide; M monomer; k reaction rate;).

The active initiator radical P* is generated by a reversible redox process, which is catalysed by a transition metal complex Y (dormant initiator[13]). Y reacts with X, which is abstracted by a one-electron-oxidation of P-X. [16] Most of the time the reaction remains on the left side of the reaction, which minimises the possibility for termination. This control via termination is the main benefit of ATRP, as well as that only one radical is formed during activation.[13]

[16] Matyjaszewski, K.; *Chem. Rev.*, **2001,** *vol. 101,* p. 2921.

3. Results and discussion

Two bifunctional monomers were synthesised (2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (HEMA-Nbe) and *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide (DCI-Et-MI-Nbe)). Their norbornene groups were functionalised with acrylates and styrene. The second functional group (C=C double bond) was polymerised by ATRP.

The HEMA-Nbe[17, 18, 19] was synthesised via two different pathways. The DCI-Et-MI-Nbe[20, 21] has been tried to synthesise once with the *exo* and once with the *endo* educt. In a next step the norbornene moiety of the *endo*-intermediate was reacted in a cross metathesis with acrylates (methyl metacrylate (MMA) and ethyl acrylate (EA)) and styrene.

In order to identify appropriate reaction conditions for ATRP, different model polymerisations were performed on MMA, styrene and EA. In this regard a four molar reaction, which is intiated with the ligand *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), was found as the most suitable for this polymerisation technique.

In this section the synthesis of the monomers, the functionalisation and the polymerisation are discussed as well as some unexpected issues which we faced during the experimental work. NMR (^{1}H, ^{13}C-APT) spectroscopy was mainly used for structural characterisation of the synthesised molecules. GPC was used in order to characterise the polymers reagarding the average molecular weight, molecular weight distribution (both by weight (M_w) and numbers (M_n)) and polydispersity index (PDI)

Detailed reactions are mentioned in chapter 5, including condtions and reaction equations.

[17] Davis, R. D.; Jarrett, W. L.; Mathias, L. J.; Steadman, S. J.; Redfearn, R. D.; & Bunn, A.; *Macromolecules*, **2004**, *vol. 37*, # 10, p. 3699 – 3706.

[18] Sinner, F.; Buchmeiser, M. R.; Tessadri, R.; Mupa, M.; Wurst, K.; & Bonn, G. K.; *J. Am. Chem. Soc.*, **2008**, *vol. 120*, p. 2790-2797.

[19] Xia, Y.; & Larock, R. C.; *Polymer Preprints*, **2010**, *vol. 51 (1)*, p. 764-765.

[20] Patil, S.V.; Mahale, K.A.; Gosavi, K.S.; Deshmukh, G. B.; & Patil, N. S.; *Organic Preparations and Procedures International*, **2013,** *vol. 45,* p. 314-320.

[21] Schaefer, M.; Hanik, N.; Kilbinger, A. F. M.; *Macromolecules,* **2012,** *vol. 45*, p. 6807-6818.

3.1. Preparation

3.1.1. Synthesis of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate

HEMA-Nbe was synthesised on two different pathways. The first pathway included cyclopentadiene and acryloyl chloride as starting materials. Norborn-5-ene-acyl chloride was formed by Diels-Alder reaction, which can only be performed if cyclopentadiene was freshly cracked. Cyclopentadiene dimerises to dicyclopentadiene within a few hours at room temperature[22] (Figure 5).

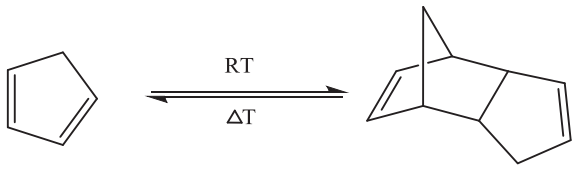


Figure 5: Diels-Alder reaction of cyclopentadiene to dicyclopentadiene.

Another problem occured, during this pathway of the synthesis. For purification of the intermediate the reaction was extracted with aqueous $NaHCO_3$. An odour of HCl was recognised and it was guessed that the chloride of the intermediate after the reaction with acryloyl chloride was abstracted and replaced by hydroxide. This hypothesis was proven by ^{1}H-NMR analysis; Figure 6.

[22] https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/enrgtop.htm; downloaded 22.07.2014

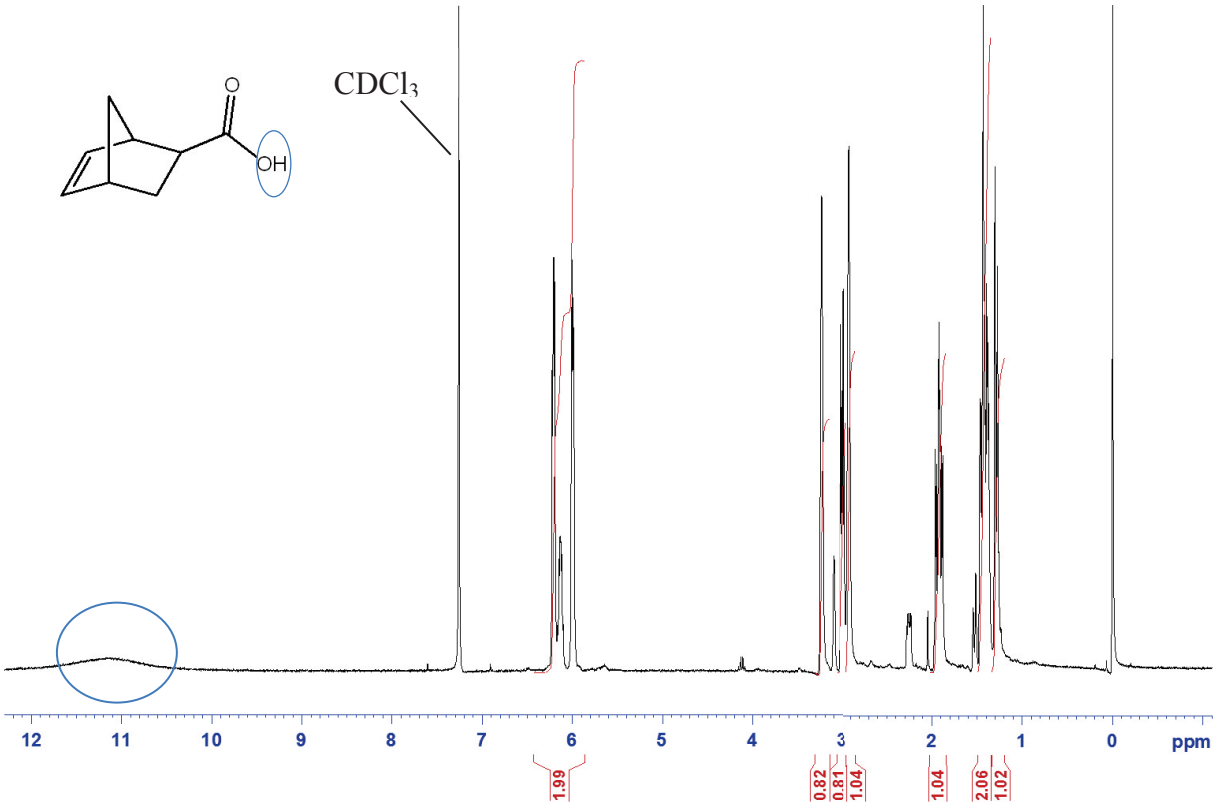


Figure 6: ^{1}H-NMR of norborn-5-ene-2-carboxylate.

Therefore a new experiment was performed and the intermediate was successfully purified this time by distillation; Figure 7.

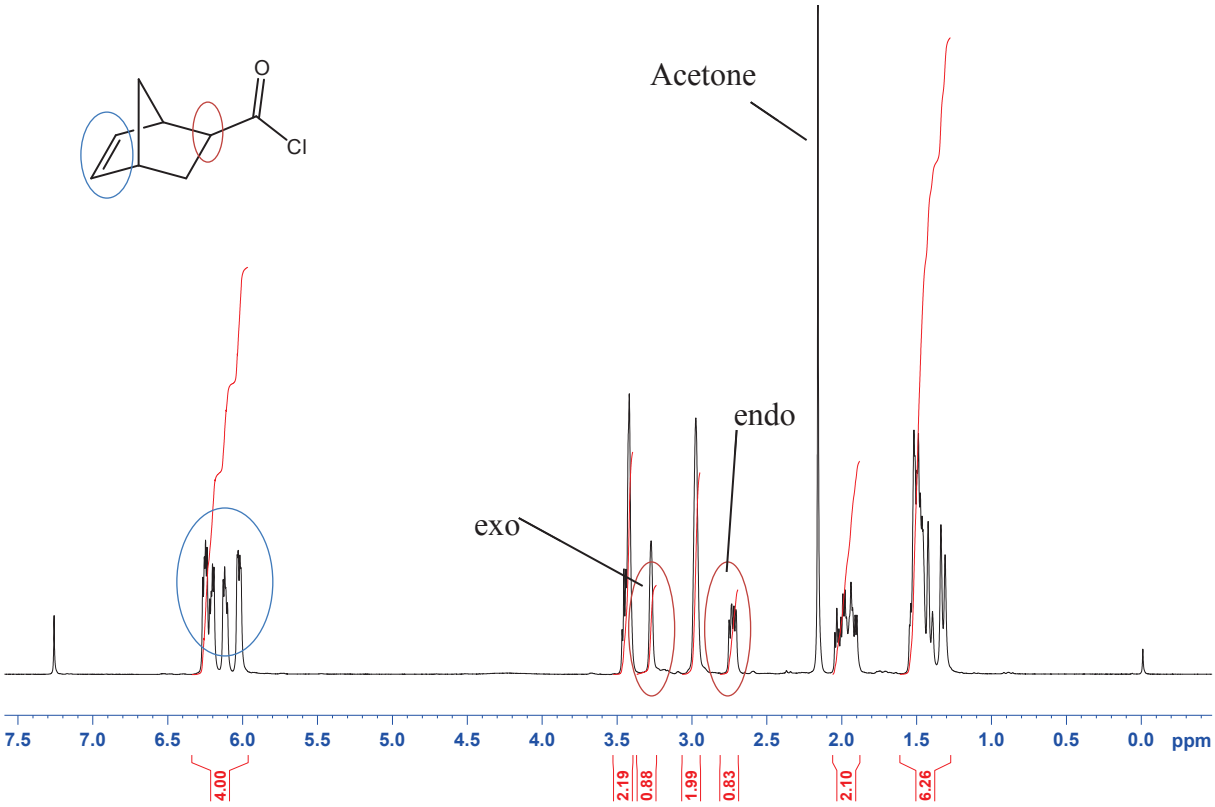


Figure 7: ^{1}H-NMR of norborn-5-ene-acyl chloride.

Both the *exo* and the *endo* acyl chloride were synthesised. Therefore it was assumed that the norbornene peaks at 6.00 ppm are equal to four protons. The *exo* and the *endo* product form two different peaks at 3.28 and 2.76 ppm. The correlation was proved with COSI-NMR; Figure 8.

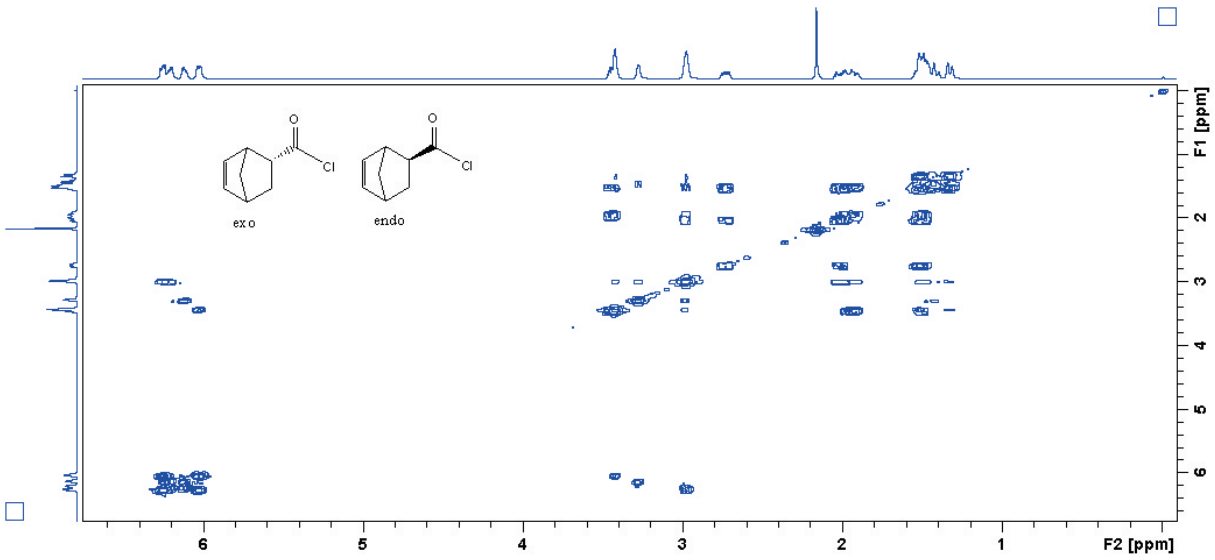


Figure 8: COSI-NMR of norborn-5-ene-acyl chloride.

Finally hydroxyethylmetacrylate (HEMA) was added and the product HEMA-Nbe (monomer 1) was formed; Figure 9.

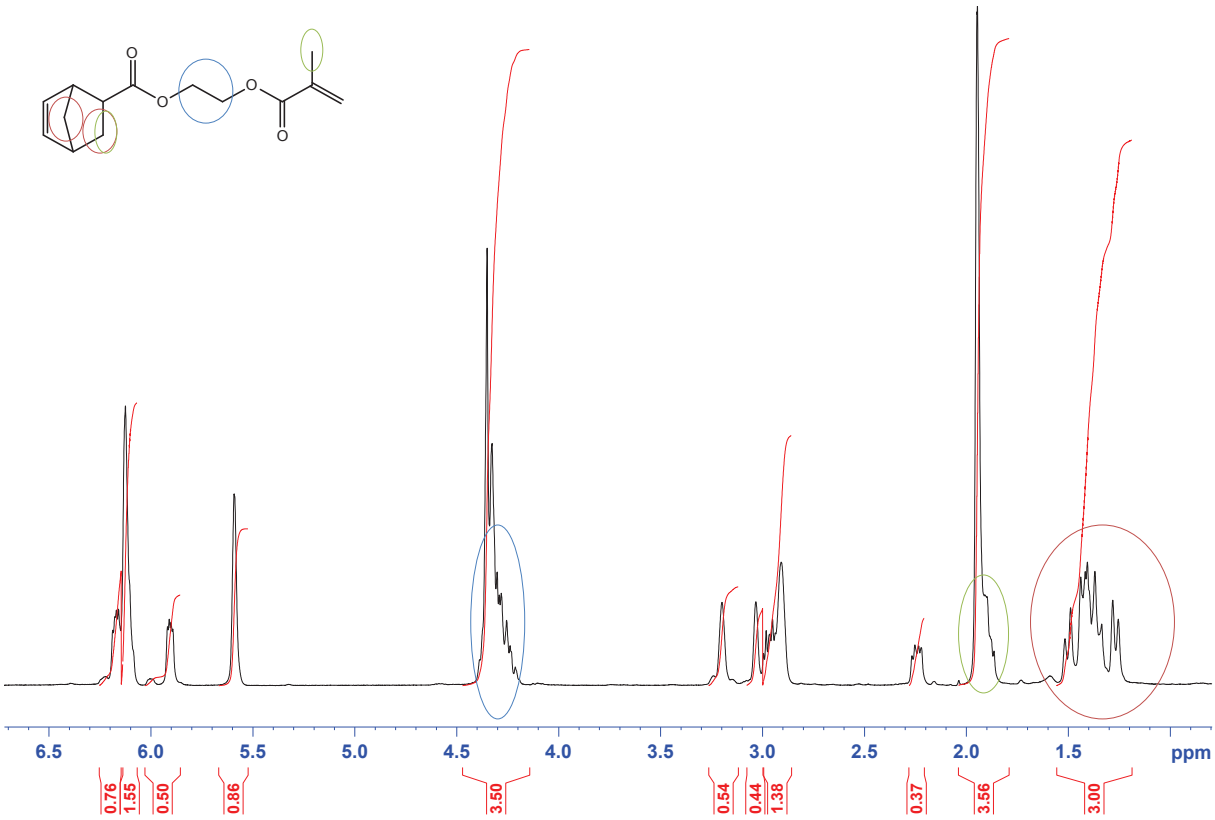


Figure 9: ^{1}H-NMR of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

Because of the high scent impact of the acyl chloride and the low yield, it was decided to investigate the reverse way of synthesis, starting with HEMA and acryloyl chloride; Figure 10. This synthesis pathway was simpler and needed only one purification step, which was done by extraction with HCl and $NaHCO_3$ saturated. HEMA was stirred in dichloro methane together with triethylamine as acid scavenger. Attention must be paid during the addition of acryloyl chloride. The reaction itself is cooled, because

- of the high reactivity of acryloyl chloride with HEMA and
- to avoid polymerisation of acryloyl chloride's[23].

Therefore the addition was slowly done. Otherwise some of the educts will be lost (In the case of too fast addition HCl gas was formed. The gas was immediately visible). After the extraction the dried product is directly used in the Diels-Alder reaction. The Diels-Alder

[23] Kraus, N.; Mueller, U.; Noll, B.; Plaschnick, D.; Raetzsch, M.; Schmidt, M.; Wohlfarth, B.; & (VEB Filmfabrik Wolften Fotochemisches Kombinat); *Ger. (East) Patent,* DD248,581; *Chem. Abstr.*, **1988**, *109*, 54328a.

reaction is also done at low temperatures to avoid unwanted polymerisation reactions of educt and aduct. Cyclopentadiene was freshly cracked and added to toluene and 2-(acryloyloxy)ethyl metacrylateat low temperatures. After the reaction was heated and stirred over night, before it was evaporated under reduced pressure.

The storage of the monomer must be in a cooled, light protected environment and a stabilisator should be added to prevent polymerisation.

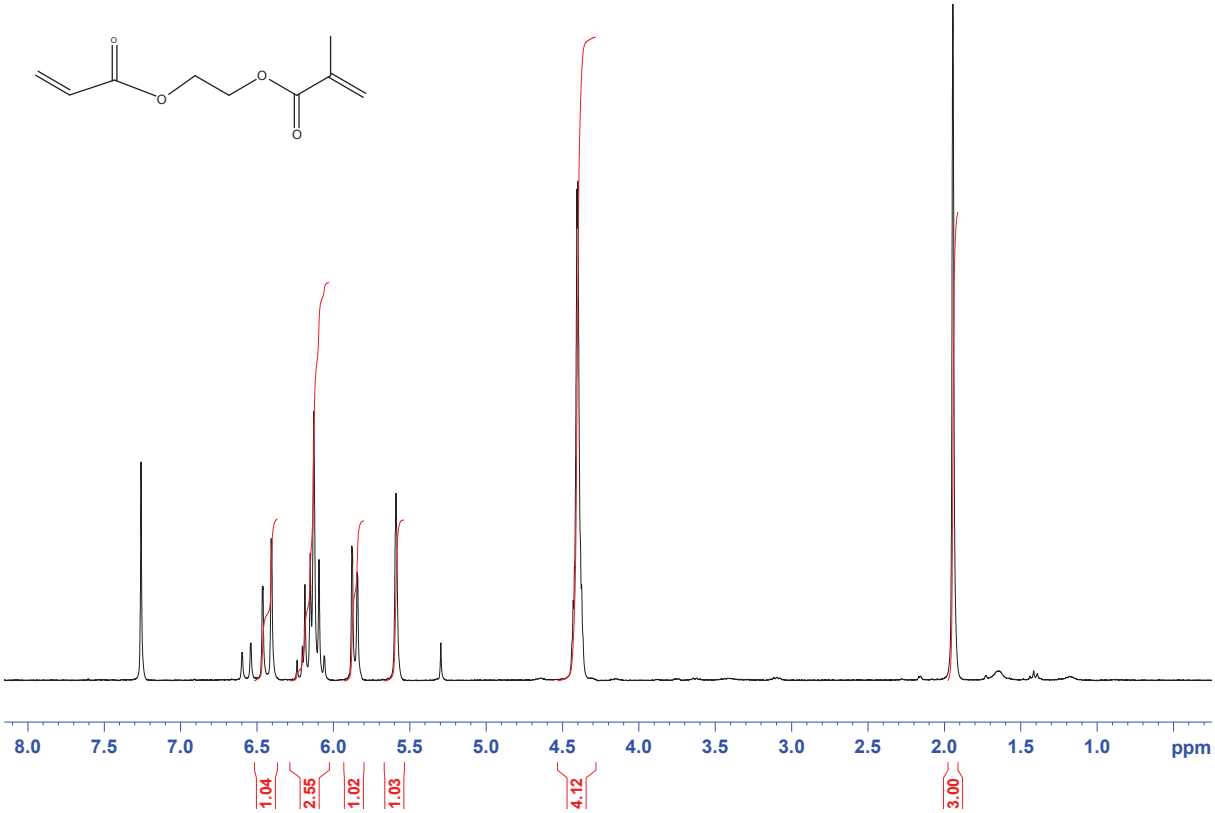


Figure 10: ^{1}H-NMR of 2-(acryloyloxy)ethyl metacrylate.

3.1.2. Synthesis of *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide

The maleimide-containing monomer 2 was synthesised in a three-step reaction. The reaction of *endo*-carbic anhydride with ethylenediamine was followed by the reaction with maleic anhydride in DMF. This reaction resulted in an open-ring intermediate. The open ring of the intermediate was closed with acetic anhydride.

Before the synthesis succeeded several trials failed. This will be discussed in the following section. As mentioned in Schaefer[21] pure *exo*-carbic anhydride was used for the synthesis. The synthesis failed probably, because no purification steps of the educts have been done.

One problem, which occured during the synthesis, was that the carbic anhydride (*exo* as well as *endo*) was hardly soluble in cold toluene. The carbic anhydride was as well as hardly soluble in chloroform and dichloro methane. We investigated these halogenated solvent on purpose. They can be used after reaction to separate between the product which is soluble and the educt, which is insoluble. Overnight the carbic anhydride solved under Dean-Stark conditions, Figure 11.

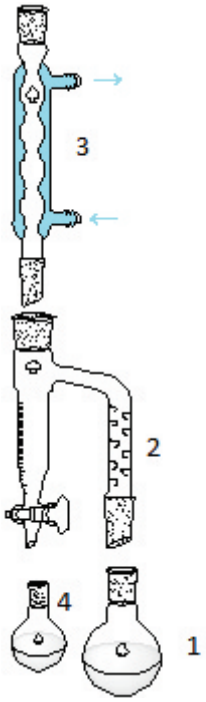


Figure 11: Dean-Stark apparatus (1: Round bottom flask; 2: Fractionating vigreux column; 3: condenser; 4: collection vessel;).

After leaving the reaction for a certain time the reaction was recrystallised in ethanol. White crystals were formed in a yellowish liquid. Firstly it was assumed that the crystals happened to be the product. Because of the low yield the liquid was purified by column chromatography.

Different fractions were obtained and used in the synthesis of the targeted maleimide-containing monomer 2, but after characterisation with NMR spectroscopy, it was obvious no DCI-Et-MI-Nbe has been formed.

We continued with *endo* carbic anhydride.

The synthesis was started by using freshly distilled tehylenediamine and the product was formed; Figure 12 (It might be important to use freshly distilled ethylenediamine, because small amounts of oxidation products, like amine oxides, would at least reduce the yield or cause unknown and unwished side reactions.).

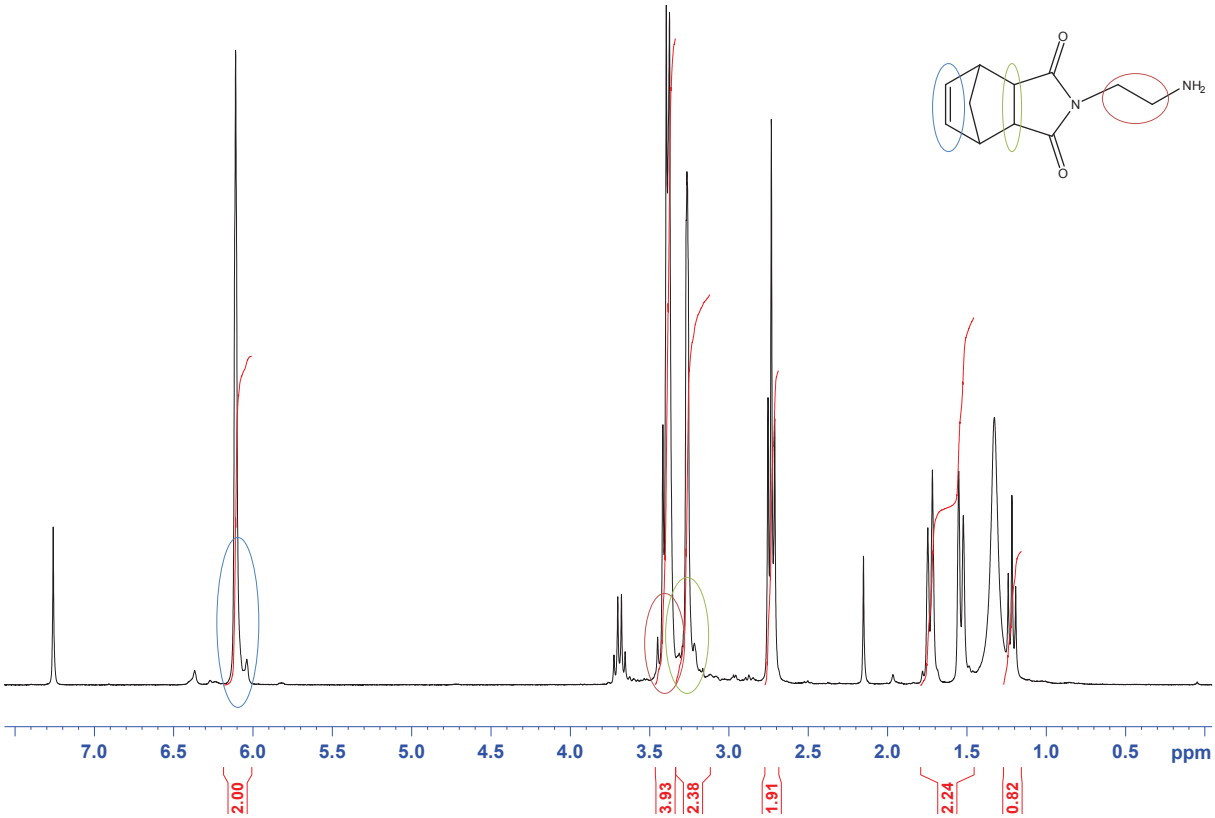


Figure 12: ^{1}H-NMR of *endo*-*N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide.

The dicarboximide is soluble in dichloro methane. The ^{1}HNMR spectra proofed that the targed product was formed. After purification the product was used for the next step, the addition and ring opening of the maleimide. The intermediate was extracted with dichloro methane and evaporated under reduced pressure; Figure 13. To get rid of DMF (which has very distinctive peaks in the ^{1}H-NMR (8.02, 2.96 and 2.88 ppm) and disturbs the reaction) toluene was added. Because of its high boiling point DMF is not easy to get rid off. Toluene has a close boiling point and drags DMF.

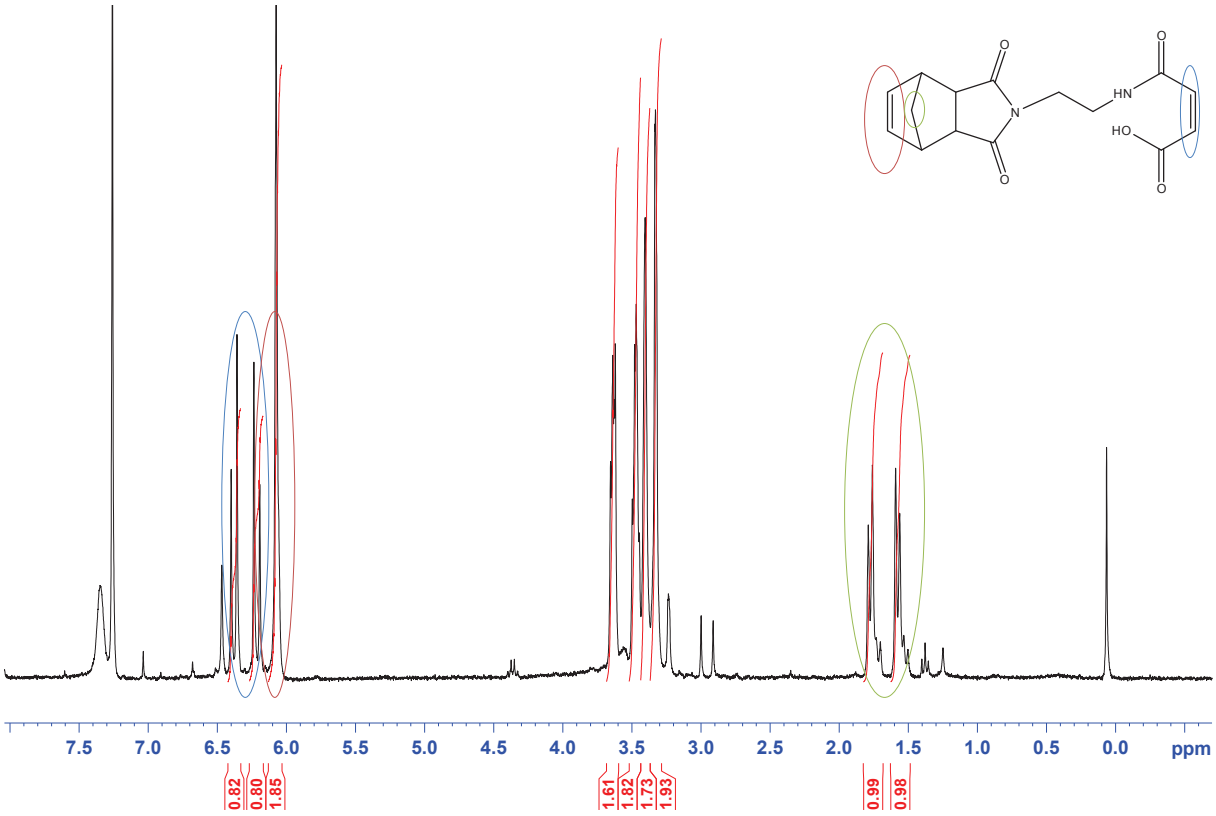


Figure 13: ^{1}H-NMR of (*Z*)-4-((2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisoindol-2-yl)ethyl)amino)-4-oxobut-2-enoic acid.

The final step of the synthesis was the ring closing. This was done in acetic acid in presence of sodium acetate. Afterwards the final product was extracted. We used hydrochloric acid and neutralised with sodium bicarbonate. However, the adition of potassium carbonate was much more effective than sodium bicarbonate to neutralise the excess of acetic acid. After evaporating under reduced pressure the monomer was characterised by ^{1}H-NMR spectroscopy; Figure 14.

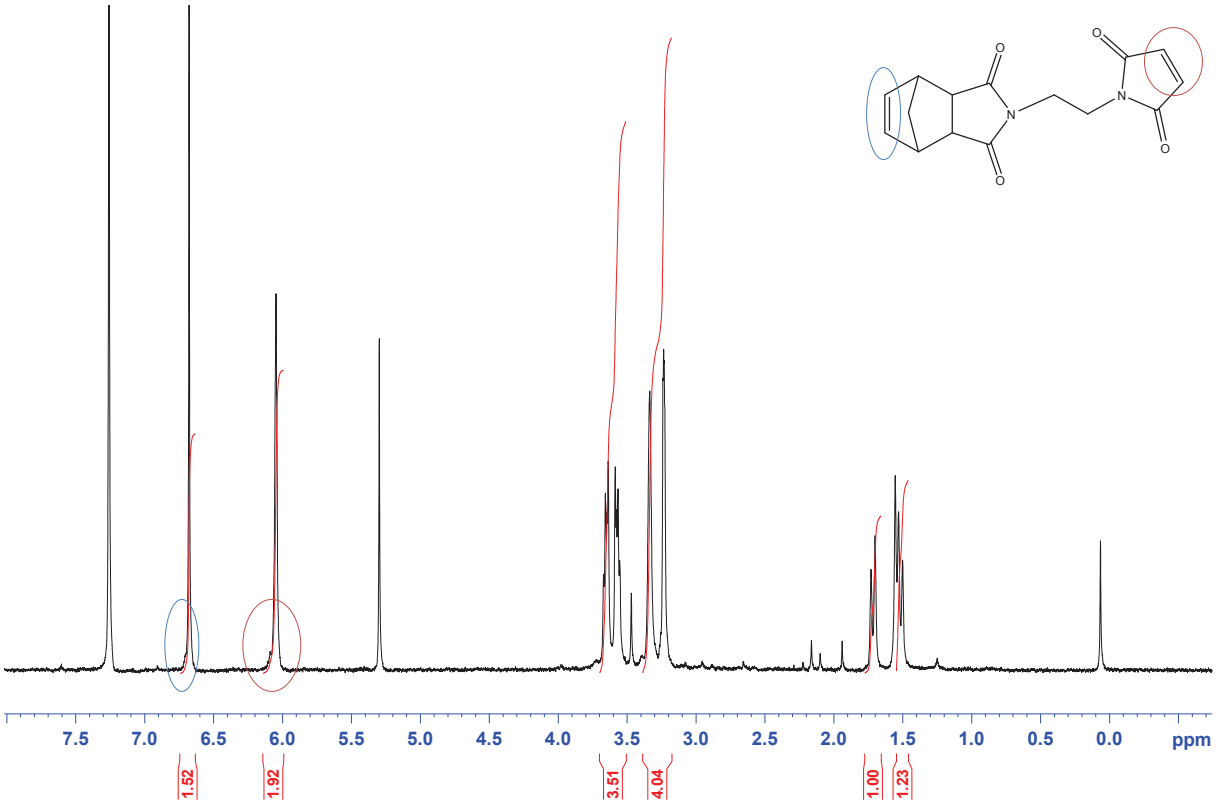


Figure 14: ^{1}H-NMR of *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide.

The blue marker indicates the double bond of the opened maleimid. The peaks are shifted to lower field regions after ring closing, while the double bond of the norbornene moiety stays at the same shift.

3.2. Polymerisation

3.2.1. Testpolymerisations

Before ATRP were started with our synthesised monomers, we checked the polymerisation conditions by using several monomer comodities (MMA, styrene and EA). Several conditions of polymerisation were done to find the optimum. One of the problems, which was expected and confirmed by our experiments, that low monomer concentrations prevents high conversion. Molarities of 0.2, 0.5 and 4 M (Figure 15) were investigated. We expected and found that higher concentrations lead to quicker polymerisation. Based on our experiments we found amonomer concentration of 4M as an optimum.

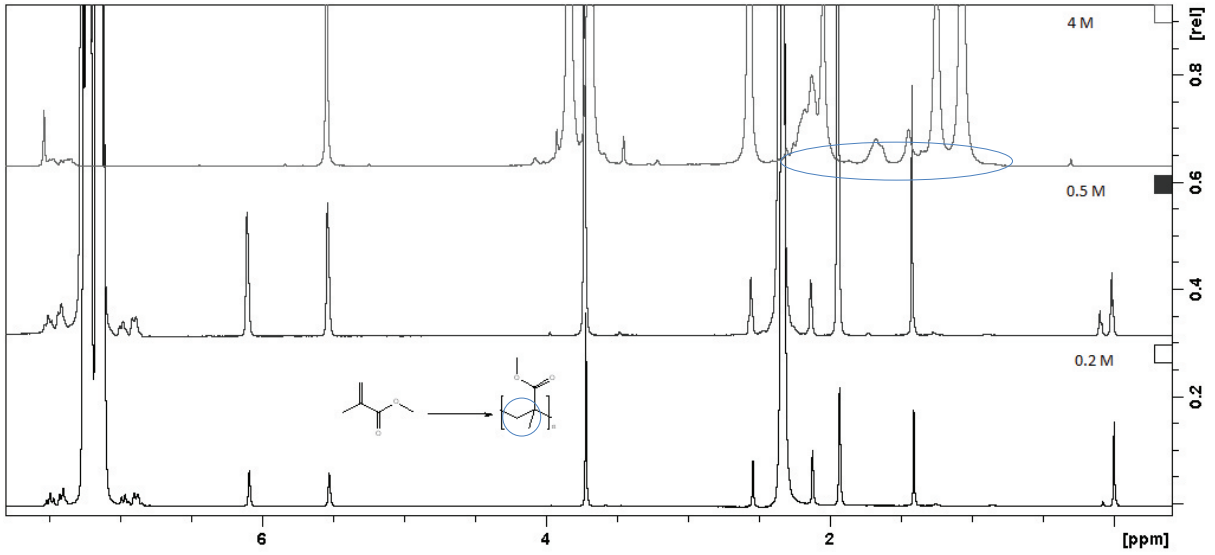


Figure 15: ^{1}H-NMR of poly methyl metacrylate with different molarities.

Another point was the change of the initiation. An ATRP system consists of a multicomponent system, which includes the initator, the monomers, the catalyst, the solvent, sometimes an additive and the temperature.[9] The catalyst consists on three components. There is on the one hand the transition metal species, which increases its oxidation state and can expand its coordination sphere as well. On the other hand there is its counterpart of the transition metal species, which can form either an ionic or a covalent bond with the metal center. And finally there is the ligand, which is complexing with the transition metal. [24]

In this case the system could be initiated either by the initator or by the ligand. Best results were obtained by the initation with the ligand.

[24] Braunecker, W. A.; & Matyjaszewski, K.; *Prog. Polym. Sci.,* **2007**, *vol. 32*, p.93-146.

3.2.2. Polymerisations of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate

Our monomer 1 (2-(Methacryloyloxy)ethyl norborn-5-ene-2-carboxylate) was copolymerised with three different monomers (MMA, styrene and 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate itself). The copolymerisation with styrene was successfull. The ratio between styrene and the norbornene containing monomer was 10:1 (as well as with methyl metacrylate: norbornene containing monomer).

The two doublets in the ^{1}H-NMR spectra at 5.78 and 5.23 ppm (Figure 16) show that still some styrene monomer was not polymerised. The broadening peaks (compared to Figure 9) prove that polymerisation has undergone. The region between 7.5-6.5 ppm show the aromatic ring of styrene, which of course is built into the copolymer much more than 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate due to the higher molecular percentage.

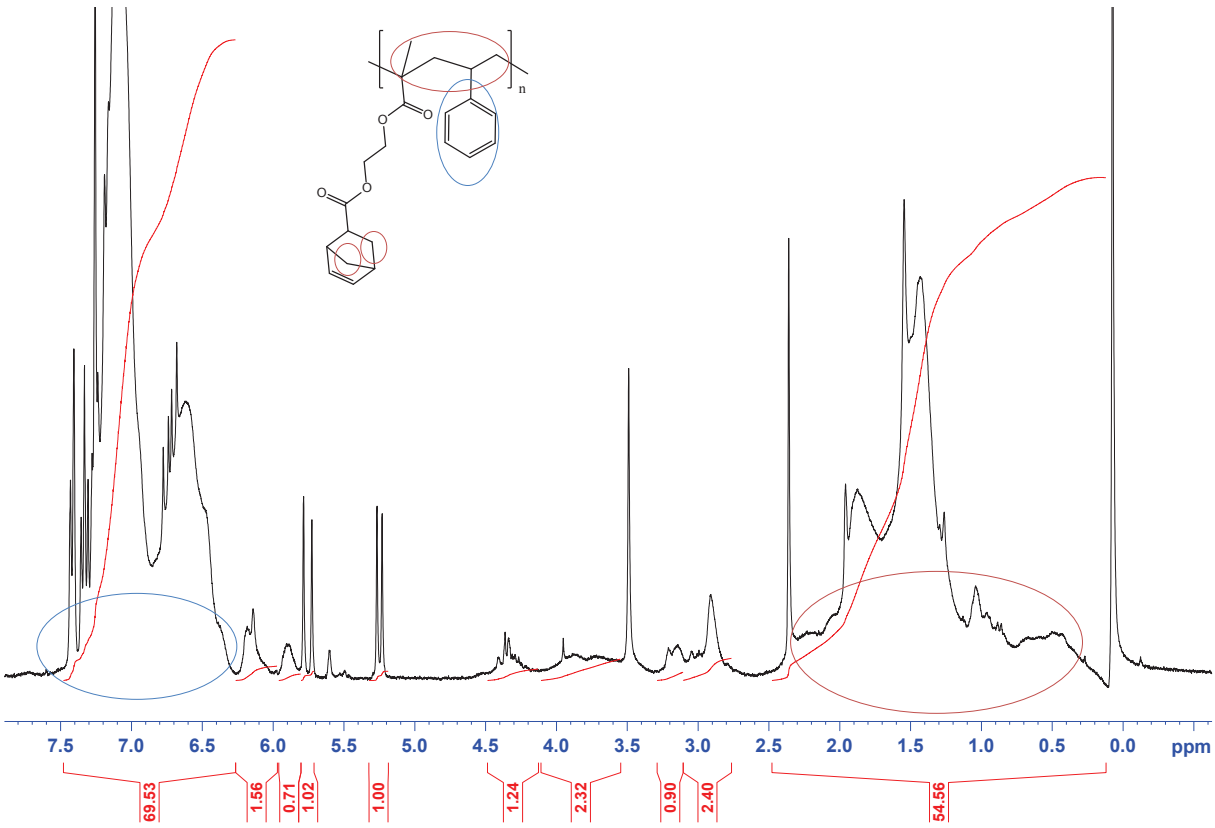


Figure 16: ^{1}H-NMR of copolymerisation of styrene and 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

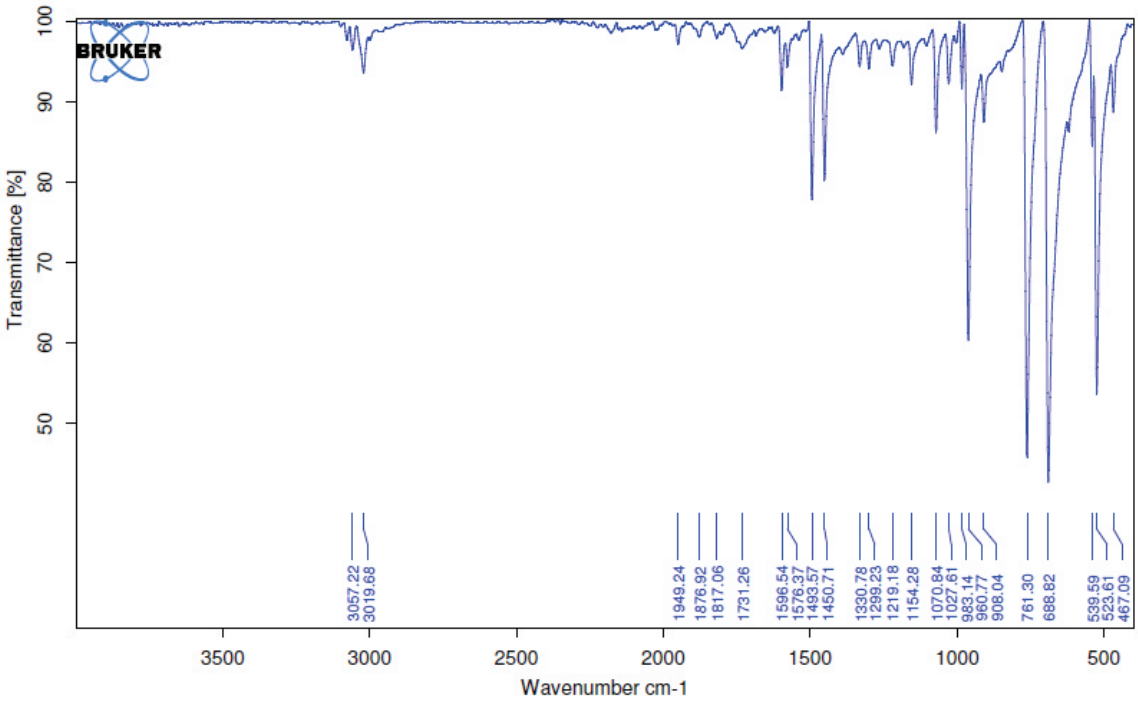


Figure 17: FTIR of copolymerisation of styrene and 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

The copolymerisation was also characterised by FTIR spectroscopy; Figure 17. The peaks about 1731 cm^{-1} indicate the keto-functional groups of the HEMA group while between 3069-2851 cm^{-1} are C-H stretching vibrations. The aromatic vibrations are about 800-700 cm^{-1}.

The measurements with GPC showed a very low PDI of 1.055, which is desired, because it means that the chainlength are equally long.

The trials of homopolymerisations of the synthesised monomer 1 as well as the copolymerisation with MMA resulted unexpectedly; Figure 18 and Figure 19.

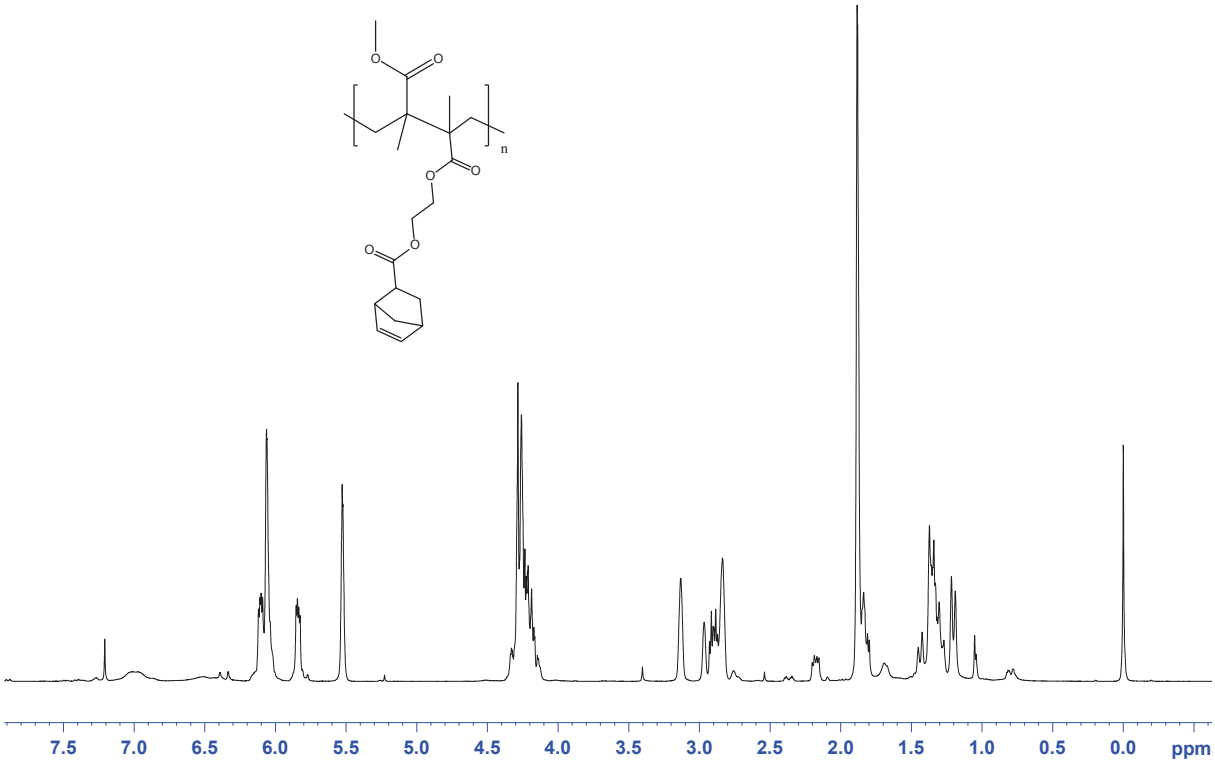


Figure 18: ^{1}H-NMR of copolymerisation of methyl metacrylate and 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

The copolymerisation with MMA turned to a gel like solid after 19 hours. This leads to the conclusion that the norbornene double bond polymerised as well and crosslinking started over night. Due to the insolubility of the crosslinked product no ^{1}H-NMR could be obtained.

The GPC data proof as well that crosslinking occurred because of the high PDI of nearly 9. This means that the chainlengths have different lengths.

No crosslinking could be observed while redoing the experiment under the same condtions again. The reaction was left at 80°C for four days and no conversion was observable; Figure 18. One reason of this (no polymerisation) might be that in the recent trial the monomer was freshly synthesised while the monomer at the first trials was already several weeks old and might have started selfpolymerisation. Therefore the copolymerisation could undergo the crosslinking during the first trials.

As mentioned in chapter 3.2.1 the lower concentration of the monomer might explains this. The monomer was only 0.4 M; raising to higher molarity might lead to better conversion. Braunecker mentiones that transfer radical polymerisations (especially the radical coupling and disproportionation termination reactions) are essentially diffusion controlled. [24]

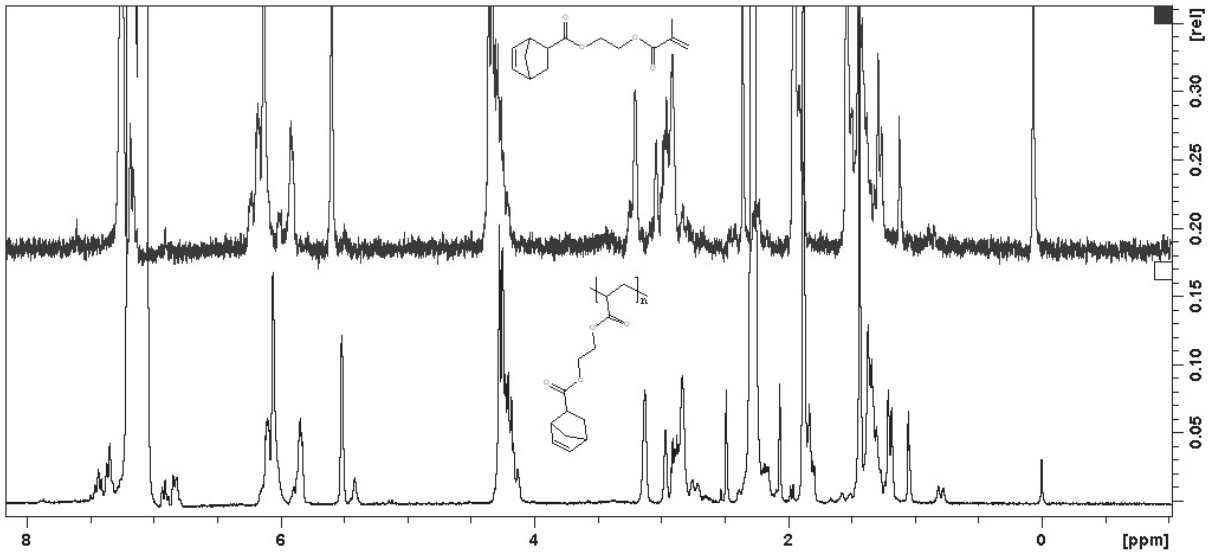


Figure 19: ^{1}H-NMR of polymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

The polymerisation of the monomer was done on the one hand uncontrolled and on the other hand under ATRP conditions. The uncontrolled polymerisation leads to an unsoluble gel. Therefore no ^{1}H-NMR could be measured. The polymerisation by ATRP-technique was not successfull at all, which can be seen in Figure 19. There is no peak broadening in the polymerisation. Probably the molarity of monomer was too low as well.

3.2.3. Polymerisation of *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide

The copolymerisation with styrene[25] was successfull. The ratio between styrene and the norbornene containing monomer was 10:1 (as well as with methyl metacrylate: norbornene containing monomer). This is proofed as well by the PDI which is between 1.6-1.2. This means that the chainlengths are not as different as the copolymerisation of HEMA-Nbe with MMA.

The two doublets at 5.78 and 5.23 ppm (Figure 20) show that still the styrene monomer is unpolymerised. The broadening peaks (compared to Figure 14) prove that polymerisation has taken place. The region between 7.5-6.5 ppm are the aromatic compound of styrene, which of course is built into the copolymer much more than *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide due to the higher molpercentage.

The maleimide double bond is opening and copolymerising with the double bond of styrene.

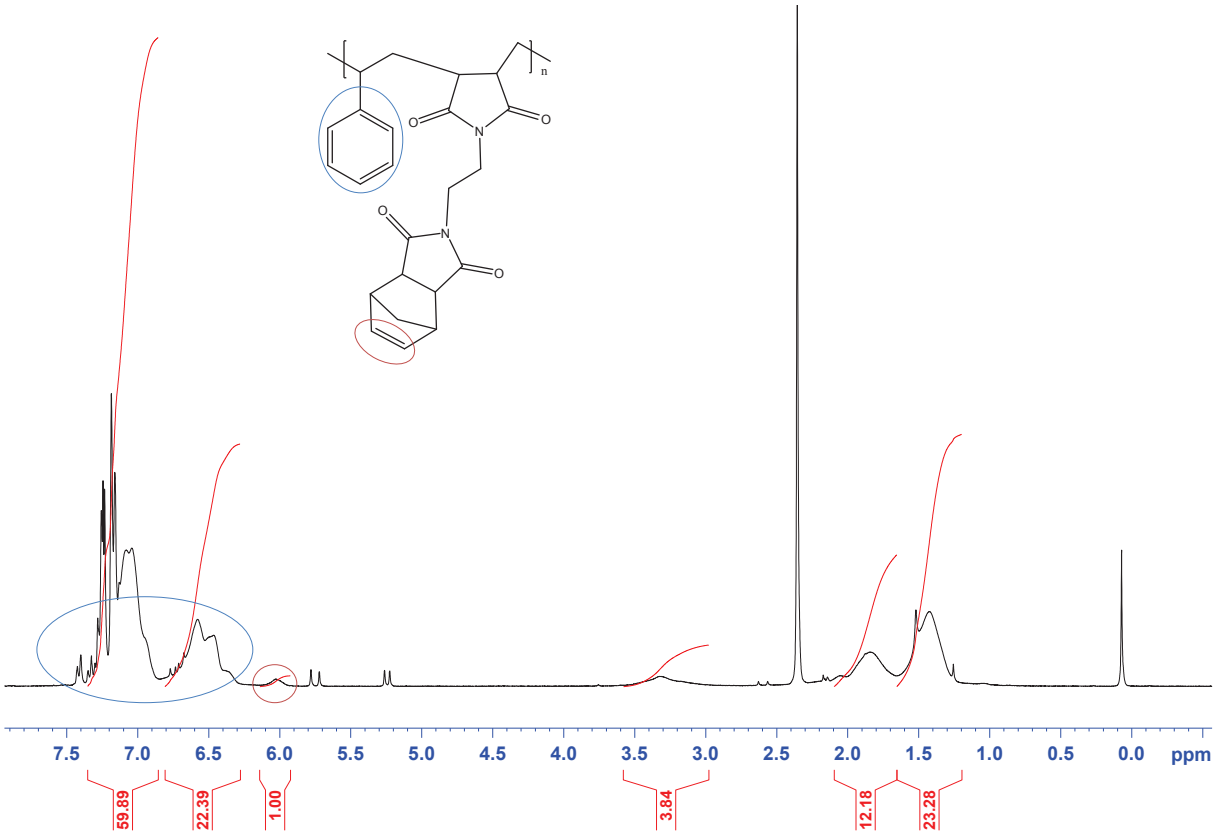


Figure 20: ^{1}H-NMR of copolymerisation of styrene and *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide.

[25] Leitgeb, A.; *Laboratory Journal,* **Alternating ATRP of styrene and bi-functional maleimide-norbornene-monomer**.

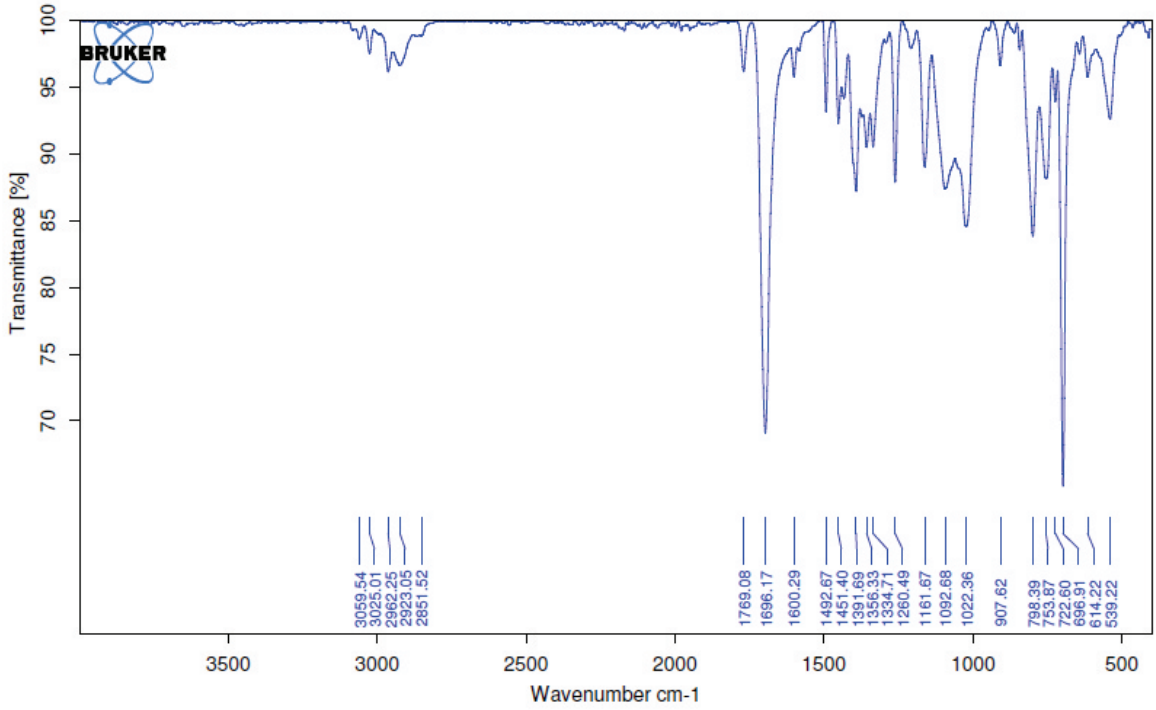


Figure 21: FTIR of copolymerisation of styrene and *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide.

An infrared spectrum of the copolymerisation has been obtained (Figure 21). The peak at 1699 cm^{-1} indicates the keto-functional groups of the maleimide containing substance while the peaks between 3069-2851 cm^{-1} are C-H stretching vibrations. The aromatic vibrations are about 800-700 cm^{-1}.

3.3. Functionalisation

3.3.1. Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with ethyl acrylate

For the functionalisation[26] everything beside the catalyst was given to a Schlenk flask. The monomer 1 and an excessive amount of EA (6 mol equivalents) were degassed by several cycles of vacuum-nitrogen. The catalyst was added to the Schlenk flask after the reaction temperature reached 80°C. The reaction turned immediately red and was left for 30 minutes until the colour changed to yellow. This indicated the end of the reaction. As seen in Figure 22 peak broadening occured which points to the fact that oligomerisation and polymerisation happened.

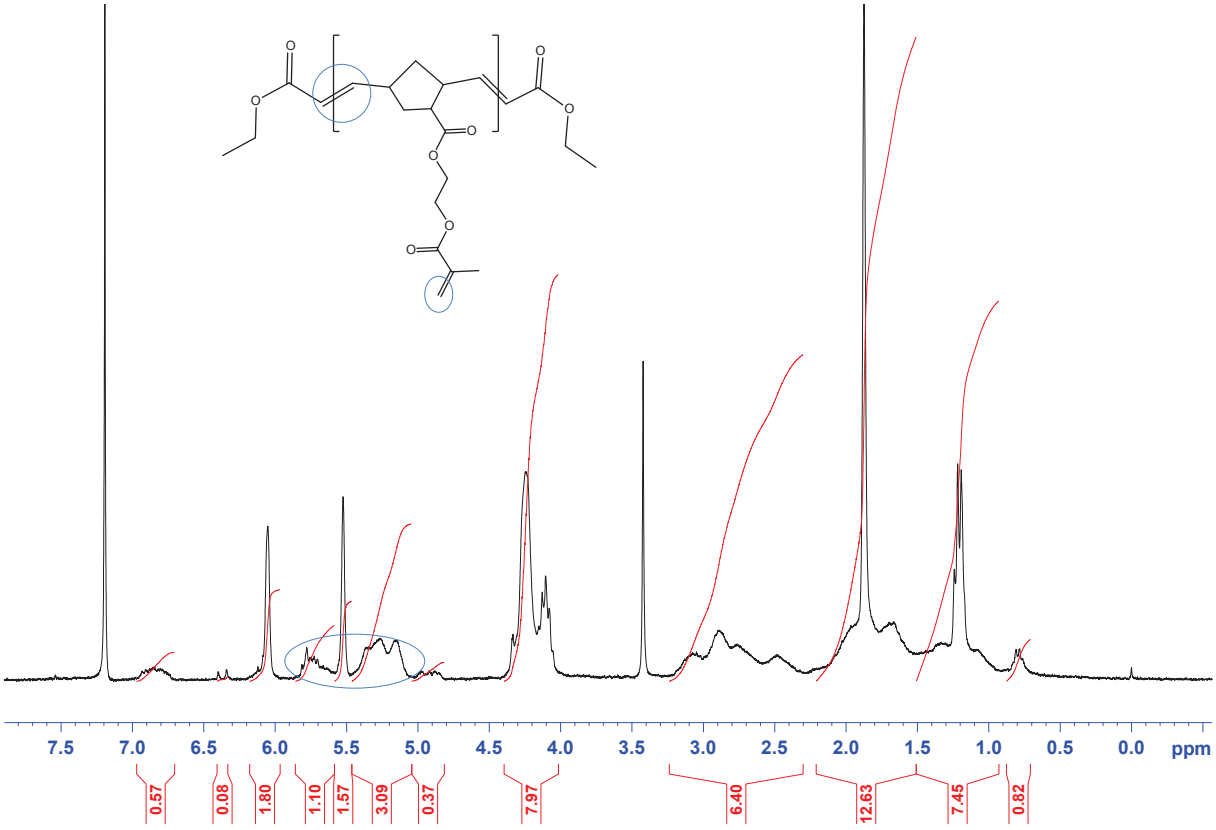


Figure 22: ^{1}H-NMR of functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with ethyl acrylate.

This means that several norbornene moieties polimerised by so-called ring opening metathesis polymerisation (ROMP); Figure 23.

[26] Lexer, C.; Saf, R.; & Slugovc, C.; *Journal of Polymer Science: Part A: Polymer Chemistry*, **2009**, *vol. 47*, p. 299-305.

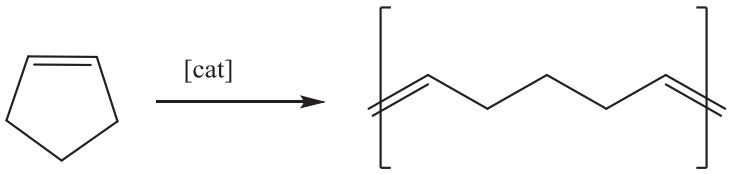


Figure 23: Mechanism of ring opening metathesis polymerisation.

3.3.2. Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with styrene

The aromatic unit of the styrene is very dominant. Still some of the functionalisation occured. As mentionend in chapter 3.3.1 some oligomerisation occured as well.

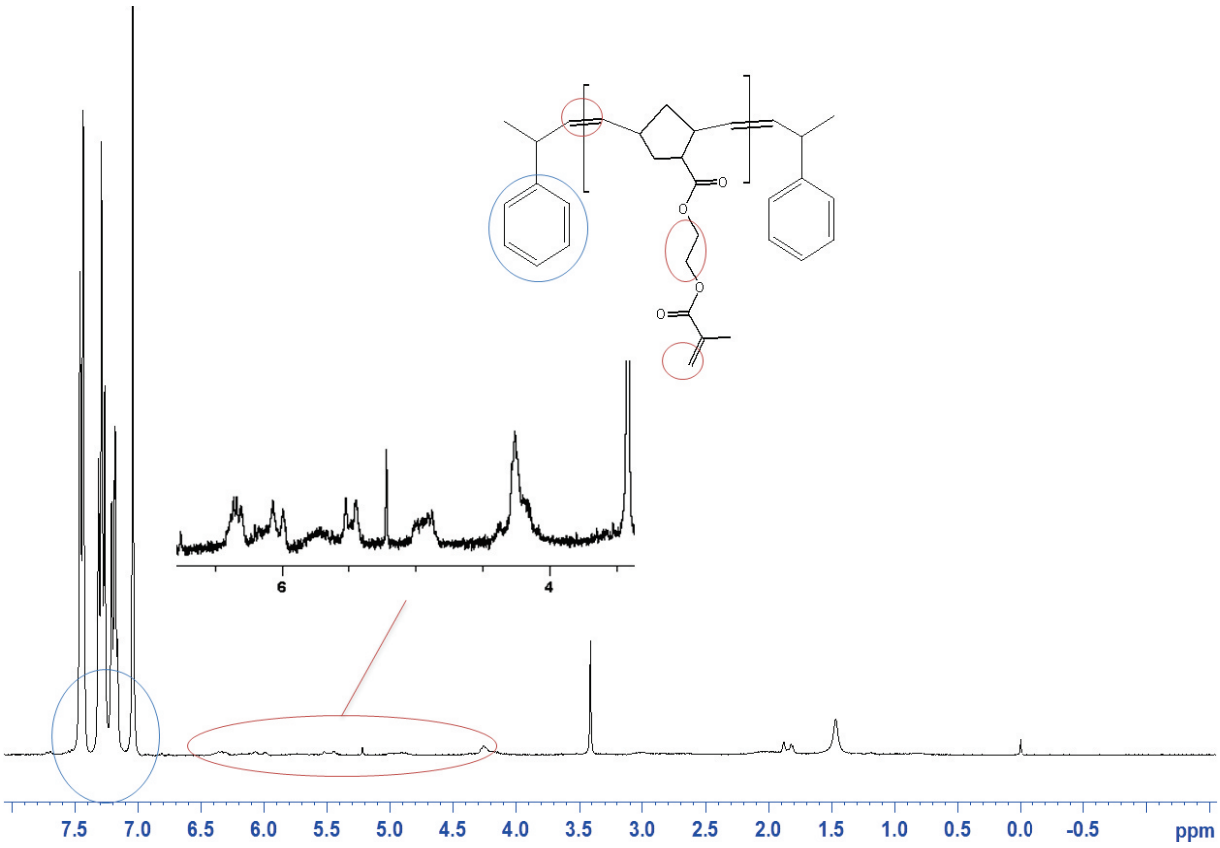


Figure 24: ^{1}H-NMR of functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with styrene.

The dominance of the aromatic compound in Figure 24 leads to the conclusion that nearly all excessive styrene can be found in a polymerchain. However, based on this we cannot conclude if it was block polymerisation of styrene and HEMA-Nbe or a statisctical distribution of styrene and our monomer 1. Still, the polymerisation has been rather unexpected and undesired.

3.3.3. Functionalisation of *endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide with ethyl acrylate

The functionalisation[25] of the dicarboximide did not occur. This can be concluded based on Figure 25. The double bond peak of the norbornene in the ^{1}H-NMR spectra should disappear during the reaction. However, the ratio of the norbornene to the maleimide double bond is the same. In Leitgeb[25] the copolymer was functionalised. The functionalisation was done in toluene and with a different Ruthenium catalyst, which was dissolved in dichloro methane and EA.

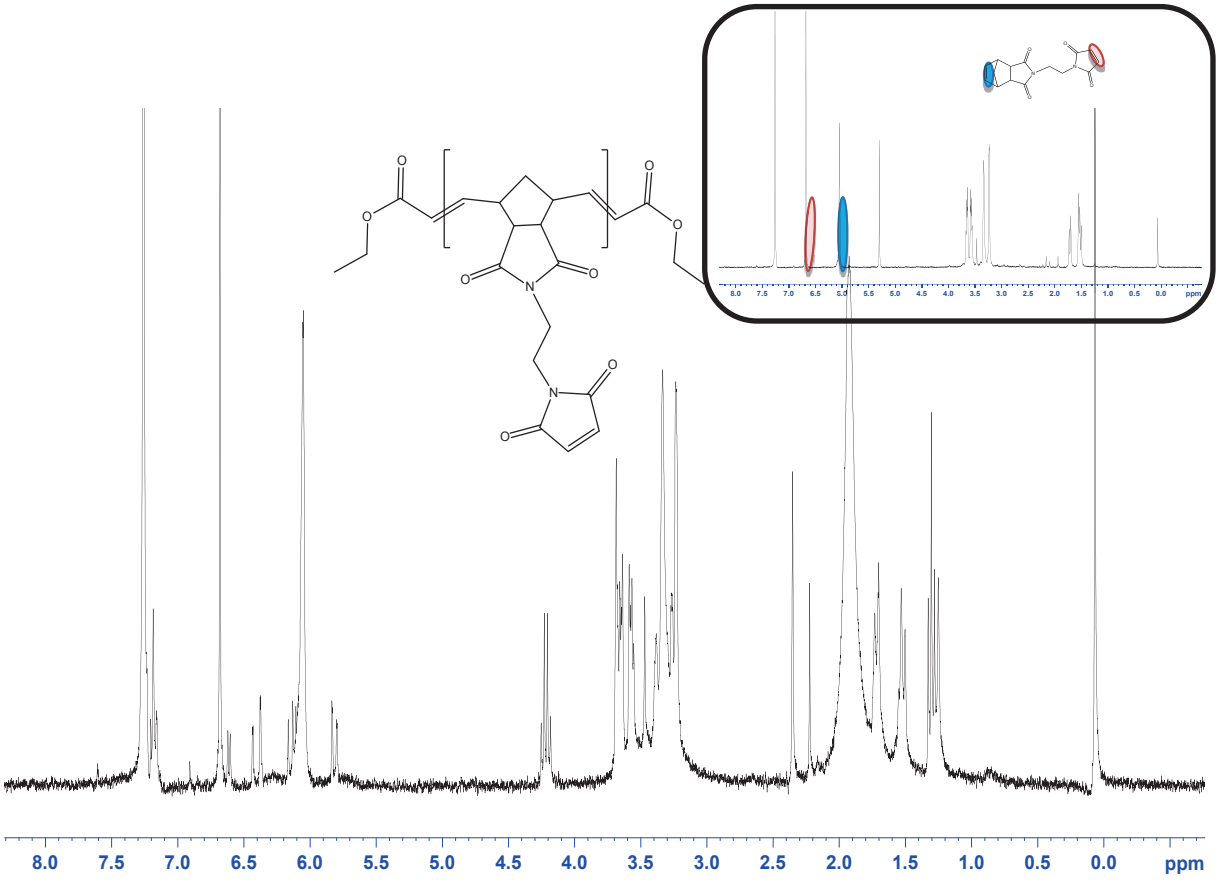


Figure 25: ^{1}H-NMR of functionalisation of *endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide with ethyl acrylate.

4. Conclusion and outlook

In order to summarise our investigations we found that the synthesis of the two bifunctional monomers (2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and *endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide) was successfull, even some difficulties appeared during the reaction.

The monomers were built incorporated in copolymers with styrene. However the copolymerisation of HEMA-Nbe with MMA was not fully successfull. Partially successfull was as well the functionalisation of the monomer 1 with styrene and EA. Notably, the monomer 1 started to oligomerise after opening the norbornene double bond.

No functionalisation of DCI-Et-MI-Nbe with EA could be observed.

There are several points which can be done in further experiments. As mentioned in chapter 3.2.2 higher concentrations of the HEMA-Nbe can be used to undergo a homopolymerisation. A change to higher temperatures during the polymerisation (110°C) can be applied as well. As mentioned in chapter 3.2.1 ATRP is a multicomponent system, consisting of a variety of monomers, temperatures, solvents, catalysts and initators. Therefore a change of one of these compounds can be considered. Different solvents like DMF[27], anisole[28], DMSO[29] or aqueous media[30] were used in literature we mentioned befre and can be applied as well.

In order to complete the investigation of copolymerisation, different polymerisation techniques can be used on the bifunctional monomers. In order to get a controlled distribution of block lengths the initiation must be fast, while the propagation has to be relatively slow compared to the initiation step, which can be achieved with alkyl lithium initiators in non-polar solvents. Due to these conditions ion pairs, which can be considered as dormant species, or their aggregates are formed. In comparison with the propagation, the exchange between dormant and active species is fast enough and therefore materials with low polydispersity can be produced.[24] Anionic polymerisation can be applied on the methacryloyloxy moiety of the

[27] Jakubowski, W.; Tsarevsky, N. V.; McCarthy, P.; & Matyjaszweski, K.; *Sigma-Aldrich*, ATRP for Everyone: Ligands and Initiators for the Clean Synthesis of Fucntional Polymers; **Controlled Radical Polymerization Guide**.

28 Li, A.; Ma, J.; & Wooley, K. L.; *Macromolecules*, **2009**, *vol. 42*, p. 5433-5436.

29 Matyjaszweski, K.; *Macromolecules*, dx.doi.org/10.1021/ma3001719 .

30 Airaud, C.; Ibarboure, E.; Gaillard, C.; & Héroguez, V.; *Macromol. Symp*., **2009**, *vol. 281*, p. 31-38.

carboxylate with an alkyl lithium[31, 32] /DMSO system as initator[33], as well as at different temperatures[34]. The copolymerisation with styrene can be done as well with anionic polymerisation.[35]

The functionalisation of copolymers is another opportunity. It can be obtained the very same way as the functionalisation of the monomers by using 100 mg of the copolymer with a high excess of the acrylate or the styrene. [25]

31 Bywater, S.; Black, P. E.; & Wiles, D. M.; *Canadian Journal of Chemistry*, **1966**, *vol. 44*, p. 695-702.

32 Yu, Y.; Dubois, P.; Teyssié, P.; & Jérôme, R.; *Macromolecules*, **1997**, *vol. 30*, p. 4254-4261.

33 Nugay, T.; Nugay, N.; & Jérôme, R.; *Polymer Bulletin*, **2002**, *vol. 48*, p. 457-462.

34 Baskaran, D.; & Sivaram, S.; *Macromolecules*, **1997**, *vol. 30*, p. 1550-1555.

35 Ott, C.; Pavlov, G. M.; Guerrero-Sanchez, C.; & Schubert, U. S.; *Journal of Polymer Science*, **2009**, *vol. 47*, p. 3691-3701.

5. Experimental

5.1. General Information

All chemicals which were not synthesised by us were purchased from commercial sources (Fluka, Sigma Aldrich, ABCR, Alfa Aesar, Arcos Organics). They were used without any further purification, unless specified otherwise. (*E*)-(1,3-dimesitylimidazolidin-2-yl)(3-phenyl-1*H*-inden-1-ylidene)(tricyclohexyl-l5-phosphanyl)ruthenium(VI) chloride as initator for the functionalisation was available for use by Eva Pump, TU Graz. Solvents and auxiliary materials were used as purchased, unless specified otherwise.

Thin layer chromatography was performed on aluminium sheets with silica gel 60 F_{254} from Merck. The spots were visualised via UV light irradiation at 365 nm and a 1% $KMnO_4$ solution.

For purification with column chromatography, silica gel 60 (220-440 mesh ASTM) was used. Nitrogen was used for reactions performed in am inert atmosphere.

Polydispersity indices (PDI) and molecular weight were obtained by gel permeation chromatography (GPC) using THF as eluent. The device setup is composed of a refreactive index detector from Wyatt Technology, separation columns of Polymer Standards Service (5 µm grade size) and a Merck Hitachi L6000 pump (delivery volume: 1 mL/min). Polystyrene standards from Polymer Standard Service were used for calibration.

For FTIR spectroscopy a Bruker ALPHA FTIR Spectrometer was used. Measurements were done in ATR mode.

NMR spectroscopy (^{1}H, ^{13}C-APT, COSY) was made by using a Bruker Avance III 300 MHz spectrometer. Deuterated solvents ($CDCl_3$, DMSO) were purchased from Cambridge Isotope Laboratories, Inc., and remaining peaks were referenced according to literature.[36] To indicate different peak shapes, the following abbreviations are used: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets).

[36] Gottlieb, H. E.; Kotlyar, A.; & Nudelman, A.; *J. Org. Chem.,* **1997**, *vol. 62*, p. 7512.

5.2. General procedure for atom transfer radical polymerisation (ATRP)

Copper(I)bromide is washed with acetic acid, methanol and diethylether and dried in vacuum. One equivalent of CuBr is weighed into a Schlenk flask, as well as absolute toluene (4M; absolute toluene is set under N_2 atmosphere by putting a syringe into the solvent and flushed with gas), the respective monomer (50 eq, in case of styrene the monomer is filtrated over Al_2O_3 to separate the stabiliser from the monomer) and (1-bromoethyl)benzene (1eq). Three cycles of freeze-pump-thaw (Figure 26) are applied. Therefore the Schlenk is submersed in liquid N_2, while the vacuum tap is closed. The tap is opened, after the solvent is fully frozen, vacuum is applied for ten minutes and finally the tap is closed afterwards and the liquid N_2 is exchanged with tepid water to thaw the reaction which is accompanied by bubble formation in the reaction mixture. The procedure is repeated at least twice until no further bubbles are formed upon thawing. Then the mixture is stirred and heated to 110 °C in an oil bath. 1.04 eq of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) are added to initiate the polymerisation.

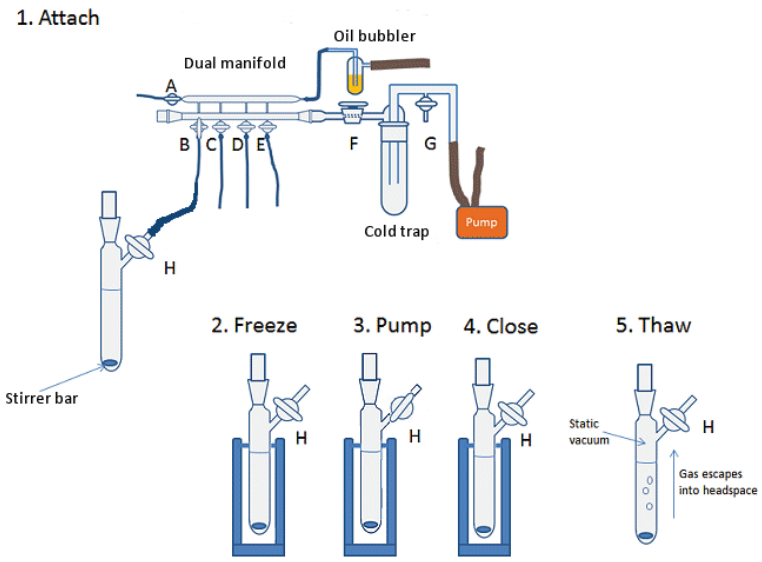


Figure 26: Freeze-Pump-Thaw[37].

The conversion progress is followed by NMR spectroscopy. Therefore a small amount of the reaction mixture is filtrated over Al_2O_3 and analysed in $CDCl_3$.

[37] http://www.chemistryviews.org/details/education/4308331/Tips_and_Tricks_for_the_Lab_Air-Sensitive_Techniques_2.html , 23.06.2014

Finally the reaction is

- filtrated over Al_2O_3,[38]
- evaporated under reduced pressure,
- dissolved in millilitre dichloro methane and
- precipitated into cold methanol.

The polymer preciptitates as a white solid whereas impurities remain dissolved in the solvent. The solid is dried and the PDI is measured with GPC in tetrahydrofuran (THF). ^{1}H-NMR spectra is taken as well for characterisation.

[38] Matyjasewski, K.; Pintauer, T.; & Gaynor, S.; *Macromolecules*, **2000**, *vol. 33*, p.1476-1478.

5.3. Synthesis of Monomers

5.3.1. Synthesis of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate

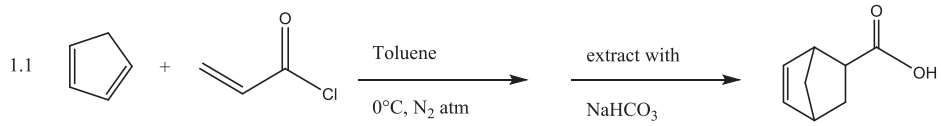


Figure 27: Synthesis of norbornene-5-carbonylhydroxide.

Norborn-5-ene-carbonylhydroxide: Dicyclopentadiene is cracked to cyclopentadiene via distillation at 195 °C. A 50 mL three-neck flask is set under N_2 atmosphere and cooled on an ice bath. Acryloyl chloride (2.0 mL, 24.7 mmol) is stirred and cyclopentadiene (3.6 mL, 43.6 mmol) is added dropwise. The ice bath is removed after 1.5 hours. The reaction is stirred at room temperature for 2 hours and then heated to 40 °C at the kryostat overnight. The reaction progress is followed by thin layer chromatography (TLC, cyclohexane/ethyl acetate 3:1) and ^{1}H-NMR. The reaction is stopped after 48 hours and extracted. It is extracted with $NaHCO_3$ saturated (in aqua dist., 100 mL), which is accompanied by odour of hydrochloric acid and a change of the solution to a brownish colour, and dichloro methane (analytical reagent grade, 100 mL). Next the organic layer is extracted by NaCl saturated (in aqua dist., 100 mL). The organic layer turns grey-greenish and is dried over Na_2SO_4 anhydrous. Afterwards the product is filtrated and evaporated under reduced pressure. The yield of a brownish liquid is 8.6852 g and purified by column chromatography (cylcohexane/ethyl acetate, 3:1). The combined layers are evaporated under reduced pressure and at the vacuum line. The brown oil is yielded with 4.1157 g (83.0 % of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 11.07 (s, 1H, OH), 6.21-5.99 (dm, 2H, HC=CH), 3.24 (s, 1H, =CH-C**H**-$(CH_2)_2$), 3.24 (s, 1H, *endo*-HC-C=O), 3.03-2.97 (m, 1H, *exo*-HC-C=O), 2.92 (s, 1H, =CH-C**H**-(CH_2)-CH), 1.96-1.88 (m, 1H, HC-C**H**H-CH-(C=O)), 1.46-1.37 (m, 2H, bridge-head C**H**H, and HC-CH**H**-CH-(C=O)), 1.30-1.28 (m, 1H, bridge-head CH**H**).

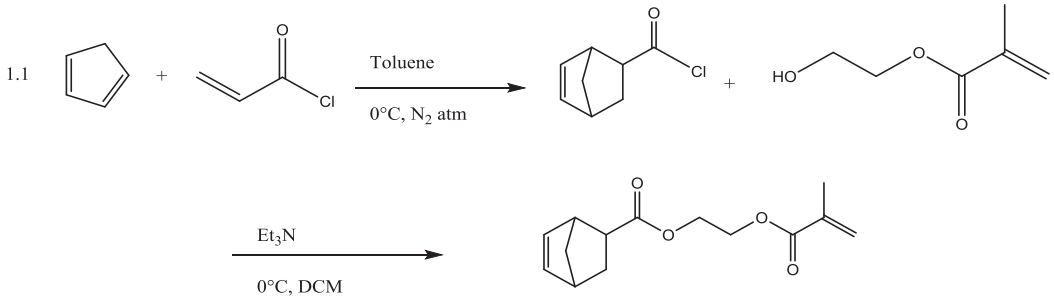


Figure 28: Synthesis of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

Norborn-5-ene-carbonylchloride: Dicyclopentadiene is cracked to cyclopentadiene via distillation at 195 °C. A 100 mL three-neck flask is filled with toluene (30 mL) and acryloyl chloride (12 mL, 148.5 mmol). The flask is cooled on an ice bath and set under N_2 atmosphere. Freshly cracked cyclopentadiene (14 mL, 169.4 mmol) is added dropwise. The reaction mixture is stirred for two hours at room temperature and afterwards heated to 100 °C. It is kept at this temperature at the cryostat over the weekend and distilled afterwards at 110 °C. The clear liquid is yielded with 7.6745g (41.4% of theory). Both *exo* and *endo* product are obtained and included in the NMR-spectroscopy interpretation.

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.28-6.02 (m, 4H, HC=CH), 3.47-3.43 (s, 2H, =CH-C**H**-$(CH_2)_2$), 3.28 (s, 1H, *endo*-HC-C=O), 2.99 (s, 2H, =CH-C**H**-(CH_2)-CH), 2.76-2.72 (q, 1H, *exo*-HC-C=O), 2.06-1.91 (m, 2H, HC-C**H**H-CH-(C=O)), 1.55-1.47 (m, 4H, bridge-head C**H**H, and HC-CH**H**-CH-(C=O)), 1.43-1.32 (m, 2H, bridge-head CH**H**).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 176.78-175.01, 139.04-138.69, 134.89-131.62, 56.43-56.32, 49.22, 47.15-46.90, 46.29, 42.89, 41.86, 31.22, 30.09.

2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate: A 100 mL three-neck flask is filled with dichloro methane (42 mL). HEMA (1.4 mL, 11.5 mmol) and Et_3N (1.8 mL, 13.0 mmol) are added and stirred on an ice bath. Norbornene-5-acyl chloride (2.0801 g, 13.3 mmol) is added via syringe. The reaction mixture is stirred for 2 hours. The mixture is extracted with 0.3M HCl (25 mL). The organic layer is washed three times with $NaHCO_3$ saturated (in aqua dist., 25 mL). The aqueous layer is washed with diethylether (50 mL). The organic layers are combined and dried over Na_2SO_4 anhydrous, filtrated and evaporated under reduced pressure. The product is purified by liquid chromatography (cyclohexane/ethyl acetate 3:1). The solid is yielded with 2.4506 g (62.6% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.17 (m, 1H, HC=CH), 6.13 (s, 1H, O=C-C=C**H**H), 5.91 (m, 1H, HC=CH), 5.59 (s, 1H, O=C-C=CH**H**), 4.35 (m, 4H, H_2C-CH_2), 3.20 (s, 1H, =CH-C**H**-(CH_2)-CH), 3.03 (s, 1H, =CH-C**H**-$(CH_2)_2$), 2.98-2.22 (m, 1H, CH-(CH_2)-**H**C-C(=O)-O), 1.95 (m, 4H, HC-C**H**H-CH-(C=O) and CH_3), 1.51-1.40 (m, 2H, bridge-head C**H**H, and HC-CH**H**-CH-(C=O)), 1.37-1.26 (m, 1H, bridge-head CH**H**).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 138.12, 137.85, 135.70, 125.99, 62.49, 62.04, 61.87, 49.62, 46.65, 46.34, 45.72, 43.26, 43.09, 42.54, 41.65, 30.33, 29.23, 18.27.

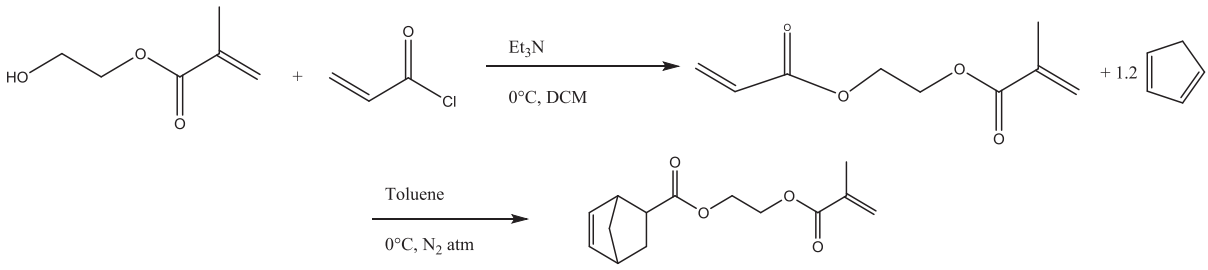


Figure 29: Synthesis of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

2-(acryloyloxy)ethyl metacrylate: Dichloro methane (40 mL), HEMA (2.54 mL, 20.9 mmol), Et_3N (3.19 mL, 23.0 mmol) and acryloyl chloride (slow addition via syringe, 1.9 mL, 23.5 mmol) are stirred in a three-neck flask equipped with a drying tube ($CaCl_2$) on an ice bath. The mixture is very reactive. After two hours stirring the ice bath is removed. The reaction is stirred over night and extracted with 1.8 M HCl (45 mL). The organic layer is washed with $NaHCO_3$ saturated (in aqua dist., 3x25 mL). The aqueous layers are washed with dichloro methane (100 mL). The combined organic layers are dried over Na_2SO_4 anhydrous, filtrated and evaporated under reduced pressure. The solid is yielded with 3.1437 g (81.7% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.47-6.40 (d, 1H, **H**HC-CH-C=O), 6.24-6.06 (m, 2H, H_3C-C=C**H_2**), 5.88-5.84 (d, 1H, H**H**C-CH-C=O), 5.59 (s, 1H, H_2C=C**H**), 4.41 (dd, 4H, H_2C-CH_2), 1.94 (s, 3H, CH_3).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 134.61, 131.32, 128.03, 126.06, 62.37, 18.26.

2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate: A 50 mL three-neck flask is filled with toluene (25 mL) and 2-(acryloyloxy)ethyl metacrylate (1.9450 g, 10.6 mmol). The reaction mixture is stirred under N_2 atmosphere and cooled on an ice bath. Freshly cracked cyclopentadiene (1.55 mL, 24.6 mmol) is added and the reaction is stirred for 1.5 h on an ice bath. Afterwards it is heated to 100 °C for four hours. The reaction mixture is evaporated under reduced pressure. The yellowish gel is yielded with 2.8769 g (63.0% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.23-6.15 (m, 1H, HC=CH), 6.13 (s, 1H, O=C-C=C**H**H), 5.92-5.84 (m, 1H, HC=CH), 5.60 (s, 1H, O=C-C=CH**H**), 4.43-4.22 (m, 4H, H_2C-CH_2), 3.20 (s, 1H, =CH-C**H**-(CH_2)-CH), 3.03 (s, 1H, =CH-C**H**-(CH_2)$_2$), 2.99-2.22 (m, 1H, CH-(CH_2)-**H**C-C(=O)-O), 1.95 (m, 4H, HC-C**H**H-CH-(C=O) and CH_3), 1.49-1.41 (m, 2H, bridge-head C**H**H, and HC-CH**H**-CH-(C=O)), 1.39-1.26 (m, 1H, bridge-head CH**H**).

5.3.2. Synthesis of *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide

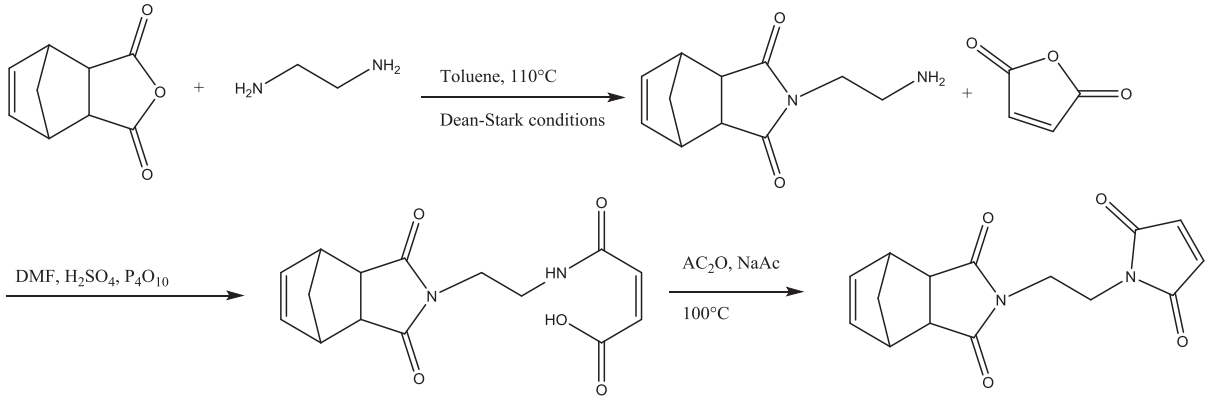


Figure 30: Synthesis of *endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide.

***endo*-*N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide:** Ethylenediamine is distilled at 116 °C. *Endo*-carbic anhydride (1 eq, 10 g, 60.9 mmol) is added rapidly in toluene (200 mL) and ethylenediamine (8.2 eq, 33.5 mL, 501.5 mmol) in a two-neck flask with a fractionating column. The reaction mixture is stirred at 110 °C under Dean-Stark-conditions (Figure 11) for 48 hours. It is concentrated under reduced pressure. The yellowish liquid is dissolved in dichloro methane, filtrated and evaporated under reduced pressure. The yellow-orange solid is washed with cold ethanol and is yielded with 10.4001 g (82.8% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.11 (s, 2H, HC=CH), 3.40-3.37 (m, 4H, H_2C-CH_2), 3.26 (s, 2H, 2x CH-C=O), 2.73 (m, 2H, 2xCH-CH=), 1.75-1.52 (dd, 2H, bridge-head CH_2), 1.24-1.19 (t, 1H, NH_2)

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 176.91, 133.54, 51.27, 44.92, 43.90, 43.64, 40.67, 39.11, 35.32.

(*Z*)-4-((2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisoindol-2-yl)ethyl)amino)-4-oxobut-2-enoic acid: *Endo*-*N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide (1 eq, 5.0338 g, 24.4 mmol) and maleic anhydride (1.2 eq, 2.8254 g, 29.1 mmol) are dissolved in DMF (9 mL) and stirred in a three-neck flask equipped with a dropping funnel and a condenser on an ice bath under inert atmosphere. Phosphorous pentoxide (0.1 eq, 0.7966 g, 2.8 mmol) and sulfuric acid (0.17 eq, 0.258 mL, 4.8 mmol) in DMF (9 mL) are added to the solution via dropping funnel and the reaction is heated to a temperature of 70 °C. After two hours of stirring at 70 °C the mixture is poured on ice and left over the weekend. The formed crystals are dissolved and extracted three times with dichloro methane, dried over Na_2SO_4,

filtrated and evaporated under reduced pressure. Toluene is added several times and removed under reduced pressure to reduce the amount of DMF. The fawn product is dried with finally 4.9759 g (67.0% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.47-6.40 (d, 1H, O=C-**H**C=CH), 6.24-6.19 (d, 1H, O=C-HC=C**H**), 6.08 (s, 2H, CH=CH), 3.66-3.62 (m, 2H, N-CH_2), 3.50-3.47 (m, 2H, 2xCH-C**H**-C(=O)-N), 3.40 (s, 2H, C**H$_2$**-NH), 3.33 (m, 2H, =CH-C**H**), 1.79-1.76 (m, 1H, HC-C**H**$_2$-CH), 1.59-1.56 (m, 1H, HC-C**H**$_2$-CH).

***endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide:** (*Z*)-4-((2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisoindol-2-yl)ethyl)amino)-4-oxobut-2-enoic acid (1 eq, 4.9617 g, 16.3 mmol) and sodium acetate (0.1 eq, 136 mg, 1.7 mmol) are dissolved in acetic acid (25 mL) and heated in a round bottom flask equipped with a condenser to 100 °C. The solution turned dark brown. After two hours the solution is cooled down to room temperature and dichloro methane is added. The organic phase is extracted twice with HCl (37%ic) and twice with $NaHCO_3$ saturated (in aqua dist.). K_2CO_3 (solid) and water are added to neutralise acetic acid. The organic layer is evaporated under reduced pressure. The red powder is yielded 4.1375 g (88.6% of theory).

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.68 (s, 2H, O=C-**H**C=C**H**), 6.05 (s, 2H, CH=CH), 3.67-3.56 (m, 4H, H_2C-CH_2), 3.34-3.23 (d, 4H, 2xC**H**-C**H**-C(=O)-N), 1.73-1.70 (d, 1H, HC-C**H**$_2$-CH), 1.55-1.50 (d, 1H, HC-C**H**$_2$-CH).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 177.54, 176.61, 133.43, 51.31, 44.90, 43.90, 43.66, 36.67, 35.72, 35.34, 35.09.

5.3.3. Failed Synthesis of *exo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide

In order to produce the maleimid containing monomer several trials are performed and will be mentioned below. They will be numbered from 1 to 4. As seen in Figure 31 the attempt failed at binding the ethylendiamin to the carbic anhydride.

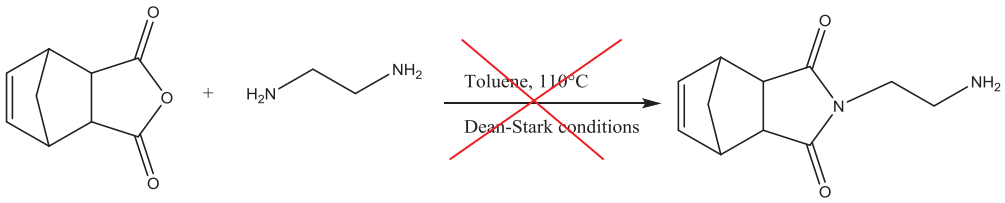


Figure 31: Failed synthesis of *exo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide.

Trial 1: *Exo*-carbic anhydride (1 eq, 5 g, 24.2 mmol) is dissolved in toluene (75 mL) in a two-neck flask with a fractionating column. The white solid does not solve properly and could not be dissolved neither during the treadment with ultrasonic irradiation nor by vigorous stirring. Upon heating to 50 °C the compound dissolves.

Ethylene diamine (8.2 eq, 33.5 mL. 501.5 mmol) is put into a 500 mL two neck flask. A dropping funnel and a Dean-Stark apparatus (Figure 11) are added. *Exo*-carbic anhydride is added by the dropping funnel and toluene (50 mL) is used to wash the funnel. The reaction is heated to 50 °C while the anhydride is added. Another 5 g of *exo*-carbic anhydride are solved in toluene (100 mL) by stirring and heating up to 50 °C before they are added to the flask via the dropping funnel. The reaction is heated to 103 °C. A white jelly like solid is formed. Another 50 mL of toluene (preheated) are added. The reaction is stirred over night. The suspension turns to a clear solution, but lacked water formation. The reaction is stirred for 40 hours and then is evaporated under reduced pressure. The yellow solid is dissolved in 50 mL of ethanol and put in the fridge over night. White crystals are formed in the yellow liquid. The white crystals are yielded in 2.3357 g. The liquid is purified by liquid chromatography (ethyl acetate/methanol 3:1 and a small amount of triethylamine). Three fractions are isolated (compare Table 1).

Table 1: Mass of fractions.

	Mass [g]	Description
Crystals	2.3357	White crystals
Fraction 1	0.5707	Beige powder
Fraction 2	5.4946	Yellow solid
Fraction 3	1.8720	Yellow liquid

Neither of the fractions contained the desired compound with ethylenediamine.

Trial 2: A 25 mL three-neck flask equipped with a condenser and a dropping funnel is put under N_2 atmosphere. The product of trial 1 (2.312 g, 11.2 mmol, fraction: crystals), maleic anhydride (0.9662 g, 9.9 mmol) and DMF (6 mL) are put into the flask. Phosphorous pentoxide (0.2332 g, 4.8 mmol), sulfuric acid (71.5 µL, 1.3 mmol) and DMF (6 mL) are put into the dropping funnel and added dropwise. The reaction is stirred at 70 °C over night with reflux. Next it is poured onto ice and extracted with chloroform (3x50 mL). The organic layer is dried over Na_2SO_4 anhydrous. DMF is removed by adding toluene and evaporating under reduced pressure for several times. This works because of the two high boiling points of the solvents. White solid, which was identified as educt by ^{1}H-NMR, is yielded and reused in trial 3.

Trial 3: The crystals (2.312 g, 11.2 mmol) are solved in acetic acid (28 mL) and are stirred vigorously. Maleic anhydride (0.9734 g, 9.9 mmol) is added. The reaction is heated to 45 °C and stirred for 10 minutes. Sulfuric acid (1 mL, 18.8 mmol) is added and the reaction temperature is raised to 60 °C for one hour. The beige suspension turned to a yellow liquid and is poured on ice. A white solid is formed and filtrated and washed with $NaHCO_3$ saturated (in aqua dist.) and H_2O. To dissolve the solid properly it is solved in ethanol and heated to 40 °C. Ethanol is removed and replaced by dicholoromethane. The organic layer is extracted with $NaHCO_3$ saturated (in aqua dist.), dried over Na_2SO_4 anhydrous and characterised with ^{1}H-NMR. A solid is yielded with 2.1394 g and the characterisation shows that it is still the educt and ethylene diamin did not bind to the *exo*-carbic anhydride.

Trial 4: The possible *exo*-*N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide (Fraction 2 of trial 1, 2.2700 g, 11.0 mmol) and maleic anhydride (0.9515 g, 9.7 mmol) are dissolved in

DMF (6 mL) and stirred for about one hour . An ice bath is put under the three neck flask, which is equipped with a dropping funnel, a condenser and is put under N_2 atmosphere. Phosphorous pentoxide (0.265 g, 0.9 mmol), sulfuric acid (71.5 µL, 1.3 mmol) and DMF (6 mL) are added through the dropping funnel and the system is heated to 70 °C. The reaction turns to an orange-yellowish liquid. After two hours of stirring the reaction is poured onto ice and a beige solid is formed, which is extracted with dichloro methane. Afterwards the organic layer is dried over Na_2SO_4 anhydrous and evaporated under reduced pressure. DMF is removed by adding toluene and evaporating under reduced pressure for several times. 2.9014 g of yellow liquid are isolated. The product is used in the ring-closing step. All of it as well as acetic anhydride (23 mL) and sodium acetate (80.7 mg, 1.0 mmol) are stirred at 100 °C over night. The reaction is extracted in dichloro methane with 1M HCl (3x 50 mL), $NaHCO_3$ saturated in aqua dist. (3x 50 mL) and brine saturated (in aqua dist., 3x 50 mL). Because acetic anhydride still stays in the organic layer K_2CO_3 (solid) is added. In a next step the product is again extracted with dichloro methane (3x 50 mL) and distilled water (2x 50 mL). Afterwards it is dried over Na_2SO_4 anhydrous and under reduced pressure. The solid is 2.5265 g, but according to ^{1}H-NMR no product is formed, because ethylene diamine did not bind to *exo*-carbic anhydride.

5.4. Synthesis of Polymers

The aim of this thesis is to synthesise alternating copolymers which can be functionalised. Both monomers have in common that they have a norbornene moiety which can be opened and therefore functionalised by, in example, cross metathesis. Some monomers (ethyl acrylate, methyl metacrylate and styrene) are polymerised in prior tests to get used to the polymerisation technology. As polymerisation methods ATRP (atom transfer radical polymerisation) and uncontrolled polymerisation are chosen. Finally the tested monomers are copolymerised with the monomers synthesised as described above in chapter 5.3.

5.4.1. Polymerisation of methyl methacryltate

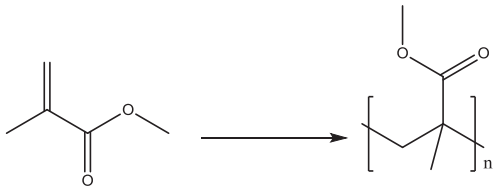


Figure 32: Polymerisation of methyl metacrylate to poly(methyl metacrylate) (PMMA).

ATRP: The procedure of ATRP is optimised. Therefore different variables are altered like the molarity of the reaction, an alternating order of the addition of chemicals and the monomer and its purification.

The polymerisation is performed like mentioned in chapter 5.2. The polymerisation of reaction 1 and 2 does not lead to the formation of the desired procuct because of the low molarity of the monomers. The molarity is raised to about 4M. Another problem occurs working with the MMA. The MMA - used in reaction 1, 2 and 5 – has been older than 15 (!) years. However, we do not really know ho this MMA was stored all over this time. Even after purification trials by extraction the polymerisation progress was very limited. Therefore new MMA was purchased and used in reactions 3, 4 and 6. A final step to optimise the ATRP procedure is to change the order of addition of chemicals.

CuBr is added to absolute toluene and MMA into the Schlenk flask. Either the ligand *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA; 1, 2 and 3) or the initiator (1-bromoethyl)benzene (4, 5 and 6) is added. After the three cycles of freeze-pump-thaw are done the reaction is heated to the temperature given in Table 2. The polymerisation is either initiated by the initatior (1, 2 and 3) or by the ligand (4, 5 and 6). All reactions were stirred for a couple of days before they were quenched with cold methanol, filtrated over Al_2O_3, washed

with dichloro methane, evaporated under reduced pressure, re-dissolved in dichloro methane and precipitated in cold methanol before GPC and NMR investigations were started.

Table 2: Amount of educts (MMA=methyl metacrylate; PMDETA= *N,N,N′,N′,N″*-pentamethyldiethylenetriamine; BEB=(1-bromoethyl)benzene; abs.=absolute; [a] CuBr is freshly washed as mentioned above 5.2; [b] Absolute toluene is degassed as mentioned above 5.2; [c] old MMA, stored under unknown conditions since at least March 1999; [d] is stirred over several days; [e] old MMA (stored under unknown conditions since at least March 1999) is extracted with 1M NaOH and distilled water, dried with Na_2SO_4, filtrated and set under N_2 atmosphere; [f] fresh MMA;).

	1[a,b,c, d]	2[c,d,e]	3[d,f]		4[d,f]	5[c,d,e]	6[a,b,d,f]
Monomer [M]	0.2	0.5	3.8	Monomer [M]	3.8	3.8	4.2
CuBr [mg]	28.3	26.5	133.2	CuBr [mg]	137.9	133.0	8.8
Toluene abs. [mL]	45	19	12	Toluene abs. [mL]	12	12	0.7
MMA [mL]	1	1	5	MMA [mL]	5	5	0.323
PMDETA [µL]	39.0	38.8	194.0	BEB [µL]	126.8	126.8	8.2
BEB [µL]	25	25	126.8	PMDETA [µL]	194.0	194.0	12.5
Temperature [°C]	110	110	110	Temperature [°C]	110	110	80

No data of 1, 2, 5 and 6 are obtained, because not enough polymer was obtained due to low conversions.

Uncontrolled radical polymerisation: As mentioned above two different batches of MMA are used. To see if polymerisation takes place at all, an uncontrolled radical polymerisation is performed with the old and new batch of MMA. The older batch of MMA is extracted as mentionened above (ATRP of MMA).

A 50 mL Schlenk flask is set under N_2 atmosphere. Absolute toluene (chapter 5.2), MMA and benzoyl peroxide (BPO) are put into the Schlenk flask. The reaction is heated to 60 °C and stirred for 24 hours. It is quenched with cold methanol to purify the polymer.

Table 3: Amount of the uncontrolled radical polymerisation (BPO=benzoyl peroxide, MMA=methyl metacrylate; [a] old MMA (stored under unknown conditions since at least March 1999); [b] fresh MMA;).

	7[a]	8[b]
Toluene abs. [mL]	4	4
MMA [mL]	1	1
BPO [mg]	24.5	21.9

Table 4: GPC data of polymerisation of methyl metacrylate.

	PDI	M_n [10^3 g/mol]
3	1.794	8.980
4	1.587	8.180
7	1.936	58.940
8	1.594	53.220

5.4.2. Polymerisation of styrene

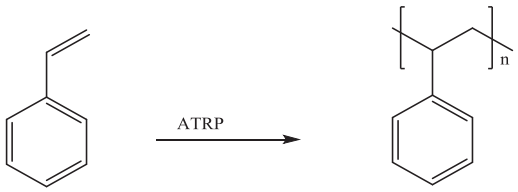


Figure 33: Synthesis of polystyrene.

Polystyrene: CuBr, absolute toluene and styrene are put into the Schlenk flask. The initiator (1-bromoethyl)benzene is added. After the three cycles of freeze-pump-thaw are done the reaction is heated to the temperature (Table 5). After reaching the temperature the polymerisation is initiated by PMDETA. All reactions are stirred for the time given in Table 5 before they are quenched with cold methanol, filtrated over Al_2O_3, washed with dichloro methane, evaporated under reduced pressure, re-dissolved in dichloro methane and precipitated in cold methanol before GPC and NMR analysis were done.

Table 5: Amount of educts (PMDETA= *N*,*N*,*N′*,*N′*,*N″*-pentamethyldiethylenetriamine; BEB=(1-bromoethyl)benzene; abs.=absolute; [a] CuBr is freshly washed as mentioned at 5.2; [b] Absolute toluene is degassed as mentioned in 5.2; [c] Styrene is filtrated over Al_2O_3 to get rid of any stabilisators; [d] shaken immediately after addition of PMDETA;).

	1[a, b, c]	2[c]	3[a, c, d]		4[c, d]	5[a, b, c, d]	6[a, b, d]
CuBr [mg]	19.0	18.1	39.7	CuBr [mg]	38.6	38.0	37.8
Toluene abs. [mL]	3	3	3.3	Toluene abs. [mL]	3.3	3.4	3.4
Styrene [mL]	1.500	1.436	1.516	Styrene [mL]	1.516	1.516	1.516
BEB [µL]	18.1	17.1	36.2	BEB [µL]	36.2	36.2	36.2
PMDETA [µL]	28.8	27.2	57.5	PMDETA [µL]	57.5	57.5	57.5
Temperature [°C]	110	110	110	Temperature [°C]	110	110	110
Time [h]	40.5	20	2.5	Time [h]	17	66.5	66.5

Table 6: GPC data of polymerisation of styrene.

	PDI	M_n [10^4 g/mol]
1	1.544	1.639
2	1.232	1.204
3	1.259	0.441
4	1.160	0.218
5	1.135	0.191
6	1.366	0.810

5.4.3. Polymerisation of ethyl acrylate

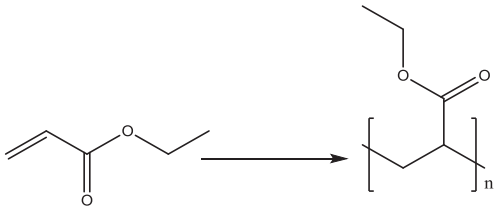


Figure 34: Synthesis of poly ethyl acrylate.

Polyethyl acrylate: CuBr, absolute toluene and EA are put into the Schlenk flask, which is set under N_2 atmosphere. PMDETA is added. After the three cycles of freeze-pump-thaw are done the reaction is heated to 110 °C. After reaching the temperature the system is initiated by (1-bromoethyl) benzene. The reactions are stirred for a couple of days. The reaction is followed by ^{1}H-NMR and no conversion is observed.

Table 7: Amount of the educts (EA=ethyl acrylate; PMDETA= *N*,*N*,*N'*,*N'*,*N''*-pentamethyldiethylenetriamine; BEB=(1-bromoethyl)benzene; abs.=absolute; [a] CuBr is freshly washed as mentioned above 5.2; [b] Absolute toluene is degassed as mentioned above 5.2; [c] is stirred over several days; [d] EA is extracted with 1M NaOH and distilled water, dried with Na_2SO_4, filtrated and set under N_2 atmosphere;).

	1[a,b,c]	2[c,d]
Molarity [M]	0.5	0.5
CuBr [mg]	32.3	25.5
Toluene abs. [mL]	23	19
EA [mL]	1	1
PMDETA [µL]	45.1	38.8
BEB [µL]	29.5	25

5.4.4. Polymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate

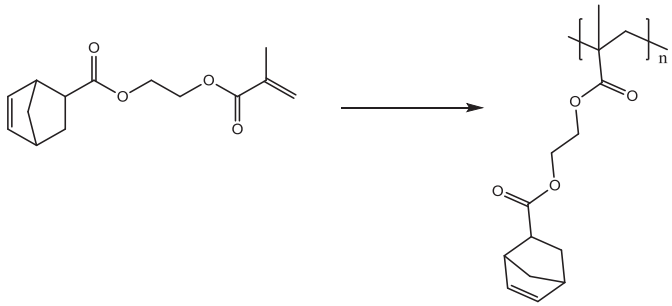


Figure 35: Synthesis of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate.

ATRP: Absolute toluene is set under N_2 atmosphere by putting a syringe into the solvent and is flushed with gas. A 10 mL Schlenk flask is put under N_2 atmosphere. CuBr, 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and absolute toluene are added to the 10 mL Schlenk flask. (1-bromoethyl)benzene is added and three freeze-pump-thaw cycles are done. The solution is heated to the temperature given in Table 8. PMDETA is added after the temperature is reached.

Table 8: Amount of substances (Monomer A=synthesised like described in chapter 5.3.1, starting material cyclopentadiene; B=synthesised like described in chapter 5.3.1, starting material HEMA;).

	A	B
CuBr [mg]	2.1	4.5
Absolute toluene [mL]	0.6	1.2
Monomer [mg]	154.9	305.6
(1-bromoethyl)benzene [µL]	1.6	3.3
PMDETA [µL]	2.5	5.0
Temperature [°C]	110	80

Heating is stopped after 4 hours and ^{1}H-NMR samples are taken for reaction control on a regular basis (each hour). The reaction is stirred at room temperature until purification for a total of 24 hours. The reaction is controlled by thin layer chromatography (cyclohexane/ethyl acetate 3:1). The polymer stays at the bottom line while the monomer is having a higher R_f (ratio of fronts) value. This happens because of the high molecular weight.

Afterwards the reaction is filtrated over Al_2O_3 and washed with dichloro methane several times. Then the product is evaporated under reduced pressure and dissolved in a minimum of dichloro methane and precipitated in cold methanol. No GPC has been performed because ^{1}H-NMR shows no polymerisation (Figure 19).

Uncontrolled radical polymerisation: 300 µL of absolute toluene, 2.9 mg of benzoyl peroxide and 162.8 mg of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (synthesised as described in chapter 5.3.1, starting material cyclopentadiene) are put into a 10 mL Schlenk flask and stirred at a temperature of 60 °C. The reaction turns gel like which suggests that cross linking happened.

No NMR and GPC have been performed, because the polymer is insoluble in THF and $CDCl_3$.

5.4.5. Copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and methyl metacrylate

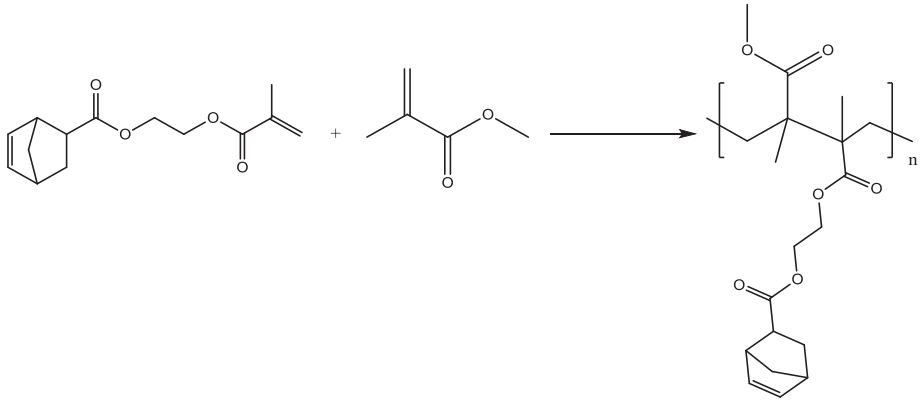


Figure 36: Copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and methyl metacrylate.

ATRP: Freshly washed (chapter 5.2) CuBr (38.7 mg), methyl metacrylate (1.552 mL, filtrated over Al_2O_3) and (1-bromoethyl)benzene (36.2 µL) are dissolved in absolute toluene (3.2 mL) in a 10 mL Schlenk flask under N_2 atmosphere. Three cycles of freeze-pump-thaw are done and the reaction is heated to 80 °C afterwards. PMDETA (57.6 µL) is added. After ten minutes 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (348.6 mg) is added and the reaction is left over night for a total of 19 hours. The product becomes a greenish gel. It is dissolved in a minimum of dichloro methane and precipitated in cold methanol before GPC has been performed.

The polymer turned to a gel like solid and is not soluble in $CDCl_3$. Therefore no NMR measurements are performed.

A second trial under the same conditions do not form any gel. ^{1}H-NMR is performed and showed no copolymerisation; Figure 18.

Table 9: GPC data of copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and methyl metacrylate.

	PDI	M_n [10^3 g/mol]
Polymer	8.768	5.671

5.4.6. Copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and styrene

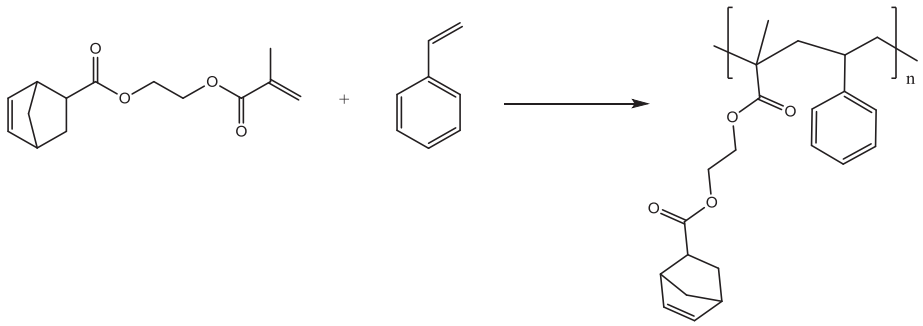


Figure 37: Copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and styrene.

ATRP: Freshly washed (chapter 5.2) CuBr (38.0 mg), styrene (1.516 mL, filtrated over Al_2O_3) and (1-bromoethyl)benzene (36.2 µL) are dissolved in absolute toluene (3.4 mL) in a 10 mL Schlenk flask under N_2 atmosphere. Three cycles of freeze-pump-thaw are done and the reaction is heated to 80 °C afterwards. PMDETA (57.6 µL) is added. After ten minutes 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (306.9 mg) is added and the reaction is left over night for a total of 21 hours at 80 °C. Afterwards it is filtrated over Al_2O_3, evaporated under reduced pressure, dissolved in one millilitre of dichloro methane and precipitated in cold methanol, before GPC and NMR are performed.

Table 10: GPC data of copolymerisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate and styrene.

	PDI	M_n [10^2 g/mol]
Polymer	1.055	3.007

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 7.41-6.62 (C_6H_5 of styrene), 6.18-6.14 (CH=CH of norbornene), 5.78-5.23 (CH=CH of monomer styrene), 4.41-3.72 (O- H_2C-CH_2-O), 3.21-2.80 (=CH-C**H**-(CH_2)-C**H**), 2.36-0.27 (H_3C-C-CH_2-CH-CH_2, bridge-head CH_2, C**H_2**-CH-C=O).

5.4.7. Copolymerisation of *endo-N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide with styrene

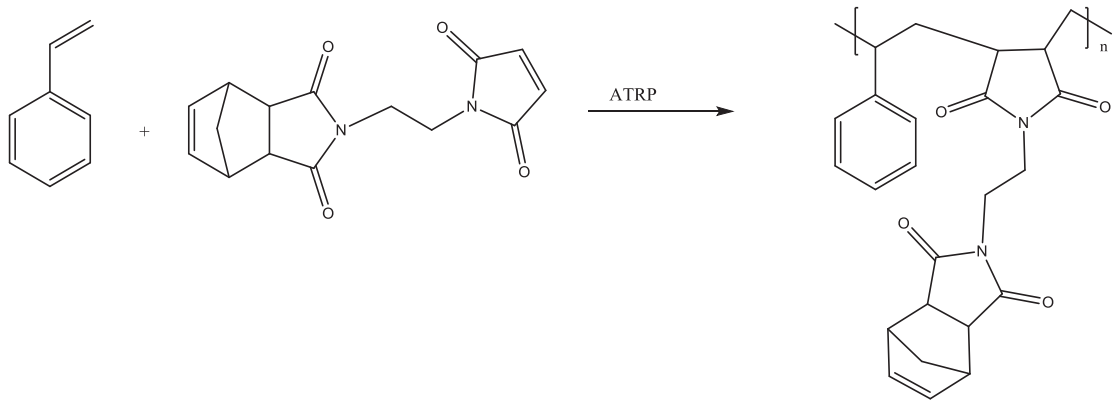


Figure 38: Copolymerisation of *endo-N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide and styrene.

ATRP: CuBr, styrene (filtrated over Al_2O_3) and (1-bromoethyl)benzene are dissolved in absolute toluene in a 10 mL Schlenk flask under N_2 atmosphere. Three cycles of freeze-pump-thaw are done and the reaction is heated to a given temperature (Table 11) afterwards. PMDETA is added and afterwards (Table 11) 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate is added and the reaction is left for 48 hours. It is filtrated over Al_2O_3, evaporated under reduced pressure, dissolved in one millilitre of dichloro methane and precipitated in cold methanol before GPC and NMR are performed.

Table 11: Amount of the educts ([a] CuBr is freshly washed as mentioned above 5.2; [b] Absolute toluene is degassed as mentioned above 5.2).

	1[a, b]	2	3
CuBr [mg]	19.3	38.5	38.8
Toluene abs [mL]	3.3	3.3	3.4
Styrene [mL]	1.516	1.516	1.516
(1-bromoethyl)benzene [µL]	18.1	36.2	36.2
PMDETA [µL]	28.8	57.5	57.5
Monomer [mg]	75.5	380.5	382.5
Time [min]	120	10	10
T [°C]	110	110	80

Table 12: GPC data of copolymerisation of *endo-N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide and styrene.

	PDI	M_n [10^4 g/mol]
Polymer 1	1.584	2.830
Polymer 2	1.563	4.667
Polymer 3	1.262	1.264

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 7.23-6.46 (C_6H_5 of styrene), 6.02 (CH=CH of norbornene), 5.78-5.23 (CH=CH of monomer styrene), 3.32 (N-H_2C-CH_2-N), 1.84 (backbone chain of maleimide and styrene), 1.52-1.26 (bridge-head CH_2, -(CH_2)-C**H**-C**H**-C=O).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ (ppm): 145.23, 129.07, 128.54, 128.26-127.73, 125.65, 125.33, 40.46, 21.49.

5.5. Synthesis of functionalised monomers

The two monomers are functionalised with ethyl acrylate and styrene. Therefore the monomer and the functionalising group (in high excess, 6 eq) are put into a Schlenk flask under N_2 atmosphere and heated up to a given temperature before the functionalisation is started with the Ruthenium catalyst (Figure 39). The reaction is completed when the colour changed from red to yellow.

[Ru] :

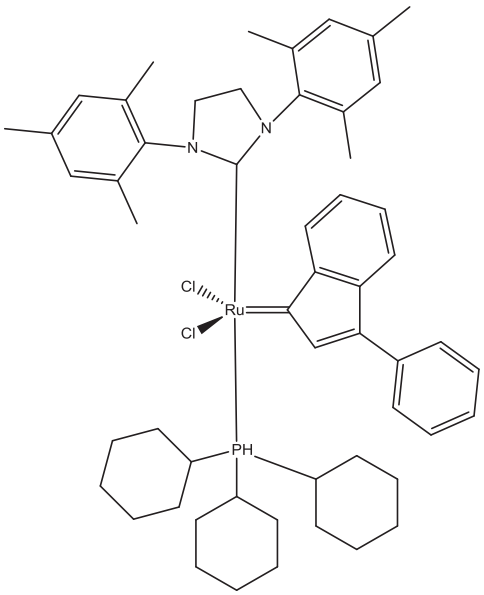


Figure 39: Ruthenium catalyst, (*E*)-(1,3-dimesitylimidazolidin-2-yl)(3-phenyl-1*H*-inden-1-ylidene)(tricyclohexyl-l5-phosphanyl)ruthenium(VI) chloride.

5.5.1. Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with ethyl acrylate

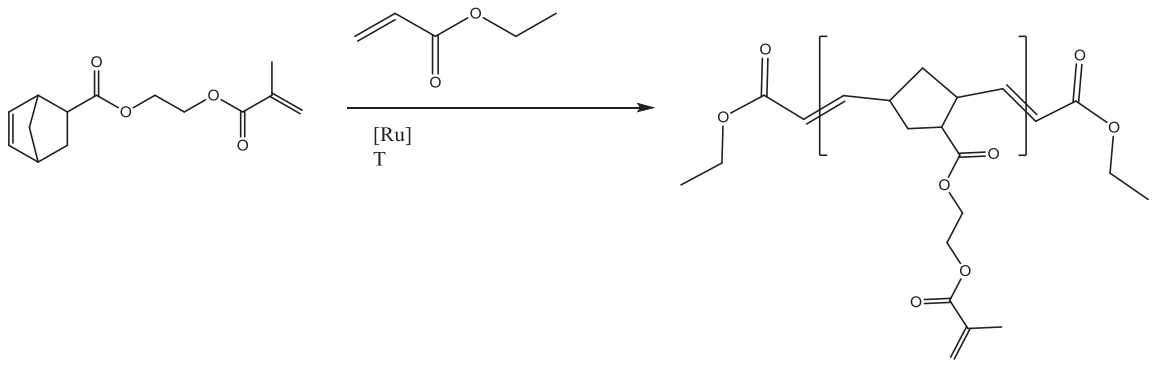


Figure 40: Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (T=different temperatures) with ethyl acrylate.

Functionalisation: The monomer (about 100 mg) is weighed into a 10 mL Schlenk flask and EA (1 mL, purification see Table 7) is added. The flask is degassed by several cycles of

changing between vacuum and N_2 atmosphere. Afterwards the [Ru] catalyst (2-3 mg) is added and the reaction turned red. The reaction is heated by an oil bath at a temperature given in Table 13 and the flask is put into it afterwards. The reaction is stopped after the colour turned yellow, which indicates that the functionalisation is finished. Ethyl acrylate is removed under reduced pressure.

Table 13: Amount of the educts (RT= room temperature; [a] the monomer is polymerised. It turns to a clear gel like solid; [b] a stabilisator, butylated hydroxytoluene, is additionally added to the mixture; [c] the monomer, which is polymerised in former experiments, is re-synthesised; [d] the functionalisation is left at room temperature for over a week. It does not turn yellow;).

	Monomer [mg]	[Ru] [mg]	T [°C]	Time [h]
1[a]	102.2	3.5	80	0.5
2[a, b]	111.4	2.3	60	0.5
3[c]	102.0	2.4	60	1.0
4[c,d]	110.6	2.7	RT	[d]
5[c]	130.7	2.3	40	0.5

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm): 6.93-4.88 (=CH_2, CH=CH), 4.33-4.08 (O-CH_2, O-CH_2-CH_2-O), 3.07-0.69 (cyclopentane, O=C-CH=, CH_2-pentane, CH_3).

5.5.2. Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate with styrene

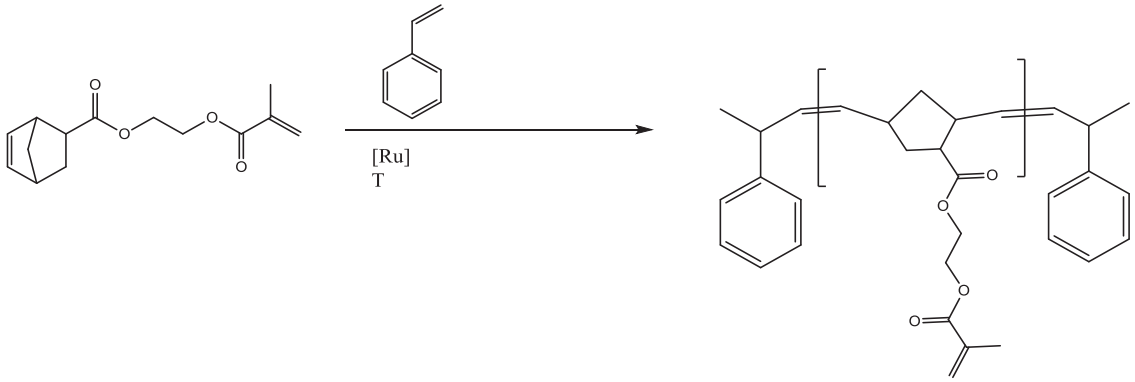


Figure 41: Functionalisation of 2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate (T=different temperatures) with styrene.

Functionalisation: The monomer (about 100 mg) is weighed into a 10 mL Schlenk flask and styrene (1 mL, purified by filtration over Al_2O_3) and dichloro methane (1 mL) are added. The flask is degassed by several cycles of changing between vacuum and N_2 atmosphere. Afterwards the [Ru] catalyst (2-3 mg) is added and the reaction turned red. An oil bath is raised to a given temperature (Table 14) and the flask is put into it afterwards. The reaction is stopped after the colour turned yellow, which indicates that the functionalisation is finished. Styrene is removed under reduced pressure.

Table 14: Amount of the educts (RT= room temperature; [a] the monomer, which is polymerised in former experiments, is re-synthesised; [b] the functionalisation is left at room temperature for over a week. It does not turn yellow; [c] the reaction turns to a gel like solid;).

	Monomer [mg]	[Ru] [mg]	T [°C]	Time [h]
1[a,b]	114.9	3.5	RT	[b]
2[a,c]	111.4	2.3	40	18.5

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm):.7.45-7.04 (C_6H_5), 6.36-4.11 (=CH_2, CH=CH, O-CH_2, O-CH_2-CH_2-O), 3.04-0.80 (cyclopentane, O=C-CH=, CH_2-pentane, CH_3, C**H**-(CH_3)-C**H**-(C_5H_6)-C**H$_2$**).

5.5.3. Functionalisation of *endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide with ethyl acrylate

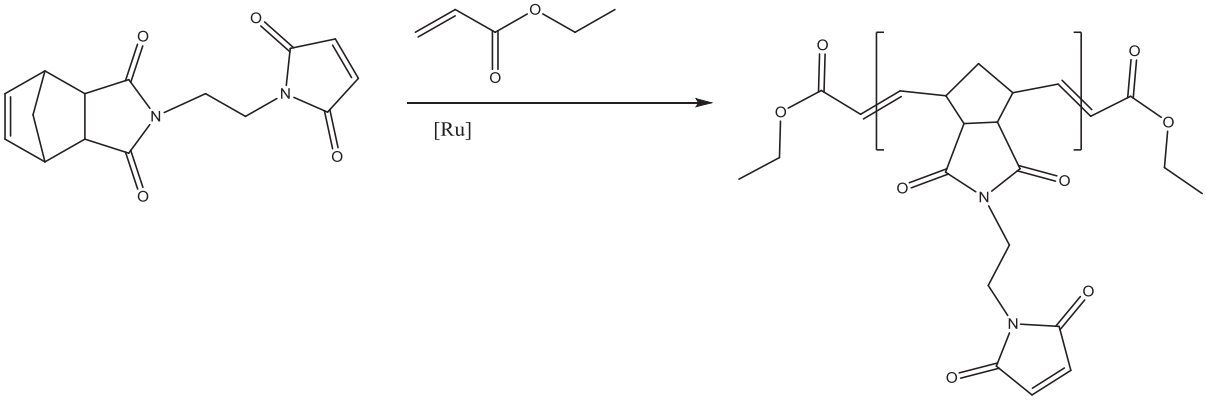


Figure 42: Functionalisation of *endo-N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide with ethyl acrylate.

Functionalisation: Monomer (100.2 mg) is weighed into a 10 mL Schlenk flask and ethyl acrylate (1 mL, purification see Table 7) and absolute toluene (0.5 mL) are added. The flask is degassed by several cycles of changing between vacuum and N_2 atmosphere. Afterwards [Ru] catalyst (1.9 mg) is added and the reaction turned red. An oil bath is raised to 60 °C and the flask is put into it after reaching the temperature. The reaction is stopped after the colour turns yellow 30 minutes later, which indicates that the functionalisation is finished. Ethyl acrylate is removed under reduced pressure.

^{1}H NMR (300.36 MHz, $CDCl_3$) δ (ppm):.7.45-7.04 (C_6H_5), 6.36-4.11 (=CH_2, CH=CH, O-CH_2, O-CH_2-CH_2-O), 3.04-0.80 (cyclopentane, O=C-CH=, CH_2-pentane, CH_3, C**H**-(CH_3)-C**H**-(C_5H_6)-C**H$_2$**).

6. Appendix

6.1. List of Abbreviations

ATRP	Atom Transfer Radical Polymerisation
BPO	Benzoyl peroxide
DCI-Et-MI-Nbe	*endo*-*N*-[2-(1*H*-Pyrrole-2,5-dione)ethyl]-5-norbornene-2,3-dicarboximide
DMF	Dimethylformamide
EA	Ethyl acrylate
Et_3N	Triethylene amine
GPC	Gel permeation chromatography
HEMA	Hydroxyethylmetacrylate
HEMA-Nbe	2-(methacryloyloxy)ethyl norborn-5-ene-2-carboxylate
MMA	Methyl metacrylate
PDI	Poly dispersity index
PMDETA	*N,N,N′,N′,N″*-pentamethyldiethylenetriamine
R_f	Ratio of fronts
ROMP	Ring opening metathesis polymerisation
THF	Tetrahydrofuran
TLC	Thin layer chromatography

6.2. List of Tables

6.3. List of Figures