Fast Responsive Redox Actuators

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Abstract

The aim of this work is to improve the swelling response of redox active hydrogel actuators. At the moment, complete swelling of our quinone based actuators takes about 150 minutes and that of our 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) based actuators takes about 60 minutes. The aim is to reduce the response time to a few minutes or seconds. To do this, hydrogels are microstructured in order to enhance the solvent and ion diffusion into the hydrogel network and in this way to increase the swelling response rate of the hydrogels.

Four methods will be investigated: an emulsion templating method that employs poly(methyl methacrylate)-b-poly(lauryl methacrylate) (PMMA-b-PLMA) block copolymers that were synthesized under atom transfer radical polymerization conditions, a poly(ethylene glycol) (PEG) templating method, a novel nylon 6,6 templating method, as well as freeze-drying using water or dimethyl sulfoxide (DMSO) as the porogen. All four methods will be tested on simple poly(2-hydroxyethyl acrylate) (PHEA) hydrogels first, and if found to be suitable subsequently applied to the redox-responsive actuators.

It was found that all four methods are suitable to create porous PHEA hydrogels and all but the PEG templating methods can be used to prepare hydrogels with a swelling rate that is increased compared to nonporous PHEA hydrogels. For the PHEA hydrogels, the very good effect of freeze-drying with DMSO as the solvent should be pointed out, which leads to PHEA hydrogels that swell to equilibrium in only 6 minutes compared to 50
hours for the nonporous reference. For the quinone actuator device it was found that both, the emulsion templating method with PMMA-\textit{b}-PLMA block copolymers as the surfactant as well as freeze-drying with DMSO, can decrease the time until equilibrium swelling is reached to 60 minutes, with almost complete swelling after already 20 minutes, compared to 150 minutes for the nonporous quinone actuator. For the TEMPO actuator device first results indicate a similar efficiency of freeze-drying with DMSO, with almost complete swelling after 10 to 20 minutes, however those results should be verified with further experiments.
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Thanks to Sébastien, Frances, Sarah, Jan, Florian and Lucas for being my friends.
For my mother and for Sébastien.
In memory of my father.
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Abbreviations

δD ............... dispersion solubility parameter
δH ............... hydrogen bonding solubility parameter
δP ............... polar solubility parameter
Δµ_{elastic} ........ elastic contribution to the chemical potential change in a swelling gel
Δµ_{ion} ........... ionic contribution to the chemical potential change in a swelling gel
Δµ_{mix} ........... mixing contribution to the chemical potential change in a swelling gel
η ............... viscosity of a solution
\frac{\partial l}{\partial t} ............ rate of fluid uptake
γl ............... surface tension of a liquid
µε ............... microemulsion
µ1 ............... chemical potential of the fluid within a gel
µ_{1,0} ........... chemical potential of pure fluid
τ ............... characteristic time for swelling of a gel
θ ............... contact angle between hydrogel and fluid
DP ............... degree of polymerization
DP ............... degree of polymerization
G ............... coefficient friction between a polymer and a solvent
K ............... bulk modulus of a gel
l ............... length of a capillary
M_n ............... average molecular weight by number
MW(M) ........... molecular weight of the monomer unit
$MW(M)$ ...... molecular weight of the monomer unit
$Q$ .............. swelling degree of a hydrogel
$Q$ .............. swelling degree of a hydrogel
$Q_{eq}$ ............ equilibrium swelling degree of a hydrogel
$Q_{eq}$ ............ equilibrium swelling degree of a hydrogel
$m_0$ ............ initial (dry) mass of a gel
$m_0$ ............ initial (dry) mass of a gel
$m_x$ ............ mass of a gel after complete swelling
$m_x$ ............ mass of a gel after complete swelling
$m_t$ ............ wet mass of a gel at time $t$
$m_t$ ............ wet mass of a gel at time $t$
$V_0$ ............ initial (dry) gel volume
$V_0$ ............ initial (dry) volume of a gel
$V_x$ ............ volume of a gel after complete swelling
$V_x$ ............ volume of gel after complete swelling
$[I]$ ............. (monovalent) initiator concentration
$[M]_0$ ........... initial monomer concentration
$m_{CPBA}$ ....... meta-chloroperoxybenzoic acid
$a$ ............... characteristic length of the gel
ABCN ........... 1,1'-azobis(cyclohexane cyanonitrile)
ACN ............ acetonitrile
AIBN ........... 2,2'-azobis(2-methylpropionitrile)
AM ............. acrylamide
ATRP ........... atom transfer radical polymerization
C ............... cubic
CMWNT ........ carbon multi walled nanotube
D ............... solvent diffusion coefficient in the gel network
d ............. diameter
<table>
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<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>EtBBr</td>
<td>ethyl 2-bromoisobutyrate</td>
</tr>
<tr>
<td>EAP</td>
<td>electroactive polymer</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
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<tr>
<td>f</td>
<td>coefficient friction between the polymer and the solvent</td>
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<td>Fe*</td>
<td>decamethylferrocene</td>
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<td>lamellar</td>
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<tr>
<td>l</td>
<td>length of capillary</td>
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<tr>
<td>LMA</td>
<td>lauryl methacrylate</td>
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<tr>
<td>LP</td>
<td>living polymerization</td>
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<td>$M_n$</td>
<td>number average molecular weight</td>
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<tr>
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<td>methanol</td>
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<td>MMA</td>
<td>methyl methacrylate</td>
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<td>NMR</td>
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<tr>
<td>nylon 6,6</td>
<td>polyamide 6.6</td>
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<tr>
<td>O</td>
<td>oil</td>
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O/W ............ oil-in-water emulsion
P ............... polymer
PD ............... polydispersity index
PD ............... polydispersity
PEG ............... poly(ethylene glycol)
PEGDA ............... poly(ethylene glycol) diacrylate
PHEA ............... poly (2-hydroxyethyl acrylate)
PMDETA ....... N,N,N',N'',N''-pentamethyldiethylenetriamine
PMMA-b-PLMA poly(methyl methacrylate)-b-poly(lauryl methacrylate)
PVP ............... poly(4-vinylpyridine)
quinone ........... 3-(2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)propyl methacrylate
RAFT .............. reversible addition fragmentation chain transfer
S ................. surfactant
SEM .............. scanning electron microscopy
TEMPA ........... N-(2,2,6,6-tetramethylpiperidin-4-yl) acrylamide
TEMPO ........... 2,2,6,6-tetramethyl-piperidine-1-oxyl
THF .............. tetrahydrofuran
v/v ............... volume to volume
W ................. water
w/w ............... weight per weight
Chapter 1

Introduction to Thesis

Cross-linked, polymeric networks that are able to absorb large amounts of water (up to 99% of their own weight), so called hydrogels, are a fascinating material. The uptake of water, briefly swelling, of hydrogels has already been used in a variety of applications in food processing, cosmetics, pharmaceuticals, bio-technology, agriculture and paint manufacturing.

In addition to this, the fact that swelling can be caused by a diversity of triggers such as temperature, pH, light, magnetic or electric field and that the process of swelling is reversible makes hydrogels even more attractive for industrial applications. The here presented work focuses on redox-responsive hydrogel actuators. That are hydrogels that can transduce electrochemical stimuli into mechanical work. In order to be able to transduce electrochemical energy into mechanical work, the hydrogels focused on in this work contain redox groups that can reversibly switch between two chemical states. With the redox groups in the hydrogel in one or the other chemical state, the hydrogel can either be in a swellable or in a nonswellable state. As a result, it is possible to trigger swelling or shrinking externally by applying different voltages. The redox active groups investigated in the presented work are quinone and 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) based redox groups. A special feature of the hydrogel actuators investigated in our group is that they are of size in the centimeter range and that they exert linear actuation. Figure 1.1 shows an example of a linear hydrogel actuator investigated in our group.

If this kind of redox-hydrogels should be used as actuators, systems that signal a change of external stimuli by mechanical work, then the triggering process should occur fast.
Figure 1.1: Linear gel actuator based on benzoquinone/hydroquinone redox system. The gel expands upon reduction (right) and shrinks upon oxidation (left).

However, the actuator devices of our group need almost 2 hours (quinone) or one hour (TEMPO) for complete swelling at the moment. This response time is distinctly too long to actually use these devices as actuators. Therefore, the overall aim of this work is to investigate strategies to reduce the response time of the actuator devices to minutes or even seconds.

The here presented work is structured in the following way. Chapter 2 will give an introduction on hydrogels, their chemical composition, synthesis and properties. Because the focus of this work lies on actuators, Chapter 2 will then explain in more detail what an actuator is and compare it to conventional, non-hydrogel, actuators. Because the drawback of our hydrogel actuators is their response time Chapter 2 will then physico-chemically analyze the swelling process of hydrogels. Subsequently, the functional principles of the four methods that will be used in this work to increase the response time of the gels will be explained. Because one of the methods that will be investigated requires the synthesis of block copolymers the end of Chapter 2 will give a short introduction on living polymerizations. Two living polymerizations will be introduced, reversible addition fragmentation chain transfer polymerization (RAFT) and atom transfer radical polymerization (ATRP)

Chapter 3 will discuss the results of the living polymerizations used for the synthe-
sis of the block copolymers. The molecular weights, polydispersity indices and GPC traces of the synthesized polymers will be discussed. Chapter 4 will give detailed information about the experimental conditions of the RAFT and ATRP polymerizations.

Chapter 5 discusses the results of the four methods used to increase the swelling response of the hydrogels. To do so, the four methods will first be tested on simple poly (2-hydroxyethyl acrylate) (PHEA) hydrogels and the effectiveness of the methods will be evaluated by the swelling responses of the PHEA gels and by cryo-SEM analysis of the hydrogel surface structures. Subsequently, the methods that have proved to be effective will be tested on the redox responsive hydrogel actuators. Chapter 6 will give information on the preparation and characterization methods of the hydrogels.
References


Chapter 2

Introduction

2.1 What is a Hydrogel

A hydrogel is a hydrophilic, insoluble, crosslinked polymeric network that is able to absorb or release large amounts of water. Hydrogels can be either neutral or ionic, and their crosslinks can be made up either by chemical bonds or physical interactions such as entanglements, crystallites or weak bonds such as Van der Waals forces or hydrogen bonds.\footnote{The volume change of hydrogels can be the result of a variety of changes of external stimuli such as pH, temperature, ion concentration, electrical field, solvent composition, or light.} Because of this, hydrogels can be used in biosensors, separation membranes, artificial muscles, drug delivery devices and many other applications. As a result, terms such as ”smart”, ”intelligent” or ”stimuli-responsive” are frequently used to describe those environmentally sensitive hydrogels.\footnote{Because of this, hydrogels can be used in biosensors, separation membranes, artificial muscles, drug delivery devices and many other applications. As a result, terms such as ”smart”, ”intelligent” or ”stimuli-responsive” are frequently used to describe those environmentally sensitive hydrogels.}

2.2 Classification and Preparation of Hydrogels

Hydrogels can be classified according to four different criteria: 1) on the basis of their preparation and composition method into homo-, co- or multi-polymer hydrogels or interpenetrating networks; 2) whether they are charged or neutral; 3) by the nature of the crosslinks in the gel which can be chemical or physical and 4) according to the physical structure of the resulting gel which can be amorphous, semi-crystalline or hydrogen bonded.\footnote{Hydrogels can be classified according to four different criteria: 1) on the basis of their preparation and composition method into homo-, co- or multi-polymer hydrogels or interpenetrating networks; 2) whether they are charged or neutral; 3) by the nature of the crosslinks in the gel which can be chemical or physical and 4) according to the physical structure of the resulting gel which can be amorphous, semi-crystalline or hydrogen bonded.}
When classified according to the method of preparation, hydrogels can either be homopolymers when only one major monomer has been reacted, copolymers when mainly two monomers build the gel structure or multipolymers when three or more monomer units form the network. Interpenetrated networks (IPNs) are blends of two different polymer networks without covalent bonds between the two of them which can be prepared by simultaneous or sequential crosslinking of the two different polymers.

Hydrogels can be neutral, anionic, cationic, or ampholytic. Ampholytic means that anionic and cationic moieties (or the corresponding ionizable groups) are simultaneously present in the hydrogel. Common monomers used in nonionic hydrogels include 2-hydroxyethyl acrylate (HEA), hydroxyethyl methacrylate, acrylamide (AM) and ethylene oxide. Typical monomers that form anionic gels include acrylic acid, methacrylic acid and their sodium, potassium or ammonium salts. Natural polymers such as alginate and pectin also form anionic gels. Ethylenimine, diallyldimethylammonium chloride and chitosan are representative monomers that form cationic gels. Ampholytic gels can for example be obtained by synthesizing an interpenetrated polymer network that contains an anionic and a cationic polymer chain. Wu et al. synthesized an ampholytic gel made of a copolymer of AM and acrylic acid which was reacted to form a polymer mesh with poly(allylammonium chloride). Some typical monomers and polymers for the synthesis of hydrogels can be seen in Figure 2.1.

To finally synthesize the polymer hydrogel, crosslinks between polymer chains have to be created. The crosslinks can be of chemical or physical nature. Chemical crosslinkers can be any bi- or multivalent molecule that can react with the growing polymer chains under appropriate reaction conditions thereby forming the polymer network. Crosslinking reactions can be initiated either chemically or via irradiation (photocrosslinking).

There are three typical ways of preparing hydrogels through radical photocrosslinking. These are the irradiation of the starting monomer (in bulk or solution) containing smaller levels of a bifunctional crosslinker, the irradiation of the polymer itself, or of a polymer aqueous solution.

Chemical crosslinking can be done by reaction of crosslinkers with monomers, prepolymers or already existing polymers. Typical chemical crosslinkers are poly(ethylene
**Figure 2.1:** Molecular structures of some typical monomers and polymers for hydrogel synthesis.

Physical crosslinking is a result of secondary weak bond interactions such as hydrogen bonds, Van der Waals or electrostatic forces, but also of molecular entanglements for example. Examples include polymers that contain hydrophobically modified sidegroups. Those groups have the ability to aggregate or associate below a temperature at which polymer-polymer interactions are favored over polymer-solvent interactions (sol-gel-temperature). This leads to the precipitation of the gel and is schematically shown in **Figure 2.3**. Examples of building blocks that form such thermally responsive hydrogels are N-isopropylacrylamide, poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymers, agarose or gelatin, and cellulose monomers such as methyl cellulose or hydroxyl propyl methylcellulose. Permanent crosslinking can be achieved by successive chemical crosslinking after the initial gel set.
Figure 2.2: Molecular structures of some commonly used crosslinkers.

Figure 2.3: A schematic representation of physical crosslinking. The polymer chains entangle upon transition of the sol-gel temperature (decrease of temperature from left to right).
2.3 Key Gel Properties

Hydrogels can be characterized by a variety of properties such as the degree of swelling, swelling kinetics, diffusion coefficients (for example of drugs) and mechanical properties (i.e. moduli). The degree of swelling is the property of often the greatest importance as it is the one that changes most dramatically and because it affects the other properties.

It is defined as:

\[ Q = \frac{m_t - m_0}{m_0} \times 100 \]  

(2.1)

\( Q \) is the degree of swelling, \( m_t \) is the wet mass of the gel at time \( t \) and \( m_0 \) is the initial (dry) mass of the gel.

The swelling is dependent on the solvent used and the chemical composition of the polymer. At a certain degree of swelling the polymer chains will have extended to the greatest possible extent and only minor interactions will take place between the chains. In this state the swelling pressure on the polymer is counteracted by the crosslinks in the hydrogel and no further swelling will occur. The degree of swelling at this stage is called the equilibrium swelling degree and is defined as:

\[ Q_{eq} = \frac{m_{\infty}}{m_0} = \frac{V_{\infty}}{V_0} \]  

(2.2)

\( Q_{eq} \) is the equilibrium degree of swelling, \( m_{\infty} \) is the mass of the gel after complete swelling, \( m_0 \) is the initial (dry) mass of the gel, \( V_{\infty} \) is the gel volume after complete swelling and \( V_0 \) is the initial (dry) gel volume.

The equilibrium degree of swelling is primarily determined by the hydrophilic/lipophilic balance of the base polymer, the concentration of crosslinks, and for hydrogels containing ionized groups the concentration of counterions.
2.3.1 Volume Change in Response to Changes in Solvent Composition

Nonionic hydrogels that contain hydrophilic side groups are swellable in hydrophilic solvents such as water, DMF or DMSO. Examples include polymers made from acrylates, methacrylates or acrylamides. Addition of a nonsolvent such as methanol (MeOH), ethanol, acetone or tetrahydrofuran (THF) leads to shrinkage or eventually precipitation of the polymer.

The factors responsible for the solubility of a polymer can be related to the swellability of the corresponding hydrogel. Those factors include polymer solvent interactions, electrostatic forces and the osmotic pressure. Therefore, a polymer exhibiting good solubility in a solvent system potentially results in a hydrogel that swells in this solvent system. However, hydrogels contain multiple crosslinks which generate an elastic force in the hydrogel upon swelling and because of this the solubility of the polymer and the swellability of its corresponding hydrogel cannot be correlated directly.

2.3.2 Volume Change of Redox Gels

Redox gels contain moieties that can be reversibly transferred between an oxidized and a reduced form. By changing the oxidation state the molecules also change affinity to their surrounding medium and hence can be used in hydrogel applications. This change in the oxidation state can be induced either chemically or electrochemically. Because this change can be induced electrochemically it offers a great opportunity in the application of actuators. Quinone for example can be reversibly reduced to hydroquinone. Hydroquinone in its ionized form is hydrophilic, in contrast to quinone which is hydrophobic. Incorporated in a hydrogel, this moiety could be used as a trigger for electrochemically induced volume changes of a gel with the ionized hydroquinone state causing swelling and the quinone state causing shrinking of the gel. Examples of electroactive groups that have already been tested in hydrogels are the just mentioned quinones but also ferrocenes, nitroxides, metal complexes and conducting polymers. Section 2.4 will give a definition of actuators, and also give more detailed examples of the functional principle of redox hydrogels.
2.4 Actuators

2.4.1 Conventional and Hydrogel Actuators

‘Actuators are materials, devices or systems that are able to act upon their external environment by transducing input energy into external mechanical work’. Conventional actuator elements are found in thermochemical motors (combustion engines), electromagnetic drives and hydraulic/pneumatic machines and have high power and complex peripheral device requirements. In addition to this, the increasing demand of new actuation technologies for use in fields such as mechatronics, robotics or biomedical engineering requires the development of new actuation technologies. Actuators for applications in those fields should be easily scalable, structurally simple and mechanically compliant and at the same time exhibit high power-to-mass and power-to-volume ratios as well as fine control capability.

Hydrogels which can respond to external stimuli by reversible volume changes as described in section offer a promising alternative to conventional actuators for several reasons. Their performance as well as the obtained power densities are close to that of a human muscle making it a promising material for the construction of artificial muscles. It is possible to obtain large displacements because of the high water content of the polymer matrix. The volume changes are abrupt, large and reversible and often do not require the use of an external power supply. If an external power supply is needed they often can operate in a low power consuming mode (between 1 and 3 V). They are soft and flexible, inexpensive, of low mass, their size and shape are easily tunable and they operate noiseless, which offers usage in many fields.

Multiple applications of hydrogel actuators have already been realized. Examples are actuators that try to resemble natural muscles or actuators used for microfluidic applications. Examples of hydrogel applications that try to imitate natural muscles already exist such as a gel fish, a gel hand and a gel motor. However, those applications are far away from actual practical use because they fail to respond as fast as natural muscles do. Applications in microfluidics including valves, transistors and sensors are at the moment more applicable because they integrate smaller hydrogels that respond quickly to external stimuli.
For the technical production of devices, it is often desired to construct devices that can be controlled electronically in order to be capable of remote and fine control. By incorporating redox elements into a gel electrochemical stimuli can be used to induce swelling. This makes the actuator responses easier to control. Advantages of electrochemical stimulation over chemical stimulation is that the switching between the redox states can occur rapid and reversibly and that it can be controlled externally for example by a computer. Furthermore, the synthesis of redox responsive devices can be achieved on the nanoscale which potentially leads to the design of miniaturized devices.

A great deal of has been performed in the area of redox polymers, because they can be used in a variety of applications aside from actuators, including batteries and electrochromic displays. The use of redox groups in actuator techniques takes advantage of the fact that oxidation or reduction of the redox centres causes a change in charge. This requires migration of counterions to balance the charge which then causes the solvent to move into or out of the network structure depending on whether the new electrochemical state of the active group (including counterions) attracts or repels the medium. Examples of electroactive groups are quinones, ferrocenes, nitroxides, metal complexes and conducting polymers.

For example, Hempenius et al. successfully created a gel actuator based on a ferrocene redox active group in the polymer main chain. They tested a permanently negatively charged poly(ferrocenylsilane) hydrogel on its mechanical response to electrochemical oxidation and reduction of the ferrocene group. Poly(ferrocenylsilane) polymers are made up of alternating ferrocene and silane units in the main chain. The permanent anionic charge of the hydrogel that they employed is caused by sulfonate sidegroups. The structure of the hydrogel they tested can be seen in Figure 2.4.

Upon oxidation, electrostatic attractions between the positively charged oxidized ferrocene group and the negatively charged sulfonate sidegroups causes the gel to collapse. Following reduction of the gel the ferrocene group is neutralized. The electrostatic attractions to the sidegroups are thereby removed. As a result, the gel expands and they measured that this process exerts a pressure of 50 Pa.

One example that proves the applicability of the hydroquinone/benzoquinone redox
Figure 2.4: Structure of the anionic poly(ferrocenylsilane) gel used by Hempenius et al. They synthesized a pH responsive poly(acrylic acid) hydrogel in such a way that it stuck onto the surface of an Au-coated film electrode. In a following step they soaked this hydrogel in a hydroquinone solution, thereby incorporating hydroquinone molecules into the hydrogel structure. Poly(acrylic acid) hydrogels collapse at low pH and swell at high pH. When the hydroquinone group, that was entrapped in the hydrogel, was electrochemically oxidized protons were released. This decreased the pH and caused the hydrogel to shrink. When the resulting benzoquinone was subsequently reduced, the pH increased and caused swelling of the poly(acrylic acid) hydrogel. These changes are caused by changes in osmotic pressure, the hydrophilicity of the hydrogel and changes in electrostatic repulsion.

Because the hydrogel changes volume but the electrode stays at constant volume, this system can be used as a bending mode actuator (see Figure 2.3). The advantages of this actuator are that stretching takes only 15 minutes, only small voltages (+1.0 V for reduction, -0.3 V for oxidation) need to be applied and contraction-expansion cycles
can be repeated at least nine times (see Figure 2.6). However, a big disadvantage of this actuator is that the redox active substance is not covalently bonded to the hydrogel structure and that it has to be trapped in the polymer network after complete gel formation. It would be better to covalently attach the quinone moieties to the gel.

![Bending mode actuator invented by Takada et al. It is based on a benzoquinone/hydroquinone redox system and bends upon oxidation (-0.3 V) and expands upon reduction (+1.0 V) (arrow between left and right picture indicates potential switch).](image)

**Figure 2.5:** Bending mode actuator invented by Takada et al. It is based on a benzoquinone/hydroquinone redox system and bends upon oxidation (-0.3 V) and expands upon reduction (+1.0 V) (arrow between left and right picture indicates potential switch).
Figure 2.6: Time cycles of bending mode actuator invented by Takada et al. The actuator bends and stretches upon repeated oxidation and reduction, respectively. $\Delta \theta$ is the displacement in the central angle and $i$ is the electric current.

2.4.2 Linear Hydrogel Actuators

To generate hydrogel actuators that can generate high strain and are mechanically stable, the dimensions of the hydrogel actuator should be of considerable size (in the range of millimeters to several centimeters). It is also sometimes required to perform linear actuation under high stress. Linear actuation is a form of actuation where most of the expansion and thereby most of the force is directed across only one axis, whereas it is normally directed to all three spatial directions simultaneously. For example, if by the swelling of a hydrogel high strain is obtained, the swelling or shrinking of a hydrogel could be used to open or close a valve, or to push a piston.

In our group we investigate the electrochemically induced actuator response of linear redox actuators of dimensions in the centimeter range. Two redox responsive hydrogels will be investigated as actuator systems in this work. The first one is based on a copolymer hydrogel of HEA with a monomer including a quinone redox group 3-(2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)propyl methacrylate (abbreviated hence as "quinone monomer" or "quinone"). The other one is a copolymer gel of AM and
a monomer that contains an amine group \( N-(2,2,6,6\text{-tetramethylpiperidin-4-yl}) \) acrylamide ("TEMPA"). This copolymer can be chemically oxidized to its corresponding nitroxide form \( \text{P}(\text{AM-co-(2,2,6,6-tetramethylpiperidine4-yl acrylamide)}) \). When referring to "TEMPO" in the following we will be referring to the gel or monomer in its nitroxide form.\(^\text{[\text{\textsuperscript{31}}]}\)

In our group redox hydrogel actuators are prepared that contain a Pt spring. To obtain such actuators a Pt spring is placed into the reaction vessel, covered with the pre-hydrogel solution and then heated to start polymerization of the hydrogel. The incorporation of a Pt spring has two crucial advantages. Firstly, it acts as an electrode and conductive pathway into the gel. Secondly, it directs the expansion of the gel, turning the expected isotropic expansion into a linear one.

**Actuator Based on Quinone Redox Chemistry**

A quinone based hydrogel can be reduced from the benzoquinone to the hydroquinone form and oxidized back to the benzoquinone form as can be seen in [Scheme 2.1.](#) If put in the right solvent system under basic conditions it then swells when in the reduced and ionized form and shrinks when in the oxidized form.

**Scheme 2.1:** Redox chemistry of quinone moiety (depicted is the quinone group already covalently bond to the polymer network).

However, this gel has an intrinsically low electrical conductivity. Therefore, in order to increase the conductivity of the gel, we incorporate carbon multi walled nanotubes (CMWNTs) into the gel structure. [Figure 2.7](#) shows a typical \( \text{P(HEA-co-quinone)} \) gel actuator and its volume change when electrochemically reduced from the quinone to
the hydroquinone form.

**Figure 2.7:** Linear gel actuator based on benzoquinone/hydroquinone redox system. The gel expands upon reduction (right) and shrinks upon oxidation (left). The dark color is caused by CMWNTs that increase the conductivity of the gel.

**Actuator Based on TEMPO Redox Chemistry**

An electrochemically induced change of the TEMPO group between the nitroxide form and the oxoammonium cation form can also be used in our gel actuators. The change in charge between the nitroxide and the oxoammonium cation form causes swelling and shrinking of the hydrogel (see Scheme 2.2). The intrinsic conductivity of this gel is high enough to use it as an actuator without having to incorporate CMWNTs (measurements of the conductivity of our hydrogels have not yet been done). A typical TEMPO based actuator can be seen in Figure 2.8.

The large drawback of hydrogel actuators of centimeter or larger length is that complete swelling takes up to several hours. For example, as can be seen in Figure 2.9, the swelling and shrinking for the actuator based on the quinone system takes about 2.5 hours. This is due to slow solvent and ion diffusion in the polymeric network.

Some applications require not only high actuation forces and swelling degrees but also that the swelling proceeds fast. For instance, if redox hydrogels are to be used to
Scheme 2.2: Redox chemistry of TEMPA moiety. After initial chemical oxidation of the hydroxylamine to the nitroxide with *meta*-chloroperoxybenzoic acid (*m*-CPBA), electrochemical oxidation results in the oxoammonium cation state (reversible).\textsuperscript{[a]}

Figure 2.8: Linear gel actuator based on nitroxide/oxoammonium cation redox system.\textsuperscript{[a]}

resemble human muscles, response times should be in the range of milliseconds. Standard hydrogels are not yet suitable for applications that require fast swelling responses. Methods have to be found to increase the response rate of larger hydrogels if fast responses are required.

To understand the process of the swelling of hydrogels and to be able to increase the swelling response, the thermodynamic and kinetic aspects of the process have to be understood. The next sections explain the chemophysical aspects of the swelling process. Furthermore, four methods used in this work to increase the swelling response of
2.5 Physicochemical Aspects of the Swelling Process

2.5.1 Thermodynamics and Swelling Kinetics of Nonporous Gels

The swelling of hydrogels is a result of diffusion of the polymer into the solvent and *vice versa*. As a result, after placing a dry hydrogel into a suitable solvent, it changes its state from glassy to rubbery (see *Figure 2.10*) (glassy polymers are polymers below their glass transition temperature, they are hard, rigid and brittle; rubbery polymers are polymers above their glass transition temperature; they are soft and flexible). When the solvent has penetrated the polymer network the polymer is in its rubbery state. The polymer is glassy in the areas the solvent has not reached yet. Over time either all solvent is absorbed or the hydrogel reaches chemical equilibrium. At this state the hydrogel and the fluid form a uniform phase. Under the assumption of a Gaussian distribution of the polymer chains, the change of
Figure 2.10: Diffusion of polymer into solvent. Upon progress of the solvent front the gel changes from the glassy (I) to the rubbery (III) state; II is a transition state between the two forms.

The chemical potential of the gel can be described as an interplay of the thermodynamic compatibility of polymer and solvent molecules and the elastic retractive forces caused by the polymer chains. The former is the driving force for the solvent to penetrate the polymer network and the latter is the limiting parameter for the swelling. At swelling equilibrium the polymer chains have extended to the greatest possible amount. At this stage the swelling process stops. In other words, if the elastic and mixing contributions to the chemical potential will balance each other, swelling equilibrium is reached and no further swelling will occur (see eq. 2.3).

\[
\mu_1 - \mu_{1,0} = \Delta \mu_{\text{elastic}} + \Delta \mu_{\text{mix}} \tag{2.3}
\]

\(\mu_1\) is the chemical potential of the fluid within the gel, \(\mu_{1,0}\) is the chemical potential of the pure fluid, \(\Delta \mu_{\text{elastic}}\) is the elastic contribution to the chemical potential change and \(\Delta \mu_{\text{mix}}\) is the mixing contribution to the chemical potential change.

For ionic hydrogels, under the same assumption of Gaussian distribution of the polymer chains, ionic contributions have to be considered as well. This changes equation 2.3 to 2.4. For swelling equilibrium to be achieved the contributions to the chemical potential must add up to zero.
\[ \mu_1 - \mu_{1,0} = \Delta \mu_{\text{elastic}} + \Delta \mu_{\text{mix}} + \Delta \mu_{\text{ion}} \]  

(2.4)

\( \mu_1 \) is the chemical potential of the fluid within the gel, \( \mu_{1,0} \) is the chemical potential of the pure fluid, \( \Delta \mu_{\text{elastic}} \) is the elastic contribution to the chemical potential change, \( \Delta \mu_{\text{mix}} \) is the mixing contribution to the chemical potential change and \( \Delta \mu_{\text{ion}} \) is the ionic contribution to the chemical potential change.

The characteristic time for the swelling process can be related to the gel length, \( a \), and the diffusion coefficient in the network, \( D \), which relates to mechanical properties of the hydrogel and the coefficient of friction between the polymer and the solvent (eq. 2.5 and 2.6).

\[ D = \frac{K + \frac{4G}{3}}{f} \]  

(2.5)

\( D \) is the solvent diffusion coefficient in the gel network, \( K \) is the bulk modulus of the gel, \( G \) is the shear modulus of the gel and \( f \) is the coefficient friction between the polymer and the solvent.

\[ \tau = \frac{a^2}{D} \]  

(2.6)

\( \tau \) is the characteristic time for swelling, \( a \) is the characteristic length of the gel and \( D \) is the diffusion coefficient in the network.

### 2.5.2 Swelling Kinetics of Porous Hydrogels

The swelling response time of a gel is directly proportional to the square of the hydrogel length, \( a \), and inversely proportional to the diffusion coefficient of the polymeric network in the solvent, \( D \), as can be seen from equation 2.6. One obvious way to increase swelling response is therefore to decrease the hydrogel dimensions as reported by Tanake et al. for instance. However, the reduction of the hydrogel size is not always a convenient method, because applications where high strains are necessary require relatively large hydrogel dimensions. Two ways are known to generate high strain and fast response times simultaneously. The first method uses a low dimensional bending mode actuator (and thus thin films) but couples several of those to one larger actuator that gives a linear response. This has already been successfully done by Yamakito et al. in ionic and electrostatic actuators. However, to my best knowledge this has not
yet been applied to hydrogel actuators.

A second way is to increase the diffusion coefficient of the polymer network in the solvent, as can be seen in Equation 2.6. This can be achieved by generating a porous microstructure in the hydrogel. The concept behind this is that bulk diffusion of a molecule in a polymer network is many times slower than in a pure fluid. It is furthermore very advantageous if the microstructure contains interconnected (bicontinuous) pores rather than closed pores. This makes the hydrogel surface accessible to the solvent through capillary effects. Because the capillary rise is much faster than the diffusion process a bicontinuous microstructure has a very positive effect on the swelling rate of hydrogels. After the initial capillary rise the solvent then diffuses into the polymer network from the pores. This process is similar to the diffusion in nonporous gels but only shorter diffusion distances are present. It has to be considered that for capillary rise to be really efficient the viscosity of the solvent should be as low as possible as can be seen in equation 2.7.

\[
\frac{\partial l}{\partial t} = \frac{d \gamma l \cos \theta}{8 \eta l}
\]

\(\frac{\partial l}{\partial t}\) is the rate of fluid uptake, \(d\) is the diameter of the capillary, \(\gamma\) is the surface tension of the liquid, \(\theta\) is the contact angle between hydrogel and fluid, \(\eta\) is the viscosity of the solution and \(l\) is the length of the capillary.

Many methods have already been investigated to generate porous microstructures in hydrogels. Those include phase separation techniques, photopatterning methods, stereolithography, synthesis of the polymer network in the presence of an inert filler (“porogen”) and many others. While an increase in the porosity will certainly increase the swelling kinetics, this may be at the expense of the strength of the gel.

### 2.6 Porogen Methods to Create Porous Hydrogels

Using inert fillers, also called ”porogens” to create porosity in hydrogels is a commonly applied method. Porogens in general have to be inert to the reaction medium and must be easily extractable after complete reaction without affecting the hydrogel itself. Porogens can be ice crystals (freeze-drying), polymers (e.g. poly(ethylene...
glycol), salts (e.g. sodium bicarbonate), silica, and many others. Four possible methods to prepare microstructured hydrogels will be discussed in further detail in the following sections.

### 2.6.1 Solid Organic Fibers as Porogen

Another, rather uncommon, porogen leaching method is the incorporation of solid organic fibers into the hydrogel structure and post-polymerization extraction of the filler. The advantage of this method is that the resulting porous structure immediately shows an interconnected tubular structure as long as fiber size and distribution are chosen properly. Hence, in addition to the diffusion of the solvent into the hydrogel network structure, solvent convection into the structure is enabled, too, thereby strongly increasing the swelling kinetics.

To my best knowledge, until now only two paper have reported the use of fibers to create porous hydrogel structures and one paper has reported the use for porous hydrogel nanocomposite networks. Studenovska et al. reported the use of poly(L-lactide) fibers to create porous poly(2-hydroxyethyl methacrylate) hydrogels. As a result, they obtained anisotropic tubular pores in the gel. However, they did not investigate the influence of this type of microstructure on the swelling behavior of the gel. Flynn et al. employed polycaprolactone fibers to prepare porous poly(2-hydroxyethyl methacrylate) hydrogels, but they, too, did not investigate the swelling behavior of the hydrogels. Rodriguez et al. described the use of sintered polyamide-6 fibresheets to generate interconnected pores in a PHEA/silica nanocomposite network. They obtained highly ordered cylindrical pores aligned like a mesh.

Another solid organic fiber that can be used as a porogen is polyamide 6.6 (nylon 6.6). Nylon 6,6 has not yet been used as a solid organic fiber porogen in the preparation of porous hydrogels. It is an inexpensive, commercially available fiber and can be dissolved out with suitable solvents such as 2,2,2-trifluoroethanol or 2,2,2-trichloroethanol under mild conditions. Therefore, nylon 6,6 can potentially be used as an inert filler for the preparation of porous hydrogels. Importantly to us, it is commercially available in very fine fiber diameters.
2.6.2 PEG as Porogen

The incorporation of poly(ethylene glycol) (PEG) into a pre-hydrogel solution as an inert filler is a common method to introduce porosity into hydrogels. It is a simple method because the porogen is easy to incorporate into most pre-hydrogel mixtures and because the hydrophilic nature of PEG makes it easy to extract after complete polymerization. Furthermore, by varying the molecular weight of PEG as well as its content it is possible to tune the porous microstructure of the hydrogels to a certain extent.

Several groups have already successfully applied PEG as a porogen in hydrogels based on poly(vinyl alcohol), poly(N-isopropylacrylamide-co-acrylic acid), polyamide, poly(N-isopropylacrylamide), and poly(ethylene oxide). The molecular weights of the PEG used in those works varied between 300 and 35000 g mol\(^{-1}\) and the amounts applied vary between 1 and 13 wt\%. In all of those papers it was described that the porous microstructure caused an increase in the swelling ratios, swelling rates or diffusion coefficients. Therefore, usage of PEG as a porogen seems to be a promising and simple method to create microporous polymeric network structures.

2.6.3 Freeze-Drying

Freeze-drying, also called "lyophilization", is another common method to microstructure hydrogels. To do this, the hydrogel is swollen in a suitable solvent, frozen and subsequently freeze dried at a pressure below the triple point of the solvent. The solvent crystals act as a porogen leaving behind a porous structure. Many groups have already reported the usage of freeze-drying for the preparation of porous hydrogels. Porous chitosan-poly(ethylene oxide), gelatin, [poly(vinylpyridine-co-methacrylic acid) poly(N-isopropylacrylamide)] semi-IPN, poly(N-isopropylacrylamide) and cellulose ether hydrogels have already been reported. It was often observed that the swelling kinetics of freeze dried hydrogels are tremendously accelerated compared to the reference samples. Moreover, it was often observed that the amount of water in the gel during the freezing is the key factor to control the microstructure and hence the swelling response of the gels.

The freezing temperature and thereby the rate of freezing, also has a large impact on
the microstructure. The size and shape of the ice crystals formed depend on the speed of the freezing process. Quick freezing results in the growth of many small ice crystals whereas slow freezing results in fewer but bigger ice crystals. Ikada et al. observed that with a higher freezing temperature the pore size of the hydrogels increased. Furthermore, Wu. et al. reported the creation of open pore structures when freezing the samples at -20 °C and -80 °C but parallel sheet structures when the samples were frozen at -196 °C. As the parallel sheet structure results in less contact surface area compared to the open pore structure they also observed a decrease of the swelling ratio for the hydrogels frozen in liquid nitrogen.

Normally the whole hydrogel sample is frozen uniformly. However, Tuszynski et al. applied uniaxial freeze-drying to agarose gels with water as porogen. To do this, they put only one end of the gel in contact with dry ice so that ice crystals formed linearly upwards. As a result, they obtained a highly linear, tubular pore structure. Even though freeze-drying is disadvantageous in regard of tunability (the water content cannot be adjusted for all kinds of hydrogels), resulting mechanical stability and the amount of energy used, it is a technique easy to apply and requires only a few preparation steps.

### 2.6.4 Emulsion Templating Method

Synthesizing a hydrogel in a continuous-discontinuous phase system, such as water with a non-aqueous nonmiscible oil medium as porogen, is a promising method to create microporous hydrogel structures.

To achieve this, an oil-in-water (O/W) emulsion is formed by dispersing the oil phase as a porogen in the aqueous pre-gel phase using a suitable surfactant. Then the gel is synthesized under conditions such as if no porogen was present. After complete polymerization, the porogen is removed by appropriate washing steps thereby creating a porous hydrogel structure (see Figure 2.11).

The most critical part of this procedure is to find a stable emulsion system for the solvent used. The emulsion stability depends on the nature of the solvent phases employed and the chemical composition of the stabilizing surfactant.

The nature of the solvent system depends on the reaction conditions. The aqueous
Figure 2.11: Schematic illustration of the preparation of porous hydrogels using the emulsion templating method. The pre-gel solution contains oil droplets that can be extracted after polymerization to create pores.

Phase must be a solute for the reactants and must therefore be a suitable reaction medium. The oil phase must be non-miscible with the aqueous phase, must not react with the reactants and must have a boiling point above the polymerization temperature. Common nonpolar phases employed include hydrocarbons and supercritical carbon dioxide, but others are possible as well.

The Hydrophile-Lypophile Balance (HLB) of a surfactant is a value based on the weight ratio of the hydrophilic to the hydrophobic groups in the surfactant molecule. It allows a prediction of the surfactant behavior in oil/water systems. According to this, a surfactant having a HLB value between 12-16 might be able to stabilize O/W emulsions. However, it only predicts the behavior expected rather than the efficiency by which this will be accomplished. Even though two surfactants can possess the same HLB value they can differ extremely in their molecular weight, from low molecular weight surfactants to very high molecular weight (polymeric) surfactants.

Block copolymer surfactants are high molecular weight amphiphilic molecules and perform distinctly better compared to low molecular weight surfactants of the same HLB. This can be attributed to the fact that the polar block of the copolymer is solubilized by the polar solvent and on the other hand the nonpolar block in the nonpolar solvent, both attempting to form separate random coils. This may cause an increase in viscosity and slow down desorption kinetics at the water/oil interface resulting in a higher stability of the emulsion.
While the HLB value gives information about the weight ratio of the hydrophilic to the lipophilic groups in a surfactant molecule needed to stabilize an oil-in-water emulsion, it does not give information on the chemical makeup of the surfactant needed to effectively stabilize an emulsion of known composition. This information can be obtained by the so called Hansen Solubility Parameter (HSP). It predicts polymer solubility properties on the basis of the total energy of vaporization. If materials have similar HSPs, more precisely if their three parameters $\delta_D$ (dispersion solubility parameter), $\delta_P$ (polar solubility parameter) and $\delta_H$ (hydrogen bonding solubility parameter) are similar to each other, they have a high affinity for each other.\(^5\)

Once a block-copolymer of suitable chemical composition and HLB value has been found the microstructure of the hydrogel and thereby the swelling properties can be controlled by varying the O/W volume ratio as well as the amount of added surfactant.\(^6\) As can be seen in Figure 2.12 emulsions can exist in different phases. The phase that is interesting in this context is the bicontinuous microstructure (e). However, as can be seen in Figure 2.13, the bicontinuous phase (as part of $\mu$) only exist in a small range of the phase diagram of the solvents and the emulsifier and the position of this range varies for different emulsion systems.

Because the block copolymers used for the emulsion templating method in this work have been synthesized by living polymerization methods, namely atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT), the following section will give an introduction on living polymerizations with special focus on the two mentioned polymerization strategies. The results of the polymerizations will be shown in Section 3.

2.7 "Controlled" or "Living" Polymerization

In conventional polymerization methods the three main steps initiation, propagation and termination occur simultaneously and proceed until either all the initiator or all the monomer is consumed. Because of the simultaneity of those three reaction steps new chains appear at all times. They permanently grow and eventually stop growing by either termination or transfer reactions whereby the lifetime of a propagating center can be very short. Because of this, a disadvantage of uncontrolled polymerizations is
Figure 2.12: Idealized microstructures of emulsion phases. (a): lamellar; (b) hexagonal; (c) microemulsion (droplets of oil in water); (d) microemulsion (droplets of water in oil); (e) microemulsion (bicontinuous); (O=oil; W=water).

Figure 2.13: Schematic phase diagram for an oil-water-surfactant (O-W-S) mixture in the composition triangle at constant temperature.

That the resulting polymers have a broad molecular weight distribution and that polymer weights and architectures cannot be controlled. When the propagating active centers do not undergo termination or transfer and when the initiation step is quick compared to the rate of propagation, the resulting polymer has a narrow molecular weight distribution and the polymerization is called "controlled" or "living" (LP) and was first reported by Szwarc in 1956.
The key point of living polymerizations is that the rate of initiation must exceed
the rate of propagation and that no termination steps occur. Under those
conditions the polymerization will proceed until all monomer has been
consumed leaving behind active polymer chain ends. Those can then be used to
continue the polymerization after further addition of monomer. As a result,
polymers synthesized under LP conditions have narrow molecular weight
distributions, controlled molecular weights and end functionalities and it is
possible to create complex molecular architectures such as block or
star polymers.\textsuperscript{6,85}

Under the assumption of complete conversion the degree of polymerization, $DP_n$,
and the average molecular weight by number, $M_n$, can be calculated as follows:\textsuperscript{85}

\begin{equation}
DP_n = \frac{[M]_0}{[I]} \quad (2.8)
\end{equation}

$DP_n$ is the degree of polymerization, $[M]_0$ is the initial monomer concentration and $[I]$ is the (monovalent) initiator concentration.

\begin{equation}
M_n = DP_n \times MW(M) \quad (2.9)
\end{equation}

$MW(M)$ is the molecular weight of the monomer unit.

Many different types of LPs, such as controlled anionic, cationic, coordination and ring
opening polymerizations, have been successfully applied for the synthesis of complex
polymer architectures. However, because radical polymerizations are quite tolerant of
functional groups and impurities and because it is the leading method to produce poly-
mers in industry, much investigation has been done to find a controlled/living radical
polymerization method.\textsuperscript{57}

A combination of fast initiation and an absence of termination is contradictory to
the principles of free radical polymerization. Nevertheless, by establishing a dynamic
equilibrium between a small amount of propagating radicals and a large majority of
dormant species a controlled radical polymerization can be obtained. This equilibrium
may either be established by reversibly trapping the radical in a deactivation/activation
process (see Figure 2.14) (e.g. ATRP) or by involving it in a "reversible transfer" degenerative exchange process (see Figure 2.15) (e.g. RAFT). If the radicals are in their active form they propagate and terminate with rate constants as in conventional free radical polymerization. Even though termination still occurs, under appropriate conditions its contribution will be small so that these radical polymerizations behave as nearly living.

**Figure 2.14:** Dynamic equilibrium of controlled radical polymerization by reversibly trapping the radical in a deactivation/activation process. $P_n^*$ is the growing, active radical species, $X$ is a (pseudo)halide atom, $P_n-X$ is the deactivated (trapped) species of the growing polymer chains, $M$ is the monomer and $k_p$, $k_t$, $k_{deact}$ and $k_{act}$ are the rate constants for the polymerization, termination, deactivation and activation process, respectively.

**Figure 2.15:** Dynamic equilibrium of controlled radical polymerization by involving the radical a "reversible transfer" degenerative exchange process. $P_n^*$ and $P_m^*$ are the growing, active radical species, $X$ is a (pseudo)halide atom, $P_n-X$ is the deactivated (trapped) species of the growing polymer chains, $M$ is the monomer and $k_p$, $k_t$ and $k_{ex}$ are the rate constants for the polymerization, termination and the exchange process, respectively.
2.8 The Reversible Addition Chain Transfer Process

Reversible Addition Chain Transfer (RAFT) is a type of LP that will be tested for the synthesis of our block polymers. It was discovered in 1998 by the group of Rizzardo and coworkers at the CSIRO institute.\(^\text{89}\) A RAFT polymerization is conducted under conditions as for conventional free radical polymerization but by addition of a definite amount of an appropriate RAFT agent. The same monomers, initiators, solvents and temperatures are used. The RAFT agent is a thiocarbonylthio compound and can be for instance a dithioester, thiocarbamate or a xanthate, all of which act as a reversible chain transfer agent. This dithio compound must have a good homolytic leaving group, R, whose radical must be capable of initiating a polymerization reaction (see Figure 2.16).\(^\text{90}\)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{raft_agent_diagram.png}
\caption{General structure and features of RAFT agents and of the intermediate radical. The thiocarbonylthio RAFT agent and the active radical species are in equilibrium with the deactivated radical species.\(^\text{91}\)}
\end{figure}

Initiation and radical-radical termination take place as in free radical polymerization. The key feature of the RAFT process is a sequence of addition-fragmentation equilibria between the active propagating radicals (P\(^\cdot\)_n and P\(^\cdot\)_m, see Figure 2.19) and the dormant species thereby providing equal probability of growing all the chains and hence causing the polymerization to be living.\(^\text{92}\) The mechanism of RAFT is depicted in Figure 2.17 and can be described as follows:
Initiation:
In the initiation step a conventional radical initiator such as azobisisobutyronitrile (AIBN) or 1,1'-azobis (cyclohexane carbonitrile) (ABCN) forms radicals. Those then add to the monomer and thereby start the polymer chains $P^-_n$ to grow.

Addition Fragmentation:
The thus formed active polymer chain $P^-_n$ adds to the dithio compound and leads to an intermediate product which is capable of homolytic cleavage of either the leaving group $R^-$ or the polymer chain itself.

Reinitiation:
Upon homolytic cleavage of $R^-$ this group then reacts with free monomer thereby starting another active polymer chain $P^-_m$. This active polymer chain can then undergo either addition fragmentation or equilibration.

Equilibration:
This step is the fundamental step of the RAFT process. The active species $P^-_m$ adds to the dithio compound thereby releasing either $P^-_m$ itself or $P^-_n$. It thereby traps the majority of active species $P^-_n$ and transforms it into the dormant species and limits the probability of chain termination. As a result, the polymerization proceeds in a controlled manner.

Termination
Termination occurs as in conventional free radical polymerization but its probability is lower due to the majority of the polymer chains being trapped in a dormant species.

Because of this, RAFT polymerization can provide polymers with controlled molecular weight and narrow molecular weight distribution can be obtained and complex molecular structures can be designed. The molecular weight of the polymer can be adjusted by the ratio of monomer to initiator and for complete conversion can be calculated as shown in equation 2.3. After polymerization, the product itself is a RAFT agent because it retains the thiocarbonylthio group as an end group (see structure 1 in Figure 2.17). By sequential monomer addition it is therefore possible to synthesize block polymers as shown in Figure 2.18.
Figure 2.17: Mechanism of RAFT process. It includes initiation and propagation, reversible chain transfer, reinitiation, chain equilibration and termination.

2.9 Atom Transfer Radical Polymerization

Atom Transfer Radical Polymerization (ATRP) is another controlled polymerization and was first established in 1995 by Sawamote and Matyjaszenski independently. Main components of an ATRP reaction mixture are an initiator R-X, a transition metal/ligand complex \( L_n M^{+z} \) and the monomer. The polymerization is initiated by a reversible (pseudo)halogen transfer from the initiator R-X to the transition metal/ligand complex \( L_n M^{+z} \) thereby forming the propagating active species \( R^* \) and the metal complex in a higher oxidation state with an additionally coordinated halide ligand \( L_n M^{+z(z+1)}X \). The radical species is then able to propagate with the monomer as in a normal free radical polymerization. After a very short time it then converts back to the dormant species \( P_n-X \) via reversible (pseudo)halogen atom transfer from \( L_n M^{+z(z+1)}X \). \( P_n-X \) again can be converted to the active species \( P^*_n \) via reversible atom transfer. By this, a dynamic equilibrium between the activated and deactivated species is formed.
Figure 2.18: Mechanism of block-polymer preparation by the RAFT process. The reaction steps are the same as for RAFT homopolymerization and include initiation and propagation, reversible chain transfer, reinitiation, chain equilibration and termination.

Because the equilibrium between the dormant and the active species lies strongly to the side of the dormant species, ATRP is a convenient strategy to create living polymers with controllable molecular weight and end group, narrow molecular weight distribution and is thereby a good method for the creation of complex molecular architectures.

After synthesis of the polymer with an active (pseudo)halogen end group it can then be used as an ATRP macroinitiator for the synthesis of complex molecular architectures such as graft, block and starpolymers.
Figure 2.19: Mechanism of ATRP. It includes initiation, propagation and termination.
References


Chapter 3

Results and Discussion for Radical Polymerizations

One of the key methods planned to be used to increase the porosity of the gels is emulsion templating. This involves the emulsification of the hydrogel precursor solution with a nonsolvent, polymerization of the mixture, and extraction of the nonsolvent. As the monomers are organic soluble, a water-organic or organic-organic solvent mixture is possible. As the comonomers are soluble in water, it was decided to use an organic-organic blend. Because \( n \)-octane and DMSO are incompatible and stable to 80 °C (temperature for polymerization of hydrogels), this was decided as the starting point.

The choice to synthesize poly(methyl methacrylate)-\( b \)-poly(lauryl methacrylate) PMMA-\( b \)-PLMA block copolymers was made according to their HSP parameters. By comparison of the \( \delta_D \), \( \delta_P \) and \( \delta_H \) values we found that PMMA would be a polymer with good solubility in DMSO and that PLMA would show good solubility in \( n \)-octane (see Table 3.1). The choice of target chain lengths of the polymers was rather random and the initial intend was to observe a chain length dependence of the stability of emulsions.

<table>
<thead>
<tr>
<th>chemical</th>
<th>( \delta_D )</th>
<th>( \delta_P )</th>
<th>( \delta_H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
</tr>
<tr>
<td>PMMA</td>
<td>18.64</td>
<td>10.52</td>
<td>7.51</td>
</tr>
<tr>
<td>( n )-octane</td>
<td>15.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>LMA</td>
<td>14.4</td>
<td>2.2</td>
<td>5.1</td>
</tr>
</tbody>
</table>
In the following, the results of the RAFT and ATRP reactions will be discussed. The molecular weights of the polymers will be shown and have been determined by GPC ($M_{n,GPC}$). In addition, the theoretical molecular weights ($M_{n,\text{theo}}$) will be shown as well, to compare it to the actually obtained weights. The theoretical molecular weights for 100% conversion will be shown, too, as it was sometimes noticed that they are similar to the actually obtained molecular weights, which is an indication for us that workup strategies should be optimized for specific cases. As a measure of the molecular weight distribution of the polymers the polydispersity index PD will be shown. It is calculated as the ratio of the weight average molecular weight of the polymer ($M_w$) to the number average molecular weight of the polymer ($M_n$) (see (3.1)). The PD values listed in this work have been taken from the GPC results and have not been calculated manually.

$$PD = \frac{M_w}{M_n}$$  \hspace{1cm} (3.1)

PD is the polydispersity index, $M_w$ is the weight average molecular weight of a polymer, $M_n$ is the number average molecular weight of a polymer.

The PD value is an indication for the livingness of the polymerization. As a rule of thumb it can be said that a polymerization has proceeded under controlled conditions, when the PD of the obtained polymer is below 1.5 (final conclusions on the livingness of a polymerization however can only be made by plotting the molecular weights against conversion). Furthermore, gel permeation chromatography (GPC) traces will be shown for the polymers. They are especially helpful to determine whether, for the block polymers, chain extension has occurred, but also to see whether only one major polymer species has been synthesized. One major peak is an indication that only one main product might have been synthesized (however not a proof of this e.g. isomers). This has been the case for all the polymers synthesized in this section as will be shown in the respective graphs. Also, for the copolymers, the presence of only one major peak indicates successful purification of the copolymer and/or complete conversion of the macroinitiator polymer, otherwise the peak of the macroinitiator would be visible as well. The GPC traces that will be shown depict the response signal (as a measure of the concentration of the substance) against the retention time of the eluent (as a measure of the molecular weight of the substance). By means of a suitable calibration curve,
the retention times can be converted into the according molecular weights. A sample calibration curve that has been used for this work, using polystyrene standards, is depicted below (see Figure 3.1). The retention time of polystyrene standards of different molecular weights in chloroform as the eluent is plotted against the molecular weight of the standards. The greater the molecular weight, the shorter is the retention time. The GPC traces depicted in this work will contain the peaks for the macroinitiators and the block-copolymers simultaneously. If the peak of the block-copolymer is at a shorter retention time compared to the peak of the corresponding macroinitiator, it can be assumed that chain extension has occurred.

![Figure 3.1: GPC calibration with polystyrene standards. After calibration of the GPC instrument, retention times (RT) can then be set in relation to molecular weights (MW).](image)

### 3.1 Results RAFT Homo- and Copolymerizations

The controlled radical homopolymerization of methyl methacrylate (MMA) under RAFT conditions initiated with the RAFT agent S-1-dodecyl-S’-(a,a’dimethyl-a”-acetic acid) trithiocarbonate and ABCN with different amounts of ABCN and different solvents was studied first. The yields of block polymers and theoretical molecular weights of the polymers were calculated as shown in Section 4.2.
The RAFT polymerization of MMA using \( S-1\text{-dodecyl-S}^\prime-(a,a\text{'}dimeethyl-a\text{''}-acetic acid) \) trithiocarbonate was investigated by Dr. Shi using AIBN as initiator. However, because ABCN is the radical initiator, a suitable ABCN concentration to initiate the RAFT polymerization had to be found first. Typical mol\% of ABCN in regard to RAFT agents that have been used in current literature vary between 11 and 500 mol\% and we therefore randomly chose to employ 40 mol\% (R-PMMA1), 90 mol\% (R-PMMA2) and 210 mol\% (R-PMMA3) of ABCN in regard to S-1-dodecyl-S’-(a,a’-dimethyl-a”-acetic acid) trithiocarbonate.

The influence of the solvent on the polymerization of MMA under RAFT conditions at 40 mol\% of ABCN was also investigated. Therefore, R-PMMA1 was reacted in toluene, R-PMMA4 in acetonitrile (ACN) and R-PMMA5 in DMF. The yields, molecular weights and polydispersity indices of those polymerizations can be seen in Table 3.2.

All polymers exhibit relatively high polydispersities indicating that the polymerizations proceeded uncontrolled. Only R-PMMA1 had a molecular weight close to the theoretical molecular weight for 100\% conversion all other samples had either a distinctly lower or higher molecular weight. R-PMMA3 stands out with a PD of 2.4 clearly indicating that the polymerization employing 210 mol\% of ABCN proceeded under free radical polymerization conditions. Despite this, the yields and PDs of R-PMMA1-3 do not follow any rational trend. Even though R-PMMA2 exhibits the highest yield and smallest polydispersity, this method still employs a relatively high amount of ABCN which is unfavourable in regard of the amount of dead chain ends produced during the polymerization. At 40 mol\% of ABCN ACN seems to be the best solvent for the polymerization because it generates the PMMA with the lowest PD (1.6).

Based on the yields, molecular weights and molecular weight distributions obtained by the RAFT polymerizations of MMA using \( S-1\text{-dodecyl-S}^\prime-(a,a\text{'}dimeethyl-a\text{''}-acetic acid) \) trithiocarbonate as the RAFT agent it can be concluded that the polymerizations under the applied conditions proceeded uncontrolled. This might result in inability of the PMMA macroinitiators to reinitiate and therefore the chain extension of R-PMMA1 with lauryl methacrylate (LMA) under similar conditions as for R-PMMA1 was investigated. As a result, R-PMMA1-\( b\)-PLMA1 block copolymer with narrow molecular weight distribution (PD=1.3) was obtained in very low yield (mass of blockpolymer recovered lower than mass of macroinitiator used, possibly due to inability of THF to elude all polymer from the silica). The molecular weight of R-PMMA1-\( b\)-PLMA1 is
Table 3.2: Effect of ABCN concentration and solvent on RAFT polymerization of MMA by S-1-dodecyl-S’-(a,a’dimethyl-α”-acetic acid) trithiocarbonate.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>ABCN mol %</th>
<th>solvent</th>
<th>Yield (%)</th>
<th>(M_n,\text{theo}^b) (g mol(^{-1}))</th>
<th>(M_{n,\text{theo}}(100%)^c) (g mol(^{-1}))</th>
<th>(M_{n,GPC}) (g mol(^{-1}))</th>
<th>(M_{w,GPC}) (g mol(^{-1}))</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-PMMA1</td>
<td>40</td>
<td>toluene</td>
<td>47</td>
<td>4750</td>
<td>10100</td>
<td>11400</td>
<td>20000</td>
<td>1.8</td>
</tr>
<tr>
<td>R-PMMA2</td>
<td>90</td>
<td>toluene</td>
<td>75</td>
<td>7610</td>
<td>10100</td>
<td>13900</td>
<td>21900</td>
<td>1.6</td>
</tr>
<tr>
<td>R-PMMA3</td>
<td>210</td>
<td>toluene</td>
<td>12</td>
<td>1180</td>
<td>10100</td>
<td>4760</td>
<td>11300</td>
<td>2.4</td>
</tr>
<tr>
<td>R-PMMA4</td>
<td>40</td>
<td>ACN</td>
<td>69</td>
<td>7050</td>
<td>14900</td>
<td>10200</td>
<td>24401</td>
<td>1.6</td>
</tr>
<tr>
<td>R-PMMA5</td>
<td>40</td>
<td>DMF</td>
<td>79</td>
<td>12700</td>
<td>16100</td>
<td>10300</td>
<td>16100</td>
<td>1.9</td>
</tr>
</tbody>
</table>

\(^a\)The polymerizations were carried out at 80 °C for 24 h.

\(^b\)based on yield

\(^c\)calculated for 100% conversion

\(^d\)mol % in regard to RAFT agent.

23600 g mol\(^{-1}\) which is distinctly lower compared to the theoretical molecular weight for 100% conversion (31700 g mol\(^{-1}\)). The GPC traces (Figure 3.2) show that chain extension of R-PMMA1 has occured. Surprisingly, \(^1\)H NMR of R-PMMA1-\(b\)-PLMA1 (see 4.4.3) does not show any peaks for PLMA, which is in contrast to the GPC results obtained. One reason for this could be that the GPC traces obtained show polymer chains that could have resulted from dimerisation of R-PMMA1 instead of PMMA-\(b\)-PLMA. However further experiments would have to prove this.

![Figure 3.2: GPC traces of R-PMMA1 and R-PMMA1-b-PLMA1.](image)

It was then tried to approach the RAFT synthesis of PMMA-\(b\)-PLMA by polymerizing LMA under RAFT conditions first. Therefore, LMA was reacted with the RAFT agent and ABCN at a molar ratio of 1/0.4/100 (RAFT/ABCN/LMA) at 80 °C in toluene. Under those conditions no polymerization occured.
It can be concluded that under the employed reaction conditions PMMA can only be obtained with broad molecular weight distributions, PLMA could not be obtained at all and the molecular weight of the polymers synthesized could not be controlled. It could be tried to further decrease the ABCN concentration and to conduct the RAFT polymerization in different solvents and at different temperatures. However, because good control employing the ATRP method was obtained (see section 3.2) no further work was carried out on the RAFT polymerizations.

3.2 Results ATRP Homo- and Copolymerizations

This section shows the results for the ATRP synthesis of PMMA macroinitiators of different molecular weights, the block copolymerization thereof with LMA as well as the synthesis of PLMA macroinitiators via ATRP and the block copolymerization with MMA. The yields of block polymers and theoretical molecular weights of the polymers were calculated as shown in Section 4.2.

3.2.1 Results ATRP Homo and Copolymerizations for Polymers with PMMA molecular weight of ca. 3000 g mol\(^{-1}\)

The controlled radical polymerization of MMA by ATRP using EiBBr and CuCl as initiator and PMDETA as ligand aiming for a molecular weight of approximately 3000 g mol\(^{-1}\) was studied first (A-PMMA1). The polymerization was carried out at 90 °C for 1h. A-PMMA1 was obtained with 48% yield. The molecular weight of A-PMMA1 is 4160 g mol\(^{-1}\), which is 1.5 times higher then what was aimed for, and the PD is 1.3. To test whether A-PMMA1 is capable to chain extend we used it as a macroinitiator for the ATRP polymerization with MMA itself. It was aimed at obtaining a block polymer with two polymer chains of approximately the same length. Because A-PMMA1 was obtained with approximately 50% yield after 1 h, A-PMMA1 and MMA was therefore reacted in the weight ratio 1:2 and stopped the reaction after 1 h as well. The resulting polymer A-PMMA1-\(b\)-PMMA1 was obtained with 29% yield and GPC analysis showed that chain extension occured from 4160 g mol\(^{-1}\) to 7560 g mol\(^{-1}\) which is what has been aimed for (see Table 3.3). The low yield results possibly from the fact that the polymerization was stopped before 100% conversion and maybe because the workup conditions might not be optimized (adherence of product on silica possible).
Because chain extension proceeded with the test polymerization, the synthesis of A-PMMA1 (A-PMMA2) was repeated and block copolymerization of A-PMMA2 with LMA was tested. A-PMMA2 ($M_{n,GPC} = 4470 \text{ g mol}^{-1}$, $PD = 1.2$; see Table 3.3) was then used as macroinitiator for the ATRP polymerization with LMA. Again it was aimed at obtaining a block copolymer with polymer blocks of the same $M_n$ and therefore reacted A-PMMA2 with LMA in the weight ratio 1:2 and stopped the reaction after 1 h. The block copolymer obtained had a $M_{n,GPC}$ of 11100 g mol$^{-1}$ which is slightly lower than the $M_n$ for 100% conversion (13400 g mol$^{-1}$; see Table 3.3). A reason for this could be that not all A-PMMA2 polymer chains might have had contained active chain ends which might result from side reactions during the synthesis of A-PMMA2 also from the fact that different monomers react under different kinetical conditions and so LMA might polymerize faster than MMA under similar conditions which could also explain the higher yield. Another reason could be the irreversible oxidation of the active Cu(I) species to Cu(II).

A-PMMA2-$b$-PLMA1 was tested on its ability to stabilize DMSO/$n$-octane emulsions of the volume ratio 7/3 (v,v DMSO/$n$-octane). Emulsions with 2 wt%, 4 wt% and 6 wt% emulsifier were tested. An emulsion employing 11 wt% could not be tested because even after 5 h of sonication, no homogeneous emulsion was obtained. The emulsion with 2 wt% and with 4 wt% emulsifier became unstable after 5 min and the emulsion with 6 wt% became unstable after ca. 15 min.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>Yield</th>
<th>$M_{n,\text{theo}}$ g mol$^{-1}$</th>
<th>$M_{n,\text{theo(100%)}_{\text{I}}}$ g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ g mol$^{-1}$</th>
<th>$M_{w,\text{GPC}}$ g mol$^{-1}$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PMMA1</td>
<td>48</td>
<td>1320</td>
<td>2760</td>
<td>4160</td>
<td>5320</td>
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<td>A-PMMA2</td>
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<td>3060</td>
<td>4470</td>
<td>5300</td>
<td>1.2</td>
</tr>
<tr>
<td>A-PMMA1-$b$-PMMA1</td>
<td>29</td>
<td>5050</td>
<td>7260</td>
<td>7560</td>
<td>10200</td>
<td>1.3</td>
</tr>
<tr>
<td>A-PMMA2-$b$-PLMA1</td>
<td>47</td>
<td>8650</td>
<td>13400</td>
<td>11100</td>
<td>14000</td>
<td>1.3</td>
</tr>
</tbody>
</table>

aData The polymerizations were carried out at 90 °C for 1 h.

bCalculated for 100% conversion
3.2.2 Results ATRP Homo- and Copolymerizations for Polymers with PMMA molecular weight of ca. 6000 g mol$^{-1}$

A-PMMA3 of molecular weight 5670 g mol$^{-1}$ with relatively low molecular weight distribution (PD=1.4) was synthesized. A-PMMA3 was then used as macroinitiator for the synthesis of two emulsifiers, A-PMMA3-b-PLMA1 and A-PMMA3-b-PLMA2. The weight ratio for the synthesis of A-PMMA3-b-PLMA1 was 1:0.5 (A-PMMA3:LMA) whereas it was 1:1 for A-PMMA3-b-PLMA2 (A-PMMA3:LMA). Under the assumption of 100% conversion this would lead to A-PMMA3-b-PLMA1 of molecular weight 8460 g mol$^{-1}$ and to A-PMMA3-b-PLMA2 of molecular weight 11300 g mol$^{-1}$.

The molecular weights obtained are 9060 g mol$^{-1}$ for A-PMMA3-b-PLMA1 and 10900 g mol$^{-1}$ for A-PMMA3-b-PLMA2 which is in good agreement with the theoretical $M_n$ for 100% conversion. The GPC traces (Figure 3.3) show single peaks for the macroinitiator A-PMMA3 and the block copolymers and show that A-PMMA3-b-PLMA1 and A-PMMA3-b-PLMA2 have a molar mass greater than A-PMMA3 indicating successful chain extension. Both emulsifiers were obtained with narrow molecular weight distributions (PD=1.3). The molecular weights and molecular weight distributions of the emulsifiers indicate that the polymerizations proceeded controlled. In disagreement with this are the relatively low yields of the polymerizations, which in regard of the molecular weights and molecular weight distributions (that indicate complete conversions) could be explained by the inability of the experimental workup to recover all of the emulsifier (see Table 3.4).

Because A-PMMA3-b-PLMA1 and A-PMMA3-b-PLMA2 both contain PMMA of similar chain length and PLMA in varying chain length (PLMA shorter for A-PMMA3-b-PLMA1) it gave an interesting starting point to investigate the influence of the HLB of the emulsifier on the stability of our DMSO/$n$-octane emulsions. The HLB of A-PMMA3-b-PLMA1 is 12.5 and the HLB of A-PMMA3-b-PLMA2 is 10.4. According to the classification of Griffin emulsifier A-PMMA3-b-PLMA1 is therefore able to stabilize a DMSO/$n$-octane emulsions with $n$-octane as the inner phase whereas emulsifier A-PMMA3-b-PLMA2 is not. It has been tested whether those emulsifiers were able to stabilize an emulsion of the volume ratio 7/3 (v,v DMSO/$n$-octane) at 80 °C.

An emulsion with 10wt% of A-PMMA3-b-PLMA1 was stable for at least 6 hours.
whereas an emulsion with 10wt% A-PMMA3-b-PLMA2 is only stable for approximately 30 minutes. This is in agreement with Griffins theory.

Because 6 hours is a sufficient time to polymerize the hydrogels, emulsifier A-PMMA3-b-PLMA1 was employed for the emulsion templating method to create porous hydrogels as can be seen in section 5.2.

### Table 3.4: ATRP homopolymerization of MMA and chain extension with LMA II.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>Yield</th>
<th>( M_{n,\text{theo}} ) g mol(^{-1} )</th>
<th>( M_{n,\text{theo}(100%)} ) g mol(^{-1} )</th>
<th>( M_{n,GPC} ) g mol(^{-1} )</th>
<th>( M_{w,GPC} ) g mol(^{-1} )</th>
<th>PD</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PMMA3</td>
<td>49</td>
<td>3990</td>
<td>8120</td>
<td>5670</td>
<td>8030</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>A-PMMA3-b-PLMA1</td>
<td></td>
<td>/</td>
<td>8460</td>
<td>9060</td>
<td>11790</td>
<td>1.3</td>
<td>12.5</td>
</tr>
<tr>
<td>A-PMMA3-b-PLMA2</td>
<td></td>
<td>/</td>
<td>11260</td>
<td>10900</td>
<td>14600</td>
<td>1.3</td>
<td>10.4</td>
</tr>
</tbody>
</table>

\( ^a \)The polymerizations were carried out at 90 °C; 1 h for PMMA and 24 h for PMMA-b-PLMA.

\( ^b \)calculated for 100% conversion

\( ^c \)2.7 g recovered from 4.0 g A-PMMA3 and 2.0 g LMA

\( ^d \)3.2 g recovered from 4.0 g A-PMMA3 and 4.0 g LMA

![Figure 3.3: GPC traces of A-PMMA3, A-PMMA3-b-PLMA1 and A-PMMA3-b-PLMA2.](image)

3.2.3 Results ATRP Homo- and Copolymerizations for Polymers with PMMA molecular weight of ca. 20000 g mol\(^{-1}\)

It was then tried to synthesize PMMA of approximate molecular weight 20000 g mol\(^{-1}\). Because reaction conditions for this polymerization were not known,
a suitable method for the polymerization had to be found. Therefore, the educt ratio of EtBBr/MMA was maintained the influence of initially added Cu(II) species and monomer/solvent ratio on the process of the polymerization was tested. The addition of a small amount of Cu(II) at the beginning of the polymerization can reduce the amount of terminated chains, and because of this, help to keep the polymerization controlled. The ratio of solvent to monomer influences the polymerization rate. To test this, aliquots were taken from the reaction mixture after defined times and analyzed via GPC.

A-PMMA4 was reacted with CuCl₂ and with a volume ratio of MMA/toluene=1/1.6. Polymerization stopped at a molecular weight of around 1700 g mol⁻¹ which might have been due to inhibition of the polymerization by CuCl₂ or maybe because all Cu(I) activator was oxidized to Cu(II) or by loss of the halogen end group. A-PMMA5 was then reacted without initially adding CuCl₂ and with the same volume ratio of MMA to toluene. Polymerization again stopped at low molecular weight (Mₙ,GPC=4000 g mol⁻¹), however this Mₙ was already a little higher. The reason for the inability of this method to yield the desired molecular weight might be that the monomer was too dilute, which lead to retardation of the polymerization rate. This again might cause that side reactions increase in importance and therefore cause dead chain ends.

Therefore, A-PMMA6 was polymerized with the same molar ratios as for A-PMMA5 and the MMA/toluene volume ratio was decreased to 1/1. As a result, higher molecular weight PMMA of Mₙ,GPC=9000 g mol⁻¹ was obtained. However this is still distinctly lower than 20000 g mol⁻¹. The MMA/toluene volume ratio was further decreased to 1/0.2 and after 93 minutes the molecular weight of the polymer was 18200 g mol⁻¹. Polymerization was stopped at this point because the high molecular weight of the polymer caused the solution to be glassy.

A-PMMA7 was then polymerized under conditions as for A-PMMA6 and the reaction was stopped after 50 minutes to avoid a complicated workup. The polymer obtained was of molecular weight 19000 g mol⁻¹ and low PD (1.3). In a further reaction the ability of this polymer to chain extend was tested (A-PMMA7-PLMA1). The PMMA-b-PLMA block copolymer was obtained with a molecular weight distinctly below the theoretical molecular weight for 100% conversion and in bad yield (see Table 3.5).
shows that A-PMMA7-b-PLMA1 has a molar mass greater than A-PMMA7. The efficiency of emulsifier A-PMMA7-b-PLMA1 to stabilize DMSO-n-octane emulsions of the volume ratio 7/3 (v,v DMSO/n-octane) was tested. Emulsions with 5 wt% and 9 wt% of the emulsifier were tested. Phase separation of the two emulsions occurred after 5 min each.

Table 3.5: ATRP homopolymerization of MMA and chain extension with LMA III.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>Yield %</th>
<th>$M_{n,\text{theo}}$ g mol$^{-1}$</th>
<th>$M_{n,\text{theo}(100%)}$ g mol$^{-1}$</th>
<th>$M_{n,GPC}$ g mol$^{-1}$</th>
<th>$M_{w,GPC}$ g mol$^{-1}$</th>
<th>PD</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PMMA7</td>
<td>46</td>
<td>9280</td>
<td>9280</td>
<td>20000</td>
<td>19000</td>
<td>24400</td>
<td>1.3</td>
</tr>
<tr>
<td>A-PMMA7-b-PLMA1</td>
<td>37</td>
<td>3800</td>
<td>3780</td>
<td>29700</td>
<td>35700</td>
<td>3700</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*The polymerizations were carried out at 90 °C; 1 h for PMMA and 24 h for PMMA-b-PLMA.

1.0 g recovered from 1.0 g A-PMMA8 and 1.0 g LMA

*cannot be calculated for this yield

Figure 3.4: GPC traces of A-PMMA7 and A-PMMA7-b-PLMA1.

3.2.4 Results ATRP Homo- and Copolymerizations for Polymers with PMMA molecular weight of ca. 40000 g mol$^{-1}$

To synthesize PMMA of approximate molecular weight 40000 g mol$^{-1}$ a suitable procedure was to be found. The problem was approached in a similar manner as for PMMA of molecular weight 20000 g mol$^{-1}$. MMA was first polymerized by initially adding CuCl$_2$ and at a volume ratio of MMA/toluene=1/1.6 (A-PMMA9). The polymerization stopped at a molecular weight of about 5000 g mol$^{-1}$. For the same reason
as described under 3.2.3 the next approach was to polymerize MMA without initially adding CuCl₂ and under maintenance of the volume ratio of MMA to toluene (A-PMMA10). Surprisingly, this did not lead to polymerization at all. The synthesis was then tested without CuCl₂ and with less toluene (A-PMMA11) which lead to PMMA of maximum $M_n,_{GPC}$ of 5220 g mol$^{-1}$. Polymerization of MMA in bulk and without adding CuCl₂ to the reaction mixture was further tried (A-PMMA11). After 50 minutes a molecular weight of 25400 g mol$^{-1}$ was obtained and again, the reaction had to be stopped at this point because the mixture became solid.

A-PMMA13 has been reacted under conditions as for A-PMMA12 and the reaction was stopped after 50 minutes. The PMMA obtained had a molecular weight of 29200 g mol$^{-1}$ and PD of 1.4. A-PMMA13 was then reacted with LMA under ATRP conditions to test whether chain extension proceeds. A-PMMA13-b-PLMA1 was obtained with a molecular weight far below the theoretical molecular weigh for 100% conversion and in low yield. (see Table 3.6). The GPC traces for the macroinitiator and the block copolymer can be seen in Figure 3.5. The efficiency of emulsifier A-PMMA13-b-PLMA1 was tested on DMSO-$n$-octane emulsions of the volume ratio 7/3 (v,v DMSO/$n$-octane). Emulsions with 5 wt% and 9 wt% of the emulsifier were tested. Phase separation occurred after 5 min for the emulsion with 5 wt% and after 15 min for the emulsion with 9 wt%.

### Table 3.6: ATRP homopolymerization of MMA and chain extension with LMA IV.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>Yield %</th>
<th>$M_n,_{theo}$ g mol$^{-1}$</th>
<th>$M_n,_{theo}(100%)$ g mol$^{-1}$</th>
<th>$M_n,_{GPC}$ g mol$^{-1}$</th>
<th>$M_w,_{GPC}$ g mol$^{-1}$</th>
<th>PD</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PMMA13</td>
<td>60</td>
<td>12100</td>
<td>40000</td>
<td>29200</td>
<td>40000</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>A-PMMA13-b-PLMA1</td>
<td></td>
<td>0.38</td>
<td>69400</td>
<td>36900</td>
<td>50800</td>
<td>1.4</td>
<td>15.8</td>
</tr>
</tbody>
</table>

$^a$The polymerizations were carried out at 90 °C; 1 h for PMMA and 24 h for PMMA-b-PLMA.

$^b$0.38 g recovered from 0.50 g A-PMMA12 and 0.50 g LMA

$^c$cannot be calculated for this yield
3.2.5 Results ATRP Homo- and Copolymerizations for Polymers with PLMA molecular weight of ca. 8000 g mol$^{-1}$

It was of further interest whether the synthesis of PMMA-$b$-PLMA could as well be approached by synthesizing PLMA under ATRP conditions first and by using PLMA as the macroinitiator for the ATRP block polymer synthesis instead of using PMMA as macroinitiator.

A-PLMA1 was synthesized at 65 °C and at a volume ratio of LMA/toluene=1/0.3 as described by Xu et al. Under three different reaction conditions, it was then tested whether A-PLMA1 is able to initiate polymerization. Therefore, A-PLMA1-$b$-PMMA1 was synthesized by adding CuCl$_2$, A-PLMA1-$b$-PMMA2 was synthesized without adding CuCl$_2$ and A-PLMA1-$b$-PMMA3 was synthesized without adding CuCl$_2$ and with excess CuCl and excess PMDETA. All three reactions lead to chain extension of A-PLMA1. However, none of the methods resulted in A-PLMA1-$b$-PMMA with a molecular weight that was in agreement with the theoretical molecular weight and all block copolymers were obtained in low yield (see Table 3.7). The GPC traces (Figure 3.6) show that for all three block copolymers chain extension has occurred.

In conclusion, the ATRP polymerization using the initiator EiBBBr proved to be a more suitable method for the synthesis of PMMA-$b$-PLMA block polymers than the RAFT polymerization by S-1-dodecyl-S'-(a,a’dimethyl-a”-acetic acid) trithiocarbonate. The synthesis strategy of the polymers under RAFT conditions was not optimized enough to generate polymers with controlled molecular weights and narrow molecular weight.
Table 3.7: ATRP homopolymerization of LMA and chain extension with MMA.

<table>
<thead>
<tr>
<th>Results of Run</th>
<th>Yield</th>
<th>$M_{\text{n, theo}}$</th>
<th>$M_{\text{n, theo}(100%)}$</th>
<th>$M_{\text{n, GPC}}$</th>
<th>$M_{\text{w, GPC}}$</th>
<th>PD</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PLMA1</td>
<td>78%</td>
<td>6180</td>
<td>7890</td>
<td>7560</td>
<td>10200</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>A-PLMA2</td>
<td>61%</td>
<td>4850</td>
<td>7890</td>
<td>7520</td>
<td>10600</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>A-PLMA1-b-PMMA1</td>
<td>0.00%</td>
<td>7560</td>
<td>15200</td>
<td>7400</td>
<td>12800</td>
<td>1.7</td>
<td>8.3</td>
</tr>
<tr>
<td>A-PLMA2-b-PMMA1</td>
<td></td>
<td>/</td>
<td>22500</td>
<td>7400</td>
<td>12800</td>
<td>1.7</td>
<td>8.3</td>
</tr>
<tr>
<td>A-PLMA2-b-PMMA2</td>
<td></td>
<td>/</td>
<td>22500</td>
<td>11400</td>
<td>15600</td>
<td>1.4</td>
<td>10.4</td>
</tr>
<tr>
<td>A-PLMA2-b-PMMA3</td>
<td></td>
<td>/</td>
<td>15100</td>
<td>10200</td>
<td>13300</td>
<td>1.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>

\(^a\) PLMA was synthesized at 65 °C and PMMA-b-PLMA was synthesized at 90 °C.

\(^b\) 0.29 g recovered from 0.29 g A-PLMA2 and 0.60 g MMA

\(^c\) not applicable for those yields

\(^d\) 0.22 g recovered from 0.30 g A-PLMA2 and 0.60 g MMA

\(^e\) not applicable for those yields

\(^f\) 0.15 g recovered from 0.30 g A-PLMA2 and 0.30 g LMA

Figure 3.6: GPC traces of A-PLMA2 and A-PLMA2-b-PMMA1.

distributions. By means of ATRP synthesis using EiBBr as initiator it was possible to obtain PMMA-b-PLMA block polymers that could be used as an emulsifier in DMSO/n-octane emulsions. Moreover, at this stage it is more sufficient to use PMMA as macroinitiator for the synthesis of PMMA-b-PLMA block polymers under ATRP conditions then using PLMA as macroinitiator. However, this is most likely due to the fact that the polymerization conditions are not yet optimized for the latter case. The demonstrated ATRP methods need to be optimized to obtain higher yields of the products.

It should be noted that the molecular weights obtained for the PLMA and PMMA-b-PLMA block copolymers could be actually higher then the $M_n$ that were obtained from
GPC analysis due to differences of the bulkiness of PLMA to the polystyrene standards. Mahabadi et al. showed that the actual molecular weight of PLMA could be up to 1.8 times higher than the $M_{n,GPC}$ obtained by GPC analysis with polystyrene standards. As a result, detailed statements about the actual $M_{n,GPC}$ of our polymers that contain PLMA is complicated at this stage.

Why the emulsifiers A-PMMA8-$b$-PLMA1 and A-PMMA13-$b$-PLMA1 could not stabilize DMSO/$n$-octane emulsion even though according to their HLB values they should is not obvious at the moment.
References


Chapter 4

Experimental Section for Radical Polymerizations

4.1 Polymerization Methods

4.1.1 General Experimental Methodology

All solvents used were dry and degassed and all reactions were performed under argon. The molecular weight of the polymers were determined by Gel Permeation Chromatography (GPC) analysis using a PL-GPC 50 (A Varian, Inc. Company) integrated GPC system, coupled with UV and RI detectors. CHCl$_3$ was used as eluent and the flow rate of the CHCl$_3$ solution of polymers (2 mg of polymer in 1 mL of CHCl$_3$; 300 $\mu$L injected in each run) was 1 mL/min. The $M_n$,$GPC$ was determined against a calibration plot of polystyrene standards. $^1$H NMR spectra were recorded on Varian Unity Inova 400 MHz spectrometer in CDCl$_3$ (7.26 ppm) at 25°C.

4.1.2 General Procedures for Synthesis of Polymers by RAFT Polymerization

MMA was distilled under reduced pressure. MMA and LMA were purged with Argon for at least ten minutes prior to use. The RAFT agent S-1-dodecyl-S’-(a,a’dimethyl-a”-acetic acid) trithiocarbonate was synthesized in the group. ABCN was used as received. All solvents used were dry and degassed. The chemicals used for the RAFT syntheses can be seen in Figure 4.1.
RAFT Homopolymerizations

Method 1: RAFT Homopolymerization of MMA

A Schlenk tube equipped with ABCN, RAFT agent, magnetic stirrer and rubber septum was purged with argon. MMA and solvent were added to the schlenk tube. The solution was degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 80 °C for 24 h. The reaction was stopped by cooling the tube to room temperature. Afterwards, the tube was opened and the content was dissolved in THF. The solvent was evaporated in vacuo. The residue was redissolved in THF and precipitated in petroleum ether (three times). The polymer was dried in vacuo and characterized.

Method 2: RAFT Homopolymerization of LMA

A Schlenk tube equipped with ABCN, RAFT agent, magnetic stirrer and rubber septum was purged with argon. LMA and toluene were added to the schlenk tube. The solution was then degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 80 °C for 24 h. The reaction was stopped by cooling the tube to room temperature. Afterwards, the tube was opened and the content was dissolved in THF. The solvent was evaporated in vacuo. The residue was redissolved in about 0.1 mL of THF and precipitated in MeOH (three times). The polymer was dried in vacuo and characterized.

Figure 4.1: Molecular Structure of the chemicals used for RAFT polymerizations.
RAFT Copolymerization

Method 3: RAFT synthesis of PMMA-\(b\)-PLMA by PMMA macroinitiator

A Schlenk tube equipped with RAFT macroinitiator R-PMMA1, ABCN, magnetic stirrer and rubber septum was purged with argon. LMA and toluene were added to the schlenk tube. The solution was then degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 80 °C for 24 h. The reaction was stopped by cooling the tube to room temperature. Afterwards, the tube was opened and the content was dissolved in THF. The solvent was evaporated \textit{in vacuo}. The residue was redissolved in THF and precipitated in MeOH (three times). The polymer was dried \textit{in vacuo} at 30°C and characterized.

4.1.3 General Procedures for Synthesis of Polymers by ATRP Polymerization

MMA was distilled under reduced pressure. MMA and LMA were purged with argon for at least ten minutes prior to use. E\(r\)BBr, PMDETA, CuCl and CuCl\(_2\) were used as received. The chemicals used for the ATRP syntheses can be seen in Figure 4.2. All solvents used were dry and degassed.

![Figure 4.2: Molecular Structure of the chemicals used for ATRP syntheses.](image)
ATRP Homopolymerizations

Method 4: ATRP homopolymerization of MMA (when CuCl$_2$ is initially added)

A Schlenk tube equipped with magnetic stirrer and rubber septum was purged with argon and filled with MMA, E$i$BBr half of the PMDETA and toluene. In a separate glass vial CuCl$_2$, the second half of PMDETA and MeOH were mixed and ultrasonicated until formation of a homogeneous solution. This solution was then added to the schlenk tube. CuCl was added and the mixture was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 90°C. The reaction was stopped at a desired time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some EtOAc and filtered over silica (SiO$_2$) in a sintered glass Buchner funnel to remove the Cu complex. The filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in petroleum ether (three times). The polymer was dried in vacuo and characterized.

Method 5: ATRP homopolymerization of MMA (without initially adding CuCl$_2$)

A Schlenk tube equipped with magnetic stirrer and rubber septum was purged with argon and filled with MMA, E$i$BBr, PMDETA and toluene. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 90°C. The reaction was stopped at a desired time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some EtOAc and filtered over silica (SiO$_2$) in a sintered glass Buchner funnel to remove the Cu complex. The filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in petroleum ether (three times). The polymer was dried in vacuo and characterized.
Method 6: ATRP homopolymerization of MMA (without initially adding CuCl₂; in bulk)

A Schlenk tube equipped with magnetic stirrer and rubber septum was purged with argon and filled with MMA, EtBBBr and PMDETA. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 90°C. The reaction was stopped at a desired time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some EtOAc and filtered over silica (SiO₂) in a sintered glass Buchner funnel to remove the Cu complex. The solvent of the filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in petroleum ether (three times). The polymer was dried in vacuo and characterized.

Method 7: ATRP homopolymerization of LMA (when CuCl₂ is initially added)

A Schlenk tube equipped with magnetic stirrer and rubber septum was purged with argon and filled with LMA, EtBBBr, half of the PMDETA and toluene. In a separate glass vial CuCl₂, the second half of PMDETA and MeOH were mixed and ultrasonicated until formation of a homogeneous solution. This solution was then added to the schlenk tube. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at the desired temperature. The reaction was stopped after a certain time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some THF and filtered over silica (SiO₂) in a sintered glass Buchner funnel to remove the Cu complex. The filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in MeOH (three times). The polymer was dried at 30°C in vacuo and characterized.

Method 8: ATRP homopolymerization of LMA (without initially adding CuCl₂)

A Schlenk tube equipped with magnetic stirrer and a rubber septum was purged with argon and filled with LMA, EtBBBr, PMDETA and toluene. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and
the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at the desired temperature. The reaction was stopped after a certain time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some THF and filtered over silica ($\text{SiO}_2$) in a sintered glass Buchner funnel to remove the Cu complex. The solvent of the filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in MeOH (three times). The polymer was dried at 30°C in vacuo and characterized.

Method 9: Synthesis of PMMA-\textit{b}-PMMA by PMMA macroinitiator

A Schlenk tube equipped with PMMA macroinitiator, magnetic stirrer and rubber septum was purged with argon and filled with MMA, EiBBr, half of the PMDETA and toluene. In a separate glass vial CuCl$_2$, the second half of PMDETA and MeOH were mixed and ultrasonicated until formation of a homogeneous solution. This solution was then added to the schlenk tube. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 90°C. The reaction was stopped at a desired time by cooling the tube in liquid nitrogen. Afterwards, the tube was opened and the content was dissolved in some EtOAc and filtered over silica ($\text{SiO}_2$) in a sintered glass Buchner funnel to remove the Cu complex. The filtrate was evaporated in vacuo. The residue was redissolved in THF and the polymer was precipitated in MeOH (three times). The polymer was dried in vacuo and characterized.

Method 10: Synthesis of PMMA-\textit{b}-PLMA by PMMA macroinitiator

A Schlenk tube equipped with PMMA macroinitiator, magnetic stirrer and rubber septum was purged with argon and filled with LMA, half of the PMDETA and toluene. In a separate glass vial CuCl$_2$, the second half of PMDETA and MeOH were mixed and ultrasonicated until formation of a homogeneous solution. This solution was added to the schlenk tube. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at 90°C. The reaction was stopped at a desired time by cooling the tube in liquid nitrogen. Afterwards, the tubes were opened and the content was dissolved in THF and filtered over silica in a sintered glass
Buchner funnel. The filtrate was evaporated \textit{in vacuo}. The residue was redissolved in THF and the polymer was precipitated in MeOH (three times). The polymer was dried at 30°C \textit{in vacuo} and characterized.

**Method 11: Synthesis of PLMA-\textit{b}-PMMA (when CuCl}_2 \text{ is initially added)**

A Schlenk tube equipped with PLMA macroinitiator, magnetic stirrer and rubber septum was purged with argon and filled with MMA, half of the PMDETA and toluene. In a separate glass vial CuCl\textsubscript{2}, the second half of PMDETA and MeOH were mixed and ultrasonicated until formation of homogeneous solution. This solution was added to the schlenk tube. CuCl was added and the solution was immediately degassed with at least three freeze-evacuate-thaw cycles and the tube was finally charged with argon and sealed. The schlenk tube was placed in an oil bath at the desired temperature. The reaction was stopped after a certain time by cooling the tube in liquid nitrogen. Afterwards, the tubes were opened and the content was dissolved in THF and filtered over silica (SiO\textsubscript{2}) in a sintered glass Buchner funnel to remove the Cu complex. The solvent of the filtrate was evaporated \textit{in vacuo}. The residue was redissolved in THF and the polymer was precipitated in MeOH (three times). The polymer was dried at 30°C \textit{in vacuo} and characterized.

4.2 Calculation of Polymer Molecular Weight

**Homopolymer theoretical M\textsubscript{n} calculation**

\[
M_{n,\text{theo}} = M_w(\text{monomer}) \times \frac{\text{[monomer]}}{[\text{initiator}]} \times \text{yield (or conversion)} \tag{4.1}
\]

**Block-polymer theoretical M\textsubscript{n} calculation**

\[
M_{n,\text{theo}} = (M_w(\text{monomer}) \times \frac{\text{[monomer]}}{[\text{macroinitiator}]} \times \text{yield} + M_{n,\text{macroinitiator}} \tag{4.2}
\]

Yield is based on the weight increase of the recovered polymer in regard to the macroinitiator used.
Calculation of monomer/initiator ratio by $^1$H NMR

(a) PMMA

$$ratio(\text{MMA} : \text{EiBBr}) = \frac{\text{integral of methyl group in PMMA}}{\frac{3}{2} \text{integral of methylene group in EiBBr}}$$  \hfill (4.3)

The methyl group (OMe) in PMMA usually appears at 3.6 ppm and the methylene group in EiBBr usually appears at 4.1 ppm.

(b) PMMA-$b$-PLMA block copolymers

The ratio between MMA to LMA monomer units in PMMA-$b$-PLMA block copolymers can be calculated as follows:

$$ratio(\text{MMA} : \text{LMA}) = \frac{\text{integral of methyl group in PMMA}}{\frac{3}{2} \text{integral of methylene group in PLMA}}$$  \hfill (4.4)

The methyl group (OMe) in PMMA usually appears at 3.6 ppm and the methylene group (OCH$_2$) in PLMA usually appears at 3.9 ppm.

4.3 Calculation of Hydrophile Lipophile Balance

According to Griffin\textsuperscript{2} the HLB value for emulsifiers can be calculated as follows:

$$HLB = 20 \times (1 - \frac{M(\text{hydrophobic polymer block})}{M(\text{block polymer})})$$  \hfill (4.5)

For the emulsifiers synthesized in this work this becomes:

$$HLB = 20 \times (1 - \frac{M(\text{PLMA block})}{M(\text{PMMA-$b$-PLMA})})$$  \hfill (4.6)

The HLB values are calculated using the molecular weights determined by GPC.
4.4 Conditions and Results of RAFT Polymerizations

4.4.1 RAFT homopolymerization of MMA by S-1-dodecyl-S’-(a,a’dimethyl-a”-acetic acid) trithiocarbonate

![Figure 4.3: General structure of RAFT PMMA.](image)

General $^1$H NMR spectrum of RAFT PMMA

$^1$H NMR (δ ppm, CDCl$_3$, 400 MHz): 3.60 (s, OCH$_3$), 2.10-0.83 (CH$_2$ ethylene backbone, α- CH$_3$, S(CH$_2$)$_{11}$, CH$_2$CH$_3$, C(CH$_3$)$_2$)

R-PMMA1

The polymer was synthesized according to method 1.

RAFT/ABCN/MMA (0.75 mL, 7.0 mmol)=1/0.4/101. Toluene: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 47%. Anal. GPC assay CHCl$_3$: $M_n$,$GPC$=11400 g mol$^{-1}$, $M_w$,$GPC$=20000 g mol$^{-1}$, PD=1.8. Theoretical $M_n$=5120 g mol$^{-1}$, Theoretical $M_n$(100%)=10100 g mol$^{-1}$.

R-PMMA2

The polymer was synthesized according to method 1.

RAFT/ABCN/MMA (0.75 mL, 7.0 mmol)=1/0.9/101. Toluene: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 75%. Anal. GPC assay CHCl$_3$: $M_n$,$GPC$=14000 g mol$^{-1}$, $M_w$,$GPC$=21900 g mol$^{-1}$, PD=1.6. Theoretical $M_n$=7970 g mol$^{-1}$, Theoretical $M_n$(100%)=10100 g mol$^{-1}$.
R-PMMA3

The polymer was synthesized according to method 1.

RAFT/ABCN/MMA (0.75 mL, 7.0 mmol)=1/2.1/101. Toluene: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 12%. Anal. GPC assay CHCl₃: $M_n,GPC=4760$ g mol⁻¹, $M_w,GPC=11300$ g mol⁻¹, PD=2.4. Theoretical $M_n=1540$ g mol⁻¹, Theoretical $M_n(100%)=10100$ g mol⁻¹.

R-PMMA4

The polymer was synthesized according to method 1.

RAFT/ABCN/MMA (0.75 mL, 7.0 mmol)=1/0.4/102. ACN: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 69%. Anal. GPC assay CHCl₃: $M_n,GPC=14900$ g mol⁻¹, $M_w,GPC=24400$ g mol⁻¹, PD=1.6. Theoretical $M_n=7420$ g mol⁻¹, Theoretical $M_n(100%)=10200$ g mol⁻¹.

R-PMMA5

The polymer was synthesized according to method 1.

RAFT/ABCN/MMA (0.75 mL, 7.0 mmol)=1/0.4/103. DMF: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 79%. Anal. GPC assay CHCl₃: $M_n,GPC=16100$ g mol⁻¹, $M_w,GPC=31200$ g mol⁻¹, PD=1.9. Theoretical $M_n=8470$ g mol⁻¹, Theoretical $M_n(100%)=10300$ g mol⁻¹.

4.4.2 RAFT homopolymerization of LMA by S-1-dodecyl-S’-(a,a’dimethyl-a”-acetic acid) trithiocarbonate

R-PLMA1

The polymer was synthesized according to method 2.
RAFT/ABCN/LMA (0.75 mL, 7.0 mmol)=1/0.4/100. Toluene: 1.25 mL, Temperature: 80 °C, Time: 24 h, Yield: 0%.

### 4.4.3 RAFT Synthesis of PMMA-b-PLMA by PMMA macroinitiator

![General structure of RAFT PLMA.](image)

**Figure 4.4:** General structure of RAFT PLMA.

**Figure 4.5:** General structure of RAFT PMMA-b-PLMA.

General $^1$H NMR spectrum of RAFT PMMA-b-PLMA

$^1$H NMR (δ ppm, CDCl$_3$, 400 MHz): 3.60 (s, OCH$_3$), 2.10-0.83 (CH$_2$ ethylene backbone, α- CH$_3$, S(CH$_2$)$_{11}$, CH$_2$CH$_3$, C(CH$_3$)$_2$)

**R-PMMA1-b-PLMA1**

The polymer was synthesized according to method 3.

R-PMMA1 (M$_{n,GPC}$=11384 g mol$^{-1}$)/ABCN/LMA (0.51 mL, 1.8 mmol)=1/0.5/100. Toluene: 1.60 mL, Temperature: 80 °C, Time: 24 h, Yield: 0.12 g PMMA-co-PLMA could be recovered from 0.2 g macroinitiator R-PMMA1 and 0.44 g LMA. Anal. GPC
Theoretical $M_n=16000 \text{ g mol}^{-1}$. Analysis of the $^1\text{H}$ NMR spectrum indicates the ratio between PLMA and initiator is 0.

### 4.5 Conditions and Results of ATRP Polymerizations

#### 4.5.1 ATRP Homopolymerization of MMA by $\text{EtBr}/\text{CuCl}/\text{CuCl}_2/\text{PMDETA}/\text{MMA}$

General $^1\text{H}$ NMR spectrum of ATRP-PMMA

$^1\text{H}$ NMR ($\delta$ ppm, CDCl$_3$, 400 MHz): 4.10-4.07 (m, CH$_2$OCO), 3.60 (s, OCH$_3$), 2.10-1.83 (CH$_2$ ethylene backbone), 1.60-0.83 (CH$_3$CH$_2$, C(CH$_3$)$_2$, $\alpha$- CH$_3$)

**A-PMMA1**

The polymer was synthesized according to method 4.

EtBr/ CuCl/ CuCl$_2$/ PMDETA/ MMA (1.0 mL, 9.4 mmol) = 1/0.9/1.0/1.8/27.6. Toluene: 1.60 mL, MeOH: 0.4 mL, Temperature: 90 °C, Time: 1 h, Yield: 48%. Anal. GPC assay CHCl$_3$: $M_n,GPC=4160$ g mol$^{-1}$, $M_w,GPC=5320$ g mol$^{-1}$, PD=1.3. Theoretical $M_n=1320$ g mol$^{-1}$. Analysis of the $^1\text{H}$ NMR spectrum indicates the ratio between PMMA and initiator is 37:1.

**A-PMMA2**

The polymer was synthesized according to method 4.
EtBBBr/CuCl/CuCl₂/PMDETA/MMA (2.0 mL, 18.8 mmol)=1/1.0/1.0/2.0/30.6. Toluene: 3.20 mL, MeOH: 0.4 mL, Temperature: 90 °C, Time: 1 h, Yield: 47%. Anal. GPC assay CHCl₃: $M_n,GPC=4470$ g mol⁻¹, $M_w,GPC=5300$ g mol⁻¹, PD=1.2. Theoretical $M_n=1430$ g mol⁻¹. Analysis of the $^1$H NMR spectrum indicates the ratio between PMMA and initiator is 39:1.

A-PMMA3

The polymer was synthesized according to method 4.

EtBBBr/CuCl/CuCl₂/PMDETA/MMA (20.0 mL, 187.8 mmol)=1/1.0/1.0/2.0/81.1. Toluene: 32.0 mL, MeOH: 5.0 mL, Temperature: 90 °C, Time: 1 h, Yield: 49%. Anal. GPC assay CHCl₃: $M_n,GPC=5670$ g mol⁻¹, $M_w,GPC=8030$ g mol⁻¹, PD=1.4. Theoretical $M_n=3990$ g mol⁻¹, Theoretical $M_n$(100%conversion)=8120 g mol⁻¹. Analysis of the $^1$H NMR spectrum indicates the ratio between PMMA and initiator is 68:1.

A-PMMA4

The polymer was synthesized according to method 4.

EtBBBr/CuCl/CuCl₂/PMDETA/MMA (5.0 mL, 46.9 mmol)=1/1.0/1.0/2.0/200. Toluene: 8.0 mL, MeOH: 0.3 mL, Temperature: 90 °C, Time: 8 h. Theoretical $M_n$(100% conversion)=20000 g mol⁻¹. Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: $M_n,GPC$(4 h 35 min)=1830 g mol⁻¹, PD=1.4; $M_n,GPC$(8 h)=1690 g mol⁻¹, PD=1.5.

A-PMMA5

The polymer was synthesized according to method 5.

EtBBBr/CuCl/PMDETA/MMA (5.0 mL, 46.9 mmol)=1/1.0/1.0/200. Toluene: 8.0 mL, Temperature: 90 °C, Time: 22 h 15 min. Theoretical $M_n$(100% conversion)=20000 g mol⁻¹. Aliquots were taken after defined times, precipitated in petroleum ether and analyzed
via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: \( M_n,\text{GPC}(8 \text{ h}) = 1070 \text{ g mol}^{-1}, \text{PD}=1.8; M_n,\text{GPC}(22 \text{ h 15 min}) = 4000 \text{ g mol}^{-1}, \text{PD}=1.3.\)

**A-PMMA6**

The polymer was synthesized according to method 5.

\[ \text{EtBBBr/CuCl/PMDETA/MMA (2.5 mL, 23.4 mmol)=1/1.3/2.4/200. Toluene: 2.5 mL, Temperature: 90 °C, Time: 7 h 45 min. Theoretical } M_n(100\% \text{ conversion})=20000 \text{ g mol}^{-1}. \]

Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: \( M_n,\text{GPC}(6 \text{ h 18 min}) = 9180 \text{ g mol}^{-1}, \text{PD}=1.5; M_n,\text{GPC}(7 \text{ h 45 min}) = 9090 \text{ g mol}^{-1}, \text{PD}=1.5.\)

**A-PMMA7**

The polymer was synthesized according to method 5.

\[ \text{EtBBBr/CuCl/PMDETA/MMA (2.5 mL, 23.4 mmol)=1/1.4/2.4/200. Toluene: 0.5 mL, Temperature: 90 °C, Time: 93 min. Theoretical } M_n(100\% \text{ conversion})=20024 \text{ g mol}^{-1}. \]

Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: \( M_n,\text{GPC}(15 \text{ min}) = 9010 \text{ g mol}^{-1}, \text{PD}=1.4; M_n,\text{GPC}(30 \text{ min}) = 11500 \text{ g mol}^{-1}, \text{PD}=1.4; M_n,\text{GPC}(62 \text{ min}) = 17400 \text{ g mol}^{-1}, \text{PD}=1.3; M_n,\text{GPC}(93 \text{ min}) = 18200 \text{ g mol}^{-1}, \text{PD}=1.4.\)

**A-PMMA8**

The polymer was synthesized according to method 5.

\[ \text{EtBBBr/CuCl/PMDETA/MMA (2.5 mL, 23.4 mmol)=1/1.4/2.4/200. Toluene: 0.5 mL, Temperature: 90 °C, Time: 50 min, Yield: 46\%. Anal. GPC assay CHCl₃: } M_n,\text{GPC}=19000 \text{ g mol}^{-1}, M_w,\text{GPC}=24400 \text{ g mol}^{-1}, \text{PD}=1.3. \text{ Theoretical } M_n = 9270 \text{ g mol}^{-1}.\)

**A-PMMA9**

The polymer was synthesized according to method 4.
EtBBr/CuCl/CuCl₂/PMDETA/MMA (5.0 mL, 46.9 mmol)=1/1.0/1.0/2.0/400. Toluene: 8.0 mL, MeOH: 0.15 mL, Temperature: 90 °C, Time: 24 h. Theoretical $M_n$(100% conversion)=40000 g mol$^{-1}$. Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: $M_{n,GPC}$(11 h)=648 g mol$^{-1}$, PD=1.3; $M_{n,GPC}$(24 h)=5180 g mol$^{-1}$, PD=1.6.

A-PMMA10

The polymer was synthesized according to method 5.

EtBBr/CuCl/PMDETA/MMA (5.0 mL, 46.9 mmol)=1/1.1/1.0/400. Toluene: 8.0 mL, Temperature: 90 °C, Time: 7 h 15 min. Theoretical $M_n$(100% conversion)=40000 g mol$^{-1}$. Aliquots were taken after defined times and petroleum ether was added to the aliquots. No precipitation.

A-PMMA11

The polymer was synthesized according to method 5.

EtBBr/CuCl/PMDETA/MMA (2.5 mL, 23.4 mmol)=1/1.6/2.7/400. Toluene: 0.5 mL, Temperature: 90 °C, Time: 21 h 5 min. Theoretical $M_n$(100% conversion)=40000 g mol$^{-1}$. Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: $M_{n,GPC}$(2 h)=4940 g mol$^{-1}$, PD=1.3; $M_{n,GPC}$(21 h 5 min)=5220 g mol$^{-1}$, PD=1.3.

A-PMMA12

The polymer was synthesized according to method 5.

EtBBr/CuCl/PMDETA/MMA (5.0 mL, 46.9 mmol)=1/1.4/2.6/400. In bulk, Temperature: 90 °C, Time: 50 min. Theoretical $M_n$(100% conversion)=40000 g mol$^{-1}$. Aliquots were taken after defined times, precipitated in petroleum ether and analyzed via GPC to see whether polymerization proceeds. Anal. GPC assay CHCl₃: $M_{n,GPC}$(15
min) = 10700 g mol⁻¹, PD = 1.4; Mₙ,GPC(40 min) = 20500 g mol⁻¹, PD = 1.4; Mₙ,GPC(50 min) = 25400 g mol⁻¹, PD = 1.4; 50 min stopped because solid.
A-PMMA13

The polymer was synthesized according to method 5.

\[
\text{EtBBr/CuCl/PMDETA/MMA (2.5 mL, 23.4 mmol)=1/1.7/2.6/400. Toluene: 0.5 mL, Temperature: 90 ^\circ\text{C}, Time: 50 min, Yield: 60\%. Anal. GPC assay CHCl}_3:\ M_n,GPC=29200 \text{ g mol}^{-1}, M_{w,GPC}=40000 \text{ g mol}^{-1}, \text{PD}=1.4. \text{ Theoretical } M_n=12100 \text{ g mol}^{-1}.
\]

4.5.2 Conditions and Results of ATRP homopolymerizations of LMA by EtBBr

![General structure of ATRP PLMA.](image)

**Figure 4.7:** General structure of ATRP PLMA.

General \(^1\text{H}\) NMR spectrum of ATRP-PLMA

\(^1\text{H}\) NMR (δ ppm, CDCl\(_3\), 400 MHz): 4.10-4.07 (m, CH\(_2\)OCO), 3.90 (m, OCH\(_2\)), 2.10-1.83 (CH\(_2\) ethylene backbone), 1.65-0.70 (CH\(_3\)CH\(_2\)O, C(CH\(_3\))\(_2\), α-CH\(_3\), OCH\(_2\)CH\(_2\), CH\(_2\)(CH\(_2\))\(_{10}\), (CH\(_2\))\(_{10}\)CH\(_3\))

A-PLMA1

The polymer was synthesized according to method 8.

\[
\text{EtBBr/CuCl/PMDETA/LMA (1 mL, 3.4 mmol)=1/1.0/1.0/31. Toluene: 0.3 mL, Temperature: 90 ^\circ\text{C}, Time: 1 h, Yield: 7800\%. Anal. GPC assay CHCl}_3: M_{n,GPC}=7560 \text{ g mol}^{-1}, M_{w,GPC}=10200 \text{ g mol}^{-1}, \text{PD}=1.3. \text{ Theoretical } M_n=6180 \text{ g mol}^{-1}.
\]
4.5.3 ATRP Synthesis of PMMA by PMMA macroinitiator

![Image of chemical structure]

**Figure 4.8:** General structure of ATRP PMMA synthesized by PMMA macroinitiator.

General $^1$H NMR spectrum of ATRP-PMMA

$^1$H NMR ($\delta$ ppm, CDCl$_3$, 400 MHz): 4.10-4.07 (m, CH$_2$OCO), 3.60 (s, OCH$_3$), 2.10-1.83 (CH$_2$ ethylene backbone), 1.60-0.83 (CH$_3$CH$_2$, C(CH$_3$)$_2$, \(\alpha\)-CH$_3$)

**A-PMMA1-b-PMMA1**

The polymer was synthesized according to method 9.

A-PMMA1 $M_{n,GPC}=4161$ g mol$^{-1}$/CuCl/CuCl$_2$/PMDETA/MMA (1.0 mL, 3.4 mmol)=-1/1.1/1.0/31. Toluene: 0.3 mL, Temperature: 90 °C, Time: 1 h, Yield: 29%. Anal. GPC assay CHCl$_3$: $M_{n,GPC}=7560$ g mol$^{-1}$, $M_{w,GPC}=10200$ g mol$^{-1}$, PD=1.3. Theoretical $M_n=5050$ g mol$^{-1}$, Theoretical $M_n$(100% conversion)=7260 g mol$^{-1}$. Analysis of the $^1$H NMR spectrum indicates the ratio between PMMA and initiator EtBBR is 66.7:1.

4.5.4 ATRP Synthesis of PMMA-b-PLMA by PMMA macroinitiator

$^1$H NMR ($\delta$ ppm, CDCl$_3$, 400 MHz): 4.10-4.07 (m, CH$_2$OCO), 3.90 (m, OCH$_2$), 3.60 (s, OCH$_3$), 2.10-1.83 (CH$_2$ ethylene backbone), 1.65-0.70 (CH$_3$CH$_2$O, C(CH$_3$)$_2$, \(\alpha\)-CH$_3$, OCH$_2$CH$_2$, CH$_2$(CH$_2$)$_{10}$, (CH$_2$)$_{10}$CH$_3$)
A-PMMA2-b-PLMA1

The polymer was synthesized according to method 10.

A-PMMA2 ($M_{n,GPC}=4470$ g mol$^{-1}$)/CuCl/CuCl$_2$/PMDETA/LMA (1.1 mL, 3.8 mmol) =1/2.8/3.0/5.6/35. Toluene: 1.60 mL, MeOH: 0.4 mL, Temperature: 90 °C, Time: 1 h, Yield: 47%. Anal. GPC assay CHCl$_3$: $M_{n,GPC}=11100$ g mol$^{-1}$, $M_{w,GPC}=14000$ g mol$^{-1}$, PD=1.3, HLB=8.1. Theoretical $M_n=8650$ g mol$^{-1}$, Theoretical $M_n$(100% conversion)$=13400$ g mol$^{-1}$. Analysis of the $^1$H NMR spectrum indicates the ratio between PLMA and initiator is 1.06:1.

A-PMMA3-b-PLMA1

The polymer was synthesized according to method 10.

A-PMMA4 ($M_{n,GPC}=5670$ g mol$^{-1}$)/CuCl/CuCl$_2$/PMDETA/LMA (2.3 mL, 7.9 mmol) =1/0.99/1.0/2.0/11.2. Toluene: 8.50 mL, MeOH: 0.8 mL, Temperature: 90 °C, Time: 24 h, Yield: 2.7 g recovered (4 g A-PMMA4, 2 g LMA). Anal. GPC assay CHCl$_3$: $M_{n,GPC}=9060$ g mol$^{-1}$, $M_{w,GPC}=11800$ g mol$^{-1}$, PD=1.3, HLB=12.5. Theoretical $M_n=8520$ g mol$^{-1}$. Analysis of the $^1$H NMR spectrum indicates the molar ratio between PLMA and initiator is 0.20:1.

A-PMMA3-b-PLMA2

The polymer was synthesized according to method 10.

A-PMMA4 ($M_{n,GPC}=5670$ g mol$^{-1}$)/CuCl/CuCl$_2$/PMDETA/LMA (4.6 mL, 15.8 mmol) =1/1.0/1.0/2.0/22.4. Toluene: 8.50 mL, MeOH: 0.8 mL, Temperature: 90 °C, Time:
24 h, Yield: 0.60 g recovered (1.1 g A-PMMA4, 1.1 g LMA). Anal. GPC assay CHCl₃: $M_n,GPC=10900$ g mol⁻¹, $M_w,GPC=14600$ g mol⁻¹, PD=1.3, HLB=10.4. Theoretical $M_n$(100% conversion)=11400 g mol⁻¹. Analysis of the $^1$H NMR spectrum indicates the molar ratio between PLMA and initiator is 0.52:1.

**A-PMMA8-b-PLMA1**

The polymer was synthesized according to method 10.

A-PMMA8 ($M_n,GPC=19000$ g mol⁻¹)/CuCl/CuCl₂/PMDETA/LMA (0.57 mL, 1.9 mmol) =1/1.5/1.0/2.2/74. Toluene: 2.00 mL, MeOH: 0.04 mL, Temperature: 90 °C, Time: 24 h, Yield: 1.0 g recovered from 1.0 g A-PMMA8 and 1.0 g LMA. Anal. GPC assay CHCl₃: $M_n,GPC=29700$ g mol⁻¹, $M_w,GPC=35700$ g mol⁻¹, PD=1.2, HLB=12.8. Theoretical $M_n$(100% conversion)=37800 g mol⁻¹.

**A-PMMA13-b-PLMA1**

The polymer was synthesized according to method 10.

A-PMMA13 ($M_n,GPC=29200$ g mol⁻¹)/CuCl/CuCl₂/PMDETA/LMA (1.15 mL, 3.9 mmol)=1/1.3/1.0/2.2/115.4. Toluene: 4.00 mL, MeOH: 0.04 mL, Temperature: 90 °C, Time: 24 h, Yield: 0.38 g recovered from 0.50 g A-PMMA12 and 0.50 g LMA. Anal. GPC assay CHCl₃: $M_n,GPC=36900$ g mol⁻¹, $M_w,GPC=50800$ g mol⁻¹, PD=1.4, HLB=15.8. Theoretical $M_n$(100% conversion)=58600 g mol⁻¹.

### 4.5.5 Conditions and Results of ATRP Copolymerizations of PLMA macroinitiator with MMA

**General $^1$H NMR spectrum of ATRP PMMA-b-PLMA**

$^1$H NMR (δ ppm, CDCl₃, 400 MHz): 4.10-4.07 (m, CH₂OCO), 3.90 (t, OCH₂), 3.60 (s, OCH₃), 2.10-1.83 (CH₂ ethylene backbone), 1.65-0.70 (CH₃CH₂O, C(CH₃)₂, α-CH₃, OCH₂CH₂, CH₂(CH₂)₁₀, (CH₂)₁₀CH₃)
A-PLMA1-b-PMMA1

The polymer was synthesized according to method 11.

A-PLMA2 (M_{n,GPC}=7520 \text{ g mol}^{-1})/CuCl/PMDETA/MMA (0.64 mL, 6.3 mmol) =1/1.0/1.0/150. Toluene: 1.0 mL, Temperature: 90 °C, Time: 24 h, Yield: 0.29 g recovered from 0.29 g A-PLMA2 and 0.60 g MMA. Anal. GPC assay CHCl₃: M_{n,GPC}=11400 \text{ g mol}^{-1}, M_{w,GPC}=15600 \text{ g mol}^{-1}, PD=1.4, HLB=5.8. Theoretical M_{n}=22900 \text{ g mol}^{-1}. Analysis of the $^1$H NMR spectrum indicates the ratio between PMMA and initiator is 0.40:1.

A-PLMA1-b-PMMA2

The polymer was synthesized according to method 10.

A-PLMA2 (M_{n,GPC}=7520 \text{ g mol}^{-1})/CuCl/CuCl₂/PMDETA/MMA (0.64 mL, 6.3 mmol) =1/1.0/2.0/150. Toluene: 1.0 mL, Temperature: 90 °C, Time: 24 h, Yield: 0.22 g recovered (0.30 g A-PLMA2, 0.60 g LMA). Anal. GPC assay CHCl₃: M_{n,GPC}=10600 \text{ g mol}^{-1}, M_{w,GPC}=14100 \text{ g mol}^{-1}, PD=1.3, HLB=5.8. Theoretical M_{n}=22900 \text{ g mol}^{-1}. Analysis of the $^1$H NMR spectrum indicates the ratio between PMMA and initiator is 0.06:1.

A-PLMA1-b-PMMA3

The polymer was synthesized according to method 11.

A-PLMA2 (M_{n,GPC}=7520 \text{ g mol}^{-1})/CuCl/PMDETA/MMA (0.32 mL, 3.0 mmol)
Toluene: 1.0 mL, Temperature: 90 °C, Time: 4 h, Yield: 0.15 g recovered from 0.30 g A-PLMA2 and 0.30 g LMA. Anal. GPC assay CHCl₃: $M_{n,\text{GPC}} = 10200$ g mol⁻¹, $M_{w,\text{GPC}} = 13300$ g mol⁻¹, PD=1.3, HLB=5.2. Theoretical $M_n = 15100$ g mol⁻¹.
References


Chapter 5

Hydrogel and Actuator Synthesis and Characterization

In this chapter the effect of the four previously mentioned porogen methods (see Section 2.6) on the microstructure and swelling response of hydrogels will be tested on simple PHEA hydrogel test systems. It will be investigated how the different methods alter the swelling rate of the hydrogels by swelling the gels in DMF. The degree of swelling $Q$ (see equation 2.1) will therefore be plotted against the time (measured starting with the immersion of the hydrogels in DMF) and the swelling response rate of the porous gels will be compared to that of the nonporous PHEA hydrogel system. Two graphs will always be shown for the porous PHEA hydrogels. The first will show the swelling behavior in the initial swelling stage (showing the first minutes or seconds) so that swelling rate differences to the nonporous hydrogel (named ”reference” in the graphs) can be seen more easily. The second shows the swelling of the hydrogels up to $Q_{eq}$. This is done, because it is important to determine whether nonporous and porous hydrogels exert the same $Q_{eq}$ to be able to compare the swelling rates. The microstructure of the cross-section of the samples will be investigated via scanning electron microscopy (SEM). Cryo-SEM pictures will be shown with 2000-fold (left pictures respectively) and 500-fold (right pictures respectively) magnification to more easily distinguish pore size and structure of the hydrogels and to control whether the hydrogel shows different types of patterning on different magnification scales. Cryo-SEM images can tell us whether the pores obtained are in the meso-, macro or supermacropores range. Mesopores have a diameter between 2 and 50 nm, macropores between 50 nm and 1 µm and supermacropores between 1 µm and 10 µm. If found that a method is suitable to distinctly increase the swelling rate of the test systems it will then be applied to the
quinone or the TEMPO actuator devices (section 5.6). For the redox responsive actuators the electrochemically induced length changes will be plotted against the time (measured starting with electrochemical reduction or oxidation) and the results will be compared to the nonporous actuator devices.

## 5.1 Nonporous PHEA Hydrogels

All PHEA hydrogels, nonporous and porous, were synthesized by free radical crosslinking reaction of HEA with PEGDA with an azo-initiator according to Scheme 5.1. The resulting crosslinked polymer contains many hydroxylated sidegroups that make the hydrogel hydrophilic. Because of this, the hydrophilic polymer network can swell in polar solvents such as water, DMF or DMSO and shrink in less polar solvents such as MeOH or THF. To record swelling of the hydrogels we therefore stored them in THF before swelling so that they were in a nonswollen state. For swelling to start, the hydrogels were then immersed into DMF and the change of weight was followed with the time (using a standard balance) until the equilibrium degree of swelling was reached.

\[
\begin{align*}
\text{HEA} & \quad + \quad \text{PEGDA} \\
\text{DMF or DMSO, 80 °C} & \quad \xrightarrow{\text{ABCN}} \quad \text{GEL}
\end{align*}
\]

**Scheme 5.1:** Synthesis of PHEA hydrogel.

To be able to evaluate the efficiency of a porogen method it is important to characterize the nonporous samples first. As can be seen in Figure 5.1 the solvent induced swelling of the nonporous PHEA hydrogel of size ca. 0.125 cm³ in DMF takes about 50 hours for complete swelling to a \(Q_{eq}\) of 800%, with 50% swelling occurring after 2 h. The cryo-SEM images of the nonporous PHEA hydrogel (Figure 5.2) reveal a relatively smooth surface. The wrinkles are probably caused by either the cutting of the hydrogel sample slice during the cryo-SEM measurement preparation or during the freezing process in the cryo-SEM sample preparation. However, no distinct porous structure can be seen.
5.2 Emulsion Templated PHEA Hydrogels

PMMA-\textit{b}-PLMA block copolymers were tested on their ability to stabilize DMSO/\textit{n}-octane emulsion of a volume ratio 7/3 (v/v; DMSO/\textit{n}-octane). This volume ratio was chosen so that the resulting hydrogels would still be mechanically stable. By using the block copolymer A-PMMA3-\textit{b}-PLMA1 as a surfactant in a DMSO/\textit{n}-octane emulsion of a volume ratio 7/3 (v/v; DMSO/\textit{n}-octane) we obtained a stable emulsion at 80 °C by employing 10 wt\% of the emulsifier. This emulsion was stable for at least 6 h which is a sufficient time for the hydrogel polymerization. We then prepared a porous hydrogel according to method E (sample E-PHEA) (see chapter 6.3.1). The swelling response of this hydrogel in DMF can be seen in Figure 5.3. The time for $Q_{eq}$ to be reached is the same for the porous and for the nonporous hydrogel, but the initial swelling rate is faster for the porous hydrogel. The structured hydrogel reaches 50\% of $Q_{eq}$ after \textit{ca.}
45 minutes, whereas the reference needs ca. 2 h, which correlates to an increase in the initial swelling rate of 2.6.

**Figure 5.3:** Solvent induced swelling response of emulsion templated PHEA hydrogel in DMF.

**Figure 5.4:** Solvent induced swelling response of emulsion templated PHEA hydrogel in DMSO.

The positive effect is more obvious when the hydrogels are swollen in DMSO instead of DMF (the initial swelling measurements were conducted in DMSO, however most likely due to the high viscosity of DMSO the swelling took up to several days, which is too long, so that we chose DMF as the solvent instead). As can be seen in **Figure 5.4**, $Q_{eq}$ for the porous hydrogel full swelling in DMSO is reached after 10 h, compared to 50 h for the nonporous hydrogel. Almost the same magnitude of rate increase is obtained when comparing the time needed to reach 50 % of $Q_{eq}$ (value manually extrapolated for the reference because no weight was measured at this point of time). The different behavior in the two different solvents could be explained with the different affinities of
PHEMA to DMF and DMSO.

The cryo-SEM images of the emulsion templated sample reveal a macroporous structure that can be described as lamellar and slightly sponge like. Comparison of the cryo-SEM images to SEM images in published work is not easy, because we did not freeze dry etch our samples during the cryo-SEM sample preparation as it was for example done by Tokuyama et al.\textsuperscript{3} Freeze-drying would result in the formation of additional pores which we try avoid, in order to distinguish the pore structure that results from the porogen methods alone.

![Cryo-SEM images of surface of emulsion templated PHEA hydrogel with 2000 (left) and 500 (right) manifold magnification. A lamellar interconnected microstructure can be seen.](image)

**Figure 5.5:** Cryo-SEM images of surface of emulsion templated PHEA hydrogel with 2000 (left) and 500 (right) manifold magnification. A lamellar interconnected microstructure can be seen.

### 5.3 PEG Templated PHEMA Hydrogels

Porous PHEA hydrogels have been synthesized with PEG as the porogen according to method G (chapter 6.3.2) with PEG of varying molecular weights and in different wt\% (see Table 5.1). The swelling results obtained in DMF as solvent can be seen in Figure 5.6. Surprisingly, apart from samples 10.1.3 and 10.2.2, all the other PEG microstructured hydrogels swelled to a $Q_{eq}$ that was lower compared to the reference (down to 500\% for sample 10.1.2), which seems in contrast to published work. \textsuperscript{4,5,6} Samples 10.2.3 and 10.3.3 turned white after refluxing with either water, THF or chloroform, respectively, which was done to remove the PEG. This was observed repeatedly and it probably indicates crosslinking of the filler with the hydrogel network.
This probably leads to an increase of the rigidity of the hydrogel and could explain
the swelling response of sample 10.2.3 (sample 10.3.3 was not measured for this reason).

Table 5.1: PEG molecular weights and contents used for hydrogel synthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ [g/mol]</th>
<th>wt%PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1.1</td>
<td>1000</td>
<td>4.04</td>
</tr>
<tr>
<td>10.1.2</td>
<td>1000</td>
<td>7.71</td>
</tr>
<tr>
<td>10.1.3</td>
<td>1000</td>
<td>14.16</td>
</tr>
<tr>
<td>10.2.1</td>
<td>4500</td>
<td>4.00</td>
</tr>
<tr>
<td>10.2.2</td>
<td>4500</td>
<td>7.69</td>
</tr>
<tr>
<td>10.2.3</td>
<td>4500</td>
<td>14.33</td>
</tr>
<tr>
<td>10.3.1</td>
<td>8000</td>
<td>4.02</td>
</tr>
<tr>
<td>10.3.2</td>
<td>8000</td>
<td>7.65</td>
</tr>
<tr>
<td>10.3.3</td>
<td>8000</td>
<td>14.29</td>
</tr>
</tbody>
</table>

All of the samples failed to accelerate the swelling process as can be seen on the left in Figure 5.6. A reason for this could be that the microstructure consists of relatively closed pores as can be seen from the cryo-SEM image of sample 10.2.2 in Figure 5.7. Even though macropores exist they are closed pores and probably due to this, the swelling process might still be mainly diffusion controlled as it is in the nonporous system and thereby does not lead to any acceleration of the volume change rate.

Figure 5.6: Solvent induced swelling response of PEG templated PHEA hydrogels.

Further experiments could investigate an increasing content of PEG 1000 (sample 10.1.3 prepared with PEG1000 was the only sample with a higher $Q_{eq}$ compared to the reference) or a way to avoid crosslinking in the samples 10.2.3 and 10.3.3, but as can be seen on the left in Figure 5.6 even though the $Q_{eq}$ might be increased (sample 10.1.3, right) the swelling response rate in the first 330 minutes is not increased.
The discrepancy to published work\cite{4,5,6} in regard of the fact, that the rate of swelling in the here reported cases is not increased, can most likely be explained by the difference in the sample sizes. Hydrogels that were tested in the literature\cite{4,5,6} were of dimensions in the millimeter range whereas our samples were of a size in the centimeter range. It should also be noted that in those published papers the positive effect of PEG as a porogen on the swelling behaviour of the hydrogels can most likely be attributed to an increase of $Q_{eq}$ itself rather than by a change in the the swelling rate. The higher $Q_{eq}$ observed in those papers could be explained by the increased surface area of the hydrogels and that water is literally entrapped in the pores. Even though the cryo-SEM image of sample 10.2.2 reveals a porous structure (Figure 5.7), retrospectively it would have also been interesting to look at the surface morphology of a sample that exhibited a low $Q_{eq}$, such as sample, 10.1.2 for example to see whether pores are present. It could be argued that extraction of PEG might not have been sufficient; however, the swelling of sample 10.1.3, that contained more PEG than the sampled 10.1.1 and 10.1.2, indicates that the extraction of PEG with chloroform is a sufficient procedure. Therefore, reasons for the poor swelling behavior of our samples cannot be clearly determined at the moment.

![Cryo-SEM images of surface of PEG templated sample 10.2.2 with 2000 (left) and 500 (right) manifold magnification. Manifold closed macropores can be seen as dark areas encircled by white areas.](image)

**Figure 5.7:** Cryo-SEM images of surface of PEG templated sample 10.2.2 with 2000 (left) and 500 (right) manifold magnification. Manifold closed macropores can be seen as dark areas encircled by white areas.

### 5.4 Nylon 6,6 Templated PHEA Hydrogels

Three PHEA hydrogels with different amounts of nylon as porogen were synthesized according to method H (Table 5.2) (chapter 6.3.3). A problem encountered during
the preparation of those hydrogels was that after extraction of the filler, the hydrogels tended to break when directly immersed into THF due to internal stresses. Therefore, the solvent polarity had to be decreased stepwise as described in the method. We were then able to test the swelling response of the hydrogels in DMF.

The swelling response of the nylon templated PHEA hydrogels can be seen in Figure 5.8. All the hydrogels exhibited a $Q_{eq}$ comparable to the reference and needed about the same time to reach this stage. However, the initial swelling behavior of the structured hydrogels differs from the nonporous sample. Sample N3 has reached 50 % of the final swelling after ca. 1070 seconds (18 minutes). On the contrary, the reference needs ca. 7470 seconds (124 minutes) for 50 %, which is about 7 times slower. The corresponding values for the other samples can be seen in Table 5.2.

The porous structure of the PHEA hydrogel can already be seen by simple photographs with a standard camera because of the size of the nylon threads employed (see Figure 5.9). SEM images confirmed that the surface structure of the hydrogel was comparable to that of the reference (not shown).

Figure 5.8: Solvent induced swelling response of nylon templated PHEA hydrogel.
Table 5.2: Time needed for the nylon 6,6 templated hydrogels to swell to 50 % of $Q_{eq}$.

<table>
<thead>
<tr>
<th>sample</th>
<th>wt%nylon</th>
<th>$t$ [s] for 50 % swelling</th>
<th>$t_{(for,50%,swelling,,sample)}$</th>
<th>$t_{(for,50%,swelling,,reference)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>0</td>
<td>7473</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>0.33</td>
<td>3710</td>
<td>$\frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>0.72</td>
<td>1481</td>
<td>$\frac{1}{5}$</td>
<td></td>
</tr>
<tr>
<td>N3</td>
<td>1.34</td>
<td>1070</td>
<td>$\frac{1}{7}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.9: PHEA hydrogel after extraction of nylon 6,6 (MWCNTs left out of mixture for clarity).

5.5 Lyophilized PHEA Hydrogels

PHEA hydrogels have been synthesized according to method A and subsequently freeze-dried according to method K (chapter 6.3.4). Different solvents, amounts of freeze-dry cycles, freeze-drying methods and a combination with other methods have been tested.

Even though water is a good solvent for PHEA hydrogels, the normally (HW1) and repeatedly (HW2) freeze-dried samples show a swelling behavior that is similar to that of the reference (see Figure 5.10). The cryo-SEM image of sample HW1 does not reveal
a porous structure which is in agreement with the swelling results (see Figure 5.12). Some surface patterning can be seen (Figure 5.12, left), but the type of structure is difficult to discern. Reasons for those results are not obvious at the moment and have to be determined. In further agreement with this, the uniaxial freeze-dried sample (HWU) and an emulsion templated and then freeze-dried sample (HWE) show no change in their swelling rate compared to the reference (see Figure 5.11).

Figure 5.10: Solvent induced swelling response of normally and repeated freeze-dried PHEA hydrogels. The porogen used was water.

HWU was prepared in order to obtain a tubular structure in the hydrogel. Even though the pores created by this probably would not have been interconnected, we hoped to see some effect of solvent convection on the swelling rate of the hydrogel. By freeze-drying the already emulsion templated hydrogel we hoped to see an increased swelling rate compared to the emulsion templated hydrogel. However, the results obtained only confirm that freeze-drying of PHEA hydrogels with water is not a successful porogen method.

Because DMSO is a good solvent for PHEA hydrogels and because we can extract DMSO ice crystals out of the hydrogel structure by lyophilization, the influence of DMSO ice crystals as porogens has as well been investigated. Therefore, a PHEA hydrogel has been prepared according to method A and then freeze-dried according to method K (sample HD).

The swelling response of HD was very fast (see Figure 5.13). Total swelling was achieved in only 6 minutes and most of the swelling proceeded in the first 3 minutes. The reference needs about 50 hours for complete swelling which is about 250 times slower. The
**Figure 5.11:** Solvent induced swelling response of HWU and HWE PHEA hydrogels compared to the reference and the emulsion templated hydrogel. The porogen used was water.

**Figure 5.12:** SEM images of surface of PHEA hydrogel lyophilized with water as porogen with 2000 (left) and 500 (right) manifold magnification. No porous structure can be seen. The microstructure obtained seems to be highly interconnected and the pores are in the supermacroporous range, which seems to be the reason for the fast response of the gel.
5.6 Actuation Response of Nonporous and Porous Redox Actuators

Quinone hydrogels were synthesized according to method B by free radical crosslinking copolymerization of HEA and the quinone monomer with the crosslinker PEGDA initiated by ABCN (see Scheme 5.2). P(AM-co-TEMA) hydrogels were synthesized according to method C by free radical crosslinking copolymerization of AM and the TEMPA monomer with the crosslinker MBAM initiated by ABCN (see Scheme 5.3). The corresponding nonporous hydrogel actuators were prepared as described in those methods in combination with method D (actuator preparation).

To analyze the electrochemically induced swelling behavior of the redox responsive hy-
Scheme 5.2: Synthesis of P(HEA-co-quinone) hydrogel.

Scheme 5.3: Synthesis of P(AM-co-TEMPA) hydrogel.

droge actuators the reduction and oxidation potentials for the electrochemical changes between the redox states had to be determined first. This can be done by means of cyclic voltammetry measurements. The quinone hydrogel can be electrochemically reduced and oxidized between the quinone and the hydroquinone state (see Scheme 5.4). The cyclic voltammogram of the quinone monomer was conducted in dichloromethane, a good solvent for the monomer. The cyclic voltammogram is shown in Figure 5.15. It clearly shows two reversible waves at around -0.73 and -1.16 V vs decamethylferrocene (Fc*) as an internal standard (corresponding to reduction to the anion radical and to the dianion, respectively).

However, dichloromethane is not a good solvent for the swelling and shrinking experiments of the quinone hydrogel actuator. It was found that a solvent mixture of DMF/water (70/30 v/v) containing 5wt% LiOAc is a good solvent system to observe the electrochemically induced length change of the quinone actuator. The cyclic voltammogram of a quinone homopolymer was therefore measured in this solvent system and can be seen in Figure 5.16. In this protic solvent system the peaks shift and become irreversible due to fast proton transfer to the anionic species. The complete reduction to the hydroquinone appears at around -0.65 V vs Ag/AgCl. To ensure complete reduction, the actuation was studied at -0.8 V.
**Figure 5.15:** Cyclic voltammogram of quinone monomer in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (100 mVs<sup>-1</sup>). Peak at 0 V is [Fc*]<sup>0</sup>/[Fc*]<sup>+</sup> reference.

**Scheme 5.4:** Electrochemically induced change between quinone and hydroquinone.

To determine the redox potentials for the TEMPO hydrogel the cyclic voltammogram for the electrochemical change between the nitroxide and the oxoammonium cation in a P(TEMPO-co-AM) copolymer was performed in water containing 5% NaBF<sub>4</sub> and is shown in Figure 5.17. It can be seen that complete oxidation can be achieved by ap-
Figure 5.16: Cyclic voltammogram of quinone homopolymer in DMF/water (70/30 v/v), 0.3 M LiOAc (100 mVs⁻¹) vs Ag/AgCl.

Applying a potential of +0.75 V and that for complete reduction -0.70 V vs Ag/AgCl was applied, although lower voltages could be potentially used. Electrochemical actuation of the TEMPO hydrogel actuator was performed in the same solvent system.

By knowing the redox potentials we could then record the electrochemically induced length change of the nonporous quinone and TEMPO hydrogel actuators. After synthesis of the TEMPA hydrogel actuator we first had to chemically oxidize TEMPA to TEMPO with meta-chloroperoxybenzoic acid (mCPBA) before we could transfer the gel to the electrochemical cell (see Scheme 5.5). The electrochemical change between the nitroxide and the oxoammonium cation form was then achieved by applying 0.75 V for the oxidation and -0.70 V for the reduction (see Scheme 5.6). The quinone actuator could directly be used after its synthesis without further chemical modification.

The electrochemically induced length changes of the nonporous redox actuators can be seen in Figure 5.18 and Figure 5.19. The nonporous P(HEA-co-quinone) actuator device needs about 150 minutes for complete swelling and shrinking, respectively. Length
Figure 5.17: Cyclic voltammogram of P(TEMPO-co-AM) copolymer in water, 0.1 M NaBF₄ (100 mVs⁻¹) vs Ag/AgCl.

Scheme 5.5: Chemical oxidation of hydroxylamine to nitroxide.

increases proportionally with time. The nonporous TEMPO hydrogel actuator needs about 60 minutes for complete swelling and shrinking (the values for the TEMPO hydrogel actuator, especially for the reduction, are taken from initial experiments and have to be confirmed with further measurements). Those response times are too long if fast responsive actuator devices are aimed for, and ideally we would be aiming to obtain full expansion in only a few minutes or seconds.
Scheme 5.6: Electrochemically induced change between nitroxide and oxoammonium cation form.

We first tested the influence of the emulsion templating method with emulsifier A-PMMA3-\(b\)-PLMA1 in a quinone hydrogel actuator. The actuator was prepared according to method F (sample E-P(HEA-co-quinone)). The response time of this actuator was drastically improved by this method and can be seen in Figure 5.20. It takes 50 minutes for the hydrogel to expand completely. Most of the expansion already exerts in the first 20 minutes. However, for reasons to be determined, the maximum swelling is lower in the structured device compared to the nonstructured device (112% expansion for the porous device in contrast to 134% expansion for the nonporous device).

Because the TEMPO hydrogel actuators are synthesized in acetic acid, the emulsion templating method in this form (DMSO as solvent and \(n\)-octane as filler) cannot be
applied to this hydrogel. However, it could be used under other conditions such as by employing supercritical carbon dioxide CO\textsubscript{2} as the filler.

The influence of the nylon 6,6 templating method on the swelling response of the redox active actuators was tested as well. TEMPO hydrogels synthesized according to method J with different amounts of nylon 6,6 (diameter ca. 0.02 mm, length 2-5 cm) as porogen could not be achieved successfully due to disintegration of the hydrogels upon extraction of the nylon 6,6 with 2,2,-trifluoroethanol. The Pt spring and the channels created by the porogen probably caused tension in the hydrogel network when immersed into the solvent and gave starting points for the hydrogels to crack open.

A P\text{ (HEA-co-quinone)} hydrogel actuator was prepared according to method I (chapter 6.3.3) by employing 0.60 wt\% nylon 6,6 (diameter ca. 0.02 mm, length 2-5 cm). The electrochemically induced length change can be seen in Figure 5.21. To our surprise, the structured device needs the same time for complete swelling as the nonstructured device. This could be attributed to the wt\% of nylon 6,6 that we used as the filler and different results might be obtained with higher nylon 6,6 amounts. Also, for reasons to be determined, the maximum swelling of this porous actuator is lower compared to the reference.

The influence of freeze-drying with DMSO on the swelling response of a quinone actuator was tested as well. A hydrogel actuator was prepared according to methods B (chapter 6.2.2) and D (chapter 6.2.4) in combination and subsequently freeze-dried
Figure 5.21: Electrochemically induced swelling and shrinking of nylon 6,6 templated quinone actuator with DMSO (sample QD). The actuator performance was considerably improved as can be seen in Figure 5.22. The response was almost comparable to that of the emulsion templated quinone actuator. Swelling was complete after 50 minutes and most of the swelling occurred in the first 20 minutes. For this device, too, the maximum swelling was lower compared to the nonporous device (only 108% length increase for the porous hydrogel compared to 134% for the nonporous hydrogel).

Figure 5.22: Electrochemically induced swelling and shrinking of a quinone actuator freeze-dried with DMSO as porogen.

A reason for the decrease of the equilibrium swelling rate could be that due to the creation of pores also small cracks might have evolved in the polymer network struc-
ture, which could decrease the conductivity of the hydrogels and result in incomplete reduction/oxidation of the active groups and therefore to less swelling/shrinking.

It is furthermore noticeable that the swelling behavior of the emulsion templated and the freeze-dried quinone hydrogel follow a similar behavior, even though the two methods result in different behavior in the PHEA gels. It could be that there is a limiting factor that causes one of the methods to perform slower then it could in theory. Whether the conductivity of the hydrogel, the reduction or oxidation of the active groups, ion diffusion, polymer-solvent interactions or solvent intrinsic properties are the factors that prevent the device from exhibiting a better response could be determined to a certain extent by further experiments for example by increasing the amount of the conductive filler in the hydrogel, using different conductive fillers or trying different electrolyte systems. Another possibility is that the porous gels are less stiff, and because of this exert a lower swelling pressure. Thus, they find it harder to expand against the tension of the spring in an actuator. However, the results obtained by freeze-drying with DMSO and by emulsion templating are quite promising.

The effect of freeze-drying with DMSO as the solvent was also tested on the response rate of TEMPO actuators (method K sample TD, chapter 6.3.4). P(AM-co-TEMPA) gel actuators were synthesized and oxidized to the nitroxide form. Upon soaking in DMSO most of the gels broke. The actuation could be tested on one gel and first results indicate that swelling is complete after 10 to 20 minutes, however the gel was too small to obtain good pictures. Future work will investigate freeze-drying with DMSO on gels with a lower crosslinker density and it is hoped that those gels will not break when immersed in DMSO.

The PEG templating method was not tested on its efficiency to generate fast responsive redox actuators due to the poor results obtained in the model PHEA hydrogels.
References


Chapter 6

Experimental Section for Hydrogel and Actuator Synthesis and Characterization

6.1 General Experimental Procedure

All liquids used for hydrogel and actuator synthesis were degassed with argon for at least ten minutes prior to use. HEA, PEGDA (MW ca. 258 g mol\(^{-1}\)), poly(4-vinylpyridine) (PVP), AM, MBAM, ABCN, PEG of molecular weight M\(_n\)=1000, 4500 and 8000 g mol\(^{-1}\), 2,2,2-trifluoroethanol, 1,4-dioxane, mCPBA, DMSO, n-octane, dichloromethane CH\(_2\)Cl\(_2\), chloroform CHCl\(_3\), glacial acetic acid, DMF, THF, sodium tetrafluoroborate NaBF\(_4\), lithium acetate LiOAc, tetrabutylammonium hexafluorophosphate Bu\(_4\)NPF\(_6\) and Nanocyl 3100 (MWCNTs) were used as received unless otherwise stated. 3-(2,4,5-trimethyl-3,6-di-oxocyclohexa-1,4-dien-1-yl)propyl methacrylate ("quinone") (MW 276.332 g mol\(^{-1}\)) and N-(2,2,6,6-tetramethylpiperidin-4-yl) acrylamide ("TEMPA") (MW 210.316 g mol\(^{-1}\)) were prepared in our group.\(^a\) Polymer A-PMMA3-b-PLMA1 was synthesized as described in section 4.5.4. The nylon 6,6 fibers used were from a commercially available nylon 6,6 fabric. They were used as received for use in PHEA hydrogels and bleached with sodium hypochlorite NaOCl before use in the redox hydrogel actuators. All polymerization reactions were conducted in argon purged plastic tubes under argon atmosphere at 80 °C for 24 h. Ultrasonication was done in a BANDELIN SONOREX RK52 ultrasound unit. Emulsion stability tests were performed in a in a BINDER Cold-/Heat Test Chamber MK 53 (Tuttlingen, Germany). All lyophilizations were conducted in a Labconco FreeZone 12 freeze dryer.
6.2 Synthesis of Nonporous Hydrogels

6.2.1 Method A: Synthesis of PHEA Hydrogels

453 mg (3.90 mmol) HEA, 50 mg (0.19 mmol) PEGDA and 50 mg (0.20 mmol) initiator ABCN were added to 2 mL DMSO with 1wt% Nanocyl 3100 carbon nanotubes and 2.5wt% PVP. The reaction mixture was ultrasonicated for ca. 1 minute until a homogeneous solution was formed and then transferred to a 3 mL plastic tube with an inner diameter of 9 mm and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was transferred from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. (The addition of MWCNTs in this polymerization is to model the characteristics of the real actuator.)

6.2.2 Method B: Synthesis of P(HEA-co-quinone) Hydrogels

45 mg HEA (0.39 mmol), 45 mg (0.16 mmol) quinone monomer [Figure 6.1], 10 mg PEGDA (0.04 mmol) and 10 mg (0.04 mmol) initiator ABCN were added to 0.4 mL DMSO with 1wt% Nanocyl 3100 carbon nanotubes and 2.5wt% PVP. The reaction mixture was ultrasonicated for ca. 5 minutes until a homogeneous solution was formed and then transferred to a 3 mL plastic tube with an inner diameter of 9 mm and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was transferred from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process.

6.2.3 Method C: Synthesis of P(AM-co-TEMPA) hydrogel

50 mg (0.24 mmol) TEMPA monomer [Figure 6.2], 50 mg (0.70 mmol) AM, 10 mg (0.06 mmol) MBAM and 5 mg (0.02 mmol) initiator ABCN were added to 0.50 mL glacial acetic acid. The reaction mixture was ultrasonicated for ca. 1 minute until a
homogeneous solution was formed and then transferred to a 3 mL plastic tube with
an inner diameter of 9 mm and polymerized. After the polymerization, the tube was
cooled to room temperature and the hydrogel was removed from the tube and soaked
in 50 mL glacial acetic acid for 24 h to remove any unreacted monomer if present. The
acid was changed several times during this process.

Oxidation of $\text{P(AM-co-(2,2,6,6-tetramethylpiperidine4-yl acrylamide))}$ to
$\text{P(AM-co-(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide))}$

The P(AM-co-(2,2,6,6-tetramethylpiperidine4-yl acrylamide)) hydrogel was soaked in
1,4-dioxane for 24 h. The solvent was changed several times during this process. 3 g
(17.38 mmol) $m$CPBA were dissolved in 5 mL 1,4-dioxane and the hydrogel was oxi-
dized in this solution for 24 h.

6.2.4 Method D: Synthesis of Spring Actuators

In order to obtain linear actuator devices a 1 mL plastic tube with an inner diameter of
4.7 mm was fitted with a Pt spring of approximate length 2.5 cm ($d_{\text{wire}} = 0.0127$ mm, ca.
25-35 coils/cm, inner diameter of spring ca. 2.5 mm). The pre-hydrogel solutions were
prepared as described in the according methods and then poured into the tube that contain the Pt spring. The hydrogels were then polymerized and washed as described.

6.3 Polymerization Methods for Porous Hydrogels and Actuators

6.3.1 Emulsion Templating Method

Determination of Emulsifier Stability

DMSO as the polar phase and \textit{n}-octane as the nonpolar phase were mixed in a volume ratio of 7/3 (v/v DMSO/\textit{n}-octane) in a glass tube and a certain amount of PMMA-\textit{b}-PLMA block copolymer (see Section 4.5.4) was added as the emulsifier (synthesized under ATRP conditions (see Section 4.5)). Emulsion formation was achieved by ultrasonication for 2 h. After emulsion formation, the tubes were heated to 80 °C (according to polymerization temperature of hydrogels). The emulsion stability with the time was then evaluated optically. First indications of phase separation were taken as the offset of emulsion stability and the time when phase separation started was recorded.

Method E: Synthesis of emulsion templated PHEA hydrogel (E-PHEA)

222 mg of emulsifier A-PMMA3-\textit{b}-PLMA1 (see Section 4.5.3) and 0.6 mL \textit{n}-octane were added to 1.4 mL DMSO with 1wt% Nanocyl 3100 carbon nanotubes and 2.5wt% PVP and the mixture was ultrasonicated for 2 h. 317 mg (2.7 mmol) HEA and 35 mg (0.14 mmol) PEGDA were added to this emulsion and it was further ultrasonicated for 10 min. 35 mg (0.14 mmol) initiator ABCN were added and the emulsion was further sonicated for one more minute. The emulsion was transferred to a 3 mL plastic tube with an inner diameter of 9 mm and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The organic filler (\textit{n}-octane and emulsifier) was extracted by refluxing the hydrogel in 150 mL THF at 80 °C for 24 h.
Method F: Synthesis of emulsion templated P(HEA-co-quinone) hydrogel actuator (E-P(HEA-co-quinone))

25.5 mg of emulsifier A-PMMA3-b-PLMA1 (see Section 4.5.4) and 0.09 mL n-octane were added to 0.21 mL DMSO with 1wt% Nanocyl 3100 carbon nanotubes and 2.5wt% PVP and the mixture was ultrasonicated for 2 h. 24 mg (0.21 mmol) HEA, 24 mg (0.09 mmol) quinone monomer and 5 mg (0.02 mmol) PEGDA were added to this emulsion and it was further ultrasonicated for 10 min. 5 mg (0.02 mmol) initiator ABCN were added and the emulsion was further sonicated for one more minute. The emulsion was transferred to a 1 mL plastic tube with inner diameter of 4.7 mm that contained a Pt wire (see method D) and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The organic filler (n-octane and emulsifier) was extracted by refluxing the hydrogel in 150 mL THF at 80 °C for 24 h.

6.3.2 PEG as Porogen

Method G: Synthesis of PEG templated PHEA hydrogels

A PHEA pre-hydrogel solution was prepared as described in method A without the addition of initiator ABCN. A defined amount of PEG was added to this solution and the mixture was heated to 40 °C under stirring for ca. 5 minutes until all PEG was homogeneously dissolved. The solution was then cooled to room temperature and 50 mg (0.20 mmol) initiator ABCN were added. After complete dissolution of the initiator, the reaction mixture was transferred to 3 mL plastic tube with an inner diameter of 9 mm and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The hydrogels were then refluxed in 150 mL CHCl₃ for several hours (extraction with water did not lead to sufficient extraction of PEG). Hydrogels containing 4, 8 and 14 wt% PEG were prepared and PEG with molecular weight 1000, 4500 and 8000 g mol⁻¹ was employed (see Table 6.1).
Table 6.1: PEG molecular weights and wt% used for synthesis of porous PHEA hydrogels.

<table>
<thead>
<tr>
<th>sample</th>
<th>M_n</th>
<th>m_{PEG}</th>
<th>wt%_{PEG}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1.1</td>
<td>1000</td>
<td>112</td>
<td>4</td>
</tr>
<tr>
<td>10.1.2</td>
<td>1000</td>
<td>222</td>
<td>8</td>
</tr>
<tr>
<td>10.1.3</td>
<td>1000</td>
<td>438</td>
<td>14</td>
</tr>
<tr>
<td>10.2.1</td>
<td>4500</td>
<td>111</td>
<td>4</td>
</tr>
<tr>
<td>10.2.2</td>
<td>4500</td>
<td>222</td>
<td>8</td>
</tr>
<tr>
<td>10.2.3</td>
<td>4500</td>
<td>444</td>
<td>14</td>
</tr>
<tr>
<td>10.3.1</td>
<td>8000</td>
<td>111</td>
<td>4</td>
</tr>
<tr>
<td>10.3.2</td>
<td>8000</td>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td>10.3.3</td>
<td>8000</td>
<td>443</td>
<td>14</td>
</tr>
</tbody>
</table>

6.3.3 Nylon 6,6 Templated Hydrogels

Method H: Nylon 6,6 templated PHEA hydrogels

Defined amounts of fine nylon 6,6 fibers (see Table 6.2) of a length varying between 2 and 5 cm and a diameter of a single fiber of ca. 0.016 mm (however the fibers sometimes form bundles, see Figure 6.3) were distributed as evenly as possible in 3 mL plastic tubes with an inner diameter of 9 mm up to the 1 mL mark of the tubes as shown in Figure 6.4. The PHEA pre-hydrogel solution was prepared as described in method A. This solution was filled into the argon purged plastic tubes that contain the nylon 6,6 up to the 1 mL mark of tube, sealed under argon and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and then soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The gel was then put in 50 mL 2,2,2-trifluorethanol at 60 °C for 24 h to extract the nylon 6,6. For swelling measurements, after extraction of the nylon 6,6 fiber, the hydrogels were then soaked at least three times in a mixture of water/THF with slowly increasing THF content and finally soaked in THF. The polarity of the solvent had to be decreased stepwise because strong capillary effects often lead to burst of the hydrogel samples in earlier tests.
Figure 6.3: Light microscope image of nylon fibers. The image shows that single fibers have a diameter of \( \text{ca. } 0.016 \text{ mm} \).

Table 6.2: Amounts of nylon 6,6 used for synthesis of porous PHEA hydrogels.

<table>
<thead>
<tr>
<th>sample</th>
<th>( m_{\text{nylon6,6}} ) [mg]</th>
<th>( \text{wt}%_{\text{nylon6,6}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>3.7</td>
<td>0.3</td>
</tr>
<tr>
<td>N2</td>
<td>8.2</td>
<td>0.7</td>
</tr>
<tr>
<td>N3</td>
<td>15.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Method I: Nylon 6,6 templated P(HEA-co-quinone) hydrogels

3.3 mg of fine nylon 6,6 fibers of a length varying between 2 and 5 cm and a diameter of a single fiber of \( \text{ca. } 0.016 \text{ mm} \) (however the fibers sometimes form bundles, see Figure 6.3) were distributed as evenly as possible in a 1 mL plastic tube up to the 0.4 mL mark of the tube as shown in Figure 6.4. A pre-hydrogel solution was prepared as described in method B to obtain 0.4 mL of the solution. This solution was then added to the 0.4 mL mark of the argon purged plastic tube, which contains the nylon 6,6 fibers, sealed under argon and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The gel was then put in 50 mL 2,2,2-trifluoroethanol at 60 °C for 24 h to remove the nylon 6,6.
Method J: Nylon 6,6 templated P(AM-co-TEMPA) hydrogels

Amounts between 5 and 10 mg of fine nylon fibers of a length between 2 and 5 cm with diameter of a single fiber of ca. 0.016 mm (however the fibers sometimes form bundles, see Figure 6.3) were distributed as evenly as possible in a 1 mL plastic tube up to the 0.4 mL mark as shown in Figure 6.4. A pre-hydrogel solution was prepared as described in method C to obtain 0.4 mL of the solution. This solution was then added to the 0.4 mL mark of the argon purged plastic tube, which contains the nylon 6,6 fibers, sealed under argon and polymerized. After polymerization, the tube was cooled to room temperature and the hydrogel was removed from the tube and was soaked in 50 mL glacial acetic acid for 24 h to remove any unreacted monomer if present. The acid was changed several times during this process. The gel was then washed three times with water and then put in 50 mL 2,2,2-trifluorethanol at 60 °C for 24 h to remove the nylon 6,6.
6.3.4 Method K: Lyophilization

Method I: Water as Porogen (HW1, HW2, HWU, HWE)

(a) PHEA hydrogels

A PHEA hydrogel was prepared as described in method A. After polymerization, the hydrogel was soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The hydrogel was then soaked in water for at least one day. The water was changed several times during this process. The hydrogel was then frozen at -20°C for 24 h by placing it in a standard freezer and subsequently freeze-dried (HW1). For repeated freeze drying, the porous hydrogel prepared as described above (HW1) was soaked in water for at least one day, frozen at -20°C and again freeze-dried (HW2).

The effect of uniaxial ice crystal growth as described in\textsuperscript{2} on the swelling response was also investigated. Therefore, a PHEA hydrogel was prepared as described in method A and soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. It was then soaked in water for at least one day while repeatedly refreshing the water. The hydrogel was then put into a glass tube (d=19 mm, l=75 mm) standing upright. The outside of the tube was insulated with cotton wool and tinfoil and put into a clamp standing upright. The bottom of this glass tube was then put in contact with the surface of a dry ice/acetone cooling bath (-78 °C) for one h. After complete ice crystal growth the hydrogel was freeze dried (HWU). A combination of emulsion templating with freeze drying was also investigated. Therefore, E-PHEA was soaked in water for at least one day. It was then frozen at -20 °C for 24 h by placing it in a standard freezer and subsequently freeze-dried (HWE).

Method II: DMSO as Porogen

(a) PHEA hydrogel (HD)

A PHEA hydrogel was prepared as described in method A. After polymerization, the hydrogel was soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The gel then
soaked in DMSO for one more day. The hydrogel was frozen at 4 °C overnight using a standard fridge and subsequently freeze dried.

(b) P(HEA-co-quinone) hydrogel actuator (QD)

A P(HEA-co-quinone) hydrogel actuator was synthesized according to method B in combination with method D. After polymerization, the hydrogel was soaked in 50 mL DMSO for 24 h to remove any unreacted monomer if present. The DMSO was changed several times during this process. The gel then soaked in DMSO for one more day. The hydrogel was then frozen at 4 °C overnight using a standard fridge and subsequently freeze dried.

(b) P(AM-co-TEMPO) hydrogel actuator (TD)

A P(AA-co-TEMPA) hydrogel was synthesized as described in method C in combination with method D and oxidized to its nitroxide form as described in method C. After oxidation, it was washed with 1,4-dioxane for 24 h. The 1,4-dioxane was changed several times during this process. The hydrogel was subsequently soaked in DMSO for 24 h ($Q_{eq}$ for swelling: 54). The DMSO was changed several times during this process. The hydrogel was frozen at 4 °C overnight using a standard fridge and subsequently freeze dried. After freeze drying, the gel was stored in 5 mL of 3.5 molar solution of $m$-CPBA in 1,4-dioxane.

Table 6.3 summarizes the different freeze-drying conditions:

<table>
<thead>
<tr>
<th>sample</th>
<th>hydrogel type</th>
<th>solvent</th>
<th>$\theta$[°C]</th>
<th>freeze-drying cycles</th>
<th>uniaxial</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW1</td>
<td>PHEA</td>
<td>water</td>
<td>-20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>HW2</td>
<td>PHEA</td>
<td>water</td>
<td>-20</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>HWU</td>
<td>PHEA</td>
<td>water</td>
<td>-78</td>
<td>1</td>
<td>x</td>
</tr>
<tr>
<td>HWE</td>
<td>E-PHEA</td>
<td>water</td>
<td>-20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>PHEA</td>
<td>DMSO</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>QD</td>
<td>P(HEA-co-quinone)</td>
<td>DMSO</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>TD</td>
<td>P(AM-co-TEMPO)</td>
<td>DMSO</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Hydrogel and Actuator Characterization

6.4.1 Solvent Induced Swelling Measurements of Nonporous and Porous PHEA Hydrogels

The PHEA hydrogels were equilibrated in THF before swelling. Samples of ca. 0.125 cm$^3$ were used for the swelling measurement. Before swelling, the hydrogels were wiped with tissue and the initial mass was recorded. The pre-weighed hydrogel sample was then immersed into 100 mL DMF (or DMSO) at room temperature until equilibrium swelling was achieved. The mass of the samples was taken after certain periods of time during the swelling. Therefore, excessive surface DMF (or DMSO) was removed from the gel with tissue and the gel was then weighed and subsequently immersed back into the solvent. The swelling was performed without shaking.

6.4.2 SEM

Small nonporous and porous PHEA hydrogel discs were soaked in DMSO before SEM analyses. Gels samples were prepared in brass rivets, then plunge frozen in liquid propane using a Leica KF80 specimen plunge-freezing device (Leica Microsystems, Vienna, Austria). Samples were mounted in a brass cryo holder, then transferred to a Gatan Alto 2500 cryo-preparation chamber/cryo stage (Gatan Inc, Pleasanton, California, USA). The chamber was kept at a constant temperature of -135°C. The top of the sample was fractured using a cooled blade. The sample was then coated with 3 nm of gold palladium. The sample was then introduced to the chamber of the JEOL JSM-6700F field emission scanning electron microscope (JEOL Ltd, Tokyo, Japan) at a voltage of 3.0 kV at -135°C.

6.4.3 Cyclic Voltammetry Measurements of Quinone Monomer

Cyclic voltammetric experiments were performed at 20°C in CH$_2$Cl$_2$ degassed with nitrogen. A three-electrode cell was used with Cypress Systems 1.4 mm diameter glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was ca. 10$^{-3}$ M in electroactive material and contained 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials were referenced to the reversible formal
potential (taken as $E^\circ = 0.00$ V) for the decamethylferrocene [$\text{Fc*}^+]_{\text{2}}/0$ process.

6.4.4 Cyclic Voltammetry Measurements of Quinone Homopolymer

Cyclic voltammetric experiments were performed at $20^\circ$C in a DMF/water solution of a volume ratio of 7/3 (v/v DMF/water) degassed with nitrogen. A three-electrode cell was used with Cypress Systems 1.4 mm diameter glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was $ca. \ 10^{-3}$ M in electroactive material and contained 0.3 M LiOAc as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials are direct as measured (vs Ag/AgCl).

6.4.5 Cyclic Voltammetry Measurements of P(AM-co-TEMPO) Copolymer

For the TEMPO copolymer (synthesis see below), a solution of the polymer was allowed to evaporate on the electrode surface. A three-electrode cell was used with Cypress Systems 1.4 mm diameter glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was $ca. \ 10^{-3}$ M in electroactive material and contained 0.1 M NaBF$_4$ as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials are direct as measured (vs Ag/AgCl).

Synthesis of TEMPO Copolymer

TEMPA (320 mg) and AM (320 mg) were dissolved in glacial acetic acid (1.0 mL). ABCN (1.6 mg) was added to the solution. The glass ampoule containing the solution was sealed. The solution was then heated for 4 h at 70°C. The solvent was removed and the residue was dissolved in a small amount of chloroform. The solution was dropwise added to chloroform/diethylether (1/1 v/v 100 mL). The precipitate was collected by filtration and dried under reduced pressure for 12 h. P(TEMPA-co-AM) was obtained as a white powder (400 mg).

P(TEMPA-co-AM) (150 mg) was then added to an ice-cold solution of mCPBA (620 mg) in THF (5 mL) and stirred for 3 h at room temperature. The polymer was dissolved in
THF with oxidation. The solution was dropwise added to diethylether/hexane (1/1 v/v 200 mL). The precipitate was collected by filtration and dried under reduced pressure for 12 h. P(TEMPO-co-AM) was obtained as an orange powder (140 mg).

6.4.6 Electrochemically Induced Actuation of P(HEA-co-quinone) Hydrogels

2 g of LiOAc were dissolved in 100 mL of a DMF/water mixture 7/3 v/v. The quinone actuator device was soaked in this solution for at least one day. Electrochemical actuation was performed in a three-electrode undivided electrochemical cell (Pt foil as counter electrode, Pt wire as quasi-reference electrode). The just described DMF/water/LiOAc solution was used as electrolyte. Reduction of the actuator device was performed at -0.8 V and pictures were taken after defined intervals of time to follow the length change of the hydrogel upon reduction. Reduction was performed for at least 2 h after which no more swelling occurred. Then the potential was switched to +0.8 V to start oxidation of the hydrogel. Again, pictures were taken at certain intervals of time to follow shrinking of the device.

6.4.7 Electrochemically Induced Actuation of P(AM-co-TEMPO) Hydrogels

5.5 g of NaBF₄ were dissolved in 100 mL of a water. The actuator device was soaked in this solution for at least one day. Electrochemical actuation was performed in a three-electrode undivided electrochemical cell (Pt foil as counter electrode, Pt wire as quasi-reference electrode). The just mentioned NaBF₄ solution was used as electrolyte. Oxidation of the actuator device was performed at 0.75 V and pictures were taken after defined intervals of time to follow the length change of the hydrogel upon oxidation. Oxidation was performed for at least 1.5 h after which no more swelling occurred. Then the potential was switched to -0.70 V to start reduction of the hydrogel. Again, pictures were taken at certain intervals of time to follow shrinking of the device.
References


Chapter 7

Conclusions and Future Work

7.1 Conclusions

Four methods have been tested on their efficiency and applicability to increase the swelling response rate of solvent responsive PHEA and of redox responsive hydrogel actuators.

The emulsion templating method was successfully applied to increase the solvent induced swelling response of the PHEA and of the electrochemically induced swelling of P(HEA-co-quinone) redox hydrogel and was especially successful for the redox active hydrogel. The emulsifier synthesis that preceded the emulsion based synthesis of porous hydrogels was first tried under RAFT and then under ATRP conditions. The RAFT syntheses did not result in polymers of controlled molecular weights and narrow molecular weight distributions, however this was most likely due to the RAFT agent used, the ABCN concentrations employed and the solvents used. ATRP synthesis under the employed reaction conditions proved suitable enough to generate PMMA-\textit{b}-PLMA block copolymers in sufficient yields, controllable molecular weights and narrow molecular weight distributions. Even though reaction conditions were not totally optimized we where then able to use one of the block copolymers for the synthesis of porous hydrogels with interconnected microstructure that enabled better solvent and ion diffusion and hence better response times of the hydrogels. Hence, for the first time PMMA-\textit{b}-PLMA block polymers were synthesized under the described ATRP conditions and could successfully be used for the emulsion templating method of PHEA and of P(HEA-co-quinone) hydrogels.
The PEG templating method, which has been reported in the current literature as a simple and convenient method to increase the swelling response of hydrogels could not be applied successfully to PHEA hydrogels. Even though the SEM image shows that a distinctive porous microstructure was obtained, this did not seem advantageous to enhance solvent diffusion into the hydrogel network which is most likely due to the fact that the pores are not interconnected. The discrepancy with the literature could be explained by the fact that we have been testing hydrogels of dimensions in the centimeter range whereas in the literature mostly hydrogel discs or beads were investigated.

A new method using fine nylon 6,6 threads as porogens has been investigated for the first time to increase the swelling response of PHEA hydrogels. A moderate increase of the swelling response rate of those hydrogels could be observed and is most likely due to capillary effects caused by the channels that were generated. However, this method did not prove to be sufficient to increase the swelling rate of the P(HEA-co-quinone) hydrogel and could not be applied to the TEMPO hydrogel at all due to difficulties in the preparation method.

Freeze drying was finally investigated as a method to increase the swelling response of our hydrogels. Even though water did not prove to be applicable, which is in contrast to many results in the literature, we found that DMSO is a really suitable solvent for freeze drying and has been used for the first time to microstructure hydrogels. The swelling response of both, PHEA and P(HEA-co-quinone) hydrogels, could be increased considerably.

In total, we found that freeze drying with DMSO proved to be the most easy, cost effective, time saving and sufficient method to microstructure our hydrogels and to improve the response rate of our solvent and redox responsive hydrogels.

7.2 Future Work

There are many interesting aspects that could be investigated in future work. First, with regard to the emulsion templating method the synthesis of the emulsifiers could be optimized including detailed kinetical investigations. The synthesized block copolymers could be tested in emulsions with varying DMSO/n-octane ratios and also on emulsions of DMF with n-octane. However, it would be time saving to synthesize
PMMA-\textit{co}-PLMA block copolymers under known conditions for example under RAFT conditions or to use commercially available surfactants or combinations thereof. An emulsion templating method that is applicable for the TEMPO redox hydrogels could be found as well. Possible for this system could be to employ supercritical CO\textsubscript{2} as the porogen.

The preparation of P(AM-\textit{b}-TEMPO) actuators by the nylon 6,6 templating method could be tested in further detail and P(HEA-\textit{co}-quinone) redox actuators employing more nylon 6,6 porogen could be prepared and tested on their swelling behaviour. Furthermore, a strategy that employs nylon 6,6 in a more controllable manner such as fiber meshes could be investigated. This would circumvent the problem of our method that the fiber distribution is hard to control.

The problem that the swelling response in our microstructured redox actuators is lower compared to the nonstructured actuators should be investigated as well. The influence of the concentration of the redox active group as well as of the crosslinkers, the comonomer used as well as the amount, nature of conductive filler (\textit{e.g.} using conductive polymers as fillers or finding a way to incorporate more carbon nanotubes) and the nature of the electrolyte could be investigated in future work as well.

Moreover, methods that are totally different from the methods described in this work could also be investigated. One example for this could be to synthesize cryogels which seems to be a simple and efficient method for the creation of interconnected macropores.

Another aspect of the gels which is unsatisfactory at the moment is their toughness, and under certain techniques mentioned above they can fall apart. A way of increasing the strength such as using clay dispersions might be highly desirable.