Light switchable coatings

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4-HEMUMA 4-hydroxy ethyl 4-methyl umbelliferone methacrylate
4-MU 4-methyl umbelliferone; 7-hydroxy 4-methyl coumarin
4-MUA 4-methyl umbelliferone acrylate
4-MUMA 4-methyl umbelliferone methacrylate
AGET activator generated by electron transfer
AIBN $\alpha,\alpha'$-azobis(isobutyronitrile)
ARGET activator regenerated by electron transfer
ATRA atom transfer radical addition
ATRP atom transfer radical polymerization
DBU 1,8-diazabicyclo (5.4.0)undec-7-ene
DCM dichloro methane
DIBTTC S-dodecyl S'-(isobutyric acid) trithiocarbonate
DMAEMA N,N-dimethyl amino ethyl methacrylate
DMF N,N-dimethyl formamide
DMSO dimethyl sulfoxide
DP degree of polymerization
DRI differential refractive index
DSC differential scanning calorimetry
eBiB ethyl bromo isobutyryl bromide
ESR electron spin resonance
EVM error-in-variables model
f Functionality
HEA hydroxy ethyl acrylate
hh head-to-head
HMTETA 1,1,4,7,10,10-hexamethyltriethylene tetramine
ht head-to-tail
$\alpha$BMA iso-butyl methacrylate
ICAR initiators for continuous activator regeneration
IRT intermediate radical termination
$k_{act}$ activation rate constant
$k_b$ fragmentation rate constant
$k_{deact}$ deactivation rate constant
$k_i$ initiation rate constant
$k_p$ propagation rate constant
$k_t$ termination rate constant
$k_{tr}$ transfer rate constant
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<thead>
<tr>
<th><strong>Glossary</strong></th>
<th><strong>Definition</strong></th>
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<tr>
<td>MALDI-ToF-MS</td>
<td>matrix assisted laser desorption-ionization time-of-flight mass spectroscopy</td>
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<tr>
<td>Me₆TREN</td>
<td>tris [2-(dimethylamino) ethyl] amine</td>
</tr>
<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number average molecular weight</td>
</tr>
<tr>
<td>MP</td>
<td>melting point</td>
</tr>
<tr>
<td>MRR</td>
<td>monomer reactivity ratio</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight average molecular weight</td>
</tr>
<tr>
<td>$n$-BA</td>
<td>$n$- butyl acrylate</td>
</tr>
<tr>
<td>NBD</td>
<td>7-nitro-1,2,3-benzoxadiazole</td>
</tr>
<tr>
<td>NBD-MAE</td>
<td>4-(N-methyl N-(2-hydroxy-ethylamine)-7-nitro-1,2,3-benzoxadiazole</td>
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<tr>
<td>NLLS</td>
<td>nonlinear least square</td>
</tr>
<tr>
<td>NMP</td>
<td>nitroxide mediated polymerization</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>pBA</td>
<td>poly (butyl acrylate)</td>
</tr>
<tr>
<td>pBMA</td>
<td>poly (butyl methacrylate)</td>
</tr>
<tr>
<td>PDI</td>
<td>poly dispersity index</td>
</tr>
<tr>
<td>pDMAEMA</td>
<td>poly (N,N-dimethyl amino ethyl methacrylate)</td>
</tr>
<tr>
<td>piBMA</td>
<td>poly(iso-butyl methacrylate)</td>
</tr>
<tr>
<td>PMDETA</td>
<td>N,N,N',N'',N''-pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>pMMA</td>
<td>poly (methyl methacrylate)</td>
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<tr>
<td>propyl ligand</td>
<td>$N_n$-pyridyl methanimine</td>
</tr>
<tr>
<td>pSTY</td>
<td>poly (styrene)</td>
</tr>
<tr>
<td>RAFT</td>
<td>reversible addition-fragmentation chain transfer</td>
</tr>
<tr>
<td>RT</td>
<td>ambient temperature</td>
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<tr>
<td>SEC-ESI-MS</td>
<td>size exclusion chromatography electron spray ionization mass spectroscopy</td>
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<tr>
<td>SR &amp; NI</td>
<td>simultaneous reverse and normal initiation</td>
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<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
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<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethylpiperidine-1-oxyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UV</td>
<td>ultra violet</td>
</tr>
<tr>
<td>VAZO-88</td>
<td>$\alpha,\alpha'$-azobis(cyclohexanecarbonitrile)</td>
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In this chapter the major goal and final purpose of the project are presented. The developments in the use of coumarin as an added functionality in polymers will be discussed together with the possibilities of their use in coatings.
1.1 Switchable coatings

In recent years a lot of attention has been paid to coatings having an additional functionality next to being scratch resistant, high gloss, impact resistant etc. Coatings contain a number of ingredients that make up the formulation and provide the final coating properties. A functionality that can be thought of is reversibility of a property by means of an external trigger. This functionality can be incorporated through addition as a diluent, crosslinker or as a functional group on the polymer structure used in the coating system. Polymers make up the main ingredient of the coating. When introducing an additional functionality to the coating, introduction of this functionality can easily be done by changing or modifying the polymer.

When adding a new functionality that responds to an external trigger, we want to introduce a change to the system on demand. Triggers can for instance be temperature, electrical current, impact or UV light. When UV light is used as the external trigger, there are various compounds that have the ability to undergo a photo chemically induced chemical transformation e.g. dimerization:

- Anthracene\cite{1,2}
- Cinnamic acid\cite{3,5}
- Coumarin\cite{6,7}
- Thymine\cite{8,9}

All of the above mentioned compounds can undergo a photo dimerization by either a [4+4] or [2+2] mechanism and to certain extent can undergo the reverse reaction, \textit{i.e.} photo cleavage. In the case of anthracene this cleavage can also occur by either irradiation with UV light ($\lambda < 320$ nm) or by heating as shown in figure 1.1.
The result of this photo chemical reaction can be for instance crosslinking on demand or orientation of the molecule in the polymeric film. The concept of orientation is being used in the orientation of liquid crystals.

Coumarin compounds are available in many derivatives and are already widely used for the preparation of liquid crystals (because of their photo alignment) or fluorescent dyes (because of their fluorescent behavior). However, the reversible dimerization is of particular interest, since it has not widely been studied in combination with coatings and thin polymer films.

Coumarin is known for its ability to go from one form to the other by means of UV irradiation. The irradiation by UV light ($\lambda > 300$ nm) causes a [2+2] cycloaddition of the double bonds, at the 3, 4 position, to form a cyclobutane ring, which produces a dimer. In most cases this reaction can be reverted by irradiation with a different wavelength of UV light ($\lambda < 300$ nm). The starting structure for the preparation of most of the functionalized coumarins used in the work described in this thesis is umbelliferone, which contains a hydroxyl group at the 7 position, see figure 1.2.
Chapter 1

Coumarin has its natural occurrence in plants such as lavender and coriander or fruits such as strawberries, apricots and cherries. Next to its use in perfumes, because of its sweet sent, coumarin is applied medically. The coumarin derivatives are very well known for its anti-coagulant and anti-tumor properties.

The dimerization of low molecular weight derivatives of coumarin is well described in literature. The various factors that can influence the photo product, conversion and rate of the dimerization are well documented. Much less is known on their behavior in solid thin films.

1.2 Objective and outline

The main objective of the work described in this thesis was to prepare polymers that contain either coumarin or coumarin dimer moieties that can make that a coating can be reversibly crosslinked under the influence of UV light.

In order to prepare well defined polymers with a specific number of functional groups, we made use of controlled radical polymerization. In this way we can pre-determine the molecular weight and the exact known number of coumarin groups per polymer chain. In Chapter 2 we discuss what is described in the literature about coumarins and polymers. Next to that we discuss controlled radical polymerization as this is the technique we have used to prepare our polymers.

As we started with the controlled radical polymerization using the RAFT (Reversible Addition- Fragmentation chain Transfer) process, we came across the discussion on the cause of retardation and whether this is caused by intermediate radical termination (IRT). In Chapter 3 we show the proof we found on IRT and the initial problems we had employing RAFT agent containing coumarin based leaving groups.

For the preparation of polymers that have the ability to form a network, we need to introduce multiple functional groups into the polymers. In Chapter 4 we describe the different pathways that we have explored in order to make star polymers that have coumarin
functional groups on the chain ends. We describe the synthesis of these star polymers by both the arms first and the core first method. For both methods we make use of a combination of click chemistry and ATRP.

In Chapter 5 we describe a number of (block) copolymers that can be compared to the star polymers we have made in chapter 4. We also looked at the reactivity ratios of both MMA and 4-MUMA (4-methyl umbelliferone methacrylate) by means of the Jaacks method.

Chapter 6 will discuss the dimerization and photo cleavage of model polymers bearing one coumarin functionality or a fully dimerized coumarin functional group. Further we discuss the dimerization of the (block) copolymers of which the preparation has been described in chapter 5 and chapter 6, respectively and the star polymers prepared in chapter 4. We finally report the results of the investigations of the reversibility of the dimerization process in the case of the star polymers.

In the Epilogue we summarize and discuss the most important results and some recommendations for future work.

1.3 References

Abstract

Coumarin is an interesting compound for the introduction of additional functionality in polymers. In this chapter the use of coumarin in different fields is addressed. Specific examples are given in combination with polymers and the typical reversible photo dimerization is explained. As controlled radical polymerization is used as a tool to prepare the desired polymer, the three main controlled polymerization techniques are introduced.
2.1 Introduction

The first discovery of coumarin was made in the 1820’s, in the Tonka bean\cite{1}. Coumarin appeared to be present in a number of natural sources such as woodruff, lavender, sweet clover grass, celery and licorice. It is also found in citrus fruits, strawberries, apricots, cherries, and cinnamon. The coumarin parent structure is given in figure 2.1, together with 4-methyl umbelliferone and Warfarin, both important derivatives of coumarin.

![Figure 2.1: The structure of coumarin and two of its derivatives.](image)

Warfarin is one of the most known derivatives of coumarin and known for its anti-coagulation properties\cite{2} it is used as a rodenticide or, in lower dosage, as a medicine for blood thinning. The family of derivatives called khellactone coumarins, are notable for their extensive bio-activities such as anti-HIV properties, anti-tumor promoting and anti-platelet aggregation\cite{3}. In polymer science coumarins are used to produce liquid crystals\cite{4-8} as the coumarin group can undergo photo alignment. In the 1990’s, studies were initiated to incorporate coumarin derived monomers into polymer networks in order to harvest and transfer solar energy\cite{9-11}. Due to the tunability of their absorbance and fluorescence (as due to changes of substituents at the coumarin the fluorescence band shifts) they are particularly interesting for use in laser dyes and light emitting diodes (LEDs)\cite{12}.

A very specific property of coumarin, that has received quite some attention over the last years, is its ability to undergo reversible dimerization. At wavelengths above 300 nm it undergoes a [2+2] photo dimerization, and at wavelengths below 260 nm the reverse reaction takes place\cite{13-21}.
The reversible photo dimerization phenomenon was utilized to act as a drug release mechanism\textsuperscript{[22]}. For this application the pore voids of a hybrid mesoporous material, called MCM-41, were functionalized with approximately 4 wt% of 7-[(3-triethoxysilyl) propoxy] coumarin. Controlled release experiments were performed using the steroid cholestane. The coumarin functionalities controlled the storage/release of the cholestane in the voids of the mesoporous material.

In order to study the reversible photo dimerization of coumarin in coating systems we aim at the introduction of coumarin derivatives in polymer chains via various routes. To efficiently study the effect of coumarin we make use of well defined polymers made by means of controlled radical polymerization.

In this chapter we aim to give an overview of the applications of coumarin, primarily in the field of polymers. In particular, we focus on the specific property of reversible photo dimerization. In addition we briefly review the three different types of controlled radical polymerization.

### 2.2 Photo dimerization and photo cleavage

The photo dimerization of coumarin was discovered by Ciamician and Silber in 1902\textsuperscript{[24]}. This photo dimerization has been extensively studied in various systems and employing various conditions\textsuperscript{[18, 20, 25, 26]}. An important feature of the dimerization of coumarin is that it is reversible. The wavelength used for irradiation determines whether dimerization or cleavage occurs (see figure 2.2).

**Figure 2.2:** Reversible photo dimerization of 4-methyl umbelliferone
The conditions have a major influence on the dimerization behavior as the coumarin chromophore has the possibility to dimerize such that four isomers are formed. The four possibilities are given in figure 2.3.

Figure 2.3: Four isomers formed after photo dimerization of coumarin.

a) syn head-to-head b) anti head-to-head c) syn head-to-tail d) anti head-to-tail.

- In solution, the configuration is determined by the solvent. Upon irradiation in polar solvents the coumarin is excited to the singlet state and predominantly forms syn photo dimers.
- In polar media the syn/anti ratio increases when using high concentrations and a low temperature.
- Irradiation in nonpolar solvents brings the coumarin to the triplet excited state and the major product formed is the anti photo dimer. When photo sensitizers are used (in both nonpolar and polar solvents) the triplet state is favored leading to predominantly anti photo dimers.
- Substituents next to the double bond of the coumarin influence the possibility to dimerize and the rate of dimerization\(^\text{[27]}\).
Figure 2.4: Schematic representation of the possible transitions of coumarin, upon irradiation.

An important side reaction during the irradiation is self-quenching\textsuperscript{[18, 20]}. Self-quenching is a bimolecular reaction between an excited molecule and a molecule in its ground state. The two molecules both will return to their ground state and the excitation energy is released without product formation.

There are two possible pathways of self quenching:

- Via excimer formation (excited dimer): \[ C^*(1) + C \rightarrow CC^* \]
  \[ CC^* \rightarrow 2C + \text{energy} \text{ (polar solvents)} \]

- Bimolecular reaction: \[ C^*(1) + C \rightarrow 2C + \text{energy} \]
  \( \text{ (non polar solvents) } \)

This side reaction lowers the quantum yield of the dimerization significantly and therefore long irradiation times are required for the dimerization. In order to increase the quantum yield, photo sensitizers such as benzophenone are commonly used\textsuperscript{[26, 28, 29]}. 
Benzophenone is extensively studied as a photo sensitizer in the dimerization reaction of coumarins. Photo sensitzers are easily excited to the triplet state at which point they can transfer their energy to another molecule in the ground state and allow this molecule to convert to the triplet excited state. However, it turns out that in the case of coumarin, benzophenone does not act as a photo sensitizer in the usual sense\textsuperscript{[26]}. The energy that is absorbed by coumarin is transferred to benzophenone as singlet excitation and after intersystem crossing is returned to coumarin as triplet excitation (intersystem crossing is the conversion of one state to another with a different spin multiplicity).

![Figure 2.5: Schematic representation of energy conversions using benzophenone to mediate inter system crossing.](image)

Unlike the photo dimerization, the photo cleavage of coumarin dimers has not been very extensively studied. The main difference from the dimerization reaction is the choice of wavelength used. For the cleavage the most used wavelength is 254 nm (or $\leq 260$ nm in general). Kim et al.\textsuperscript{[30]} used a Nd:YAG laser at 532 nm to cleave the photo dimers, however the dose needed for the cleavage was much higher than when 266 nm was used.

Instead of solvents as discussed earlier, in the solid film state the polymers used will determine the environment of the coumarin that needs to be dimerized (or cleaved). The effect of the environment can be split into two main contributions. First the glass transition
temperature ($T_g$) will influence the mobility of the polymer chain\cite{31} and secondly, the choice of the monomer determines the surrounding polarity of the coumarin. In chapter 6 these two properties are studied and discussed in depth.

### 2.3 Application of coumarin in polymer systems

Extensive work on polymer systems has been reported by Chen and coworkers\cite{32}. They studied the reversible photo cross-linking and photo cleavage of coumarins in various polymeric systems. Initially they studied coumarin derivatives (bearing different lengths of alkyl chains) dispersed in poly (vinyl acetate)\cite{33}, using UV-Vis spectroscopy to follow the dimerization and cleavage of the coumarin. Using their knowledge from these systems they prepared a number of copolymers of (meth)acrylates and 7-acyloxy-4-methylcoumarin\cite{31}.

![Figure 2.6: Reversible dimerization scheme of copolymers of (meth)acrylates and 7-acyloxy-4-methylcoumarin.](image)

Next to proving the reversible photo dimerization in a number of cycles these authors showed that the photo cleavage reaction is influenced by a dynamic equilibrium. At 254 nm both cross-linking and cleavage can occur. The different cycles we show in figure 2.7.
Upon increasing the incorporation of the pendant 4-methylcoumarin groups into the copolymers the glass transition temperatures ($T_g$) were increased. When dimerization was followed in the film state it was found that the rate and ultimate fraction of cross linking depended on the chain mobility.

In their study on polyurethanes containing coumarin components[34] Chen et al. used a different approach. They started with coumarin dimers, with and without a methyl group on C4 of the coumarin (see figure 2.2), and used the dimer in the poly addition reaction to prepare the polyurethanes, as is represented in figure 2.8.

These polymers were dissolved in 1,4-dioxane and subjected to 254 nm UV light. Upon irradiation the photo cleavage was followed by UV-Vis spectroscopy. It was observed, for
the unsubstituted coumarin, that after 1 minute of irradiation a maximum absorbance was obtained and upon further irradiation the absorbance leveled out to an equilibrium value. For the 4-methyl substituted coumarin the maximum absorbance was obtained after only 33 seconds of irradiation but also in this case the absorbance leveled out to an equilibrium value. This decrease indicated the dynamic equilibrium photo cleavage and photo dimerization.

After the photo cleavage they re-photo polymerized the photo cleaved products and made a comparison between irradiations using $\lambda_{\text{max}}$ 300 and 350 nm UV light. They followed the photo polymerization again by measuring the UV-Vis absorbance. When 300 nm light was used, the equilibrium was reached within 15 minutes as compared to 140 minutes when using 350 nm light. This is ascribed to the higher absorbance efficiency at 300 nm, which is near to the $\lambda_{\text{max}}$ of coumarin chromophores (315 nm).

Trenor et al.\cite{35,36} used poly (ethylene glycol) diol and modified the chain ends with coumarin. The functionalized polymers that were obtained were casted from solution into films and upon photo dimerization they chain extended the polymers. They were able to identify the amounts of dimers, trimers and higher molecular weight species and were able to demonstrate the reversibility by photo cleavage using 254 nm UV light. Using this chain extension principle the authors demonstrated to be able to synthesize pressure sensitive adhesives and they used the photo reversibility to regain the adhesive strength on demand by photo cleavage.

Zhao et al.\cite{37} used diblock copolymers with incorporated coumarin moieties to make micelles. These micelles were then reversibly dimerized. The amphiphilic diblock copolymers were synthesized using ATRP. A hydrophilic block poly (ethylene oxide) was used and the hydrophobic block was either a poly (coumarin methacrylate) (CMA) or a random copolymer of methyl methacrylate (MMA) and CMA.
They prepared micelles by adding water to a polymer solution in DMSO or THF (depending on the composition of the hydrophobic block) and exposed these solutions to light with $\lambda > 310$ nm (2000 mW from a UV-Vis spot curing system). After 800 seconds a maximum dimerization of $\sim 78\%$ was reached. Upon irradiation using 254 nm UV light they observed a decrease in dimerization degree from 78% to 30%. The micellar solution was repeatedly irradiated with alternating UV light of $\lambda > 310$ nm and $\lambda < 260$ nm. These experiments demonstrated a reversible change in dimerization degree as shown in figure 2.7.

As seen in the studies by Chen et al.\textsuperscript{[32], [34]} the coumarin reaches a photo stationary state due to the occurrence of dimerization at the irradiation wavelength $< 260$ nm.

Recently Cheng-Mei et al.\textsuperscript{[38]} reported on a polystyrene coumarin end-capped system made by ATRP. A polystyrene chain with a coumarin end group was obtained by using an ATRP initiator derived from coumarin, see figure 2.10.
Upon irradiation dimerization of the polymer was observed. However, the reaction was hindered due to the high $T_g$ (and thus low mobility) in the solid state resulting in a $M_n$ lower than predicted.

The large majority of work on the coumarin dimerization has been done in solution and only some research groups have investigated the polymers in a film or solid state. Additionally, most of the polymers investigated were synthesized using either free radical polymerization or addition polymerization yielding polymers having a broad polydispersity and high molecular weights.

To study a range of (meth)acrylic polymers we have used the same approach as been described by Cheng-Mei et al. We prepared a coumarin based ATRP initiator. Starting with this initiator, (meth) acrylic polymers with coumarin chain end functionality were synthesized. The synthesis of these polymers and their photo dimerization as well as photo cleavage properties are described in chapters 4 and 6, respectively.

In the next section we describe Nitroxide Mediated polymerization (NMP), ATRP and Reversible Addition-Fragmentation chain Transfer (RAFT) mediated polymerization. NMP, ATRP and RAFT are the three most commonly used controlled radical polymerization techniques for producing polymers with a low molecular weight polydispersity from a wide range of vinyl monomers. In the present work we used ATRP and RAFT to make the polymers studied.

### 2.4 Controlled Radical polymerization

For the study of model systems, well defined polymers are required. In order to make well defined polymers, controlled/ living radical polymerization results into good control over the molecular weight and the end groups. There are two major mechanisms of controlling the polymerization, i.e. by reversibly trapping the radicals or by reversible ‘transfer’ of the radicals (degenerative exchange process).
Two of the main controlled radical polymerization techniques, NMP and ATRP, make use of reversibly trapping the radicals.

The third technique of controlled radical polymerization is RAFT. This system makes use of reversible transfer also called the degenerative exchange process.

A specific characteristic of controlled polymerizations is the relation between the monomer concentration and time, see equation (2.1). Next to this the molecular weight also increases linearly with monomer conversion proving the concept that all polymer chains grow simultaneously and good control is achieved. Because of the simultaneous growth of the polymer chains a low polydispersity is obtained throughout the polymerization.

\[ \ln \frac{c_M}{c_{M_0}} \sim t \]  

(2.1)

### 2.4.1 Nitroxide Mediated Polymerization

In the nitroxide mediated polymerization the propagating radicals that are formed, by an alkoxyamine, are trapped in a deactivation state by a nitroxide species. In the polymerization of styrene, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was first used in 1993 by Georges et al.\cite{39} based on the work of Moad et al.\cite{40} TEMPO acted as an end-capping molecule for the growing chains and creates the dormant species. These dormant species are thermally unstable and at high temperatures they cleave homolytically to yield the active species, see figure 2.11.

![Figure 2.11: General mechanism for nitroxide mediated polymerization.](image-url)
As the use of TEMPO was limited to a number of monomers, a library of new nitroxides was designed\cite{41}. These new alkoxyamines have more labile C-O bonds in order to polymerize monomers having a lower equilibrium constant, such as acrylates and dienes\cite{42,43}.

The use of these alkoxyamines proved to be very efficient in controlling the polymerization and more importantly, they are not only able to act as an end-capping group but also as an initiator. Another advantage of NMP is that the alkoxyamines can withstand conditions used for ATRP and RAFT and therefore can be combined with these techniques to make block copolymers\cite{44-46}.

### 2.4.2 Atom Transfer Radical Polymerization

Similar to NMP, in ATRP the propagating radicals are trapped. The principle of ATRP is based on Atom Transfer Radical Addition (ATRA) which is a widely used reaction in organic chemistry\cite{47}. ATRA is a metal catalyzed reaction to form stoichiometric adducts of alkyl halides and alkenes. The metal catalyst generates a radical species from the alkyl halide which in turn reacts with the unsaturated compound. In the case of ATRP the radicals are also trapped by the halide but this halide is positioned on an initiator that ensures that the product after addition can be reactivated. Not only the transition metal is needed but it is used in combination with a suitable ligand that forms a complex with the metal. This metal-ligand complex provides the transfer of the halogen atom from the dormant polymer chain to produce an active chain end (i.e. radical). This active chain end can then propagate or terminate. As the equilibrium in this transfer process is strongly shifted towards the dormant species termination is negligible. Figure 2.12 shows the mechanism for ATRP.
A big advantage of ATRP is that most of its catalysts and ligands are commercially available. Because of the wide range of ligands and initiators a wide range of monomers can be used. Only a few monomers are not tolerated in ATRP such as monomers having a carboxylic groups, vinyl acetate and certain ionic monomers.

Next to the commercially available initiators, other initiators are readily synthesized, including multi-functional initiators producing star polymers. The main problem when the standard conditions are used in an ATRP, is the catalyst removal after polymerization. To circumvent catalyst removal, systems have been developed to minimize the amount of catalyst needed. Activator ReGenerated by Electron Transfer (ARGET) \cite{48, 49} ATRP uses only ppm quantities of copper as it makes use of reducing agents such as glucose, ascorbic acid or tin (II) 2-ethylhexanoate. Other methods include ICAR (Initiators for Continuous Activator Regeneration) ATRP \cite{49}.

ICAR ATRP or “reverse” ARGET ATRP provides the use of low amounts of copper (10-50 ppm) along with a free radical source and reducing agents.

Table 2.1 gives a comparison of the different methods based on ATRP.
Table 2.1: Comparison of the different systems of ATRP (all values are molar ratios).

<table>
<thead>
<tr>
<th></th>
<th>M/R-X/Cu'X/Cu''X</th>
<th>Ligand</th>
<th>Reducing agent</th>
<th>Free radical initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘normal’ ATRP</td>
<td>200/1/1/—</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Reverse ATRP&lt;sup&gt;1&lt;/sup&gt;</td>
<td>200/—/—/1</td>
<td>1</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td>SR &amp; NI&lt;sup&gt;2&lt;/sup&gt; ATRP</td>
<td>200/1/—/0.2</td>
<td>0.2</td>
<td>—</td>
<td>0.1</td>
</tr>
<tr>
<td>AGET ATRP</td>
<td>200/1/—/0.2</td>
<td>0.2</td>
<td>0.18</td>
<td>—</td>
</tr>
<tr>
<td>ARGΣET ATRP</td>
<td>200/1/—/0.01</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>—</td>
</tr>
<tr>
<td>ICAR ATRP</td>
<td>200/1/—/0.01</td>
<td>0.01</td>
<td>—</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

<sup>1</sup>: Makes use of a free radical initiator and copper (II). <sup>2</sup>: simultaneous reverse and normal initiation

2.4.3 Reversible Addition-Fragmentation chain Transfer mediated polymerization

RAFT makes use of reversible chain transfer, also called the degenerative exchange process. RAFT was introduced by Rizzardo et al.<sup>[50]</sup> in 1998 making the RAFT process the youngest of the three controlled radical polymerization techniques. Figure 2.13 shows the general mechanism for the RAFT mediated polymerization.

To initiate the reaction, a free radical source is used. However, the amount of initiator is relatively low. The generally used concentration ratio of the RAFT agent and the initiator is 1:5 or 1:10. The RAFT agent provides the controlled character of the polymerization as it controls the main equilibrium.
After radicals have been formed by the free radical source, the propagating radicals add to the RAFT agent and form the intermediate radical. Upon fragmentation of this intermediate radical, a new propagating radical and a dormant species are forming. This transfer process is very important as it controls the simultaneous growth of the polymer chains, which results in polymers with low polydispersity. The target molecular weight can be easily tuned by the ratio of the RAFT-agent and the monomer as every molecule of RAFT should ideally initialize one polymer chain.

The RAFT agent has the general structure \( Z-C(=S)-S-R \), so called thiocarbonyl thio compounds, and is always tuned to the polymeric system used in order to provide proper control. The \( R/P_n/P_m \) groups are the leaving groups and should be weakly bound to the...
sulphur atom. This provides a high fragmentation rate of the intermediate radical \( (k_\beta) \) and should ensure a low amount of side reactions. After fragmentation of the R-group, the radical produced should be able to efficiently re-initiate the polymerization. This re-initiation can be altered by the chemical structure of the leaving group and therefore must be tuned to the monomer used. The Z group controls the activation or deactivation of the C=S group and therefore influences the addition and fragmentation rates. Both the Z- and R-group can be used to introduce specific functional groups into the polymer chain, see Chapter 3.

Because of the use of the free radical initiator a small amount of termination cannot be avoided. Next to termination, retardation and inhibition are known phenomena in RAFT mediated polymerizations. These side-reactions are mainly dependent on the choice of the RAFT-agent, the monomer and reaction conditions. In the ongoing debate on the cause of retardation of the polymerization, there are two general schools of thought:

- Slow fragmentation of the intermediate radical
- Termination of the intermediate radical

In chapter 3 the postulated intermediate radical termination is described in more detail and evidence is given for the termination products formed.

One major disadvantage is that there are only a few RAFT agents commercially available and the synthesis of the RAFT agents can be very inefficient and lengthy\(^{[51, 52]}\). Another drawback is that after polymerization the RAFT moiety is remaining on the polymer chain end giving the material color. There is also the risk that degradation of the RAFT moiety over time leads to the release of a bad odor. However, there are methods available to remove the RAFT moiety\(^{[53]}\).

As compared to the other two controlled polymerization techniques the widest range of monomers can be polymerized using RAFT. Only primary and secondary amines can not be polymerized. Also the tolerance towards most functional groups that can be incorporated into the RAFT agent is a benefit. There is also a wide range of reaction conditions that can be employed including heterogeneous systems like emulsion and mini emulsion polymerizations\(^{[54-56]}\).
By using polymers made by controlled radical polymerization we produced well defined polymers and we aimed to study the relationship between the molecular weight, amount of coumarins incorporated and the rate of dimerization in the different polymers prepared.

2.5 References


Aspects of RAFT mediated polymerization

Abstract

The mechanism of RAFT was investigated with regards to the intermediate radical termination and proof of this is described. Problems encountered when combining coumarin and living radical polymerization are described.

Part of this chapter is based on: Patricia Geelen and Bert Klumperman Macromolecules 2007, 40 (11), 3914.
3.1 Introduction

Reversible Addition-Fragmentation Chain Transfer (RAFT) mediated polymerization is a controlled/ living radical polymerization that can be used for many monomer/ initiator combinations and is easily performed in heterogeneous systems such as emulsions. The generally accepted mechanism for RAFT is given in figure 3.1.

**Initiation:**

\[
\text{Initiator} \quad \rightarrow \text{I}^* \quad \overset{M}{\rightarrow} \quad \overset{M}{\rightarrow} \quad \text{p}_n^*
\]

**Reversible chain transfer:**

\[
\begin{align*}
\text{p}_m^* + S \overset{k_{-\text{add}}}{\rightarrow} S-P_n & \quad \overset{k_{\text{add}}}{\rightarrow} \quad P_m-S-P_n \\
& \quad \overset{k_p}{\rightarrow} \quad p_n^* + S
\end{align*}
\]

**Termination:**

\[
2 \text{P}^* \quad \overset{k_p}{\rightarrow} \quad \text{P-P (dead polymer)}
\]

Figure 3.1: General mechanism for RAFT- mediated polymerization.

As the RAFT mediated polymerization technique is recently developed, its mechanism is still not fully elucidated. We took a closer look at one of the big questions regarding the mechanism. In certain combinations of a dithiobenzoate RAFT agent and acrylate monomers, retardation of the polymerization is observed. The use of a RAFT agent with a UV-label allowed us to answer the question what happens to the intermediate radical during RAFT polymerization. The results and conclusions of this study are given in this chapter.

Many studies have been done on coumarins in combination with polymers. However, most of these polymers are not made by controlled/living polymerization but with conventional free radical polymerization. As we want to use well defined polymers and to make sure that we only have one coumarin per polymer chain, we decided to use RAFT mediated polymerization for this. We looked at the difference in RAFT agents when using substituents.
aspects in RAFT mediated polymerization

at the double bond of the coumarin. The problems encountered are also described in this chapter.

3.2 Intermediate Radical Termination in RAFT (IRT)

In the field of living/controlled radical polymerizations, extensive research has been done on reversible addition-fragmentation chain transfer (RAFT) mediated polymerization as a highly versatile method. Recently, an important focus has been on the elucidation of the reaction mechanism. Special interest has been given to the fate of the intermediate radical, as this is a potential source for side-reactions. These potential side-reactions of the intermediate radical could be the cause of rate retardation phenomena.

In the ongoing debate on the cause of rate retardation, there are two general schools of thought:

- Slow fragmentation of the intermediate radical
- Termination reactions of the intermediate radical (figure 3.2)

Many different techniques have been used to elucidate the RAFT mechanism, e.g. NMR\(^{[1,2]}\), UV-Vis spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF-MS)\(^{[3]}\), electron spin resonance (ESR) spectroscopy\(^{[4-6]}\), and size exclusion chromatography electron spray ionization mass spectrometry (SEC-ESI-MS)\(^{[7]}\).

Barner-Kowollik \textit{et al.}\(^{[7]}\) studied polymerizations mediated by a rate-retarding RAFT agent (dithiobenzoate), and by a non-rate-retarding RAFT agent (phenyl dithioacetate). Predict\(^{5}\) was used to predict concentrations of the three-arm stars that would result from the termination of intermediate radicals. Theoretically predicted concentrations of terminated products were compared with experimentally determined concentration, by SEC-ESI-MS. In their experimental work, Barner-Kowollik \textit{et al.} were unable to find evidence for termination products originating from the intermediate radical. Drache \textit{et al.}\(^{[8]}\) used Monte Carlo simulations to predict the concentrations of termination products resulting from intermediate radical termination. These calculations predicted several percents of terminated species at lower conversions (up to 25% monomer conversion).
Figure 3.2: Proposed mechanism for the RAFT process with intermediate radical termination.

Other authors used model systems favoring the formation of intermediate radical termination products to show the chemical pathway that leads to these termination products. These model systems do not necessarily represent the mechanisms taking place in real polymerization systems because monomer was absent in these studies.[3, 9]

Rate retardation almost exclusively occurs with RAFT agents that carry a phenyl group as a radical stabilizing group (see figure 3.2) (i.e. dithiobenzoates). Elucidation of the origin of rate retardation is important to obtain a deeper understanding of the RAFT mechanism as has been reviewed recently by Vana et al.[10] It is tempting to relate the present study to ab initio quantum chemical calculations from Coote et al.[11, 12] However, it needs to be stressed that these calculations are focused on the initialization process, or the so-called pre-equilibrium. The current study focuses on the post-initiation stages, often referred to as the main equilibrium.

On the basis of previous research, there are strong indications that intermediate radical termination products can occur in RAFT mediated polymerizations. However, despite the many efforts in earlier research, the structure of possible termination products (three- and four-arm stars) has experimentally not been confirmed. Next to this, hardly any experimental
proof was given of termination products in a real polymerization system, in the presence of monomer.\textsuperscript{[13]} Barner-Kowollik \textit{et al.}\textsuperscript{[14]} discussed their results of a similar experiment as the one we will be discussing in this chapter. However, they were not able to detect any termination products. In a recent publication, Arita and Buback\textsuperscript{[15]} point at the possibility that three- and four-arm stars in dithiobenzoate-mediated polymerization can undergo side reactions. These side reactions will lower the concentration of star-shaped polymers and will lead to the formation of chains that are potentially difficult to distinguish from products of conventional bimolecular termination.

In continuation of previous work in our group,\textsuperscript{[3]} we polymerized n-butyl acrylate (BA) in the presence of a dithiobenzoate RAFT agent (3)(see figure 3.3).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.3}
\caption{Synthesis of RAFT agent (3) with 7-nitro-1,2,3-benzoxadiazole (NBD) moiety.}
\end{figure}

The use of the 7-nitro-1,2,3-benzoxadiazole (NBD)\textsuperscript{[16]} moiety as part of the leaving group provides a UV absorbing group with a $\lambda_{\text{max}}$ of 470 nm, which is present at virtually every polymer chain end. The C=S group of the RAFT agent has a $\lambda_{\text{max}}$ of 305 nm. This means that the two different chromophores can be measured simultaneously during an SEC
experiment, and therefore the ratio can be determined as a function of elution time. Due to the disappearance of the 305 nm chromophore upon (intermediate radical) termination (IRT), this ratio provides an entry into the study of IRT. We subsequently fractionated polymers by SEC and analyzed some relevant fractions by MALDI-ToF-MS.

3.3 Identification of termination products in IRT

Poly (\(n\)-butyl acrylate) synthesized in the presence of RAFT-agent (3) was analyzed by SEC (\(M_n = 4980\) g/mol; PDI = 1.12). The polymerization showed a living character, as evidenced by a linear increase of molar mass with monomer conversion and a low polydispersity index throughout the whole reaction. It should be kept in mind that reactions were stopped at reasonably low conversions (65%) and that no bimodality was observed in the SEC trace.

To determine the presence and location of products from intermediate radical termination in the molar mass distribution, we carried out SEC with UV-detection. Detection at 305 nm allows the selective detection of the thiocarbonyl thio moiety of the RAFT agent. Detection at 470 nm, on the other hand, shows the presence of the chromophore in the leaving group of the RAFT-agent (3). The ratio of UV470/UV305 as a function of elution time in SEC will provide information on the possible evidence of products from intermediate radical termination.

The expected (i.e., linear) polymer is anticipated to include both UV chromophores in a 1:1 ratio. However, when termination occurs at the intermediate radical position, the polymer chain will lose its thiocarbonyl thio chromophore and a three or four-arm star will be formed that contains three or four UV470 chromophores, respectively (see figure 3.2). Therefore the UV470/UV305 ratio will change and can be used to detect possible termination products. Note also that bimolecular termination of propagating polymer chains will also lead to a decrease in the UV470/UV305 ratio. It is therefore necessary to identify the nature of the chains that cause the decrease in UV470/UV305 ratio.
The normalized SEC data measured at two different wavelengths is given in figure 3.4. There is a significant difference in UV absorption noticed at both lower elution time (i.e. higher molar mass) and at higher elution time (i.e. lower molar mass).

**Figure 3.4:** SEC chromatogram of a pBA sample at 62 % conversion measured at wavelength of 470 nm and of 305 nm ($M_n = 4981$ g/mol, PDI = 1.12). The straight vertical lines represent the positions of the collected SEC fractions that were analyzed with MALDI-ToF-MS.

The difference in UV absorption, present at both the higher and lower molar mass, is most likely caused by a disappearance of the thiocarbonyl thio moiety due to termination reactions of some of the chains. Fractionation was used to isolate samples at the higher molecular weight end of the distribution where the deviation between the two UV absorptions is the highest. Next to the difference in UV absorption, it is important to measure at the higher molecular weight end of the distribution rather than around the peak maximum, since at the peak maximum the concentration of linear chains is large therefore no termination products will be observed. The fractions from SEC were analyzed with MALDI-ToF-MS to identify possible termination products.

The first fraction is taken at an elution time of 21.5 min. Its mass spectrum is shown in Figure 3.5. Very clearly, two distributions are observed. The high molar mass distribution
can be assigned to terminated chains carrying three UV$_{470}$ chromophores. Next to that there is one thiocarbonyl thio moiety present. The molar mass of this distribution is in agreement with products resulting from intermediate radical termination with a propagating polymer chain. The comparison between experimental and theoretical isotope pattern is shown figure 3.5$^a$ and 3.5$^c$, respectively.

Figure 3.5: a) MALDI-ToF mass spectrum of fractionated pBA-RAFT sample (conversion of sample 62 %) at SEC elution time 21.5 min. b) expansion between 9500 and 9700 g/ mol c) calculated isotopic patterns for poly(BA) termination product between intermediate radical.

The first distribution at lower molar mass is linear pBA. The bimodal distribution observed can be explained by the hydrodynamic volume of the two different chain architectures. It is known that star polymers have a lower hydrodynamic volume compared to their linear equivalent having the same molecular weight. In our case, the stars produced by the intermediate radical termination having a higher molecular weight have the same hydrodynamic volume as the linear polymer of lower molecular weight. Therefore, the two
Aspects in RAFT mediated polymerization

distributions elute at the same elution time in SEC. It needs to be stressed that the origin of
the seemingly narrow distributions in the MALDI spectra lies in the fractionation by SEC.
The second fraction at an elution time of 21.9 min also shows a bimodal distribution. The
first distribution is assigned to linear poly (BA), whereas the second distribution with higher
molecular weight corresponds with the termination product carrying four UV470
chromophores and two thiocarbonyl thio moieties, see figure 3.2. This product is most likely
formed via termination by combination between two intermediate radicals. The mass
spectrum and a relevant expansion of the termination product are shown in Figure 3.6.

Figure 3.6: a) MALDI-ToF mass spectrum of fractionated pBA sample (conversion of
sample 62 %) at elution time 21.9 min. b) expansion between 8350 and 8550 g mol -1. c)
calculated isotopic pattern for poly (BA) termination product between two intermediate
radicals (4-arm star from figure 3.2).

It is expected that intermediate radical termination occurs throughout the whole
polymerization and therefore termination products should be found over the whole
molecular weight range. This is also the case as we found in our study. Even at very low
conversion we observe the termination product of an intermediate radical bearing only two
monomer units and three leaving groups (shown in figure 3.7). These termination products
are found in the different samples taken during the polymerization, having an increasing conversion, confirming that the termination products formed are irreversible. Unfortunately, the MALDI-ToF-MS analysis only provides information on the total molar mass and therefore an exact structural representation of the terminated product cannot be given.

A similar study by Ah Toy et al.\textsuperscript{[14]} employed SEC with online ESI-MS detection. In their sample, they identified a large number of polymer species carrying different types of end groups, and originating from various side reactions. In our spectra, there are some species that coincide with the observations of Ah Toy et al. (e.g., trace amounts of the oxidized RAFT agents can be identified in the low molar mass fraction) (see Figure 3.7). Other species that they observe cannot be identified in the current spectra, such as the intermediate radical terminated with a hydrogen atom. However, in the present spectra, there seems to be clear evidence for three- and four arm stars that are absent in the Ah Toy study. It is difficult to pinpoint the origin of these discrepancies, but it could be due to difficulties with mass spectrometry such as ionization method, sensitivity, and mass range of the different instruments.

\textbf{Figure 3.7}: a) MALDI-ToF mass spectrum of fractionated pBA sample at elution time 23.1 minutes together b) expansion between 1530 and 1680 g/mol. The expansion shows the terminated product (3-arm star from figure 3.2) together with the linear pBA (conversion = 25%).
As known from previous literature, a number of other explanations can be given for the formation of polymer chains bearing multiple leaving groups on one chain. One of the explanations is that of chain transfer to polymer of acrylates during a (living) radical polymerization. Chain transfer to polymer occurs in two possible pathways. The first one is via intramolecular chain transfer to polymer or backbiting. This backbiting takes place at higher monomer conversion (≈ 80%) and higher temperature (≈ 80°C) and results in bimodality observed in the SEC traces. At the higher temperatures, beta scission of the mid-chain radical can also occur, which leads to the formation of macro monomers. These macro monomers can subsequently copolymerize, which leads to the introduction of multiple end groups.

The second pathway is via an intermolecular chain transfer to polymer, which leads to a mid-chain radical.\(^{17}\) This long-lived radical can undergo termination reactions with propagating chains, again leading to the introduction of multiple chain ends.

In our case, no bimodality can be observed in the SEC traces (only in the MALDI-ToF-MS analyses) and therefore we assume no significant chain transfer to polymer occurred in the system causing branching as observed by O’Shea et al.\(^{18}\) (see also the discussion below). To confirm that the products found are specific for the RAFT process, a control experiment is performed. ATRP is chosen as the technique for the control experiments as it is an alternative well-known living radical polymerization technique for acrylates. Therefore, the evolution of molar mass as a function of conversion is the same as in the case of RAFT-mediated polymerization. Also, polymerization conditions can be tuned in such a way that conversion versus time is comparable, which means that the propagating radical concentration is similar.

ATRP polymerization was performed under similar conditions as the RAFT mediated polymerization, and the samples taken during different times of conversion were handled in the same manner.

As expected the polymerization showed a living character having a low polydispersity index and having an increasing \(M_n\) with increasing conversion. In Figure 3.8 a typical MALDI-
ToF-MS spectrum is given of a sample at 72% conversion. The main distribution found corresponds to linear (dormant) polymer having the initiator fragment on the one side and a bromine chain end. The minor distribution is explained by the same linear chain end but where the bromine chain end is replaced by hydrogen. The latter distribution can be formed during the analysis or during the polymerization. As shown in Figure 3.9 the corresponding SEC hardly shows any bimodality.

Figure 3.8: MALDI-ToF mass spectrum of pBA sample before fractionation at a conversion of 72 % (M_n = 3551 g/mol, PDI = 1.11).

To obtain a good comparison with the RAFT experiments, samples were fractionated at the higher molar mass end of the SEC distribution to find any possible termination products. A typical MALDI-ToF mass spectrum of a relevant fraction is given in Figure 3.10. The same pattern is found as in the unfractionated sample. The main distribution is the linear (dormant) pBA. The minor distribution is explained by the linear chain having bromine replaced by hydrogen. Close inspection of the minor peaks in the spectra shows that there are no significant signals that point to the presence of chains carrying more than one initiator fragment. The tiny peaks that are seen among the two main distributions are most likely due to post source fragmentation, as judged from the poor resolution. This confirms the earlier conclusion that under the conditions of the present experiments chain transfer to polymer and subsequent reactions[17, 18] are insignificant.
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Figure 3.9: SEC traces of pBA samples taken during ATRP polymerization (the vertical line represents the position of the fractionated sample).

Figure 3.10: MALDI-ToF mass spectrum of fractionated pBA sample, taken at the end of the polymerization shown in Figure 3.9.

Hence, the control experiment makes it clear that the termination products found in the RAFT mediated polymerization are not caused by chain transfer to polymer and subsequent termination processes and are inherent to the RAFT process.
3.4 RAFT and coumarin

In order to incorporate coumarins into a polymer, monomer derivatives can be used. In literature examples are styrene or acrylate derivatives of coumarin are reported\[^{19-26}\]. This we chose as our approach to make (block) - copolymers. Next to copolymers we also investigated polymers having only one coumarin moiety as model material in order to get a better insight into the reversible photo dimerization. This was obtained by using a RAFT agent with a coumarin as a leaving group. The RAFT agents we used to introduce the coumarin moiety on the polymers are depicted in figure 3.11.

![Figure 3.11: Structures of trithiocarbonate RAFT agents without (5) and with 4-methyl substitution (6) of the coumarin leaving group.](image)

After performing polymerizations using RAFT agent 5 (without the 4-methyl substitution), problems were encountered. In many cases, there was a very large inhibition time (over 4 hours no polymerization occurred) and broad molecular weight distributions were obtained. The increased polydispersities can be explained by the additional amount of initiator added, when using AIBN as the (free) radical source.
Figure 3.12: SEC traces of RAFT mediated polymerization using coumarin RAFT (5).

The inhibition can be caused by the presence of the double bond of the coumarin. In literature examples are given that this double bond can copolymerize with styrene\textsuperscript{[27]}. To solve this problem the 4-methyl substituted coumarin is used as this will provide sterical hindrance and therefore decrease reactivity of the double bond.

Inhibition\textsuperscript{[2, 28, 29]} normally can be circumvented by using higher reaction temperatures. We performed different reactions employing higher reaction temperatures in combination with V-40 (also known as VAZO-88; 1,1'-azobis(cyclohexanecarbonitrile)), a free radical source having a half-life time of 10 hours at 88°C\textsuperscript{*}. Figure 3.14 shows the two reactions using RAFT agent 6 (see figure 3.11) at two different temperatures. Still a long inhibition period is observed.

\textsuperscript{*} Data obtained from Wako chemicals
Figure 3.13: SEC traces of RAFT mediated polymerization using coumarin RAFT (6). Reaction time = 23 hours final conversion of 91.6%.

Figure 3.14: RAFT mediated polymerization of BA employing RAFT agent (6), reactions performed at 90°C and 75°C.
Another issue can be the use of the high RAFT agent concentration causing the inhibition period. Perrier et al.\textsuperscript{[28]} showed that employing different concentrations of RAFT agent in the polymerization of methyl acrylate (MA) inhibition can be circumvented.

Figure 3.15 shows the polymerization of BA employing different concentrations of RAFT agent 6. The results demonstrate that the lower RAFT agent concentration indeed shows no inhibition; on the other hand it can be seen that at the lower concentrations the rate of polymerization is influenced.

To further understand the possible influence of the presence of coumarin in the polymerization we have performed some polymerizations using a non-retarding RAFT agent DIBTTC (S- dodecyl S'- (isobutyric acid) trithiocarbonate) and addition of free coumarin and 4-MU to the reaction mixture. Figure 3.16 shows the polymerization employing RAFT agent 6 (based on 4-MU) having the inhibition period together with the polymerizations where we have used the DIBTTC together with the free coumarin (7-hydroxy coumarin) and 4-MU (4-methyl umbelliferone). It shows that the presence of the different coumarins does
not influence the radical polymerization as we expected and the inhibition only depends on the purity of the RAFT agent that we have prepared.

![Graph]

**Figure 3.16:** RAFT mediated polymerization of BA employing RAFT agent 6 (*) and DIBTTC in combination with free coumarin (●) and 4-MU (∗) added to the reaction mixture.

### 3.5 Conclusions

The present results provide additional proof of intermediate radical termination in a real polymerization system, *i.e.* in the presence of monomer. In addition, evidence of termination products formed from the early stages of polymerization onwards and remaining unchanged throughout. Therefore our results support the hypothesis of intermediate radical termination as a possible source for retardation of the polymerization and provide further insight in the complete RAFT mechanism. Furthermore, the results support Predici© simulations predicting termination products of intermediate radicals and the terminated products found are in agreement with model systems previously used to mimic intermediate terminated products. The control experiment confirmed that the termination products found are inherent to the RAFT mediated process and were not caused by chain transfer to polymer.
RAFT agents containing the coumarin based leaving group show inhibition when employed at high concentrations. We have seen that higher reaction temperatures do not show any improvement as would be expected for inhibition. Addition of free coumarin to a RAFT mediated polymerization employing DIBTTC showed no inhibition, indicating that the coumarin does not interfere with the radicals in the polymerization system.

3.6 Experimental section

3.6.1 Materials

All solvents and reagents were purchased from Aldrich Chemical Co. and used without further purification (unless mentioned otherwise). BA (99%) was filtered before use through a column for removing hydroquinone and mono methyl ether hydroquinone (Aldrich), to remove the radical inhibitor. 4-(N-methyl N-(2-hydroxy-ethylamine)-7-nitro-1,2,3-benzoaxadiazole (NBD-MAE) (1) was prepared as described in literature.\cite{16} The RAFT agent DIBTTC was prepared as described in literature.\cite{30} Details on the methods used for analysis can be found in Appendix 1.

3.6.2 Synthesis of chlorophenyl acetyl NBD-MAE ester (2)

![Figure 3.17: Synthesis of NBD-MAE ester (2)](image)

A solution of chlorophenyl acetylchloride (6.08 g, 32.16 mmol) was added dropwise to a solution of NBD-MAE (1; 8.24 g, 34.6 mmol) and triethylamine (10.46 g, 103.4 mmol) in dry THF (300 ml). The reaction mixture was kept at 40 °C for three hours and left to react.
overnight at ambient temperature. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (300 mL). The solution was extracted twice with brine (300 mL). The organic phase was dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure. The product was isolated as a bright orange solid in 90% yield (11.30 g, 28.9 mmol). ¹H NMR (CDCl₃, 400 MHz): δ 8.35 (d, 1H, Ph (H)), δ 7.30 (m, 5H, Ph (H)), δ 6.04 (d, 1H, Ph (H)), δ 5.25 (s, 1H, PhCHCl), δ 4.66 (m, 2H, COCH₂CH₂) δ 4.47 (m, 2H, CH₂CH₂N), δ 3.27 (S, 3H, PhNCMe).

3.6.3 Synthesis of RAFT agent (3)

Phenyl magnesium bromide was synthesized from bromobenzene (2.63 g, 16.7 mmol) and magnesium turnings (0.33 g, 13.4 mmol) in dry THF (10 mL). Carbon disulfide (0.99 g, 13.0 mmol) was added to the solution maintaining the reaction temperature below 35 °C. NBD-MAE ester (2, 4.99 g, 12.8 mmol) dissolved in THF (40 mL) was then added into the solution. The reaction temperature was raised to 75 °C and maintained for 72 h. Ice water was then added to the solution. After removal of THF the water layer was extracted twice with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. After solvent removal a dark orange solid was obtained in 85% yield (5.5 g, 10.8 mmol). ¹H NMR (CDCl₃, 400 MHz): δ 8.23 (d, 1H, Ph (H)), δ 7.90 (m, 5H, Ph (H)), δ 7.5 (m, 5H, Ph (H)), δ 6.0 (d, 1H, NPh (H) NO₂), δ 5.52 (s, 1H, PhCH₂), δ 4.58 (m, 2H, OCOC (H2) CH₂), δ 4.30 (m, 2H, OCOCH₂C (H2)), δ 3.30 (s, 1H, NC (H3)).
3.6.4 Synthesis of NBD-MAE initiator for ATRP (4)

![Diagram of NBD-MAE initiator synthesis](image)

Figure 3.19: Synthesis of NBD-MAE ATRP initiator.

NBD-MAE (1; 4 g, 16.8 mmol) was dissolved in THF (30 mL) together with triethylamine (2.56 mL, 18.5 mmol). To this, the bromo isobutyryl bromide was added (2.3 mL, 18.6 mmol) slowly. The product precipitated from the solution upon reaction. The product was filtered off and stirred in petroleum ether to remove unreacted starting materials. The product isolated was a bright orange solid in 45% yield (2.95 g, 7.6 mmol). $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.46 (d, 1H, Ph (H)), δ 6.23 (d, 1H, Ph (H)), δ 4.56 (s, 4H, C(CH$_2$CH$_2$)O), δ 3.50 (s, 3H, C(CH$_3$)), δ 1.85 (s, 6H, COC(CH$_3$)$_2$Br).

3.6.5 Synthesis of 7-hydroxy coumarin ester

7-Hydroxy coumarin (3.00 g, 18.5 mmol), 0.5 M NaOH solution (52 mL), and dichloromethane (42 mL) were mixed in a three-necked round bottom flask under cooling in an ice bath. Chloro phenyl acetylchloride (3.50 g, 18.5 mmol) was added dropwise and left to react for 2 hours. The two phases were separated and the water phase was extracted twice with dichloromethane. After collecting the organic phases, the solvent was removed under reduced pressure. The residue was recrystallized from ethanol (50 mL) yielding 3.14 g (54%) white solid after filtration. $^1$H NMR (CDCl$_3$, 400 MHz): δ 5.35 (s, 1H, CH), 6.17 (d, 1H, CH), 7.0 (d, 1H, CH), 7.17 (m, 2H, CH), 7.25 (m, 2H, CH), 7.40 (m, 2H, CH), 7.57 (dd, 2H, CH).
3.6.6 Synthesis of RAFT agent (5)

1-Dodecanethiol (1.1 g, 5.5 mmol), acetone (30 mL), and crushed NaOH (0.22 g, 5.50 mmol) were mixed in a three-necked round bottom flask under cooling in an ice bath. Upon reaction of 30 minutes the sodium salt of the dodecanethiol precipitated. CS$_2$ (0.41 g, 5.50 mmol) was added dropwise to the reaction mixture and left to react for another hour. Slowly added 7-hydroxy coumarin ester (1.5 g, 4.8 mmol) dissolved in acetone (30 mL) using a syringe. Upon reaction the mixture turned dark red and NaCl precipitated. The solution was filtered to remove the NaCl and the solvent was removed under reduced pressure. The product was washed with heptane to remove residual dodecan thiol and yielded 0.83 g of yellow/orange solid (31%). $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 0.88 (t, 3H, CH$_3$), 1.2 (m, 20H, CH$_2$), 1.74 (m, 2H, CH$_2$), 3.28 (t, 2H, CH$_2$), 6.0 (s, 1H, CH), 6.43 (d, 1H, CH), 7.03- 7.1 (m, 4H, CH), 7.35- 7.5 (m, 4H, CH), 7.6 (s, 1H, CH).

3.6.7 Synthesis of RAFT agent (6)

The same procedure was followed as described in 3.6.6 for RAFT agent 5. Starting material was 4-methyl umbelliferone. After work up, a yellow solid was obtained in 33 % yield. $^1$H NMR (CDCl$_3$ 400 MHz): $\delta$ 0.88 (t, 3H, CH$_3$), 1.2 (m, 20H, CH$_2$), 1.74 (m, 2H, CH$_2$), 2.4 (s, 3H, CH$_3$), 3.28 (t, 2H, CH$_2$), 6.0 (s, 1H, CH), 6.43 (d, 1H, CH), 7.03- 7.1 (m, 4H, CH), 7.35- 7.5 (m, 3H, CH), 7.6 (s, 1H, CH).

3.6.8 Polymerization using RAFT agent (3)

Butyl acrylate (9.5 g, 74 mmol), RAFT agent (3, 1.02 g, 2.0 mmol) and $\alpha$, $\alpha'$-azobis(isobutyronitrile) (AIBN) (0.066 g, 0.4 mmol) were added into a three-necked round bottom flask together with toluene (8.5 mL). The flask was deoxygenated by flushing with argon for approximately 30 minutes the flask was placed in a preheated oil bath at 70 °C. During the polymerization, samples were taken at different times of conversion which were further used for analysis. The reaction was stopped after 6 h by cooling the flask in an ice bath and addition of a small portion of THF (2 mL) (Conversion = 65 %; $M_n$ = 5500 g/mol; PDI = 1.12).
3.6.9 Polymerization using ATRP (control experiment)

Butyl acrylate (9 g, 70.2 mmol), NBD-MAE initiator (0.73 g, 1.88 mmol) and CuIBr (0.2 g, 1.39 mmol) were added into a Schlenck tube together with toluene (10 mL) and THF (4 mL). The Schlenck tube was deoxygenated by flushing with argon for 45 minutes. The Schlenck tube was then immersed in a preheated oil bath of 70 °C and PMDETA (0.32 mL, 1.43 mmol) was added to initiate the reaction. Samples were taken at different times of conversion and used for analysis purposes. The samples were analyzed with SEC. Some samples were fractionated prior to analysis with MALDI-ToF-MS. The polymerization was stopped after 3 hours and 45 minutes (final conversion = 76 %).

3.7 References


In this chapter we describe the synthesis of star polymers containing coumarin end groups. Two main methods were used to prepare end functional coumarin groups: the arms first and the core first methods. In both cases a combination of ATRP and click chemistry is employed. A third method using the core first approach and ATRP is also described.
4.1 Introduction

A star polymer is a multifunctional core bearing several polymer chains in the shape of a star. The number of functionalities of the core molecule determines the number of polymer arms. Star polymers have some improved characteristics, like compact morphology, reduced solution viscosity (compared to their linear analogues because of a lower hydrodynamic volume) and higher shear stability than linear analogs \cite{1, 2}.

Our objective is to introduce coumarin moieties at the chain ends of the arms of star polymers. In this way we prepare polymers with multiple coumarin functionalities and therefore in the film state we can introduce network formation if we have an average functionality larger than 2 \((f > 2)\).

The literature describes two main ways to produce star polymers. The first way is called the arms first method. Examples of this method are controlled cross-linking of linear polymers\cite{3} and attachment of linear polymers to a core molecule utilizing click chemistry\cite{4} or other high selective chemical reactions. The second method is the core first method. Examples of this method are ATRP (Atom Transfer Radical Polymerization) or RAFT (Reversible Addition-Fragmentation chain Transfer) mediated polymerizations that make use of multifunctional initiators (ATRP) or chain transfer agents (RAFT) and in that way grow the star polymers in a controlled manner \cite{5-10}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{star_polymer_schematic}
\caption{Schematic representation of two different ways to synthesize star polymers. Coumarin functional groups (○), multifunctional core molecule (●) and azide functionality (△).}
\end{figure}
Star polymers containing coumarin end groups

We have investigated a combination of several methods, our objective was not only to make star polymers; we also aimed at having one coumarin functional group per polymer chain end.

The arms first method as well as the core first method will be explained in the following sections, together with the introduction of coumarin groups in both cases as chain end functionalities. For the core first method, we have used two approaches. The first synthetic route we used is click chemistry using a mono-functional coumarin alkyne. For the second approach, we used modified ATRP conditions in order to ensure the selective reaction of one monomer unit to the chain end.

4.2 Arms first approach

For the arms first approach we need to take a couple of steps in order to make a star polymer bearing coumarin chain end functionalities. The consecutive steps that we used are:

- Synthesis of a coumarin based ATRP initiator.
- Use of the coumarin initiator to make the linear polymers (the arms).
- Conversion of the bromine chain end of the arms into an azide.
- Synthesis of the multi functional core alkyne.
- Click reaction of the arms to the multi functional core molecule.

These steps are shown in figure 4.2.
Figure 4.2: Steps taken in the arms first method, employing linear pMMA initiated by a coumarin derived ATRP initiator and difunctional alkyne as core molecule.

Initiator 1 was successfully synthesized and several polymerizations were performed to test the suitability of this initiator for ATRP. As mentioned before these polymerizations will typically show linear increase of \( \ln \left( \frac{[M_0]}{[M]} \right) \) with time, see figure 4.3. Next to this first order kinetics we showed a clear shift of the molecular weight distribution upon conversion, with respect to the monomer concentration, figure 4.4.
Figure 4.3: ATRP of MMA using coumarin based initiator (I) in toluene solution.

Figure 4.4: Molar mass distributions measured at different conversions of a typical pMMA ATRP polymerization using a 4-methyl umbelliferone initiator (I).

The initiator (I) was also used for other monomers to investigate its versatility. The results of various polymerizations using different monomers and different target molecular weights are collected in table 4.1.
Table 4.1: Results of ATRP using different monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$M_n, \text{th}$ (g/mol)</th>
<th>$M_n, \text{exp}$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>iBMA</td>
<td>4912</td>
<td>5340</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>6206</td>
<td>7180</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>2500</td>
<td>3270</td>
<td>1.15</td>
</tr>
<tr>
<td>MMA</td>
<td>6810</td>
<td>8270</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>2500</td>
<td>2660</td>
<td>1.15</td>
</tr>
<tr>
<td>BMA</td>
<td>4266</td>
<td>5220</td>
<td>1.17</td>
</tr>
<tr>
<td>BA</td>
<td>6878</td>
<td>5180</td>
<td>1.49</td>
</tr>
</tbody>
</table>

*: standard conditions: 4- MU initiator, propyl ligand or PMDETA, CuBr, toluene (50 v/v %) 80 °C.

Additionally we wanted to investigate the influence of $T_g$ on the photo dimerization of coumarin carrying polymer. $T_g$s of the different polymers are determined with DSC and are given in table 4.2.

Table 4.2: $T_g$s of different polymers measured with DSC

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>piBMA</td>
<td>5580</td>
<td>40.5</td>
</tr>
<tr>
<td>pMMA</td>
<td>4260</td>
<td>85.2</td>
</tr>
<tr>
<td>pBMA</td>
<td>5220</td>
<td>12.0</td>
</tr>
<tr>
<td>pBA</td>
<td>5180</td>
<td>-58.7</td>
</tr>
</tbody>
</table>

* All $T_g$ values were determined using the half height method.

The target molecular weight was varied to obtain polymers with higher and lower molecular weights. The polymers with shorter arms allowed the use of MALDI-ToF-MS after formation of the star polymers. Upon formation of the star polymers, the resulting polymers may reach high molecular weights. In literature many examples are reported where they successfully employ click chemistry for the synthesis of star polymers\[11-13\]. In contradiction it is also reported that click reactions performed on higher molecular weight polymers can
Star polymers containing coumarin end groups cause incomplete conversion \[^{14}\]. For this reason we tried both low and higher molecular weight polymer chains.

In all reactions with azide functionalization, the azide end group was introduced at the end of the polymer chain by nucleophilic substitution of the bromide. The isotopic patterns in the MALDI-ToF-MS spectra are predicted and compared to the corresponding isotope pattern of the product. As can be seen in figure 4.5 the second prediction is of the polymer chain without an azide, the loss of end functionality results in an unsaturated chain end. This loss of chain end functionality can occur during the polymerization or during the analysis \[^{15}\]. Another issue is that MALDI-ToF-MS analysis is not quantitative and therefore we cannot draw any conclusions on the total conversion of the azide functionalization.

Figure 4.5: a) MALDI-ToF-MS spectrum of 4- MU initiated pMMA with azide chain end. b) Prediction of product with azide end group. c) Prediction of product with unsaturated chain end.
In order to tune the reaction conditions of the click reaction, model reactions were performed, by using a linear polymer and a mono-functional alkyne. In this case the coumarin alkyne (4) was clicked to the polymer. It was then analyzed by MALDI-ToF-MS (figure 4.6), which showed that the desired product was formed. Two additional large peaks are visible which can be assigned to azide substituted polymer chains and polymer chains with an unsaturated chain end, after comparison with calculated isotope patterns. The end-groups of these non-substituted chains could be formed during the polymerization or during the MALDI-ToF-MS experiment. It must be stressed that due to fragmentation the isotopic patterns of the samples measured are of a very poor quality and conclusions can not be drawn solely from the MALDI-ToF-MS measurements.

Click reaction of the linear polymer and coumarin alkyne (4) showed full conversion overnight. The absence of coumarin alkyne, after overnight reaction, in the HLPC analysis confirmed the full conversion.

After the model click reactions, we synthesized multi-functional alkyne cores 5, 6 and 7 bearing 3, 2 and 4 alkyne functionalities respectively, followed by click reactions.
When employing the multifunctional alkynes, higher molecular weight star polymers are formed. To follow the progress of these reactions we analyzed the samples with SEC to see whether the starting polymer peak moves towards higher molecular weight. In SEC, the elution volume of the chains will decrease with increasing hydrodynamic volume. Note that for star polymers the hydrodynamic volume is smaller than that of their linear analogues, because of their relative compact structure.

Two arm and four arm star polymers did not show any peak shift to higher molecular weight at all. The failure of click reaction with a central composition of neopentylglycol and pentaerythritol was reported earlier by both Matyjaszewski and Sharpless\textsuperscript{[4, 14]}. Reasons for this are not yet elucidated.

Star polymers synthesized with multifunctional core 5 resulting in three arm polymers, showed only a small movement to higher molecular weight. However, the coupling reaction did not go to complete conversion. Changing the solvent from THF to DMF and addition
of L-ascorbic acid showed a small improvement, but still the measured molecular weight was only the twofold of the original molecular weight instead of threefold, see figure 4.8. After 4 days 15 % of the starting material was left; 30 % of double molecular weight fraction is present and 55 % of the targeted triple molecular weight is present (conversion determined by deconvolution of polymeric peaks).

![Figure 4.8: Molar mass distribution of reaction mixture from the click reaction to tri functional alkyne core molecule (5) and linear pMMA followed over time.](image)

In order to investigate these reactions, and identify the products using MALDI-ToF-MS measurements, we are limited in the final molecular weight we can use for analysis. In order to ensure that MALDI-ToF-MS can be applied on the resulting products, we performed some click reactions using lower molecular weight polymers. Also in this case no three armed stars are formed but only a double molecular weight was obtained as can be seen in figure 4.9. The starting material has a molecular weight of 3270 g/mol, and in the MALDI spectrum only the original distribution, and that with double the original molar mass is observed.
Figure 4.9: MALDI-ToF-MS spectrum of click reaction of linear pMMA initiated with 4-methyl umbelliferone initiator with tri functional alkyne core molecule, performed in DMF.

From the results obtained above we can conclude that the combination of linear polymers with azide chain end and the consecutive click reaction with multifunctional alkyne core molecules do not lead to the desired products.

4.3 Core first method (click chemistry)

The steps that need to be taken to make the coumarin functional star polymers via a core first method are:

- Synthesis of the multifunctional (ATRP) initiator
- Polymerization
- Chain end modification into azide
- Synthesis of coumarin alkyne
- Click reaction of coumarin to chain ends

These steps for a three arm star polymer are given in figure 4.9.
Figure 4.10: Reaction steps in the core first method, employing a three functional initiator to produce star shaped pMMA and consecutive click reaction with 4-methyl umbelliferone alkyne after chain end functionalization with an azide.

When we want to use the core first method we need to take some considerations. When we make the star polymers we use multifunctional initiators. In literature\(^1\) it is reported that when performing the polymerization, employing these multifunctional initiators, the conversion is preferably kept below 50% as above this conversion broadening of the molecular weight distribution is observed. This broadening is caused by star-star reaction. Subsequently, when the star polymers are made, determination of the molecular weight under standard SEC conditions gives a deviation from the real molecular weight. The reason for this deviation is the low hydrodynamic volume of the star polymers when compared to linear polymers. A correction for this deviation in molecular weight demands for a light scattering detector. Finally, to determine the chain end functionalization, the molecular weight of the star polymer is too high to get a proper resolution in MALDI-ToF-MS analysis.
ATRP with the core-first method was performed with a three and a five functional core initiator. These core initiators result in a star polymer with three arms and with five arms. The results in table 4.3 demonstrate that polymers with a low polydispersity index were obtained.

Table 4.3: Results of ATRP using multifunctional initiators.

<table>
<thead>
<tr>
<th>Monomer ( # of arms)</th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA (5)</td>
<td>13400</td>
<td>1.14</td>
</tr>
<tr>
<td>PMMA (5)</td>
<td>11600</td>
<td>1.15</td>
</tr>
<tr>
<td>PMMA (3)</td>
<td>11850</td>
<td>1.19</td>
</tr>
</tbody>
</table>

* : The molecular weights of the star polymers were determined compared to linear pMMA standards.

The synthesized star polymers after ATRP have no coumarin functionality yet. To ensure this, two reaction steps are necessary. The first step is changing the chain end functionality from a bromide into an azide. No analytical method is known to quantitatively determine whether the bromide is substituted by the azide. Only after the second step we know whether the chain-end was functionalized with an azide, because the second step is clicking the coumarin alkyne (4) to the polymer chain-end. Figure 4.10 shows the UV signal from a SEC chromatogram. The dashed signal shows the star polymer with azide end functionality and thus having no UV absorption at 315 nm. Upon effective click reaction of the coumarin alkyne to the star polymer we can see UV absorption at 315 nm caused by the coumarin: the solid line in figure 4.11.
Figure 4.11: SEC UV-Vis detection at 315 nm, clicking of the coumarin to the star polymer.

A quantification of the coumarin groups on the star polymers with UV-Vis spectroscopy (a comparison was made with the UV-Vis spectrum of a polymer bearing one coumarin functional group) points to an average functionality of one per star polymer, indicating that the conversion of the click reaction is approximately 30%.

4.4 Core first method (monomer addition)

As the functional star polymers obtained with click chemistry did not show complete conversion, an alternative to replace the click chemistry in the core first method should be found.

We propose the following consecutive steps to produce the coumarin functional star polymers:

- Synthesis of the multifunctional (ATRP) initiator
- Controlled polymerization of MMA with ATRP
- Synthesis of coumarin based monomer
- Single addition of coumarin (meth)acrylate to chain ends employing adjusted ATRP conditions

![Chemical structure of the copolymer](image1.png)

**Figure 4.12:** Steps taken in the core first method, employing a multi-functional initiator to produce star shaped pMMA and consecutive selective monomer addition of 4-methyl umbelliferone methacrylate.

In order to ensure only the addition of one monomer unit to the polymer chain end, we make use of the well known principles of ATRP. In the ATRP mechanism, upon radical formation caused by the homolytic cleavage of the carbon-halogen bond (R-X), the metal moves to a higher oxidation state. The presence of the metal in two oxidation states controls the equilibrium. When an increased amount of the metal in a higher oxidation state (in our case copper (II)) is used, the equilibrium will shift to the dormant state and slows down propagation. By making use of an increased amount of Cu (II) we want to ensure that the addition of the second coumarin monomer is much slower than the first one.
To enable the selective reaction of the coumarin (meth) acrylate monomer, we have screened several modified reaction conditions based on the standard ATRP conditions. A number of variables were changed to optimize the reaction of the chain end. These include the equivalents of monomer (to the polymer chain end), the ratio of copper (I) to copper (II) and the nature of the ligands. We also looked at the difference between the use of an acrylate and a methacrylate coumarin derivative. The 4-methyl umbelliferone derivative was used as the parent structure.

Three different coumarin monomers were synthesized; two of them are methacrylate-based (4-MUMA (8) and 4-HEMUMA (10)) and one of them is an acrylate-based (4-MUA (11)) monomer, see figure 4.13. The reason for using different monomers for the same system was to compare methacrylates with acrylates (4-MUMA vs 4-MUA) and also to see whether a spacer makes any difference in methacrylic monomers in terms of reactivity (4-MUMA vs 4-HEMUMA).

![Figure 4.13: Structures of the monomers 4-MUMA (8), 4-HEMUMA (10) and 4-MUA (11).](image)

One of the challenges was to quantify the chain end functionality after the reaction with the different coumarin monomers. Two different methods were used to determine the number of coumarin molecules at the chain-end: UV-Vis spectroscopy and SEC. How the functionality of the chains was determined with these techniques is described below.
Determination of chain end functionality using SEC measurements.

To determine the functionality after reaction, the SEC, DRI (differential refractive index) and UV-Vis signals (measured at 315 nm) were used. We determine the ratio between the DRI and UV signal as a measure for the functionality. We used a model compound, containing only one coumarin functionality, in order to determine this ratio. To do this we measure the DRI and UV signal. First we have to divide the DRI signal by the molecular weight, at the local molecular weight, in this way we obtain a number distribution. Next we have to make a correction for the elution time of the UV signal, since these detectors are placed in series, so the peaks overlap. The functionality of the polymer is then determined by dividing the UV signal by the adjusted DRI signal. For the model compound, bearing one coumarin functional group, we find a ratio of 3.49. The same calculation was repeated for all the other reactions and the obtained value was divided by 3.49 to determine the average functionality per polymer chain end.

As a model system, linear pMMA was chain extended with coumarin monomers first and analyzed. The experimental conditions that showed the most promising results were applied to 3-arm star pMMA.

For all the reactions we analyzed the SEC data as discussed above and in this way determine the functionality ($f$). All experiments are summarized and the values obtained are given in table 4.4-4.9.

The general trend that can be observed when using HMTETA (1,1,4,7,10,10-hexamethyltriethylene tetramine) as the ligand is that with an increasing amount of monomer equivalents an increase is found in the number of monomer units per polymer chain, independent of the amount of copper that is used. Next to this the reproducibility is not good as can be seen when MUMA-5 and MUMA-6 are compared. To make a robust system we need to have reproducible results and therefore we investigated other ligands suitable for chain extending the pMMA macro initiator.
Table 4.4: Linear pMMA with 4-MUMA using HMTETA ligand (the equivalents are given with respect to polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. of 4-MUMA</th>
<th>Eq. of Cu</th>
<th>Cu(I):Cu(II) f(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MUMA-1</td>
<td>1</td>
<td>1.9</td>
<td>1.1 : 1 0.46</td>
</tr>
<tr>
<td>MUMA-2</td>
<td>2</td>
<td>1.9</td>
<td>1.1 : 1 0.88</td>
</tr>
<tr>
<td>MUMA-3</td>
<td>5</td>
<td>1.9</td>
<td>1.1 : 1 1.46</td>
</tr>
<tr>
<td>MUMA-4</td>
<td>1</td>
<td>1</td>
<td>1 : 9 0.48</td>
</tr>
<tr>
<td>MUMA-5</td>
<td>2</td>
<td>1</td>
<td>1 : 9 0.99</td>
</tr>
<tr>
<td>MUMA-6</td>
<td>2</td>
<td>1</td>
<td>1 : 9 2.1</td>
</tr>
<tr>
<td>MUMA-7</td>
<td>5</td>
<td>1</td>
<td>1 : 9 2.86</td>
</tr>
<tr>
<td>MUMA-8</td>
<td>5</td>
<td>1</td>
<td>1 : 1 1.69</td>
</tr>
</tbody>
</table>

Table 4.5 compares the results of different ligands employing the same amount of copper and monomer equivalents. We can say that, even though it is reported \cite{16} that Me₆TREN (tris [2-(dimethylamino) ethyl] amine) is a relatively poor ligand for methacrylates as it forms a too active complex and may lead to radical termination at early stages of polymerization and hence the loss of control over the polymerization, Me₆TREN gave a value close to 1. The propyl ligand (N-(n-propyl)-2-pyridylmethanimine) has shown to be very effective for the controlled polymerization of a range of methacrylates in the literature \cite{17, 18}. However, here it showed a poor activity in our system and almost no chain extension of pMMA with 4-MUMA was observed.
Table 4.5: Chain-end functionalization of linear pMMA with 4-MUMA in the presence of different ligands. (The equivalents are given with respect to the polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. of 4-MUMA</th>
<th>Eq. of Cu</th>
<th>Cu(I):Cu(II)</th>
<th>Eq. of Ligand</th>
<th>Ligand</th>
<th>f(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MUMA-5</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>1</td>
<td>HMTETA</td>
<td>0.99</td>
</tr>
<tr>
<td>MUMA-9</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>1.2</td>
<td>PMDETA</td>
<td>0.72</td>
</tr>
<tr>
<td>MUMA-10</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>2.1</td>
<td>Propyl</td>
<td>0.15</td>
</tr>
<tr>
<td>MUMA-11</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0.95</td>
</tr>
<tr>
<td>MUMA-12</td>
<td>5</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>1</td>
</tr>
</tbody>
</table>

As well as the methacrylate we also tested the coumarin acrylate derivative (4-MUA) using Me₆TREN and propyl ligand. As demonstrated by the results collected in Table 4.6 Me₆TREN does not provide monomer addition to the polymer chain end and in contrast to the results with the 4-MUMA (see table 4.5) propyl ligand gives good results with 4-MUA.

Table 4.6: Chain-end functionalization of linear pMMA with 4-MUA in the presence of propyl ligand and Me₆TREN. (The equivalents are given with respect to polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. of 4-MUA</th>
<th>Eq. of Cu</th>
<th>Cu(I):Cu(II)</th>
<th>Eq. of Ligand</th>
<th>Ligand</th>
<th>f(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MUA-1</td>
<td>5</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0.11</td>
</tr>
<tr>
<td>MUA-2</td>
<td>2</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0</td>
</tr>
<tr>
<td>MUA-3</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0</td>
</tr>
<tr>
<td>MUA-4</td>
<td>5</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>2.1</td>
<td>propyl</td>
<td>0.91</td>
</tr>
<tr>
<td>MUA-5</td>
<td>2</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>2.1</td>
<td>propyl</td>
<td>0.36</td>
</tr>
<tr>
<td>MUA-6</td>
<td>2</td>
<td>1</td>
<td>1 : 9</td>
<td>2.1</td>
<td>propyl</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Considering the structure of the coumarin monomers it is possible that the bulky side group hinders the reactivity of the vinyl bond in the controlled radical polymerization. For this reason we tested the 4-MUMA with a spacer between the coumarin group and the methacrylate. The results are given in table 4.7.
Table 4.7: Chain-end functionalization of linear pMMA with 4-HEMUMA in the presence of HMTETA and PMDETA. (The equivalents are given with respect to polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. of 4-HEMUMA</th>
<th>Eq. of Cu</th>
<th>Cu(I):Cu(II)</th>
<th>Eq. of Ligand</th>
<th>Ligand</th>
<th>(f) SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMUMA-1</td>
<td>3.53</td>
<td>1.5</td>
<td>1.1 : 1</td>
<td>1.2</td>
<td>PMDETA</td>
<td>1.74</td>
</tr>
<tr>
<td>HEMUMA-2</td>
<td>1.8</td>
<td>1</td>
<td>1 : 9</td>
<td>1.2</td>
<td>PMDETA</td>
<td>0.3</td>
</tr>
<tr>
<td>HEMUMA-3</td>
<td>1.8</td>
<td>1.9</td>
<td>1.1 : 1</td>
<td>1</td>
<td>HMTETA</td>
<td>1.86</td>
</tr>
<tr>
<td>HEMUMA-4</td>
<td>1.8</td>
<td>1</td>
<td>1 : 9</td>
<td>1</td>
<td>HMTETA</td>
<td>1.68</td>
</tr>
</tbody>
</table>

It is very difficult to draw a conclusion from these results as they do not show a clear trend. In general the functionality that we obtained with these systems is ≥ 1. In case of MAHEMU-3 and 4, increasing the amount of Cu (II) resulted in a slight decrease in functionality. More experiments should be performed to draw a plausible conclusion and find the optimal conditions for HEMUMA.

Concerning the effect of the spacer, it might be said that a spacer makes the reaction easier so that functionality reaches a higher value in the case of HEMUMA in the presence of HMTETA (MUMA-5 vs HEMUMA-4).

PMDETA and Me₆TREN were employed in the chain extension of 3-arm pMMA with 4-MUA. The results obtained are given in table 4.8.
Table 4.8: Chain-end functionalization of 3-arm pMMA with 4-MUA. (The equivalents are given with respect to polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Eq. of 4-MU per arm</th>
<th>Eq. of Cu per arm</th>
<th>Cu(I):Cu(II)</th>
<th>Eq. of Ligand</th>
<th>Ligand</th>
<th>f(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3star-1</td>
<td>5</td>
<td>1.9</td>
<td>1.1:1</td>
<td>1.2</td>
<td>PMDETA</td>
<td>0.95</td>
</tr>
<tr>
<td>3star-2</td>
<td>5</td>
<td>1.9</td>
<td>1.1:1</td>
<td>1.2</td>
<td>PMDETA</td>
<td>0.69</td>
</tr>
<tr>
<td>3star-3</td>
<td>5</td>
<td>1</td>
<td>1:5</td>
<td>1.2</td>
<td>PMDETA</td>
<td>0.72</td>
</tr>
<tr>
<td>3star-3</td>
<td>5</td>
<td>1.9</td>
<td>1.1:1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0.64</td>
</tr>
<tr>
<td>3star-4</td>
<td>2</td>
<td>1.0</td>
<td>1:9</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>1.25</td>
</tr>
<tr>
<td>3star-5</td>
<td>2</td>
<td>1.0</td>
<td>1:9</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>0.64</td>
</tr>
</tbody>
</table>

As we have seen from the results discussed above, the reaction conditions using Me₆TREN as ligand with 5 equivalents of 4-MUMA to the polymer chain end (entry MUMA-12) give the best (and most reproducible) result. When we determined the functionality after 2 and 4 hours of reaction time the functionality = 1. This means that after the addition of the one 4-MUMA the equilibrium is apparently strongly on the dormant side and no propagation occurs. This was also tested on the star polymers. The results are given in table 4.9.

Table 4.9: Chain-end functionalization of 3 and 5-arm pMMA with 4-MUMA. (The equivalents are given with respect to polymer chain end)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting Mₙ (g/mol)</th>
<th>Eq. of 4-MUMA</th>
<th>Eq. of Cu</th>
<th>Cu(I) : Cu(II)</th>
<th>Eq. of ligand</th>
<th>Ligand</th>
<th>f(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3star-6</td>
<td>11100</td>
<td>5</td>
<td>1.9</td>
<td>1.1:1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>1</td>
</tr>
<tr>
<td>5star-1</td>
<td>11600</td>
<td>5</td>
<td>1.9</td>
<td>1.1:1</td>
<td>1.1</td>
<td>Me₆TREN</td>
<td>1</td>
</tr>
</tbody>
</table>

The equivalents given in the table are calculated per arm of the star polymer.

As we expected, in the case of the star polymers, the polymer chains remain dormant after one monomer addition.
4.5 Conclusions

Both the coumarin-based initiator (1) for the arm-first method and the multifunctional initiators for the core-first method showed typical properties for ATRP, i.e. correlation between \( \ln([M]_0/[M]) \) and time, and all the polymers obtained show a linear increase in \( M_n \) with conversion and a low PDI.

For the arms first method, the substitution of the bromide by the azide was performed and in all cases the substitution took place, only the amount of bromide substituted by azide is unknown. Finding a way to quantify the degree of substitution should be investigated.

After the chain end functionalization with the azide, click reactions were performed using coumarin alkyne (6). With MALDI-ToF-MS we were able to prove that the click reaction was successful. The main problem encountered was that the azide functionalization did not reach completion and therefore we cannot say anything on the conversion and thus the yield of the reaction.

Pentaerythritol derivatives do not work when used in click reaction to make star polymers as described before by Matyjaszewski and Sharpless. As a result, the arm-first click reaction with two arms and four arms failed. Click reaction with three arms showed a small shift to higher molecular weight, but this molecular weight did not correspond with the expected molecular weight of the product. Changing the solvent for the reaction from THF to DMF showed an improvement on the conversion of the reaction. The use of L-ascorbic acid showed a slight positive effect on the conversion and the fraction of higher molar mass material increased, but still no pure three arm polymer was obtained. MALDI-ToF-MS did not show the presence of the product and thus the synthesis of the three arm polymer using the arms first method did not succeed.

The multifunctional initiators used for the core-first method were successfully employed to make star polymers. SEC shows chain end functionalization of star polymer with click chemistry, implying that the azide chain end substitution did work. We are not able to
quantify the chain end after the azide functionalization and subsequently we cannot say anything about the yield of the click reaction.

Three coumarin derived monomers were successfully synthesized. Experiments were conducted to functionalize the polymer chain-end with one coumarin monomer. In most of the experiments a higher functionality was obtained when an excess of the monomer was employed and an increase of the amount of copper did not lead to a pronounced effect on the functionality obtained. Although the propyl ligand is known to be very effective for the controlled polymerization of a range of methacrylates, it showed a poor activity in the chain extension of pMMA with 4-MUMA. Me₆TREN gave good results although it is known to be a relatively poor ligand for methacrylates. In contrast, Me₆TREN acted as a poor ligand with 4-MUA and almost no chain extension occurred. A spacer was found to result in an increase in the functionality when HEMUMA was compared to 4-MUMA.

After fine tuning the reaction conditions it can be concluded that we successfully chain extended the polymer chain ends with one 4-methyl umbelliferone methacrylate of both linear and 3 and 5 arm pMMA. For complete chain extension we employed 5 equivalents of a coumarin modified methacrylate monomer to the polymer chain end in combination with a ratio Cu'IBr: Cu''Br of 1.1 to 1 and Me₆TREN as the ligand.
4.6 Experimental

4.6.1 Materials

All solvents and reagents were purchased from Aldrich Chemical Co. and used without further purification (unless mentioned otherwise). All the monomers used were purified prior to use by means of purification over a column packed with neutral (or basic) aluminum oxide. All characterization techniques are described in Appendix 1.

4.6.2 4-methyl-coumarin-7-yl 2-bromo-2-methylpropanoate (I).

![Figure 4.14: Synthesis of coumarin initiator.](image)

4-Methylumbelliferone (0.066 mol; 12 g) and triethyl amine (0.10 mol; 14 mL) were dissolved in 400 mL THF and placed together in a 3-necked round-bottom flask. The mixture was magnetically stirred and was left to react at ambient temperature for about 30 minutes. The temperature was cooled to 0 °C and 2-bromo isobutyrylbromide (0.10 mol; 12.4 mL) was added dropwise to the mixture. This was allowed to react for an hour. Triethylammonium bromide was formed, and upon completion, the ammonium salt was removed by filtration. THF was removed under reduced pressure and DCM was added. Two extractions were performed. The first extraction was with 1M HCl, the second one with brine. DCM was removed under reduced pressure. The product was re-crystallized from methanol and dried in the vacuum-oven. White crystals were obtained in a yield of 62%. MP 112 °C; $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 2.0 (s, 6H, CH$_3$), 2.4 (s, 3H, CH$_3$), 6.3 (s, 1H, CH), 7.1 (s, 1H, CH), 7.0 (d, 1H, CH), 7.6 (d, 1H, CH).
4.6.3 Tri-functional initiator (2).

Figure 4.15: Synthesis of initiator with three functional groups.

Tris(hydroxymethyl)ethane (50 mmol; 6.1 g) and triethylamine (166 mmol; 23 mL) were dissolved in 100 mL tetrahydrofuran in a 3-necked round bottom flask. The flask was cooled using an ice bath and drop wise, 2-bromoisobutyrylbromide (165 mmol; 20.4 mL) was added in 30 minutes. After addition, the reaction was allowed to warm up to ambient temperature and left to react overnight. The ammonium salt was filtered off. The filtrate was filtered over a basic aluminum oxide column, followed by the removing the solvent under reduced pressure. DCM was added and extraction was done using 1 M HCl. The organic layer was dried on MgSO4 and the solvent was removed under reduced pressure. The solids obtained were re-crystallized from methanol, which yielded white crystals. Yield: 22.9% MP 53 ºC; $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 1.2 (s, 3H, CH$_3$), 2.0 (s, 6H, CH$_2$), 4.2 (s, 18H, CH$_3$).

4.6.4 Synthesis of N-n-propyl-2-pyridyl-methanimine (propyl ligand) (3)

Figure 4.16: Synthesis of propyl ligand.

Pyridine-2-carboxyaldehyde (20 mL, 0.21 mol) was dissolved in diethyl ether (20 mL) and cooled in an ice bath. n- Propyl amine (20.5 mL, 0.25 mol) was added to the reaction mixture dropwise. Then Na$_2$SO$_4$ was added to dry the reaction mixture and the reaction was left
overnight at ambient temperature under argon flow. Na$_2$SO$_4$ was filtered off and diethyl ether was evaporated under reduced pressure. Finally a vacuum distillation at a pressure of $7.7 \times 10^{-1}$ mbar was performed for purification. The temperature of oil bath was 82.6°C and the fraction coming at 45-50 °C was collected. $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 1.0 (d, 3H, CH$_3$), 1.7 (t, 2H, CH$_2$), 3.6 (d, 2H, CH$_2$), 7.2 (t, 1H, CH), 7.7 (t, 1H, CH), 8.0 (s, 1H, CH), 8.3 (d, 1H, CH), 8.6 (d, 1H, CH).

### 4.6.5 General polymerization procedure

Initiator (1) (1.26 mmol; 410 mg), Cu(I)Br (1.25 mmol; 180 mg), iso-butyl methacrylate (62.4 mmol; 10 mL) and 40 mL of toluene were charged to a Schlenck tube at the same time. Oxygen is removed by purging with argon for 25-30 minutes. The propyl ligand (3) (2.63 mmol; 0.41 mL) was added to start the reaction. The reaction was maintained at 70 ºC for seven hours. The reaction was stopped by a flow of air through the mixture and by dilution with THF. The catalyst was removed by passing the diluted reaction mixture over a basic aluminum oxide column and subsequently the solvent is removed under reduced pressure. The product was obtained by precipitation in cold methanol: water (2:1). The polymer is dried in a vacuum-oven. Conversion: 70%. $M_n = 5570$ g/mol; PDI = 1.11.

### 4.6.6 Azide functionalization

![Figure 4.17: Nucleophilic substitution of bromide chain-end.](image)

Poly iso-butyl methacrylate (0.54 mmol; 3.0 g; $M_n=5570$) and NaN$_3$ (1.85 mmol; 0.12 g) were put in a 50 mL 3-necked round bottom flask and dissolved in 40 mL of N,N-di methyl formamide (DMF). Reaction was allowed to react at 40 ºC for two days. Water was added and extraction was done with diethyl ether: dichloromethane 4:1 (v/v). The organic layers
were collected and the solvent was removed under reduced pressure. Precipitation was done in cold methanol: water 2:1 (v/v) and the product was dried under vacuum.

4.6.7 Synthesis of 4-methyl-7-(prop-2-ynyloxy) coumarin (4)

![Synthesis of coumarin-alkyne](image)

4-Methyl umbelliferone (15.1 mmol; 2.45 g) was dissolved in 70 mL DMF and cooled to 0 °C. In small portions, sodium hydride (15.9 mmol; 0.63 g; 60% wt in mineral oil) was added. The reaction was kept at 0 °C for 30 minutes. Propargyl bromide (23.2 mmol; 2.0 mL; 80% wt in toluene) was slowly added maintaining the low temperature. After addition the mixture was allowed to warm up to ambient temperature and left to react for 3.5 hours. Water (400 mL) was added which resulted in precipitation of the product. The product was filtered off and dried under vacuum. A white solid was obtained in 98% yield (14.9 mmol; 3 g). MP 132 °C; \(^1\)H NMR (CDCl\(_3\), 298 K, 400 MHz) δ 2.4 (s, 3H, CH\(_3\)), 2.6 (s, 1H, CH), 4.8 (s, 2H, CH\(_2\)), 6.2 (s, 2H, CH\(_2\)), 6.8 (s, 1H, CH), 6.9 (s, 1H, CH), 7.5 (s, 1H, CH).
4.6.8 Synthesis of tri functional alkyne (5)

![Chemical structure of tri functional alkyne (5)](image)

**Figure 4.19:** Synthesis of tri-alkyne

4-((N, N-dimethylamino)pyridine (24.5 mmol; 3.0 g) and 1,1,1-tris(4-hydroxyphenyl)ethane (3.26 mmol; 1.0 g) dissolved in 100 mL dichloromethane were put together in a 3-necked round bottom flask. The mixture was cooled to -15 °C and propargyl chloroformate (19.6 mmol; 1.9 mL) was added drop wise in twenty minutes. The reaction was allowed to warm up to ambient temperature and reacted for 24 hours. Extraction was carried out with 1 M HCl. The organic layer was collected and extracted with brine. The organic layer was dried using MgSO₄ and filtered after drying. The solvent was removed under reduced pressure. A viscous colorless liquid was left which later on crystallized. MP 79-84 ºC. $^1$H NMR (CDCl₃, 298 K, 400 MHz) δ 2.27 (s, 3H, CH₃), 2.77 (s, 3H, CH), 4.72 (s, 6H, CH₂), 7.07 (dd, 6H, CH), 7.18 (dd, 6H, CH).

4.6.9 Synthesis of di functional alkyne (6)

The synthetic procedure was followed as described for the synthesis of di functional alkyne (5) except that the starting material was neopentyl glycol. $^1$H NMR (CDCl₃, 298 K, 400 MHz) δ 0.9 (s, 6H, CH₃), 2.5 (s, 2H, CH), 3.9 (s, 4H, CH₂), 4.7 (s, 4H, CH₂).
4.6.10 Synthesis of tetra functional alkyne (7)

The synthetic procedure was followed as described for the synthesis of tetra functional alkyne (5) except that the starting material was pentaerythritol. $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) $\delta$ 2.7 (s, 4H, CH), 4.7 (dd, 16H, CH$_2$).

4.6.11 Click reactions

![Click Reaction Diagram]

Figure 4.20: Click reaction of alkyne

piBMA-N$_3$ (0.31 mmol; 1.00 g), coumarin-alkyne 4 (0.34 mmol; 73.0 mg) and Cu(I)Br (0.136 mmol; 20.0 mg) were put together with 30 mL THF in a Schlenck tube. The mixture was magnetically stirred and the reaction was purged with argon for twenty minutes. 1,8-diazabicyclo[5.4.1]-undec-7-en was added and the reaction was kept at ambient temperature for seven days under argon atmosphere. The reaction was stopped by a flow of air through the mixture, deactivating the Cu(I)Br catalyst. It was put over a basic aluminum oxide column to remove the catalyst and the solvent was removed under reduced pressure. The product was obtained by precipitation from cold methanol: water (2:1). Volatiles were removed in a vacuum-oven.
4.6.12 4-methyl umbelliferone methacrylate (4-MUMA) (8)

![Chemical structure of 4-MUMA](image)

**Figure 4.21**: Synthesis of 4-MUMA.

The round bottom flask was charged with 4-MU (20.013 g, 0.082 mol), triethylamine (20.8 mL, 0.206 mol) and THF (400 mL). The reaction mixture was stirred at ambient temperature for 1 hour and then immersed in an ice bath. Methacryloyl chloride (13 mL, 0.132 mol) was added dropwise and left to react for 1 h at ambient temperature. The amine salt removed by filtration and THF by evaporation. The residue was dissolved in DCM and extracted twice with 1M HCl and once with brine. The organic layer was concentrated under vacuum after drying with Na$_2$SO$_4$ and 27 grams of white solid was obtained (yield = 97.2 % with a purity of >98%). \textsuperscript{1}H NMR (CDCl$_3$, 298 K, 400 MHz) δ 2.0 (s, 3H, CH$_3$), 2.4 (s, 3H, CH$_3$), 5.6 (s, 1H, CH), 6.2 (s, 1H, CH), 6.4 (s, 1H, CH), 7.1 (m, 2H, CH), 7.8 (d, 1H, CH).

4.6.13 Hydroxy ethyl 4-methyl umbelliferone (HEMU) (9)

Despite reports in the literature\textsuperscript{[19-21]}, it was not possible to achieve high yields for the synthesis of HEMU, although different procedures employing different solvents (THF, EtOH, DMF), base systems (K$_2$CO$_3$/NaI, NaH) and reaction times were studied.

![Chemical structure of HEMU](image)

**Figure 4.22**: Synthesis of HEMU
The round bottom flask was charged with 4-MU (10.06 g, 0.057 mol), K$_2$CO$_3$ (6.013 g, 0.043 mol), KI (0.501 g, 0.003 mol) and THF (100mL) and the system which was a clear yellow liquid with white solid at the bottom was refluxed under argon flow. After 2 hours mixing, bromo ethanol (5.75 mL, 0.081 mol) was added and after 1 day another 5.75 mL (0.081 mol) of bromo ethanol was added. The reaction stopped after 2 days. The color turned to very pale yellow. The salt was filtered off and THF was evaporated. The residual solid was dissolved in chloroform (partially) and extracted with water. Organic layers were combined, dried with Na$_2$SO$_4$ and the solvent was evaporated. To purify the product it was recrystallized from MeOH and white crystals were obtained in a yield of 20%. $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 1.9 (s, 1H, OH), 2.4 (s, 3H, CH$_3$), 4.0 (t, 2H, CH$_2$), 4.2 (t, 2H, CH$_2$), 6.2 (s, 1H, CH), 6.8 (s, 1H, CH), 6.9 (d, 1H, CH), 7.5 (d, 1H, CH).

4.6.14 Hydroxy ethyl 4-methyl umbelliferone methacrylate (HEMUMA)(10)

The same procedure was used as described in 4.6.12. Starting material was 4-HEMU (9). $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 2.0 (s, 3H, CH$_3$), 2.4 (s, 3H, CH$_3$), 4.3 (t, 2H, CH$_2$), 4.5 (t, 2H, CH$_2$), 5.6 and 6.8 (s, 2H, CH$_2$), 6.2 (s, 1H, CH), 6.8 (s, 1H, CH), 6.9 (d, 1H, CH), 7.5 (d, 1H, CH).

4.6.15 4-methyl umbelliferone acrylate (4-MUA) (11)

The same procedure was used as described in 4.6.12 except methacryloyl chloride was used instead of acryloyl chloride. $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) δ 2.4 (s, 3H, CH$_3$), 6.1 and 6.7 (s, 2H, CH$_2$), 6.4 (s, 1H, CH), 6.4 (t, 1H, CH), 7.1 (d, 1H, CH), 7.2 (s, 1H, CH), 7.6 (d, 1H, CH).

4.6.16 Functionalization of linear and star pMMA-Br end with coumarin monomers

The insertion of (Meth) acrylate-coumarin monomers was done in toluene via modified ATRP conditions. The ratio of the monomer used to the polymer chain end and the ratio of
monomer to Cu(I) and Cu(II) were varied and the different types of ligands were studied to make a comparison. After the reaction was done, toluene was removed under vacuum. The polymer was dissolved in THF and precipitated twice from MeOH: water (2:1).

4.7 References

Abstract

Coumarin is an interesting compound for the introduction of additional functionality in polymers. In this chapter the use of 4-methyl umbelliferone as a monomer in the synthesis of (block) copolymers is described. The monomer reactivity ratios of MMA and 4-methyl umbelliferone methacrylate are given as determined using the Jaacks method.
5.1 Introduction

In this chapter we describe the synthesis of various (block) copolymers of methacrylates (MMA and DMAEMA) and 4-methyl umbellifereone methacrylate (4-MUMA). The general purpose is to investigate the crosslinking behavior of these polymers. In order to provide crosslinking characteristics we must ensure an average content of > 2 umbelliferone moieties per polymer chain in order to obey the requirement for network formation\cite{1}.

The network can be formed in solution resulting in an insoluble gel ('hydrogel' when crosslinking occurs in aqueous environment\cite{2}) or a crosslinked coating when performed in the solid state.

In literature some examples are given of the crosslinking of (block) copolymers employing coumarin derivatives. Zhao et al.\cite{3} reported on the stabilization of polymer micelles by using block copolymers of pEO (ethylene oxide) and HEMUMA (7-(2-methacryloyloxyethoxy)-4-methylcoumarin). They used the different solubilities of the separate blocks and in that manner made micelles that crosslinked upon irradiation.

Chen et al.\cite{4,5} reported on the copolymerizability of 7-acryloyloxy-4-methylcoumarin and N-\((1\text{-phenylethyl})\text{acrylamide}\) and later on the copolymerizability of acrylates. In both cases they used free radical copolymerization to produce the copolymers. Most recently Long et al.\cite{6} reported on the random poly(alkyl (meth)acrylate)s containing coumarin moieties, they first prepared random copolymers by free radical polymerization of \(n\)-BA (butyl acrylate) and 2-HEA (hydroxy ethyl acrylate) and functionalized the HEA moieties afterwards with an acid chloride derivative of 4-methyl coumarin.

In all the cases the dimerization behavior is studied of the polymers made. In general not much is known on the behavior of coumarin functional monomers in controlled radical polymerizations and the monomer reactivity ratios. In order to predict the copolymerization behavior of 4-MUMA with MMA we need to measure the reactivity ratios of both monomers.
5.2 Determination of reactivity ratios of MMA and 4-MUMA

The instantaneous composition of a copolymer build-up from two monomers \(M_1\) and \(M_2\) can be described by the Mayo-Lewis equation\[^7\] using the terminal model. The two monomers, \(M_1\) and \(M_2\) can react in four different fundamental steps with corresponding rate coefficients \(k_{ij}\):

\[
\begin{align*}
\text{M}_1^* + M_1 & \xrightarrow{k_{11}} \text{M}_1^* \\
\text{M}_1^* + M_2 & \xrightarrow{k_{12}} \text{M}_2^* \\
\text{M}_2^* + M_1 & \xrightarrow{k_{21}} \text{M}_1^* \\
\text{M}_2^* + M_2 & \xrightarrow{k_{22}} \text{M}_2^*
\end{align*}
\]

The reactivity ratios are defined as:

\[
\begin{align*}
 r_1 &= \frac{k_{11}}{k_{12}} \\
 r_2 &= \frac{k_{22}}{k_{21}}
\end{align*}
\]

For the copolymer the instantaneous composition can be given following the Mayo-Lewis equation:

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_1] + r_2[M_2])}
\]

As mentioned above the reactivity of a monomer determines the copolymer composition. There are several methods available for the determination of the reactivity ratio. There can be made a division between the linearized and non-linearized methods. Examples of the linearized methods are described by:

- Kelen–Tüdos\[^8\]
- Fineman–Ross\[^9\]
- O’Driscoll–Reilly\[^10\]
Examples of the non-linearized methods are:

- nonlinear least square (NLLS) by Tidwell\textsuperscript{[11]}
- error--in--variables model (EVM) by Patino-Leal \textit{et al.}\textsuperscript{[12]}

Many more methods that are largely variations on and combinations of the methods mentioned above are reported in the literature\textsuperscript{[13]}. We make use of another linearized method according to Jaacks\textsuperscript{[14]} to get an initial parameter estimate for the reactivity ratios of MMA and 4-MUMA. In the Jaacks method we make use of $^1$H NMR to determine the residual monomer during the polymerization and follow the conversion of both monomers in time.

The linear expression\textsuperscript{[15]} to determine the monomer reactivity ratio (MRR) is:

$$\ln \left\{ \frac{[M_1]}{[M_2]} \right\} = r_1 \times \ln \left\{ \frac{[M_2]}{[M_1]} \right\}$$

There are a number of restrictions in the Jaacks method that need to be taken into account:

- appropriate excess of the monomer to be evaluated
- ability of homopolymerization of the monomer used in excess
- polymerizations are required to proceed to high conversions (\textit{ca.} 80 \%)

For the controlled radical polymerizations we have compared ATRP and RAFT mediated polymerization employing two different RAFT agents. Both RAFT agents and the ATRP initiator we have used are given in Figure 5.1.

\textbf{Figure 5.1:} Structures of RAFT agents DIBTTC and ethyl isobutyryl dithiobenzoate and ATRP initiator eBiB.
We performed all polymerizations using an initial molar ratio of 0.965 to 0.035 of MMA to 4-MUMA. The reactions were performed at 65 °C and are followed to high conversion. In this way we obey the requirements needed for the Jaacks method.

From the linear expression we showed before we can determine the reactivity ratio of the monomer used in excess. Figure 5.2 shows a typical Jaacks plot resulting from the ATRP and giving the conversion of both monomers. From the slope of the plot we determine the reactivity ratio of MMA \( r_{\text{MMA}} \) as being 0.44 for an initial molar fraction of 0.965.

![Jaacks plot of MMA: 4-MUMA (96.5: 3.5) with ATRP at 65 °C.](image)

**Figure 5.2:** Jaacks plot of MMA: 4-MUMA (96.5: 3.5) with ATRP at 65 °C.

Similar to the ATRP, we determined the reactivity ratio of MMA from the Jaacks plot when employing the RAFT agents. The results obtained from the polymerizations are given in table 5.1.
Table 5.1: Reactivity ratios of MMA \( r_{\text{MMA}} \) in ATRP and RAFT mediated copolymerizations with 4-MUMA as the comonomer. \( r_{\text{MMA}} \) determined according to the Jaacks method.

<table>
<thead>
<tr>
<th>Polymerization</th>
<th>Final conversion MMA</th>
<th>Final conversion 4-MUMA</th>
<th>( r_{\text{MMA}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAFT (1)</td>
<td>86</td>
<td>99</td>
<td>0.410</td>
</tr>
<tr>
<td>RAFT (2)</td>
<td>48</td>
<td>77</td>
<td>0.44</td>
</tr>
<tr>
<td>ATRP</td>
<td>65</td>
<td>91</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The values for the reactivity ratio of MMA that we have found are similar for the ATRP and RAFT mediated polymerization. As the copolymerization of MMA and 4- MUMA is not described in the literature, to the best of our knowledge, we cannot directly compare the values with reported values. The copolymer system that comes close is a copolymerization of MMA with HEMA giving a \( r_{\text{MMA}} \) of 0.63, see entry 1 in table 5.2. Compared to HEMA, 4-MUMA has an extra bulky group that can influence the reactivity and this bulky group is perhaps the reason for the difference in reactivity of the MMA. Some other important values we found in the literature are also collected in table 5.2. The differences with the literature can be attributed to the difference in the polymerization medium and the co-monomer combination.

Table 5.2: Literature values of MMA monomer reactivity ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Type of polymerization</th>
<th>Co-monomer</th>
<th>Solvent</th>
<th>( r_{\text{MMA}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NMP</td>
<td>HEMA[16]</td>
<td>Toluene</td>
<td>0.63</td>
</tr>
<tr>
<td>2</td>
<td>Free radical</td>
<td>HEMA[16]</td>
<td>Toluene</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>Free radical</td>
<td>4-MUA[8]</td>
<td>DMF</td>
<td>1.68</td>
</tr>
<tr>
<td>4</td>
<td>ATRP</td>
<td>MA[17]</td>
<td>bulk</td>
<td>1.88-2.09</td>
</tr>
</tbody>
</table>

With the reactivity ratio of MMA we determined from the Jaacks method we estimated the monomer reactivity of 4-MUMA using the integrated conversion equation:

\[
\text{Conversion} = 1 - \frac{1}{r_{\text{MMA}}}
\]
In the equation $f_{i,0}$ and $f_i$ are the initial and instantaneous molar fractions of monomer $i$ in the feed.

$$\alpha = \frac{r_2}{1-r_2}, \quad \beta = \frac{r_1}{1-r_1}, \quad \delta = \frac{1-r_1 \cdot r_2}{(1-r_1) \cdot (1-r_2)} \text{ and } \gamma = \frac{1-r_2}{2-r_1-r_2}$$

From the copolymers we have synthesized we have used the values for $f_{i,0}$ and $f_i$ of both MMA and 4-MUMA and from this we found an average value of $0.88 \pm 0.1$ for $r_{4\text{-MUMA}}$.

From both the MRR of MMA and 4-MUMA we can show now in a Mayo-Lewis plot how the reactivity ratios affect the copolymer composition. When we say that $F_1$ and $F_2$ are the molar fractions of MMA and 4-MUMA in the copolymer, respectively and $f_1$ and $f_2$ the corresponding instantaneous molar fractions of the monomers in the feed, we can then use the copolymerization equation to predict $F_1$ and $F_2$:

$$F_i = \frac{(r_i f_1^2 + f_i f_2)}{(r_i f_1^2 + 2 f_i f_2 + r_2 f_2^2)}$$

The resulting plot from the copolymerization equation is shown in figure 5.3.

![Figure 5.3: Mayo-Lewis plot of the MMA-4-MUMA copolymerization.](image)
Chapter 5

The point where \( F_{\text{MMA}} = f_{\text{MMA}} \) is the azeotropic copolymer composition and when employing a copolymerization at this composition the resulting copolymer will have that exact composition and will have no heterogeneity caused by composition drift.

5.3 Synthesis of (block) copolymers of MMA, DMAEMA and 4-MUMA

For coating applications we prepared copolymers of MMA with 4-MUMA. In order for the polymers to be able to crosslink they should have an average functionality of \( > 2 \). The molar fractions of 4-MUMA within the copolymers we have chosen are comparable to the star shaped polymers that we have prepared as described in Chapter 4. The 3 arm and 5 arm star polymers bearing 4-MUMA groups, which we prepared, have 6.5 and 10 mol\% 4-MUMA respectively. In order to directly compare the properties of the star polymers and random or block copolymers in the reversible dimerization we have tuned the amount of 4-MUMA to match the molar amount of the star polymers.

In table 5.3 we give the properties of the copolymers we have prepared. We also prepared a copolymer of 4-MUMA and DMAEMA as we expect that the polarity will positively influence the dimerization behavior of the coumarin. Copolymers 1-3 (in table 5.3) are copolymers of MMA \((x + R1)\) and 4-MUMA \((y)\), copolymer \( R2 \) is a copolymer of DMAEMA \((x + R2)\) and 4-MUMA \((y)\). The block copolymer in table 5.3 is a homopolymer.

**Figure 5.4:** Structure of the (block) copolymer of MMA \((x + R1)\) or DMAEMA \((x + R2)\) and 4-MUMA \((y)\) with ATRP.
of MMA (x + R1) chain extended with 4-MUMA (y). The values in the columns x and y, in table 5.3, represent the number of repeating units of the monomers in the (block) copolymers.

**Table 5.3:** Properties of (block) copolymers of MMA, DMAEMA and 4-MUMA made with ATRP.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>x</th>
<th>y</th>
<th>Mol % 4-MUMA</th>
<th>$M_n$ (g/mol)</th>
<th>$M_n/M_w$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer 1</td>
<td>84</td>
<td>5</td>
<td>6.5</td>
<td>8220</td>
<td>1.74</td>
<td>115.3</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>32</td>
<td>3</td>
<td>10</td>
<td>4220</td>
<td>1.54</td>
<td>99.9</td>
</tr>
<tr>
<td>Copolymer 3</td>
<td>16</td>
<td>4</td>
<td>20</td>
<td>2440</td>
<td>1.45</td>
<td>96.8</td>
</tr>
<tr>
<td>Copolymer R</td>
<td>32</td>
<td>4</td>
<td>16</td>
<td>7020$^*$</td>
<td>1.40</td>
<td>28.2</td>
</tr>
<tr>
<td>Block copolymer 1</td>
<td>23</td>
<td>3</td>
<td>22.5</td>
<td>3260</td>
<td>1.27</td>
<td>109.2</td>
</tr>
</tbody>
</table>

$^*$: $M_n$ determined based on PSTY standards

From the copolymerization we can say the incorporation of coumarin provides an increase in the $T_g$. When we compare the value of copolymer 2, having three 4-MUMA monomer units, with the model compound described in chapter 4 (entry pMMA in table 4.1) having a similar molecular weight but only one 4-MUMA unit and having a $T_g$ of 85.2°C an increase of the final $T_g$ of the copolymer is observed. This conclusion is certainly valid in the case of DMAEMA, where the homopolymer of DMAEMA (containing no 4-MUMA) has a $T_g$ of 9-11°C, with a similar molecular weight, and the $T_g$ for the copolymers is 28.2°C.

**5.4 Conclusions**

Determination of the reactivity ratio of MMA was done utilizing the linearized Jaacks method. We have used two different RAFT agents in the RAFT mediated polymerization in order to determine whether the RAFT agent has any influence on the reactivity ratio. The reactivity ratio of MMA had a value = 0.41 and 0.44 for DIBTTC and ethyl isobutyryl dithiobenzoate, respectively. When employing ATRP we find a reactivity ratio = 0.44 for MMA. In literature, to the best of our knowledge, no reactivity ratios are given for this
specific system, the one system that comes the closest is described by Ydens \textit{et al.}\textsuperscript{[10]} describing the copolymerization of MMA and HEMA. They found a value \(= 0.63\) for the MRR of MMA employing NMP.

After determining the reactivity ratio of MMA using the Jaacks method we used the integrated conversion equation to determine the reactivity ratio of 4-MUMA as 0.88.

We successfully prepared a range of copolymers that can be used for crosslinking experiments. The (block) copolymers all had more than two 4-MUMA groups in order to be able to form networks upon dimerization. The molar ratios were chosen in such a way that they correspond to the molar ratios of the star polymers we have prepared as described in chapter 4.

5.5 Experimental

All chemicals were used as received unless mentioned otherwise. MMA was purified by means of removal of the inhibitor over a column packed with basic alumina. 4-MUMA was prepared as described in Chapter 4 section 4.6.12. Details on the methods used for analysis can be found in Appendix 1. The trithiocarbonate RAFT agent DIBTTC was prepared as described in literature\textsuperscript{[18]}.

5.5.1 Synthesis of isobutyrate dithiobenzoate (2)

Phenyl magnesium bromide was synthesized from bromobenzene (6.3 g, 40 mmol) and magnesium turnings (1.00 g, 40.6 mmol) in dry THF (30 mL). Carbon disulfide (3.00 g, 39.4 mmol) was added to the solution maintaining the reaction temperature below 35 °C. Ethyl -2-bromoisobutyrate (7.00 g, 35.9 mmol) is placed in a dropping funnel and added slowly to the reaction mixture. After addition, the mixture is heated to 75 °C and left to react for two days. The reaction mixture is cooled to ambient temperature and the solvent is removed by evaporation under reduced pressure. To the concentrate, ice water is added (50 mL) and the water phase is extracted three times with diethyl ether (3 times 50 mL). the combined organic extracts are washed with brine and dried over anhydrous magnesium sulphate. After
filtration the solvent is removed under reduced pressure yielding a dark red viscous liquid in 65% yield (6.26 g, 23.3 mmol). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.2 (t, 3H, CH$_3$), 1.8 (s, 6H, CH$_3$), 4.2 (q, 2H, CH$_2$), 7.2 (dd, 1H, CH), 7.3 (m, 2H, CH), 7.8 (m, 2H, CH).

5.5.2 RAFT mediated copolymerization of MMA and 4-MUMA

In a Schlenck tube the MMA (5.0 mL; 49 mmol) and 4-MUMA (0.43 g, 1.76 mmol) were put together with AIBN (33 mg, 0.2 mmol), toluene (5 mL) and the RAFT agent (I; 0.37 g, 1.0 mmol). The reaction mixture was degassed at ambient temperature for 30 minutes and afterwards was inserted into a preheated oil bath at 65 °C. At regular intervals samples were taken and the conversion of both monomers was determined with $^1$H NMR.

5.5.3 ATRP copolymerization of MMA and 4-MUMA

In a Schlenck tube the MMA (5.0 mL; 49 mmol) and 4-MUMA (0.43 g, 1.76 mmol) were put together with Cu$^\text{I}$Br (0.144 g, 1.00 mmol), ethyl bromoisobutyrate (3, 0.195 g, 1.00 mmol) and toluene (5 mL). The reaction mixture was degassed at ambient temperature for 30 minutes and was inserted afterwards into a preheated oil bath at 65 °C. The reaction was started by adding the ligand (N-(n-propyl)-2-pyridylmethanimine; 0.16 g, 1.0 mmol). At regular intervals samples were taken and the conversion of both monomers was determined with $^1$H NMR.
5.6 References

Abstract

In this chapter we look at the dimerization and photo cleavage of model polymers. These polymers contain one coumarin or a fully dimerized coumarin functional group. Next to the model compounds we look at the dimerization of the (block) copolymers and star polymers of which the preparation was described in the previous chapters. Finally we look at the reversible character of star polymers.
6.1 Introduction

In this chapter we discuss the reversible dimerization properties of the polymers synthesized as described in the previous chapters. We study the dimerization and photo cleavage of model compounds and compare the reversible dimerization of (block) copolymers and star polymers.

With the model compounds we look at different (meth)acrylate polymers and the influence of $T_g^{[1, 2]}$ and polarity$^{[3]}$ on the surroundings of the coumarin functionality and the dimerization. In this way we aim to determine the possibilities and limitations of the reversible dimerization process. Figure 6.1 shows the reversible dimerization of the 4-MU (4-methyl umbelliferone) initiator under the influence of UV light of different wavelength.

![Figure 6.1: Reversible dimerization of 4-MU ATRP initiator (1)](image)

As we described in Chapter 4, star polymers have improved properties compared to their linear analogs. Here we look at the dimerization and subsequent photo cleavage of these star polymers bearing one coumarin functional group at the polymer chain ends of the arms. We then compare these star polymers bearing coumarin functional chain ends to copolymers having the same molar amount of coumarin functional groups incorporated in the polymer backbone.
6.2 Dimerization in solution

In literature a lot of results are described on the dimerization of low molecular weight coumarin molecules in solution and the different effects that play a role in the dimerization, such as:

- Polarity (solvent effects)\(^\text{[3]}\)
- Coumarin substituents on the 4 and 7 position\(^\text{[4]}\)
- Use of photo sensitizer\(^\text{[5-7]}\)
- Wavelength used for irradiation

We have discussed these influences in detail in Chapter 2.

We describe here the effects of two different photo sensitizers used. Figure 6.2 shows the structures of the two photo sensitizers we have used. First we have performed dimerizations of the 4-methyl umbelliferone initiator using the standard photo sensitizer benzophenone. This sensitzing agent has a broad overlap in UV absorbance with the 4-MU initiator to be dimerized, see figure 6.3. We think that this overlap in absorbance is the cause that benzophenone does not really act as a classical sensitizing agent as we have described in chapter 2.2. For this reason we have tested a substituted benzophenone, \(i.e.\) 4,4\(^\prime\)-bis(dimethylamino) benzophenone, which has only partial overlap in UV absorbance with the initiator. We have performed several dimerizations in dry dichloromethane at ambient temperature with and without photo sensitizer.

![Figure 6.2: Structure of Benzophenone (3) and substituted Benzophenone (4)](image-url)
Figure 6.3: Overlaid UV-Vis spectra of substituted benzophenone, Benzophenone, pMMA-4-MUMA and pMMA dimerized.

In order to quantify the extent of reaction, we need to determine the conversion of the coumarin. This can be done in several ways:

- UV-Vis spectroscopy
- IR spectroscopy
- $^1$H NMR spectroscopy
- Size exclusion chromatography (SEC)

Contrary to what we expected, the substituted benzophenone did not give any dimerization. We checked the dimerization during an irradiation period of 22 hours using UV-Vis and $^1$H NMR spectroscopy. We did not observe any conversion to the desired dimerized product. We also performed some dimerization experiments under the same conditions without any photo sensitizer present and also here we did not observe any conversion to the dimer.

Even when using the benzophenone as photo sensitizer, the dimerization reaches only 60 % conversion after 22 hours. We followed the conversion with $^1$H NMR, we did not measure UV-Vis because of the overlap in absorbance of the 4-MU initiator and the benzophenone.
Figure 6.4: Dimerization of 4-MU initiator (1).

Figure 6.5 shows the dimerization of the 4-MU initiator with the numbers showing the protons of the 4-MU initiator. The letters correspond with the protons in the dimerized 4-MU initiator, shown in the corresponding $^1$H NMR spectra, before and after dimerization using benzophenone, see figure 6.6.

![Diagram of 4-MU initiator and its dimerization](image)

**Figure 6.5:** Dimerization of 4-MU initiator under influence of UV A light.

In spectrum a) we show the $^1$H NMR spectrum of the reaction mixture (after evaporation of the dichloromethane) consisting of benzophenone, 4-MU initiator and dimerized 4-MU initiator. In spectrum b) we show the pure starting material and in c) the purified product. The most important shift is the peak at 6.3 ppm of the $\text{-CH=C}$ moving upfield to 3.5 ppm. These peaks are used to determine the conversion.
Figure 6.6: $^1$H NMR spectra of a) reaction mixture consisting of benzophenone, 55.3 % 4-MU-initiator and 44.7 % 4-MU initiator dimer; b) 4-MU initiator; c) 4-MU init. dimer with a trace of benzophenone.
6.3 Dimerization of model compounds

Next to dimerization in solution we looked at the dimerization in polymeric solid thin films. We studied the dimerization behavior of both model compounds, bearing only one coumarin functional group per polymer chain and (block) copolymers containing multiple coumarin functionalities per polymer chain. The dimerization of the model compound, bearing one coumarin moiety, is depicted in figure 6.7.

![Dimerization of pMMA with 4-MU initiator under the influence of UV A light.](image)

**Figure 6.7:** Dimerization of pMMA with 4-MU initiator under the influence of UV A light.

When using UV-Vis spectroscopy we can look at the decrease of the double bond in the lactone ring that is converted into the cyclobutane ring as we can see in figure 6.8.

![UV-Vis spectroscopy of pMMA in solid film; Irradiation using UV A light.](image)

**Figure 6.8:** UV-Vis spectroscopy of pMMA in solid film; Irradiation using UV A light.
To verify that this decrease is caused by the conversion of the double bond and not by degradation of the polymer backbone and/or the coumarin functional group, we used some other techniques to verify the decrease of the UV absorbance. We dimerized a model compound and analyzed it with SEC and MALDI-TOF-MS. Upon dimerization we expect to obtain the double molecular weight of the starting material. We observed this as can be seen in figure 6.9 and 6.10.

**Figure 6.9:** SEC traces before and after dimerization of pMMA bearing a coumarin functional end group.

The sample after dimerization was subjected to fractionation before analysis with MALDI-TOF-MS. In figure 6.10 we can clearly see the starting material with the lower molecular weight and the double molecular weight resulting from the dimerization. With this we prove that the decrease in UV absorbance is caused by the dimerization.
Figure 6.10: MALDI-ToF-MS of pMMA after 4 hours of dimerization. The sample after dimerization was fractionated before MALDI-ToF-MS analysis.

To investigate the influence of mobility we prepared a range of (meth)acrylate polymers bearing a coumarin chain end functionality. The different polymers that were synthesized and tested on their dimerization are given in Table 6.1. The molecular weights are in the range from 3000 to 6000 g/mol and were synthesized using the 4-MU initiator (I). The different monomers chosen provided a wide range of glass transition temperatures from -58 to 85 °C.

Table 6.1: Different polymers made with 4-MU initiator.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_n (g/mol)</th>
<th>M_w/M_n</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pMMA-1</td>
<td>4260</td>
<td>1.15</td>
<td>85.2</td>
</tr>
<tr>
<td>pBA-1</td>
<td>5180</td>
<td>1.50</td>
<td>-57.7</td>
</tr>
<tr>
<td>piBMA-1</td>
<td>5570</td>
<td>1.11</td>
<td>40.5</td>
</tr>
<tr>
<td>ptBMA-1</td>
<td>2670</td>
<td>1.66</td>
<td>45.6</td>
</tr>
<tr>
<td>pDMAEMA-1</td>
<td>9480*</td>
<td>1.33</td>
<td>11</td>
</tr>
</tbody>
</table>

* M_n determined based on PSTY standards and thus overestimated.

In Figure 6.11 we show the comparison in the dimerization behavior of the various model compounds. The results demonstrate that there is not much difference in the final
conversion and that the main differences occur in the initial stages of the dimerization process. There is a significant difference between the polymers with a \( T_g \) above and those with a \( T_g \) below ambient temperature. As can be seen, the polymers with a \( T_g \) below ambient temperature reach their maximum conversion much faster than compared to the polymers in the glassy state during the dimerization.

![Figure 6.11: Dimerization of different polymers bearing one coumarin moiety.](image)

When we compare the two polymers with the low \( T_g \) we would expect solely on the glass transition temperature that pBA (with the lower \( T_g \)) would have more mobility and thus reach the maximum conversion faster than pDMAEMA. The results show the opposite. We think this is due to the polarity of the polymer chain. As we know from the dimerization in solution, as described in literature, the polarity of the surroundings of the coumarin has an influence on the dimerization process\(^3\).

Long et al\(^2\) recently reported on similar polymers containing coumarin functionalities in different (meth) acrylates. They prepared them by copolymerization of the (meth) acrylate with hydroxyl ethyl acrylate (HEA) and afterwards modified the HEA with an acid chloride derivative of coumarin. The results they found are similar to what we have presented for the model compounds. However, they stop only after a short time of irradiation and do not say
anything about prolonged irradiation. They also relate the amount of dimerization to the
dosage of UV light and report the different copolymers after a total of 22 J cm\(^{-2}\) indicating a
total irradiation time of 10 minutes. When we compare this to our results using a UV dosage
of 0.69 J cm\(^{-2}\) per minute (measured at 24 °C) this would resemble an irradiation time of ~
32 minutes. When we then look at our results (figure 6.12) after this time of irradiation we
can conclude the same as Long et al. However, we also see that upon longer irradiation times
(irradiation time of 600 minutes; total UV A dosage 414 J cm\(^{-2}\)) we see a further increase in
the dimerization reaching high levels of conversion and that when employing such a high
dosage of UV light there is no vast difference between the different polymers.

### 6.4 Dimerization of (block) copolymers and star polymers

After investigation of the model compounds we have seen that even high \(T_g\) polymers give a
high conversion of the coumarin double bond. In order to form a network we have to
investigate the dimerization behavior of polymers bearing more than one coumarin
functional groups in the polymer backbone. For this we have prepared a range of (block)
copolymers with more than 2 functional groups. The preparation of these polymers was
described in Chapter 5. In table 6.2 we have summarized the polymers being prepared and
tested on the dimerization behavior.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(M_n) (g/mol)</th>
<th>(M_w / M_n)</th>
<th>Mol % 4-MUMA</th>
<th>Type of copol.</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pMMA-2</td>
<td>8220</td>
<td>1.74</td>
<td>6.5</td>
<td>Random</td>
<td>115.3</td>
</tr>
<tr>
<td>pMMA-3</td>
<td>4220</td>
<td>1.54</td>
<td>10</td>
<td>Random</td>
<td>99.9</td>
</tr>
<tr>
<td>pMMA-4</td>
<td>2440</td>
<td>1.45</td>
<td>20</td>
<td>Random</td>
<td>96.8</td>
</tr>
<tr>
<td>pDMAEMA-2</td>
<td>7020</td>
<td>1.40</td>
<td>16</td>
<td>Random</td>
<td>28.2</td>
</tr>
<tr>
<td>pMMA-5</td>
<td>3260</td>
<td>1.27</td>
<td>22.5</td>
<td>Block</td>
<td>109.2</td>
</tr>
</tbody>
</table>

As we can see in figure 6.12 there does not seem to be a significant difference between the
different copolymers having different molar fractions of 4-MUMA. Similar to the model
compounds we can see that the copolymer of DMAEMA and 4-MUMA reaches the maximum conversion much faster than the MMA copolymers. This confirms the trend we have observed with the model compounds and as we discussed can be contributed to the lower $T_g$ in combination with the polarity of the polymer.

![Figure 6.12: Dimerization of different (block) copolymers.](image)

After testing the copolymers we have dimerized the star polymers made as we described in Chapter 4. The star polymers we investigate have 3 and 5 arms with each polymer arm bearing one 4-MUMA functional group. The molar fraction of 4-MUMA for the star polymers is 6.5 and 10 mol % for the 3 and 5 arm stars respectively. In table 6.3 we give the details of the star polymers we have used for the dimerization experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Number of arms</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$/$M_n$</th>
<th>$T_g$ (°C)</th>
<th>Mol % 4-MUMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Star-1</td>
<td>3</td>
<td>11140</td>
<td>1.16</td>
<td>117</td>
<td>6.5</td>
</tr>
<tr>
<td>Star-2</td>
<td>5</td>
<td>11600</td>
<td>1.15</td>
<td>123.1</td>
<td>10</td>
</tr>
</tbody>
</table>

108
In figure 6.13 we can see that also in this case we do not see any difference between the two polymers. In order to compare the star polymers to the copolymers we also have depicted the dimerization of the copolymers in figure 6.13. Both star and copolymers reach the same level of dimerization and no big difference can be seen in the initial stages before the maximum conversion is reached.

**Figure 6.13:** Dimerization of 3 and 5 arm star polymers and the comparison with the copolymers containing the same molar amount of 4-MUMA.
6.5 Photo cleavage of model compounds

Next to the dimerization of polymers in solid thin films we investigated the photo cleavage. As opposed to the dimerization, the photo cleavage is not that well reported in literature. Next to this, mostly the photo cleavage of coumarin is discussed as part of the dimerization and the systems described are not fully dimerized. In order to solely look at the photo cleavage we have prepared a range of model compounds.

We have dimerized the 4-MU initiator and after purification used this difunctional ATRP reagent for the preparation of different polymers containing a fully dimerized core molecule, as is depicted in figure 6.14 the dimerization of the 4-MU initiator we have described in chapter 6.2.

![Dimerization reaction](image)

**Figure 6.14:** ATRP of MMA employing dimerized 4-MU initiator (2).

After we dimerized and purified the initiator we had to test its ability to function as an ATRP initiator. For this we followed the polymerization and as can be seen in figure 6.15 we obtained a linear increase of the molar mass upon conversion and a polymer with a low polydispersity. This indicates that the initiator is suitable for ATRP.
Switching properties of coumarin polymers

Figure 6.15: Linear increase of $M_n$ upon conversion of difunctional coumarin based initiator (2) together with the theoretical $M_n$, b) and a) the evolution of polydispersity upon conversion.

We employed this bifunctional initiator to prepare a range of polymers having a range of different $T_g$. The polymers we prepared are given in Table 6.4.

Table 6.4: Different polymers made with 4-MU dimer initiator.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pMMA-5</td>
<td>8780</td>
<td>1.10</td>
<td>96.6</td>
</tr>
<tr>
<td>pMMA-6*</td>
<td>19760 (9120)</td>
<td>1.25</td>
<td>119.0</td>
</tr>
<tr>
<td>piBMA-2</td>
<td>12300</td>
<td>1.21</td>
<td>48.7</td>
</tr>
<tr>
<td>pBA-2</td>
<td>7080</td>
<td>1.14</td>
<td>-54.2</td>
</tr>
</tbody>
</table>

*A mixture of initiators was used resulting in a mixed polymerization resulting in a mixture of pMMA with a dimerized coumarin as centre and of 26 mol% half molecular weight pMMA with a 4-MU initiator chain end.
With this range of polymers we have prepared our model compounds that we want to test on their ability for photo cleavage. The photo cleavage of these polymers will take place as is depicted in figure 6.16.

![Figure 6.16: Photo cleavage of pMMA with coumarin dimer core molecule using UV C light.](image)

After successfully preparing a range of polymers, we tested the photo cleavage. As we can see in figure 6.18, the photo cleavage of the model compounds is very fast and we do not see any major difference between the different polymers tested. The amount of energy needed for the photo cleavage (0.183 J cm$^{-2}$ during one minute of irradiation) is much less than for the dimerization (552 J cm$^{-2}$ during 800 minutes of irradiation).

![Figure 6.17: Photo cleavage of different polymers employing UV C light.](image)
Similar to the dimerization experiments we wanted to confirm the photo chemical reaction with different analysis techniques. For UV-Vis spectroscopy the signal of the double bond in the coumarin will increase upon irradiation and hence indicate photo cleavage. In figure 6.18 we show typical UV spectra of samples measured in time upon photo cleavage.

![Figure 6.18](image)

**Figure 6.18:** Typical UV absorbance of pMMA containing a dimerized coumarin core molecule. Upon photo cleavage the increase, as indicated with the arrow, is observed.

As we expected the molecular weight to reduce by 50%, we analyzed the samples upon photo cleavage with SEC and determined the conversion by means of deconvolution of the polymeric peaks. The different SEC traces are depicted in figure 6.19 and show the decrease of the molecular weight upon photo cleavage. Again we confirmed here that the conversion we determined with UV measurements is in agreement with the SEC results.
Figure 6.19: SEC traces of pMMA polymer containing a dimerized coumarin core molecule.

In literature relatively few papers can be found which reported about the use of the dimerized coumarin in polymeric systems. Zhao et al.\[8\] described the synthesis of spherical hybrid nanoparticles by using a bisethoxysilyl derivative of allyloxy coumarin dimer in a sol-gel polymerization. These authors describe the photo cleavage of the nanoparticles by several minutes irradiation with 254 nm UV light. In chapter 2 we discussed the polyurethanes prepared by Chen et al.\[9\] using a dimerized coumarin for the polyaddition with diisocyanates. Similar to our work they prepared polyethers containing coumarin dimer components\[4\]. Upon photo cleavage Chen et al. observe a high conversion to the original coumarin (before dimerization) and subsequently irradiate with UV A to re-dimerize the system. They do not get back to the fully dimerized coumarin and upon repeated photo cleavage and dimerization, the maximum level of dimerization decreases. They explain this by equilibration of the photo chemical reaction.
6.6 Reversible photo dimerization

To prepare reversible networks we need to know the optimal conditions for the dimerization and the subsequent photo cleavage. For this we have dimerized the 3 star-polymer (entry star-1 in table 6.3) to different degrees of dimerization. After the dimerization we have photo cleaved the cross-linked polymer and again dimerized for a certain time. In Figure 6.20 we show a dimerization of 20 minutes and a photo cleavage of 90 seconds. As we can see, the photo cleavage does not have a high conversion and the degree of dimerization only goes from 36 back to 21 %, longer irradiation times do not show any additional cleavage. Upon the second dimerization we see that the dimerization reaches a higher level than in the first one, but again here we see that the subsequent photo cleavage does not reach high conversion.

![Figure 6.20: Reversible dimerization of 3 star pMMA; the vertical lines represent the photo cleavage reaction.](image)

Similar results as shown in figure 6.20 are obtained, when we use shorter irradiation times (10 minutes) and longer irradiation times (30 minutes) for the dimerization. From these results we must conclude that it does not seem likely that the system developed can be completely reversible. We must add to this, that this conclusion is only valid for the results we have from the solid state and we cannot conclude anything about systems in solution.
In literature\cite{1, 10-14} the problems we observed are attributed to a so-called equilibration. We tested some of our polymers in order to confirm whether equilibration plays a role in either the photo cleavage or dimerization. First of all we irradiated a pMMA prepared with the dimerized 4-MU initiator (entry pMMA-5 in table 6.4) with UV A (normally used for dimerization experiments) over a period of 15 minutes. We did not see any difference in the polymer before and after irradiation. This indicates that in this time period no photo cleavage occurs using this UV A light.

The opposite test is to irradiate a pMMA prepared with the 4-MU initiator (entry pMMA-1 in table 6.1) with UV C (normally used for photo cleavage) over a period 15 minutes. This time of irradiation is much longer than the maximum 2 minutes for the photo cleavage. We did not see any change in the polymer with both UV-Vis and SEC before and after the irradiation. From this we can conclude that no dimerization occurs with UV C light.

Since we do not see any photo cleavage when using UV A and no dimerization when using UV C we can only conclude that equilibration does not occur and the differences they see upon repeated cycles of photo cleavage and dimerization are caused by other factors.

\section*{6.7 Conclusions}

The dimerization of the 4-MU initiator when using benzophenone as co-reagent gave a conversion of approximately 60 % after 22 hours irradiation with UV A light (total UV A dosage is 911 J cm\textsuperscript{-2}). Dimerization of the initiator with a substituted benzophenone or without any photo sensitizer did not show any conversion.

After dimerizations in solution we prepared model polymers using the 4-MU initiator with \(T_g\) ranging from -58 ° to 85 °C. These polymers, bearing one coumarin functional group, were dimerized in solid thin films and their dimerization was followed using UV-Vis spectroscopy. To confirm the decrease in UV signal at 315 nm was caused by dimerization and not degradation we confirmed the conversion by SEC (deconvolution of the polymeric peaks) and identified the doubled molecular weight by MALDI-ToF-MS measurements. The
polymers reached a conversion of approximately 90 % after 600 minutes of irradiation with UV A light (total UV A dosage is 414 J cm$^{-2}$) and we did not observe any difference between the final conversion of the different polymers tested. The polymers with their $T_g$ below ambient temperature (pBA and pDMAEMA) reached the maximum conversion much earlier than the higher $T_g$ polymers. The more polar character of pDMAEMA in comparison with pBA made that this polymer reached maximum conversion after only 150 minutes (total UV A dosage is 104 J cm$^{-2}$), with pBA after 450 minutes (total UV A dosage is 311 J cm$^{-2}$).

After the dimerization of the model polymers we investigated the dimerization of the (block) copolymers and star polymers we prepared in chapter 5. The copolymers of MMA contained 6.5, 10 and 20 mol % of 4-MUMA and the MMA block copolymer contained 22.5 mol % 4-MUMA. The copolymer of DMAEMA contained 16 mol % 4-MUMA and the 3 and 5 arm star polymers contained 6.5 and 10 mol % 4-MUMA respectively. Independent of the molar fraction of 4-MUMA all the copolymers dimerized in a similar fashion and reached a maximum conversion of 90 % in 800 minutes (total UV A dosage of 552 J cm$^{-2}$). The block copolymer of MMA and 4-MUMA needed a slightly longer time to reach the same maximum conversion in 1000 minutes (total UV A dosage 690 J cm$^{-2}$). As expected, the copolymer of DMAEMA and 4-MUMA reached the maximum conversion faster (150 minutes with a total UV A dosage of 104 J cm$^{-2}$) as we already observed in the dimerization experiments of the model polymers.

For the photo cleavage we prepared a range of polymers using a dimerized 4-MU initiator (2). We used UV-Vis to follow the conversion and again we checked this using SEC (deconvolution of the polymeric peaks). The presence of not dimerized 4-MU (entry pMMA-6 in table 6.4) did not have any influence on the behavior in the photo cleavage. The maximum conversion of the photo cleavage was reached after 60 seconds of irradiation with UV C light (total UV dosage of 0.183 J cm$^{-2}$) and no difference in speed and maximum conversion was observed between pMMA, pBA and piBMA.

Combining the dimerization and the photo cleavage did not result in a fully reversible system. This is in contrast with experimental results for the two separate photo chemical
reactions. From irradiations with both UV A and UV C we can say that the hindrance in high conversion of photo cleavage after partial dimerization is not caused by simultaneous dimerization upon UV C irradiation. What is causing the hindrance in the photo cleavage is not known.

**6.8 Experimental**

All solvents and reagents were purchased from Aldrich Chemical Co. and used without further purification (unless mentioned otherwise). All the monomers used were purified prior to use by means of purification over a column packed with neutral (or basic) aluminum oxide. 4-MU initiator is synthesized as described in 4.6.2. All characterization techniques are described in Appendix 1.

**6.8.1 Dimerization of 4-methyl umbelliferone initiator (1)**

A solution of dichloromethane (100 mL), 4-MU initiator (1, 3 gram; 9.22 mmol) is put together with benzophenone (0.314 gram; 1.84 mmol) in a jacketed reactor with a quartz lid. The reaction mixture was kept at ambient temperature during irradiation. Samples were taken in time and the conversion was determined using UV spectroscopy. After 8 hours of irradiation 51 % dimer was formed. The solvent was removed under reduced pressure and the solids are recrystallized from methanol. The solid obtained is the starting material. The mother liquid is concentrated and the solids are washed with diethyl ether to remove the benzophenone. After drying a pale yellow solid is obtained in 30% yield. Mp = 168 °C. \(^{1}\text{H} \text{NMR (CDCl}_3, 298 \text{K, 400 MHz)} \delta 1.33 (s, 6H, CH}_3), 2.07 (s, 12 H, CH}_3), 3.51 (s, 2H, CH), 6.95 (d, 2H, CH), 7.03-7.06 (dd, 2H, CH), 7.16 (d, 2H, CH).

**6.8.2 Polymerization using dimerized initiator (2)**

In a Schlenck tube, dimer initiator (2, 0.261 gram; 0.4 mmol), copper (I) bromide (0.057 gram; 0.4 mmol), methyl methacrylate (MMA; 5 mL; 49 mmol) and toluene (20 mL) were put together and purged with argon for 30 minutes. After degassing and bringing the
reaction mixture to 80 °C the ligand (N-n-pyridyl methanimine; 0.12 mL; 0.77 mmol) was added to start the reaction. GC was used to determine the conversion. After 5.5 hours the reaction was stopped by purging with air and cooling of the reaction mixture. The final conversion was 60.2 %. The mixture was put over a column containing basic aluminum oxide to remove the copper. The filtrate was concentrated and precipitated from cold methanol: water, 2:1. The final polymer had a \( M_n \) of 8780 g/mol and a PDI = 1.10.

### 6.8.3 Dimerization and photo cleavage

For the dimerization UV A light was employed. And for photo cleavage UV C light was employed. The details of the lamps and UV intensities are given in Appendix 1. The polymers are dissolved in THF at 15 wt% and cast onto a quartz cuvet. In some cases the polymer was applied as a film onto aluminum foil employing a doctor blade with a height of 60 µm (resulting in films of ~4 µm).

### 6.9 References

The main objective of this project was to prepare polymers that contain either coumarin or coumarin dimer moieties that can make that the coating can be reversibly crosslinked under the influence of UV light. In this work we have focused on the synthesis of the well defined polymers and we went into the details of the reversible photo dimerization of the coumarin functional groups in the polymers.

For the synthesis of the well defined polymer systems we used controlled radical polymerizations. In this way we could predefine the molecular weights and control the number of coumarins per polymer chain. As we initially started with RAFT (reversible addition-fragmentation chain transfer) mediated polymerization we could after preparation of the polymers, cleave off the RAFT agent moiety and perform crosslinking. We came across problems with the combination of RAFT and coumarin such as inhibition when using a RAFT agent derived from coumarin and when using coumarin based monomers we did not get any incorporation into the polymer chain. This made us decide to prepare our polymers using another controlled radical technique, called ATRP (atom transfer radical polymerization).

Using the ATRP method we prepared coumarin and coumarin dimer based ATRP initiators. In this way we were able to prepare model polymers which we could use for the study of the reversible photo dimerization. We looked at (meth) acrylate polymers having a range of $T_g$ values from -58 °C to 85 °C.

To dimerize the polymers we used UV A light and monitored the decrease of the double bond of coumarin with UV-Vis spectroscopy. The dimerization reached a conversion of
approximately 90 \% after 600 minutes of irradiation with UV A light (total UV A dosage is 414 J cm$^{-2}$) and we did not observe any difference among the various polymers in terms of final conversion. The polymers with their $T_g$ below ambient temperature (pBA and pDMAEMA) reached the maximum conversion much earlier than the higher $T_g$ polymers. The more polar character of pDMAEMA compared to pBA made that this polymer reached maximum conversion after only 150 minutes (total UV A dosage is 104 J cm$^{-2}$), with pBA after 450 minutes (total UV A dosage is 311 J cm$^{-2}$).

The polymers made with the coumarin dimer initiator were tested on their photo cleavage behavior using irradiation with UV C light. The maximum conversion of the photo cleavage was reached after 60 seconds of irradiation with UV C light (total UV dosage of 0.183 J cm$^{-2}$) and no difference in rate and maximum conversion was observed among pMMA, pBA and piBMA.

Next to the model compounds we prepared (block) copolymers and star polymers containing coumarin functional groups. The copolymers of coumarin (4-MUMA) and MMA contained 6.5, 10 and 20 mol\% of coumarin. The copolymer we prepared of coumarin and DMAEMA contained 22.5 mol\% of coumarin. The 3 arm and 5 arm star polymer contained 6.5 and 10 mol\% of coumarin respectively, the coumarin functional groups were positioned on the chain end of the arms.

In the preparation of the star polymers we explored two different approaches. The first approach, the arms first method, started with the synthesis of linear polymers using ATRP using a coumarin based initiator. The chain ends needed to be converted from bromide to an azide in order to click onto the multi functional alkyne core molecule. The main problem with this method was the determination of the conversion from the bromide to the azide chain end. When this conversion is not complete, the consecutive step of clicking to the core molecule cannot lead to 100\% chain end functionalization.

The second approach, the core first method, starts out with a multi-functional core ATRP initiator and after polymerization the star polymer is obtained. The next step is to functionalize the chain ends of the star polymer with the coumarin functionality. One way to
do this is with a click reaction. For this, first the chain ends of the star polymer have to be converted from bromine to an azide and afterwards they have to be clicked with a coumarin functional alkyne. This gives again rise to the problem that there is no good way to determine the chain end conversion to the azide. The additional problem for the chain end functionalization of the star polymers is the high molecular weight which reduces the number of analytical methods available for the determination of the conversion of the chain end functionalization.

In order to ensure a coumarin functional group on each chain end of the star polymer we looked at the selective monomer addition using altered ATRP conditions. For this method we made use of coumarin derived monomers and we conducted experiments to functionalize the polymer chain-end with one coumarin monomer. After fine tuning the reaction conditions it can be concluded that we successfully chain extended the polymer chain ends with one 4-methyl umbelliferone methacrylate of both linear and 3 and 5-arm pMMA. Employing 5 equivalents of methacrylate monomer to the polymer chain end in combination with a ratio Cu\(^{+}\): Cu\(^{-}\)Br of 1.1 to 1 and Me\(_6\)TREN as the ligand.

The (block) copolymers and the star polymers all had more than two coumarin groups in order to be able to form networks upon dimerization. Independent of the molar fraction of coumarin all the copolymers dimerized in a similar fashion and reached a maximum conversion of 90 % in 800 minutes (total UV A dosage of 552 J cm\(^{-2}\)). The block copolymer of MMA and 4-MUMA needed a slightly longer time to reach the same maximum conversion in 1000 minutes (total UV A dosage 690 J cm\(^{-2}\)). As expected, the copolymer of DMAEMA and 4-MUMA reached the maximum conversion faster (150 minutes with a total UV A dosage of 104 J cm\(^{-2}\)) as we already observed in the dimerization experiments of the model polymers.

The combination of dimerization and photo cleavage did not result in a fully reversible system. This in contrast to when we look at the two separate photo chemical reactions. From irradiations with both UV A and UV C we can say that the limited conversion of photo cleavage after partial dimerization is not caused by simultaneous dimerization upon
UV C irradiation. What is causing the limited conversion in the photo cleavage is not yet known.

Recommendations

Looking at the initial objective of this project we still have some questions that need to be answered and experiments that need to be done in order to use coumarins in a functional coating system. The first main question is: why is the dimerization not completely reversible?

In literature there are many answers postulated as to why complete reversibility of the dimerized products is not possible. The main explanation given is simultaneous dimerization and photo cleavage in both UV A and UV C. We have shown with our model compounds that this is not the case and when we look at solely the dimerization or the photo cleavage high conversions are obtained.

Our vision is that during the photo chemical reactions something happens to the coumarin that prohibits both the reactions. In literature some call these products “degenerates” but no identification of these side products is given. A first way in understanding what happens would be the thorough analysis of lower molecular weight polymers after dimerization using MALDI-ToF-MS, and NMR spectroscopy methods. In this way possible side products and thus side reactions could be identified.

Another option would be to look into the combination of monomers having different polarity or having different polar segments, this because we see a major influence in the rate of dimerization when employing DMAEMA in combination with the coumarin. When the time for the dimerization can be made shorter this also can then possibly decrease the contribution of side reactions and in this way optimize the reversibility for coating applications.
Appendix 1: Characterization techniques

Gas Chromatography (GC)

GC was used to determine monomer conversion by determination of the residual monomer. The analysis was carried out on a Hewlett-Packard (HP 5890) GC Series II, equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 µm) and equipped with a split injector (injection temperature was 180 °C) and autosampler. The injection volume was 1.0 µL, and Helium was used as the mobile phase. Detection was done using a FID (flame ionization detector) with a detection temperature of 280 °C and toluene was used as internal reference.

The following temperature program was used:
- initial temperature 40 °C
- heat to 100 °C at a rate of 5 °C/ minute
- heat to 250 °C at a rate of 25 °C/ minute
- keep at 250 °C for 2 minutes
- cool down to 40 °C

Size Exclusion Chromatography (SEC)

The polymer solution was diluted in tetrahydrofuran (THF, Biosolve) to a concentration of approximately 1 mg/mL. The solution was filtered over a 0.2 µm PTFE syringe filter. The analysis was carried out using a Waters 2695 Alliance pump and injector, a model 2996 photo diode array detector (at 305 and 470 nm) and a model 410 refractive index detector. The columns used were two PLgel Mixed-C (Polymer Laboratories, 5 µm particles) 300 × 7.5 mm followed by a PLgel Mixed-D
Appendix 1: Characterization techniques

(Polymer Laboratories, 5 µm particles) 300 × 7.5 mm in series (which were maintained at 40 °C for analysis). THF was used as an eluent (flow rate 1.0 mL/min). Data acquisition was performed using Waters Empower 1 software. Calibration was carried out using narrow MWD (pSTY) standards ranging from 2450 to 16.5 × 104 g/mol. The molecular weights were calculated using the universal calibration principle and Mark-Houwink parameters [pBA: K = 1.22 × 10^{-4} dL/g, a = 0.700; pSTY: K = 1.14 × 10^{-4} dL/g, a = 0.716]. Molecular weights were calculated relative to the relevant homopolymer (in this case pBA).

SEC fractionation

In some instances, the obtained polymers were fractionated prior to MALDI-ToF-MS analysis using SEC. The SEC setup consisted of the same series of columns used for the determination of the molecular weights. The system also consisted of an isocratic pump (Waters 590, flow rate of 1.0 mL/min), UV detector (Linear Instruments Corporation UV-vis 200, 254 nm). THF was used as a solvent at a flow rate of 1.0 mL/min. A fraction collector (Millipore) was used to collect 40 fractions at equal volume intervals of 0.4 mL.

(MALDI-ToF-MS

Measurements were performed on a Voyager-DE STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. Positive ion spectra were acquired in reflector mode. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] Malononitrile) (Aldrich, ≥ 99%) was chosen as the matrix and recrystallized prior to use. Potassium trifluoroacetate (Aldrich, 98%) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg/mL. Potassium trifluoroacetate was added to THF at a concentration of 1 mg/mL. The dissolved polymer concentration in THF was 1 mg/mL. In a typical MALDI-ToF-MS experiment, the matrix, salt and polymer solutions were premixed in the ratio 5 µL sample: 5 µL matrix: 1 µL salt. Approximately 0.3 µL of the obtained mixture was hand-spotted on the target plate. For each spectrum 1000 laser shots were accumulated.
Appendix 1: characterization techniques

Differential scanning calorimetry (DSC)

Glass transition temperatures were determined by DSC measurement on a DSC Q100 from TA instruments. Samples of 3-6 mg were heated with a heating rate of 20 °C/ minute in the appropriate temperature range for the specific polymer.

Proton nuclear magnetic resonance (1H NMR)

1H NMR spectra were recorded on a Varian Mercury Vx spectrometer (400 MHz) using TMS as an internal standard. Deuterated chloroform (CDCl₃) was used as the solvent.

InfraRed (IR)

Samples were measured by attenuated total reflection Fourier- Transform InfraRed spectroscopy (ATR- FTIR) on a Bio- Rad Excalibur FTS3000MX infrared spectrometer using the golden gate setup (100 scans per spectrum with a resolution of 4 cm⁻¹) equipped with an ATR diamond unit. The polymers were either measured as a powder or were casted from solution on to the ATR crystal.

UV- Vis spectroscopy

UV- Vis absorbance spectra were recorded with a Hewlett Packard 8453 spectrometer operating between 200 and 1100 nm.

UV irradiation

Dimerization:
For the dimerization experiments we made use of a Philips HPR-125 mercury discharge lamp. The lamp has an output of 125 W/ 1.15 Amps. The light intensities were measured with a UV power puck radiometer at a temperature of 24°C. The readings are given in the table below.

* More details can be found on: http://www.lamptech.co.uk/Spec%20Sheets/Philips%20HPR125.htm
Appendix 1: Characterization techniques

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>UV dosage (J cm(^{-2}) min(^{-1}))</th>
<th>UV dosage (W cm(^{-2}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV A 320 - 390</td>
<td>0.690</td>
<td>0.011</td>
</tr>
<tr>
<td>UV B 280 – 320</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UV C 250 – 260</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UV V 395 - 445</td>
<td>0.375</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Photo cleavage:
For the photo cleavage experiments we made use a UV bench lamp XX-15S from UVP. The bench lamp contained two lamps of 15 W/ 0.6 Amps** each. The light intensities were measured with a UV power puck radiometer at a temperature of 21°C. The readings are given in the table below.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>UV dosage (J cm(^{-2}) min(^{-1}))</th>
<th>UV dosage (W cm(^{-2}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV A 320 - 390</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UV B 280 – 320</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UV C 250 – 260</td>
<td>0.183</td>
<td>0.003</td>
</tr>
<tr>
<td>UV V 395 - 445</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

** More details can be found on: [http://uvp.com/xxseries.html](http://uvp.com/xxseries.html)
In this work we describe the successful preparation of a range of model polymers, copolymers and star polymers containing one or more coumarin functional groups. The work was done as part of the project #494 of DPI (Dutch Polymer Institute).

As we aimed to make a coating system that upon irradiation can de-crosslink we wanted to make well defined polymers utilizing controlled radical polymerization. In RAFT mediated polymerization there are problems with retardation of the polymerization rate, when using certain combinations of RAFT agents and monomers. The present results provide additional proof of intermediate radical termination in a real polymerization system, i.e. in the presence of monomer. In addition, evidence of termination products formed from the early stages of polymerization onwards and remains unchanged throughout.

For the introduction of the coumarin group onto the polymer chains we made use of RAFT agents containing a coumarin based leaving group. The problem we observed is that these RAFT agents show inhibition when employed at high concentrations. As we encountered these problems with the RAFT mediated polymerizations we decided to make use of another controlled radical polymerization, called ATRP.

For the synthesis of star polymers containing coumarin chain ends, that are able to form networks upon dimerization, we looked at two different methods. In the first method, called the arms first method, we first make the arms using ATRP and then employing click reactions to multifunctional alkynes to prepare the star polymers. The second method, the so-called core first method starts with the use of a multifunctional ATRP initiator where after polymerization the star polymers are obtained. After chain end conversion, the
cocomin is introduced through click reaction to the chain end of the star polymer. The main problem we encountered in both methods is the incomplete conversion of the chain end of the polymer (for both the linear and star polymers) in the functionalization with an azide. This then causes incomplete click reaction and in the case of the arms first method we do not obtain star polymers and in the case of the core first method we have star polymers without cocomin functionality.

As both the arms first method and the core first method did not give the desired star polymers having cocomin functionalities on every chain end, we looked at another way for functionalization of the chain ends. In this method we follow the core first method but instead of using click chemistry to introduce the cocomins, we make use of ATRP employing altered conditions. After fine tuning the reaction conditions it can be concluded that we successfully chain extended the polymer chain ends with one cocomin (4-MUMA) of both linear and 3 and 5-arm pMMA. Employing 5 equivalents of methacrylate monomer to the polymer chain end in combination with a ratio CuBr: CuBr of 1.1 to 1 and Me₆TREN as the ligand.

After successfully preparing the star polymers we continued with (block) copolymers. To get an insight on the copolymerization behavior of MMA and cocomin (4-MUMA) we determined the reactivity ratio of MMA utilizing the linearized Jaacks method. We have used two different RAFT agents in the RAFT mediated polymerization. The reactivity ratio of MMA had a value of 0.41 and 0.44 for DIBTTC and ethyl isobutyryl diithiobenzoate respectively. When employing ATRP we find a reactivity ratio of 0.44 for MMA. After determining the reactivity ratio of MMA using the Jaacks method we used the integrated conversion equation to determine the reactivity ratio of 4-MUMA as 0.88.

We successfully prepared a range of copolymers that can be used for crosslinking experiments. The (block) copolymers all had more than two 4- MUMA groups in order to be able to form networks upon dimerization. The molar ratios were chosen in such a way that they correspond to the molar ratios of the star polymers we prepared.
Model polymers were made, using the coumarin based initiator, with $T_g$'s ranging from -58 °C to 85 °C. The polymers reached a conversion of approximately 90 % after 600 minutes of irradiation with UV A light (total UV A dosage is 414 J cm$^{-2}$) and we did not observe any difference between the different polymers. The polymers with their $T_g$ below ambient temperature (pBA and pDMAEMA) reached the maximum conversion much earlier than the higher $T_g$ polymers.

After the dimerization of the model polymers we looked at the dimerization of the (block) copolymers and star polymers we prepared. Independent of the molar fraction of 4-MUMA all the copolymers dimerized in a similar fashion and reached a maximum conversion of 90 % in 800 minutes (total UV A dosage of 552 J cm$^{-2}$).

For the photo cleavage we prepared a range of polymers using a dimerized coumarin base initiator. The maximum conversion of 90- 95 % of the photo cleavage was reached after 60 seconds of irradiation with UV C light (total UV dosage of 0.183 J cm$^{-2}$) and no difference in speed and maximum conversion was observed between pMMA, pBA and piBMA.

Combining the dimerization and the photo cleavage of a star polymer, did not result in a fully reversible system. This in contrary to when we look at the two separate photo chemical reactions. From irradiations with both UV A and UV C we can say that the hindrance in high conversion of photo cleavage after partial dimerization is not caused by simultaneous dimerization upon UV C irradiation. What is causing the hindrance in the photo cleavage is not known.
Als onderdeel van het onderzoek #494 binnen DPI (Dutch Polymer Institute), beschrijven we de geslaagde bereiding van een reeks model polymeren, copolymeren en ster polymeren die allemaal 1 of meer coumarine moleculen bevatten.

We hadden als doel het maken van een coating systeem dat door bestraling met twee verschillende golflengtes van UV licht kan wisselen tussen het vormen of verbreken van het polymere netwerk. Om dit te bestuderen wilden we gebruik maken van goed gedefinieerde polymeren door deze te maken met gecontroleerde radicaal polymerisatie. In RAFT polymerisatie zijn er problemen met vertraging van de polymerisatiesnelheid wanneer een specifieke combinatie van RAFT agens en monomeren gebruikt wordt. De huidige resultaten geven aanvullend bewijs van terminatie van het intermediaire radicaal in een werkelijk polymerisatie systeem, in aanwezigheid van monomeer. Daarnaast hebben we terminatie producten aangetoond in alle fases van de polymerisatie en we hebben laten zien dat deze onveranderd blijven na terminatie.

Om een coumarine groep te introduceren op het keteneinde van de polymeren hebben we gebruik gemaakt van RAFT agens die een vertrekkende groep hadden gebaseerd op coumarine. Het probleem wat naar voren kwam wanneer we deze RAFT agentia gebruikten in hogere concentraties was inhibitie van de polymerisatie. Naar aanleiding hiervan hebben we besloten om gebruik te maken van ATRP, een ander type gecontroleerde radicaal polymerisatie.

Voor de synthese van ster polymeren die coumarine groepen bevatten op het keteneinde, waardoor ze geschikt zijn voor netwerk vorming, hebben we gebruik gemaakt van twee methodes. De eerste methode heet de arm eerst methode. Bij deze methode maken we eerst
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de armen met ATRP waarna we m.b.v. clickchemie de armen, nadat we de broom hebben vervangen door een azide, bevestigen aan een multifunctioneel centrum molecuul. De tweede methode heet de centrum eerst methode. Hierbij maken we gebruik van een multifunctionele ATRP initiator waarmee na polymerisatie de sterpolymeren gevormd zijn. Nadat de keteneinden vervangen zijn met een azide word m.b.v. clickchemie de coumarine op het keteneinde gebracht. Het grootste probleem bij beide methodes is de incomplete omzetting van het keteneinde naar een azide. Hierdoor ontstaan er problemen met de clickchemie waardoor deze ook niet volledig zal zijn. Als gevolg van de onvolledige clickreactie worden bij de armen eerst methode geen sterpolymeren verkregen en bij de centrum eerst methode geen coumarines geïntroduceerd op de keteneinden.

Aangezien we met de beide methodes niet succesvol waren in het bereiden van de gewenste steropolymeren hebben we gezocht naar een andere methode om de keteneindes te functionaliseren. Bij deze methode werken we volgens de centrum eerst methode, met dit verschil dat we in plaats van de clickreactie nu een ATRP gebruiken met aangepaste condities. Nadat we de condities hebben geoptimaliseerd, kunnen we concluderen dat we met succes de keteneindes van de sterpolymeren hebben gefunctionaliseerd met 1 coumarine (4-MUMA). Hiervoor gebruiken we 5 equivalenten coumarine monomeer t.o.v. het keteneinde in combinatie met een verhouding van Cu$^{1}$Br en Cu$^{II}$Br van 1.1 tot 1 en Me$_{6}$TREN als ligand.

Nadat we de sterpolymeren hebben gemaakt zijn we verder gegaan met het maken van (block) copolymeren. Om een beter inzicht te krijgen van het copolymerisatie gedrag van MMA met coumarin hebben we de reactiviteit ratio bepaald met de gelineariseerde Jaacks methode. We hebben twee verschillende RAFT agentia gebruikt in de RAFT polymerisatie. De reactiviteit ratio van MMA had een waarde van 0.41 en 0.44 voor DIBTTC en ethyl isobutryl dithiobenzoate. Bij gebruik van ATRP als polymerisatie methode vonden we een reactiviteit ratio van 0.44 voor MMA. Nadat we de reactiviteit ratio hebben bepaald van MMA hebben we gebruik gemaakt van de geïntegreerde conversie vergelijking om de reactiviteit ratio te bepalen van coumarine. Deze bedroeg 0.88.
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We hebben een variatie van (blok) copolymeren bereid die allemaal meer dan twee coumarine eenheden bevatten en daardoor netwerken kunnen vormen door dimerisatie. De molaire verhoudingen werden zo gekozen dat die in overeenstemming waren met de eerder bereide sterpolymeren.

Door het gebruik van een op een coumarine gebaseerde initiator, hebben we een range aan polymeren bereid met $T_g$'s variërend van -58 °C tot 85 °C. De polymeren bereikten een conversie van ongeveer 90 % na 600 minuten bestraling met UV A licht (de totale UV A dosering is 414 J cm$^{-2}$) verder zagen we geen verschil tussen de verschillende polymeren. De polymeren met een $T_g$ beneden kamer temperatuur (pBA en pDMAEMA) bereikten de maximale conversie veel eerder dan de andere polymeren met een hogere $T_g$.

Na de dimerisatie van de modelverbindingen hebben we onderzoek gedaan naar de dimerisatie van de (blok) copolymeren en sterpolymeren die we hadden bereid. Onafhankelijk van de molaire fractie van coumarine dimeriseerden alle polymeren met een zelfde snelheid en bereikten de maximale conversie van 90 % in 800 minuten (de totale UV A dosering is 552 J cm$^{-2}$).

Voor de terugreactie (photo cleavage) hebben een reeks polymeren bereid waarbij we een dimeer coumarin gebaseerde initiator hebben gebruikt. De maximum conversie van de terugreactie was ongeveer 90-95% na slechts 60 seconden bestraling met UV C licht (de totale UV dosering is 0.183 J cm$^{-2}$). In dit geval zagen we geen verschil in snelheid en maximum conversie van de verschillende polymeren.

Wanneer we de dimerisatie en de terug reactie achtereenvolgens meerdere malen uitvoeren van een sterpolymeer, observeren we geen volledige reversibiliteit van het systeem. Dit in tegenstelling tot wanneer we naar de twee afzonderlijke fotochemische reacties kijken en daar een hoge conversie vinden. Als gevolg van bestraling van model verbindingen met zowel UV A en UV C kunnen we concluderen dat de hindering in de terugreactie niet wordt veroorzaakt door gelijktijdige dimerisatie. Wat hiervan wel de oorzaak is, is tot op heden niet bekend.
Samenvatting
Het is zover, ik ben klaar. Nu moet ik eraan geloven ‘het echte werk’ gaat nu beginnen……

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P.