Chapter 8

Towards new polymers for enhanced oil recovery

Abstract

The progress booked in this project is discussed in terms of the problems that have been overcome. Control of the acrylamide (AM) polymerization was accomplished and this allows the preparation of polyacrylamide (PAM) with variations in its chemical structure and molecular architecture. Branching in PAM is presented as a new tool to significantly improve the solution viscosity without changing the chemical structure of the polymer.

The non-ionic nature of the branched PAM renders it insensitive to the presence of salt. More specifically, the solution viscosity and the elastic response are not affected by the presence of salt. The rheological properties of aqueous solutions are maintained when increasing the amount of salt whereas those of the commercial HPAM are dependent on the salt concentration.

The AM units in HPAM are also highly susceptible to alkaline hydrolysis at high temperatures (T > 50 °C). N,N-dimethyl acrylamide (DMA), as a hydrolysis resistant moiety, is a viable option especially in combination with the increase thickening efficiency through branching. The oil recovery efficiency of the branched PDMA polymers is similar to branched PAMs, as evaluated using a 2D flow-cell that simulates residual oil trapped in dead-ends. This makes them interesting polymers for application in EOR where alkaline agents are used to in situ generate surfactants.

The obtained results constitute a breakthrough in the general field of chemical product design for EOR. However, a further refinement of the used criteria can be envisaged on the basis of the changing legislation (e.g. currently in Norway). This implies the use of biologically degradable polymers for underground injection as fitting a general “sustainability” concept for this application. In this context, the potential of different biopolymers for EOR where synthetic polymers cannot be used is briefly discussed. All the currently investigated biopolymers are based on polysaccharides, albeit with slightly different molecular structures. The thickening capability and
resistance towards salt and temperature of the biopolymers are a strong function of the molecular weight and their ability to form helical structures in aqueous solutions. The elasticity of the biopolymer solutions are a strong function of the molecular weight of the biopolymer, with the higher molecular weight ones displaying a more pronounced elastic response.
8.1. Introduction

Water soluble polymers in EOR have been investigated and applied in different techniques, i.e. Polymer Flooding, Alkaline Surfactant Polymer (ASP) Flooding, and Surfactant Polymer (SP) Flooding. When water soluble polymers are applied in any of the former techniques, several different aspects have to be considered. In the context of this dissertation, i.e. EOR, the important ones (amongst others) are: the solution viscosity as a function of the polymer concentration, the dependency of the solution viscosity on the presence of salt (mono- and divalent ions), and the resistance (in terms of solution viscosity) towards higher temperatures (T > 50 °C).

The dependency of the solution viscosity on the polymer concentration is in general well known for homopolymers. The rheological properties depend on the concentration regime in which the solution is. In general four different concentration regimes can be distinguished (Figure 8.1).

\[ \frac{\eta}{\eta_0} = 1 + 2.5 \cdot \phi \]  \hspace{1cm} (8.1)

where \( \eta \) = viscosity of the solution, \( \eta_0 \) = viscosity of the solvent and \( \phi \) = the volume fraction of the particles.

At these low concentrations, the solution viscosity depends solely on the volume fraction of the spheres, i.e. the polymer coils, and not on their size. The polymer concentration at which the polymer coils start to touch (overlap) each other is defined as the first critical overlap concentration (C*). According to several estimations, the values for C* generally range between
0.1 up to 5.0 wt.%\(^3\) When the polymer concentration is increased beyond \(C^*\), overlapping of the polymer coils becomes more prominent and the solution viscosity increases significantly. The concentration regime starting from the \(C^*\) up to a second critical concentration \((C^{**}, \) above which a gel is formed) is defined as the semi-dilute regime. The viscosity of a polymeric solution in this regime is governed by the relaxation, i.e. reptation\(^4\), of the entanglements in response to disturbances caused by deformation forces (stresses). At higher concentrations \((c > C^{**}, \) polymer concentration \([p] \geq 50 \text{ wt.\%}\)^3\)), the rheological properties resemble those observed for polymers in the melt state.\(^3, 5, 6\) However, when making allowances for the desired application (i.e. EOR), the increase in the polymer concentration can lead to significant problems in the reservoir. The propagation of polymer coils through narrow pore throats “presses” the coils closer to each other. If the coils are large enough, bridging (Figure 8.2) can arise which leads to blockage of pores.\(^7 - 10\)

![Figure 8.2: Bridging in porous media\(^{10}\)](image)

An increase in the polymer concentration is also detrimental for the economics of a flooding project given the scale of such projects (e.g. for the Marmul field pilot-project \(\sim 25\) ton/day of dry polymer has been used\(^11, 12\)).

The molecular weight also affects the rheological properties of water soluble polymers. In general, the solution viscosity increases with the molecular weight of the polymer, and the dependency can be described using the reptation model of de Gennes.\(^4\) At equal polymer concentration, an
increase in the molecular weight will lead to an increase in the overlap density, which in turn leads to longer relaxation times (synonymous of higher viscosities). Nevertheless, the molecular weight of the polymers cannot be increased indefinitely without leading to problems. Sensitivity towards mechanical degradation becomes a significant problem as the molecular weight of the polymers increases.\textsuperscript{13-17} In addition, the aforementioned problem with bridging will be augmented with an increase in the molecular weight.\textsuperscript{8, 9} In practice, high molecular weight HPAM leads to filter cake formation on the surface (face plugging) of cores, especially low permeable ones, and cannot be applied in a reservoir field with similar rock properties.\textsuperscript{18}

The introduction of charges (in PAM, the hydrolysis degree) in a polymer backbone will lead to an increase in the solution viscosity compared to its uncharged analogue.\textsuperscript{19} The higher the amount of charged moieties, the more stretched the polymer coil will be and thus the higher the solution viscosity. This enables the use of lower molecular weight polymers without jeopardizing the thickening capability. However, for the polymer to remain insensitive towards salinity and hardness of the brine, the hydrolysis degree cannot be too high (e.g. higher than 40 mol\%).\textsuperscript{20} Therefore, although beneficial for the thickening capability in de-ionized water, the presence of charged moieties will result in sensitivity issues towards electrolytes. In the presence of divalent ions (such as Ca\textsuperscript{2+}), even precipitation can arise, due to inter-chain complexation\textsuperscript{21}, eventually leading to a complete loss of solution viscosity. In practice the hydrolysis degree is fixed at 30 mol\%. Nevertheless, to date partially hydrolyzed polyacrylamide (HPAM) is the polymer of choice for chemical EOR, mainly in connection to its relatively low price (2 - 4 €/kg).

This project started with identifying the limitations of the currently used HPAM in enhanced oil recovery (\textit{vida supra}). The main objective of this dissertation was to tackle a couple of these limitations and present new solutions. Firstly the controlled polymerization of acrylamide (AM) was accomplished through the use of atomic transfer radical polymerization (ATRP) in water. In addition, the “living” character of the polymerization process offered the possibility of adding a second block of $N$-isopropylacrylamide (NIPAM). The controlled polymerization of AM enabled the design of different molecular architectures of polyacrylamide (PAM). Subsequently evidence for the increased thickening capability of branched PAM \textit{versus} linear PAM could be provided. In addition, the presence of branches ($N > 8$) increased the elastic response of aqueous solutions of the polymers. Given the uncharged nature of the branched PAMs (compared to the commercial HPAM with $\sim$ 30 mol\% of charged moieties), the presence of
salt does not influence the solution properties making these polymers particularly suitable for high salinity reservoirs.

Another limitation related to HPAM is the temperature stability. The use of copolymers of AM and NIPAM provides polymers that display thermo-thickening up to 80 °C, and are therefore resistant (in terms of solution viscosity) to higher temperatures (T > 50 °C). In addition, the oil recovery efficiency at high temperatures using the thermo-responsive copolymers is significantly improved compared to a branched PAM analogue.

In the following sections, the branched PAMs prepared in this thesis are discussed in terms of their rheological properties compared to either linear PAMs or commercial linear HPAMs. Unresolved problems related to the use of AM as a monomer are discussed and preliminary results on improvements are presented. In addition, new preliminary results for other acrylamide-based materials as well as several different biopolymers are presented in terms of rheological behavior and oil recovery performance.

### 8.2. Thickening capability, comb-shaped PAM

The thickening capability of the currently used HPAM is due to its high to ultra-high molecular weight (3.5 – 20·10^6 g/mol) and the presence of charged (25-35 mol%) moieties. According to the general theory of polyelectrolyte solutions, the presence of the charged moieties leads to electrostatic repulsions and subsequently to prominent chain stretching. However, when dissolved in salt solutions the thickening capability is significantly hampered (due to the electrostatic screening of the charged moieties). Other ways of increasing the thickening capability of a polymer is the introduction of hydrophobic moieties that will lead to aggregate formation. In this thesis (chapter 3 & 4, Figure 8.3), a new approach to improve the thickening capability (in water solutions) of a polymer has been developed.

The thickening capabilities of the branched PAMs depend on the functionalization (number of arms) degree. A low number of arms (\(N \leq 8\)) leads to polymers which display a lower solution viscosity compared to linear PAMs of equal theoretical overall molecular weight. This is attributed to the inherent lower hydrodynamic volume of branched polymers. For larger number of arms (\(N \geq 12\)), a higher solution viscosity is found when compared to linear analogues. The branched PAMs with a relatively high number of arms (\(N = 12, 13\) and 17) possessed a higher hydrodynamic radius compared to the branched PAMs with a low (\(N = 4\) and 8) number of arms at equal total molecular weight.
In Chapter 1, the thickening capabilities of several different water soluble polymers were plotted against each other in Figure 1.11. With the results of Chapter 3 & 4 a comparison of the branched PAM with other (non-hydrophobic) AM based polymers is performed and the results are displayed in Figure 8.4.

As can be observed in Figure 8.4 A, the thickening capability of the HPAM is the highest of the three included in the comparison. Remarkably, the thickening capability of the branched PAM (with a lower molecular weight than that of the linear PAM) is seven times as high as that of the linear PAM. This demonstrates that the molecular architecture is a strong tool to improve the thickening capabilities of water-soluble polymers in the concentration regime useful for EOR. The thickening capabilities of the branched PAMs have been extensively discussed in Chapters 3 & 4. Here the focus will be on the salt resistance of the branched PAMs in terms of solution viscosity and the viscoelastic response of aqueous solutions containing them.

**Figure 8.3**: New approach to increase the solution viscosity of aqueous solutions
8.3. Salt resistance, comb-shaped PAM

The salt sensitivity of HPAM is a well know problem given its ionic character.\(^1\) The solution viscosity decreases significantly as the salt concentration increases. Given that in all oil reservoirs brine (salt water) is used, it is not a problem that can be circumvented by using deionized water. In addition, in the presence of weak bases (such as sodium carbonate) hydrolysis of the acrylamide moieties occurs which becomes extensive at elevated temperatures (T > 60 °C) The injection of non-hydrolyzed PAM,
rather than HPAM, has been proposed as a new method for EOR.\textsuperscript{26} The non-hydrolyzed PAM will be hydrolyzed \textit{in-situ} and the viscosity of the solution will increase. For oil reservoirs where a high amount of salt is present the use of pristine PAM can represent a good option. However, the low thickening capability of linear PAM compared to linear HPAM will be detrimental for a project given the higher amount of linear PAM required to match the viscosity of the aqueous phase to that of the oil. Therefore, we propose the use of branched PAM with its better thickening capability compared to linear PAM for high salinity applications (Figure 8.5).

\textbf{Figure 8.5:} A; the solution viscosity ($\dot{\gamma} = 10 \; \text{s}^{-1}$) as a function of the salt (NaCl) concentration for HPAM and branched PAM, and B; the viscosity functions of 2 charged HPAMs and 2 uncharged branched PAMs
As evident in Figure 8.5 A, the solution viscosity of the uncharged branched PAMs (PK30-g₁₃-(PAM23810) and PK30-g₁₃-(PAM49225)) is not affected by the presence of salt (up to 12 wt.% of NaCl). The solution viscosities (\( \dot{\gamma} = 10 \) s\(^{-1} \), \([p] = 5000 \) ppm) of the charged linear HPAM are all higher than the branched PAMs in de-ionized water. However, as the amount of salt increases the solution viscosities of the branched PAMs remain constant while that of the charged HPAMs decreases significantly. Remarkably, the solution viscosity of a charged HPAM with a molecular weight between 8 \( - 10 \cdot 10^6 \) g/mol decreases to values lower than that of the PK30-g₁₃-(PAM49225) \( (M_n \approx 3.5 \cdot 10^6 \) g/mol). This demonstrates the suitability in terms of the solution viscosity of the branched PAMs for application in high salinity environments.

The shear thinning behavior of the aqueous solutions has also been probed. As can be observed in Figure 8.5 B, this pseudoplasticity of the branched PAM is similar to that of the charged HPAM with a molecular weight either 2 or 3 times as high as that of the branched PAM. In actual applications the pseudoplastic behavior is preferred, given that a low viscosity at high shear rates will require less pumping energy.

Another important parameter identified for an efficient oil recovery is the viscoelasticity of the aqueous phase. In Figure 8.6, the viscoelastic response of aqueous solutions containing either a linear HPAM or a branched PAM is displayed.

As can be observed in Figure 8.6 A, the viscoelastic response of the HPAM solution is dependent on the salt concentration. A significant decrease in the elasticity of the solution can be clearly distinguished as the concentration of the salt increases. The reduction in the hydrodynamic volume of the polymer coils, due to electrostatic screening, is the accepted explanation of the observed behaviour. The effective size of the polymer in solution is smaller, and therefore the extent of overlapping is suppressed which leads to a lower elastic response.

The results for the uncharged branched PAM (Figure 8.6 B) demonstrate that the elastic response of the aqueous solution is not affected by the presence of salt.
Figure 8.6: (A) the viscoelasticity as a function of the salt (NaCl) concentration for HPAM ($M_w = 3.2\cdot10^6$ g/mol, $[p] = 1.0$ wt.%), and (B) the viscoelasticity as a function of the salt (NaCl) concentration of a branched PAM ($M_w = 1.7\cdot10^6$ g/mol, $[p] = 1.0$ wt.%)

8.4. Hydrolysis resistance, comb-shaped PAM

The hydrolysis reaction of PAM is a well-known reaction that can be catalysed either by an acid or a base.$^{35}$ The hydrolysis reaction (Scheme 8.1) leads to the formation of ammonia.

In ASP floods most often sodium carbonate is used as the alkali agent. Therefore, the resistance to base catalysed hydrolysis of PAM is important. In general there are two stages of the hydrolysis reaction.$^{35}$ The first one (high
rate) reaches hydrolysis degrees up to 40 mol% and is accelerated by neighbouring carboxylate groups.

**Scheme 8.1: Base catalysed hydrolysis of PAM**

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{O} \\
\text{n} \\
\end{array} + m \text{NaOH} \rightleftharpoons \begin{array}{c}
\text{H}_2\text{N} \quad \text{O} \\
\text{n-m} \quad \text{O} \\
\end{array} + m \text{NH}_3
\]

The second stage displays a ten times lower rate. This is suppressed by the electrostatic repulsion between the carboxylate groups and the base, and the increased viscosity due to chain stretching driven by electrostatic repulsion of the carboxylate groups leads to mass transfer limitations. The parameters that have been identified to accelerate the hydrolysis rate are high temperatures, the presence of salts, polymer concentration, and high base/polymer ratio.\textsuperscript{35-37} The characteristics of chemical EOR usually are a low polymer concentration for economic reasons, temperatures above 50 °C found for many oil reservoirs, and the presence of salts in the water used as the displacing fluid. Therefore, it is obvious that the challenge to design a polymer that can resist the base hydrolysis under the conditions in EOR is important at an industrial level.

The use of other monomeric units that can withstand alkaline hydrolysis is a viable option. Investigations towards novel multiblock co- and terpolymers have demonstrated the effectiveness of changing the AM units into other more resistant moieties.\textsuperscript{38, 39} Several different acrylamide based monomers have been investigated as hydrolysis resistant ones (Figure 8.7).\textsuperscript{40-42}

However, the homopolymers of DMA and AM display a markedly different behaviour under the same conditions. After 50 hours, the hydrolysis degree of poly(\(N,N\)-dimethylacrylamide) (PDMA) is only 2 mol%, while that of PAM reached a hydrolysis degree of 30 mol% after only 2 minutes.\textsuperscript{43, 44} The reactivity of PAM towards alkaline hydrolysis is 500 times higher compared to that of PDMA and PAAEE.\textsuperscript{43, 44} The synthesis of the polymers have all been through free radical polymerization. In order to benefit from the improved thickening capability of branched polymers compared with linear ones, the controlled polymerization of the hydrolysis resistant monomers is required. The controlled polymerization of DMA, NIPAM and AAE has been demonstrated already.\textsuperscript{45-50}
8.4.1. Results and discussion

**Macroinitiators.** The synthesis of the macroinitiators was performed according to the Paal-Knorr reaction (Scheme 8.2) of a halogenated primary amine with aliphatic perfectly alternating polyketones. The carbonyl conversion was determined using elemental analysis. The characterization of the macroinitiators has been extensively investigated in Chapter 3 & 4 and therefore will not be discussed here. The properties of the macroinitiators used in the synthesis of branched PDMA are listed in Table 8.1.

**Table 8.1: Properties of the macro-initiators**

<table>
<thead>
<tr>
<th>Polyketone sample (PK30-Cl(^a))</th>
<th>Elemental composition (C : H : N, wt%)</th>
<th>(X_{\text{CO}}) (%)(^b)</th>
<th>Pyrrole units(^c)</th>
<th>(M_{n,\text{GPC}})</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30 (virgin)</td>
<td>67.0 : 8.4 : 0.0</td>
<td>-</td>
<td>0</td>
<td>2 797</td>
<td>1.74</td>
</tr>
<tr>
<td>PK30-Cl(_4)</td>
<td>58.6 : 7.1 : 1.6</td>
<td>18.87</td>
<td>4</td>
<td>2 447</td>
<td>2.02</td>
</tr>
<tr>
<td>PK30-Cl(_8)</td>
<td>64.0 : 7.9 : 3.3</td>
<td>37.21</td>
<td>8</td>
<td>2 244</td>
<td>2.01</td>
</tr>
<tr>
<td>PK30-Cl(_{13})</td>
<td>62.9 : 7.6 : 4.9</td>
<td>61.14</td>
<td>13</td>
<td>2 072</td>
<td>1.97</td>
</tr>
</tbody>
</table>

\(a\). Number indicates the ethylene content (\%)

\(b\). The conversion of the carbonyl groups of the polyketone

\(c\). Average number of pyrrole units per chain
The obtained, chemically modified polyketones are used as macroinitiators in the ATRP of DMA for the preparation of comb-shaped polymers with a different number of side chains. The synthesis of linear and comb-like PDMA was performed according to Scheme 8.2.

**Table 8.2: Characteristics of the linear and branched PDMA**

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Entry</th>
<th>[M]0/[I]0/[CuCl]0/[Me6TREN]0</th>
<th>M/s1/s2 (wt:vol:vol); T; Time (min)</th>
<th>Conv (%)</th>
<th>M_n,tot</th>
<th>M_n,SPAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>1</td>
<td>22 919:1:1.5:1.5</td>
<td>1:5; 25 °C; 180</td>
<td>58.4</td>
<td>1 326 825</td>
<td>1 326 825</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>88 515:1:3.0:3.0</td>
<td>1:5; 25 °C; 180</td>
<td>47.0</td>
<td>4 124 011</td>
<td>4 124 011</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>79 351:1:3.0:3.0</td>
<td>1:4:1/10; 25 °C; 60</td>
<td>70.1</td>
<td>5 514 111</td>
<td>2 759 853</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>79 213:1:3.0:3.0</td>
<td>1:4:1/10; 25 °C; 60</td>
<td>64.5</td>
<td>5 064 788</td>
<td>1 268 994</td>
</tr>
<tr>
<td>4-arm</td>
<td>6</td>
<td>19 969:1:1.5:1.5</td>
<td>1:6:1/6; 25 °C; 130</td>
<td>39.9</td>
<td>789 831b</td>
<td>124 310</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>49 905:1:1.5:1.5</td>
<td>1:5:1/10; 25 °C; 180</td>
<td>46.3</td>
<td>2 290 499</td>
<td>355 181</td>
</tr>
<tr>
<td>13-arm</td>
<td>8</td>
<td>99 226:1:3.0:3.0</td>
<td>1:5:1/20; 25 °C; 150</td>
<td>49.9</td>
<td>4 908 300</td>
<td>757 920</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>200 000:1:3.0:3.0</td>
<td>1:5:1/40; 25 °C; 180</td>
<td>30.3</td>
<td>6 007 278</td>
<td>926 993</td>
</tr>
<tr>
<td>17-arm</td>
<td>10</td>
<td>100 030:1:1.5:3.0</td>
<td>1:4:1/20; 25 °C; 180</td>
<td>41.0</td>
<td>4 065 549</td>
<td>481 097</td>
</tr>
</tbody>
</table>

*a. M/s1/s2 = Monomer / solvent 1 / solvent 2 = N,N-dimethylacrylamide / water / acetone  
b. M_n,GPC = 771 300 g/mol and the PDI = 1.80 as determined by aqueous GPC*

The ratio between the initiator (or the macroinitiator) and the monomer was varied in order to synthesize linear and comb-shaped PDMA with different...
molecular weights. The linear polymers were prepared using MCIPr as the initiator while the comb PDMA as the polyketone based macronitiators were used. Table 8.2 lists the results for the different polymers prepared.

The polymerization of DMA in water at room temperature using the polymerization process described in Chapter 2 & 3 allows for the preparation of linear and branched PDMA with relatively low dispersity indices. The rheological properties depend on the number of arms (Figure 8.8).

Increasing the number of arms (from \(N = 4\) to 17) leads to a higher solution viscosity at equal polymer concentration and molecular weight, similar to the results obtained for the branched PAMs (Chapter 4). This is evident from the
comparison between a 13-arm (entry 7) and a 17-arm (entry 10) branched PDMAs with their corresponding linear analogues (entries 2 and 3 respectively). The comparison between a 4, 8 and 13-arm branched PDMA further demonstrates the effect of the number of branches on the solution viscosity.

The hydrolysis resistance of the linear and branched PDMA were investigated under conditions resembling those found in actual chemical EOR (Figure 8.9).

Figure 8.9: (A) Solution viscosity (in percentages from the starting value) as a function of hydrolysis time for a linear and a branched PAM and a branched PDMA, \([p]=5000 \text{ ppm}\), (B); the hydrolysis degree of the linear and branched PAM as a function of temperature as measured by \(^{13}\text{C}-\text{NMR}-\text{spectroscopy}\)
The aqueous solution used in EOR usually remains for extensive times in the reservoir. Periods of several months onshore, and up to more than one year offshore have been stated.\textsuperscript{22, 51} The most important parameter for maintaining the success of the polymer flood is the solution viscosity of the aqueous phase.

Upon hydrolysis charged groups are randomly introduced in the polymer. This will lead to electrostatic repulsion\textsuperscript{3} thus increasing the hydrodynamic volume of the coils in solution and this is synonymous to a higher solution viscosity. The increase in the solution viscosity as a function of the hydrolysis time is significantly more pronounced for the linear PAM (PAM21445) when compared to the branched PAM (PK30-$g_{13}$-PAM23810) and PDMA (PK30-$g_{13}$-PDMA48515). The solution viscosity increases by more than 300 $\%$ of the original value, both with and without CaCl\textsubscript{2}. This is strong evidence that the hydrolysis of the linear PAM is extensive (while that of the branched analogue is not), since in the absence of salt the solution viscosity increases with an increase in the hydrolysis degree (up to a limiting value).\textsuperscript{26} The differences in the solution viscosities between the presence of NaCl or NaCl-CaCl\textsubscript{2} suggest that either the hydrolysis is suppressed by the presence of CaCl\textsubscript{2} or part of the polymer precipitates by complex formation with Ca$^{2+}$.\textsuperscript{52} The relatively low increase in the solution viscosity of the branched PAM suggests a lower hydrolysis rate compared to the linear analogue. However, the increase in solution viscosity with an increase in the hydrolysis rate not necessarily has to be equal for both the linear and the branched PAM. Therefore, the direct measurement of the hydrolysis degree (by $^{13}$C-NMR) was carried out for the two samples (Figure 8.9 B). The increase in the hydrolysis degree is similar during the first couple of hours. After 50 hours the hydrolysis degree of the linear PAM surpasses that of the branched PAM indicating that the branched PAM is more resistance to alkaline hydrolysis compared to the linear analogue. As can be observed in Figure 8.9 A, the change in the solution viscosity of the branched PDMA is limited. This is strong evidence that the branched PDMA is resistant towards alkaline hydrolysis, which is in line with earlier reports.\textsuperscript{44}

Increasing the residence time under the harsh conditions and the salt concentration leads to a significant increase in the solution viscosity (Figure 8.10) for the linear PAM.
Figure 8.10: (A) Solution viscosity (in percentages from the starting value) as a function of hydrolysis time for a linear ([p] = 5000 ppm) and a branched PAM ([p] = 4900 ppm) and a linear ([p] = 5900 ppm) and a branched PDMA ([p] = 4500 ppm), at equal molar concentration, (B) Solution viscosity (in percentages from the starting value) as a function of the hydrolysis time for a linear ([p] = 10000 ppm) and a branched PDMA ([p] = 6500 ppm) and a commercial HPAM ([p] = 5500 ppm), at equal starting solution viscosity (measured at $\dot{\gamma} = 10 \text{ s}^{-1}$)

The branched PAM (with similar molecular weight) displays at first an increase in the solution viscosity (albeit less pronounced compared to its linear analogue) and decreases slowly to below the starting viscosity.

The hydrolysis degree of the 62 days samples was determined by $^{13}$C-NMR as being 38 and 33 mol% for, respectively, the linear and the branched PAM. The solution viscosity of the linear and branched PDMA is not
significantly affected by the conditions applied, even after more than 60 days. This suggests that little, if any, hydrolysis takes place. This is confirmed by $^{13}$C-NMR where no carboxylate units could be detected (i.e. below the detection limit of $^{13}$C-NMR) for the 62 days samples.

The presence of CaCl$_2$ also affected the solution viscosity of the samples; however the differences between the samples with CaCl$_2$ and the ones without were not large. Although the presence of CaCl$_2$ did not significantly affect the solution viscosity of the samples, precipitation was observed in the case of PAM-based polymers (Figure 8.11).

![Figure 8.11: Precipitation of the commercial HPAM (with CaCl$_2$) sample after 42 days](image)

The solutions of the linear and branched PDMA stayed clear even after 62 days in the oven, whereas the linear HPAM became more turbid. This indicates the formation of large aggregates.

### 8.5. Oil recovery, 2D flow-cell

The efficiency of the branched hydrolysis resistant PDMA in recovering oil out of dead-ends was evaluated using the flow-cell (Chapter 7). In addition, the oil recovery at higher temperatures (i.e. $T = 70$ °C) using the thermo-responsive block copolymers (Chapter 6) was also evaluated.

#### 8.5.1. Oil recovery efficiency

The efficiency in recovering residual oil by branched PDMA (at room temperature) and branched random copolymer of AM and NIPAM (at room temperature and 70 °C) has been evaluated (Figure 8.12).
Figure 8.12: Oil recovery out of dead ends using branched PDMA ([3]) compared to brine ([1]) and the commercial polymer ([2]) at room temperature using crude oil, and branched copolymers of AM and NIPAM ([6] and [9]) compared to water ([4] and [7]) and branched PAM of similar molecular weight ([5] and [8]) both at room temperature and at 70 °C using a mixture of crude oil and cyclo octane (2-1 vol.%)

The efficiency of the recovery of residual oil using the branched PDMA ([3] PK30-g₁₃-(PDMA23105)) is similar to that of the branched PAM (Chapter 7, [D] PK30-g₁₃-(PAM35275) and that of the commercial polymer ([2], poly(AM31515-co-AA13320). However, the polymer concentration required to match the solution viscosity of the water phase with that of the oil is higher compared to a branched PAM of the same molecular weight. Nevertheless, the ability to recover part of the residual oil makes these hydrolysis resistant branched PMDA polymers potential candidates for EOR where alkali is also used to generate in situ surfactants.

The residual oil recovery efficiency of the branched thermo-responsive copolymers is slightly higher compared to a branched PAM ([5] PK30-g₁₃-(PAM3275), similar molecular weight). However, when performing the
comparison at 70 °C, different recovery efficiencies are observed for the branched PAM and thermo-responsive copolymer. The recovery efficiency of the branched PAM increases from 4.8 to 8.6 %. This can be attributed to the improved mobility ratio (equation 1.3, Chapter 1) due to the lower viscosity of the oil (the decrease in the oil viscosity is more pronounced that the decrease of the polymer solution viscosity).

When comparing the recovery efficiency of the branched thermo-responsive copolymer a significantly higher efficiency is observed. This cannot reside only in the decrease of the oil viscosity at higher temperatures. The higher oil recovery efficiency of the branched copolymer ([9] PK30-g13- (PAM1405-co-PNIPAM1405)) at 70 °C is therefore attributed to the increased solution viscosity (Chapter 6). The mobility ratio is lower than unity (and thus lower at 70 °C compared to at RT) given the higher solution viscosity, and thus a better displacement of the oil takes place. However, from a practical point of view, the polymer concentration can be decreased until the solution viscosity at 70 °C matches that of the oil.

The increase in oil recovery efficiency at higher temperatures makes these types of copolymers interesting candidates for application in EOR where the reservoir temperatures are high (i.e. T ≥ 50 °C).

8.6. Biopolymers for EOR

In certain regions of the world regulations stipulate that if a polymer is used in recovering oil, it has to be reusable or biodegradable. If a synthetic polymer is used, the produced mixture of oil and water (containing the synthetic polymer) has to be separated and the water phase must be reinjected. However, in most field application the polymer that is produced along with the oil has been either chemically or thermally degraded and therefore cannot be re-injected. Therefore, the use of biopolymers is almost inevitable and a lot of effort has been put in developing biopolymers for EOR. Although there are many examples of biopolymers that can be used for EOR, only xanthan gum has been applied in actual oil reservoirs, although there are current (pilot) projects under way with other water soluble biopolymers, such as schizophyllan.

8.6.1. Thickening capability and viscoelasticity

Most of the biopolymers that have been considered so far for EOR are polysaccharides. The ability of these type of polymers to increase the viscosity of an aqueous solution is based on their high molecular weight and in some cases the rigidity of the polymeric chains. Although there are many
different types and sources of biopolymers, not all of them are soluble in cold water. In many cases boiling water is required before complete dissolution of the polymeric chains is obtained. From an economical and practical (remote locations of many oil reservoirs) point of view, the dissolution in cold water is preferred. Although only xanthan gum has been applied so far in chemical EOR, there are many other different biopolymers that might be suitable. The thickening capability of several different biopolymers is displayed in Figure 8.13.

![Figure 8.13: Thickening capabilities (viscosity measured at $\dot{\gamma} = 10$ s$^{-1}$) of different biopolymers at a polymer concentration of 1 wt.\%](image)

As can be observed in Figure 8.12, there are several other biopolymers that can significantly increase the viscosity of a water solution. Scleroglucan, a $\beta$-1,3 linked D-glucose with single D-glucose side chains linked $\beta$-1,6 every third unit, has long been seen as a good substitute for xanthan gum, especially in oil reservoirs where high temperature and high salt concentration (given the non-ionic character of scleroglucan) are found.

Another biopolymer that has been identified as a suitable biopolymer for EOR is schizophyllan (chemically the same as scleroglucan). This resides mainly in its ability to increase the solution viscosity even at very low polymer concentration (i.e. a solution viscosity of 10 mPa.s, $\dot{\gamma} = 10$ s$^{-1}$ and a $[p] = 200$ ppm). In addition, the solution viscosity of an aqueous solution containing schizophyllan only decreases by 10 % when heated up to 130
By comparison, an aqueous solution of xanthan gum decreases by 95%.

Carboxy-methyl cellulose (CM cellulose) has also been considered as a good candidate for EOR. The addition of carboxy-methyl groups to cellulose makes the biopolymer soluble in cold water. This makes it attractive for EOR since no specialty dissolution equipment is required. However, given the ionic character of carboxy-methylcellulose, the solution viscosity is sensitive to the presence of salt. Depending on the molecular weight (low or high [LM or HM]) of the parent cellulose polymer a different thickening capability is observed.

Chitosan has also been shown to increase the solution viscosity of a water solution significantly. However, chitosan is only soluble in acidic media (i.e. pH < 6.0) which will significantly hamper its application in EOR. Nevertheless, the high thickening capability of chitosan still makes it an interesting polymer as a rheology modifier.

Methyl-cellulose, on the other hand, is soluble in cold neutral water. Although its capability to increase the solution viscosity is less than most of the biopolymers, its low molecular weight might make it suitable for low permeable reservoirs. A peculiar behaviour of methyl-cellulose is its gelation (in water solution) upon heating due to hydrophobic associations. The gelation is reversible; upon cooling the aqueous solution will return to its original state. Nevertheless, the hydrophobic character of parts of the biopolymer might lead to enhanced adsorption (higher resistant factors, indicating a higher layer thickness) on the rock surface similar to that observed for hydrophobically modified polymers.

Guar gum has also been investigated for application in EOR. It is used already to control the rheological properties of drilling muds. The thickening capability of guar gum is higher than xanthan gum, but in solution of high salinity guar gum is highly sensitive towards high temperatures limiting its application.

Little effort has been aimed at investigating the viscoelasticity of aqueous solutions containing biopolymers. Experiments and mathematical models have demonstrated the importance of the viscoelasticity of the solution on the recovery of residual oil, although so far no consensus has been reached. The viscoelasticity of some commercial biopolymers has been evaluated and the results are displayed in Figure 8.14.

The results suggest that the elastic response of the aqueous solutions increases as the molecular weight increase. This indicates that the extent of overlapping is higher for the higher molecular weight polymers. Although the
molecular weight of xanthan gum is not as high as that of CM cellulose, its elastic response is much more pronounced. A possible explanation for this is the rigidity of the polymeric chains. Xantham gum is known to form helices in water solutions.\textsuperscript{68-71}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/Figure_8.14.png}
\caption{(A), the loss and elastic modulus as a function of the frequency of different biopolymers ([p]=1.0 wt.\%) and (B), the phase angle as a function of the frequency of the same biopolymers}
\end{figure}

8.7. Conclusion

Currently used partially hydrolyzed polyacrylamide (HPAM) in EOR has several limitations. The main objective of this dissertation was to design new acrylamide based polymers that provide solutions to the limitation of the
aforementioned polymer. The first hurdle that had to be passed was the controlled polymerization of AM. This was accomplished through the use of atomic transfer radical polymerization (ATRP) in water at room temperature. Furthermore, given the “living” character of the polymerization process a second block of \(N\)-isopropylacrylamide (NIPAM) can be added to the first AM block. With the accomplishment of controlled polymerization of AM, PAM with different molecular architecture could be envisaged. This was achieved through the use of functionalized (with halogens) alternating aliphatic polyketones. Subsequently, evidence for the increased thickening capability of bottle-brush PAM compared to a linear analogue was provided. The presence of branches \((N > 8)\) increased the elastic response of aqueous solutions of the polymers. Also, given the uncharged nature of the bottle-brush PAMs (compared to the commercial HPAM [~30 mol% charged moieties]), the presence of salt does not influence the solution properties making these polymers particularly suitable for high salinity reservoirs. Another limitation related to HPAM is the temperature stability. Rheological characterization demonstrated that copolymers of AM and NIPAM display thermo-thickening behavior up to 80 °C, and are therefore resistant (in terms of solution viscosity) to higher temperatures \((T > 50 \, ^\circ C)\). The increased oil recovery efficiency at high temperature \((T = 70 \, ^\circ C)\) demonstrates the potential of the thermo-responsive polymers for EOR.

Since in many cases alkaline agents are used in combination with polymers, hydrolysis of the AM units in HPAM is extensive, especially at high temperatures \((T > 50 \, ^\circ C)\). The use of hydrolysis resistant moieties such as DMA is promising, more so in combination with the increased thickening capability through branching. The oil recovery efficiency of the branched PDMA polymers is similar to branched PAMs, and these are therefore good candidates for application in EOR where alkaline agents are used to generate \textit{in situ} surfactants.

The potential of using biopolymers for EOR where synthetic polymers cannot be applied is briefly discussed. Most of the investigated biopolymers are polysaccharides, with the differences being the source and molecular structure of the polymeric chains. Their thickening capability is a function of the molecular weight and the resistance towards salt depends on their ability to form helical structures in aqueous solutions.

\section{8.8. Acknowledgements}

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8.9. References

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Appendix 8.A

8.A.1. Experimental section

Chemicals. \( N,N \)-dimethylacrylamide (DMA, \( \geq 99\% \)), copper(I) bromide (CuBr, 98%), copper(I) chloride (CuCl, 98%), methyl 2-chloropropionate (MeClPr, 97%), sodium chloride (NaCl, \( \geq 99.5\% \)), glacial acetic acid, ethanol, and diethyl ether were purchased from Sigma Aldrich. Calcium chloride dihydrate (\( \text{CaCl}_2 \cdot 2 \text{H}_2\text{O} \), 99%) and sodium bicarbonate (NaHCO\(_3\), \( \geq 99\% \)) were purchased from Merck. CuBr & CuCl were purified by stirring in glacial acetic acid for at least 5 hours, filtering, and washing with glacial acetic acid, ethanol and diethyl ether (in that order) and then dried at reduced pressure.\(^{46}\) All the other chemicals were reagent grade and used without further purification.

Linear polymerization. A 250-mL three-necked flask was charged with demineralized water and DMA. Subsequently, the mixture was degassed by three freeze-pump-thaw cycles. A nitrogen atmosphere was maintained throughout the remainder of the reaction steps. CuCl and the ligand (Me\(_6\)TREN) were then added to the flask and the mixture was stirred for 10 minutes. The flask was then placed in an oil bath at 25 °C. The reaction was started by the addition of the initiator (MeClPr) using a syringe. After the pre-set reaction time, the mixture was exposed to air and milli-Q water was added. The contents were then purified via dialysis using membrane tubing Spectra/Por® Dialysis Membrane (molecular weight cut off [MWCO] = 12 000 – 14 000 g/mol). The product was then dried in an oven at 65 °C until constant weight and then ground.

Macroinitiators. The PK30 functionalization was performed according (Scheme 8.A.1) to the published method. The reactions were performed in a sealed 250 ml round bottom glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating.

For the preparation of PK30-Cl\(_{12}\) (taken here as an example) 3-chloropropylamine hydrochloride (9.89 g, 53.6 mmol) was dissolved in methanol (90 ml) to which an equimolar amount of sodium hydroxide (2.15 g, 53.6 mmol) was added. After the polyketone (10 g, 76 mmol of dicarbonyl units) was preheated to the liquid state at the employed reaction temperature (100 °C), the amine was added drop wise (with a drop funnel) into the reactor in the first 20 min. The stirring speed was set at a constant value of 500 RPM. During the reaction, the mixture of the reactants changed from the slight yellowish, low viscous state, into a highly viscous brown homogeneous paste. The product was dissolved in chloroform and afterwards washed with demineralized water. The two phases (organic & water) were
separated in a separatory funnel. The polymer was isolated by evaporating the chloroform at reduced pressure at room temperature. The product, a brown viscous paste (low degree of functionalization) or a brown powder (high degree of functionalization), was finally freeze dried and stored at -18 °C until further use. Some properties of the macro-initiators are given in Table 1. The macro-initiators were characterized using elemental analysis and \(^{1}H\)-NMR spectroscopy (in chloroform).

**Scheme 8.A.1: Synthesis of the macro-initiators**

The conversion of carbonyl groups of the polyketone was determined using the following formula:

\[
x_{CO} = \frac{2^{y}}{x+2^{y}} \cdot 100 = \frac{\left( \frac{2}{mol_{N}} \cdot \frac{N(wt.\%)}{mol_{N}} \right)}{\left( \frac{N(wt.\%)}{mol_{N}} \cdot \frac{C(wt.\%)}{mol_{C}} \right) + \left( \frac{2}{mol_{N}} \cdot \frac{N(wt.\%)}{mol_{N}} \right)} \cdot 100
\]  

\( \bar{n}_{C}^{n-m} = 3.7, \) is the average number of carbons in \( n-m \) (see Scheme 8.2)

\( \bar{n}_{C}^{m} = 10.4, \) is the average number of carbons in \( m \) (see Scheme 8.2)

mol\(_{N}\) = molecular weight of nitrogen

mol\(_{C}\) = molecular weight of carbon

The number of pyrrole units was determined using the conversion of the carbonyl groups of the polyketone and formula 2:

\[
N_{pyrrole \ units} = \left( \frac{M_{PK}}{M_{repeating \ unit \ PK}} \right) \cdot x_{CO}
\]  

\( M_{PK} = \) the average molecular weight of the parent (unmodified) polyketone

\( M_{repeating \ unit \ PK} = \) the average molecular weight of the repeating unit of polyketone
Comb polymerization. A 250-mL three-necked flask was charged with the macro-initiator. Enough acetone (typically 5-10 ml) was added to dissolve the macro-initiator. Demineralized water and DMA were then added to the solution. Subsequently, the mixture was degassed by three freeze-pump-thaw cycles. A nitrogen atmosphere was maintained throughout the remainder of the reaction steps. CuBr was then added to the flask and the mixture stirred for 10 minutes. The flask was then placed in an oil bath at 25 °C. The reaction was started by the addition of the ligand (Me₆TREN) using a syringe. After the pre-set reaction time, the mixture was exposed to air and the mixture was diluted with demineralized water. The reaction mixture was then purified via dialysis using membrane tubing Spectra/Por® Dialysis Membrane (molecular weight cut off [MWCO] = 12 000 – 14 000 g/mol). The product was then dried in an oven at 65 °C until constant weight and then grounded.

Characterization. The DMA conversion was measured by using Gas Chromatography (GC). The samples were injected on a Hewlett Packard 5890 GC with an Elite-Wax ETR column with pentadecane as an internal standard. The total molecular weight ($M_{n,tot}$) is calculated using the DMA conversion (monomer-initiator ratio multiply by the conversion). The span molecular weight ($M_{n,SPAN}$) is calculated using the $M_{n,tot}$ and is defined as two times the molecular weight of one arm plus the molecular weight of the macro-initiator (comb PDMA).

Gel permeation chromatography (GPC) analysis of one (entry 6, $M_{n,th}$ falls in the range of the calibration curve of the GPC while the $M_{n,th}$ of the rest of the entries are all higher than the range) of the water-soluble samples was performed on a Agilent 1200 system with Polymer Standard Service (PSS) columns (guard, 104 and 103 Å) with a 50 mM NaNO₃ aqueous solution as the eluent. The columns were operated at 40 °C with a flow-rate of 1.00 ml/min, and a refractive index (RI) detector (Agilent 1200) was used at 40 °C. The apparent molecular weights and dispersities were determined using a polyacrylamide (PAM) based calibration with WinGPC software (PSS).

Carbon (13) nuclear magnetic resonance ($^{13}$C-NMR) spectroscopy was performed on a Varian Mercury Plus 500 MHz spectrometer. For analysis D₂O was used as the solvent. The delay time was set at 2s and at least 10000 scans were performed (overnight). The polymer samples were swelled for 1 day and stirred for another day at room temperature. In order to obtain a high signal to noise ratio, a high polymer concentration was used. The hydrolysis degree was determined through the integration method reported in literature.⁷²
Rheological characterization. The aqueous polymeric solutions were prepared by swelling the polymers in water for one day and afterwards gently stirring the solution for another day. Viscometric measurements were performed on a HAAKE Mars III (ThermoScientific) rheometer, equipped with a cone-and-plate geometry (diameter 60 mm, angle 2°). Flow curves were measured by increasing the shear stress by regular steps and waiting for equilibrium at each step. The shear rate (\(\dot{\gamma}\)) was varied between 0.1 – 1750 s\(^{-1}\). Dynamic measurements were performed with frequencies ranging between 0.04 – 100 rad/s (i.e., 6.37·10\(^{-3}\) – 15.92 Hz). It must be noted that all the dynamic measurements were preceded by an oscillation stress sweep to identify the linear viscoelastic response of each sample and to ensure that the dynamic measurements were conducted in the linear response region of the samples.

Alkaline hydrolysis. Stock solutions of the different polymers were prepared by swelling the polymers for a day in the alkali-salt mixtures and gently stirring for another day. The polymer concentration was set at 5000 ppm. NaHCO\(_3\) was used as the alkali agent and the concentration was fixed at 3000 ppm. One solution further contained 5000 ppm NaCl and the other one contained 4925 ppm NaCl and 75 ppm CaCl\(_2\). The solutions were divided into 8 different vials (sealed) and placed in an oven at 70 °C. At set time intervals a sample vial was removed from the oven and cooled to room temperature. The viscosity function of the sample was then recorded. Both solutions were evaluated for a total of 192 hours. The viscosity retention was evaluated for the samples using equation 8.A.3:

\[
Viscosity\ retention = \frac{\eta_{t0}}{\eta_{t,x}}
\]  

(8.A.3)

where \(\eta_{t0}\) = the solution viscosity (measured at \(\dot{\gamma} = 10\) s\(^{-1}\)) of the virgin polymer samples and \(\eta_{t,x}\) = the solution viscosity (measured at \(\dot{\gamma} = 10\) s\(^{-1}\)) of the polymer sample treated for the specified number of days.

Four other solutions were prepared in order to evaluate for longer periods. Two sets of comparison were performed. In the first one, the polymer concentration (in terms of monomeric moles) was set equal between the different polymers and the other one the solution viscosity (at \(\dot{\gamma} = 10\) s\(^{-1}\)) was kept equal. Again NaHCO\(_3\) was used as the alkali agent and the concentration was fixed at 3000 ppm. One solution further contained 10000 ppm NaCl and the other one contained 9850 ppm NaCl and 150 ppm CaCl\(_2\). The solutions were divided into 8 different vials (sealed) and placed in an oven at 70 °C. At set time intervals a sample vial was removed from the
oven and cooled to room temperature. The viscosity function of the sample was then recorded. Both solutions were evaluated for more than 63 days.
Appendix 8.B

8.B.1. Experimental section

Chemicals. Cyclo octane (≥ 99.5 %), guar gum, methyl cellulose, xanthan gum and sodium carboxy methyl cellulose were purchased from Sigma Aldrich. The crude oil is a medium oil (API gravity equals 27.8) and originates from the Berkel oil field in the southwest of the Netherlands. The viscosity of the oil is 71 mPa.s at 20 °C. The branched non-ionic water soluble (co)polymers used in the flow cell were previously synthesized using atomic transfer radical polymerization (Chapters 6, and section 8.4).

Solution preparation. The polymeric solutions were prepared by swelling the polymers for at least 12 hours in demineralized water and subsequently stirred for another 12 hours.

Rheological characterization. Viscometric measurements were performed on a HAAKE Mars III (ThermoScientific) rheometer, equipped with a cone-and-plate geometry (diameter 60 mm, angle 2°). Flow curves were measured by increasing the shear stress by regular steps and waiting for equilibrium at each step. The shear rate was varied between 0.1 – 1750 s⁻¹. Dynamic measurements were performed with frequencies ranging between 0.04 – 100 rad/s (i.e. 6.37·10⁻³ – 15.92 Hz). It must be noted that all the dynamic measurements were preceded by an oscillation stress sweep to identify the linear viscoelastic response of each sample and to ensure that the dynamic measurements were conducted in the linear response region of the samples.

Flow-cell experiments. A schematic presentation of the flow-cell (with the dimensions) is given in Figure 7.2. The flow cell has been adapted from the original ones presented in literature to resemble dead ends (Figure 1.4) that are present in oil reservoirs. The bottom part of the flow-cell is made out of aluminum while the cover is glass. The depth of the chamber (designated as blue in Figure 7.2) is set at 0.5 mm. The chamber is first filled with oil and afterwards flooded with water or polymer solutions. For the branched PDMA crude oil was used, and for the copolymers of AM and NIPAM a 1-2 (volume%) mixture of cyclo-octane and crude oil was used (η = 17 mPa.s). The linear velocity was set at 1 foot per day. Each flood (either water or polymer) was continued for at 24 hours at room temperature (RT). The oil recovery out of the different cells was visually determined by taking high definition pictures (before and after the floods). Analysis (pixel count) of the image using Adobe allows the calculation of the amount of oil left behind in the flow-cell.
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