Synthesis of novel branched polymers for enhanced oil recovery
van Mastrigt, Frank

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Abstract

Polymer flooding, being one of the most widely applied enhanced oil recovery (EOR) techniques, finds application in a wide range of oil fields. The currently applied hydrolysed polyacrylamide (HPAM), however, suffers from some limitations. Current research is focussed on overcoming these limitations by altering the topology and chemical structure of the polymer. For delivering control over the molecular architecture and the reaction, controlled radical polymerisation (CRP) techniques have proven very valuable. The majority of current research considers atom transfer radical polymerisation (ATRP). Reversible addition-fragmentation chain-transfer (RAFT) polymerisation, on the other hand, has high potential because of its versatility and high industrial relevance. Little is known about the application of RAFT polymerisation in the synthesis of water soluble polymers for application in EOR. Therefore, this introduction considers the application of RAFT polymerisation in the synthesis of water soluble polymers.
1.1 Energy

In the last decade, whilst the overall world economy grew, emissions related to energy production and consumption started to decrease for the first time.\(^1\) Human-induced global warming, however, impacts the average global temperature of the earth, thereby reaching record high temperatures in recent years.\(^2\) General consensus dictates that a rigorous approach is required in order to limit the mean rise in global temperature to 2 °C.\(^3\)–\(^7\) While awareness regarding emissions is increasing, continuing the production of petroleum, coal and natural gas is inevitable.\(^8\)

In figure 1, an overview of the current primary consumption, versus a prediction for 2030 is displayed. While a relative increase in renewable energy becomes apparent, nearly 80% of consumption is in the form of petroleum, coal, and natural gas, the latter three in equal quantities. While one might argue that, indeed, the share of petroleum is slightly decreasing, the total primary energy consumption is projected to increase by 56% between 2010 and 2040.\(^9\) More specifically, world petroleum (and other liquid fuel) consumption is predicted to increase by 23.7% between 2010 and 2030.\(^10\) Even in a very optimistic scenario, with a significant change in environmental policies around the globe, mankind will be to a high degree relying on petroleum in the near future.\(^11\)

**Figure 1:** World primary energy consumption in 2014\(^{12}\) and 2030 (projection\(^8\))

1.2 Oil production

In 2014, global oil production equalled 93 million barrels per day, approaching a 20% increase since the year 2000.\(^13\) This oil originates from reservoirs, consisting of permeable porous rock, in which oil is accumulated. Sandstone is the most common rock found in oil fields, accounting for approximately 80% of oil reservoirs, followed
CHAPTER 1. INTRODUCTION

1.1 Energy

In the last decade, whilst the overall world economy grew, emissions related to energy production and consumption started to decrease for the first time. Human-induced global warming, however, impacts the average global temperature of the earth, thereby reaching record high temperatures in recent years. General consensus dictates that a rigorous approach is required in order to limit the mean rise in global temperature to $2\,^{\circ}\text{C}$. While awareness regarding emissions is increasing, continuing the production of petroleum, coal and natural gas is inevitable. In figure 1, an overview of the current primary consumption, versus a prediction for 2030 is displayed. While a relative increase in renewable energy becomes apparent, nearly 80% of consumption is in the form of petroleum, coal, and natural gas, the latter three in equal quantities. While one might argue that, indeed, the share of petroleum is slightly decreasing, the total primary energy consumption is projected to increase by 56% between 2010 and 2040.

More specifically, world petroleum (and other liquid fuel) consumption is predicted to increase by 23.7% between 2010 and 2030.

Even in a very optimistic scenario, with a significant change in environmental policies around the globe, mankind will be to a high degree relying on petroleum in the near future.

1.2 OIL PRODUCTION

In 2014, global oil production equalled 93 million barrels per day, approaching a 20% increase since the year 2000. This oil originates from reservoirs, consisting of permeable porous rock, in which oil is accumulated. Sandstone is the most common rock found in oil fields, accounting for approximately 80% of oil reservoirs, followed by carbonates. The reservoir is enclosed on the upper face by an impermeable cap. In case of saturation, oil and gas are present as two layers and the top layer is referred to as the gas cap. Water is generally present as a bottom layer, denominated the aquifer, besides a film on the surface of the rock. Oil recovery from oilfields undergoes three distinct phases before reaching maturity, referred to as the primary, secondary, and tertiary stage.

1.2.1 Primary recovery

In primary recovery, natural pressure is the driving force behind production (figure 2), as the pressure at the bottom of the well exceeds the hydrostatic pressure exerted by the oil in the well. With pressure above the bubble point, production will consist predominantly of oil. Falling pressure, however, results in dissolved gas coming out of solution and dominating production due to its lower viscosity. The latter is accelerated by the increase in viscosity of the oil above the bubble point, reducing its mobility. The declining pressure difference between well and atmosphere is backed up by artificial lift techniques, e.g. pumps, and production is continued until the oil cut (i.e. fraction of oil) at the wellbore reaches uneconomically low values. Typical primary recovery factors range from 5 to 15% of the original oil in place (OOIP).
1.2.2 Secondary recovery

Before reaching the bubble point, generally, the secondary recovery stage is initiated. At this stage, reservoir pressure is maintained by injection of pressurised gas at the top of the reservoir, or water in the lower areas of the reservoir, as is schematically illustrated in figure 3. Production is continued until water is produced and the oil cut becomes uneconomical. Depending on the exact oil field, total recovery after the secondary stage is 20 to 40% of the OOIP. Any technique applied after secondary recovery, is referred to as tertiary recovery.

![Secondary oil production](image)

Figure 3: Secondary oil production

1.3 Enhanced oil recovery

According to Lake (1989), enhanced oil recovery (EOR) is the recovery of oil from an oilfield, by injecting materials that are not normally present in the reservoir. While EOR is often used mistakenly as a synonym for tertiary recovery, it can be applied in each stage of oil recovery. World proven oil reserves are approximately 1.3 trillion barrels, with an annual consumption of nearly 34 billion barrels (2014). Conventional oil reserves total 7 to 8 trillion barrels, which can be partly recovered by improved techniques (e.g. EOR). Typical recovery potential by EOR for light oils is 45%, however, for heavy oils 90% is reported, and for tar sands 100% of the OOIP, resulting from low recoveries during the primary and secondary stages. EOR methods can be divided into two groups, thermal and non-thermal ones. Thermal methods are predominantly applied for heavy oils and tar sands, while non-thermal ones are more suitable for lighter oils. Thermal methods include...
hot water drive, steam injection, in situ combustion, and electrical heating. Non-thermal methods range from miscible flooding to chemical flooding, immiscible flooding and other methods such as microbial EOR and foam flooding. Within non-thermal recovery, polymer flooding is the most widely applied method, with successful applications over the last decades in the United States of America, China, Angola, and Oman.

1.3. Polymer flooding

Because of its effectivity in increasing oil production, its applicability in a wide range of oil fields, and its low cost, water flooding is the most commonly applied secondary recovery technique. The effectiveness of water flooding is determined by both microscopic and macroscopic characteristics. The microscopic efficiency is a function of interfacial tension, wettability, contact angle, and viscosity. The macroscopic efficiency depends on the reservoir dimensions, differences in permeability within the field, and the mobility ratio. The microscopic efficiency denotes the capability of water to remove oil from pores, while the macroscopic efficiency is related to the displacement of (microscopically) mobilised oil to the production well.

\[ \lambda = \frac{k_i}{\mu_i} \]  

Especially of importance is the mobility ratio (Eq. 1.1), defined as the relative permeability of a fluid \( k_i \), divided by its viscosity \( \mu_i \). The water to oil mobility ratio relates the mobility ratio of water to the oil and is calculated by dividing the mobility ratio of water by that of the oil in the designated field (Eq. 1.2).

\[ M = \frac{k_w}{\mu_w} \frac{\mu_o}{k_o} \]  

where \( k_w \) is the relative permeability of water, \( k_o \) the relative permeability of oil, \( \mu_w \) the viscosity of water, and \( \mu_o \) the viscosity of oil.

A mobility ratio \( \leq 1 \) is desirable, as the displacing phase is less mobile than the displaced phase, resulting in the displaced oil to move more easily through the reservoir. Because of the low viscosity of water, the water to oil mobility ratio is generally above 1, leading to instabilities in the flow and a phenomenon named ‘viscous fingering’ as depicted in figure 4. The latter originates from water finding pathways with the least resistance, thereby bypassing the majority of the oil. The high mobility ratio results in a decreasing oil cut and eventually the production of injected water.

By decreasing the water to oil mobility ratio, sweep efficiency is improved and a piston like displacement is obtained (figure 5). The mobility ratio can be improved...
by altering the permeability of the porous media, decreasing the viscosity of the displaced fluid, or increasing the viscosity of the displacing fluid. While it is possible to affect the permeability of porous media, in commercial applications one of the latter approaches is applied.

By dissolving a polymer in the injected water, the viscosity of the displacing fluid is increased, thereby decreasing the water to oil mobility ratio. As a consequence, oil recovery rate is elevated and additional oil is produced before breakthrough of the fluid (polymer) at the production well occurs. The latter implies a lower residual oil saturation after a polymer flood compared with a water flood. Residual oil can be present in several forms, depending on the structure of the oil field. Generally, residual oil is present in dead ends, in ganglia in pore throats, at corners of pores, and in the form of a film on the surface of the walls. Ideally, applied polymers are suitable for application in various types of reservoirs. Relevant characteristics of polymers for EOR are temperature resistance, salt resistance, solution stability over a prolonged period (hydrol-
1.3. ENHANCED OIL RECOVERY

Viscous fingering by altering the permeability of the porous media, decreasing the viscosity of the displaced fluid, or increasing the viscosity of the displacing fluid. While it is possible to affect the permeability of porous media, in commercial applications one of the latter approaches is applied.

Figure 5: Piston-like displacement

By dissolving a polymer in the injected water, the viscosity of the displacing fluid is increased, thereby decreasing the water to oil mobility ratio. As a consequence, oil recovery rate is elevated and additional oil is produced before breakthrough of the fluid (polymer) at the production well occurs. The latter implies a lower residual oil saturation after a polymer flood compared with a water flood.

Residual oil can be present in several forms, depending on the structure of the oil field. Generally, residual oil is present in dead ends, in ganglia in pore throats, at corners of pores, and in the form of a film on the surface of the walls. Ideally, applied polymers are suitable for application in various types of reservoirs. Relevant characteristics of polymers for EOR are temperature resistance, salt resistance, solution stability over a prolonged period (hydrolysis resistance), applicability in low-permeable reservoirs, and suitability over a broad range of oil viscosities. Currently applied polymers are high molecular weight anionic polymers based on acrylamide, or xanthan gum. The most used polymer consists of acrylamide (AM) and acrylic acid (AA) in a ratio of 70:30. The latter copolymer, generally referred to as hydrolysed polyacrylamide (HPAM), suffers from high sensitivity to salts and low temperature resistance. For application in reservoirs at more severe conditions, however, copolymers containing 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and N-vinylpyrrolidone (NVP) are available, as well as the biopolymer xanthan gum.

Polyacrylamide

The viscosifying effect of polyacrylamide (PAM) arises from its very high molecular weight ($>10^7$). In order to enhance solution viscosity and facilitate a high rate of dissolution, acrylid acid (AA) is introduced during synthesis, or a post-hydrolysis step is performed. This latter polymer, partially hydrolysed polyacrylamide (HPAM, depicted in figure 6), contains randomly distributed negative charges along the backbone, leading to stretching of the polymer coil because of electrostatic repulsion. Increased repulsion within coils enhances the hydrodynamic volume of the latter, offering a pronounced increase in solution viscosity. The latter effect is limited by a certain threshold value, occurring at $>70\%$ degree of hydrolysis, referred to as counterion condensation. In current practice, between 15 and 35\% of the monomeric units is negatively charged, affording an optimum between solution viscosity and stability of the coils in presence of ions. An increased ionic strength of the solution, namely, results in increased shielding of the repulsion and inversely affects the polymer coil size.

Figure 6: Structure of partially hydrolysed polyacrylamide (HPAM)

Next to the adverse effect of salts on solution viscosity, hardness (presence of divalent ions, e.g. Mg$^{2+}$ and especially Ca$^{2+}$) limits the applicability of HPAM at elevated temperatures. Based on cloud-point measurements, hardness limits are at 2,000, 500, and 270 mg/L for temperatures of 75, 88, and 96°C respectively. At higher concentrations of divalent ions, gel formation or polymer precipitation is observed, and the solution viscosity is found to decrease. At elevated temperatures, i.e. those present in reservoirs, hydrolysis progresses, leading to an increase in anionicity of the polymer. The latter leads to more pronounced salt sensitiv-
ity and precipitation in presence of lower concentrations of divalent ions.\textsuperscript{76} The rheology of HPAM solutions in porous media was found to deviate from that measured with a viscometer.\textsuperscript{77} In porous media, at low velocities, slight shear thinning behaviour is reported,\textsuperscript{78} as well as (near) Newtonian behaviour.\textsuperscript{79} Bulk rheology follows the same trend, however, at a certain shear rate bulk viscosity starts to decline, displaying a clear shear thinning trend. The apparent viscosity in porous media, on the other hand, starts to increase at average to high flow rates, displaying shear thickening behaviour.\textsuperscript{79–81} At low flow rates, in porous media with low permeability (55 mD), HPAM displays shear thinning behaviour, attributed to the presence of very high molecular weight polymer chains. Because of mechanical degradation, these chains are not anticipated to penetrate far into the reservoir.\textsuperscript{82} At higher flow rates, shear thinning in porous media is only observed at low salinity or high polymer concentration. In practice, however, the degree of shear thinning is considered negligible.\textsuperscript{82} HPAM is relatively resistant to bacterial degradation,\textsuperscript{83} especially compared with the more rigid and less ionic xanthan gum. The latter polymer, however, has a high resistance to salts or hardness.\textsuperscript{84}

Xanthan gum

Xanthan gum, an extracellular polysaccharide, is produced by the microorganism Xanthomonas campestris amongst others\textsuperscript{66} and consists of a cellulose backbone, which is substituted with charged side chains containing trisaccharides, rendering the polymer a polyelectrolyte\textsuperscript{85} (displayed in figure 7). Contrarily to the vast majority of polyelectrolytes, xanthan gum does not display a loss in viscosifying behaviour in solutions at high ionic strength. The latter effect is ascribed to a conformational change of the polymer, from disordered to ordered, in presence of salts.\textsuperscript{85} Moreover, xanthan gum solutions are known for their viscosity insensitivity to temperature, especially at high salt concentrations.\textsuperscript{86} Up to temperatures of 80 to 90 °C and in presence of salts, viscosity of samples was retained to a high degree over a period of 800 days.\textsuperscript{87} However, pronounced degradation at temperatures of 100 °C and above was reported. Aqueous solutions of the polymer were found to display properties of pseudoplastic and plastic polymer solutions.\textsuperscript{86} The viscosifying behaviour of xanthan gum stems to a high degree from its high molecular weight. Molecular weights ranging from $2 \times 10^6$ to $2 \times 10^7$ Da are reported,\textsuperscript{86,88,89} whereby the higher values might be attributed to association phenomena.\textsuperscript{90} Because of the high molecular weight of the polymers, dispersities are difficult to measure, however, values of 2.25 and 2.8 are reported in literature.\textsuperscript{91,92}

The ordered conformation of xanthan gum is reported to be more shear stable than its unordered equivalent,\textsuperscript{85} and is reported to withstand shearing at 5,000 s\textsuperscript{-1} for 30 min. Furthermore, the conformation has a pronounced effect on the solution viscosity. Predominantly at low shear rates, higher viscosities are obtained with the
disordered conformation. At higher shear rates (>3,000 s\(^{-1}\)), comparable viscosities are obtained for both analogues. Compared to HPAM, less data from actual oil fields are available. However, xanthan gum has been applied as viscosifying agent in polymer flooding in some instances over the last decades. Pilot studies in the Yumen and Shengli oil fields in China were reported to be successful.\(^{63,93}\)

### 1.3.2 Topology

In order to improve the properties of HPAM, modification of the polymer has been proposed, referring to alterations of the topology or chemical structure. The main attention is directed towards rendering the polymer more shear resistant and enhancing its viscosifying effect, salt tolerance, and temperature resistance.\(^{67,94-97}\) Regarding topology, altering the molecular architectures has been receiving much attention, whereby structures ranging from comb to block, star and hyperbranched were synthesised.\(^{98,99}\) A schematic representation of the latter structures is displayed in figure 8. From an application point of view, (hyper)branched water soluble polymers are relevant, as they display unique rheological properties compared with linear equivalents, expressed in more predominant elastic behaviour and in some instances a reported higher viscosifying effect.\(^{100-102}\)

Recently, branched hydrophobically modified polyacrylamide was synthesised by free radical polymerisation of a branched core, AM, AA and an hydrophobic monomer.\(^{103}\) The resulting polymer was found to display higher temperature and salt resistance than a commercial HPAM equivalent, as well as a more pronounced viscosifying behaviour. Furthermore, higher viscoelasticity was reported, attributed to extended relaxation times of deformation induced by the high degree of branching. Similar results were obtained for comb-shaped hydrolysed acrylamide polymers, synthesised by free radical polymerisation.\(^{104}\) Comb polymers were found
to be more efficient viscosifiers than linear HPAM, especially when the hydrophobic arms are sufficiently long and hydrophobic interactions afford strong association between polymers. Even at comparable degree of hydrolysis, higher salt resistance and temperature resistance was reported for the branched equivalents, attributed to steric hindrance and intermolecular associations. Unfortunately, molecular weights were not listed and viscoelastic properties of the polymers were not investigated, making the comparison to a commercial polymer at least challenging.

Free radical polymerisation was employed in the synthesis of core-shell hyperbranched polymers consisting of a core of nano-SiO$_2$, hyperbranched polyamidoamine (PAMAM) as subshell, and linear arms of AM, AA and 2-acrylamide-2-methylpropanesulfonic acid (AMPS).\textsuperscript{105} Polymers were found to display excellent shear, salt, and temperature resistance, as well as more elastic behaviour compared with a linear polymer consisting of AM, AA, and AMPS. Moreover, oil recovery from porous rock was found to be higher than for the linear analogue.

In order to synthesise well defined polymers, traditional methods such as anionic, cationic, and group transfer polymerisations are challenging to implement at industrial scale, as these polymerisations are very sensitive to impurities and reaction conditions.\textsuperscript{106,107} Free radical polymerisation, on the other hand, fails in delivering sufficient control over the polymeric architecture and uniformity of the reaction mixture.\textsuperscript{108} In contrast to the aforementioned methods, controlled radical polymerisation (CRP) techniques as nitroxide-mediated polymerisation (NMP),\textsuperscript{109–111} atom transfer radical polymerisation (ATRP),\textsuperscript{112–114} and reversible addition-fragmentation chain transfer (RAFT) polymerisation\textsuperscript{115–117} offer control

---

**Figure 8:** Topology of polymers. A: Comb, B: Block, C: Star, D: Hyperbranched
over the architecture of the polymer, as well as its molecular weight distribution. The versatility of CRP techniques has been illustrated by the various polymer architectures that have been synthesised over the past decades.\textsuperscript{118-121}

A significant amount of literature is available in which ATRP is employed in the synthesis of polymers with different structures, e.g. comb polymers for EOR, as reported by Wever et al.\textsuperscript{122} Linear AM polymers synthesised with ATRP in aqueous medium were compared with star (4-arm) and comb (12-arm) equivalents with similar number average molecular weights. Comb polymers were found to display more pronounced elastic behaviour, compared with their linear and star analogues, especially at low shear rates ($\leq 10$ rad s$^{-1}$). The effect of a hydrophobic block was studied by synthesising random and diblock branched copolymers with 4, 8, or 13 arms with ATRP.\textsuperscript{123} Block copolymers of AM and $N$-isopropylacrylamide (NIPAM) were found to precipitate out of solution at temperatures above the lower critical solution temperature (LCST), while random copolymers were found to stay in solution and display thermothickening behaviour at low shear rates. The effect of the number of arms on the solution rheology of comb polymers has been clearly displayed.\textsuperscript{124} Intrinsic viscosity of a linear, 4 and 8 arm PAM were found to be comparable; however, 13 and 17 arm PAM equivalents displayed a significantly higher viscosity. Based on performance in a two dimensional flow-cell and sandstone cores, comb polymers of AM were found to perform comparable to or better than linear PAMs, at lower polymer concentrations.\textsuperscript{125} Moreover, well-defined diblock, triblock and four arm star amphiphilic block copolymers were synthesised by ATRP.\textsuperscript{126} Polymers were found to be very efficient viscosifiers, sol-gel transitions were obtained at very low polymer concentrations (1,000 ppm). Ionic strength and pH were found to be of great influence on the rheology of the polymer solution, solution viscosity was pronouncedly lowered by decreasing the pH or increasing salt concentration.

Limited research is available in which RAFT polymerisation is applied in the synthesis of (branched) polymers for EOR. Recently, however, RAFT was employed in the synthesis of polyzwitterions, polymers bearing both cationic and anionic functionalities, that are envisioned for application in EOR.\textsuperscript{107} In absence of salts, the latter polymers adopt a collapsed conformation. Upon the addition of electrolytes, on the other hand, random coil conformations are reported. Moreover, stimuli responsive block copolymers were successfully synthesised, displaying phase or conformational change upon a change in solution pH, electrolyte concentration, or temperature. The latter polymers, however, were not evaluated in application tests.

To the authors best knowledge, no literature is available describing the application of NMP in the synthesis of polymers designated for EOR. Since RAFT polymerisation is conceivably more versatile than NMP and ATRP,\textsuperscript{127,128} able to control the polymerisation of a broad range of monomers, the current work
emphasises on the application of the former polymerisation technique. Furthermore, RAFT polymerisation is compatible with several reaction media, ranging from organic solvents, to water, and dispersed systems. A major advantage of the application of RAFT polymerisation is its industrial relevance, because of the uncomplicated process development. Compared to a regular free radical polymerisation, the sole difference lies in the introduction of a RAFT agent. On top of that, no transition metals are required for the polymerisation, making workup of the reaction mixture more straightforward as compared with ATRP.

1.4 RAFT polymerisation

RAFT polymerisation was discovered in 1998 and employs a procedure similar to conventional free radical polymerisation. Different from the latter is the introduction of a chain transfer (RAFT) agent which mediates the polymerisation by trapping radically growing chains, making the latter dormant, thus decreasing the average concentration of actively propagating chains. In figure 9, an exemplary overview of the RAFT polymerisation of AM is shown. Polymerisation is initiated by the generation of free radicals. These radicals either react with monomers containing double bonds, or react reversibly with the RAFT agent, forming an intermediate radical. This intermediate radical can release a reinitiating group, thereby forming a dormant chain connected to the thiocarbonylthio group of the RAFT agent (1 and 2). The released reinitiating group readily polymerises with monomer, before it reacts with another dormant chain, leading to release of the dormant chain for further polymerisation, thereby settling the main RAFT equilibrium (3). Another propagating chain reacts again with the dormant chain, forcing the initial chain to start propagating. The latter equilibrium offers control over the reaction in terms of molecular weight and polydispersity index (PDI), whereby molecular weight is governed by the ratio between consumed monomer and RAFT agent. Some termination might occur, by disproportionation, recombination, or cross-termination of radical chains. The extent to which termination happens, however, can be limited by applying appropriate conditions to the polymerisation.

The selection of a suitable RAFT agent highly influences the results of a RAFT polymerisation and should be tailored to the applied monomers and reaction conditions. The structure of a RAFT agent is determined by its R-group (leaving group) and Z-group (activating group) coupled to a thiocarbonylthio group, as illustrated in figure 10 and shown for several RAFT agents in table 1.
1.4. RAFT POLYMERISATION

**Figure 9:** Exemplary reaction scheme for RAFT polymerisation of AM with 3-((benzylthio)carbonothioyl)thio) propanoic acid (BCPA) as RAFT agent and 4,4'-Azobis(4-cyanovaleric acid) (ACVA) as initiator.
1.4.1 Water soluble polymers by RAFT polymerisation

Several monomers have been reported for the synthesis of water soluble polymers by RAFT polymerisation. An overview of the majority of these monomers is depicted in the supplementary information. Moreover, water soluble polymers are polymerised with a variety of RAFT agents, ranging from a dithioacetate to xanthates and several trithiocarbonate structures. The majority of the published reactions, however, involves an aromatic dithioester RAFT agent. An overview of the RAFT agents and monomers the latter have been applied to is depicted in table 1.

![Figure 10: Addition of a radical to the RAFT agent with its characteristic R-group and Z-group, adapted from\textsuperscript{140} and\textsuperscript{131}](image)

Table 1: Overview of applied RAFT agents

<table>
<thead>
<tr>
<th>CTA</th>
<th>Z-group</th>
<th>R-group</th>
<th>Homopolymers</th>
<th>Copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPDA</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td>AM\textsuperscript{106}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dithioacetate</td>
<td></td>
</tr>
<tr>
<td>tBDB</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td>NAM\textsuperscript{141–144}</td>
<td>NAM&amp;/TBA\textsuperscript{141} TBA&amp;/NAM\textsuperscript{141}</td>
</tr>
<tr>
<td>CDB</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td>AM\textsuperscript{106}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aromatic dithioesters</td>
<td></td>
</tr>
</tbody>
</table>
1.4. RAFT POLYMERISATION

Table 1 – continued from previous page

<table>
<thead>
<tr>
<th>CTA</th>
<th>Z-group</th>
<th>R-group</th>
<th>Homopolymers</th>
<th>Copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPDB</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NIPAM&lt;sup&gt;145&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,146&lt;/sup&gt; MAM&lt;sup&gt;116&lt;/sup&gt; PEGMA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; MAPSp&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; HPMA&lt;sup&gt;148&lt;/sup&gt; DMA&lt;sup&gt;149&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; DMAPMAM&lt;sup&gt;149&lt;/sup&gt; O-M-MAMGlc&lt;sup&gt;150&lt;/sup&gt; AEMA&lt;sup&gt;151&lt;/sup&gt; APMA&lt;sup&gt;151&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt; VBT&lt;sup&gt;134&lt;/sup&gt; NIPAM&lt;sup&gt;152&lt;/sup&gt; MAA&lt;sup&gt;153&lt;/sup&gt; CTP-PEG-CTP::SSS&lt;sup&gt;153&lt;/sup&gt; DMAEMA&lt;sup&gt;154&lt;/sup&gt;</td>
</tr>
<tr>
<td>CTP</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>AM&lt;sup&gt;106,146&lt;/sup&gt; MAM&lt;sup&gt;116&lt;/sup&gt; PEGMA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; MAPSp&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; HPMA&lt;sup&gt;148&lt;/sup&gt; DMA&lt;sup&gt;149&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; DMAPMAM&lt;sup&gt;149&lt;/sup&gt; O-M-MAMGlc&lt;sup&gt;150&lt;/sup&gt; AEMA&lt;sup&gt;151&lt;/sup&gt; APMA&lt;sup&gt;151&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt; VBT&lt;sup&gt;134&lt;/sup&gt; NIPAM&lt;sup&gt;152&lt;/sup&gt; MAA&lt;sup&gt;153&lt;/sup&gt; CTP-PEG-CTP::SSS&lt;sup&gt;153&lt;/sup&gt; DMAEMA&lt;sup&gt;154&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>MDB</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NAM&lt;sup&gt;142&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,146&lt;/sup&gt; MAM&lt;sup&gt;116&lt;/sup&gt; PEGMA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; MAPSp&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; HPMA&lt;sup&gt;148&lt;/sup&gt; DMA&lt;sup&gt;149&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; DMAPMAM&lt;sup&gt;149&lt;/sup&gt; O-M-MAMGlc&lt;sup&gt;150&lt;/sup&gt; AEMA&lt;sup&gt;151&lt;/sup&gt; APMA&lt;sup&gt;151&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt; VBT&lt;sup&gt;134&lt;/sup&gt; NIPAM&lt;sup&gt;152&lt;/sup&gt; MAA&lt;sup&gt;153&lt;/sup&gt; CTP-PEG-CTP::SSS&lt;sup&gt;153&lt;/sup&gt; DMAEMA&lt;sup&gt;154&lt;/sup&gt;</td>
</tr>
<tr>
<td>CMDB</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NAM&lt;sup&gt;142&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,146&lt;/sup&gt; MAM&lt;sup&gt;116&lt;/sup&gt; PEGMA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; MAPSp&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; HPMA&lt;sup&gt;148&lt;/sup&gt; DMA&lt;sup&gt;149&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; DMAPMAM&lt;sup&gt;149&lt;/sup&gt; O-M-MAMGlc&lt;sup&gt;150&lt;/sup&gt; AEMA&lt;sup&gt;151&lt;/sup&gt; APMA&lt;sup&gt;151&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt; VBT&lt;sup&gt;134&lt;/sup&gt; NIPAM&lt;sup&gt;152&lt;/sup&gt; MAA&lt;sup&gt;153&lt;/sup&gt; CTP-PEG-CTP::SSS&lt;sup&gt;153&lt;/sup&gt; DMAEMA&lt;sup&gt;154&lt;/sup&gt;</td>
</tr>
<tr>
<td>TPB</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NAM&lt;sup&gt;142&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,146&lt;/sup&gt; MAM&lt;sup&gt;116&lt;/sup&gt; PEGMA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; MAPSp&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; HPMA&lt;sup&gt;148&lt;/sup&gt; DMA&lt;sup&gt;149&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; DMAPMAM&lt;sup&gt;149&lt;/sup&gt; O-M-MAMGlc&lt;sup&gt;150&lt;/sup&gt; AEMA&lt;sup&gt;151&lt;/sup&gt; APMA&lt;sup&gt;151&lt;/sup&gt; SSS&lt;sup&gt;134&lt;/sup&gt; VBT&lt;sup&gt;134&lt;/sup&gt; NIPAM&lt;sup&gt;152&lt;/sup&gt; MAA&lt;sup&gt;153&lt;/sup&gt; CTP-PEG-CTP::SSS&lt;sup&gt;153&lt;/sup&gt; DMAEMA&lt;sup&gt;154&lt;/sup&gt;</td>
</tr>
<tr>
<td>TSPE</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>AM&lt;sup&gt;106,156&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,156&lt;/sup&gt;</td>
</tr>
<tr>
<td>MTBSPE</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>MAM&lt;sup&gt;147&lt;/sup&gt; MEABSE&lt;sup&gt;147&lt;/sup&gt; AEMA&lt;sup&gt;147&lt;/sup&gt; DMAPMAM&lt;sup&gt;147&lt;/sup&gt; VPP&lt;sup&gt;134&lt;/sup&gt;</td>
<td>AM&lt;sup&gt;106,156&lt;/sup&gt;</td>
</tr>
<tr>
<td>TBSPNDS</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>PEGA&lt;sup&gt;147&lt;/sup&gt; APSp&lt;sup&gt;147&lt;/sup&gt; SSS&lt;sup&gt;147&lt;/sup&gt; AETA&lt;sup&gt;147&lt;/sup&gt; DMAPMAM&lt;sup&gt;147&lt;/sup&gt; VBT&lt;sup&gt;149&lt;/sup&gt; VPP&lt;sup&gt;134&lt;/sup&gt;</td>
<td>VBT&lt;sup&gt;149&lt;/sup&gt; DMA&lt;sup&gt;147&lt;/sup&gt;</td>
</tr>
<tr>
<td>MTBSMPM</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>MEABSE&lt;sup&gt;147&lt;/sup&gt; VPP&lt;sup&gt;134&lt;/sup&gt;</td>
<td>MEABSE&lt;sup&gt;147&lt;/sup&gt; VPP&lt;sup&gt;134&lt;/sup&gt;</td>
</tr>
<tr>
<td>ICAVB</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NIPAM&lt;sup&gt;157&lt;/sup&gt;</td>
<td>NIPAM &amp; 1,2-Propanediol-3-methacrylate &amp; 9-Anthryl methyl methacrylate&lt;sup&gt;158&lt;/sup&gt;</td>
</tr>
<tr>
<td>BID</td>
<td><img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
<td>NIPAM&lt;sup&gt;157&lt;/sup&gt;</td>
<td>NIPAM &amp; 1,2-Propanediol-3-methacrylate &amp; 9-Anthryl methyl methacrylate&lt;sup&gt;158&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Xanthate

| MCEX | ![Structure](image) | ![Structure](image) | AM<sup>159,160</sup> AA<sup>159</sup> DMA<sup>160</sup> NIPAM<sup>160</sup> | AM&BioAM<sup>159</sup> AA&BioAM<sup>159</sup> AM&AMPS<sup>160</sup> DMA&AMPS<sup>160</sup> NIPAM&DMA<sup>160</sup> |
Acrylamides and Methacrylamides

For polymerisation of acrylamide (AM), dithioacetate CPDA (structures corresponding with abbreviations are depicted in table 1) was employed, as well as aromatic dithioester agents CDB, CTP, and TSPE. While it was possible to polymerise up to a molecular weight of 100,000 Da with PDIs below 1.40, the best control was offered when a xanthate (MCEX) was modified with PEG to enhance its water solubility and successively applied to the partitioning of the RAFT agent into the organic phase. In water, dithiobenzoate CTP was employed to polymerise DMA up to a molecular weight of 8,200 Da (PDI: 1.68), while thiodiisobutyl dithiocarbonate DBTTC has proven to be an efficient transfer agent in the polymerisation of AM in water, initiated by Gamma radiation and an aqueous buffer with a pH of approximately 5.3. Dithiocarbamate BDAT has been employed at 45°C for polymerisation in a mixture of water and hexane. Molecular weights of almost 1,000,000 Da were reached with a claimed polydispersity of 1.12. Trithiocarbonate BDAT has been employed to polymerise MAM up to a molecular weight of 34,500 Da, with PDIs as low as 1.10. The polymer was successfully chain extended with AM. Slightly lower molecular weights were obtained with trithiocarbonate EMP and CMP. This was attributed to the partitioning of the RAFT agent into the organic phase. In water, dithiobenzoate CTP was employed to polymerise DMA up to a molecular weight of 8,200 Da (PDI: 1.20). The popular trithiocarbonate BDAT has been employed at 60°C to polymerise DMA up to a molecular weight of 60,000 Da, with PDI values below 1.40. Low temperature polymerisation was employed to polymerise MAM up to a molecular weight of 34,500 Da, with PDIs up to 1.31. Low temperature polymerisation was employed in the polymerisation of AM in water with BDAT and water/acetone with BCPA up to molecular weights of 17,000 and 37,000 Da respectively, while maintaining low polydispersities. Low temperature polymerisation was explored...
1.4. RAFT POLYMERISATION

with redox initiation of AM at 25 to 45°C in presence of trithiocarbonate BDAT. The polymers had molecular weights in good correspondence with their theoretical values, up to 13,400 Da with PDIs up to 1.31. Low temperature polymerisation was also reported up to higher molecular weights. A xanthate (MCEX) was modified with AM in a mixture of ethanol and water up to a molecular weight of 650 and subsequently applied in the polymerisation of additional AM in water, initiated by redox initiation at ambient temperature.\(^{160}\) Molecular weights of almost 1,000,000 Da were reached with a claimed polydispersity of 1.12.

Significantly less attention has been devoted to the RAFT polymerisation of methacrylamide (MAM). In an aqueous buffer (pH = 5.3), dithiobenzoate CTP was employed to polymerise MAM up to a molecular weight of 34,500 Da, with PDIs as low as 1.10.\(^{146}\) The polymer was successfully chain extended with AM. Slightly higher molecular weights were obtained with dithiobenzoate MTBSPE in water (pH = 3.0).\(^{147}\) MAM was polymerised up to a molecular weight of approximately 60,000 Da, with PDI values below 1.40.

In the polymerisation of N,N-dimethylacrylamide (DMA), generally trithiocarbonate RAFT agents are employed, whereby water is applied as solvent. In 2010, four different trithiocarbonate structures with different water solubilities were applied in the aqueous polymerisation of DMA as well as in the inverse emulsion polymerisation in a mixture of water and hexane.\(^{163}\) Molecular weights obtained in water with BDAT, EMP, and CMP ranged from 35,700 to 42,100 Da and were in good correspondence with theoretical values. Reported PDIs were 1.14, 1.06, and 1.09 respectively. In the inverse microemulsion, less control over the reaction was observed and molecular weights for BDAT, EMP, CMP, and DMP increased to 40,000 Da, 69,600, 138,100, and 399,300 Da respectively, at a similar monomer to RAFT agent ratio. The loss of control was also illustrated by the increase in PDI values of 1.68, 1.20, 1.36, and 2.46 respectively. This loss was attributed to partitioning of the RAFT agent into the organic phase. In water, dithiobenzoate CTP was employed to polymerise DMA up to a molecular weight of 8,200 Da (PDI: 1.08).\(^{149}\) The polymer was successfully chain extended with DMA up to a molecular weight of 26,700 Da with a PDI of 1.07. Chain extension with DMAPMAM, on the other hand, yielded a very high molecular weight polymer, which was attributed to loss of control of the reaction. Trithiocarbonate DMP was modified with polyethylene glycol (PEG) to enhance its water solubility and successively applied to the polymerisation of DMA at \(-15^\circ\)C, yielding molecular weights up to 37,300 Da with PDIs below 1.25.\(^{170}\) A successful chain extension with N-isopropylacrylamide (NIPAM) was performed, yielding a copolymer with a molecular weight of 62,500 Da and a PDI of 1.26. The popular trithiocarbonate BDAT has been employed at low temperatures in water\(^{171}\) and an aqueous buffer with a pH of approximately 5.\(^{170}\) At room temperature, molecular weights up to 78,000 Da were obtained, with PDIs as low as 1.05. At \(-15^\circ\)C, the highest molecular weight attained was
30,900 Da, with a PDI of 1.25. In a chain extension experiment with NIPAM, thermoresponsive copolymers with a molecular weight of 62,500 Da and a PDI of 1.26 were obtained. Significantly higher molecular weights were only reported with xanthate MCEX. The xanthate was modified with DMA in ethyl acetate (molecular weight: 1,050 Da) or NIPAM in water (13,000 Da, PDI: 1.28) and extended with DMA in water at room temperature. After polymerisation, initiated by redox, molecular weights of 826,000 and 1,021,000 Da were obtained respectively, with PDI values of 1.11 and 1.51.

In the polymerisation of NIPAM, both dithiobenzoates and trithiocarbonates are employed. NIPAM was polymerised in DMF in presence of dithiobenzoate CPDB up to a molecular weight of 31,100 Da, with a PDI of 1.27. The polymer was modified to introduce RAFT groups along the backbone and applied in the polymerisation of VA or N-vinyl-2-pyrrolidone (NVP) to yield comb-polymers. Moreover, dithiobenzoate CTP was employed in the polymerisation in dioxane, yielding thermoresponsive polymers with a molecular weight of 12,000 Da and a PDI of 1.30.

NIPAM was copolymerised with 1,2-propandiol-3-methacrylate and 9-anthryl methyl methacrylate in dioxane. The cloud points of the fluorescent copolymers were investigated and found to range from 30 to 37°C, depending on the composition. Unfortunately, molecular weights and polydispersities were not listed. Monomer VBC was polymerised with NIPAM and subsequently modified with 4(5)-Imidazole dithiocarboxylic acid to synthesise a backbone with RAFT groups. The Z-group of the dithiobenzoate RAFT agent is identical to that of RAFT agent BID. After polymerisation in DMF, comb polymers with peak molecular weights between 755,000 and 2,795,000 Da and corresponding PDI values from 3.11 to 10.34 were obtained. Unmodified BID was applied in the polymerisation of NIPAM in dioxane up to a molecular weight of 69,200 Da, with PDIs listed below 1.43. Trithiocarbonate DMP was modified with PEG to enhance its water solubility and successively applied in the polymerisation of NIPAM at −15°C up to a molecular weight of 37,300 Da with PDIs below 1.25. Subsequent chain extension with DMA yielded a copolymer with a molecular weight of 53,100 Da and a PDI of 1.22. DMP was also applied in the polymerisation of NIPAM in DMF, initiated radically or by photo initiation. Molecular weights up to 17,500 Da were reported, along with PDIs below 1.35. Using DMSO as solvent, a molecular weight of 7,000 Da was obtained, with a PDI of 1.15. A chain extension experiment was performed with tert-butyl acrylate (TBA), yielding an amphiphilic polymer with a molecular weight of 15,700 Da and a PDI of 1.11. BCPA was employed as RAFT agent in the polymerisation of NIPAM in water with 15 vol% acetone. Polymerisation was initiated by gamma radiation, yielding a molecular weight of 105,000 Da, with a PDI of 1.12.

The most commonly applied trithiocarbonate, BDAT, has been reported in
1.4. RAFT POLYMERISATION

several polymerisations of NIPAM.154,162,169,170,172 Both radical and photo initiation have been employed in DMF, yielding PNIPAM with molecular weights up to 17,500 Da and PDIs up to 1.45.168 Slightly higher molecular weights were afforded by redox initiation in distilled water. Values up to 40,700 Da were reported, with PDI values as low as 1.20.172 By applying gamma radiation in water, molecular weights up to 74,000 Da with low polydispersity (1.10) were obtained.170 Moreover, polymerisation at lower temperature was proven to be viable. At -15, BDAT was employed in the polymerisation of NIPAM in an aqueous buffer (pH = 5.0) up to a molecular weight of 33,500 Da with PDIs as low as 1.19.162 Chain extension with DMA yielded a block copolymer with a molecular weight of 65,600 Da and a PDI of 1.27. Thioiocarbonate BDAT was compared with EMP, the latter containing a different Z-group, leading to polymerisation on one side of the RAFT agent solely.162 PNIPAM with molecular weights up to approximately 75,000 Da were obtained for both RAFT agents, with PDIs below 1.10. Polymers were chain extended with DMA to yield AB (EMP) or ABA (BDAT) block copolymers. AB block copolymers had listed molecular weights up to 61,900 Da with PDIs up to 1.21. The ABA block copolymers had molecular weights up to 53,000 Da and PDI values below 1.15. The polymers are forming reversible micelles upon heating, whereby transition temperature and micelle size depend on the polymer architecture and the NIPAM block length. Star polymers consisting of NIPAM were synthesised with macro RAFT agents having four actives sites, containing thioiocarbonate groups and a R-group and Z-group similar to DMP.178 Two different macro RAFT agents, with molecular weights of 9,000 Da and 21,000 Da, where applied in dioxane. The final star polymers had reported molecular weights up to 42,000 Da and PDI values ranging from 1.05 to 1.15.

N-acryloylmorpholine (NAM) was polymerised with several dithiobenzoate RAFT agents. tBDB was employed in multiple instances, using dioxane as solvent.141–144 Molecular weights ranged from 10,000 Da (PDI < 1.15),143 to 40,500 Da (PDI: 1.03),141 up to 80,000 Da with PDI as low as 1.15144 or 1.16142 respectively. A successful chain extension experiment with N-tert-butylacrylamide (TBAm) illustrated the living character of the polymerisation.141 A PNAM homopolymer (molecular weight: 40,500 Da, PDI: 1.03) was employed in further polymerisation, yielding an amphiphilic copolymer with a molecular weight up to 50,000 Da (PDI up to 1.25). MDB was employed in the polymerisation of NAM up to a molecular weight of 40,000 Da, with PDI values up to 1.10.142 Similar PDIs were obtained, in the polymerisation with RAFT agent TPB, up to molecular weights of 70,000 Da. With CMDB, a molecular weight of 75,000 Da was reached, while maintaining polydispersities between 1.10 and 1.20.142 N-(2-aminoethyl)acrylamide (AEMA) was polymerised with dithiobenzoate CTP in water:dioxane (2:1 vol/vol).151 Polymers with molecular weights up to 22,700 Da were obtained, with polydispersities below 1.20. A macro RAFT agent with a
molecular weight of 8,600 Da (PDI: 1.20) was subjected to chain extension experiments with either AEMA, or N-(3-aminopropyl)acrylamide (APMA). After chain extension, molecular weights of 25,300 and 20,500 Da respectively were obtained with PDIs of 2.14 and 1.29. APMA was also subjected to homopolymerisations in water:dioxane (2:1 vol/vol) with CTP up to molecular weights of 26,500 Da and PDI values up to 1.31.\textsuperscript{151}

N-(2-hydroxypropyl)methacrylamide (HPMA) was polymerised with dithiobenzoate CTP in an aqueous buffer (pH = 5.2), up to molecular weights of 97,000 Da, while the polydispersity remained below 1.09.\textsuperscript{148} CTP was employed in the polymerisation N-(3-(dimethylamino)propyl) acrylamide (DMAPAM) as well.\textsuperscript{147} In aqueous KCl (pH = 3.2), molecular weights up to 80,000 Da and PDI values of approximately 1.20 by multangle laser light scattering (MALLS) and 1.50 by ASEC were stated. 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was polymerised with trithiocarbonate RAFT agents and xanthate MCEX. The latter was modified with AM and AMPS (3:1 mol/mol) in a mixture of ethanol and water\textsuperscript{160} up to a molecular weight of 700. The macro RAFT agent was employed in the redox copolymerisation of AM and AMPS, in a similar ratio to the macro RAFT agent, yielding a polymer with a molecular weight of 1,170,000 Da and a PDI of 1.36. AMPS was also copolymerised with DMA (1:10 mol/mol) by redox initiation with a macro RAFT agent of MCEX polymerised with DMA (molecular weight: 1,050 Da). A molecular weight of 1,110,000 Da and a PDI of 1.61 were reported for the latter copolymer.\textsuperscript{160} Other reported polymerisations at ambient temperature employed gamma radiation for the polymerisation with trithiocarbonate BDAT in water, or BCPA in a mixture of water and acetone.\textsuperscript{154} Two dithiobenzoate RAFT agents have been reported in the polymerisation of N-(3-(dimethylamino)propyl) methacrylamide (DMAPMAM). MTBSPE was employed in water (pH = 4.0), leading to PDMAPMAM polymers with molecular weights up to approximately 40,000 Da and PDI values below 1.40 based on end-group analysis, or below 1.50 based on ASEC.\textsuperscript{147} Higher molecular weights were obtained with CTP in water, however, control was lost.\textsuperscript{149} In an aqueous buffer, control was maintained and DMAPMAM was polymerised up to a molecular weight of 40,000 Da with a PDI up to 1.10. A PDMAPMAM macro RAFT agent (molecular weight: 8,700 Da and PDI of 1.08) was extended with DMA, (ar-vinylbenzyl)trimethylammonium chloride (VBTA), or DMAPMAM. The copolymers had reported molecular weights of 37,200, 24,600, and 58,900 Da respectively, with polydispersities of 1.14, 1.11, and 1.12.

Branching in AM polymers was introduced by copolymerising with \textit{N},\textit{N}′-methylenebisacrylamide (BisAM), a bifunctional AM monomer\textsuperscript{159,165,166} (depicted in figure 11). Xanthate MCEX was employed in a mixture of water and 2-propanol, yielding branched copolymers of AM and BisAM with a molecular weight up to 7,370, and PDI values ranging from 2.68 to 11.9. Higher molecular weights,
1.4. RAFT POLYMERISATION

![Figure 11: N,N'-methylenebisacrylamide (BisAM)](image)

ranging from 560,000 to 1,280,000 Da were obtained when BCPA was used as RAFT agent in an aqueous buffer. GPC traces displayed bimodal peaks, resulting in polydispersities ranging from 4.7 to 8.6. Next, the feeding policy of BisAM was explored. By polymerising the arms, before the addition of BisAM, star-shaped polymers with molecular weights up to 715,000 Da and PDIs ranging from 1.1 to 2.2 were obtained. In a second approach, the core was first synthesised by reaction of BisAM with the RAFT agent, followed by the addition of AM in order to grow arms from the core. The latter approach yielded polymers with molecular weights up to 579,000 Da and polydispersities between 1.6 and 2.4. In a batch approach, AM was directly copolymerised with BisAM. Molecular weights were limited to 204,000 Da (PDI: 1.9), at higher BisAM concentration gelation was observed. With a continuous feeding approach of BisAM, molecular weights up to 1,290,000 Da with polydispersities from 1.4 to 9.4 were obtained. Moreover, dithiobenzonate CTP was employed in the polymerisation in dioxane. The former yielded thermoresponsive polymers with a molecular weight of 12,000 Da and a PDI of 1.30. The polymer was subsequently crosslinked with BisAM and PEGDAC (vide infra). When solely BisAM was applied in the crosslinking, a star-shaped polymer was obtained with a molecular weight of 25,000 Da and a PDI of 1.70. The latter approach, however, introduced BisAM in the polymerisation. For experiments involving both BisAM and PEGDAC, gel structures were reported. Molecular weights for the latter polymers, were not expressed. Using trithiocarbonate TCPA as RAFT agent, NIPAM was copolymerised with BisAM to synthesise a branched macro RAFT agent. The latter was chain extended with a fresh batch of NIPAM to form a hydrogel. Unfortunately, the authors did not mention the molecular weight of the polymers. Dithiobenzonate ICAVB, bearing a pendant double bond, was applied in the polymerisation of NIPAM in dioxane. Molecular weights of the branched polymer up to 61,300 Da were listed, however, polydispersities were not mentioned.

**Acrylates**

Trithiocarbonate BDAT was employed in the polymerisation of Acrylic acid (AA) in water, initiated by gamma radiation. With this controlled reaction, a polymer with a molecular weight of 98,000 Da and a PDI of 1.10 was obtained. By applying trithiocarbonate BCPA in a mixture of water and acetone, molecular weights up to
230,000 Da were obtained with PDI values below 1.27. Poly(ethylene glycol) acrylate (PEGDA) was polymerised with dithiobenzoate TBSPNDS in aqueous KCl. Molecular weights up to 70,000 Da were reported, while the PDI remained below 1.40. Acrylate 2-hydroxyethyl acrylate (HEA) was polymerised with two different trithiocarbonate RAFT agents, initiated by gamma radiation. Polymersisation with BDAT in water yielded a polymer a molecular weight of 72,000 Da and a PDI of 1.15. When BCPA was employed in a mixture of water and acetone, a molecular weight of 50,000 Da was obtained, with a corresponding PDI of 1.12. 2-acryloyloxyethyl trimethyl ammonium (AETA) was polymerised with dithiobenzoate TBSPNDS in aqueous KCl, up to a molecular weight of 80,000 Da and a PDI of approximately 1.35. The latter RAFT agent was also employed in the polymerisation of 3-(acryloyloxy) propanesulfonate potassium salt (APSP). With TBSPNDS as well as CTP, molecular weights up to 100,000 Da were obtained, with PDIs below 1.10. However, with both RAFT agents some high molecular weight polymer was formed, attributed to competition with free radical polymerisation.

AA was polymerised in ethanol up to a molecular weight of 2,500 Da (PDI below 1.20) with xanthate MCEX. Under similar conditions, AA was copolymerised with BisAM, yielding branched polymers with molecular weights up to 5,700 Da with PDI values ranging from 1.25 to 4.27.

**Methacrylates**

For the polymerisation of methacrylic acid (MAA), both a ditbiobenzoate and a trithiocarbonate RAFT agent have been reported. The former (CTP) was applied in water, whereby molecular weights up to 15,600 Da were obtained with a low PDI value of 1.14. The trithiocarbonate CTTPA was employed in the polymerisation of MAA in water, methanol, and dioxane. Water offered the highest degree of control over the polymerisation, as well as favourable kinetics. At a pH of 4 or lower, low polydisperiesities were obtained (up to 1.27), while molecular weights of 92,000 Da were reached. At higher pH, control over the reaction was lost. CTTPA was also applied in the preparation of a macro RAFT agent containing MAA and poly(ethylene glycol) methacrylate (PEGMA) (50:50 mol/mol) up to a molecular weight of 16,000 Da. The macro RAFT agent was employed in the
emulsion polymerisation of methyl methacrylate (MMA), or MMA with styrene (St). The former polymers had molecular weights ranging from 43,100 to 187,000 Da, the latter 51,800 to 54,800 Da, with PDI values of 1.20 to 1.52 and 1.19 to 1.14 respectively. Morphology of the copolymers changed from spherical micelles, to fibers, and to vesicles with increasing hydrophobic block size, independent of the pH of the aqueous phase. Similar macro RAFT agents, containing MAA and PEGMA in a ratio of 50:50 and 33:66 were synthesised with molecular weights from 20,000 to 24,000 Da. These macro RAFT agents, with reported PDIs from 1.09 to 1.14, were chain extended with St up to a molecular weight of 117,200 Da (PDI up to 1.42), or with MMA. Molecular weights of the latter copolymers were unfortunately not listed.

Apart from being incorporated into a macro RAFT agent, PEGMA was also employed in the synthesis of homopolymers. Ditiobenzoate CTP was applied as RAFT agent in water and polymerisation was initiated by gamma radiation. Molecular weights ranged up to 50,000 Da, with low PDI values as low as 1.07. Another study reported molecular weights up to 56,000 Da, again with low polydispersities. Interestingly, polymers were reported to have a cloud point around 83 °C.

Other reported polymerisations of methacrylates involved ditiobenzoate RAFT agents. CTP was employed in the polymerisation of N,N-dimethylaminomethyl methacrylate (DMAEMA), 3-(methacryloyloxy) propanesulfonate potassium salt (MAPSP), and methyl 6-O-methacryloyl-α-D-glucoside (6-O-MAMGlc). Applying DMAEMA, a polymer with molecular weight up to 17,500 Da and a PDI as low as 1.20 was synthesised by gamma radiation in water. The radically initiated RAFT polymerisation of MAPSP in water yielded molecular weights up to approximately 100,000 Da, with PDIs below 1.10. Finally, 6-O-MAMGlc was polymerised with CTP in water. Addition of sodium carbonate or sodium hydrogen carbonate did not offer control over the reaction, while addition of approximately 10% ethanol led to conformation of the molecular weight with its theoretical value. A molecular weight of 26,300 Da was reported, with a PDI of 1.14.

CTP was furthermore employed as RAFT agent for the polymerisation of MEABSE in aqueous buffer, as well as MTBSPE and MTBSMPM in water. However, no polymer was obtained, while the distinct colour of the mixture was retained. The latter was attributed to a low rate of polymerisation at the employed temperature, which was confirmed by a very low rate of reaction when free radical polymerisation was employed with this monomer. Finally, MAETA was polymerised with MTBSPE in water up to a molecular weight of 60,000 Da, with PDI values of approximately 1.60 (determined by end-group analysis). Employing ASEC, high molecular weights and PDIs were obtained, which was attributed to aggregation of the polymer because of electrostatic interaction between anionic end-groups and the cationic polymer.
Crosslinked polymers of PEGMA were synthesised in acetonitrile, in presence of trithiocarbonate BCPA. In a first step, PEGMA was polymerised up to a molecular weight of 9,000 Da or 21,000 Da with PDI values below 1.20. Subsequently, the macro RAFT agents were crosslinked with BisAM or a biodegradable crosslinker, in presence of benzaldehyde, up to a molecular weight of 132,000 Da with polydispersity between 1.08 and 1.19.

**Other water soluble monomers**

Besides (meth)acrylamides and (meth)acrylates, other water soluble monomers are reported in literature. Some of these monomers exhibit unique properties, such as the introduction of ion exchange properties, which renders them promising candidates for several applications. Starch was modified with a xanthate group, similar to that of MCEX, and subsequently applied in the polymerisation of vinyl acetate (VA). The molecular weight of one sample was listed, namely 263,000 Da, with a PDI of 2.72. After hydrolysis, the arms were characterised and molecular weights of 18,000 to 105,000 Da were reported, with PDI values between 1.21 and 1.53. VBTA was polymerised with dithiobenzoate TBSPNDS and CTP. With the latter RAFT agent in aqueous NaBr, molecular weights up to 40,000 Da were obtained, with a PDI below 1.14. A macro RAFT agent with a molecular weight of 27,300 Da and a PDI of 1.13 was employed in the polymerisation of DMA up to a molecular weight of 124,000, with a final PDI of 1.39. CTP was applied in water, yielding a polymer with a molecular weight of 5,800 Da and a PDI of 1.08. This macro RAFT agent was used in the polymerisation of DMAPMAM and VBTA. The former polymerisation turned out to be uncontrolled, while the latter yielded a block copolymer with a molecular weight of 31,100 Da with a PDI of 1.14. Another low molecular weight macro RAFT agent was synthesised with CTP and VBTA. A chain extension experiment was conducted with N,N-dimethylvinylbenzylamine (DMVBA) up to a molecular weight of 51,000 Da and a corresponding PDI of 1.37.

Sodium 4-vinylbenzenesulfonate (SSS) was polymerised with a variety of dithiobenzoates. TBSPNDS was employed in aqueous NaBr, however, no molecular weights were reported. CTP was employed in water, yielding molecular weights up to 31,600 Da and PDI values below 1.26. A successful chain extension experiment was performed with sodium 4-vinylbenzoate (VB) and a macro RAFT agent of unknown molecular weight. The final molecular weight of the copolymer was 18,800 Da, with a PDI of 1.18. The latter research reports the polymerisation of SSS with CMDB in water as well. While a high molecular weight of 507,000 Da was obtained, conformation with its theoretical value was poor and the loss of control was confirmed by a high polydispersity. CTP, moreover, was modified with PEG, to yield a PEG chain capped between two CTP dithiobenzoate structures with a molecular weight of 10,000 Da and
A successful chain extension experiment was conducted with A chain extension experiment was conducted with A chain extension experiment was conducted with A chain extension experiment was conducted with A chain extension experiment was conducted with A chain extension experiment was conducted with A chain extension experiment was conducted with 1.24. Moreover, some unsuccessful RAFT polymerisations have been reported. Dithiobenzoates TBSPNDS, MTBSPE, and MTBSMPM have been employed in the polymerisation of VPPS in aqueous NaBr, however, even at low a pH no polymer was formed. Judging from the discolouration of the reaction mixture, failure of the reaction was attributed to degradation of the RAFT agents.

As shown in the overview above, multiple monomers have been employed in the synthesis of water soluble polymers. However, little research is devoted to the RAFT polymerisation of water soluble polymers up to high molecular weights. With respect to their application in EOR, molecular weight is one of the governing factors. On top of that, little research is directed at the synthesis of branched, water soluble polymers, especially at a desirable higher molecular weight.

1.5 Aim and scope of research

The objective of this work is to investigate the use of reversible addition-fragmentation chain-transfer (RAFT) polymerisation in the preparation of water-soluble polymers for application in enhanced oil recovery (EOR). Because of the limited results available from literature, the focus is more specifically on the introduction of branches in such polymers and on the comparison of these polymers with linear equivalents for application in EOR.

Chapter 1 gives an introduction to polymer flooding and the currently applied commercial polymers. Current polymers for EOR contain acrylamide (AM), as it is affordable and offers desirable viscosifying properties. AM can be readily polymerised by free radical polymerisation up to high molecular weights, and water can be applied as solvent. From literature, however, introducing branches in the polymers has become apparent to yield advantages related to the rheology, as well as to shear resistance and presence of salts. In order to introduce branching in an industrially-relevant polymerisation procedure, control over the reaction is required. The latter can be offered by applying a controlled radical polymerisation (CRP) approach. Therefore, the state of the art on the controlled synthesis of water soluble polymers by RAFT polymerisation has been presented.

In Chapter 2, the synthesis of three different industrially relevant RAFT agents is described. These RAFT agents are designed to offer control over the polymerisation of AM and influence the molecular weight of the final polymers.

In Chapter 3, RAFT agent 3-(((benzylthio)carbonothioyl)thio) propanoic acid (BCPA) is applied in the aqueous polymerisation of AM. Control over the reaction is investigated by linear first order kinetic plots, a linear development of the molecular weight as function of reaction time and a chain extension experiment...
of an AM macro RAFT agent with $N, N$-dimethylacrylamide (DMA). The work described in this chapter opens the door to the polymerisation of AM up to high molecular weight.

After the synthesis of linear PAM, the focus is on the introduction of branches in the polymers. To that end, hyperbranched PAM is synthesised in Chapter 4 by a facile copolymerisation of AM and $N, N'$-methylenebis (acrylamide) (BisAM) in presence of a RAFT agent. The role of the RAFT agent is investigated, as well as the degree of branching. The effectiveness of the introduction of branches is investigated by the comparison of a branched polymer to a linear equivalent (which offers a larger hydrodynamic volume than a branched counterpart).

The focus is shifted towards reaching higher molecular weights in Chapter 5, by application of a two-step synthetic approach. In the first step, a low molecular weight branched core is synthesised. This macro RAFT agent is extended with fresh AM in a second step. The effect of the degree of branching in the core, as well as the length of the arms after extension (step 2) are investigated. Rheological measurements of these polymers are performed in Chapter 6. Elastic behaviour of the SB-PAMs is evaluated based on the amount of crosslinker in the core of the polymer. The polymers are ultimately evaluated in a two-dimensional flow-cell, in order to simulate oil recovery from an oil field and more specifically from dead-end in such fields.

In Chapter 7, the properties of SB-PAMs with higher molecular weights are set in direct comparison with linear PAMs and commercial linear hydrolysed polyacrylamides (HPAMs). These comparisons are performed in flow-cell experiments and in core flood experiments, which evaluates the oil recovery of the polymer solutions from porous rock. Moreover, the effect of the addition of NaCl to the aqueous polymer solutions is investigated.

In Chapter 8, the synthesis of novel thermothickening polymers is explored, as alternative to ultra high molecular weight conventional polymers for EOR. Comb copolymers containing 17 arms (on average) of $N, N$-dimethylacrylamide (DMA) and $N$-isopropylacrylamide (NIPAM) are prepared at 0°C in water with the CRP method atom transfer radical polymerisation (ATRP). These copolymers are evaluated on their lower critical solution temperature (LCST), which is the temperature at which the solubility of the polymer deteriorates. Altering the solubility of such polymers could render these polymers interesting from an application point of view, as the polymers can be injected into oil fields with low energy consumption (high shear rate and low temperature), whereas the solution viscosity increases where it is desirable (in the oil field, at a low shear rate and high temperature).
1.6 Acknowledgement

This research forms part of the research program of the Dutch Polymer Institute, Project 778.

References

REFERENCES


[40] Liu, Q.; Dong, M.; Ma, S.; Tu, Y. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2007, 293, 63–71.


REFERENCES


[77] Sun, Y.; Saleh, L.; Bai, B. In Rheology; De Vicente, J., Ed.; InTech, 2012.


[79] Seright, R. S. Use of Polymers to Recover Viscous Oil from Unconventional Reservoirs; 2011.


REFERENCES


REFERENCES

REFERENCES

REFERENCES


### Supplementary Information Chapter 1

**Table S1: (Meth)acrylamides**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Monomer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acrylamide</td>
<td>AM</td>
</tr>
<tr>
<td></td>
<td>Methacrylamide</td>
<td>MAM</td>
</tr>
<tr>
<td></td>
<td>N,N-dimethylacrylamide</td>
<td>DMA</td>
</tr>
<tr>
<td></td>
<td>N-isopropylacrylamide</td>
<td>NIPAM</td>
</tr>
<tr>
<td></td>
<td>N-acryloylmorpholine</td>
<td>NAM</td>
</tr>
<tr>
<td></td>
<td>N-(2-aminoethyl)acrylamide</td>
<td>AEMA</td>
</tr>
<tr>
<td></td>
<td>N-(3-aminopropyl)acrylamide</td>
<td>APMA</td>
</tr>
<tr>
<td></td>
<td>N-(2-hydroxypropyl) methacrylamide</td>
<td>HPMA</td>
</tr>
<tr>
<td></td>
<td>N-(3-(dimethylamino)propyl) acrylamide</td>
<td>DMAPAM</td>
</tr>
<tr>
<td></td>
<td>2-acrylamido-2-methylpropane sulfonic acid</td>
<td>AMPS</td>
</tr>
<tr>
<td></td>
<td>N-(3-(dimethylamino)propyl) methacrylamide</td>
<td>DMAPMAM</td>
</tr>
</tbody>
</table>
1.6. *SUPPLEMENTARY INFORMATION CHAPTER 1*

**Table S2: Acrylates**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Monomer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic acid</td>
<td>AA</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycolacrylate</td>
<td>PEGA</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxyethyl acrylate</td>
<td>HEA</td>
<td></td>
</tr>
<tr>
<td>2-Acryloyloxyethyl)trimethyl ammonium chloride</td>
<td>AETA</td>
<td></td>
</tr>
<tr>
<td>3-(Acryloyloxy)propanesulfonate potassium salt</td>
<td>APSP</td>
<td></td>
</tr>
</tbody>
</table>

**Table S3: Methacrylates**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Monomer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methacrylic acid</td>
<td>MAA</td>
<td></td>
</tr>
<tr>
<td>Poly(ethyleneglycol) methacrylate</td>
<td>PEGMA</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylaminoethyl methacrylate</td>
<td>DMAEMA</td>
<td></td>
</tr>
<tr>
<td>(2-Methacryloyloxyethyl) trimethylammonium chloride</td>
<td>MAETA</td>
<td></td>
</tr>
<tr>
<td>3-(Methacryloyloxy) propanesulfonate potassium salt</td>
<td>MAPSP</td>
<td></td>
</tr>
<tr>
<td>2-Methylenesuccinic acid bis(3-sulfopropyl) ester dipotassium salt</td>
<td>MEABSE</td>
<td></td>
</tr>
<tr>
<td>Methyl 6-O-methacryloyl-α-D-glucoside</td>
<td>6-O-MAMGlc</td>
<td></td>
</tr>
</tbody>
</table>
### Table S4: Other water soluble monomers

<table>
<thead>
<tr>
<th>Structure</th>
<th>Monomer</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="vinyl-acetate" alt="Structure" /></td>
<td>Vinyl acetate</td>
<td>VA</td>
</tr>
<tr>
<td><img src="ar-vinylbenzyl-trimethylammonium-chloride" alt="Structure" /></td>
<td>(Ar-vinylbenzyl) trimethylammonium chloride</td>
<td>VBTA</td>
</tr>
<tr>
<td><img src="sodium-4-vinylbenzenesulfonate" alt="Structure" /></td>
<td>Sodium 4-vinylbenzenesulfonate</td>
<td>SSS</td>
</tr>
<tr>
<td>![Structure](3-(2-vinylpyridinio-propanesulfonate)</td>
<td>3-(2-Vinylpyridinio) propanesulfonate</td>
<td>VPPS</td>
</tr>
</tbody>
</table>