DIPLOMA THESIS IN POLYMER CHEMISTRY

Synthesis of Cyclic Polymers in miniemulsion

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October, 2013

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This diploma thesis was carried out in the time between January and October 2013 at the Max Planck Institute for Polymer Research in the research group of Prof. Dr. K. Landfester.

to my family

"When you study natural science and the miracles of creation, if you don't turn into a mystic you are not a natural scientist."

Albert Hofmann

Acknowledgments

First of all my gratitude goes to my supervisor Prof. Katharina Landfester. Many thanks for giving me the opportunity to perform my thesis in your group and for the interesting and challenging topic!

I forward my appreciation to Dr. Frederik Wurm for his constructive contribution and helpful advice.

I want to thank Matthew Hood, Beatriz Ma, Margherita Mari, Laura Preiss, Stephanie Tomcin, Sandra Seywald, Rafael Munoz-Espi, Viktor Fischer, Daniel Crespy and all other group members for their kindness, helpfulness and a nice atmosphere in the lab.

Thanks to Eugen G., Vladimir G., Helene R., Inna M., who accompanied me through the whole period of my studies.

I am deeply grateful to my family, especially my mother for her emotional and financial support.

List of abbreviations and symbols

BHT	butylhydroxytoluene
Cy	cyclohexyl
DCC	dicyclohexyl carbodiimide
DCM	dichloromethane
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EA	ethyl acetate
eq	equivalent
GPC	gel-permeation chromatography
MW	molecular weight
Mes	mesityl
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy
PLA	polylactide
PS	polystyrene
ppm	parts per million
REP	ring expansion polymerization
ROMP	ring opening metathesis polymerization
RT	room temperature
SDS	sodium dodecyl sulfate
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
THF	tetrahydrofuran

TLC	thin layer chromatography
UV-light	ultra violet light

Abstract

The present work describes the preparation of α, ω – bifunctional polymers, such as polystyrenes and polylactides, their intramolecular cyclization attempts in solution and in miniemulsion as well as the synthesis of a cyclic ruthenium alkylidene catalyst for the ring expansion polymerization. The isolation of the successfully synthesized catalyst exhibits serious difficulties remaining an unsolved problem. The formation of macrocycles via [2+2] photocycloaddition could not be achieved in either case. Cyclic polystyrene was prepared in solution via the ring closing metathesis approach by using the second generation Grubbs catalyst. The final step, the cyclization in miniemulsion, has not yet been accomplished and is still a subject of investigation.

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1 Theory

1.1 Synthetic approaches for cyclic polymers

The discovery of cyclic DNA molecules in 1962[1] inspired many scientists and launched an intense research in the field of cyclic polymers. Several synthetic strategies have been developed and tested since then in order to prepare specific macromolecules. These strategies can be devided into five categories each of which has multiple methods.[2]

1.1.1 Kinetically controlled polycondensations

Since kinetically controlled reactions do not show equilibration reactions only a main product is formed as a consequence of the fastest reaction. Almost all kinetically controlled polycondensations show a competition of cyclisation with every growing step of the polycondensation and at all concentrations.[3,4,5] Figure 1.1 shows the correlation between conversion and mol percentage of rings with the initial monomer concentration as the third parameter.

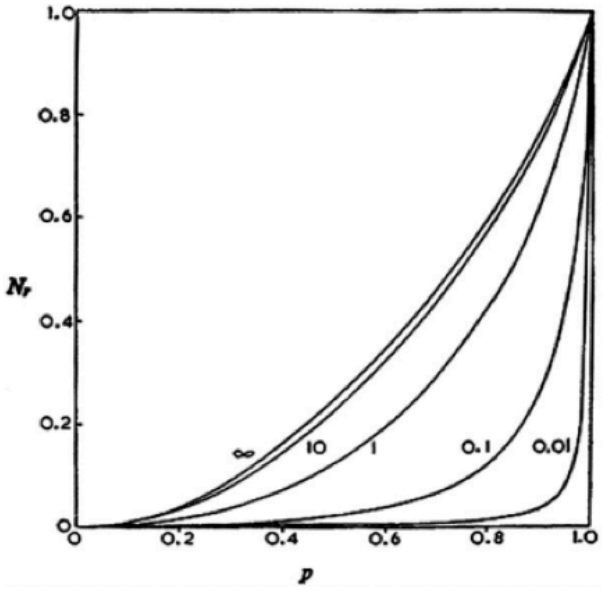


Figure 1.1 Number fraction of rings (N_r) Versus conversion (p) in kinetically controlled polycondensations with variation of the initial monomer concentration. [4,5]

One can conclude from Figure 1.1 that at conversions below 99% and especially below 90% the yield of cycles increases with lower initial monomer concentration and at conversions above 99% the weight fraction of cycles approaches 100% no matter how high the concentration of the initial monomer is. Therefore the conversion is the most important parameter which has to be regarded for an effective synthesis of macrocycles and thus experimental conditions leading to high conversions must be ensured.[2]

In order to maximize the yield of cyclic polymers, polycondensation reaction conditions and structure of monomers have been optimized over the past decade.[2] It could be shown that cyclization occurs both in solution and in bulk. An example for a polycondensation in bulk are the syntheses of polyesters from silylated diphenols and aliphatic diacid dicarboxylic acid dichlorides in the melt at temperatures above 150 °C. [6,7]

Cyclic polycarbonates were also successfully obtained in high purities using optimized synthetic approach via bisphenol-A with phosgene and hydrolytic polycondensation of bisphenol-A bischloroformate.[8,9,10,11,12] Circular polyimides have been prepared from aromatic diamines and tetracarboxylic anhydrides via direct polycondensation in refluxing m-cresol (Figure 1.2).[13,14]

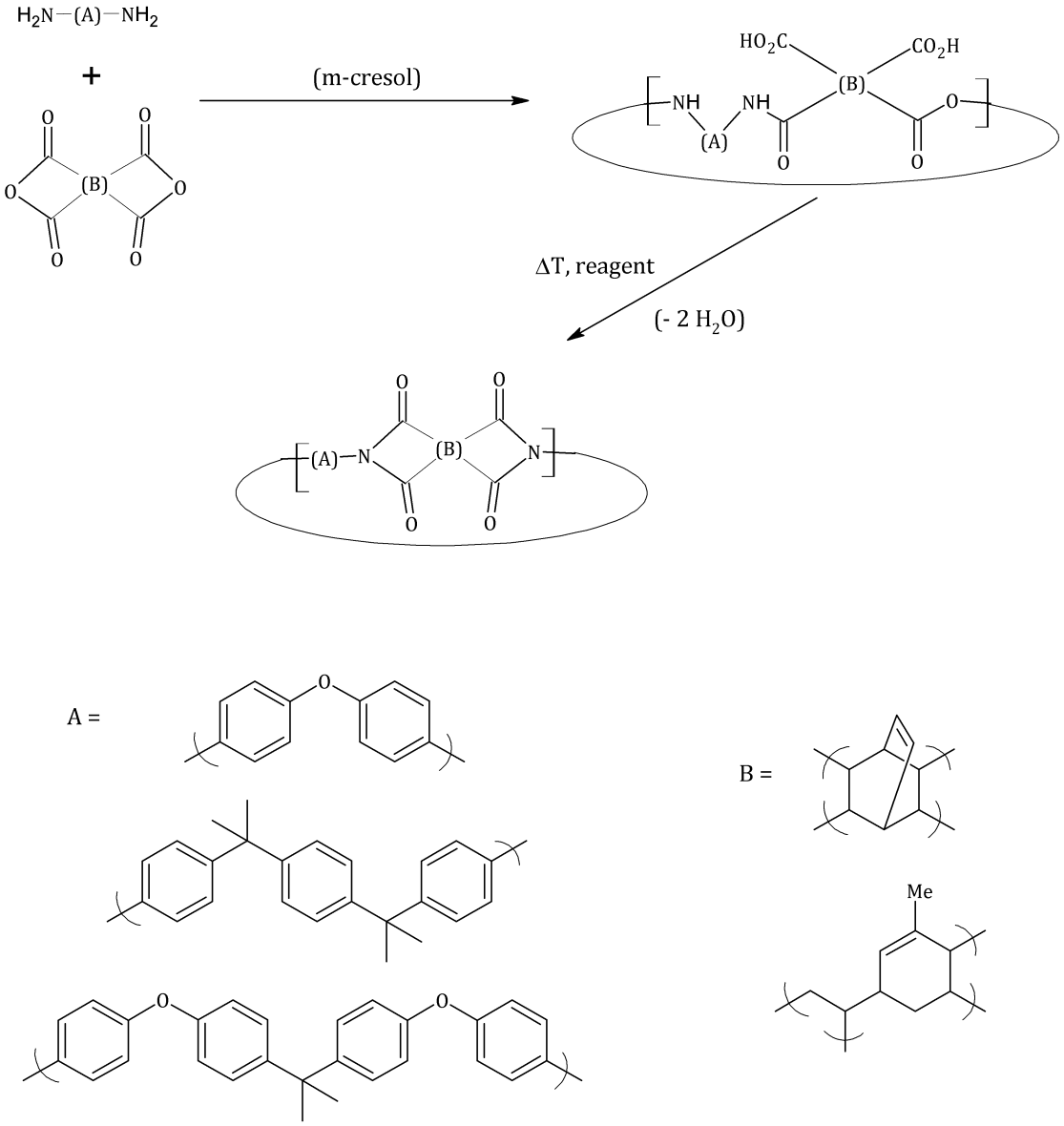


Figure 1.2 Synthesis of cyclc polyimides in boiling m-cresol.[13,14]

Furthermore, aromatic polyethers have been synthesized after prudent optimization of conversion resulting in pure cycles without linear polymers.[15,16] (Figure 1.3).

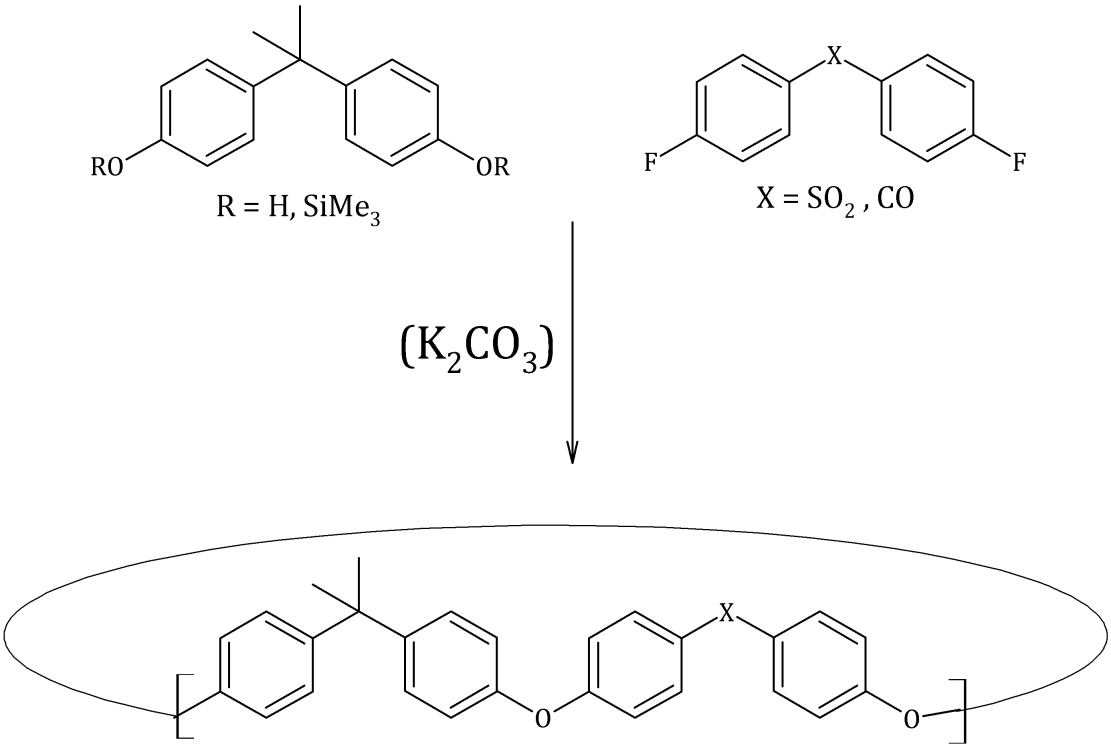


Figure 1.3 Synthesis of cyclic poly(ether sulfone)s.[15,16]

Another effective method is represented by „a^2+b^2“ reactions at low concentrations. The first example is the preparation of cyclic polystyrenes.[17,18,19] Using a bisanionic initiator bisanionic polystyrenes have been synthesized and then reacted with dichloro- or dibromoalkanes such as dibromomethane or dichloromethane. 1,2- and 1,4-bis(chloromethyl) and bis(bromomethyl) benzenes have also been used for cyclization. With the use of low initial monomer concentration cyclization occured rather than polycondensation (Figure 1.4).

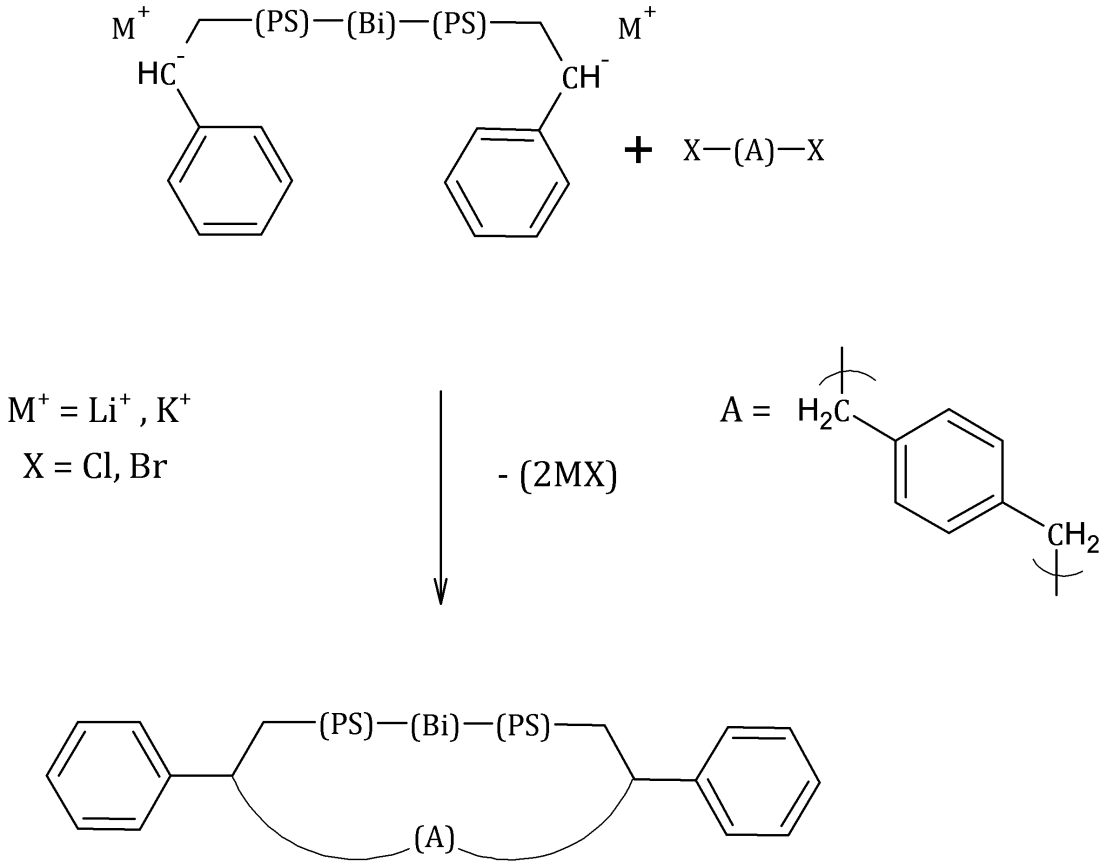


Figure 1.4 **Synthesis of cyclic polystyrenes by „a²+b²“ (poly)condensation at low initial monomer concentration. Bi = bifunctional initiator.[17,18,19]**

The big advantage of the living anionic polymerization is the low polydispersity and the size of the resulting cycles can be controlled by the monomer/initiator ratio. A number of other vinyl monomers have been used as the basis for the synthesis of cyclic polymers (Figure 1.5).[2]

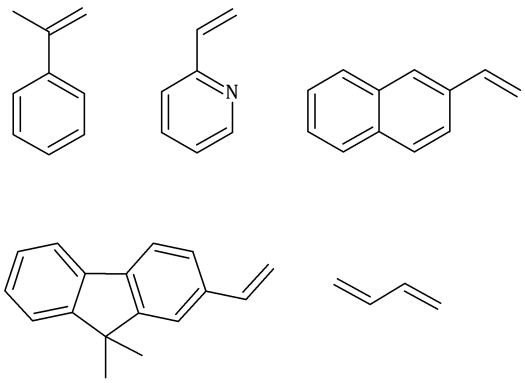


Figure 1.5 **Vinyl monomers used for the synthesis of cyclic homopolymers via „a²+b²“ (poly)condensation at low initial monomer concentrations.[2]**

For all these vinyl monomers anionic polymerization has been used to control the molecular weight and to keep the polydispersities low. The „a^2+b^2“ condensation strategy turned out to be useful in synthesizing cyclic polyethers, such as poly(ethylene oxide).[20,21,22,23] The synthesis involves commercially available poly(ethylene glycol) which is either condensed with bistosylated poly(ethylene glycol) by heating with potassium hydroxide resulting in a perfect cyclic polyether, or with potassium hydroxide and dichloromethane by closing the ring via a formal group (Figure 1.6) .

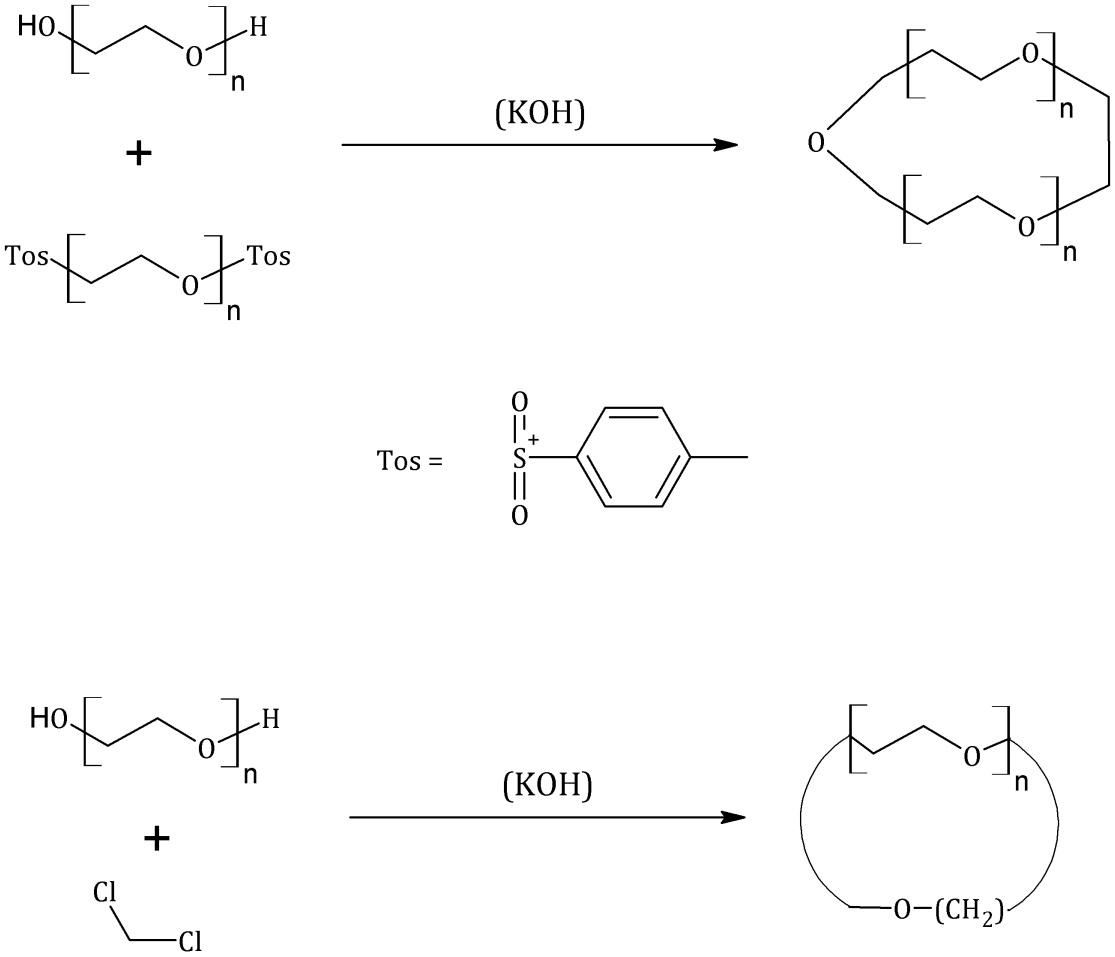


Figure 1.6 Synthesis of cyclic poly(ethylene oxide)s by „a^2+b^2“ (poly)condensation.[20,22]

Cyclic diblockcopolymers have been prepared via „a_2+b_2“ condensation of bisanionic homopolymers at low initial monomer concentration.[2] The general procedure involves the preparation of a bisanionic A-B-A triblock copolymers which is *in situ* cyclized with a coupling agent (Figure 1.7).

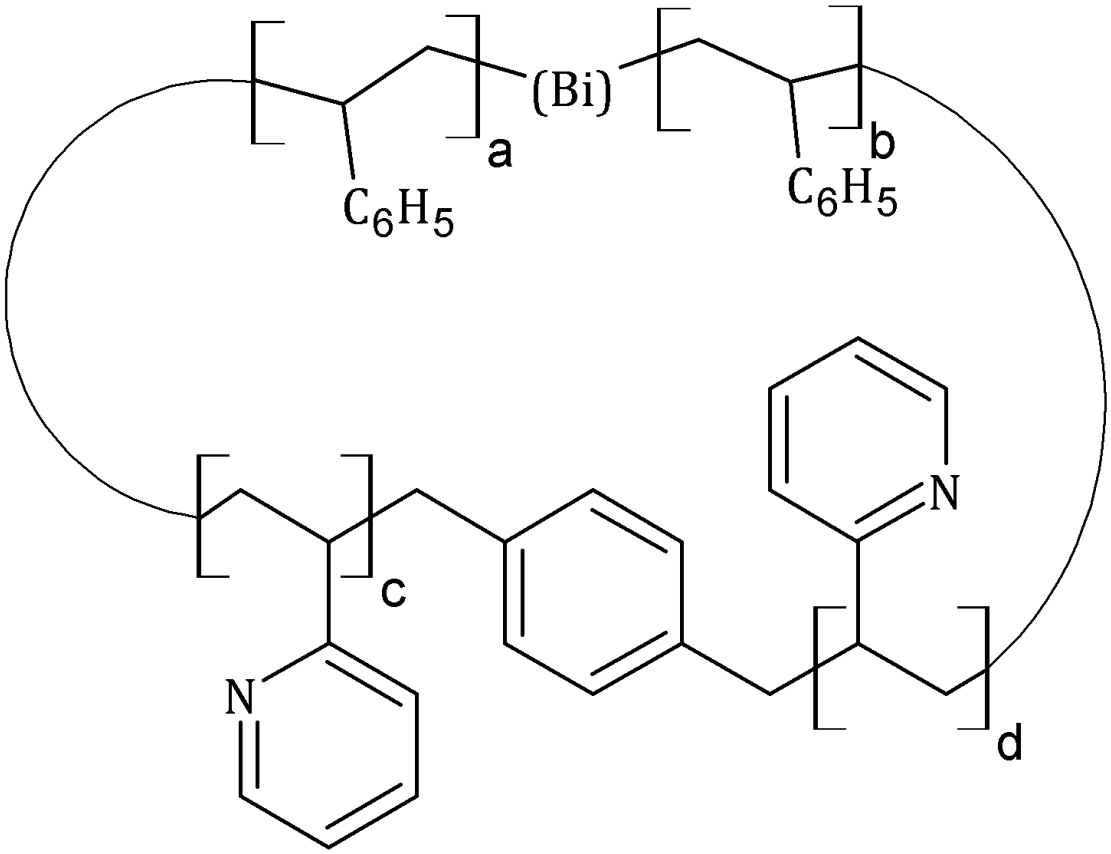


Figure 1.7 Example for a cyclic diblock copolymer prepared by (poly)condensation of bisanionic A-B-A triblock copolymer with 1,4-bis(bromomethyl) benzene.[2] (Bi) = bifunctional initiator.

The ring closure of a polymer via „a-b“ strategy can be characterized by the synthesis of a polymer containing one cyrboxylic and one amino endgroup which can react with the aid of 2-chloro-*N*-methyl pyridinium iodide.[24] A similar cyclization via cyclic amide formation is represented by poly(methyl methacrylate) involving the initial anionic polymerization of methyl methacrylate and the ring closure via an amide group (Figure 1.8).[2]

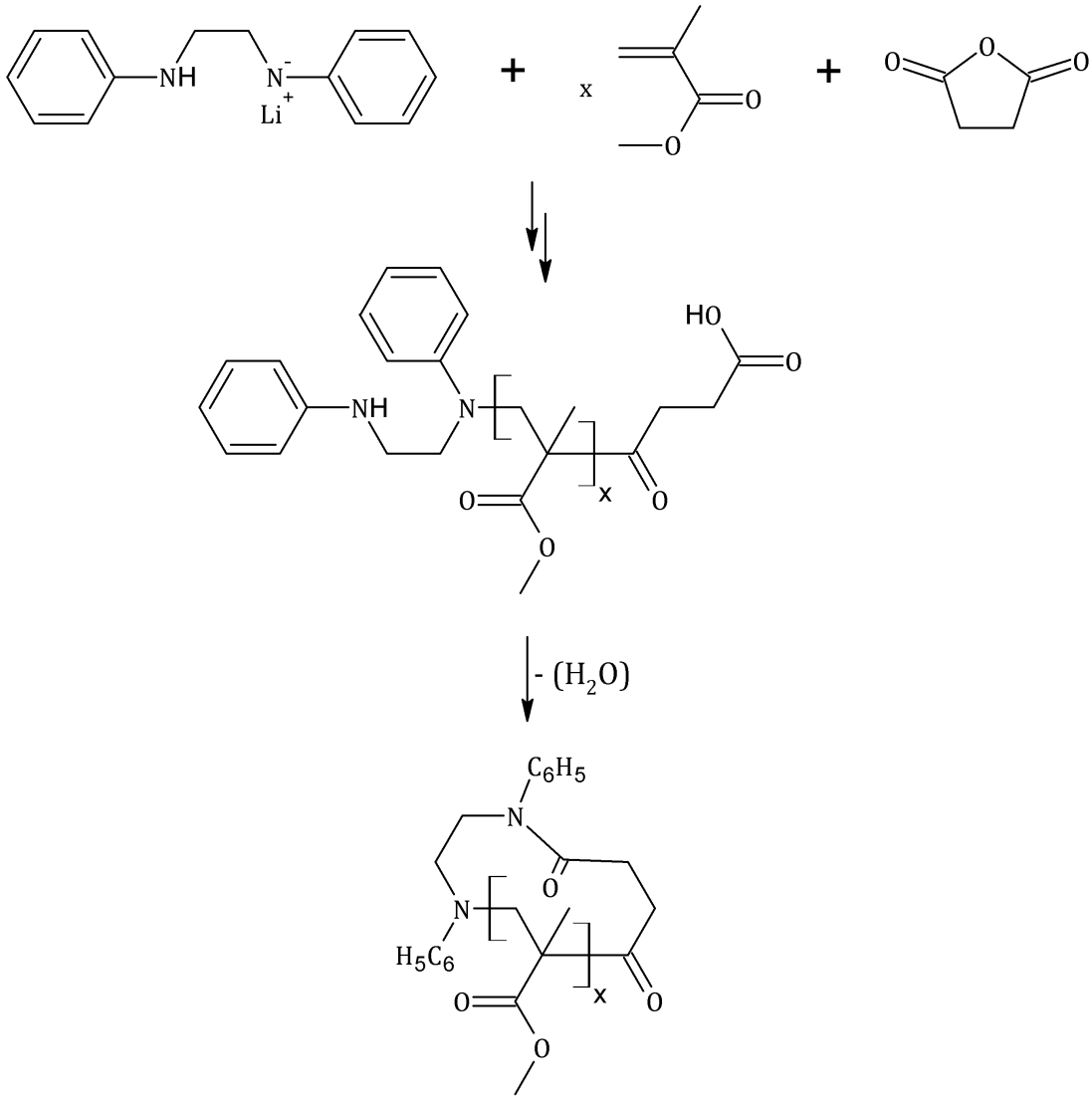


Figure 1.8 Synthesis of poly(methyl methacrylate) lactam.[2]

„a-b“ Funtionalized polymers can also be succesfully cyclized using the „click chemistry“. The 1,3-dipolar addition of an azide onto an alkine endgroup of the polymer catalized by copper (I) bromide showed the major advantages of this method as described in literature. [25]

„a²“-Polycondensation

A number of functional groups are known to be able to perform polycondensation or polyaddition reactions with themselves. An example for a kinetically-controlled „a²“-polycondensation is represented by the oxidative coupling of 1,2,3-tetracosadiyne.[26] It must be taken into account that in this oxidative cyclization no hydrogene is eliminated because of its *in situ* oxidation

making the reaction a special case of a polycondensation. Thus, cyclic oligo(ethylene)s were obtained in good yields up to the molecular weight of ca. 2k.

Metathesis condensation of polymers with two vinyl endgroups is another approach using „a²“ polycondensations. [27] As shown in Figure 1.9, poly(tetrahydrofurane) functionalized with two allyl ether groups forms a defect-free cyclic architecture via methatesis and after subsequent hydrogenation consisting only of the monomer unit.[28]

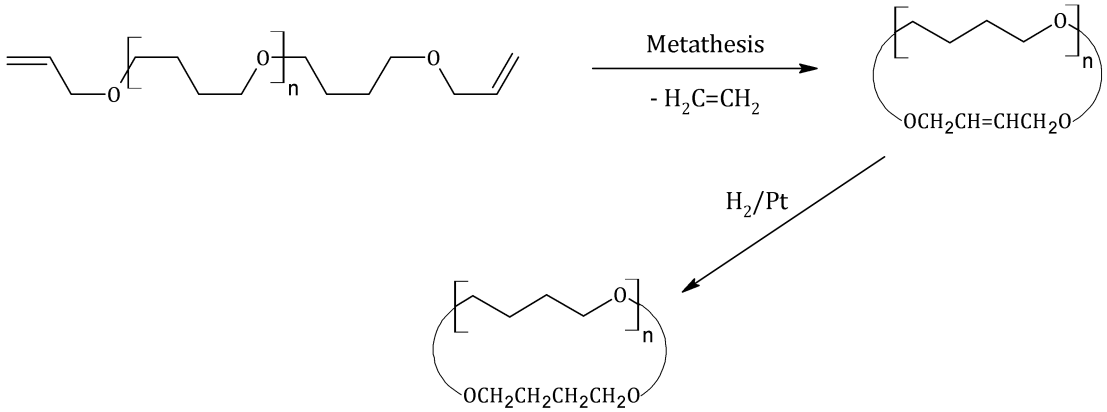


Figure 1.9 Synthesis of a cyclic poly(tetrahydrofurane) via metathesis.[28]

Furthermore, it was possible to prepare cyclic polystyrene by oxidative coupling of thiol groups under conditions of low concentration(Figure 1.10).[29]

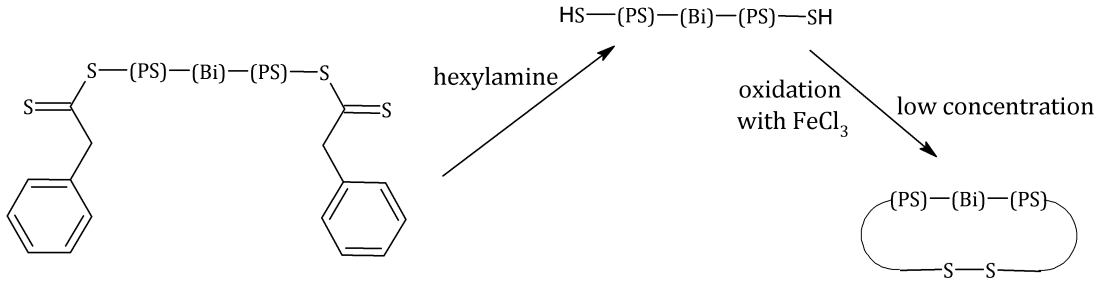


Figure 1.10 Synthesis of cyclic polystyrene via oxidation of mercapto endgroups.[29]

1.1.2 Combined ring-opening polymerization and polycondensation

A new field in the preparation strategies of cyclic polymers is the combined ring-opening polymerization and polycondensation. α–amino acid *N*-carboxyanhydrides is an advantageous group of monomers because of their stability against „back-biting“ (below 120° C) and a variety of initiators and catalyst that can be used.[30] The polymerizations initiated with primary amines or sterically nonhindered secondary amines yield linear polymers with a stable amide endgroup and one amino endgroup. [30,31] In contrast, since imidazolides of carboxylic acids are much more electrophilic than amide groups they react easily with amines at room temperature and therefore imidazol-initiated peptides can react with each other via chain extension or they form cyclic polymers. To achieve a good yield of cycles, a good solubility of the growing chains must be ensured to prevent precipitation.[32] Some polar, nucleophilic solvents such as DMF, *N*-methyl pyrrolidone and DMSO are able to catalyze polymerizations of NCAs without an initiator leading to cyclic oligopeptides.[33] A possible mechanism is shown in Figure 1.11.

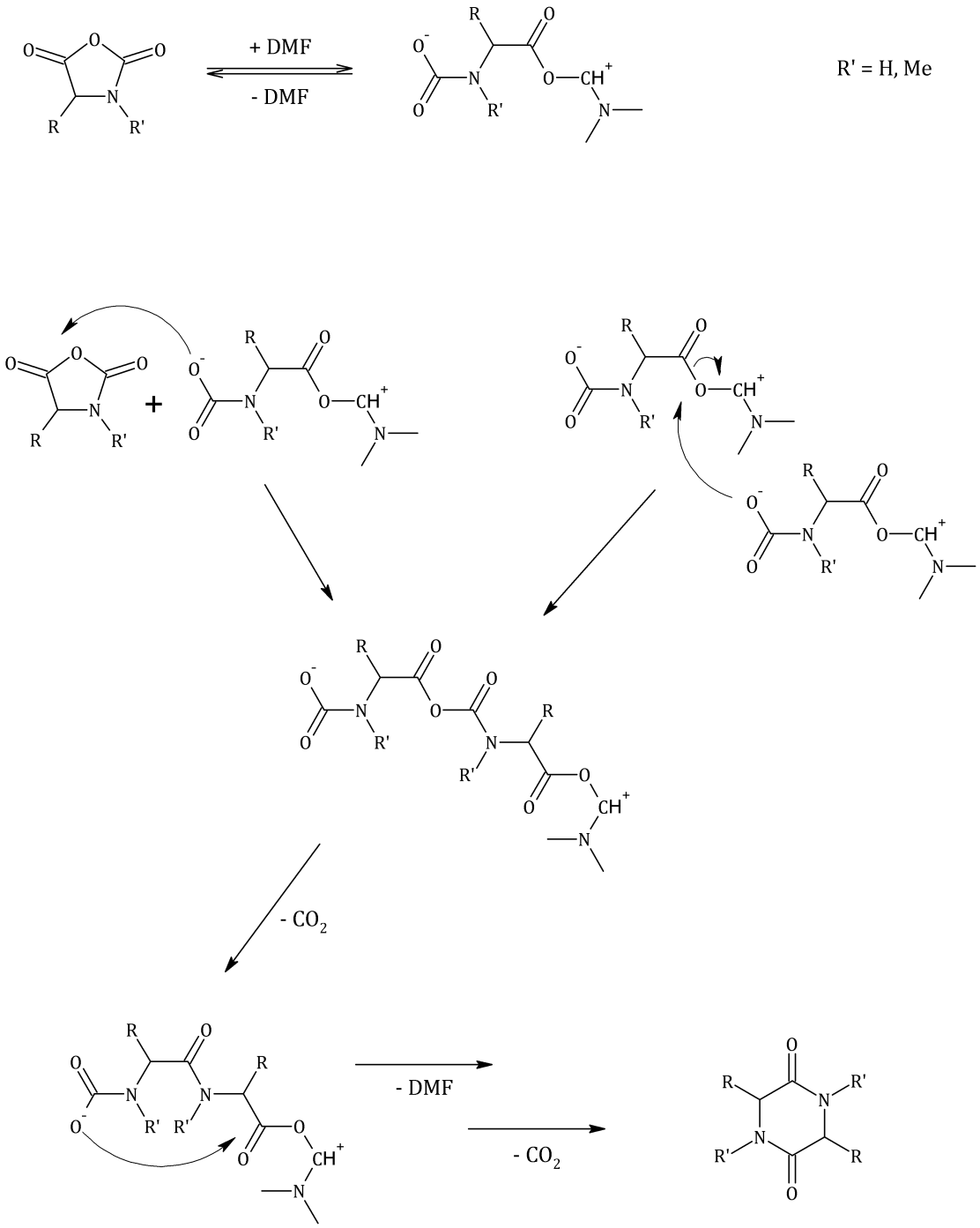


Figure 1.11 **DMF-initiated zwitterionic polymerization of α-amino acid NCAs.[2]**

If the nitrogen atom in NCA is unsubstituted the zwitterionic intermediate can form oligomers with one amino- and one *N*-acyl NCA group. Since this bifunctional oligomer has two reactive ends it can continue the ring-opening polymerization using the amino group or react inter- or intramolecularly via condensation.

The NCAs can be polymerized even without a catalyst just by heating the reaction mixture above the melting temperatures leading to cyclic polypeptides and some byproducts.[34] Once again it is speculated that the solvent (such as DMF) can catalyse the polymerization. Three other classes of cyclic anhydrides which can be polymerized via a zwitterionic mechanism using pyridine as catalyst[35,36,37,70-72] are shown in Figure 1.12.

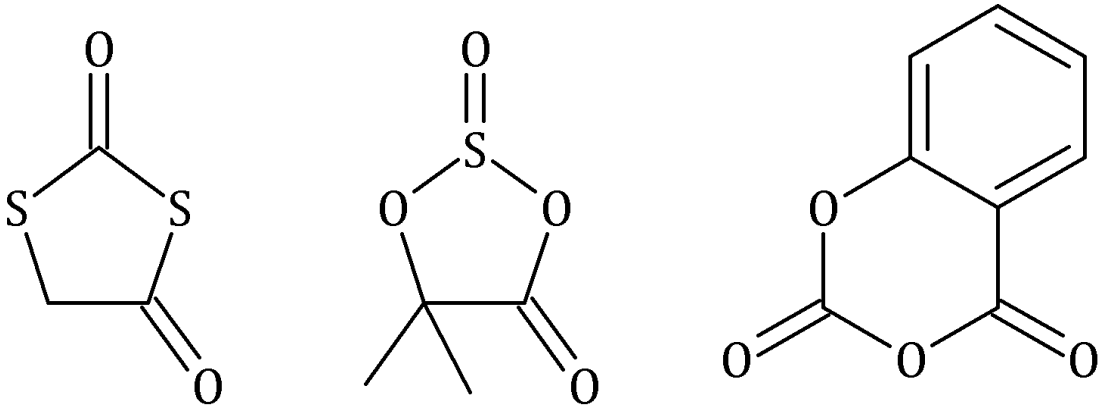


Figure 1.12 Cyclic anhydrides leading to cyclic polyesters upon thermal or pyridine-catalyzed polymerizations. [35,36,37,2]

1.1.3 Thermodynamically controlled polycondensations

TCP are characterized by fast equilibration reactions which can be classified either according to the structure of the polymer (transesterifications, transamidations etc.) or to the mechanism of the reaction. The so called „back-biting“ is the common equilibration reaction (Figure 1.13) for a reversible formation of cyclic monomers and oligomers.[2]

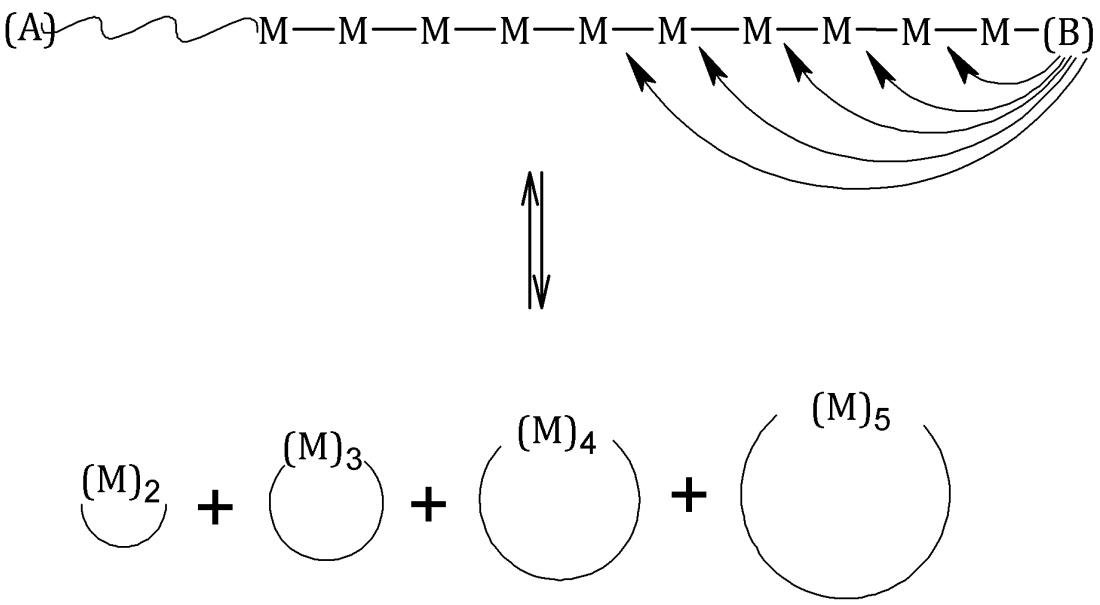


Figure 1.13 Ring-chain equilibration via „back-biting“.[2]

In agreement with the law of dilution the amount of cyclic species will increase with conversion. Since commercial polymers such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are produced at high temperatures (above 220 °C) side reaction are not avoidable under these conditions and the conversions are difficult to reach. It means that these preparation methods are not suitable for the synthesis of cyclic polymers. Nevertheless, a small scale production still could be realized for the preparation of cyclic PBT.[38]

Metal alkoxides with free d-orbitals such as tin alkoxides usually show donor-acceptor interactions which can lead e.g. to exchange reactions of the alkoxide groups. Using $Bu_2Sn(OMe)_2$ for a polycondensation with oligoethylene glycoles the equilibration reaction can be shifted to the cyclic reaction product by removing methanol which is formed as side product.[39] The formation of cyclic polyethers with one Bu_2Sn group could be proved by ^{119}Sn NMR spectroscopy based on different environments of tin due to different intramolecular donor-acceptor interaction which for their part depend on the ring size.[40] All the cyclic polyethers containing a metal are sensitive to alcohols and phenols because of the reactive metal oxygen bond and therefore the characterization of the molecular weight is hardly realizable. In the case of tin containing cycles the

replacement of the tin oxygen bond with tin sulfur bond turned out to be stabilizing.[41] An examplary procedure is shown in Figure 1.14.

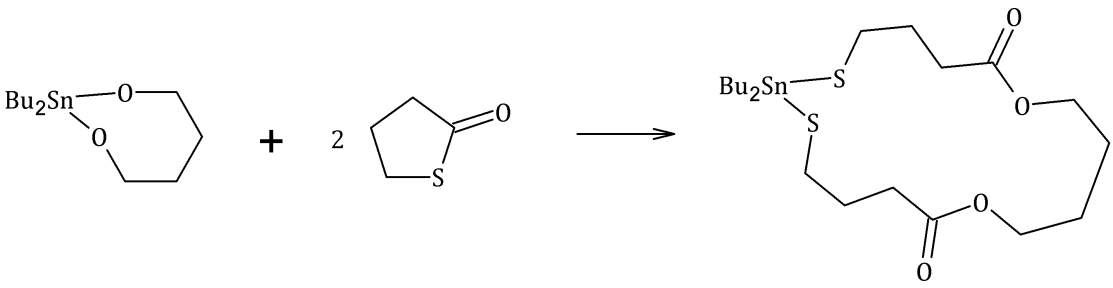


Figure 1.14 Stabilization of cyclic oligo(ether ester)s.[41]

Furthermore, cyclic polyesters with Bu_2Sn group within the polymer can be reacted with phthaloyl chloride for stabilization.[42]

Cyclization Via Electrostatic Interactions

The synthesis of cyclic polymers and even more complex cyclic composition via electrostatic interactions attracted a lot of interest. The promising method is often called „electrostatic self-assembly and covalent fixation method“ or ESA-CF. This approach involves the combination of a bifunctional polymer with two positivley charged endgroups with a monomer containing negatively charged end groups. The disadvantages of the *N*-methylpyrrolidium groups, such as the substitution of the methyl group could be avoided by using the *N*-phenyl pyrrolidinium endgroups which react only under cleavage of the pyrrolidinium ring.[43,44,45,46] Alternatively, polystyrene with chinuclidinium endgroups was successfully used to react with sodium terephthalate under cyclization.[47] The possible cyclic architectures prepared via electrostatic interactions are summarized in Figure 1.15.

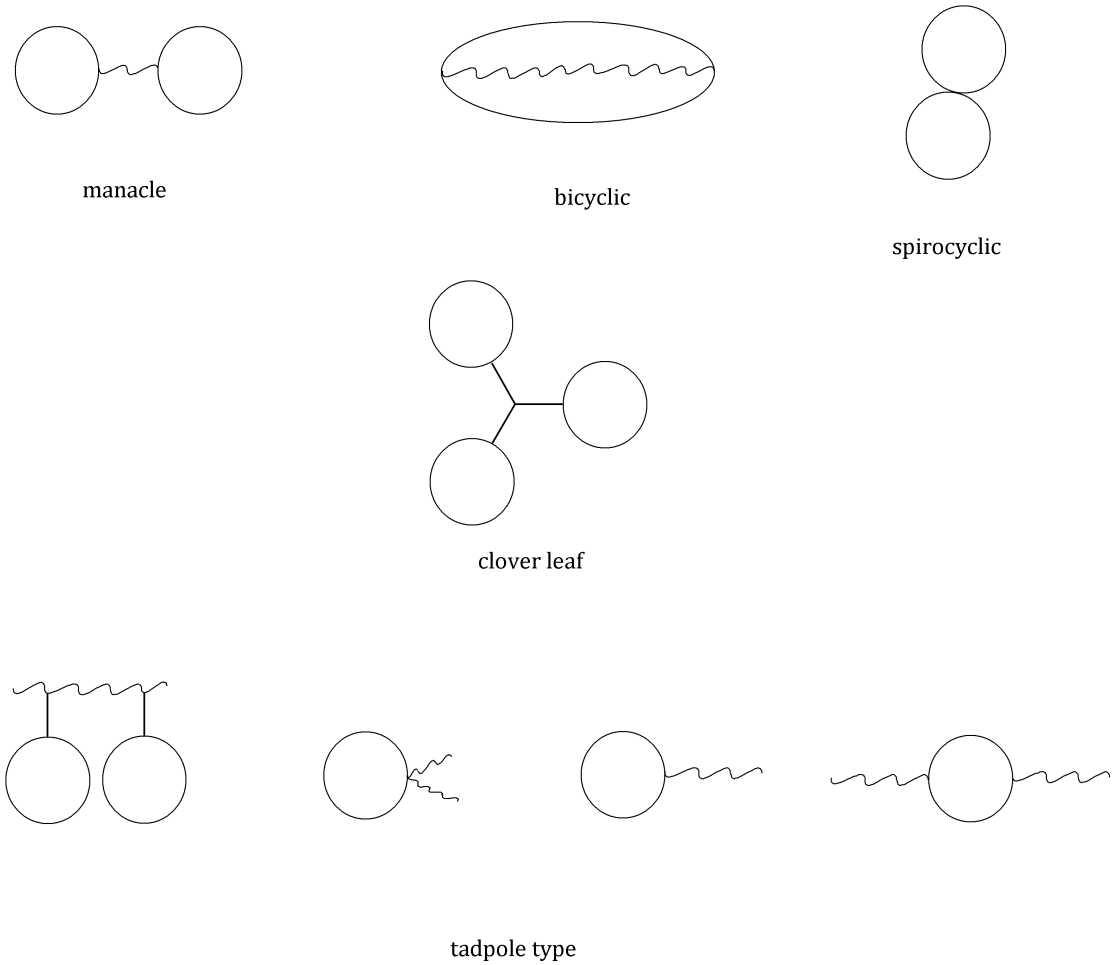


Figure 1.15 Cyclic polymer architectures synthesized from functionalized poly(tetrahydrofurane) via the ESA CF method.[2]

1.1.4 Ring-ring equilibrations

Ring-ring equilibration can be treated as a particular ring-opening polymerization with equilibration reaction rates as high as chain-growth reactions or even faster and with small catalyst concentration or its absence. As shown in Figure 1.16 1,2-ethane diol or 1,3-propane diol reacts with dibutyl tin dimethoxide to cyclic dimers without polymerization.[48,49,50,51]

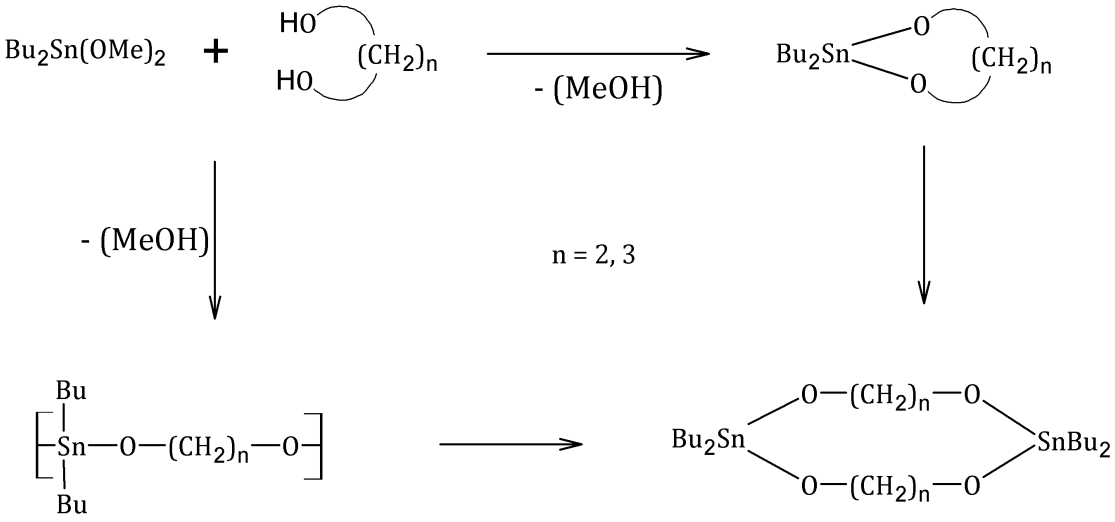


Figure 1.16 Polycondensations of $Bu_2Sn(OMe)_2$ with 1,2-ethanediol or 1,3-propanediol.[2]

Quite novel is the synthesis of cyclic polyesters by the zwitterionic ring-opening polymerization of lactide with *N*-heterocyclic carbenes (Figure 1.17).[52] In the final step, the carbene is released by intramolecular reaction of the macromolecular zwitterion yielding a cyclic polymer.

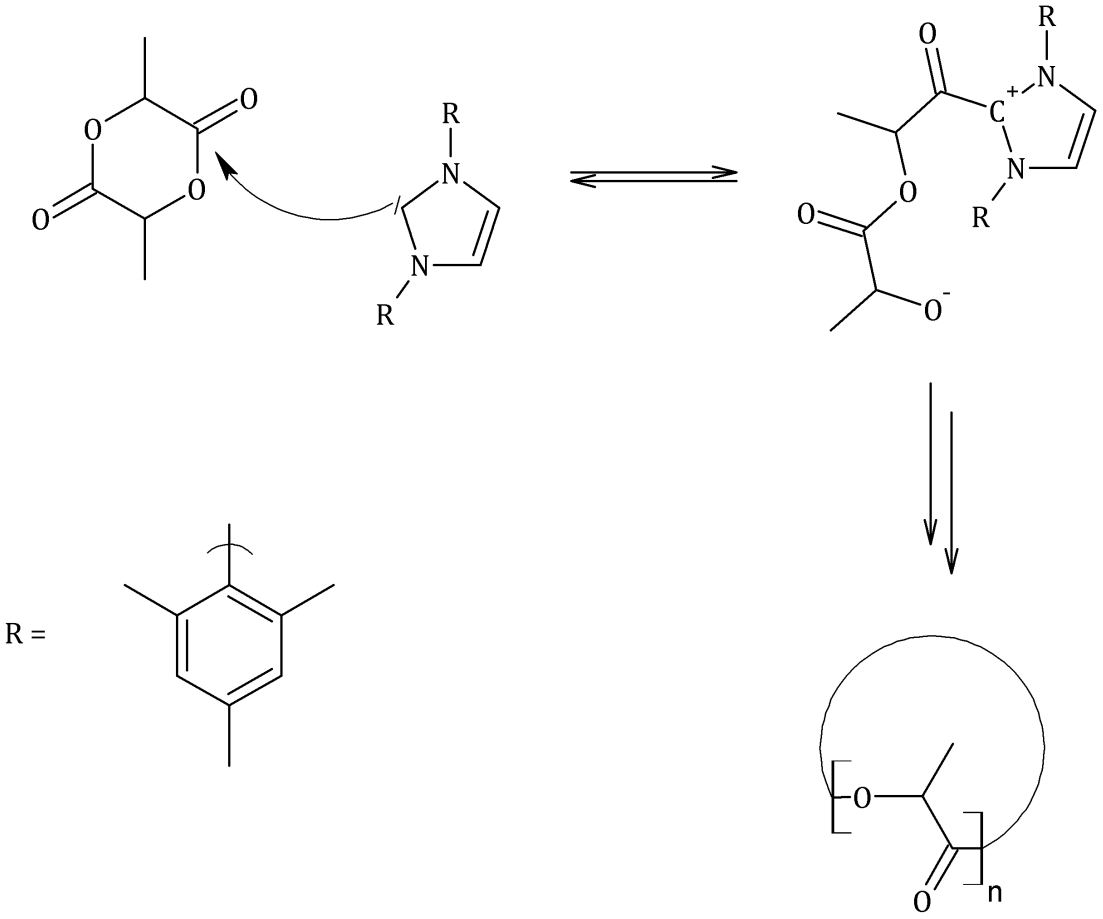


Figure 1.17 **Carbene-catalized equilibration of D,L-lactide at room temperature.**

1.1.5 Kinetically-controlled ring-expansion polymerizations (REP)

The most studied REP is the polymerization of cyclic esters using cyclic tin alkoxides. These REP initiators are shown in Figure 1.18 and were used to yield cyclic polymers out of cyclic monomers such as δ-valerolactone, ε-caprolactone, β-D,L-butyrolactone, L-lactide and trimethylene carbonate.[2]

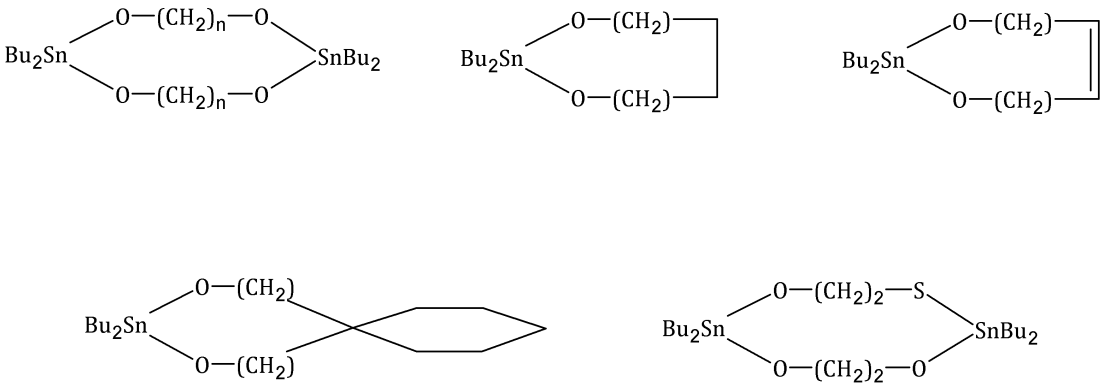


Figure 1.18 **Cyclic and spirocyclic initiators based on dibutyl tin alkoxides.[2]**

The coordination-insertion mechanism of the REPs is the same as for noncyclic metal alkoxides.[53] Since the tin-oxygen bond is very sensitive to hydrolysis dealing with tin containing cyclic polymers in air is difficult but the easy hydrolythic or methanolytic removal of Bu_2Sn groups leads to telechelic homopolyester free of tin. Furthermore, spirocyclic polyesters were prepared using spirocyclic alkoxides of germanium and zirconium as initiators[54,55,56,57] (Figure 1.19) and are potential reactive intermediates due to their hydrolytic sensitivity.

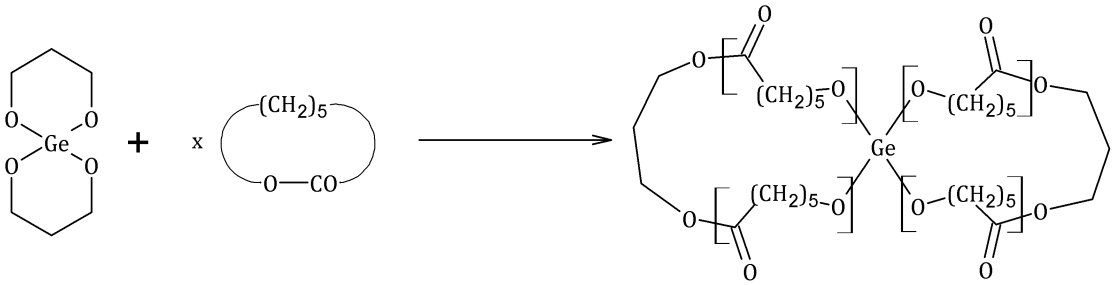


Figure 1.19 **Spirocyclic polyester via REP of ϵ-caprolactone by using of a spirocyclic Ge-propylene oxide.[54]**

Another REP procedure yielding cyclic polymers in high yields is the methatesis polymerisation of a cyclic alkene by use of a cyclic ruthenium carbene complex. Cyclic catalysts with varying tether lengths (Figure 1.20) have been synthesized for this purpose showing different catalytic activitied and stabilities.[58]

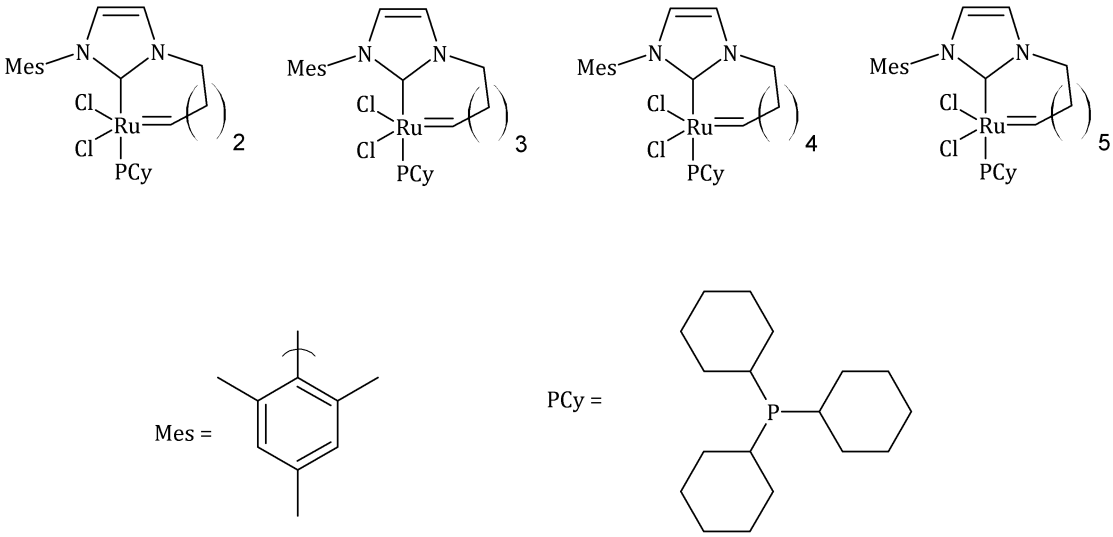


Figure 1.20 Cyclic Ru-alkylidene metathesis catalysts.[58]

The reaction mechanism by which the REMP proceeds involves basically three key steps (Figure 1.21). The polymerization is initiated via a ring-expansion of the cyclic Ru-alkylidene catalyst by a cyclic monomer. The propagation proceeds via the incorporation of the cyclic monomers into the growing cyclic polymer. When the monomers are consumed the cyclic polymer is released and the original catalyst is recovered. However, after complete conversion the molecular weight of the cyclic polymers can decrease in the presence of the cyclic catalyst due to intramolecular chain transfer reactions.

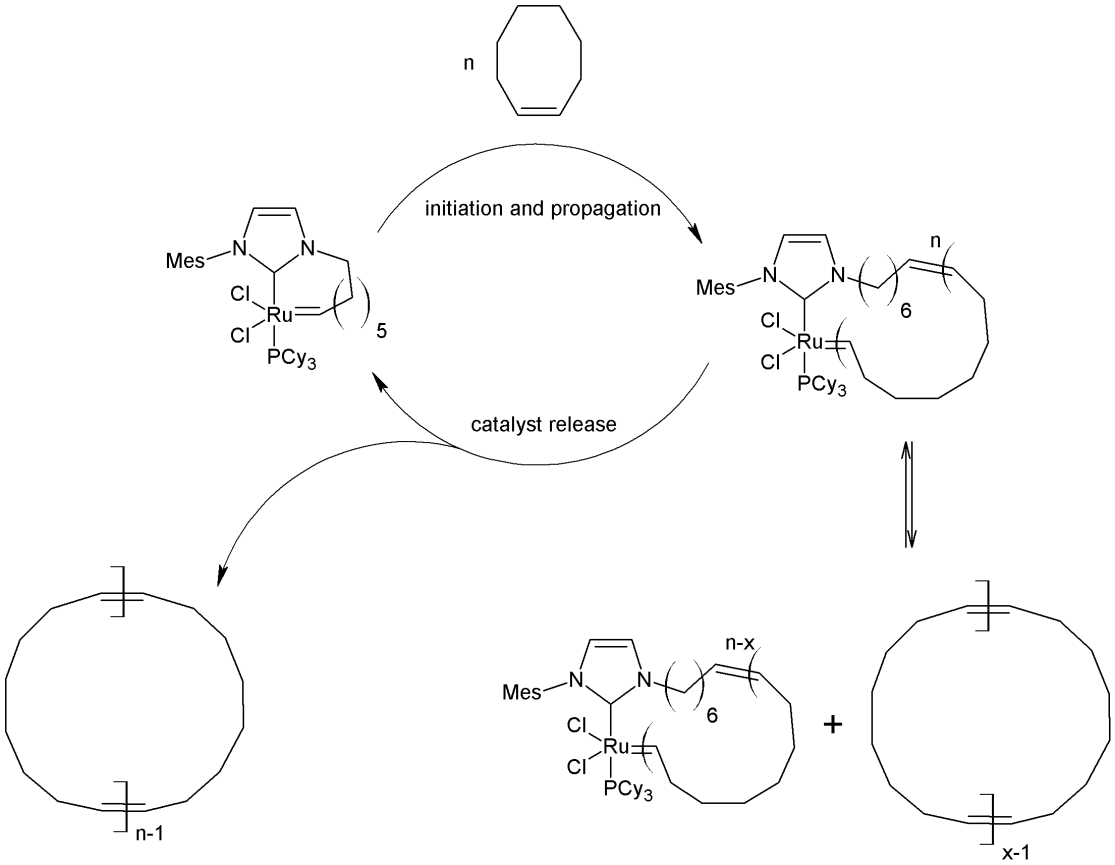


Figure 1.21 REMP catalytic cycle.[58]

It is important to understand the influence of the catalyst architecture on the kinetics of all the processes appearing in the reaction mechanism in order to controll the REMP and its products.

The tether length within the cyclic catalyst is one of the basic parameter for controlling the inherent ring strain, the relative orientations of ligands about the metal center and the rotation about the Ru-alkylidene bond. Varying the tether lengths and the ligand electronics, such as saturation of its backbone, within the cyclic catalyst can balance the polymerization efficiency.[58]

Such a catalyst can be synthesized in three steps[58,59] (Figure 1.22). Initially, mesitylamine is transformed to 1-(mesityl)imidazole, which then yields a mesitylimidazolinium salt via alkylation with a particular bromo alkene. These ionic compounds can be introduced into the Grubb's catalyst (1st generation) in a ligand exchange reaction. The final step is an intramolecular methatesis which leads to the cyclization of the catalyst.[58]

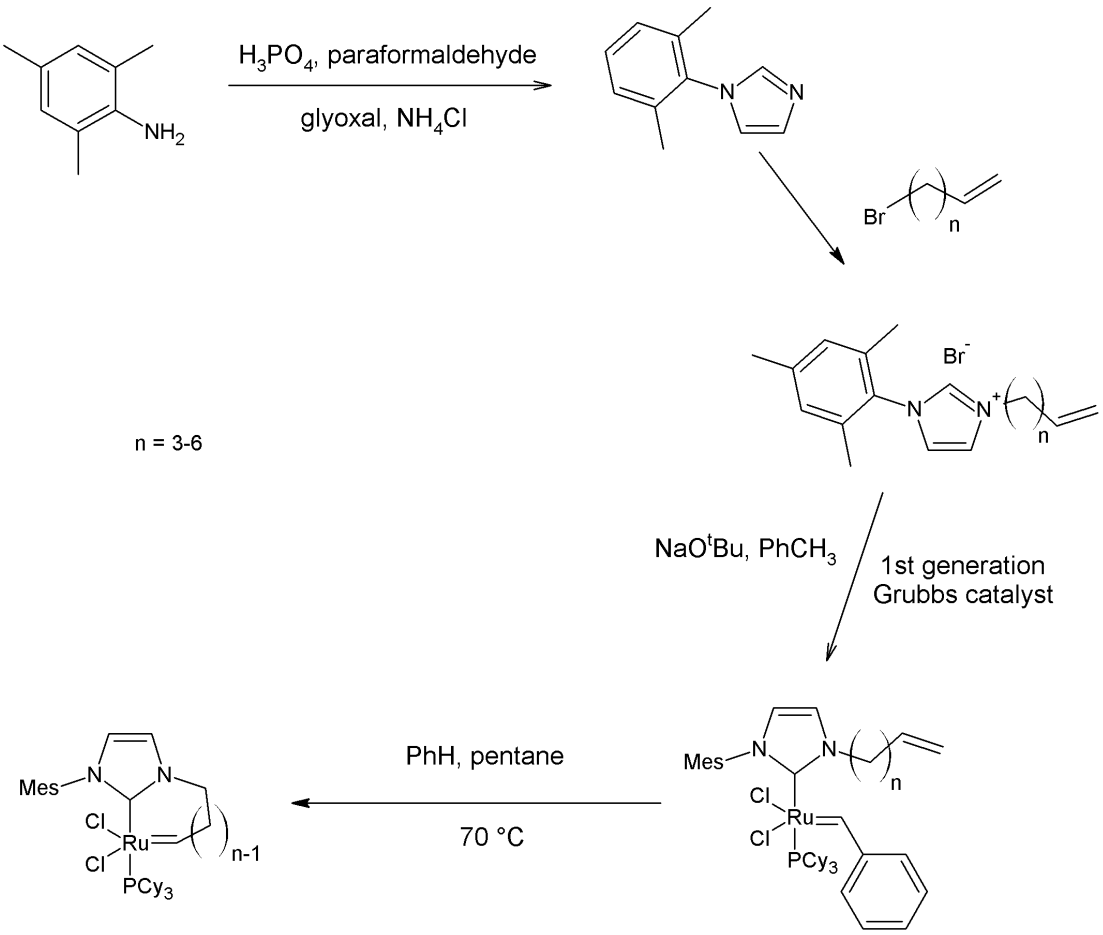


Figure 1.22 Synthesis of cyclic REMP catalysts.[58,59]

1.2 Physical properties of cyclic polymers

Cyclic polymers differ in their physical properties from their linear counterparts. The difference in volume between macrocycles and linear polymers causes different solution properties. It was found that the hydrodynamic volume of cyclic polymers is smaller and the solution viscosities are lower than those of the linear polymers with the same molecular weight.[2,17,18] Therefore size exclusion chromatographie is the common method for characterization and detection of macrocycles. The ratio of the „peak molecular weights" $(M_p)_l/(M_p)_c$ for polystyrene decreases with increasing average degree of polymerization. It means that it is easier to identify and separate the cyclic polymers from their linear counterparts for higher molecular weight polymers.[2] It is noteworthy that the different properties of cyclic and linear polymers are independent of the chemical structure of the repeat unit. It was found that the dependence of the glass temperature on the molar mass of cyclic polystyrene can be neglected for the number average molecular weight (M_n) exceeding 7 kDa.[60] Similar results were found for the cyclic forms of poly(2-vinyl naphthalene).[61] The reason for this behavior is the limited configurational freedom due to the absence of chain ends. Thus, the mobility of the cycles is similar to the mobility of a middle segment of a linear polymer chain. This leads to an interesting structure-property relationship which can be attractive for technical applications, such as melt viscosity control and simplification of the mechanical processing from the melt as well as the control of the glass transition temperature T_g. The melt viscosities of cyclic polymers show an interesting trend having a greater viscosity at low molecular weights and a smaller viscosity at high molecular weights compared to the linear form.[62] The extent of entanglements plays a role at that point and is much higher for linear chains than for cycles.[2] The blends of cyclic and linear polybutadiens with a volume fraction of cycles of 0.0-0.8 show an interesting effect, too. The melt viscosity is higher than that of linear and cyclic polymers separately.[63] It means that the characterization of physical properties of molten cyclic polymers is reliable only if linear chains are not present. Lower transition friction coefficient[62,64], higher refractive index[62], lower dipol moment at low molecular weights[62] are also the consequence of the cyclic

architecture of polymers. The thermostabilities of cyclic polymers, such as poly(2-vinyl naphthalene), measured by thermogravimetry, are a bit higher if compared to the linear analogues.[61]

Biodegradable cyclic polymers, such as polyglycolic acid, may have unique properties considering their degradation rates. They could be attractive for applications in tissue engineering or drug delivery since primary polymer chain breaks would lead to a polymer without changing the molecular weight.[62]

1.3 Miniemulsion

1.3.1 Theory of emulsions

In general, emulsions are dispersed systems with liquid droplets in another, nonmiscible liquid. Oil-in-water emulsions are called direct emulsions and water-in-oil are named inverse emulsions (Figure 1.23).

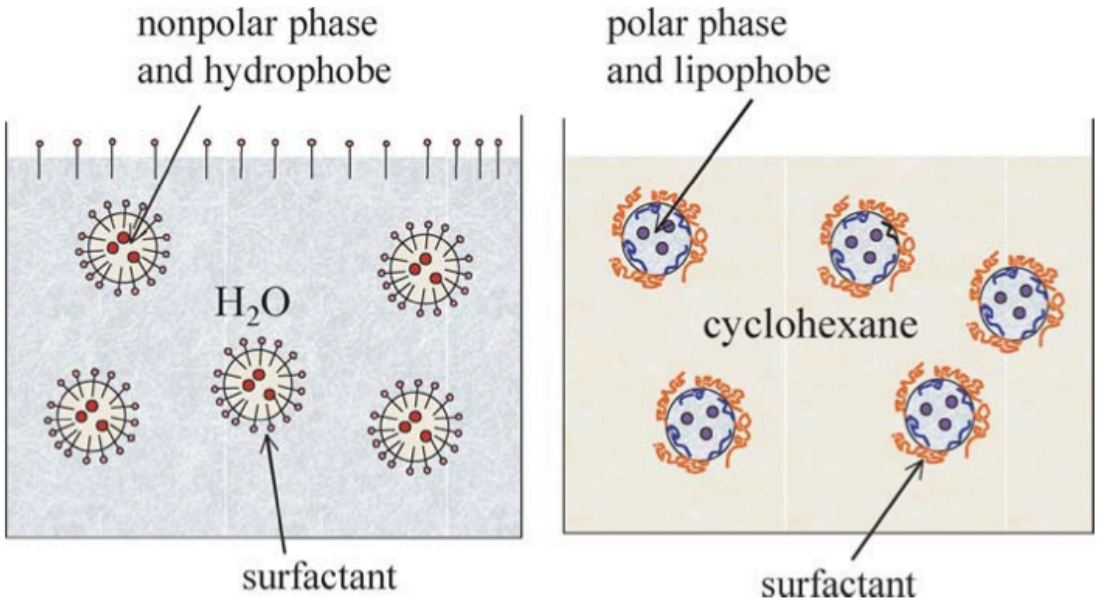


Figure 1.23 Direct and inverse miniemulsion.[65]

The droplet size in miniemulsion is ca. 50-500 nm in diameter.[66] Ostwald ripening and coalescence can destabilize and destroy emulsions. In order to prepare a stable miniemulsion consisting of small droplets, the droplets must be stabilized and protected from these two effects.

The coalescence is a process in which emulsion droplets come together by collisions forming larger droplets. Thus, the total surface of the droplets becomes smaller and the frictional resistance decreases and, as a result, the motion of the droplets causes the phase separation. The coalescence can be suppressed by the addition of an appropriate surfactant, such as sodium dodecyl sulfate (Figure 1.24), providing electrostatic or steric stabilization of the droplets.[65]

The Ostwald ripening is the growing of the droplets at the cost of the small droplets. The driving force for this process is the difference in the Laplace

pressures within the droplets of different sizes. In order to minimize the Laplace pressure, oil is diffusing from small particles into big particles. Big droplets become hereby even bigger and small droplets disappear. For example: if a lipophilic liquid is dispersed as small droplets with a low polydispersity, a slow mass exchange can be observed. The reason for that is the dependence of the Ostwald ripening on the size, polydispersity and solubility of the dispersed phase in the continuous phase. However, the addition of a third hydrophobic compound, such as hexadecane (Figure 1.24), would build up additional osmotic pressure and stabilize the system.[65]

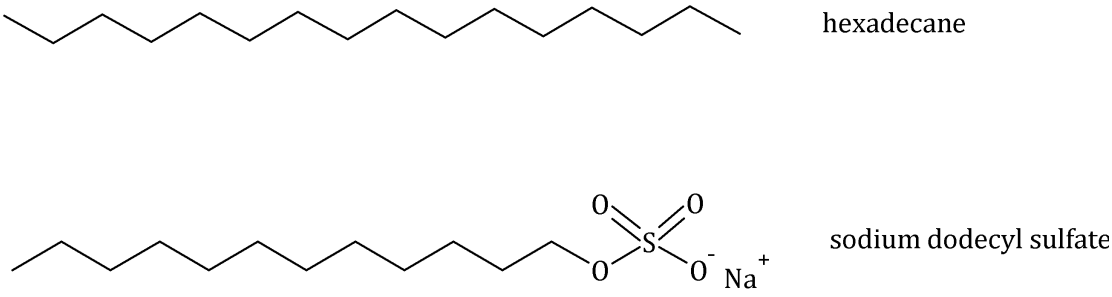


Figure 1.24 Sodium dodecyl sulfate and hexadecane.

For the preparation of miniemulsions ultrasonication is used nowadays and simple stirring is not sufficient, since high energy for homogenization is required (Figure 1.25).

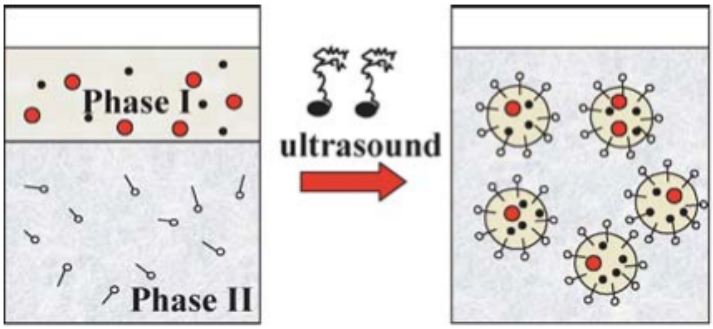


Figure 1.25 Miniemulsion process.[65]

However, for large quantities of miniemulsion rotor-stator disperser can be used.[65]

1.3.2 Synthesis of nanoparticles via miniemulsion process

The miniemulsion technique is suitable for the preparation of polymer nanoparticles[67,68] and using functional monomers can lead to nanoparticles with a functionalized surface.[69,70] Polymerization reactions in inverse miniemulsions, such as polyaddition, polycondensation and anionic polymerization, can produce nanocapsules with a hydrophilic core.[71] Miniemulsions can also be employed as spatial confinement to separate single polymer chains.[72] For this purpose, the polymer is dissolved in organic solvent, such as toluene and a miniemulsion technique is applied. After the evaporation of the solvent, the polymer chains which were in the dispersed phase can form extremely small polymeric nanoparticles with a few or only a single polymer chain (Figure 1.26).

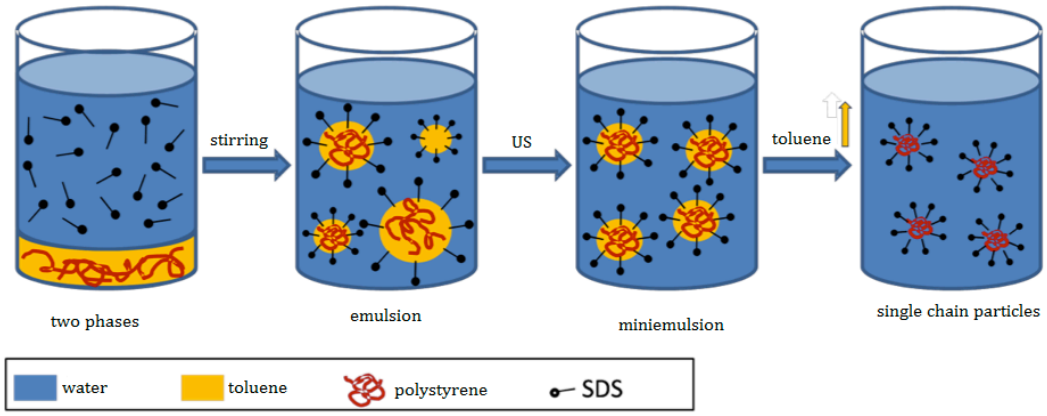


Figure 1.26 Miniemulsion and evaporation process.[72]

It is believed to be possible to use this technique in order to carry out a single molecule reaction such as intramolecular cyclisation whereby the intermolecular reaction can be successfully suppressed (Figure 1.27).[72]

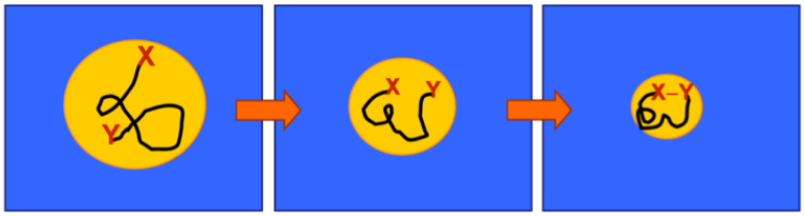


Figure 1.27 Intramolecular reaction of a separated polymer chain in a miniemulsion droplet during the evaporation of the solvent.[72]

1.4 Anionic polymerization

1.4.1 Theory of the anionic polymerization

Living anionic polymerization was presented by Szwarc and coworkers in 1956[2,73,74] and became a popular and important methode in polymer science. A remarkable feature of the living anionic polymerization is that termination reactions do not occur when carried out under the appropriate conditions. Compounds like water, alcohols, oxygen etc. react rapidly with the carbanions at the chain end and thus terminate the propagation. This is why all the reaction ingredient; i.e., the initiators, monomers and solvents, must be dried thorouphly in order to ensure a living system.

The reaction is usually initiated by a strong base whereby the chains start growing all at once by adding the monomer. The chain ends remain active when the monomer is consumed and can be used for further reactions. By this means, block copolymers can be formed by adding another monomer.

A functional group can also be easily introduced via a subsequent chemical reaction between the living anion chain end and a terminating agent of choice.[75]

Anionic polymerizations usually yield polymers with a narrow molecular weight ditribution and the molecular weight is predictable since it can be calculated by the ratio between initiator and monomer. The propagation rates are dependent on the propagating anion, counterion, solvent and temperature and can be influenced by variation of these parameters for a certain system.

The widely used anionic polymerizations besides carbanionic type involve a formation of living species with oxygene anions as reactive chain ends. The propagation rate, as shown in Figure 1.28 is proportional to the size of the counter ion since oxygene forms a stable bond preferentially with small ions according to the HSAB concept.

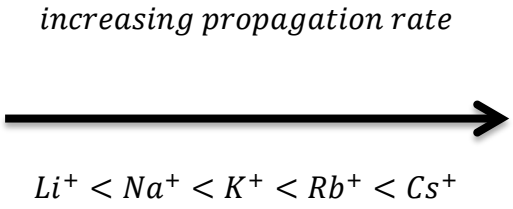


Figure 1.28 Dependance of the propagation rate on the metal ion.

Figure 1.29 shows the different forms of ion pairs which are in equilibrium with each other, as proposed by Fuoss[76,77] and Winstein[78]:

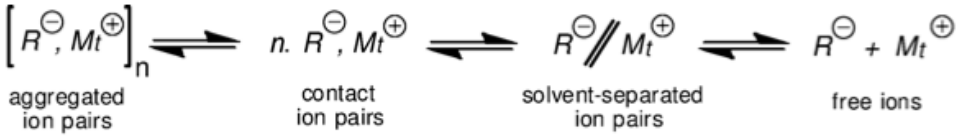


Figure 1.29 Fuoss–Winstein spectrum of anion pairs.[79]

The reactivity of the free ions and solvent-separated ion pairs is much higher compared to contact ion pairs. The position of this equilibrium can be influenced by the polarity of the solvent. Polar solvents, such as THF or DMSO can solvate ions better than nonpolar solvents like toluene or cyclohexane and therefore the speed of reaction is increased.[79]

In exceptional cases, when the solubility of the growing polymer with anionic end groups is not satisfactory in polar solvents, crown ethers or chelating ligands can be used as an aid. These compounds strongly bind certain cations forming complexes allowing the anions interact with the solvent more efficiently.[80,81]

1.4.2 Polystyrene

Polystyrene is one of the most widely used synthetic materials. It is mainly produced via radical polymerization and its production volume amounts to several million tonnes per year. Polystyrene has many applications such as packaging, toys, electronics, construction and houseware and it is also used to produce medical and pharmaceutical supplies.

Structurally, polystyrene is a vinyl polymer, consisting of a long hydrocarbon chain with a phenyl group attached to every second carbon (Figure 1.30).

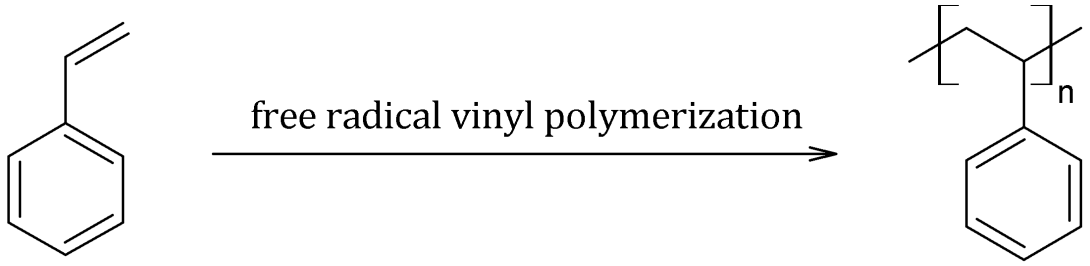
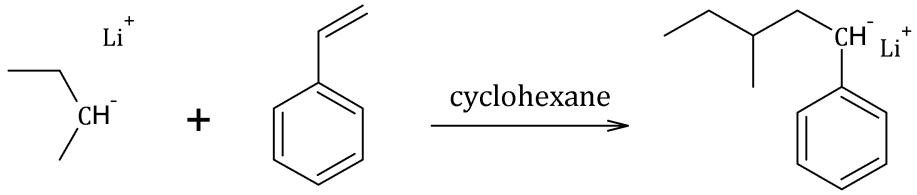


Figure 1.30 Polymerization of styrene.

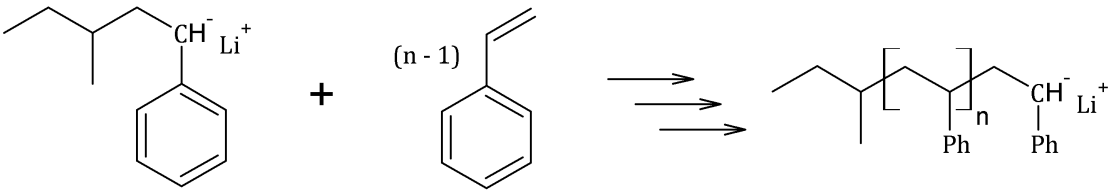
1.4.3 Anionic polymerization of styrene

The anionic polymerization is usually initiated by nucleophilic addition to the double bond of the styrene monomer by using a hydroxide, alkoxide, cyanide or carbanion as nucleophile (Figure 1.31). The alternative is represented by initiation via electron transfer which takes place when alkali metals or reducing organic salts such as sodium naphtalenide are applied (Figure 1.32).[79]

Initiation



Propagation



Termination

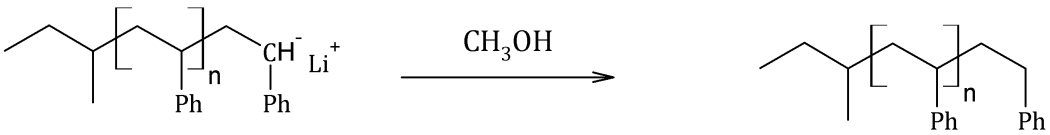


Figure 1.31 Anionic polymerization of styrene using sec-butyllithium as initiator.[79]

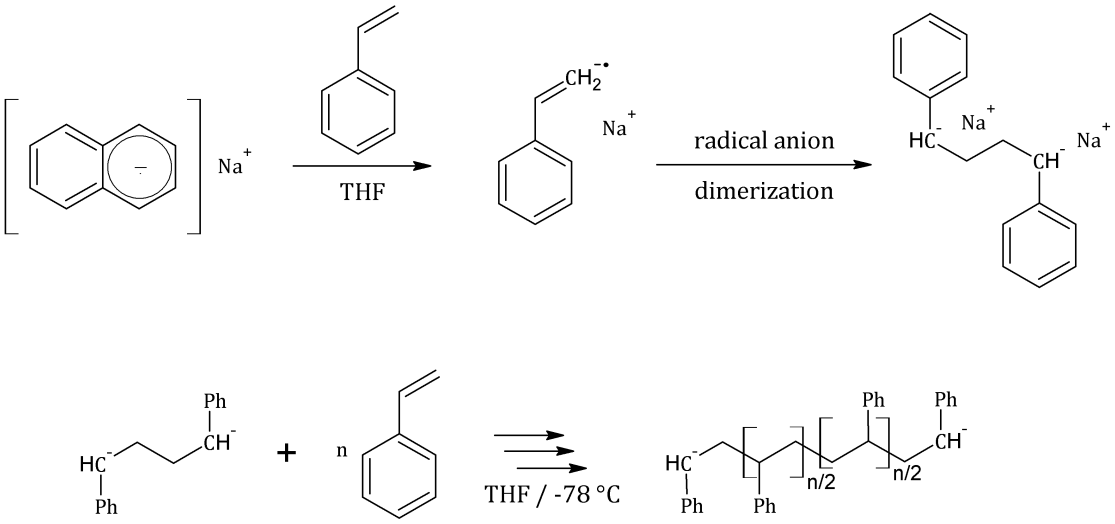
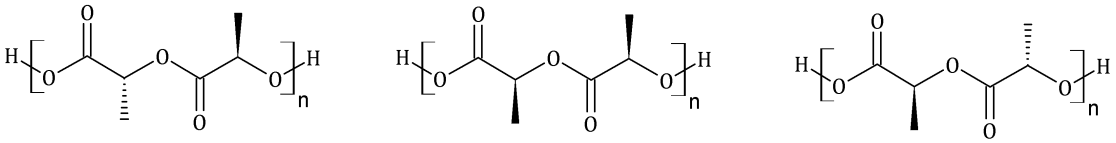


Figure 1.32 Anionic polymerization of styrene using sodium naphthalene as initiator in THF.[79]

The reaction mechanism shows that two different living anions, with one or two reactive chain ends, respectively, are possible according to how the initiation occurs. Depending on the purpose of the target molecules, mono- and α,ω-difunctional polystyrene can be easily synthesized by choosing the appropriate initiator.

1.4.4 Poly(lactide)

Polylactide is the most common bioplastic nowadays. The range of applications for polylactide is huge and it can be used to replace other polyesters. Due to its biodegradability PLA is used as medical implants and compostable packaging material. The global PLA production capacity stands at around 180,000 tons per year and is believed to increase to around 800,000 tons per year by 2020.[82] Polylactide can be synthesized from lactide via ring opening polymerization.[83] The chirality of lactide leads to structural differences within the resulting polymers entailing different physical properties, such as crystallinity, glass transition temperature, melting temperature and tensile moduli.[84] Contemplable structures of the polymers made of D-lactide, L-lactide and D,L-lactide are represented in Figure 1.33.



L-lactide D,L-lactide D-lactide

Figure 1.33 Possible structures of polylactides.

1.4.5 Anionic polymerization of lactide

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Figure 1.34) is an effective organocatalyst for the ring- opening polymerization of L-lactide.[85]

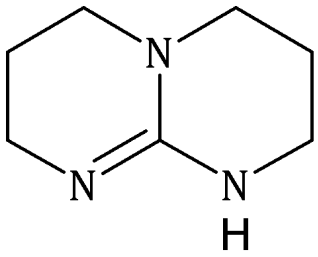


Figure 1.34 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD).

TBD is an effective acyl-transfer and transesterification catalyst and its activity can be used for the ROP of different cyclic esters (Figure 1.35).[83]

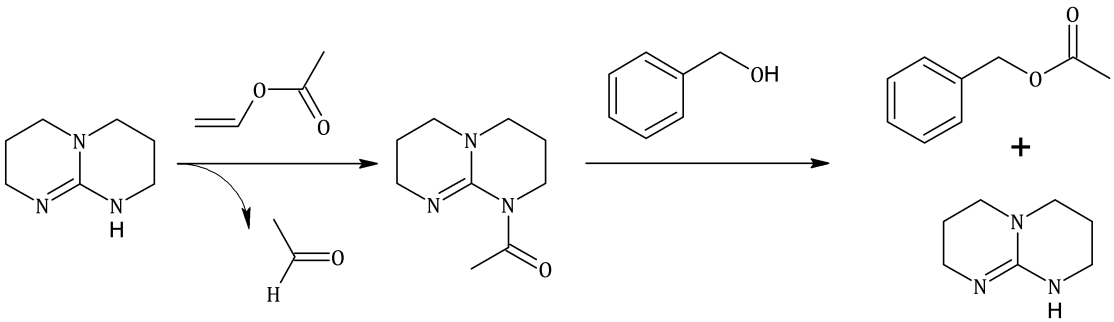


Figure 1.35 Acyl transfer reaction.[83]

Polymerization of L-lactide in DCM with TBD at only 0.1% relative to monomer with 1% of the initiator can produce poly-(L-lactide) in less than one minute with a narrow polydispersity ($\frac{M_w}{M_n} < 1.2$) and a quantitative conversion even at room temperature. The reaction mechanism[83] of the ROP of L-lactide is shown in Figure 1.36 and Figure 1.37.

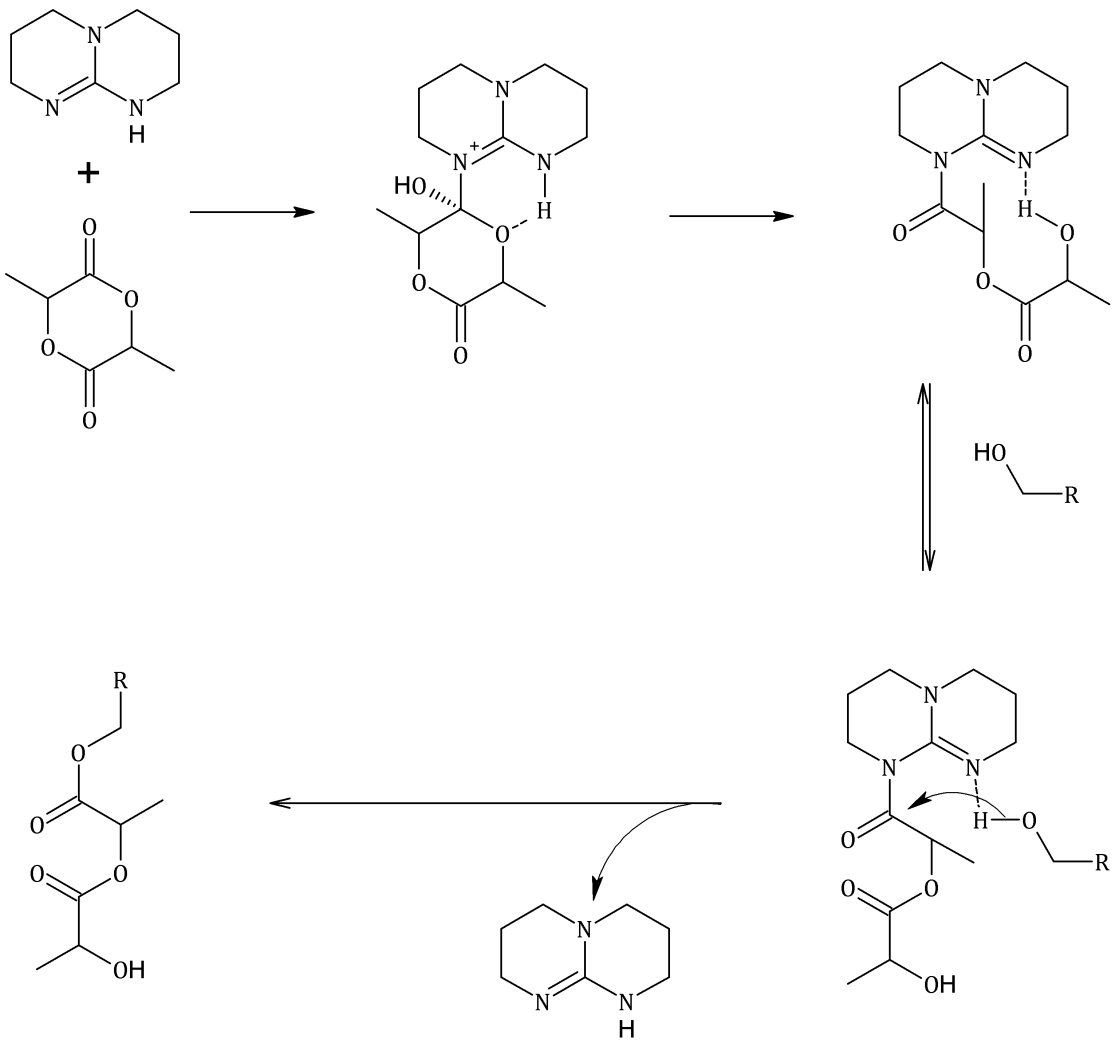


Figure 1.36 Dual activation of monomer and initiator by TBD.[83]

The broadening of the molecular weight was found to occur if the reaction mixture is left to stand for some time after complete conversion. The reason is the TBD-catalyzed transesterification with the back bone of the polyester which occurs due to the high activity of the catalyst. This problem can be circumvented by quenching the TBD with benzoic acid after short reaction times.[86]

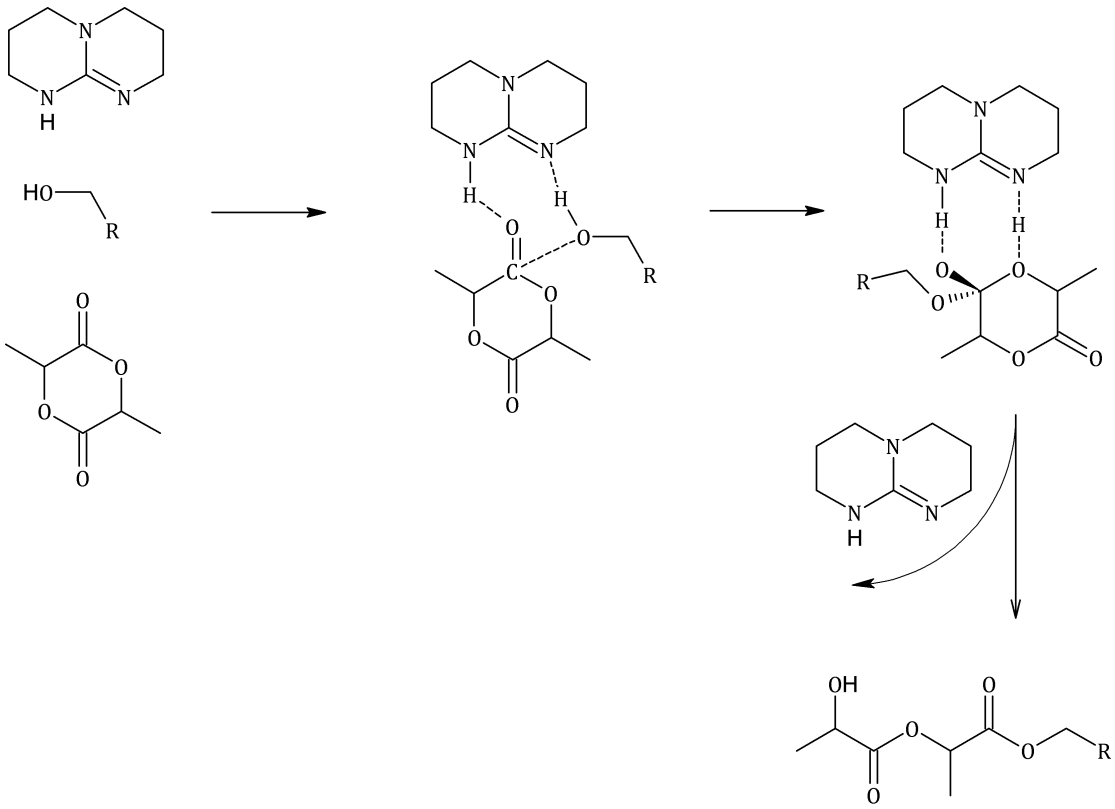


Figure 1.37 Dual activation by TBD through hydrogen bonding.[83]

2 Aims

Cyclic polymers represent an interesting class of polymers with a considerable number of potential applications. Their different physical properties compared to their linear counterparts could result in useful industrial products. However commercialization is still hindered by the lack of a method in order to produce cyclic macromolecules on large scales with controlled molecular weight distributions and with versatile chemical composition. Therefore a sustainable access to cyclic polymers would be highly desirable. Using the miniemulsion technique as a key step is a promising way to obtain cyclic polymers. Avoiding large amounts of organic solvents and replacing them by a tenside-water mixture could evolve into a „green“ method of the macrocycle preparation.
Thus, two methods should be investigated in the framework of this thesis.

A cyclic ruthenium alkylidene catalyst should be synthesized in 4 steps as shown in Figure 2.1. It should be subsequently used for the ring expansion polymerization studies of a cyclic monomer, such as cyclooctene, in miniemulsion (Figure 2.2).

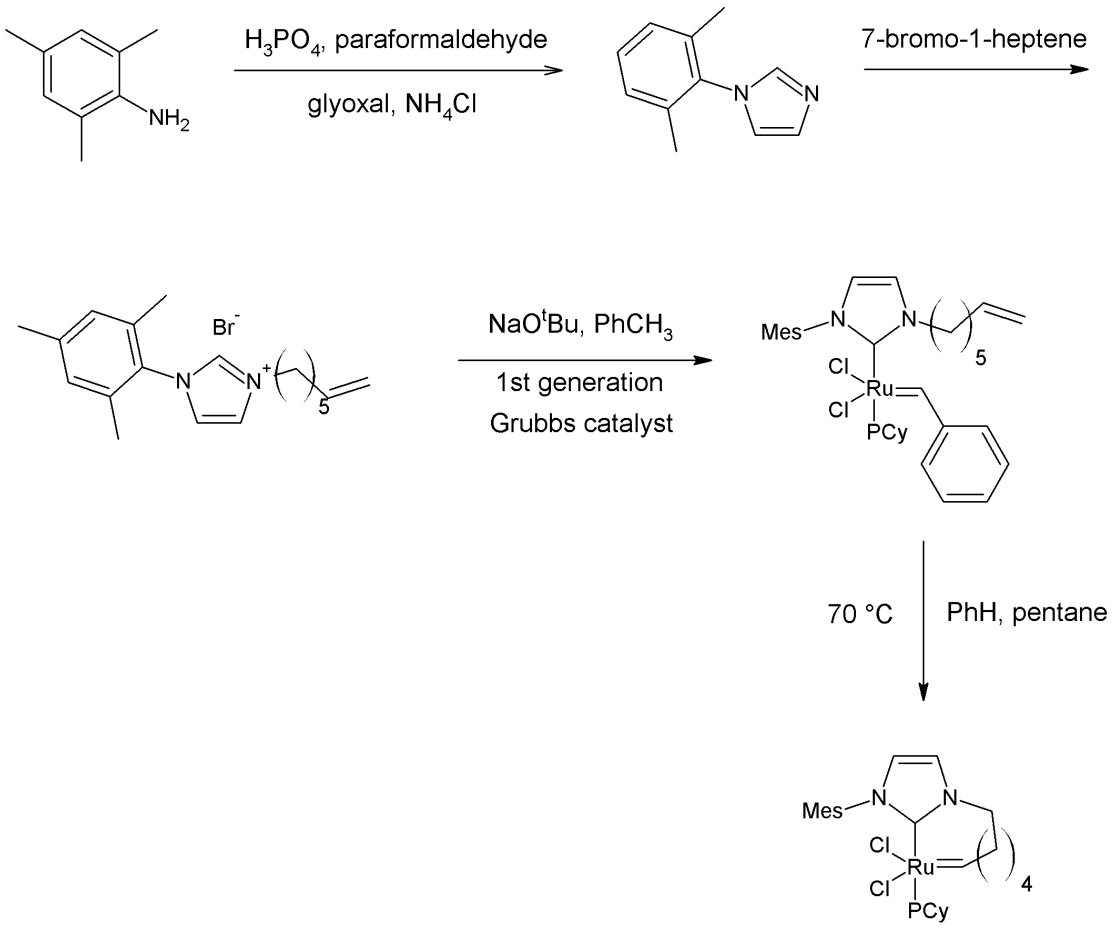


Figure 2.1 **Synthesis of a cyclic ruthenium alkylidene catalyst.**

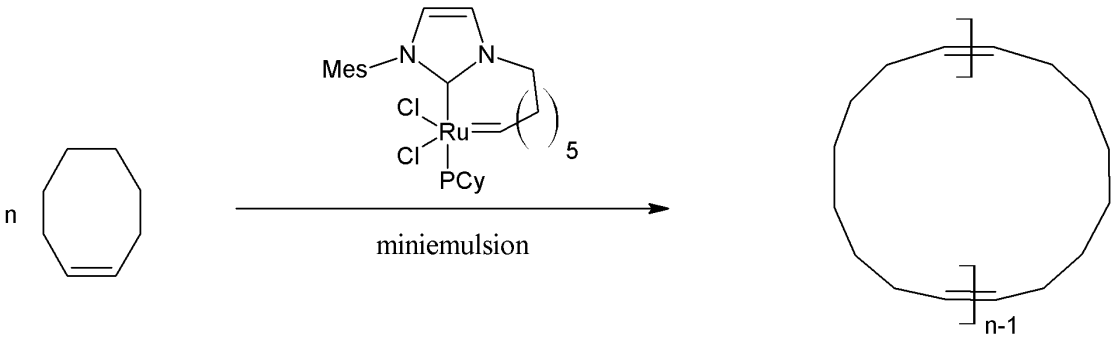


Figure 2.2 **REMP in miniemulsion.**

The second approach to cyclic polymers should be realized via a preparation of an α,ω–bifunctional polymer with terminal moieties capable of undergoing a reaction with each other. The formation of macrocycles via an intramolecular reaction was carried out in miniemulsion and studied for its efficacy and applicabilty. For this purpose, polystyrene and polylactide carrying either two terminal cinnamoyl moieties (Figure 2.3) for an intramolecular [2+2]

photocycloaddition (Figure 2.4) or terminal undecylenic moieties for the ring closing metathesis (Figure 2.5) were synthesized.

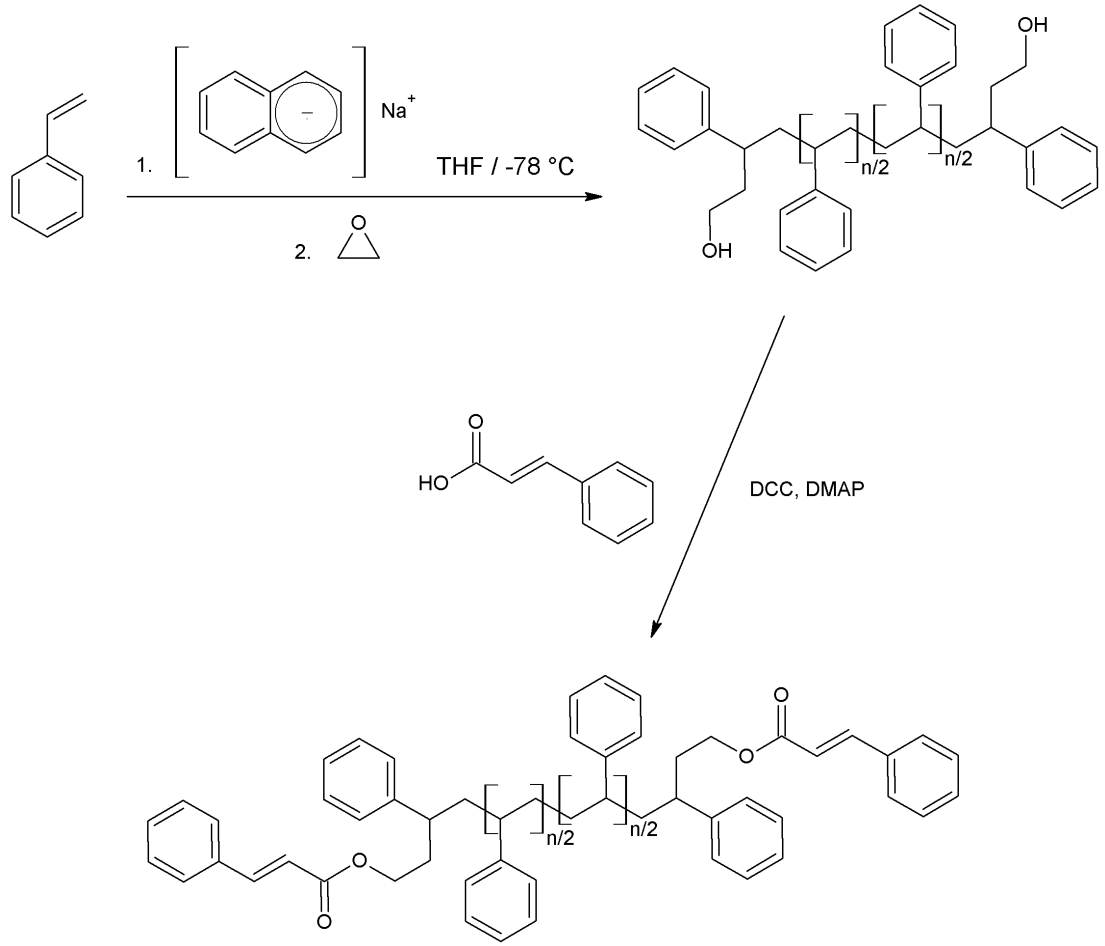


Figure 2.3 **Synthesis of an α, ω – dicinnamoyl functionalized polymer on the example of polystyrene.**

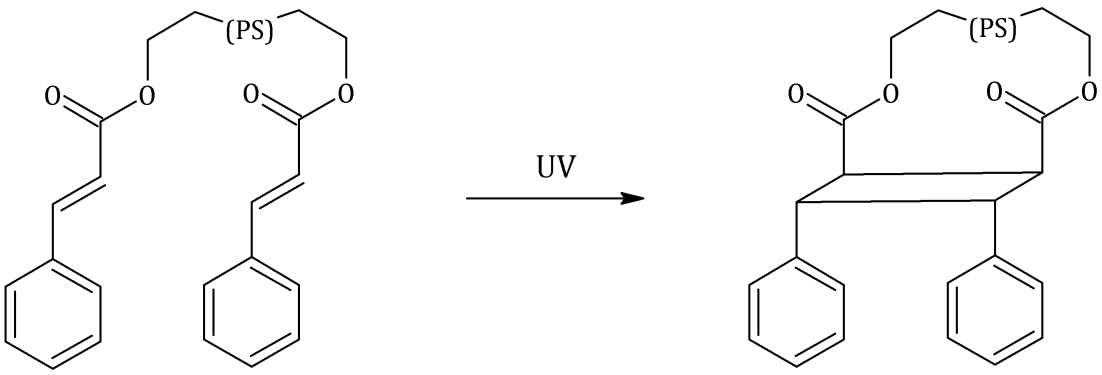


Figure 2.4 **Cyclization of the polymer via [2+2] cycloaddition of the cinnamoyl moieties on the example of polystyrene.**

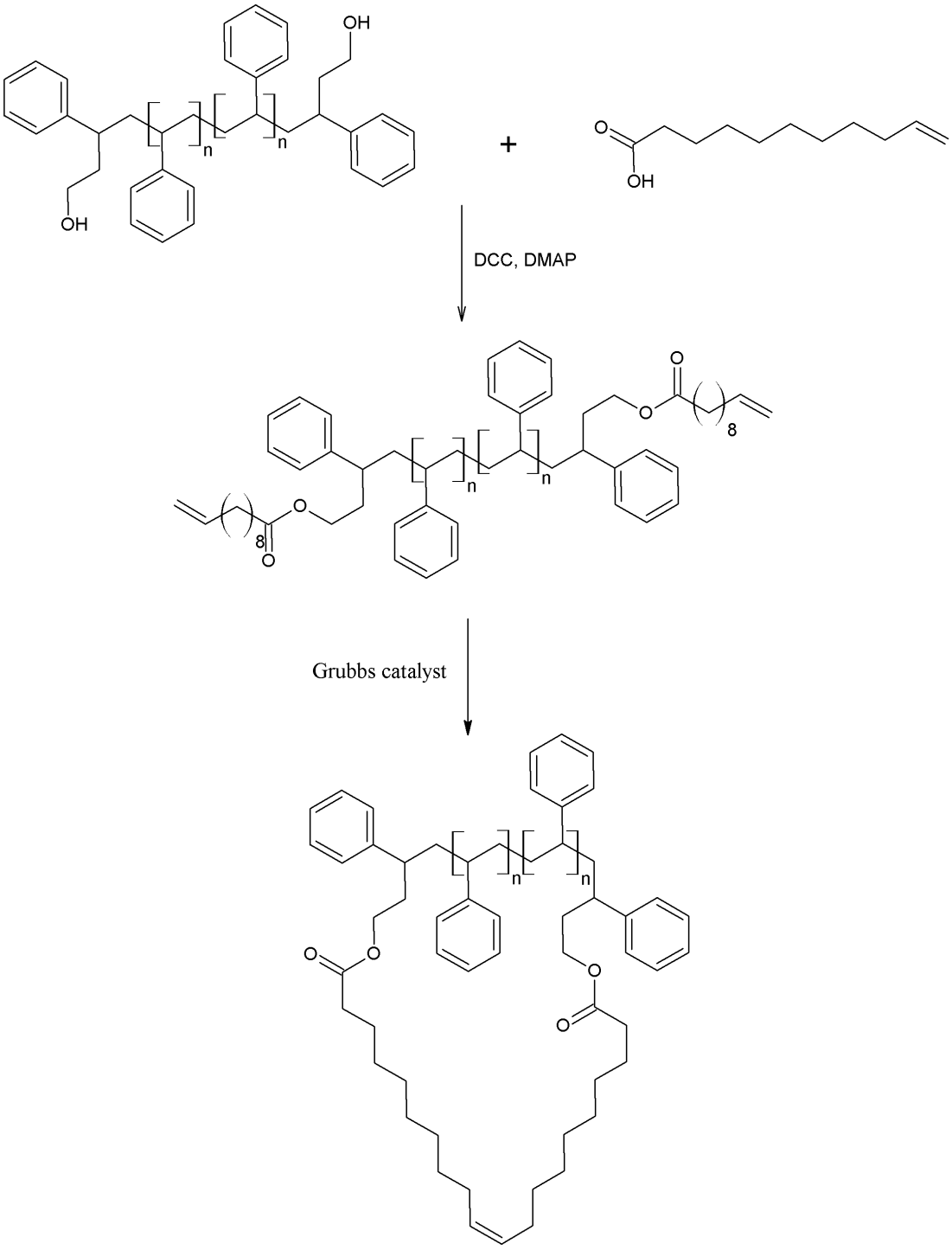


Figure 2.5 Synthesis of an α,ω–(bis)undecylenoyl functionalized polymer with a subsequent ring closing metathesis on the example of polystyrene.

3 Results and Discussion

3.1 Synthesis of the cyclic ruthenium alkylidene catalyst

The first aim of the thesis was the formation of the cyclic ruthenium catalyst for ring expansion metathesis polymerization. For this purpose the procedure reported by Michael Spiegler et al. [59] and Robert Grubbs et al.[58] was used. The procedure involves a 4-step reaction which is schematically shown in Figure 3.1.

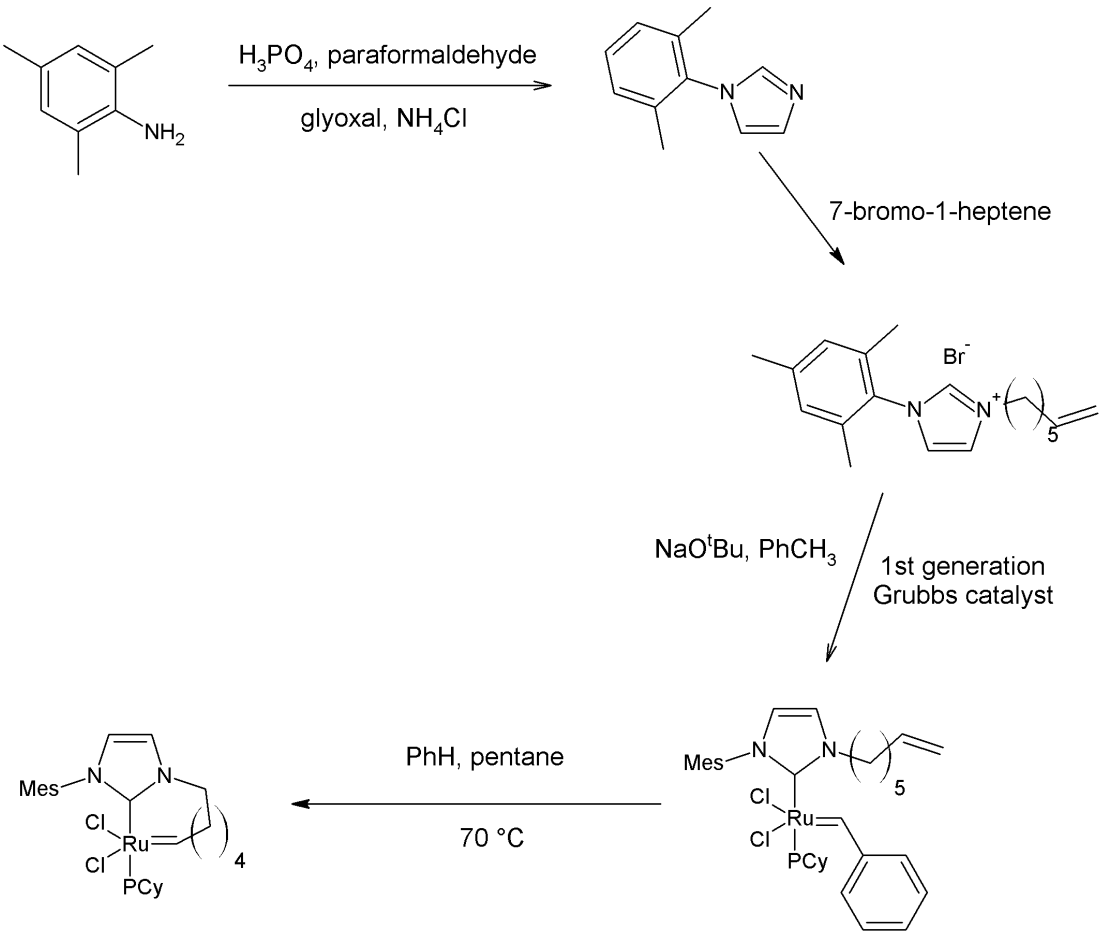


Figure 3.1 Scheme for the synthesis of the cyclic Grubbs catalyst.

3.1.1 Synthesis of 1-(mesityl)imidazol

1-(mesityl)imidazol was syntesized according to the literature protocol[59] with modified purification. Recrystallization still produced yellowish crystals instead

of a colorless solid. For that reason flash column chromatography was used in order to isolate the product. The solvent mixture DCM:EA (3:1) showed a retention factor of 0.3 for the product and was used as eluent. Since the impurities eluted before the product due to their higher retention factor, the first fractions were discarded. As soon as the impurities were not detectable in the eluate by using the TLC the eluent was exchanged with pure ethyl acetate. Since the target substance has a higher R_f in pure EE it was possible to speed up the elution. The result of this purification method was much more effective if compared with recrystallization and a colorless substance was obtained. The NMR measurements in CD_2Cl_2 confirmed the purity showing the spectrum in accordance to the reported one Figure 3.2).

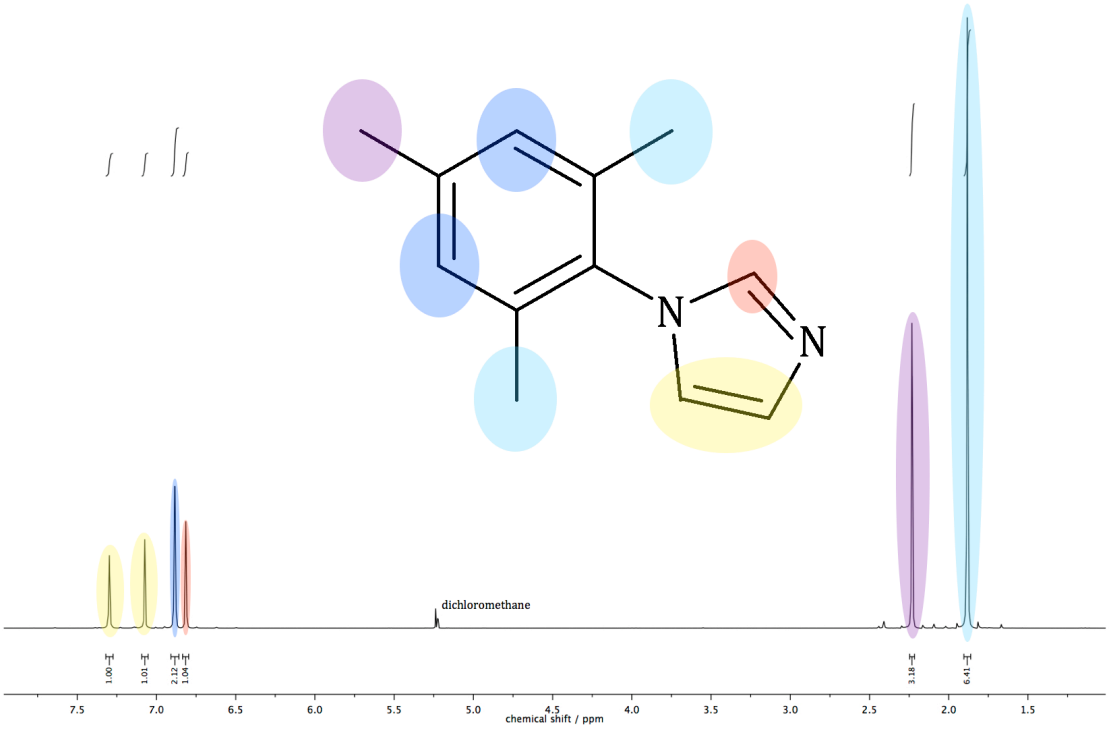


Figure 3.2 NMR spectrum of 1-(mesityl)imidazol.

The reaction sequence starts with a condensation reaction of glyoxal with ammonia and mesityl amine to generate a diimine. Since the reaction mixture contains water it reacts with the paraformaldehyde to give formaldehyde which then reacts with the diimine. The following ring closure and water elimination leads to the desired product (Figure 3.3).

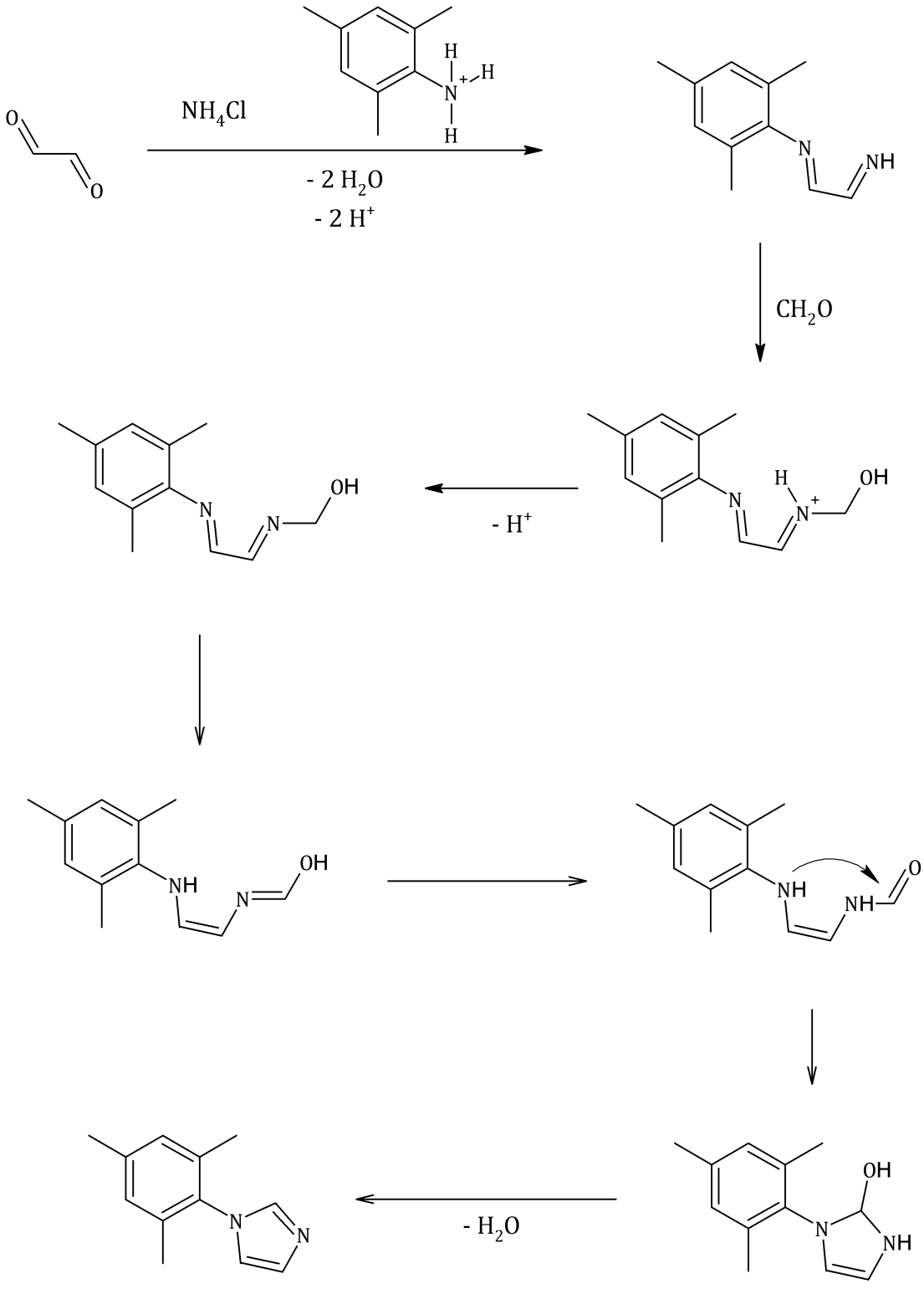


Figure 3.3 **Reaction mechanism for the formation of 1-(mesityl)imidazol.**

3.1.2 Preparation of the imidazolium salt

This compound was synthesized according to a literature procedure[87] and similar yields were obtained (ca. 78%). The solubility of the product in diethyl ether is low but it is well soluble in dichloromethane. Taking advantage of this fact the product was successfully isolated by precipitation but some difficulties appeared which were not described in literature. After running the reaction for 24 h the toluene was removed and the residue was dissolved in dichloromethane for further precipitation into diethyl ether.

The characterization of the collected white solid was performed by NMR which confirmed the purity of the product (Figure 3.4).

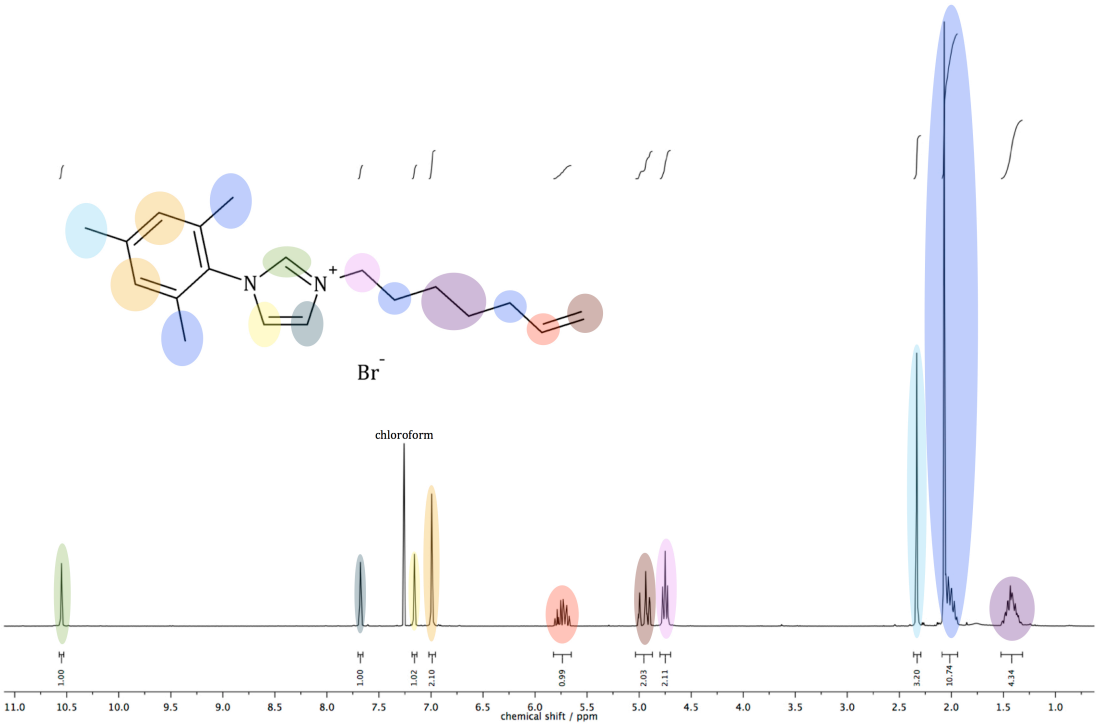


Figure 3.4 NMR spectrum of 1-(6-Heptenyl)-3-mesitylimidazolium bromide.

The compound used for this synthesis is an imidazol derivative. Imidazol is an aromatic heterocycle due to its six electrons within the planar ring structure and the lone electron pair of one of the nitrogen atoms is incorporated into the aromatic system. As one can conclude from the resonance structures below, one nitrogen atom is quite reactive due to its negative charge in one of the possible contributing structures (Figure 3.5):

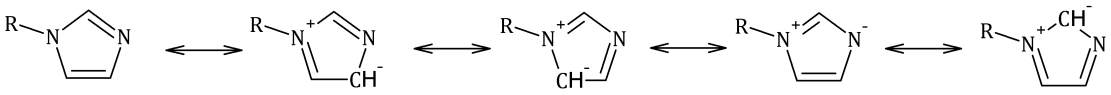


Figure 3.5 Resonance structures of imidazol and its derivatives.

This property of imidazol and its derivatives can be used for further reactions. In the reaction of 1-(mesityl)imidazole with 7-bromo-1-heptene alkylation of the nitrogen atom occurs. The high electron density near the reacted nitrogen is the reason for the nucleophilic attack on the carbon atom partially positively charged by the attached bromide. The nucleophilic substitution of the bromide atome leads to a positively charged nitrogen and the charge is resonance-stabilized which is favourable for the reaction (Figure 3.6).

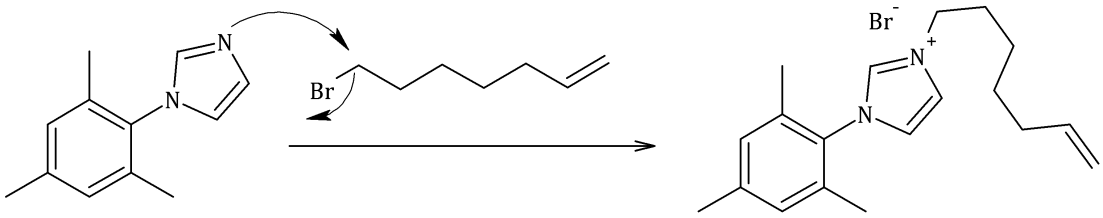


Figure 3.6 Reaction mechanism for the formation of 1-(mesityl)imidazole with 7-bromo-1-heptene.

3.1.3 Preparation of the „open“ catalyst

For this purpose the reaction of 1-(6-heptenyl)-3-mesitylimidazolium bromide with the first generation Grubbs catalyst was carried out a described by Tew et al.[87] The previously synthesized 1-(6-heptenyl)-3-mesitylimidazolium bromide belongs to the group of the so-called imidazolium salts. The carbon atom between the two nitrogen centres of the imidazolium ring is highly electron-deficient due to the positive charge. Therefore the carbon-hydrogen-bond is destabilized by these factors and can be easily broken. A base, such as potassium *tert*-butoxide can abstract the proton from this site leading to the formation of the so-called imidazol-2-ylidenes. These compounds are known as *N*-heterocyclic carbenes. Imidazole-based persistent carbenes are the most stable and the most well studied group of stable carbenes. The lone pair of carbene leads to a reaction with the First generation Grubbs catalyst by replacing one of the phosphine ligands and coordinating to the ruthenium center of the complex, as shown in Figure 3.7.

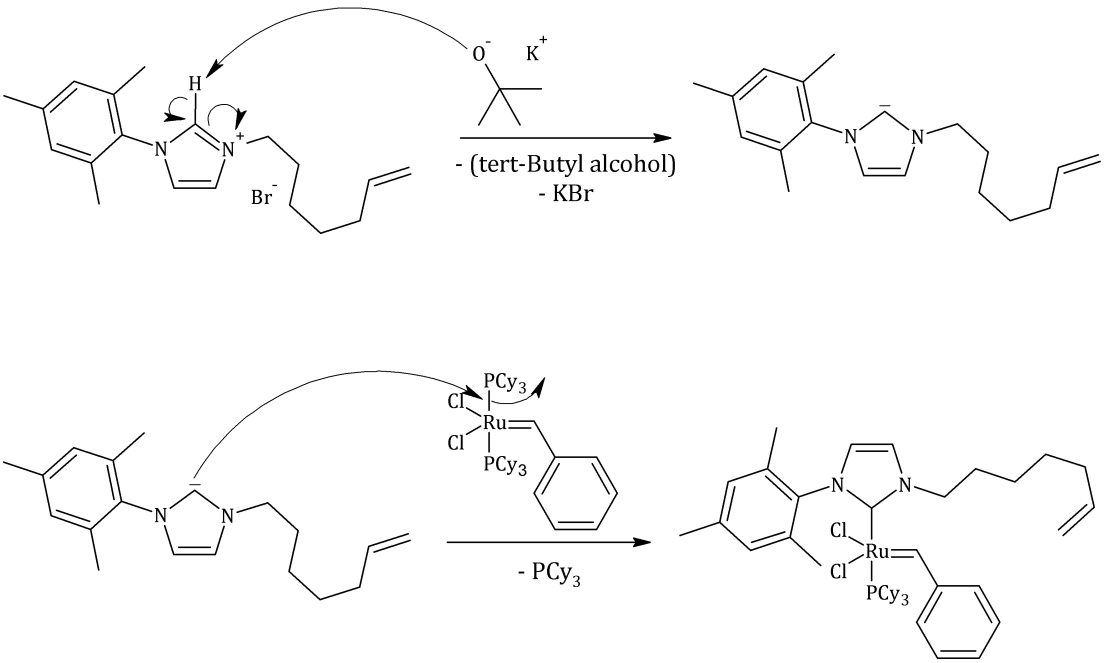


Figure 3.7 Reaction mechanism for the formation of 1-(6-heptenyl)-3-mesitylimidazolium bromide with the first generation Grubbs catalyst.

The preparation of this compound caused some difficulties especially with respect to its isolation from the reaction mixture. The first small scale test reaction was carried out in a vial which was filled with nitrogen and sealed by parafilm. After one hour the solution turned green and no product formation could be detected by TLC. The same was repeated by using a Schlenk flask resulting in a red-brown reaction mixture after stirring for one hour. The product was detected by TLC by using pentane/diethyl ether 2:1 as eluent. The retention factor of the product was ca. 0.4 under these conditions whereas the first generation grubbs catalyst showed a retention factor of ca. 0.9 but was not detected within the reaction mixture. It showed either a quantitative reaction or the catalyst used for the reaction was degraded due to its instability. Nevertheless, in both cases it was necessary to purify the reaction mixture which contained the unreacted reagent and numerous side products. The brown suspension was purified by flash column chromatography on silica under the same conditions as used for analytical thin layer chromatography. The expected red-purple solution had a brown-green color and only trace amounts of product could be detected by TLC. The same procedure was repeated by using N_2-pressure to accelerate the elution. It could be observed in both cases that the

silica turned green during the separation procedure indicating fast degradation. This assumption was verified by NMR: one of the most characteristic signals within the NMR spectrum of the target molecule arises from the akylidene proton with the chemical shift of 19.9. The absence of this signal lead to the conclusion that the carbene was absent and it confirmed the speculated degradation of the Ruthenium complex bringing up the question how the purification can be performed without product loss. For this purpose silica was replaced by aluminium oxide since it was speculated that silica could degrade the product. Running the purification with aluminium oxide the green staining of the stationary phase could be observed again, however, the NMR spectrum showed a weak signal of the alkylidene proton. The yields were poor (less than 10%) and it must be taken into account that the cleavage products which presumably originated from the interaction of the alkylidene complex with aluminium oxide still contaminated the end product. Since pH-neutral silica for column chromatography which would probably be more inert was not available it was a challenge to come up with an effective alternative purification method. The degradation of the product was the higher the longer it was exposed to the stationary phase and it was decided to use a thin layer of aluminium oxide in order to filtrate the reaction mixture through it. The first sign for the relatively high effectiveness of this method was the intense red color indicating a higher concentration of the desired product. Thus, a suitable balance between the cleavage and loss of product and contamination was achieved. Although the characterization of the isolated product by this method was again difficult due to the presence of side products it produced the best results (Figure 3.8). The NMR below shows the NMR spectrum of [1-(6-heptenyl)-3-mesitylimidazol-ylidene]$RuCl_2$(dCHPh)(PCy_3).

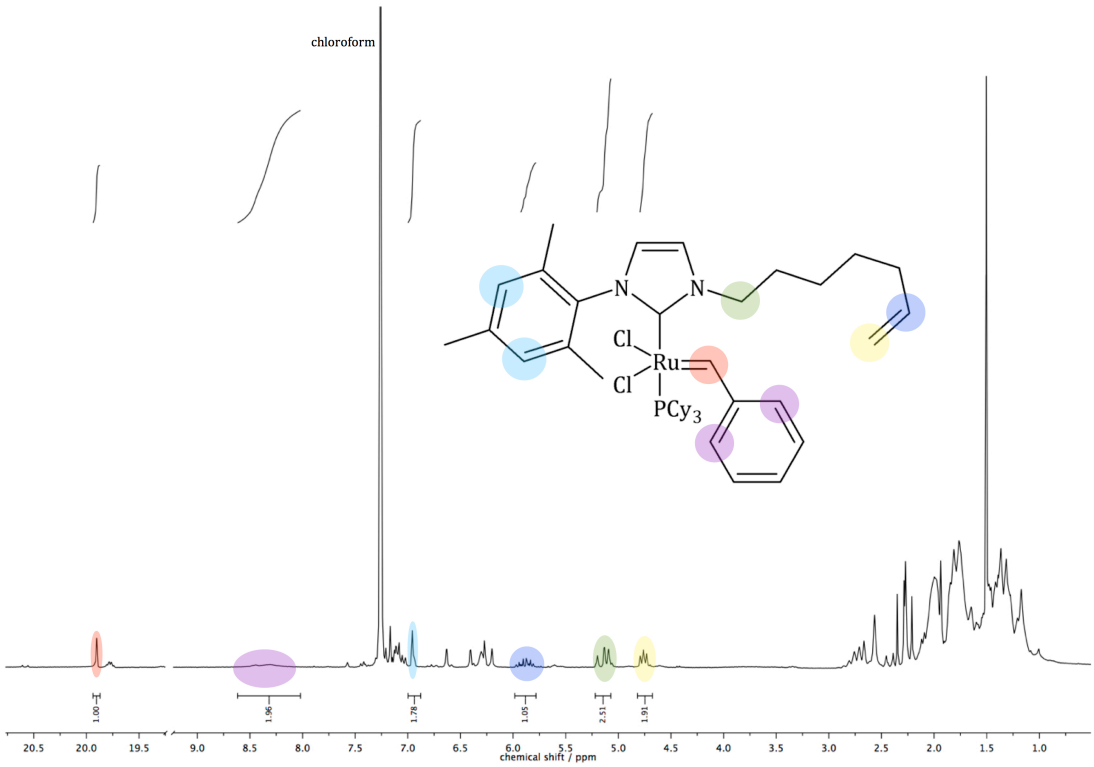


Figure 3.8 NMR spectrum of [1-(6-heptenyl)-3-mesitylimid-azolylidene]$RuCl_2$(dCHPh)(PCy_3).

The integration of the characteristic signals of this compound shows the successful product formation which can be concluded from the correct proton ratios. Unfortunately, the integration of the signals for methyl-, methylene- and some aromatic protons could not be included due to their presumed overlapping with the signals originating from the impurities providing unreasonable integral values. Furthermore, the first generation Grubbs catalyst was still present in trace amounts and since the next reaction step would be carried out under highly diluted conditions in order to ensure the intramolecular reaction it was believed that this fact should not affect the procedure.

3.1.4 Preparation of the cyclic ruthenium alkylidene catalyst

The acyclic ruthenium alkylidene complex which is also commonly called „open“ catalyst can be cyclized via an intramolecular metathesis reaction. For this purpose a highly diluted solution (ca. 1 mmol/L) is prepared in order to suppress an intermolecular reaction and to make sure that metathesis occurs only intramolecularly. The reaction mechanism starts with the direct [2+2]

cycloaddition of the alkene double bond to the ruthenium alkylidene to yield a metallacyclobutane ring. This intermediate releases the desired cyclic catalyst and styrene.

After heating the reaction mixture at 70 °C for 1 hour and removing the solvent the product formation was monitored by TLC showing a mixture of at least 4 UV active components. The retention factor of the contemplable compounds within the reaction mixture were compared by using a TLC plate. Three red to purple spots appeared as well separated fractions which later could be seen within the NMR spectra. The alkylidene region of the NMR spectrum confirmed the assumption that the compounds monitored by TLC were three different species of ruthenium complex (Figure 3.9) showing three different chemical shifts for the alkylidene proton due to their different chemical environment. Two of them could be identified as the reagent and the product i.e. the cyclic and the „open" acyclic catalyst. The third one could originate either from the First generation Grubbs catalyst or its partially degraded or modified derivative. Since all three contemplable catalysts could have been degraded the clevage products could be represented by the signals between 20.1-20.3 ppm, 19.0-19.4 ppm or in the area 16.0-16.7 ppm.

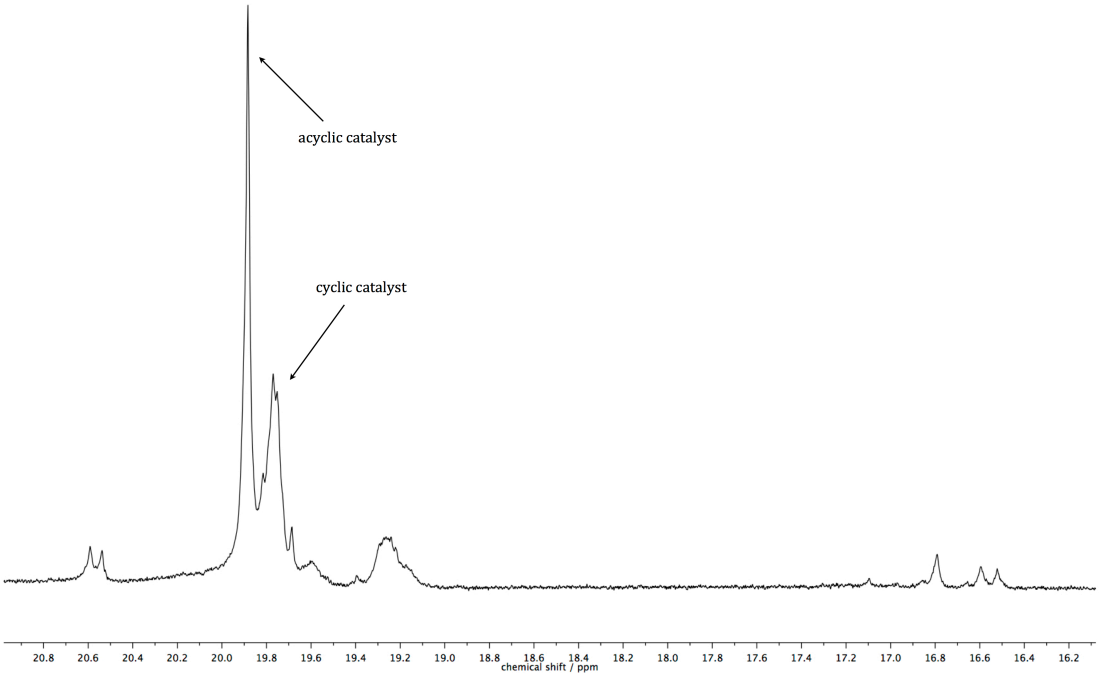


Figure 3.9 NMR spectrum for the alkylidene region of the ruthenium complexes.

The green spot at the loading site could be the previously observed cleavage product of the complex. The presence of 3 different ruthenium compounds represented even a bigger challenge for purification than it was in the case of the acyclic catalyst. The reason for that was again the fact that the flash column chromatography was unsuitable for purification applications for the previously stated reasons. The attempt to run a chromatography column resulted in complete degradation as it was the case for the attempt to recrystallize the residue. As expected, simple filtering through a thin layer of aluminium oxide did not solve the problem showing the presence of the aforementioned ruthenium compounds. Furthermore, the contact to aluminium oxide again caused degradation as could be seen in the colour change of the solution into a red to greenish solution. The integration and ratio calculation of the signals was also in this case difficult due to signal overlap. (Figure 3.10).

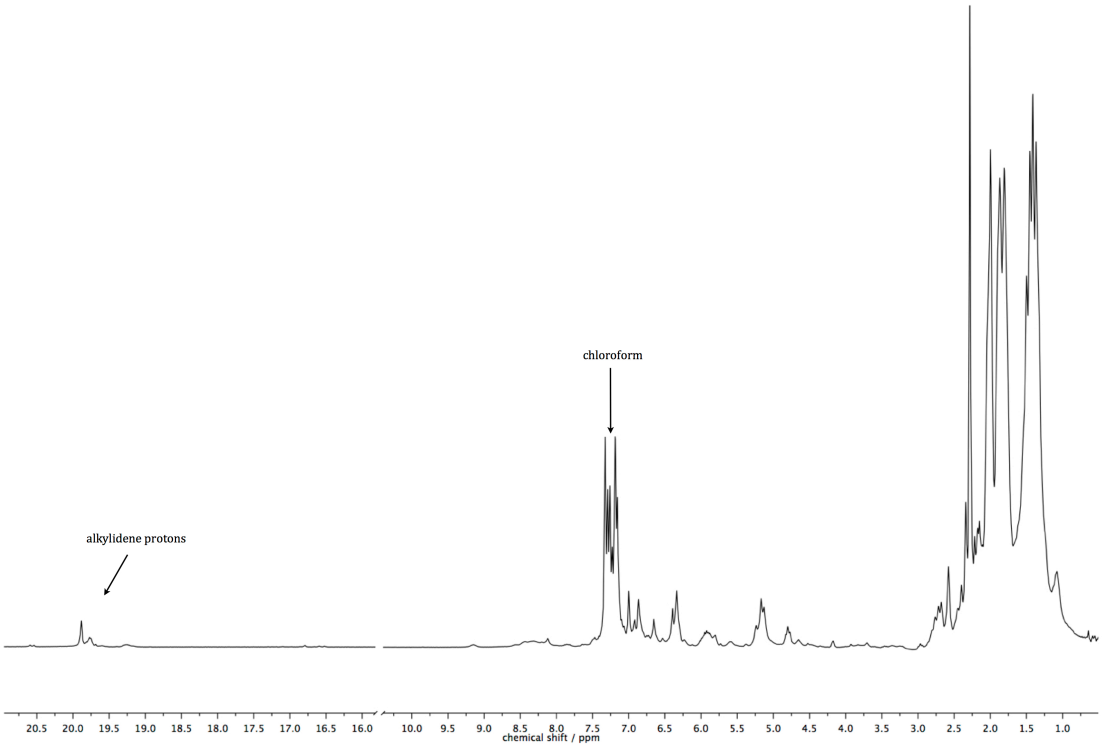


Figure 3.10 NMR spectrum of the cyclic catalyst contaminated with other ruthenium complexes.

The ring-expansion metathesis polymerization requires high purity of the catalyst to guarantee the formation of cyclic polymers only. Polymerization of cyclooctene by using the unpurified product yielded impractical PDIs of around 5 where the detection or isolation of cycles is complicated.

As described in literature[58], purification can only be solved by using neutral silica (pH 6.5-7.0). Thus, it is possible to isolate the product via conventional flash column chromatography without massive product degradation, but no supplier of neutral silica could be tracked down and therefore the purification issue is still open.

3.2 Synthesis of α, ω – dicinnamoyl – polystyrene

The second approach for the synthesis of cyclic polymers is as described in the theory part a cyclization of an α, ω –difunctional polymer. Thus, cinnamic moieties which are able to react whith each other via [2+2] cycloaddition were introduced to the polymer chain ends aiming a subsequent macrocycle formation upon irradiation. For this purpose α, ω–dihydroxy–polystyrene was synthesized by anionic polymerization of styrene using sodium naphthalenide as a bifunctional initiator and terminating the macrodianion with ethylene oxide. The obtained polystyrene was subsequently functionalized with cinnamic acid via Steglich esterification (Figure 3.11.).

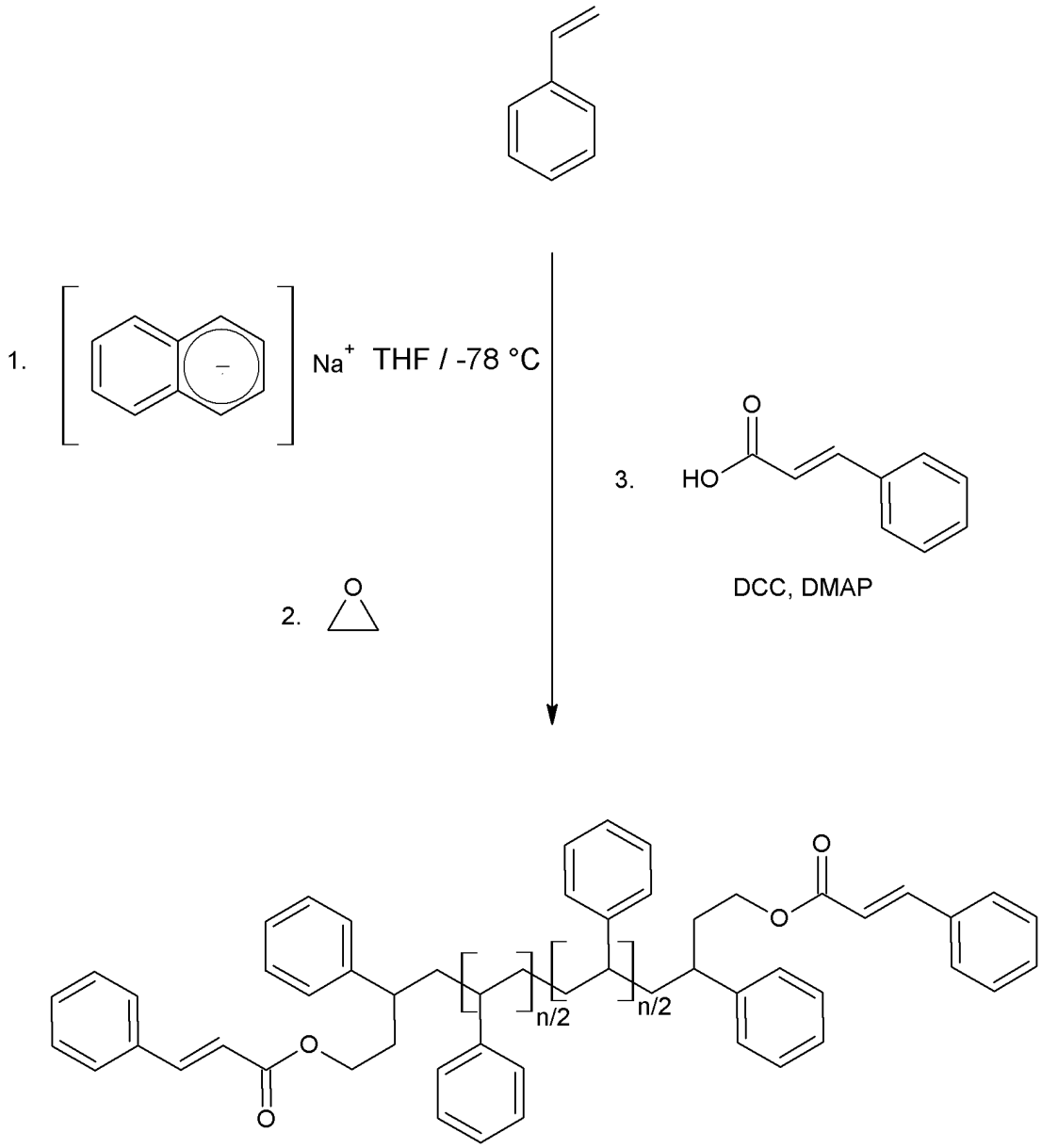


Figure 3.11 Synthesis of α, ω – dicinnamoyl-polystyrene

3.2.1 Synthesis of α, ω – dihydroxy-polystyrene

The synthesis of α, ω – dihydroxy-polystyrene first required the synthesis of the initiator from sodium mirror and naphthalene. When the dry naphthalene solution was added to sodium the reaction took place immediately which could be seen from the resulting green color. The reaction was allowed to proceed for 4 days until completion. It was important to ensure a quantitative reaction of sodium since the exact concentration of the initiator was required in order to control the molecular weight of the target polymer. As soon as no sodium mirror was visible it was assumed that the reaction was completed and the initiator was

ready to use. The first synthesis was terminated with water (Figure 3.12) producing no functionalities at the chain ends of the polymer and was used for the purpose of titration of the initiator solution. The concentration was calculated from the molecular weight of the resulted polystyrene determined via GPC measurements (Figure 3.13).

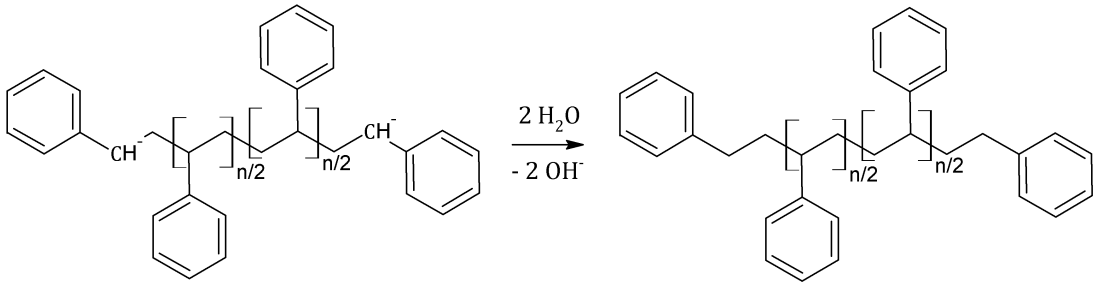


Figure 3.12 Termination of the polystyrene macrodianion with water

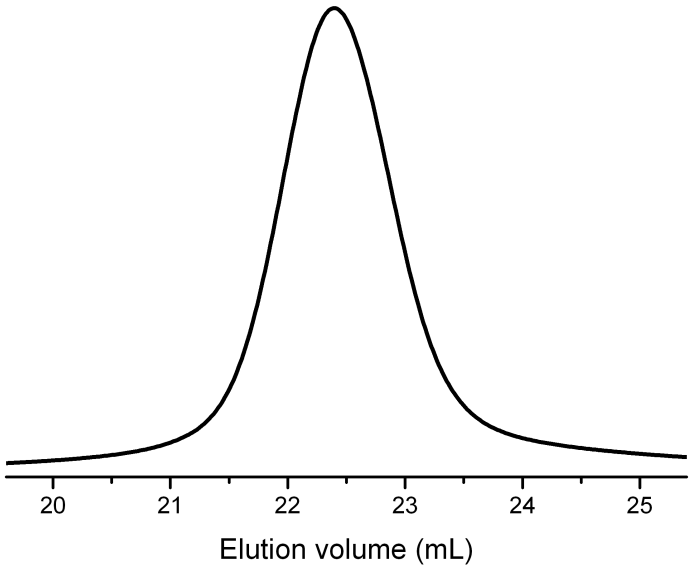


Figure 3.13 UV signal of the GPC measurement of α, ω – dihydroxy-polystyrene M_n=57800 g/mol

The next attempt was to target a molecular weight of ca. 10000 g/mol. Since the polymerization rate was very high ethylene oxide was added 10-15 minutes after the mixing of the initiator with the styrene solution. The red color of the macroanions disappeared after ca. 15-20 minutes and the polymer was isolated by precipitation into methanol.

The product was characterized both by NMR and GPC. The molecular weight approximately complied with the targeted one and the PDI of 1,23 was adequate for further studies (Figure 3.14).

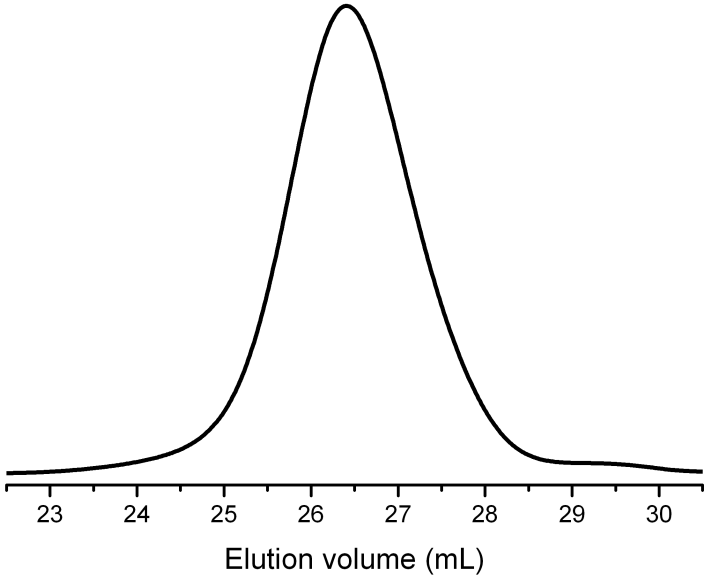


Figure 3.14 UV signal of the GPC measurement of PS–8k.

The detected molecular weight was controlled by NMR measurements (Figure 3.15). All the characteristic signals of polystyrene were identified (δ= 1.2–2.3, 3.15–3.45, 6.25–7.23) including the methylene protons (3.15-3.45 ppm) next to the hydroxyl moieties which were successfully used as reference for signal integration. The molecular weight calculated from the NMR spectrum for PS-8k (Figure 3.15) was ca. 9700 g/mol which approximately conformed with the peak molecular weight detected by GPC measurements (Table 3.1.)

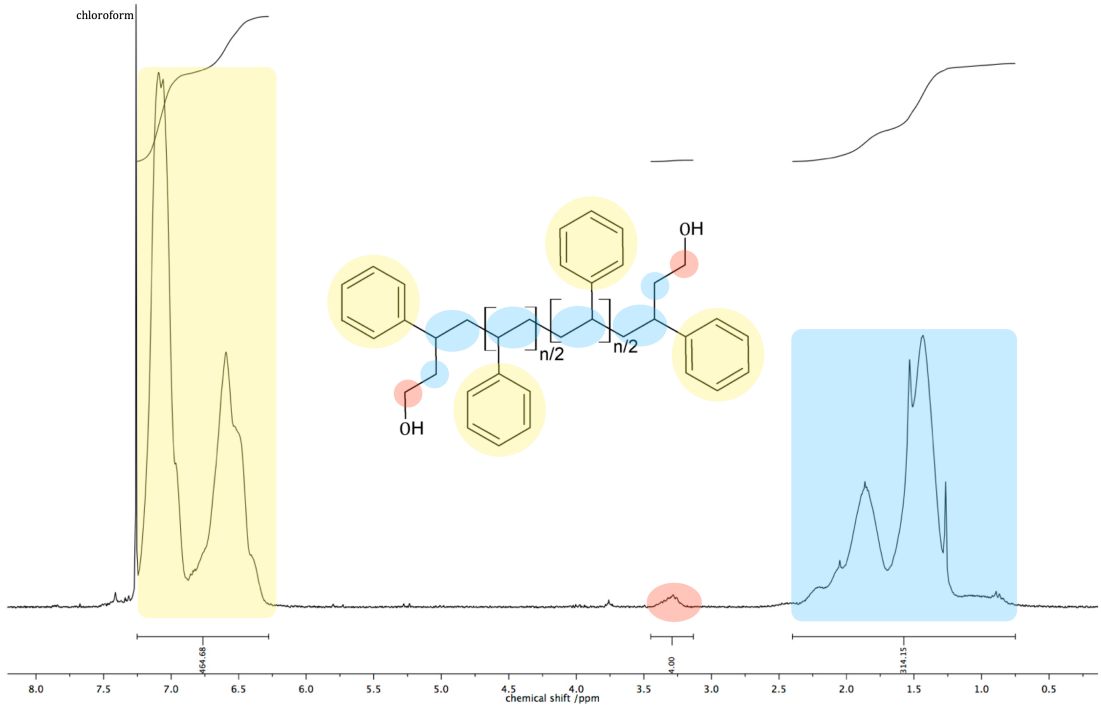


Figure 3.15 NMR spectrum of PS–8k.

Table 3.1 GPC and NMR data of the prepared polystyrenes

#	M_n	M_p	PDI	hydroxyl – endgroups
PS–57.8k	57800	72200	1.32	–
PS–8k	8000	9200	1.23	+

After the purity of the product was confirmed by NMR it was functionalized with cinnamic acid via a Steglich esterification.[88]

100-fold molar excess of cinnamic acid finally provided quantitative conversion with new resonances at 3.71–4.06 and 7.33–7.74 ppm from the cinnamic esters (Figure 3.16).

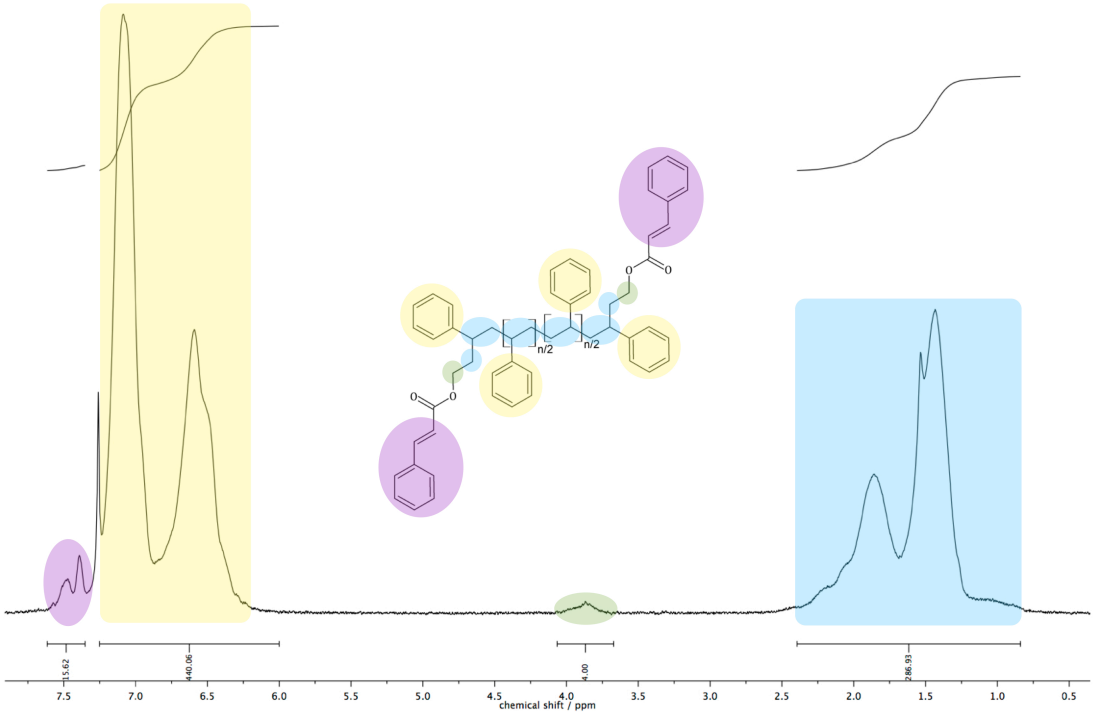


Figure 3.16 Complete esterification of PS-8k

The excess of cinnamic acid and other reagents were easily removed by precipitation of the modified polystyrene into methanol.

3.3 Cyclization of α, ω – dicinnamoyl – polystyrene via [2+2] photocycloaddition

The cyclization reaction was studied in solution and in miniemulsion. As described in the work of Kathrin Schöller, the probability of the appearance of more than one polymer chain in a miniemulsion droplet can be minimized by reducing the number of polymer chains compared to the number of the miniemulsion droplets. Therefore it is statistically likely to produce separated single chain particles in which single molecule reaction can take place. These conditions should suppress intermolecular reactions without high dilution of the reaction mixture. In order to prepare single chain particles with the synthesized polystyrene, the miniemulsion was prepared according to the procedure described in the introduction and the experimental part.

The toluene evaporation was continued until such time as the mixture became slightly turbid in order to guarantee a sufficient solvation of the polymer within the droplets. In the case of a complete removal of toluene the polymer chains and therefore their ends which are supposed to react would be hindered in moving. On the other side, the system's intense light scattering had to be minimized to ensure efficient UV absorption. However, this problem would not affect the polymer solution in chloroform which was regarded as comparative and control study.

The molecular weight decreased after the irradiation experiment in chloroform solution. In addition, the PDI increased significantly and several decomposition products were detected at high elution volumes which indicated that not the expected cyclization reaction occured. Similar results were obtained in miniemulsion but with some interesting characteristics which shall be discussed next.

The following elugram (Figure 3.17) shows the result of a 5 h irradiation in miniemulsion and in chloroform where one can see the appearance of large amounts of low molecular species in both cases indicating the degradation of the polymer.

Interestingly, the irradiation in miniemulsion produces a mixture containing a fraction of approximately the same molecular weight as the starting material and the degradation products which can be detected at higher elution volumes whereas the cleavage of the polymer during the irradiation in chloroform apparently affects all polymer chains. Furthermore, the miniemulsion elugram shows a the strong signal between 29 and 31 mL originating from the surfactant (SDS) which could not be completely removed by dialysis.

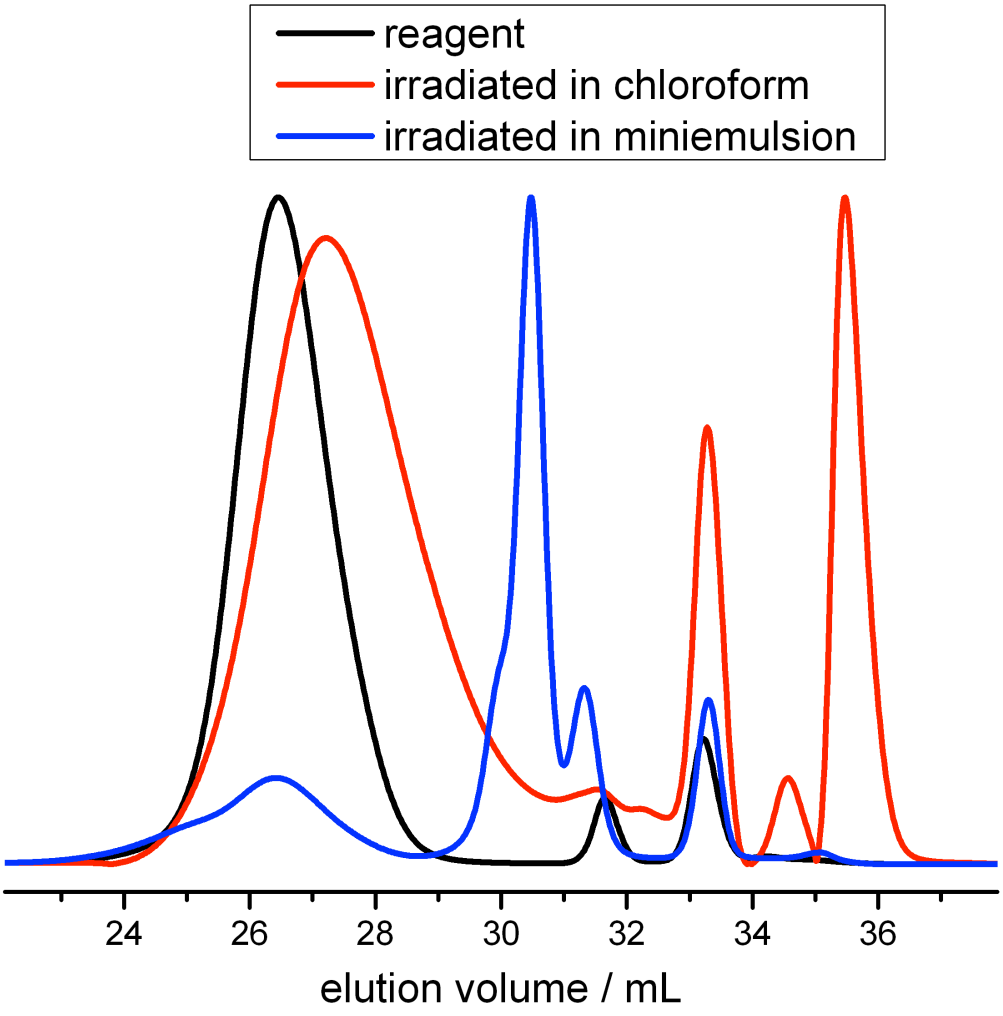


Figure 3.17 GPC data (RI signal) of irradiated polystyrenes.

The following HPLC elugram (Figure 3.18) shows the product after 5 h of irradiation in miniemulsion in comparison to the reagent. The intense signals between 27 and 34 min most likely represent oligomers originating from the polystyrene fractionation.

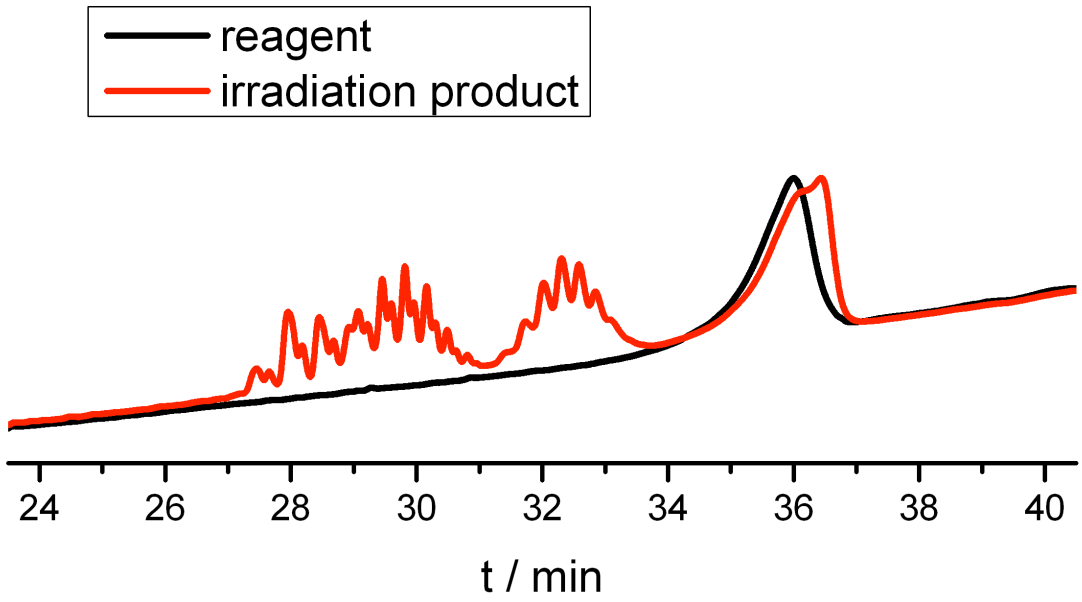


Figure 3.18 HPLC of the irradiated polystyrene.

The difference between the irradiation product in miniemulsion and chloroform could originate from the different chemical environment of the polystyrene chains. In miniemulsion the polymer chains are surrounded by the surfactant forming a shell which could partially block the UV light and protect the polystyrene from excessive degradation. In chloroform the UV light can be directly absorbed by the polymer. Additionally, chloroform is an efficient radical chain transfer agent and can induce the polymer cleavage by radical reactions.

One can see in the NMR (Figure 3.19) spectrum of the irradiated polymer that the proton signals of the cinnamic moieties dramatically decreased if compared to the reagent and new signals appear indicating the formation of other compounds than the polymer. It lead once more to the conclusion that the degradation observed within the GPC data takes place during the irradiation.

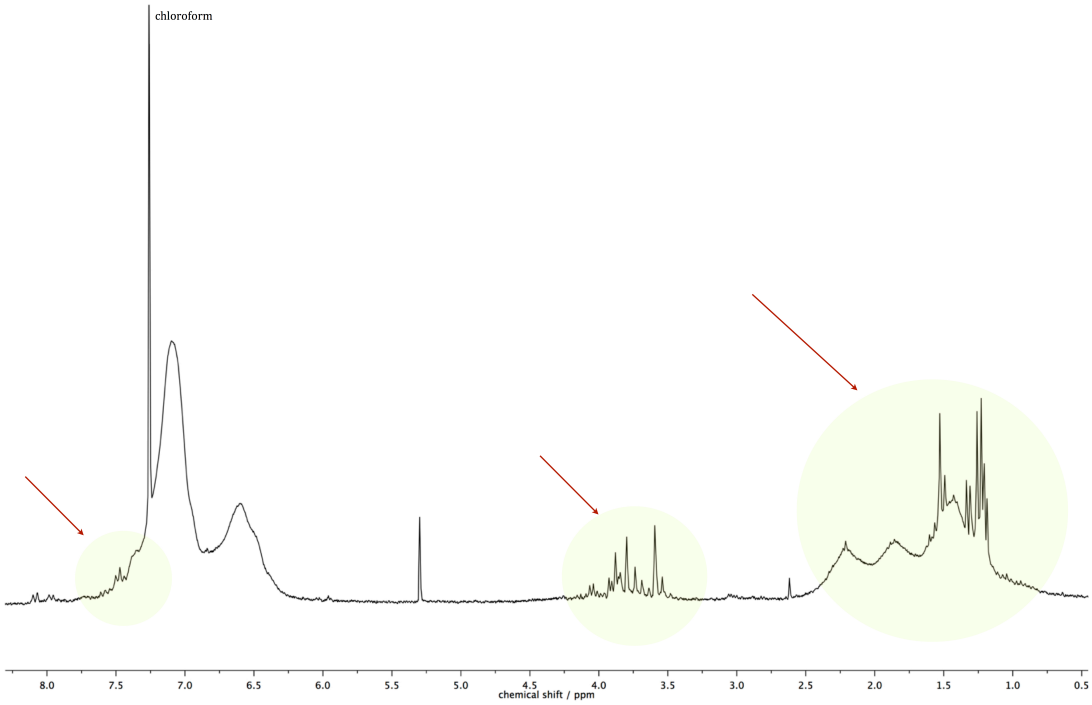


Figure 3.19 NMR spectrum of the irradiated polystyrene.

The experiments were initially carried out with a mercury short-arc lamp (200W) which was replaced with a UV hand lamp (6W). The reason was the assumption that its lower intensity would create milder conditions and preserve the polymer from unwanted side reactions. The irradiation time was varied in order to study possible reactions which unfortunately lead to similar results. The decrease of the molecular weight was proportional to the irradiation time (Figure 3.20) and therefore only short irradiation times would come into question for this system. The beginning decomposition can be detected as early as after 15 minutes of irradiation. The relevant data for short irradiation times is not shown in the figure for the sake of clarity.

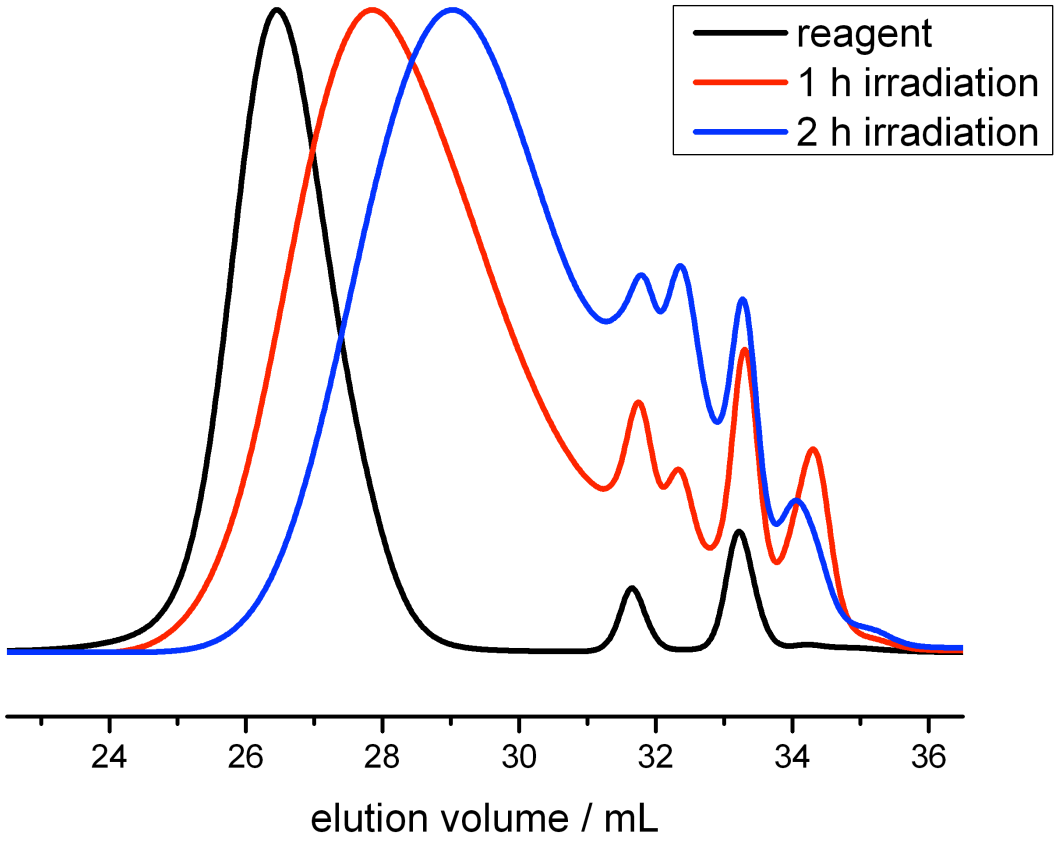


Figure 3.20 GPC data of the kinetics of the polymer degradation by irradiation with UV light.

Highly concentrated solutions were also irradiated for short times and all showed the same effect. The cleavage was again unavoidable as can be concluded from the appearance of intense signals at higher elution volumes. However, the original peak molecular weight was recovered as can be seen in the elugram, presumably due to the high number of molecules which cannot all be affected after short irradiation times (Figure 3.21).

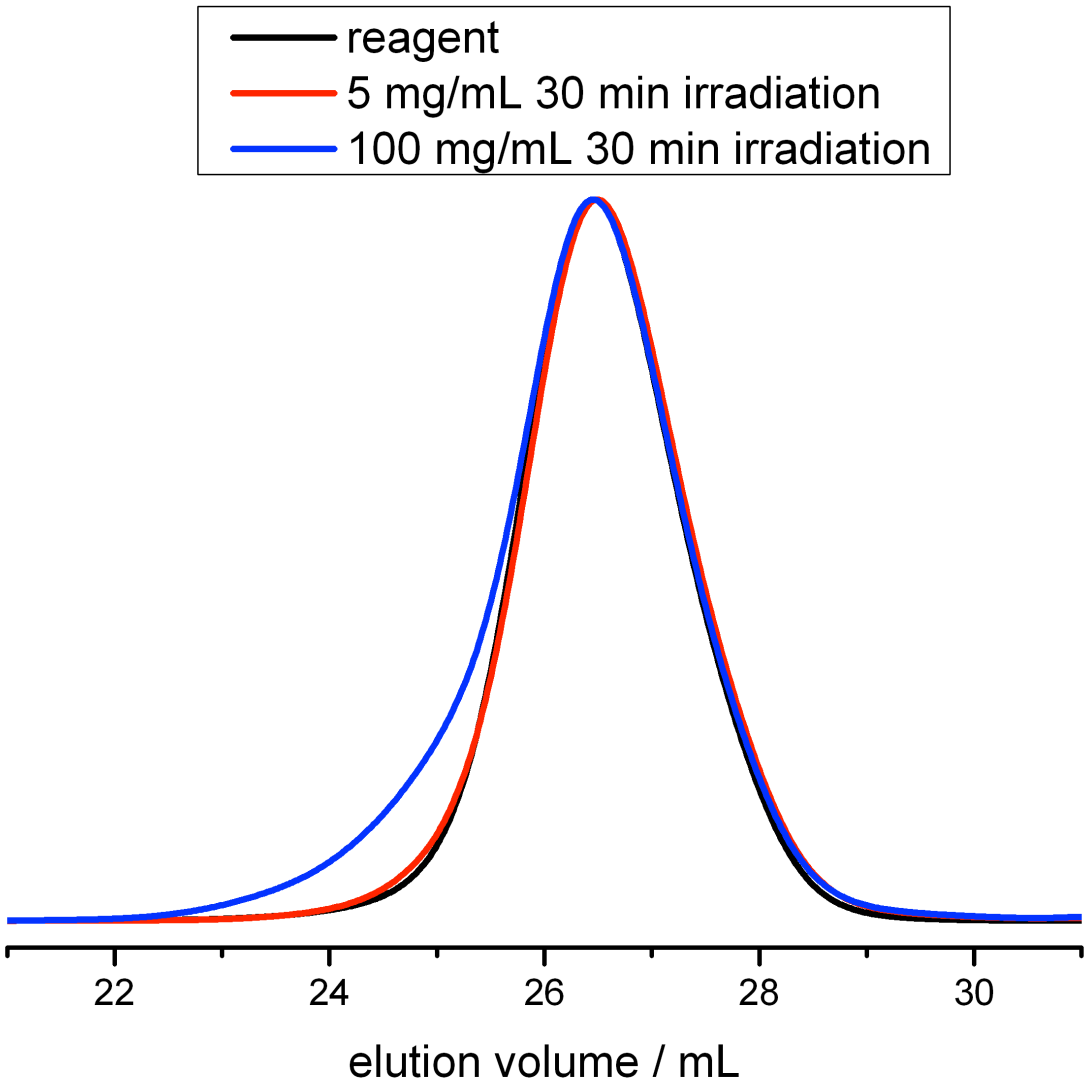


Figure 3.21 **GPC data for the irradiation product of polystyrene at high concentrations.**

It is notable that the formation of higher molecular weight species is observed and can be speculated as a result of an intermolecular reaction. As expected it is more likely for a 100 mg/mL solution than for a 5 mg/mL that the reaction occurs resulting in a broadened molar mass distribution as can be seen in the elugram. Nonetheless, the reaction seems to be slow compared to degradation.

Irradiation experiments in chloroform, dichloromethane and cyclohexane all showed similar results with resect to polymer decomposition.

Interestingly, no degradation was observed after prolonged irradiation (ca. 5 h) of the polymer in toluene as can be seen in the GPC elugram presented in Figure 3.22. It once again confirmed that the high absorption of UV light by polystyrene leads to its cleavage since the irradiation of a toluene solution represents a stable

system where toluene as solvent absorbs most of the radiation and protects the polymer. On the other hand the UV light activation needed for the reaction was probably missing and therefore anticipated cyclization of polystyrene was not achieved by this method.

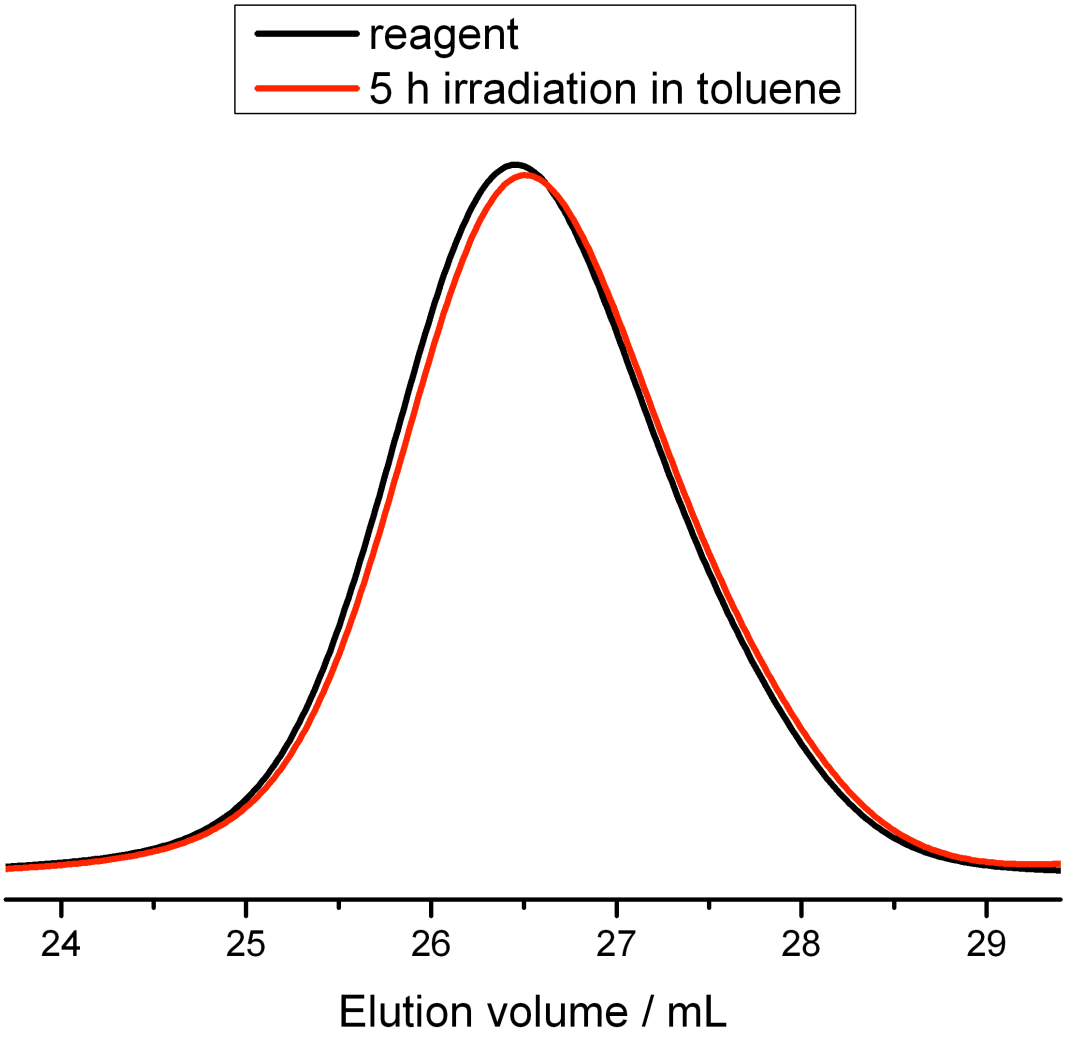


Figure 3.22 GPC data for the irradiation product of polystyrene in toluene.

Benzene and DMF also protected the polymer from degradation presumably due to their UV cut off in the region of the polystyrene absorption maximum. However, no cyclization occurred either that could be concluded from recovering the original molecular weight of the reagent due to the previously stated reasons. In summary the degradation rate of polystyrene was believed to be much higher than cyclization wherefore another polymer had to be found for this purpose. Polylactide was chosen due to its lower UV absorption and was believed to outlast the irradiation stress.

3.4 Synthesis of α, ω–dicinnamoyl–polylactide

As alternative polymer for UV-cyclization telechelic (poly)lactide with hydroxyl end groups was synthesized by anionic ring opening polymerization of lactide.

In order to prepare an α, ω–dihydroxy–polylactide a bifunctional initiator was used as it was the case for the synthesis of α, ω–dihydroxy–polystyrene. The polymerization of lactide was then carried out using poly (ethylene glycole) with M_n=600 g/mol as a bifunctional macroinitiator (Figure 3.23).

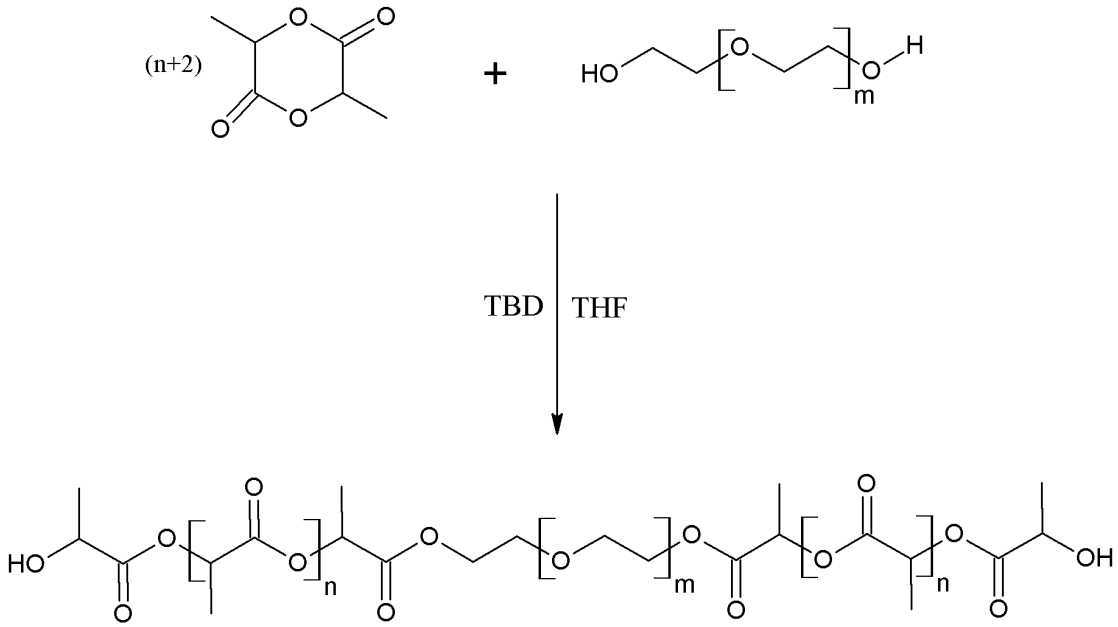


Figure 3.23 Polymerization of lactide initiated by PEG(600).

The isolated yield was rather low (ca. 5%: PEG-PLA (7.1k)) or no polymer was detected by precipitation. The reason for that could be the amphiphilicity of the resulted polylactide-block-poly (ethylene glycol)-block-polylactide (PLA-block-PEG-block-PLA). Thus, it can be assumed that the precipitation of the product into methanol was an exceedingly inefficient purification method for this compound. Due to its amphiphilicity it may be soluble in polar solvents or it may form micelles with the poly(ethylene glycol) - shell which would make them soluble.

The reaction was then carried out with 1,6-hexandediol in THF (Figure 3.24) producing better results.

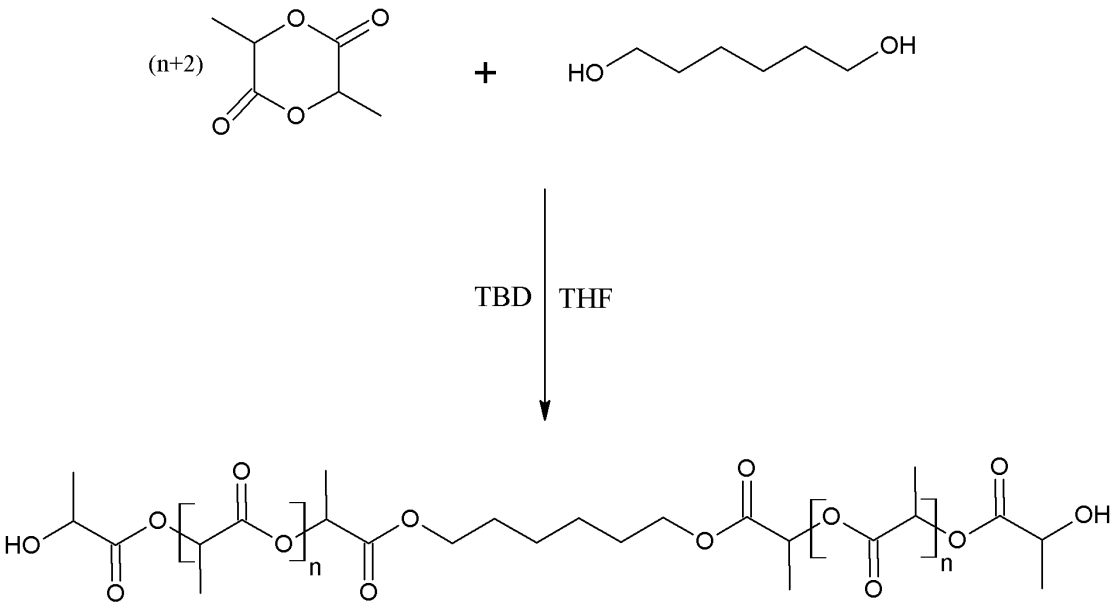


Figure 3.24 Polymerization of lactide initiated with 1,6-hexanediol.

A number of polylactides have been synthesized by this means but still the PDI could not be controlled as desired.

Molecular weights, the PDIs, the reaction conditions and the yields of the prepared polylactides are summarized in Table 3.2.

Table 3.2 List of the prepared polylactides.

#	Solvent	Initiator	**Mn**	PDI	yield
PLA(8.6k)	**THF**	**1,6-hexanediol**	8600	1.13	6%
PLA (20.4k)	**THF**	**1,6-hexanediol**	20400	1.61	14%
PLA (11.5k)	**THF**	**1,6-hexanediol**	11500	1.34	45%
PLA (9.1)	**THF**	**1,6-hexanediol**	9100	1.34	70%
PLA (11.2k)	**THF**	**1,6-hexanediol**	11200	1.54	59%
PLA (16.4k)	**THF**	**1,6-hexanediol**	16400	1.15	81%
PEG-PLA(7,1k)	**DCM**	**PEG (**M_n=600 g/mol)	7100	1,19	5%

An expemplary NMR spectrum for a prepared polylactide is represented by PLA(16.4k) in (Figure 3.25).

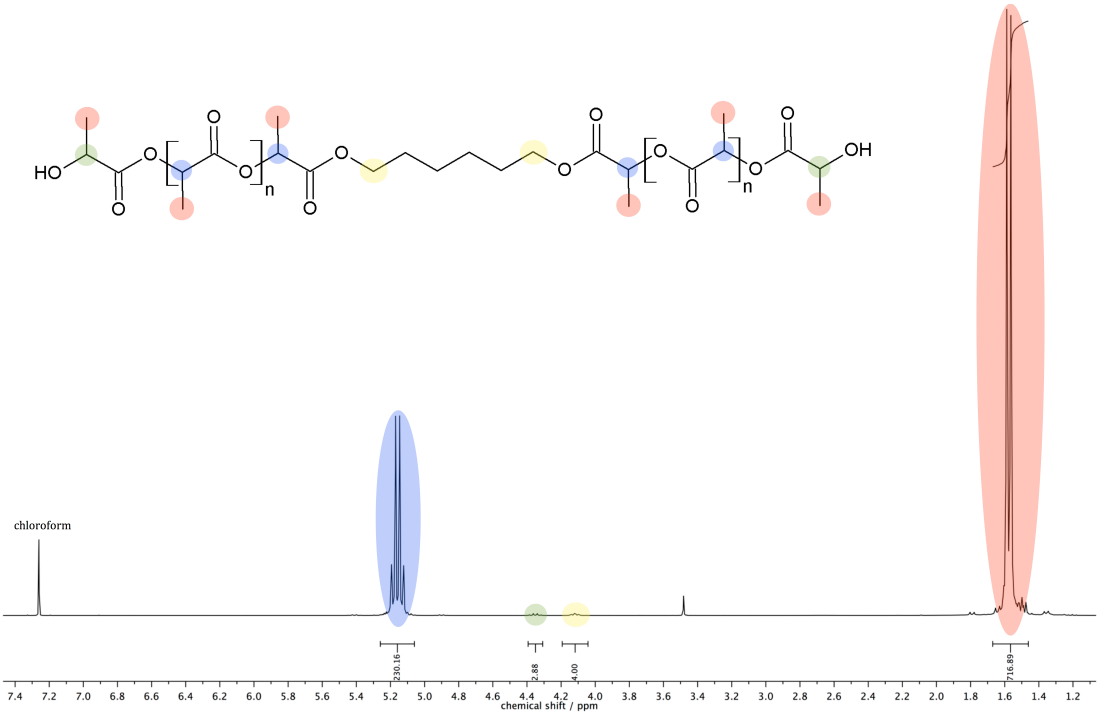


Figure 3.25 NMR spectrum of PLA (16,4k).

In order to modify the terminal hydroxyl groups of the polymer, a Steglich esterification with cinnamic acid was conducted in analogy to polystyrene. In the case of PLA, the Steglich esterification at room temperature did not lead to quantitative esterification which was percieved via NMR measurments showing an insufficient integral value for the cinnamic protons. Running the reaction at increased temperatures (ca. 60-70 °C) did not give any improvements presumably due to the sterically hindered secondary hydroxyl groups.

Therefore it was decided to use cinnamic chloride which represents an acyl chloride with a high reactivity. This method improved the reaction at room temperature but was still unsatisfying even for the high temperature reaction. The reaction of cinnamoyl chloride at elevated temperatures using DMAP as catalyst and pyridine as acid scavenger gave best results for the ester formation with an isolated yield of 89%.

The reaction mechanism is shown in Figure 3.26 and Figure 3.27.

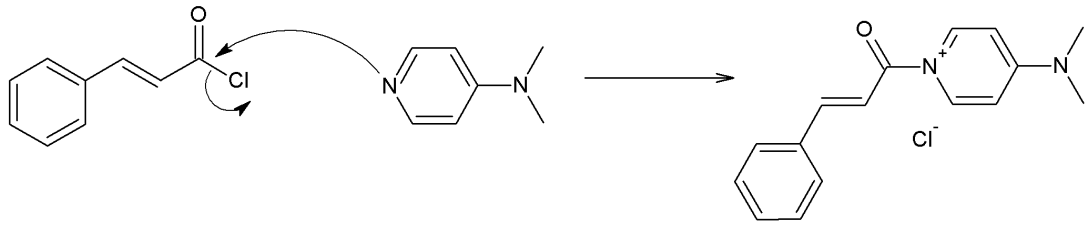


Figure 3.26 Activation of cinnamoyl chloride by DMAP.

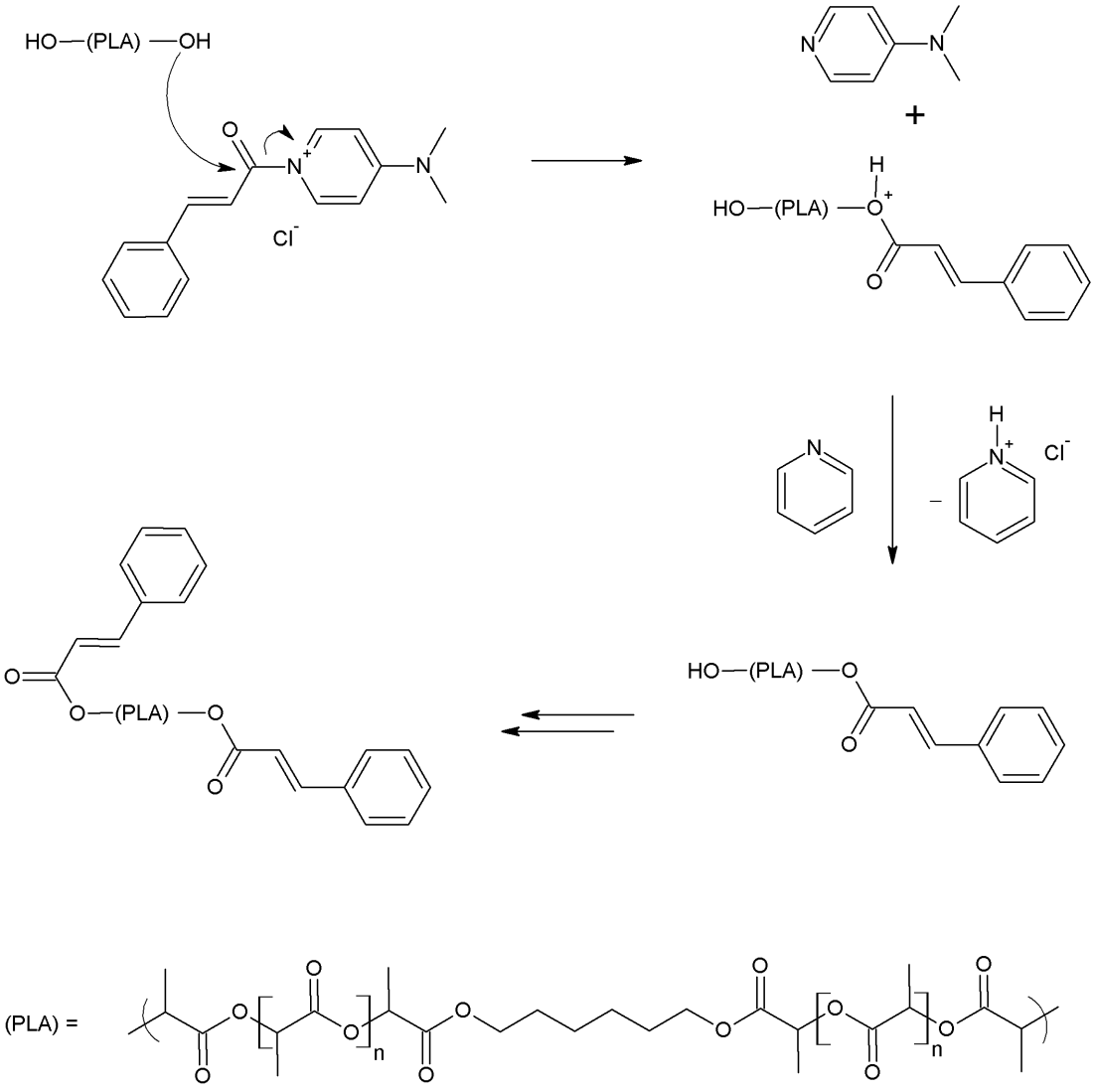


Figure 3.27 Esterification of polylactide with cinnamoyl chloride.

The successful formation of the bifunctional polymer was monitored by NMR measurements, as can be seen in Figure 3.28.

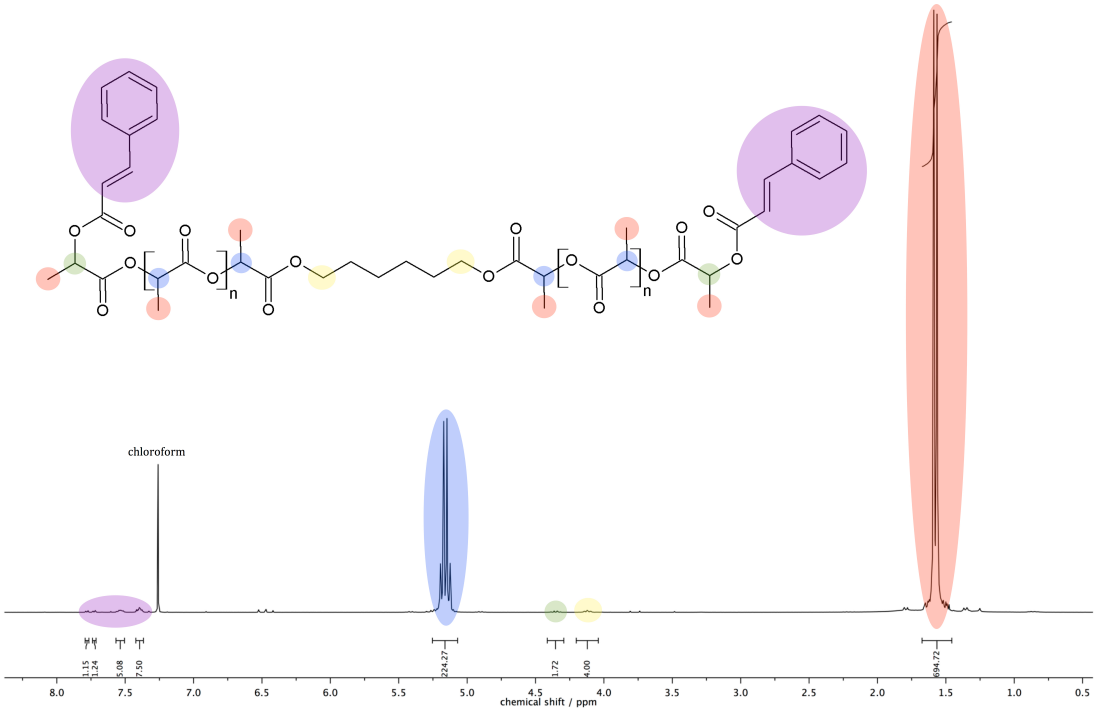


Figure 3.28 NMR spectrum of PLA(16,4k) functionalized with cinnamic acid.

3.5 Cyclization of α, ω–dicinnamoyl–polylactide via [2+2] photocycloaddition

A number of polylactides were irradiated in chloroform or dichloromethane solution and in miniemulsion in order to induce polymer cyclization via [2+2] cycloaddition of its cinnamoyl moieties all showing results similar to the previously obtained ones. The following GPC elugram (Figure 3.29) shows the data obtained after different irradiation times of a polylactide with terminal cinnamoyl moieties:

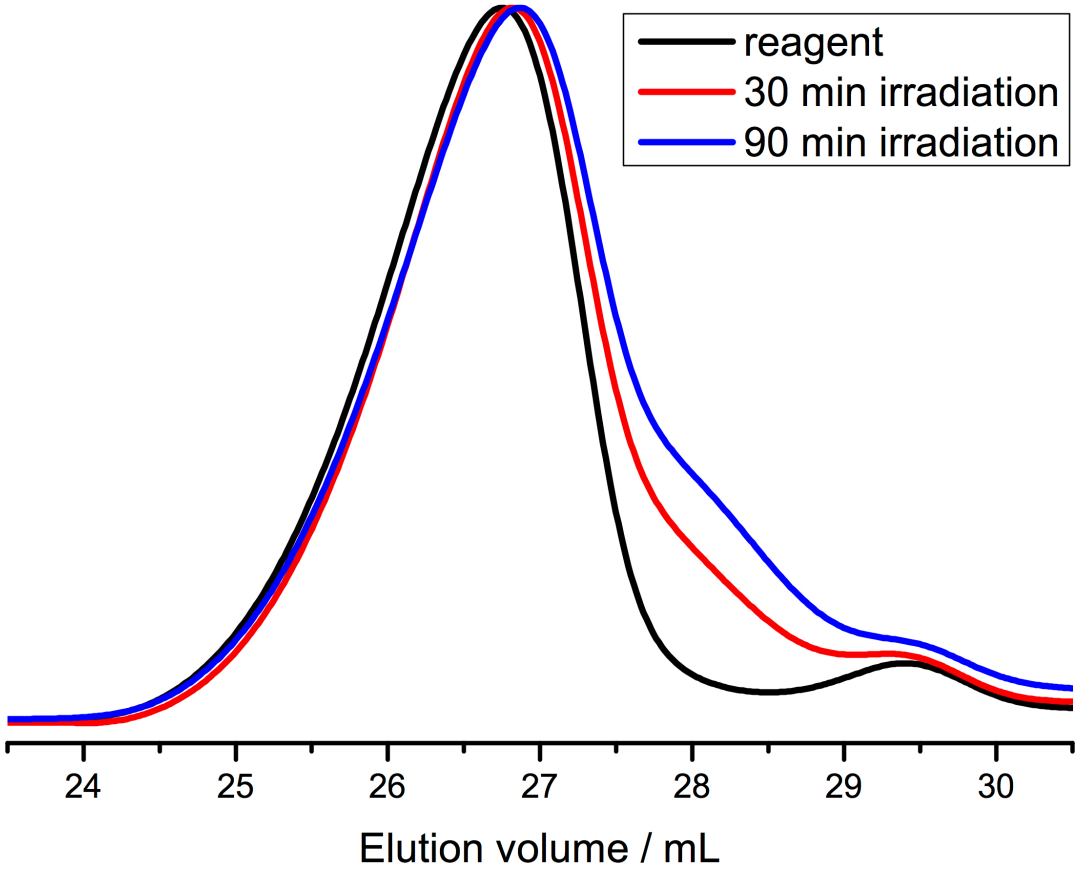


Figure 3.29 GPC data of an irradiated polylactide.

The molecular weight decreased over time with the peak molecular weight moving from 7,700 to 6,800 g/mol. Moreover, the PDI increased upon irradiation from 1.14 to 1.26 and the number average of the molecular weight decreased from 8,200 to 6,100 g/mol. From the lesson learned before the stability of the polymer under UV light had to be controlled as well. Thus, polylactide was

irradiated for prolonged times. Once again the decrease of the molecular weight continued the longer the polymer was exposed to UV light. However, in the case of a successful cyclization this process should stop at one point when the hydrodynamic volume complies with the cyclic structure. Finally, a 24 hours irradiation experiment resulted in severe degradation as can be concluded from the GPC data (Figure 3.30). As it was the case with the polystyrene fractionation and degradation one can see low molecular species at high elution volumes and the large decrease of the molecular weight that does not allow any other definite conclusion that decomposition takes place. Therefore, under these conditions it is not possible to state with any confidence that the data shown in Figure 3.29 represents the desired formation of macrocycles or just a gradual elimination of polymer fragments. Most likely, the latter must be assumed.

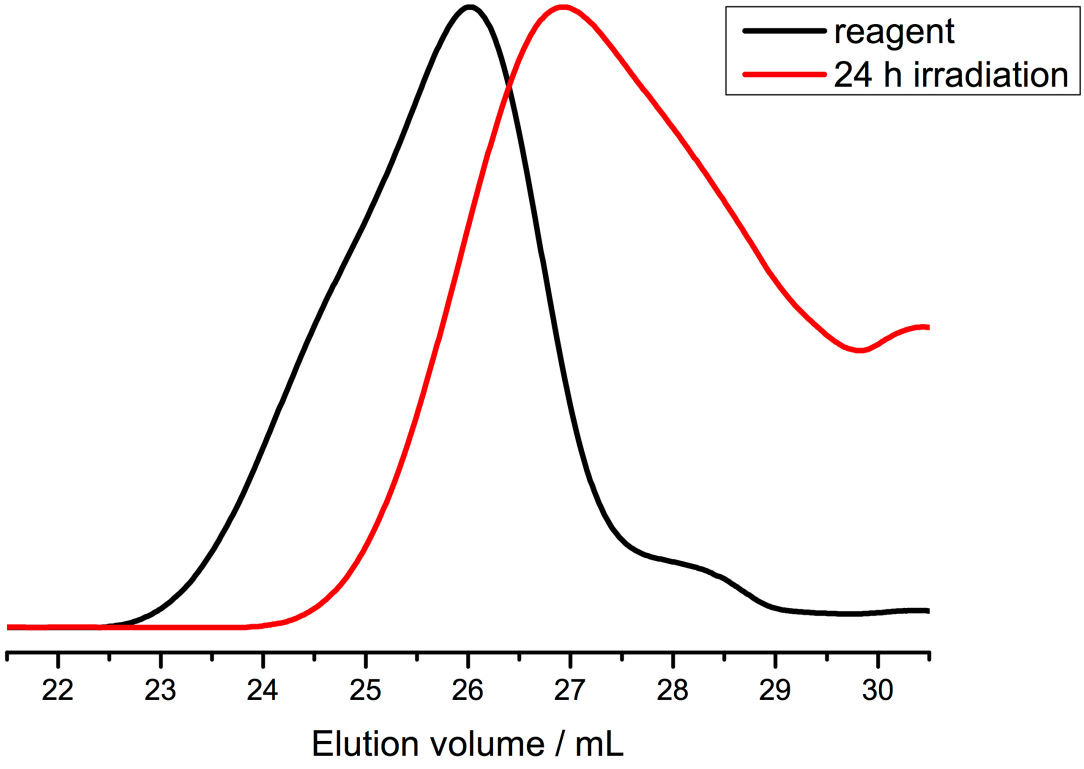


Figure 3.30 GPC data of the 24-h irradiation product of polylactide.

The NMR spectrum shows a large number of new signals if compared to the reagent representing the decomposition products (Figure 3.31).

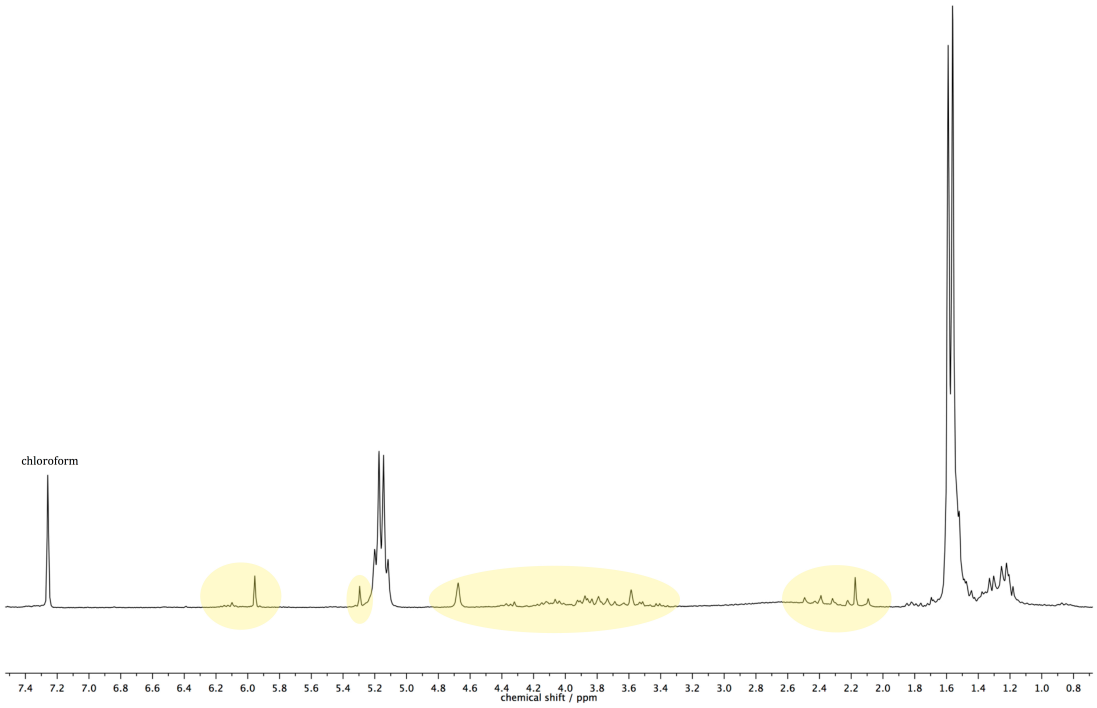


Figure 3.31 NMR spectrum of an irradiated PLA.

Irradiation of a concentrated polymer solution (ca. 70 mg/mL) was performed for a short time (ca. 1 h) in order to avoid decomposition. No cycle formation could be observed as it was the case for a diluted solution (ca. 0.2 mg/mL). It can be therefore concluded that the cycloaddition is slower than degradation under these conditions. The irradiation of the polymer in miniemulsion did also not provide cyclic polymers and only the original molecular weight of the linear meterial was detected by GPC.

According to the literature[89] the irradiation of cinnamic acid in solution leads to a *cis-trans* isomerization only whereas the irradiation of its liquid esters like ethyl cinnamate shows a [2+2] cyclization reaction. The cyclization of the ethyl cinnamate has been studied with regard to the isomerization and cyclization during the irradiation.[90] Thus, the isomerization of the liquid ethyl cinnamate was faster than cyclization at 25 °C but nevertheless the irradiation furnished cyclic dimers with up to 70 % yield if summed up all cyclic isomers. They originated from cis- and trans-isomers which both contributed to the dimer formation. Therefore, the differences between the reported system and the used one i.e. α, ω–dicinnamoyl–polylactide and –polystyrene have to be found.

The first difference is the accessibility of the cinnamoyl moieties to each other

within a polymer which needs to be discussed explicitly. Liquid ethyl cinnamate represents a system where the probability of the desired reaction is quite high since the concentration of the (small) molecules is high and all of them carry the reactive double bonds. Thus, during the irradiation the excited functionalities are close to each other and are likely to react. The system of the used polymers where a relatively large macromolecule is carrying two terminal cinnamoyl moieties exhibits a different situation in regard to the statistical probability. It can be assumed that it requires a long time for the terminal moieties to meet and react while excited and therefore irradiation times must be increased dramatically which however degrades the polymer backbone. It should be also kept in mind that the described isomerization which represents a quasi competition to cyclization must be taken into account requiring even longer irradiation times.

The same can be expected for the reaction in miniemulsion considering the applied surfactant concentration of ca. 4 mg/mL with a toluene (or chloroform) content of 20-25 vol.%. Thus, the polymer chains within the miniemulsion droplets may be partially undissolved and hindered in their motion in the course of the evaporation of the respective organic solvents representing a further problem. Moreover, the polymer could be partially protected by the surfactant which preserves it from decomposition by UV light via scattering and absorption but at the same time lowering the reaction activation.

3.6 Cyclization of polystyrene via ring closing metathesis

The final approach to cyclic polymers which was applied in this thesis is a ring closing metathesis reaction of an α, ω–functionalized polymer. According to this concept, the terminal moieties containing alkenyl groups react with each other via a olefin metathesis under highly diluted conditions to ensure intramolecular reaction to produce a cyclic polymer and suppress ADMET polymerization (Figure 3.32).

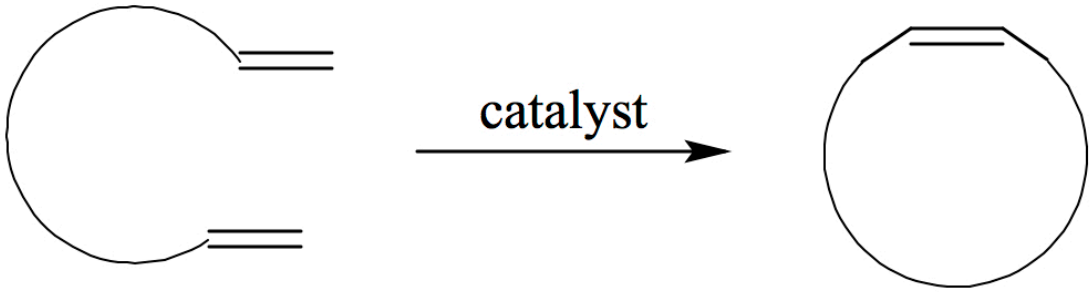


Figure 3.32 Cyclization of a polymer via a ring closing metathesis.

For this scenario, the previously synthesized α, ω–dihydroxy polystyrene was modified with undecylenic acid to introduce terminal double bonds via a Steglich esterification, as shown in Figure 3.33.

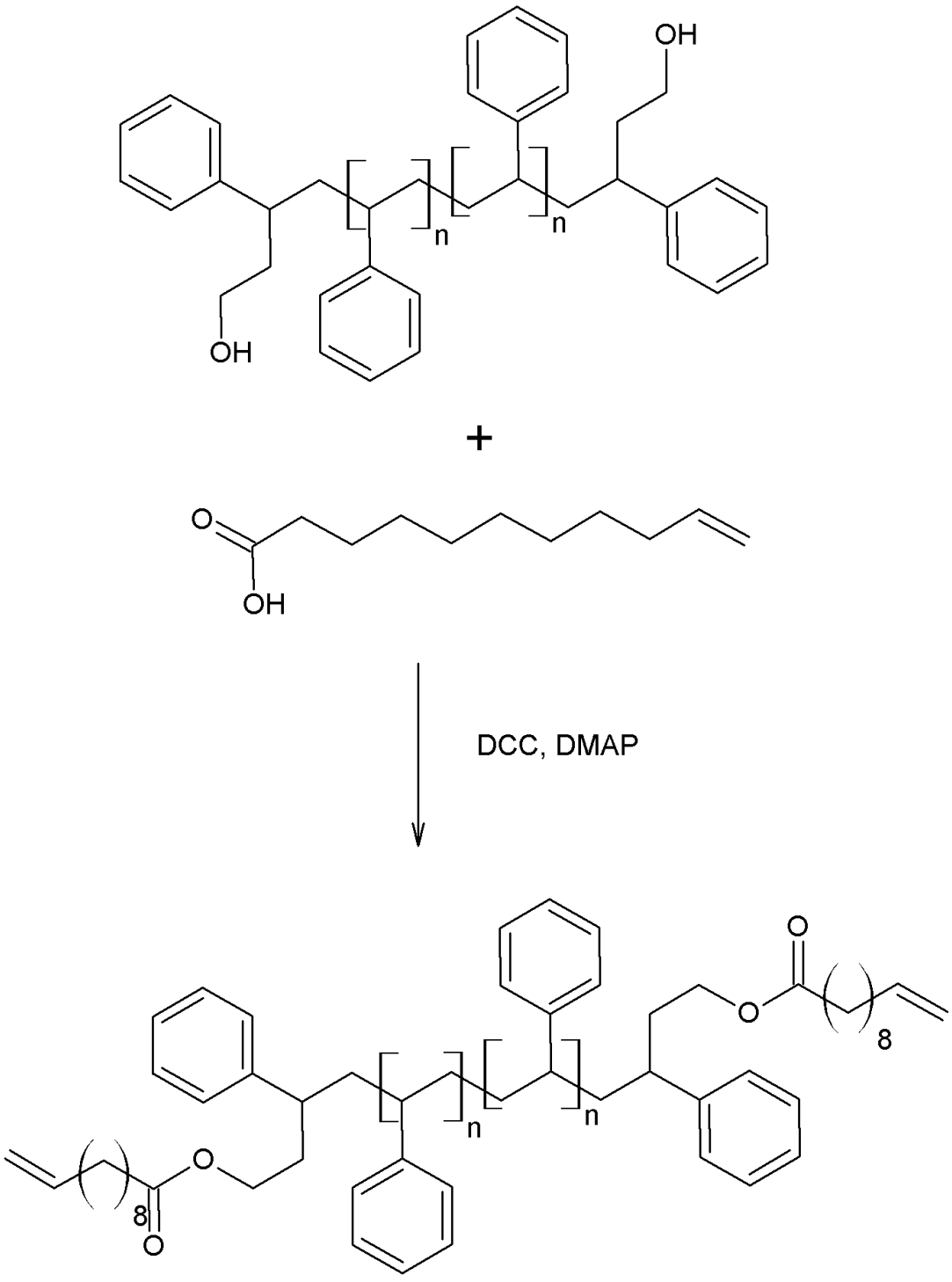


Figure 3.33 Esterification of an α, ω – dihydroxy polystyrene with undecylenic acid.

In the final step, the functionalized polymer was planned to undergo cyclization by the use of a Grubbs catalyst (Figure 3.34).

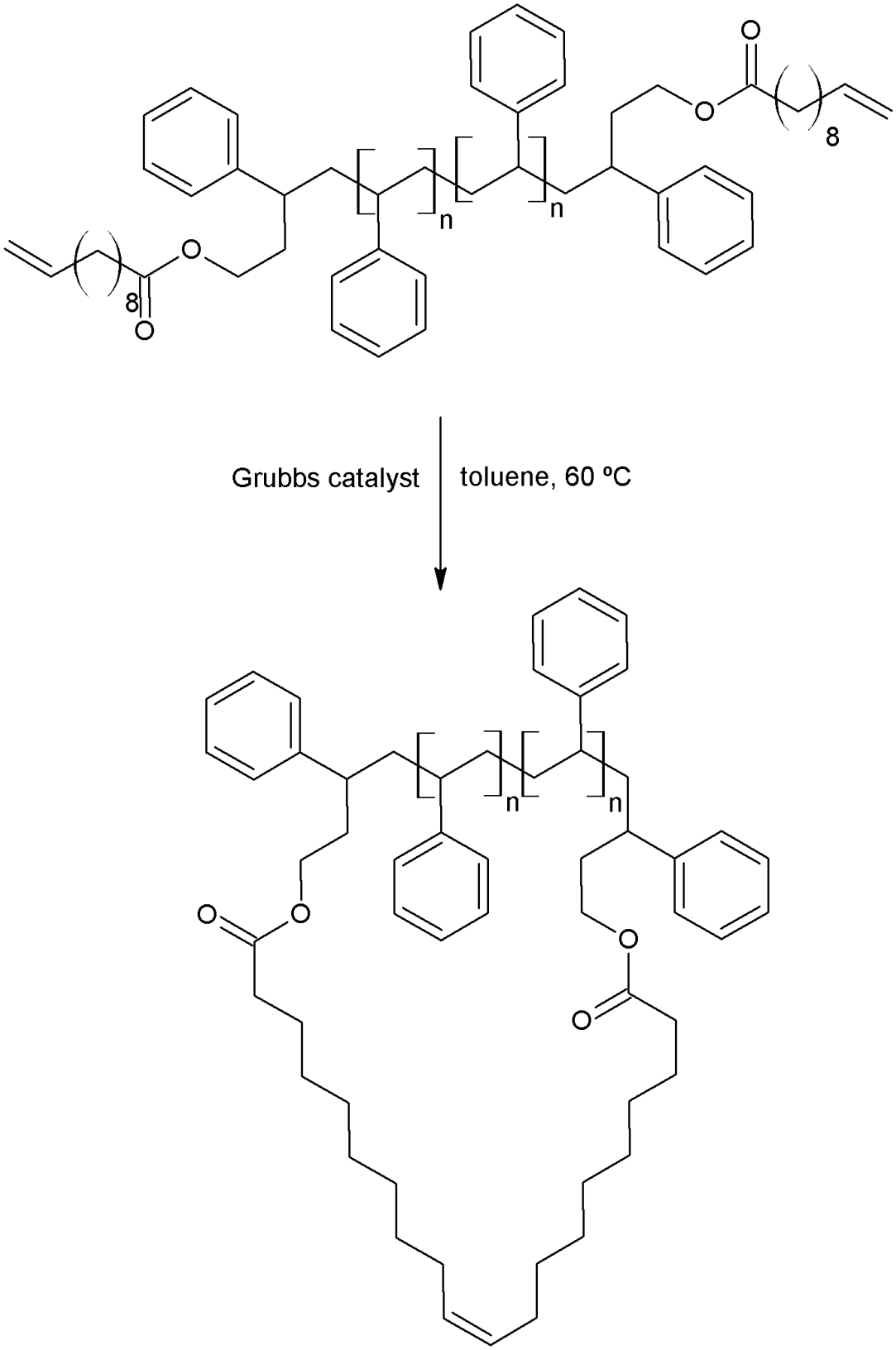


Figure 3.34 Cyclization of polystyrene via the ring closing metathesis.

To ensure quantitative esterification of the polymer, undecylenic acid was used in a high excess. The reaction provided a nearly 100% yield at room temperature

and the purification was performed without any complications. Drop-wise addition of the reaction mixture into methanol successfully precipitated the polymer and simultaneously removed the unreacted undecylenic acid.

The ^{1}H-NMR spectrum in Figure 3.35 shows the resulted bisfunctionalized polystyrene with undecylenic acid where the characteristic signals could be successfully assigned. Thus, the signals in the range of 1.09-2.36 and 6.28-7.25 ppm correspond to the methylen and phenyl protons of polystyrene respectively, whereas the multiplet in the range of 5.73-5.92 and the triplet at 4.96 ppm are represented by the alkene protons of the undecylenic moieties.

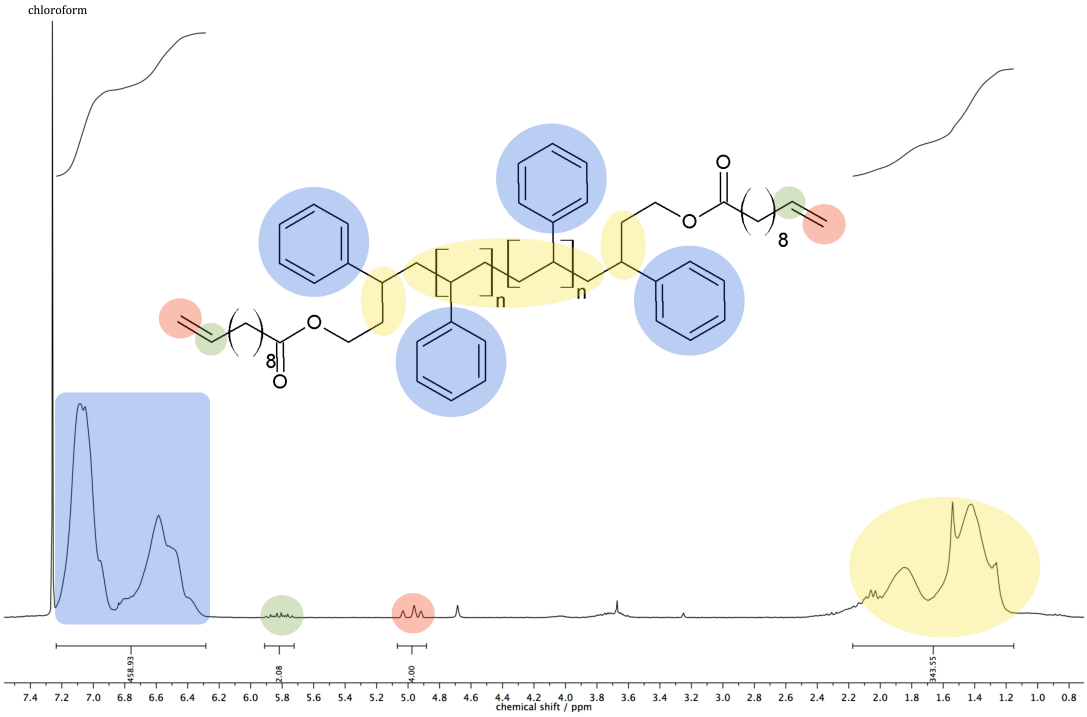


Figure 3.35 NMR spectrum of α,ω–(bis)undecylenoyl polystyrene

The first attempt to cyclize the polymer via metathesis was performed with the first generation Grubbs catalyst, however, no cyclic polymer was obtained and only the original polymer was recovered. From the ^{1}H-NMR spectrum only terminal alkenyl groups were detected. The catalyst was replaced by the second generation Grubbs catalyst which is known to be more effective in ring-closing metathesis reactions and the reaction product was analyzed by NMR spectroscopy (Figure 3.36) and GPC chromatography (Figure 3.37).

The number average of the molecular weight decreased after reaction from 8,200 g/mol to 7,300 g/mol and the ^{1}H-NMR spectrum showed the appearance of the internal alkene protons of the cyclized polystyrene. However, it could be also concluded that the reaction was incomplete since terminal double bonds were still detectable (Figure 3.36).

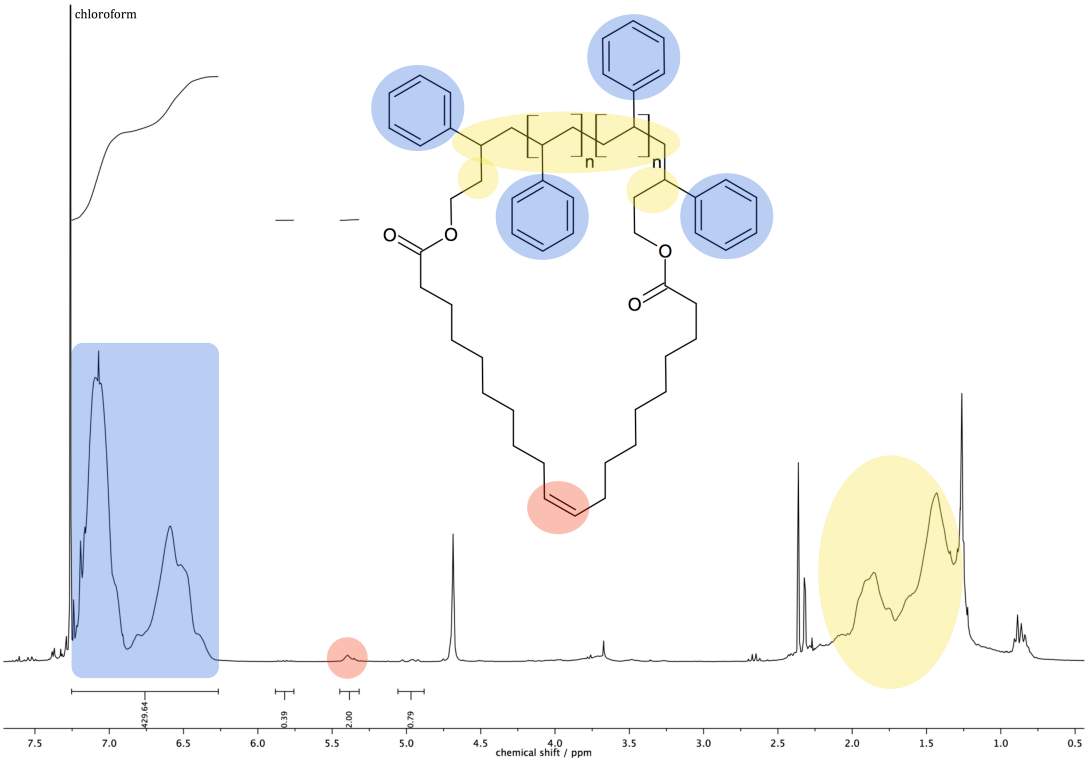


Figure 3.36 NMR spectrum of the cyclic polystyrene.

The yield was determined from the NMR spectrum by integrating the characteristic signals of the reagent and product and considering them in relation. The conversion was calculated to be 80% for the cyclic product.

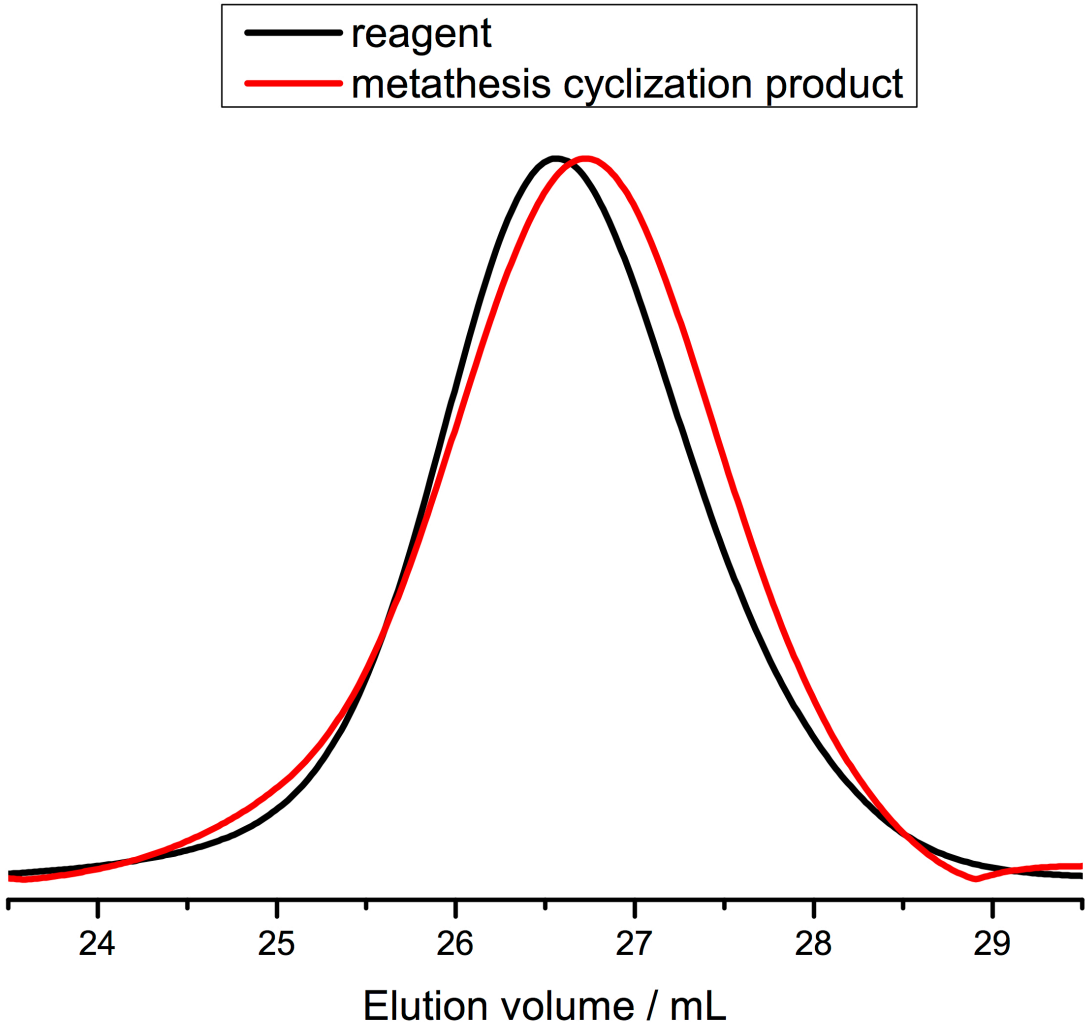


Figure 3.37 GPC data of α, ω–(bis)undecylenoyl polystyrene acid and its cyclic metathesis product.

The Grubbs second generation catalyst showed its effective applicability for the ring closing metathesis. The reaction mechanism for the macrocycle formation is shown in Figure 3.38. The structure of the catalyst which is also shown in the figure has been depicted in its simplified form throughout the reaction mechanism.

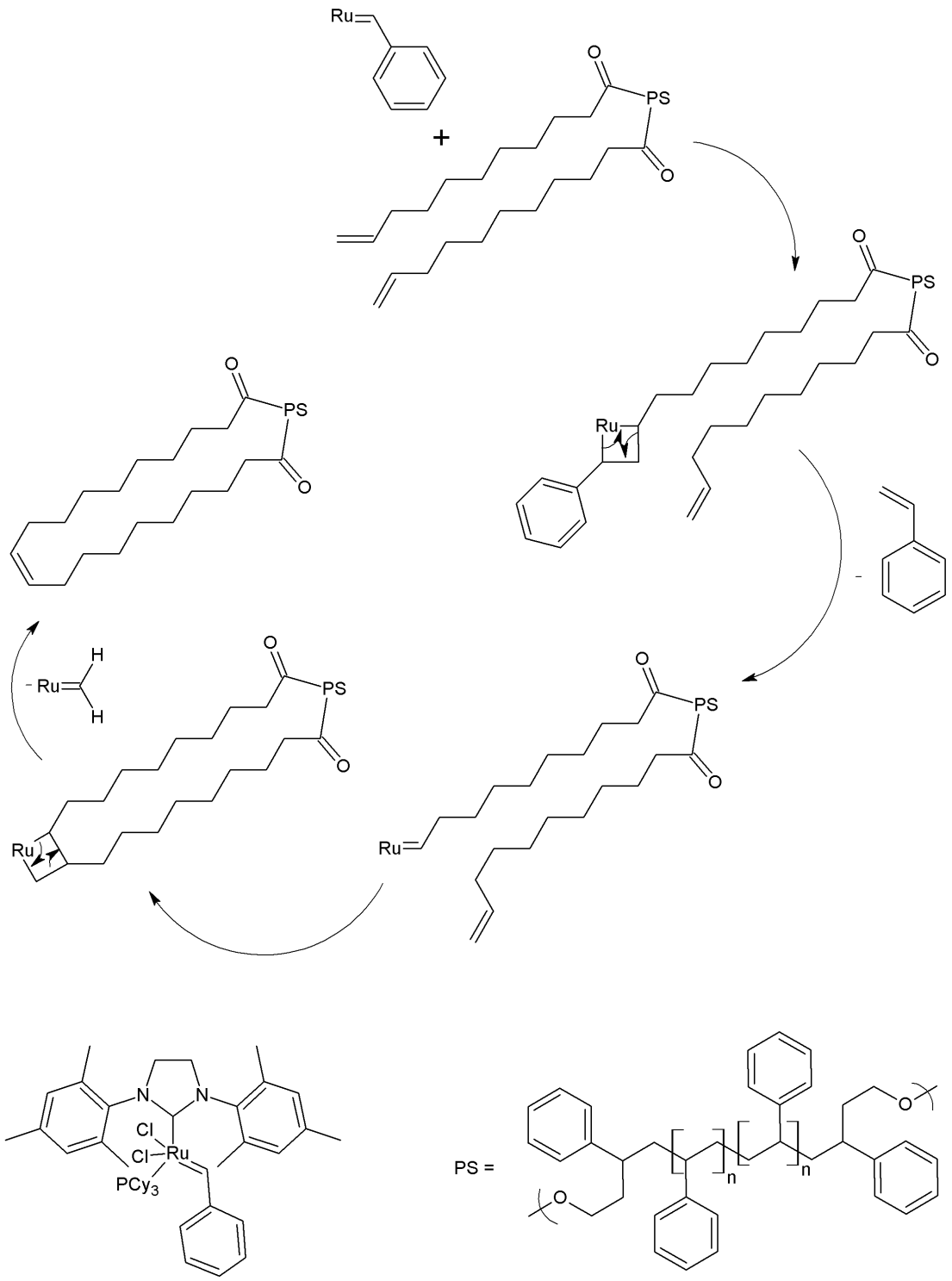


Figure 3.38 Reaction mechanism for the ring closing metathesis of α,ω–(bis)undecylenoyl polystyrene.

This method represents a convenient approach for the generation of cyclic polymers. However, the isolation of the polymer which was performed via repeated filtering of the reaction mixture and subsequent precipitation into

methanol was not satisfying. The removal of the catalyst and its degradation products is complex causing some difficulties in analyzing the NMR data.

The experiment was repeated in miniemulsion with a polymer concentration of $1.96 \cdot 10^{-5}$ mmol/mL, a catalyst (Grubbs, second generation) concentration of $2.04 \cdot 10^{-5}$ mmol/mL and with a toluene content of 20 Vol.%. The procedure involved the preparation of two miniemulsions containing the polymer and the catalyst respectively which were subsequently combined and sonicated under the same conditions. The obtained miniemulsion was heated at 60 °C for 24 h since it was a successful condition for the reaction in solution but the attempt did not give any interesting results and the original linear polymer was recovered as could be concluded from the GPC data. The reason is still unknown but factors such as a decomposition and activity loss of the catalyst during the miniemulsion preparation and the entire reaction time as well as a limited mobility of the polymer could come into question but they still are of a fairly speculative nature. The reaction in miniemulsion is still believed to be promising and should be investigated and the underlying causes for the failed cyclization must be analyzed in the future.

4 Conclusion and Outlook

4.1 Conclusion

The cyclic ruthenium catalyst for the ring expansion metathesis polymerization was successfully prepared in a 4-step reaction but the purity of the endproduct remains a challenging issue. Common purification methods, such as recrystallization and flash column chromatography, turned out to be inefficient under the provided conditions and lead to product decomposition.

α, ω – dicinnamoyl–polystyrene and – lactide could be successfully synthesized starting with the polymerization of styrene and L-lactide as monomers by using bifunctional initiators sodium naphthalenide and 1,6-hexandiol and subsequent attachment of cinnamic moieties via esterification. The esterification of the dihydroxy polystyrene could be easily realized via Steglich esterification with cinnamic acid at room temperature. The esterification reaction of the lactides required cinnamoyl chloride as a more reactive derivative of cinnamic acid in combination with higher reaction temperatures (≈60 °C), DMAP as catalyst and pyridine as acid scavenger.

The intramolecular [2+2] photocycloaddition of the terminal cinnamoyl moieties could not be achieved due to the excessive polymer degradation during the irradiation experiment. The attempts to inhibit the decomposition with the variation of solvents and the addition of an antioxidant did not give any useful results for both solution and miniemulsion system.

α, ω – undecylenoyl–polystyrene could be easily synthesized from α, ω – dihydroxy polystyrene via Steglich esterification. The product was then successfully converted into a cyclic polymer with a yield of 80% via ring closing metathesis with the Second generation Grubbs catalyst in solution. The macrocycle formation could be detected by GPC measurments showing a decrease of the molecular weight due to the decrease of the hydrodynamic volume of the polymer. NMR measurments confirmed the intramolecular cyclization via undecynoyl moieties by showing internal alkene protons. No

formation of cyclic polymers could be observed when the reaction was carried out in miniemulsion.

4.2 Outlook

The isolation of the cyclic ruthenium alkylidene catalyst was problematic due to the decomposition of the product during the purification. Nevertheless, it should be possible to solve the problem and isolate the product by using neutral silica (pH 6.5-7.0) for flash column chromatography without degradation. The formation of cyclic polymers can then be studied as planned in miniemulsion.

Although the [2+2] photocycloaddition approach to cyclic polymers was not successful it could evolve into an effective method after some improvements.
It is believed to be necessary and inevitable to construct a system where the functional groups i.e. the cinnamoyl moieties are optimally arranged in regard to their favorable orientation for the cyclization reaction in order not to be confronted with the problem of their accidental collocation. Thus the irradiation times could be reduced to a minimum in order not to destroy the polymer.

Also a UV-stable polymer would be suitable which outlasts the irradiation exposure until a cycle is generated. A possible improvement could be the modification of the cinnamic acid with polar or ionic groups. It could induce their orientation in the interface where the cycloaddition could take place. Moreover, it must be assumed that the evaporation of the organic solvent from the miniemulsion droplets could completely „freeze“ the motion making any other steps pointless since the polymer chains will remain in the same state. For this purpose quantitative studies for the solvent concentration within the miniemulsion droplets must be performed and the control of the solvent amount through the entire period of the irradiation experiment is strongly recommended. Thus, a suitable balance between mobility of the polymer and the scattering of the UV radiation could be achieved.

The cyclization of the polymer chains via ring closing metathesis in miniemulsion would once again require a strict control of the solvent concentration within the miniemulsion droplets. Furthermore, the ring closing metathesis reaction should be carried out under low temperatures in order to minimize the evaporation of the organic solvent and therefore prevent the polymer chains from immobility. Organic solvent with a higher boiling point than water, such as toluene, are highly recommended. If the obtained yields are reproducable for a miniemulsion system it could become an efficient method to synthesize cyclic polymers on a large scale. Thus, a (molar) fraction of 0.8 of cyclic polymers would drammatically change the physical properties of the polymer leading to its potential applications despite a slight „contamination“ with the linear counterparts.

5 Experimental part

5.1 Materials

All reaction vessels were cleaned with destilled water, acetone and DCM before use. All glassware used to oxygen or moisture sensitive experiments were dried on the Schlenk line with the aid of a heat gun (Steinel HG 2310 LCD, 650° C). All reactions were carried out either under argon or nitrogene atmosphere. Column chromatography was performed using silica gel (Macherey Nagel, Silica 60, 0.063-0.2 mm) and aluminium oxide (Fluka, 0.05-0.15 mm, pH=7.0±0.5). Thin layer chromatographie plates were purchased from Macherey-Nagel (Alugram® SIL G/UV_{254}, 40 x 80 mm, layer: 0.2 mm silica gel with fluorescent indicator). For irradiation experiments Spectroline ultraviolet light lamp ENF-260C UV and HBO Mercury short-arc lamp (200W) were used.

5.2 Solvents and chemicals

Prior to use, THF and cyclohexane were stirred over sodium for at least 48 h. DCM, ethyl acetate, pentane and hexane were dried over CaH_2 for 24 h. The solvents were transerred into the reaction vessel either via cryogenic destillation or the common vacuum destillation. Toluene, ethanol, methanol and chloroform were used as delivered. Unless specified otherwise, all chemicals were used as purchased from the manufactures (Acros, Aldrich, TCI). L-lactide was recrystallized from ethyl acetate and dried in vacuo prior to any experimental activities.

5.3 Equipment and substance identification

The following techniques were used for identification and characterization of reactants and products:

Gel permeation chromatography (GPC)

GPC measurements were carried out in THF at 30° C using PSS SecCurity (Agilent Technologies 1260 Infinity) with following features:

- flowrate 1 mL/min
- porosity 10^6, 10^4, 500 Å
- particle size 10 µm

The GPC instrument was calibrated by use of polystyrene standards. RI (RI-101 ERC) and UV (1260 ALS, 254 nm) detectors were used.

High performance liquid chromatography (HPLC)

HPLC measurements were carried out using a photodiode detector (Agilent Series, 260 nm) and Agilent Eclipse XDB C18 column (length 150 mm, diameter 4.6 mm, pore size 5 µm, flowrate 1 mL/min, RT). The applied gradient was: THF/water 20/80 % to 100% THF in 40 min.

NMR spectroscopy

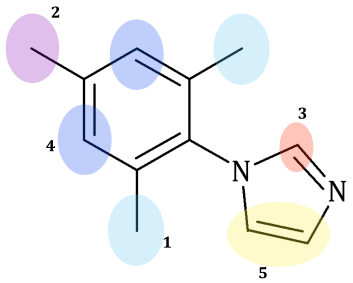
^{1}H-NMR spectra were recorded on a BRUKER spectrometer (250 MHz and 300 MHz) at room temperature. Chemical shifts (δ) are given in part per million (ppm) and are refered to deuterated chloroform (δ=7.26) and deuterated methylene chloride (δ=5.32). The observed splitting patterns were represented by their common descriptive names: s for singlet; d for doublet; t for triplet and m for multiplet. The NMR data were analyzed using Mestrenova 8.1 software.

5.4 Synthesis

Synthesis of 1-(mesityl)imidazole

13,5 g (0,10 mol) mesitylamine was dissolved in 50 mL water. To this solution phosphoric acid was added until a pH of 2 was reached. The resulting suspension

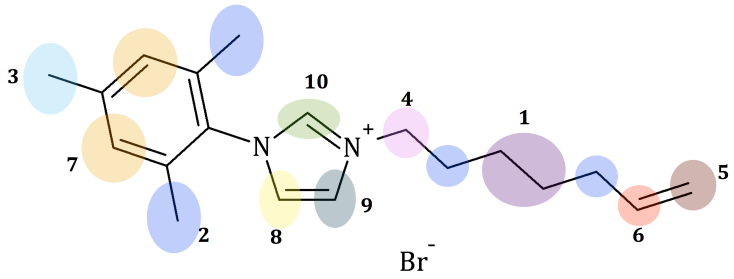
was mixed with a solution of 3,00 g paraformaldehyde in 100 mL water and 100 mL 1,4-dioxane. Subsequently glyoxal (11,5 mL of 40% aqueous solution, 0,10 mol) was added and the mixture was heated at 100 °C. An ammonium chloride solution (5.35 g, 0,10 mol, 20 mL water) was then added dropwise over 30 min. After refluxing the mixture at 110-115 °C for 1 h it was cooled down to 0 °C using an ice bath and NaOH was added until a pH of ca. 13 was obtained. Water (150 mL) was added to the reaction mixture and the product was extracted with hexane. The combined hexane extracts were dried over $MgSO_4$, filtrated and evaporated to yield a brown solid. The crude brown solid was recrystalized from ethyl acetate and purified by flash column chromatography on silica gel eluting with DCM/EA (3:1). Thus, a colourless crystalline solid was obtained (3.86 g, 21%).



^{1}H-NMR (300 MHz, CD_2Cl_2): δ 1.96 (6H, **1**), 2.31 (3H, **2**), 6.89 (1H, **3**), 6.97 (2H, **4**), 7.15, 7.38 (2x1H, **5**).

Synthesis of 1-(6-Heptenyl)-3-mesitylimidazolinium bromide

1.20 g (6.44 mmol) 1-(mesityl)imidazole and 1.37 g (7.73 mmol) 7-bromo-1-heptene were dissolved in 35 mL toluene and refluxed for 24 h. The toluene was then evaporated and the obtained brown viscous liquid was dissolved in dichloromethane. The crude product was precipitated from diethyl ether to give a white solid (1.8 g, 78%).



^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.51-1.33 (m, 4H, **1**), 2.07-1.97 (m, 10H, **2**), 2.33 (s, 3H, **3**), 4.77-4.73 (t, 2H, **4**), 4.99-4.90 (t, 2H, **5**), 5,81-5.67 (m, 1H, **6**), 6.99 (s, 2H, **7**), 7.17 (s, 1H, **8**), 7.68 (s, 1H, **9**), 10.55 (s, 1H, **10**).

General procedure for the synthesis of [1-(6-Heptenyl)-3-mesitylimidazol-ylidene]RuCl2(=CHPh)(P(Cy)$_3$)

1-(6-Heptenyl)-3-mesitylimidazolinium bromide (2.00 eq) was suspended in dry toluene under dry N_2. To this solution was added KOtBu (2.00 eq) and the mixture was stirred at RT for 12 h. Bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (Grubb's catalyst, 1st generation, 1.00 eq) was then added in a single portion and the mixture was stirred for 1 h. The resulting brown mixture was filtered through a thin pad of either silica gel or aluminium oxide using Et_2O/pentane (1:4) as eluent. The filtrate was concentrated at 18 °C using the rotary evaporator. The crude product was purified by column chromatography on either silica gel or aluminium oxide under N_2 pressure using Pentane/Et_2O (2:1) as eluent. After removing the solvent and drying under vacuum a green brown solid was obtained.

General procedure for the synthesis of the cyclic Ru-alkylidene catalyst

200 mg (0.24 mmol) [1-(6-Heptenyl)-3-mesitylimidazolylidene]-$RuCl_2$(=CHPh)(P(Cy)$_3$) were dissolved in 15 mL dry toluene, diluted with 230 mL dry hexane in a Schlenk tube under dry N_2 and placed in an oil bath. The solution was refluxed and stirred vigorously while maintaining the bath-temperature at 70 °C. After one hour the solution was cooled to RT, transferred

to a round-bottom flask and concentrated at 17-20 °C using the rotary evaporator. The residue was filtrated through a thin layer of aluminium oxide with subsequent solvent evaporation and drying under vacuum.

Synthesis of sodium naphthalenide

Sodium was cut in small pieces, washed by THF and cyclohexane in order to remove the mineral oil. Then, the cleaned sodium was collected, placed in an ampoule and dried under vacuum ($p \approx 10^{-3}$ mbar). The ampoule was then heated with a Bunsen burner to produce a sodium mirror. Yield: 1.36 g.

A solution of 9.0 g (0.062 mol) naphthalene in 30 mL benzene was given in a second ampoule. The benzene was removed on the Schlenk line and the naphthalene was allowed to dry under vacuum. The amount of naphthalene was determined by weighing and dry THF was transfered into the ampoule using the Schlenk line. After removing the cooling bath with liquid nitrogene the ampoule was placed in a metal container and allowed to reach RT yielding a colorless solution.

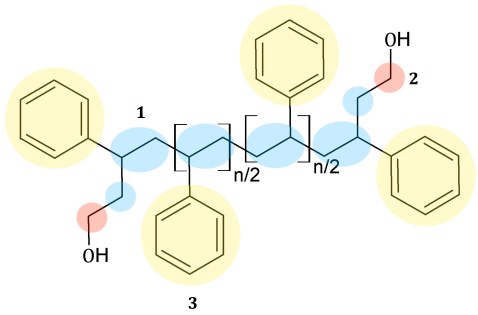
Both ampoules were then connected with a vacuum take-off adapter and the chilled naphthalene solution was allowed to react with sodium. The ampoule with the reaction mixture was kept in the ice bath for 20 min and periodically shaken. It was then disconnected and shaken for 4 days using a laboratory shaker until the sodium mirror was completely dissolved. The result was a deep green solution.

The strength of the stock solution (85 mL) was determined by a test syntesis of polystyrene and the concentration of the initiator was calculated according to the obtained molecular weight of the polymer ($9.35 \cdot 10^{-5}\ mol/L$).

Synthesis of α, ω–dihydroxy polystyrene

Styrene was placed in a round flask with calcium hydride and stirred over night. Then, dried styrene (1.6 g) and 100 mL dry THF were transferred into a Schlenk flask. The ampoule whith the initiator stock solution was connected with the Schlenk flask using a vacuum take-off adapter which was heated and evacuated afterwards. The styrene solution was placed in an ethanol bath at ca. -105 °C and

a predetermined amount (ca. 4 mL) of the initiator solution was added in one portion. In the moment of adding the reaction mixture was shaken vigorously to ensure a simultaneous chain initiation. A trace amount of ethylene oxide was then added from an ampoule to the resulting red solution using the same set up. The evacuated reaction mixture was allowed to react with ethylene oxide at RT until it turned colourless. DCM and diluted sulfuric acid were added to the viscous liquid and the reaction mixture was given dropwise into methanol to precipitate the product. After filtration, the crude product was dissolved in DCM and reprecipitated from methanol giving a white powder. Yield: 1.51 g (94 %).

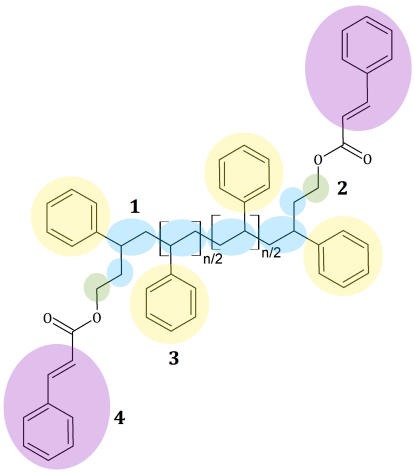


^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.2-2.3 (br, **1**), 3.15-3.45 (br, 4H, **2**), 6.25-7.23 (br, **3**)

GPC (THF): M_n=8000 g/mol, PDI=1.23.

Synthesis of α,ω–dicinnamoyl-polystyrene

606 mg α,ω-dihydroxy polystyrene ($7.58 \cdot 10^{-2}$ mmol), 1,736 g (8.38 mmol) DCC, 93 mg (0.76 mmol) DMAP and 1.13 g (7.62 mmol) cinnamic acid were dissolved in dry DCM, the round flask was filled with dry argon and the reaction mixture was stirred for 24 h. The suspension was concentrated by evaporation and filtered. The product was precipitated from methanol 3 times giving a white powder after drying under vacuum. Yield: 580 mg (93%).

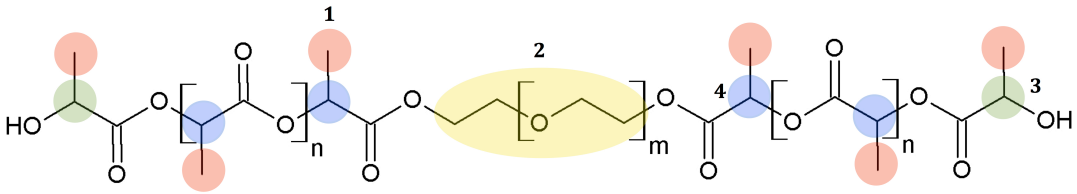


^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.11-2.3 (br, **1**), 3.71-4.06 (m, 4H, **2**), 6.23-7.25 (br, **3**), 7.33-7.74 (m, 14 H, **4**)

GPC (THF): M_n=8400 g/mol, PDI=1.23.

Synthesis of polylactide-block-poly(ethylene glycol)-block-polylactide

370 mg (2.57 mmol) L-lactide and 1 mg ($7.18 \cdot 10^{-3}$ mmol) TBD in 50 mL DCM were given into a Schlenk flask, filled with argon and covered with a septum. To this solution 25 mg (ca. 0.04 mmol) of PEG (MW: 570-630 g/mol) in 1 mL DCM were added in one portion. The reaction mixture was stirred for 12 h, concentrated under reduced pressure and the product was precipitated from methanol. Yield: 18 mg (5%) .

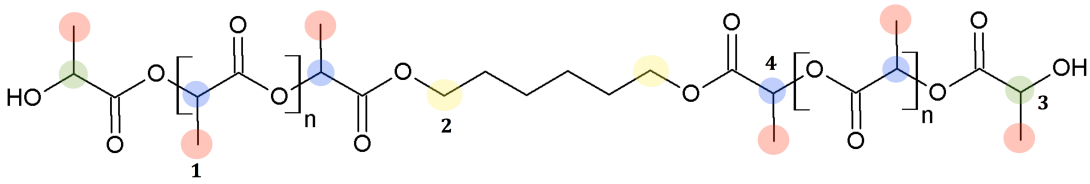


GPC (THF): M_n=7100, PDI = 1.19

^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.45-1.66 (bd, **1**), 3.56-3.71 (b, **2**), 4.35 (m, 2H, **3**), 5.08-5.23 (bq, **4**).

General procedure for the synthesis of a *α*, *ω*–dihydroxy–polylactide

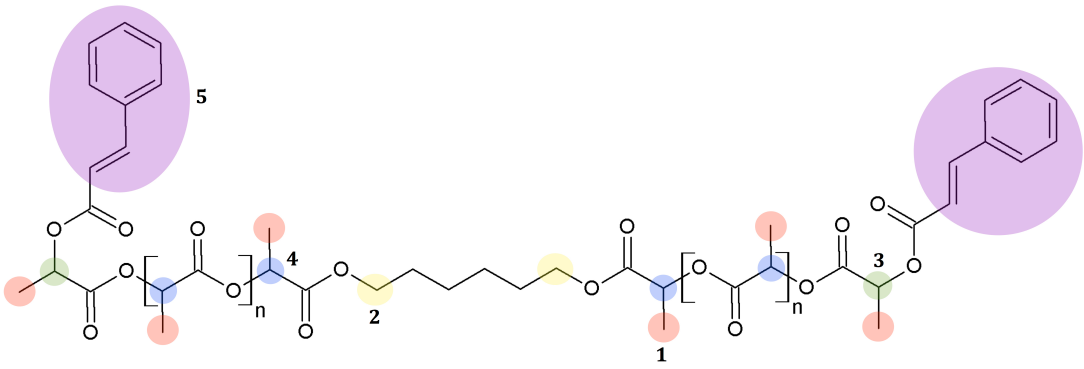
TBD (1 eq) and L-lactide (1000 eq) were given to a Schlenk flask and dissolved in THF. The initiator was dissolved in a small amount of THF and was added in one portion via septum into the reaction vessel. The reaction mixture was stirred for 12 h under dry argon and benzoic or diluted acetic acid was added. The solution was concentrated under vacuum and the residue was dissolved in DCM and precipitated from methanol 3 times. The precipitate was isolated via centrifugation and dried in vacuo.



^{1}H-NMR (250 MHz, $CDCl_3$): *δ* 1.44-1.68 (bd, **1**), 4.12 (t, 4H, **2**), 4.35 (q, 2H, **3**), 5.10-5.22 (bq, **4**).

Synthesis of *α*, *ω*–dicinnamoylpolylactide

Polylactide (1 eq) was dissolved in chloroform together with cinnamoyl chloride (100 eq), DMAP (10 eq) and pyridine (50 eq). The reaction mixture was refluxed over night, cooled to RT and concentrated in vacuo. DCM was then added to the residue and the undissolved solids were filtrated. The product was then precipitated from methanol 3 times with subsequent centrifugation and drying. Yield: 89%.



^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.45-1.66 (bd, **1**), 4.11 (t, 4H, **2**), 4.36 (q, 2H, **3**), 5.09-5.21 (bq, **4**), 7.35-7.79 (m, 14H, **5**).

General procedure of irradiation experiments in solution

$1.5 \cdot 10^{-3}$mmol of α,ω–dicinnamoylpolylactide or α,ω–dicinnamoylpolystyrene were dissolved in 65 mL chloroform and this solution was given to a quartz tube and stirred for 12 h. The sealed quartz tube was placed in 13 cm distance from the light source and irradiated at a wavelength of 254 nm while stirring the solution vigorously. After irradiation the solvent was evaporated and the residue was analyzed using NMR and gel permeation chromatography.

General procedure for the irradiation of a polymer solution with under high concentration conditions

The polymer was dissolved in 200 µL chloroform and given to a quartz cuvette. The cuvette was placed on the top of the light source (254 nm) for irradiation. After irradiation the solvent was removed and the dried residue was analyzed using NMR spectroscopy and gel permeation chromatography.

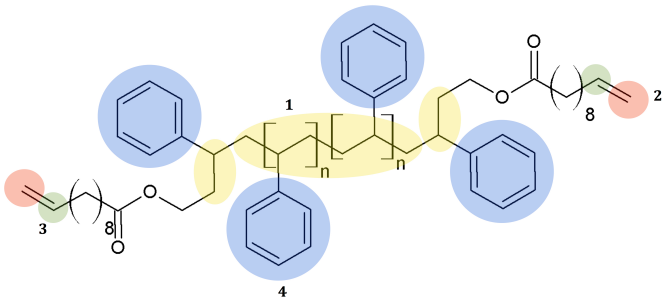
General procedure for the irradiation in miniemulsion

$1.5 \cdot 10^{-3}$ mmol of the polymer were dissolved either in 15 mL chloroform or toluene and stirred for 12 h. The polymer solution was mixed with a solution of 325 mg SDS in 65 mL water and stirred for 1 h to prepare an emulsion. This

emulsion was placed in an ice bath and sonicated (Branson Sonifier W450 Digital, ½ inch, 90% amplitude, 2 min) in order to prepare a miniemlusion. The mixture was heated while stirring at 60 °C (86°C for toluene) for 3-5 h. The resulting mixture was irradiated according to the above mentioned method. After the irradiation the reaction mixture was concentrated by freeze-drying and dialyzed for 7-10 days. The polymer was obtained via freeze-drying.

Synthesis of α,ω–(bis)–undecylenoyl–polystyrene

100 mg α,ω–dihydroxy polystyrene ($1.25 \cdot 10^{-2}$ mmol), 283 mg (1.38 mmol) DCC, 12.2 mg (0.1 mmol) DMAP and 230 mg (1.25 mmol) undecylenic acid were dissolved in dry DCM, the round flask was filled with dry argon and the reaction mixture was stirred for 24 h. The suspension was concentrated by evaporation and filtered. The product was precipitated from methanol 3 times giving a white powder after drying under vacuum. Yield: 90 mg (90%).
GPC (THF): M_n=8200, PDI = 1.21;



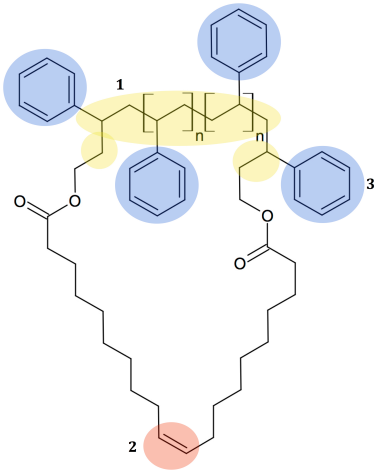
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.09-2.36 (br, **1**), 4.96 (t, 4H, **2**), 5.73-5.92 (m, 2H, **3**), 6.28-7.25 (br, **4**).

Synthesis of a cyclic polystyrene via the ring closing methatesis

12 mg ($1.46 \cdot 10^{-3}$ mmol) of α,ω–bis–undecylenoyl–polystyrene were dissolved in 70 mL toluene and stirred for 1 h. 1.3 mg ($1.53 \cdot 10^{-3}$ mmol) Second generation Grubb's Catalyst in 3 mL toluene were added and the reaction mixture was stirred at 60° C for 24 h under dry argon. The solution was

concentrated in vacuo and filtered via syringe filter (0,2 µL pore size). The filtrate was precipitated into methanol, centrifuged and dried in vacuo. Yield: ca. 80%;

GPC (THF): M_n=7300, PDI = 1.23.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.07-2.25 (br, **1**), 5.29-5.49 (b, 2H, **2**), 6.28-7.25 (br, **3**).

General procedure for the ring closing metathesis in miniemulsion

12 mg ($1.46 \cdot 10^{-3}$ mmol) of α, ω–bis–undecylenoyl–polystyrene were dissolved in 10 mL toluene and stirred overnight. 1.3 mg $1.53 \cdot 10^{-3}$ mmol Grubbs catalyst were dissolved in 5 mL toluol. Both solutions were added to the prepared solutions of 160 mg SDS in 30 mL water and stirred for 1 h to prepare an emulsion. These emulsions were placed in an ice bath and sonicated (Branson Sonifier W450 Digital, ½ inch, 90% amplitude, 2 min) in order to prepare a miniemlusion. The obtained miniemulsions were combined and the sonication procedure was repeated under the same conditions. The mixture was then heated while stirring at 60° C for 24 h. After the cooling the reaction mixture to RT it was was concentrated by freeze-drying and dialyzed for 7-10 days. The polymer was isolated via freeze-drying.

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