Synthesis of novel branched polymers for enhanced oil recovery
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Evaluation of the Performance of Novel Branched Polyacrylamides Synthesised By RAFT Polymerisation for Enhanced Oil Recovery (EOR)

Abstract

In the present chapter novel star-like branched polyacrylamides (SB-PAMs) with theoretical molecular weights of 1.3 - 11.0 million Darcy (MDa) have been evaluated for their suitability in enhanced oil recovery (EOR). Compared with Chapter 6, higher molecular weights have been targeted. Moreover, relevant aspects from an application point of view, such as resistance to shear and salt, as well as permeation through pores were investigated. Rheological measurements displayed the advantage of branching, as higher viscosities were recorded than for linear polyacrylamide (PAM) at comparable theoretical molecular weight. Oil recovery was evaluated in two-dimensional flow-cell measurements and core-flood experiments. SB-PAMs displayed superior performance in the flow-cell experiments, recovering up to 3 times more oil than a linear equivalent at lower polymer concentrations. In core flood experiments, higher recoveries were reported for the branched polymers than for a linear PAM and a linear hydrolysed polyacrylamide (HPAM), however, the HPAM required a lower polymer concentration stemming from its high molecular weight. The branched polymers displayed the lowest pressure drop over the cores, passed the filtration experiments, were stable to the addition of salt, and displayed high shear resistance. Therefore, SB-PAMs show promising characteristics for their application as viscosifying polymers in EOR.

7.1 Introduction

Oil reservoirs contain permeable porous rock, in which oil is accumulated. Sandstone is the most common rock, accounting for approximately 80% of oil reservoirs, followed by carbonates.\(^1\) Oil recovery from oilfields undergoes three distinct phases before reaching maturity, referred to as the primary, secondary, and tertiary stage.\(^2\)

After primary\(^3\) and secondary recovery (introduced in Chapter 1), 60 - 80% of the original oil in place (OOIP) is still present in the oil field.\(^4\)\(^-\)\(^6\) Any technique applied to recover oil after secondary recovery, is regarded tertiary recovery. Enhanced oil recovery (EOR) is commonly mistaken as synonym for tertiary recovery,
7.1. INTRODUCTION

However, it can be applied in each stage of oil recovery.\textsuperscript{2} Typical recovery potential by EOR for light oils is 45%.\textsuperscript{7}

The effectiveness of waterflooding, being the most commonly applied secondary recovery technique, depends on microscopic and macroscopic characteristics. Microscopic efficiency is expressed in interfacial tension, wettability, contact angle, and viscosity, whereas macroscopic efficiency depends on dimensions of reservoir, differences in permeability within the field, and the mobility ratio. The former denotes the capability of the water to remove oil from pores, while the latter is related to the displacement of (microscopically) mobilized oil to the production well.

The mobility ratio, defined as the relative permeability ($k_i$) of a fluid divided by its viscosity ($\mu_i$), is a key characteristic of a fluid (Eq. 7.1).

$$\lambda = \frac{k_i}{\mu_i}$$ \hspace{1cm} (7.1)

The water to oil mobility ratio relates the mobility ratio of water to oil and is calculated by dividing the mobility ratio of water by that of oil (Eq. 7.2).

$$M = \frac{k_w \mu_o}{\mu_w k_o}$$ \hspace{1cm} (7.2)

where $k_w =$ relative permeability of water, $k_o =$ relative permeability of oil, $\mu_w =$ viscosity of water, and $\mu_o =$ viscosity of oil.

A mobility ratio $\leq 1$ is desirable, as the displacing phase is less mobile than the displaced phase, resulting in effective displacement of oil throughout the reservoir. In practice, the water to oil mobility ratio is generally above 1, leading to instabilities in the flow and viscous fingering, whereby the water flood bypasses the majority of the oil. This high mobility ratio results in a decreasing oil cut and eventually the production of injected water.

By dissolving a polymer in the injected water, the viscosity of the displacing fluid is increased, thereby decreasing the water to oil mobility ratio.\textsuperscript{8,9} As an effect, oil recovery rate is elevated\textsuperscript{10} and additional oil is produced before breakthrough of the polymer solution at the production well occurs.\textsuperscript{11} The latter implies a lower residual oil saturation after a polymer flood compared to a water flood.\textsuperscript{12} 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 range of oil viscosities.\textsuperscript{2,13} Currently applied polymers are high molecular weight anionic polymers based on acrylamide,\textsuperscript{14} or xanthan gum.\textsuperscript{15} The majority 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. At elevated temperatures, i.e. those present in reservoirs, hydrolysis progresses, leading to an increase in anionicity of the polymer.\textsuperscript{16} The latter leads to more pronounced salt sensitivity and precipitation in presence of low concentrations of divalent ions.\textsuperscript{17}

Another characteristic of polymer flooding is the retention of polymer on the surface of the rock, leading to a reduction in reservoir permeability.\textsuperscript{18,19} A measure for this permeability reduction is the residual resistance factor (RRF), which is calculated by dividing the brine permeability before polymer flooding ($k_a$) by its permeability after polymer flooding ($k_n$), as displayed in Eq. 7.3.

\[
RRF = \frac{k_a}{k_b}
\]  
(7.3)

By altering the topology of the polymer, it is possible to tailor the characteristics of the macromolecule to its envisioned application. In that regard, branched polymers display relevant properties. Such polymers are known for their superior shear and temperature resistance compared with linear analogues.\textsuperscript{20–22} Hyperbranched copolymers of AM, AA, and N-Vinyl-2-pyrrolidinone (NVP) showed higher viscosity retention combined with improved oil recovery from a sandstone core compared with a linear equivalent of similar molecular weight.\textsuperscript{23} The effect of the degree of branching on the RRF was investigated by Lai et al.\textsuperscript{21} At a low degree of branching and low molecular weight, low RRFs were obtained and polymer retention was mainly attributed to surface adsorption. Increasing the degree of branching in the polymer was found to lead to an increase in shear resistance, as well as more pronounced intermolecular entanglements by chain ends. The latter was found to contribute to the RRF by a prominent increase in mechanical trapping. Similarly, a higher RRF was obtained with a 13-arm PAM synthesised by ATRP, compared with a linear PAM and a linear HPAM of comparable molecular weight.\textsuperscript{24} For an equivalent polymer with 17 arms, significantly higher oil recoveries from both Berea and Bentheim sandstone cores were reported compared with a linear equivalent.

In order to overcome the drawbacks associated to HPAM, the current research focusses on the performance evaluation of novel branched PAM that was synthesised by a two-step RAFT polymerisation. Because of the easy and versatile synthetic procedure, scaling up to industrial scale is anticipated to be straightforward. Moreover, as this novel polymer is built from acrylamide, it does not contain charges and its viscosity is stable to high salt concentrations and the presence of divalent ions.
7.2 Experimental

7.2.1 Materials

Acrylamide (AM, electrophoresis grade, ≥ 99%), N,N'-methylenebis (acrylamide) (BisAM, 99%), cyclooctane (≥ 99%), and sodium acetate (ReagentPlus, ≥ 99%) were purchased from Sigma-Aldrich and used as received. 4,4'-Azobis(4-cyanovaleric acid) (ACVA, ≥ 98.0%) was obtained from Sigma-Aldrich and used without further purification. The RAFT agent 3-(((benzylthio) carbonothioyl)thio)propanoic acid (BCPA) was synthesised according to the method outlined in literature, however, purification of the product was performed by recrystallisation twice from dichloromethane, obtaining the RAFT agent as a yellow solid with 66% yield. The crude oil for the oil recovery experiments was heavy oil, with a viscosity of 1,023 mPa.s at 20°C, corresponding to API gravity below 22.3° (kindly supplied by Shell Global Solution International B.V.). The viscosity of the oil was adjusted by addition of cyclooctane. Isopore membrane (polycarbonate) filters (pore size = 1.2 and 3.0 μm, D = 47 mm) were obtained from Merck Millipore. Sandstone cores (Bentheim, 5 x 30 cm) were obtained from Kocurek Industries. HPAMs (Flopaam 3130S and Flopaam 3430S, degree of hydrolysis: 25 - 35%) were kindly supplied by SNF Floeger.

7.2.2 Synthesis of the macro RAFT agent (mCTA)

A 25 mL round-bottomed flask was charged with acrylamide monomer, AM (e.g. table 1, entry 3: 0.5128 g, 0.007 mol), divinyl monomer, BisAM (0.1589 g, 1.03 mmol), RAFT agent, BCPA (0.0701 g, 0.257 mmol) and initiator, ACVA (0.0199 g, 0.071 mmol) (in that order). Monomers, RAFT agent and initiator were dissolved in a mixture of sodium acetate/acetic acid buffer solution (pH = 5) of acetic acid (0.27 M) and sodium acetate (0.73 M) and ethanol (50:50 vol%) before addition to the reaction mixture. After the addition of a magnetic stirrer, the system was degassed by purging with nitrogen gas (N2) for at least 30 minutes under vigorous stirring (1,050 rpm) and subsequently sealed. After deoxygenation, the system was placed in an oil bath at 70°C to initiate the polymerization. All reactions were performed under nitrogen. After a certain reaction time, the mixture was exposed to ambient air and diluted with demineralised water (5 mL) to terminate the reaction. A sample of 0.3 mL was taken from the solution mixture for determination of AM conversion by gas chromatography (GC) and the molecular weight and weight distribution by gel permeation chromatography (GPC). To isolate the polymerised macro RAFT agent, the solvent (buffer solution/ ethanol mixture) was evaporated at low pressure (<100 mbar). The yellowish, gel-like product was dissolved in sufficient demineralised water (typically a few drops). Afterwards, the reaction mixture was precipitated in an excess amount of methanol. Hereafter, the
precipitated product was decanted and filtered over a 0.45 μm filter by using a vacuum pump. The solid residue was finally dried in an oven at 70 °C. The detailed reaction conditions for the synthesis of the macro RAFT agent are summarised in table 1.

Table 1: Reaction conditions for the synthesis of macro RAFT agents

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(wt:vol); (%)</td>
<td></td>
<td></td>
<td>(-); (-)</td>
<td>(-); (-)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9:1:0.31:0.16</td>
<td>0.13; 70 °C; 120</td>
<td>95</td>
<td>2,700</td>
<td>8,200</td>
<td>38.2</td>
</tr>
<tr>
<td>2</td>
<td>7:1:0.25:0.13</td>
<td>0.13; 70 °C; 120</td>
<td>93</td>
<td>2,700</td>
<td>13,000</td>
<td>52.7</td>
</tr>
<tr>
<td>3</td>
<td>7:1:0.25:0.07</td>
<td>0.05; 70 °C; 240</td>
<td>91</td>
<td>2,600</td>
<td>5,700</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>5:1:0.19:0.05</td>
<td>0.05; 70 °C; 237</td>
<td>89</td>
<td>2,700</td>
<td>7,100</td>
<td>10.6</td>
</tr>
<tr>
<td>5</td>
<td>3:1:0.13:0.03</td>
<td>0.05; 70 °C; 234</td>
<td>98</td>
<td>3,100</td>
<td>7,700</td>
<td>7.4</td>
</tr>
<tr>
<td>6¹</td>
<td>0:0.22:0.11</td>
<td>0.10; 70 °C; 180</td>
<td>98</td>
<td>2,500</td>
<td>2,900</td>
<td>1.3</td>
</tr>
</tbody>
</table>

7.2.3 Star-like branched PAM (SB-PAM) polymerisation

A 250 mL three-necked flask was charged with macro RAFT agent (e.g., table 2, entry 9: 0.0499 g, 0.088 mmol), monomer, AM (30.0089 g, 0.422 mol), and initiator,
ACVA (0.0027 g, 0.0096 mmol) which were dissolved in sodium acetate/acetic acid buffer solution (300 mL) at pH=5. Subsequently, the system was purged with nitrogen gas (N₂) under vigorous stirring (1,050 rpm) for at least 30 minutes. After degassing, the system was placed in an oil bath at 80°C, to initiate the reaction. All reactions were performed under nitrogen. During the reaction, the mixture of the reactants transitioned from yellowish, to a whitish-gelatine like homogeneous paste. The viscosity of the solution visibly increased with time. After a certain reaction time, the mixture was exposed to ambient air and diluted with demineralised water to terminate the reaction. A sample of 0.3 mL was taken from the reaction mixture for determination of AM conversion by GC and the molecular weight and weight distribution by GPC. Afterwards, the product was precipitated by washing the polymer in an excess amount of methanol. Subsequently, the precipitated polymer was decanted and dried in an oven at 70°C. An overview of the polymerisation protocol is shown in figure 1.

7.2.4 Characterisation

Conversion of AM was measured using gas chromatography (GC). Samples of reaction mixtures were dissolved in acetone containing 1,000 ppm pentadecane (reference) and injected on a Hewlett-Packard 5890 GC equipped with an Elite-Wax ETR column.

(Co)polymer samples were dissolved in demineralised water containing 0.05M sodium nitrate and subjected to GPC. An Agilent 1200 system was equipped with Polymer Standard Service (PSS) columns (100 Å, 1,000 Å, and 3,000 Å, 8 x 300 mm) and an aqueous 0.05M sodium nitrate solution was used as the eluent. Column temperature was maintained at 40°C and detection of (co)polymers was conducted with a refractive index (RI) detector, operated at 40°C. AM-based calibration and WinGPC software (GPC) were used to calculate the apparent molecular weight and polydispersity (PDI) of the samples.

Dynamic viscosity measurements of (co)polymer samples (2 wt%) were performed on a ThermoScientific HAAKE Mars III, equipped with a cone-plate fixture (diameter 60 mm, angle 2° and a solvent trap. The shear rate was increased gradually from 0.1 to 1,750 s⁻¹ and at each step the equilibrium shear force was recorded in order to construct flow curves. Oscillation frequency sweep measurements were performed in order to measure the inherent viscosity of polymer solutions. Prior to all frequency sweeps, an oscillation stress sweep was performed in order to determine the linear response region for each polymer. Hereafter, the storage modulus (G’) and loss modulus (G”) were measured according to the individual pre-measured linear response region of the polymer solution (typical shear stress was 10 Pa). Shear resistance of polymer solutions was measured by shearing polymer solutions with a viscosity of approximately 120 mPa.s at 20°C, measured
Table 2: Conditions for chain extension polymerisations of different macro RAFT agents

<table>
<thead>
<tr>
<th>Entry</th>
<th>mCTA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[mCTA]&lt;sub&gt;[0]&lt;/sub&gt;[I]&lt;sub&gt;[0]&lt;/sub&gt;</th>
<th>M/solv.&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Conv.</th>
<th>[M]&lt;sub&gt;n,thor.&lt;/sub&gt;,&lt;sup&gt;d&lt;/sup&gt;</th>
<th>[M]&lt;sub&gt;n,GPC&lt;/sub&gt;</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[BisAM]&lt;sub&gt;[0]&lt;/sub&gt;</td>
<td>[AM]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>(wt:vol); (%)</td>
<td></td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>1</td>
<td>1:1.89:21.371</td>
<td>0.14: 78°C; 30</td>
<td>72</td>
<td>1.095,100</td>
<td>676,400</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:3.46:43.598</td>
<td>0.11: 78°C; 66</td>
<td>85</td>
<td>2,617,500</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:1.22:12.410</td>
<td>0.10: 80°C; 161</td>
<td>60</td>
<td>529,900</td>
<td>541,500</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1:1.63:243,017</td>
<td>0.10: 80°C; 86</td>
<td>67</td>
<td>2,365,500</td>
<td>1,143,000</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1:0.96:82,109</td>
<td>0.10: 80°C; 62</td>
<td>61</td>
<td>3,565,500</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1:1.89:22.910</td>
<td>0.17: 80°C; 60</td>
<td>80</td>
<td>1,317,700</td>
<td>1,003,000</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1:0.87:34,365</td>
<td>0.17: 80°C; 120</td>
<td>86</td>
<td>2,111,900</td>
<td>1,072,000</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1:1.39:36,621</td>
<td>0.17: 80°C; 40</td>
<td>84</td>
<td>2,180,700</td>
<td>1,250,000</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1:1.09:47,929</td>
<td>0.10: 80°C; 80</td>
<td>59</td>
<td>2,014,300</td>
<td>825,400</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1:1.18:79,61</td>
<td>0.10: 80°C; 104</td>
<td>81</td>
<td>4,611,200</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1:1.63:243,017</td>
<td>0.10: 80°C; 80</td>
<td>69</td>
<td>11,969,600</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1:1.63:60,439</td>
<td>0.10: 80°C; 92</td>
<td>81</td>
<td>3,489,000</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1:1.42:99,703</td>
<td>0.10: 80°C; 103</td>
<td>71</td>
<td>5,064,500</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1:1.49:65,086</td>
<td>0.10: 80°C; 80</td>
<td>83</td>
<td>3,851,800</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3,200,000</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>16&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10,000,000</td>
<td>12,000,000</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Macro-RAFT agent (mCTA) (table 1), ratio of [BisAM]/[AM]. Entry 1 and 2 are synthesised with a CTA (BCPA) instead of mCTA.

<sup>b</sup>Molar ratio

<sup>c</sup>M/solv. = Monomer / solvent = Acrylamide / Buffer solution (pH=5)

<sup>d</sup>Calculated from the linear equivalent theoretical molecular weight formula proposed by Stenzel et al. using Eq. 7.10

<sup>e</sup>Polimerised with entry 2 from table 1

<sup>f</sup>Polimerised with entry 3 from table 1

<sup>g</sup>Commercial linear HPAM Flopaam 3130S

<sup>h</sup>Commercial linear HPAM Flopaam 3430S

<sup>i</sup>M<sub>n,thor.</sub>, according to supplier
at a constant shear rate of 9.63 s\(^{-1}\) in 30,000 ppm brine (NaCl solution). Solutions were sheared at 154 s\(^{-1}\) for 300 s (phase 1), followed by shearing at 1750 s\(^{-1}\) for 300 s (phase 2), and again shearing at 154 s\(^{-1}\) for 300 s (phase 3). The shear resistance factor (SRF) was determined as follows:

\[
SRF = \frac{\bar{\eta}_{phase\ 3}}{\bar{\eta}_{phase\ 1}}
\]

where \(\bar{\eta}_{phase\ 3}\) denotes the average viscosity during shearing phase 3 and the SRF is a measure for the retention of the viscosity after high shear phase 2.

### 7.2.5 Modelling of flow-cell experiments

In contrast with oil, the applied polymer solutions display shear-thinning behaviour. In order to match the viscosity of the polymer solutions to the oil, a representative shear rate has to be estimated. Therefore, flow-cell experiments were modelled in COMSOL Multiphysics software, using the two-phase level-set method. For each node, Navier-Stokes and continuity equations were solved, in order to estimate shear rates and track oil recovery as a function of time. A visual representation of the recovery can be accessed through the QR code depicted in figure 3.

**Figure 2**: Oil recovery of a brine flood as modelled in COMSOL Multiphysics software. The colour red denotes the presence of oil, whereas blue corresponds with brine (i.e. the oil originally present in that location was displaced during the brine flood).

The oil recovery from the flow-cell, as modelled, is displayed in figure 2. The red colour corresponds with oil, while the blue colour illustrates the swept part of the flow-cell (brine). Related shear rates are depicted in figure 4 and clearly illustrate that the obtained shear rates in the dead-ends of the flow-cell are between 0.5 and 1.0 s\(^{-1}\). Based on these results, a shear rate of 0.85 s\(^{-1}\) is used for the evaluation of polymers in the flow-cell.
7.2.6 Flow-cell experiments

Dead end oil recovery simulations were performed using a two-dimensional flow-cell, consisting of an aluminium bottom and a transparent plastic top cover with size varied chambers to consecutively simulate dead-end pores in oil reservoirs. The flow-cell setup (figure 5) has been adapted from the original, presented by Niu et al.\textsuperscript{27} and was evaluated for EOR by Wever et al.\textsuperscript{24} The depth of the chambers (designated as dark blue in figure 5) measures 0.5 mm. The experimental procedure was as follows. First, the flow-cell was filled with crude oil. Here, it must be noted that the crude oil used for the experiment has been diluted with cyclooctane from a viscosity of approximately 15 mPa.s (shear rate = 9.63 s\textsuperscript{-1}) was as follows. First, the flow-cell was filled with crude oil. Here, it must be noted that the crude oil used for the experiment has been diluted with cyclooctane from a viscosity of 1,023 mPa.s to a viscosity of 70 mPa.s at 20 °C, measured at a constant shear rate of 0.85 s\textsuperscript{-1}. Afterwards, the flow-cell was flooded either by brine (30,000 ppm NaCl, used as reference) or polymer solution (in 30,000 ppm NaCl) using a pump to steadily inject the solution. The concentration of polymer was chosen as such, that the resulting polymer solution viscosity matched that of the crude oil.
7.2. EXPERIMENTAL

Figure 5: Schematic representation of the two-dimensional flow-cell (top view)\textsuperscript{24}

(at 20 °C and a shear rate of 0.85 s\textsuperscript{-1}). The flow rate was set to 1.00 mL/hour and experiments were continued for 24 hours to reach steady state. Flow-cell evaluation was graphically performed by taking high definition photographs from a set height point. The image analysis was performed using Adobe Photoshop CS6 via the ‘pixel count’ option to determine the amount of remaining crude oil in the chambers and consequently calculate the oil recovery according to:

\[
\text{Oil rec.\%} = \left(100 - \frac{100 \text{Pixel}_{\text{Remaining}}}{\text{Pixel}_{\text{Total}}}\right)_{\text{Polymerflood}} - \left(100 - \frac{100 \text{Pixel}_{\text{Remaining}}}{\text{Pixel}_{\text{Total}}}\right)_{\text{Waterflood}} \tag{7.5}
\]

where the oil recovery (%) is the percentage of oil recovered during polymer flood minus the water flood reference. All evaluated polymer solutions managed to remove (nearly) all oil from chamber 1 and 7 and hardly any recovery was obtained from chamber 5 and 6. In order to offer resolution and distinguish between the different samples, for the calculation of the oil recovery only chamber 2, 3, and 4 were used as consecutive examples for dead-end pores (see figure 5).

7.2.7 Filtration experiments

Permeation of the polymers through small pores was evaluated by filtration experiments. In these experiments, 250 mL polymer solution (in 30,000 ppm NaCl) with a viscosity of approximately 15 mPa.s (shear rate = 9.63 s\textsuperscript{-1}) was put in a container and pressurised to 2 bars, fitted with an Isopore membrane (polycarbonate) filter (\(d_{\text{effective}} = 41 \text{ mm}\)) as depicted in figure 6. The weight of the effluent was recorded as function of time and the filtration ratio (FR) was calculated as follows:

\[
FR = \frac{t_{w200} - t_{w180}}{t_{w80} - t_{w60}} \tag{7.6}
\]

where \(t_{w200}\) denotes the time required to reach 200 g of effluent, and FR is a measure of the decrease in permeability of the filter over time.
7.2.8 Core-flood experiments

Oil recovery experiments applying polymer flooding in a simulated oil reservoir were conducted at ambient temperature with Bentheim sandstone cores (5 x 30 cm), purchased from Kocurek Industries. Porosity of the cores was taken from Wever et al.,24 from which the pore volume (PV) was derived by relating the porosity to the total volume of the core. Brine permeability of the cores was calculated according to Darcy’s law28 (Eq. 7.7) by injecting brine (30,000 ppm NaCl) at different flow rates and measuring the corresponding pressure drop over the cores.28

\[
k_{\text{brine}} = 1000 \cdot \frac{L}{A} \cdot \eta \cdot Q \cdot \frac{1}{\Delta P}
\]

where \(k_{\text{brine}}\) is the brine permeability (mD), \(L\) the length of the core (cm), \(A\) the cross-sectional area (cm\(^2\)), \(\eta\) the viscosity of the brine (mPa.s), \(Q\) the flow rate (cm\(^3\)/s), and \(\Delta P\) the pressure drop over the core (bar). From this permeability, the average pore radius \(r\) can be determined, according to Eq. 7.8.29

\[
r = \left(\frac{8 \cdot k_{\text{brine}}}{\phi}\right)^{1/2}
\]

where \(k_{\text{brine}}\) is the brine permeability in \(\mu\)m\(^2\) and \(\phi\) the fractional porosity.
7.2. EXPERIMENTAL

A schematic overview of the core-flood setup is displayed in figure 7. Preparation of the sandstone cores was as follows. First, the core was sealed by heat shrinkable clear plastic tubes and placed in a stainless-steel core holder system. Hereafter, the core was saturated with carbon dioxide (CO₂) to remove oxygen, followed by brine (30,000 ppm NaCl) injection at low flow rate for at least 2 hours. Next, oil was pumped into the core, whereby brine flowing out of the core was collected in order to determine the initial oil saturation. The viscosity of the oil was adjusted to a viscosity of 122 mPa.s at 20°C, measured at a constant shear rate of 9.63 s⁻¹. The pressure drop over the sandstone core was recorded with digital pressure transducers (GS4200-USB) from ESI Technology Inc. The polymer flood was performed with a volumetric flow rate of 12 mL/hour (2 feet/day). The oil and polymer solution coming out of the core were collected in test tubes (fraction collector system) and visually analysed by calculating the cumulative volume. The oil recovery factor was calculated according to literature, as follows:

\[
\text{Oil recovery factor} = \frac{\text{Cumulative recovered oil}}{\text{initial oil saturation in core}} \quad (7.9)
\]

where the oil recovery factor (%) represents the additional recovery of oil after the conventional water flood, calculated by dividing the amount of oil produced during the polymer flood (mL) by the initial amount of oil present in the porous rock (mL).
7.3 Results and discussion

7.3.1 Polymerisation

Two different synthetic strategies were applied, namely direct RAFT polymerisation and the RAFT polymerisation of a low molecular weight mCTA, followed by chain extension. The polymers obtained by direct RAFT polymerisation (table 2, entry 1 and 2) are linear reference polymers. In the second approach, a core-moiety, or macro chain transfer agent (mCTA) was synthesised by either RAFT polymerisation of AM up to low molecular weight, or RAFT copolymerisation of BisAM and AM. The linear core moiety (table 1, entry 6) was used in the synthesis of linear chain extended reference polymers (table 2, entry 3, 4, and 5). Branched mCTAs with varying degrees of branching (table 1, entry 1 to 5) were applied in the synthesis of star-like branched polyacrylamide (SB-PAM), as listed in table 2 (entry 6 to 14). mCTAs with experimental molecular weights ranging from 2,769 to 13,040 Da were obtained, with PDIs ranging between 1.3 (linear mCTA) and 52.7. Especially high PDIs were obtained with entry 1 and 2 (table 1), indicating prominent branching and/or cyclisation reactions. In order to reduce excessive branching in the core, syntheses of branched core entries 3, 4, and 5 were performed at higher dilution (5 wt% instead of 13 wt%), as suggested by Li et al to suppress intramolecular cyclisation. Entry 3 clearly displays the effect of dilution on the PDI, as a pronouncedly lower PDI of 7.1 was obtained, under further similar conditions.

The mCTAs were subjected to a chain extension step, in order to synthesise SB-PAM or linear PAM, depending on the nature of the core-moiety. The experimental conditions and resulting polymers are displayed in table 2. SB-PAMS with theoretical molecular weights ranging from 1.3 to 12 MDa were obtained (calculated according to Eq. 7.10, where $M_{\text{theor.}}$ is the theoretical molecular weight of the synthesised polymer; $[M]_{0,AM}$ the initial monomer concentration of AM (mol); $M_{W,\text{BisAM}}$ is the molecular weight of BisAM; X represents the monomer conversion). It was not possible to determine the experimental molecular weight for the polymers of high molecular weight, because of limitations in the column setup of the GPC and its calibration standards. Linear chain extended polymers with theoretical molecular weights between 0.5 and 3.6 MDa were prepared and used as reference polymers (entry 3, 4, and 5). Linear polymers obtained by a direct one-pot RAFT polymerisation had theoretical molecular weights of 1.1 and 2.6 MDa and were used as a second type of reference polymer.

$$M_{\text{theor.}} = \left( \frac{[M]_{0,AM}}{[M]_{0,RAFT}} \cdot M_{w,AM} + \frac{[M]_{0,BisAM}}{[M]_{0,RAFT}} \cdot M_{w,BisAM} \right) \cdot X + M_{w,RAFT} (7.10)$$
7.3. RESULTS AND DISCUSSION

7.3.2 Rheological measurements

Polymers were dissolved in demineralised water and their viscosity was recorded as a function of shear rate at a constant concentration of 2 wt%. An overview of the results is depicted in figure 8a and 8b. In general, polymer solutions display an apparent Newtonian plateau at low shear rates, followed by a rapid decrease in viscosity upon increasing shear rate (shear thinning). As expected, solution viscosities were found to vary highly, resulting from differences in molecular weight and architecture of the polymer. The significant increase in solution viscosity from entry 3 to 4 to 5 respectively (figure 8a and 8b), clearly indicates the role of the mCTA in the obtained molecular weight of these chain extended linear polymers. A similar increase in viscosity was found for entry 2, compared with entry 1. Both linear polymers are polymerised with a RAFT agent in a one pot reaction, however, the ratio between RAFT agent and monomer was varied to obtain polymers with different molecular weights.

![Viscosity versus shear rate curves for linear and star-like branched polyacrylamide at a polymer concentration of 2 wt%](image)

**Figure 8:** Viscosity versus shear rate curves for linear and star-like branched polyacrylamide at a polymer concentration of 2 wt%

The viscosity of branched polymers synthesised with a certain mCTA (table 1) is expected to increase upon increasing the AM to mCTA ratio. A larger ratio, in theory, leads to the addition of longer arms to the core-moiety. Entry 6 and 7 (BisAM:AM = 1:9) clearly display an increase upon higher AM addition. For entry 12 and 13 (BisAM:AM = 1:5) a similar increase is obtained. With mCTA entry 3 (BisAM:AM = 1:7), an initial increase is obtained when observing entry 9 and 10. At higher AM addition (entry 11), however, this increasing trend is disrupted and a slightly lower viscosity compared with entry 10 is obtained. Judging from the large ratio between monomer and mCTA, one might reason that the concentration of mCTA was too low to effectively mediate the polymerisation. The latter could have induced loss of control over the polymerisation, leading to a larger probability
of the concurrent synthesis of linear polymer. Moreover, the results indicate that
increasing the BisAM concentration in the mCTA leads to the synthesis of final
polymers with increasing viscosity at comparable molecular weight. For instance,
increasing BisAM to AM ratio from 0 (entry 5) to 1:5 (entry 12) to 1:3 (entry 14)
yields an increase in solution viscosity at a theoretical molecular weight of approxi-
mately 3.5 MDa (figure 8b). The contribution of the polymers to the viscosity of the
solution was derived from oscillation frequency sweep measurements. From these
measurements, the intrinsic viscosity was obtained according to Martin’s Eq.:\(^{34}\)

\[
\log \frac{\eta_{sp}}{c} = \log [\eta] + k[\eta]c
\]  

(7.11)

where \(\eta_{sp}\) denotes the specific viscosity, \(c\) the polymer concentration, \(k\) the
viscosity slope constant, and \([\eta]\) the intrinsic viscosity. The intrinsic viscosity is
determined as the limit of \(\frac{\eta_{sp}}{c}\), when the polymer concentration approaches zero,\(^{35}\)
as is shown in figure 9a.

The obtained intrinsic viscosities are displayed in 9b. Similar to the viscosity
versus shear rate curves, a higher ratio of monomer to mCTA to yields polymers
with higher intrinsic viscosities (e.g. entry 6 and 7, entry 9 and 10, entry 12 and
13). At comparable theoretical molecular weight, increasing the amount of BA
in the core of the mCTA is found to increase the intrinsic viscosity (illustrated
by entry 4, 7, and 8, as well as 5, 12, and 14). Entry 11 displays a comparable
intrinsic viscosity to entry 10, while the theoretical molecular weight is more than
doubled. This observation subscribes to the theory of loss of control during the
polymerisation (vide supra), originating from the large ratio between monomer and
mCTA.

In figure 10 an overview of the shear resistance for four different polymers is
displayed. Polymer solutions are subjected to an initial shearing phase at 154 s\(^{-1}\),
followed by shearing at high shear rate (1750 s\(^{-1}\)) and finally shearing at 154 s\(^{-1}\).
From figure 10 the shear resistance factor (SRF) is determined for the polymer
solutions according to Eq. 7.4. SB-PAMs display SRFs close to unity, namely 1.00
for entry 10 and 0.99 for entry 14, confirming findings in literature.\(^{20,21,23}\) For the
linear HPAMs, the SRF was found to highly depend on the molecular weight of
the polymer. For entry 15 (3.2 MDa), a SRF of 0.96 is recorded, while entry 16
(11 MDa) shows a significant reduction in viscosity as indicated by a SRF of 0.81,
substantiating previous findings in the literature.\(^{36-38}\)

Next to shearing forces, the salt concentration highly influences the rheological
properties of the polymers. Salt tolerance for 1 wt% solutions of some polymer
solutions at a shear rate of 9.63 s\(^{-1}\) is displayed in figure 11. The initially very
high solution viscosity of entry 16 decreases dramatically upon the addition of salt.
The addition of 10 wt% NaCl results in a viscosity loss of 85%, which supports
the limitations in the application of HPAM in high salinity reservoirs.\(^{39}\) SB-PAMs
7.3. RESULTS AND DISCUSSION

Figure 9: A) Reduced viscosity versus concentration for linear an branched PAM. B) Corresponding intrinsic viscosities

Figure 10: Shear resistance of SB-PAM (entry 10, 1:7 - 4.6 MDa and 14, 1:3 - 3.9 MDa) versus linear HPAM (entry 15, 3.2 MDa and 16, 11 MDa), measured at comparable viscosity at a shear rate of 9.63 s\(^{-1}\)

entry 8 and 14 display a noticeable increase in viscosity upon the addition of salt. The addition of 10 wt% NaCl leads to an increase in viscosity of 53 and 28% respectively. In literature, a few reports are available on the increase of viscosity with ionic strength for PAM solutions. Solution viscosity was found to increase upon addition of 0.5 mol/L Na\(_2\)SO\(_4\).\(^{40}\) Moreover, an increase in intrinsic viscosities of PAM solutions was reported with increasing NaCl concentration to 0.2 and
especially 1.0 mol/L, over a broad range of molecular weights. The superb resistance of SB-PAMs towards salts compared with HPAM illustrates the suitability for application of these polymers in a highly saline environment.

**Figure 11:** NaCl tolerance for entry 8 (1:7 - 2.2 MDa), 14 (1:3 - 3.9 MDa), and 16 (Lin. HPAM - 11 MDa) at a polymer concentration of 1 wt% and a shear rate of 9.63 s⁻¹

### 7.3.3 Flow-cell experiments

Oil recovery from dead-ends was evaluated in a two-dimensional flow-cell, as depicted in figure 5, by evaluating the recovery from chamber 2, 3, and 4, relative to the recovery of a brine (30,000 ppm NaCl) flood. Polymer solutions were prepared with a viscosity comparable to that of the used oil (70 cP at 20°C) at a shear rate of 0.85 s⁻¹ (figure 12).

An overview of the recoveries of the evaluated polymers is depicted in figure 13c - 13j, in which the recoveries from chamber 2, 3, and 4 of the flow-cell (figure 5) are graphically shown. Polymer concentrations and corresponding experimental oil recoveries are demonstrated in figure 14. The storage and loss modulus (G’ and G” respectively) and the corresponding phase angles are depicted in figure 15a and 15b. As shown, actual oil recovery with a brine flood is slightly higher than the modelled recovery (16% versus 10%). With the polymer floods, different oil recoveries ranging from 1.4 to 47.2% were obtained. These differences cannot be explained by differences in the elastic responses of the polymers, in contrast to what has been reported in literature. Polymer mixtures with similar molecular weight, but different elastic responses were evaluated based on oil recovery from a core containing glass beads. Mixtures with a higher elastic response were reported to recover more oil in both secondary recovery and tertiary recovery (succeeding...
7.3. RESULTS AND DISCUSSION

Figure 12: Viscosity versus shear rate curves for flow-cell experiments

A water flood. Moreover, polymer solutions with the least pronounced elastic behaviour displayed the lowest oil recoveries from a two-dimensional flow-cell, however, solutions with the highest elastic response were not found to recover the highest amount of oil.

Figure 13: Flow-cell oil recovery from chamber 2, 3, and 4 (figure 5) at comparable viscosity (70 mPa.s at a shear rate of 0.85 s⁻¹)
Entries 15 and 16, commercial linear HPAMs, display the highest elastic responses, whereas their respective oil recoveries are 4.6 and 1.4%. The high elastic responses of the commercial HPAM can be reasoned in light of their high PDI, which is a direct cause of the elasticity of a polymer solution. In contrast, linear PAM (entry 2, of comparable molecular weight to entry 15) displays the lowest elastic response and recovers 14.9% of oil. The branched PAMs display slight differences in their elasticities.

Elastic response appears to increase with arm length, as shown by entry 8 (1:7 - 2.2 MDa) versus entry 10 (1:7 - 4.6 MDa) and entry 12 (1:5 - 3.5 MDa) versus entry 13 (1:5 - 5.1 MDa). The slightly higher elastic response of entry 14 (1:3 - 3.9 MDa) compared with entry 12 (1:5 - 3.5 MDa) appears to indicate that a higher degree of crosslinking in the core leads to more pronounced elasticity, similar to the observations made in Chapter 6. Despite the differences in elastic response, the branched polymers demonstrate higher oil recoveries than their linear counterparts (commercial linear HPAM and linear PAM synthesised by RAFT polymerisation). An additional 16.5 to 47.2% of oil is recovered compared with the brine flood. In context, with a similar flow-cell 13 and 17-arm comb-polymers containing polyacrylamide arms were found to recover 5 - 25% of the OOIP. However, applied polymer concentrations for the 13 and 17-arm PAM were 4,000 - 5,250 ppm, compared with 5,900 - 8,150 in the present work.

It needs to be stressed that the branched polymers recovered more oil than
their linear counterparts. Especially high recoveries of 40.4 and 47.2% are demonstrated by entry 8 (1:7 - 2.2 MDa) and 10 (1:7 - 4.6 MDa), respectively. Both polymers have a 1:7 ratio of BisAM to AM in the core and different levels of extension. Correspondingly, entry 10 requires a lower polymer concentration in order to afford the same solution viscosity. The latter two polymers, however, do not display pronounced elastic behaviour. While this clearly represents a counterexample of the general statement that the elasticity of the solution is responsible for the oil recovery, further experiments are required to elucidate the root cause of this phenomenon.

### 7.3.4 Filtration experiments

In order to evaluate the permeation of high molecular weight polymers through small pores, filtration experiments were performed. With regard to the applied sandstone cores in the core-floods (vide infra), two different filters with average pore sizes of 3.0 µm and 1.2 µm were selected. Polymers were dissolved in 30,000 ppm NaCl and compared at commensurate viscosity (approximately 15 mPa.s), at a shear rate of 9.63 s\(^{-1}\), which is a relevant shear rate in EOR.\(^{27,45}\) Rheological properties of the solutions are displayed in figure 16, 17a, and 17b. The results of the first screening of polymers, performed with a filter with an average pore size of 3.0 µm, are depicted in figure 18a. As shown all polymers pass the filtration experiment with filtration ratios close to unity (0.94 - 1.11). Differences in throughput time can be ascribed to slight variations in the solution viscosity of the samples, as shown in figure 16. Secondly, experiments were repeated with a filter with an average pore size of 1.2 µm. The results are displayed in figure 18b. Comparable to the wider pore size filter, all samples manage to pass the test (FR

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**Figure 15:** a) Dynamic viscosity measurements for flow-cell experiments. b) Corresponding phase angles
CHAPTER 7. EVALUATION OF BRANCHED PAMS

Figure 16: Viscosity versus shear rate curves for filtration experiments

Figure 17: a) Dynamic viscosity measurements for filtration experiments. b) Corresponding phase angles ≤ 1.230) and display similar filtration ratios (0.97 - 1.12). The latter observation indicates the applicability of these polymers in the core-flood experiments (vide infra), as the applied porous media has average pore sizes ranging from 5.40 - 9.11 μm (table 3). Prior to application in reservoirs with smaller pore size, additional filtration experiments have to be performed in order to evaluate the suitability of these polymers.

7.3. RESULTS AND DISCUSSION

Figure 18: Effluent weight recorded as function of time with filters with different average pore sizes (a) 3.0 µm, (b) 1.2 µm. Filtration ratio (FR) was calculated as described in Eq. 7.6

Figure 19: Viscosity versus shear rate curves for core-flood experiments

7.3.5 Core-flood experiments

Ultimately, the performance of the SB-PAMs in recovering oil from actual sandstone was evaluated. Core-flood experiments were performed with entry 2 (Lin. PAM - 2.6 MDa, 11,950 ppm), 9 (1:7 - 2.0 MDa, 11,000 ppm), 10 (1:7 - 4.6 MDa, 8,400 ppm), and 16 (Lin. HPAM - 11 MDa, 5,200 ppm). In these experiments, Bentheim sandstone (cylindrical, 5 x 30 cm) was saturated with oil, after which a brine flood (30,000 ppm NaCl) was performed until the oil cut was below 0.5 vol%. Subsequently, a polymer flood was performed at the same ionic strength.
7.3. RESULTS AND DISCUSSION

Figure 18: Effluent weight recorded as function of time with filters with different average pore sizes (a) 3.0 µm, (b) 1.2 µm. Filtration ratio (FR) was calculated as described in Eq. 7.6

Figure 19: Viscosity versus shear rate curves for core-flood experiments

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Polymer solutions were matched to the oil (122 mPa.s at 20°C) based on their viscosity at a representative shear rate of 9.63 s⁻¹.²⁷,⁴³ Rheological properties of the polymers are shown in figure 19, 20a, and 20b. The linear HPAM (entry 16) displays the highest degree of shear thinning, as expected because of its high molecular weight. Similarly, entry 10, having longer arms, shows to a greater extent pseudoplastic behaviour compared with entry 9. Linear PAM (entry 2) displays apparent Newtonian behaviour up to shear rates of 10 s⁻¹, followed by shear thinning, albeit to a lesser degree than for the other entries. The low polymer concentration required for the linear HPAM, can be ascribed to its significantly higher molecular weight. Furthermore, entry 10 requires a lower concentration than entry 9 to afford the same viscosity, illustrating the effect of the arm length and thus molecular weight on the viscosity. The highest concentration is required for linear PAM, stemming from the relatively low molecular weight. Compared with entry 9, the molecular weight is higher, however, the required concentration is higher as well. This illustrates the advantages of introducing branches in order to afford viscosity (Chapter 4). The linear PAM displays the least pronounced elastic response, followed by entry 9 and 10. The linear HPAM displays the highest elastic response, attributed to its high molecular weight, as reported for polystyrene in the melt,⁴⁴ as well as HPAM.⁴⁵

Properties of the applied sandstone cores are listed in table 3. The brine permeability was found to significantly vary between the different cores. In that context, the core applied for entry 9 displays the lowest brine permeability and correspondingly the lowest oil saturation. For entry 10 and 16, oil recovery as a function of pore volumes injected is displayed in figure 21. In both experiments, similar oil recoveries are obtained with the brine flood. The polymer flood with SB-PAM entry
7.3. RESULTS AND DISCUSSION

Table 3: Oil recovery results from core-flood experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Core sample</th>
<th>Polymer conc. (ppm)</th>
<th>Brine perm. (mD)</th>
<th>Oil sat. a (% of PV)</th>
<th>Oil Oil sat. b (% of PV)</th>
<th>Oil recovery c (% OOIP)</th>
<th>Oil maximum Δ, PFD</th>
<th>r-pore average (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Bentheim</td>
<td>8,400</td>
<td>1,435</td>
<td>85</td>
<td>48</td>
<td>6.0</td>
<td>0.7</td>
<td>5.8</td>
</tr>
<tr>
<td>16</td>
<td>Bentheim</td>
<td>5,200</td>
<td>1,008</td>
<td>85</td>
<td>49</td>
<td>3.6</td>
<td>0.9</td>
<td>5.8</td>
</tr>
<tr>
<td>9</td>
<td>Bentheim</td>
<td>11,000</td>
<td>886</td>
<td>61</td>
<td>25</td>
<td>6.7</td>
<td>0.4</td>
<td>5.4</td>
</tr>
<tr>
<td>2</td>
<td>Bentheim</td>
<td>11,950</td>
<td>2,525</td>
<td>83</td>
<td>49</td>
<td>5.4</td>
<td>0.7</td>
<td>9.1</td>
</tr>
</tbody>
</table>

*a The oil saturation to begin the experiment

*b The oil saturation after the brine flood

*c Oil recovery based on Eq. 7.9

*d The maximum pressure drop during the polymer flood

The brine flood is performed with 30,000 NaCl

10 manages to recovery an additional 6.0% of oil, while with the linear HPAM (entry 16) 3.6% additional oil is recovered. The maximum pressure drop for the former experiment is 0.7 bars, while for the latter 0.9 bars was recorded. Therefore, despite the lower pressure drop over the core, the SB-PAM manages to recover more oil from the core. The linear HPAM, however, requires a lower polymer concentration due to its high molecular weight. The oil recovery for linear PAM (entry 2) and a low molecular weight SB-PAM (entry 9) is illustrated in figure 22. Significant differences in the oil recovery with the brine flood are reported, stemming from the relatively low permeability of the core applied for entry 9. Despite the lower permeability, a significantly lower pressure drop is recorded for the SB-PAM compared with the linear PAM. Moreover, the polymer concentration of the former is lower, while the oil recovery is higher (6.7 versus 5.4%). These results are especially promising when taking into account the low oil saturation after the brine flood of only 24.8%, making it significantly more difficult to recover oil. The latter effect is confirmed by core-flood experiments in literature, whereby significantly less oil was recovered from cores with a lower permeability. Similarly, more oil was recovered from a high permeability core than a low permeability core in a dual core setup. Moreover, because of the lower permeability it can be reasoned that the actual porosity of the core applied in the core flood experiments with entry 9 was lower than calculated for this type of core. Therefore, the actual relative recovery is expected to be higher.

Interestingly, the linear polymers display higher pressure drops over the cores. An increase in pressure might be caused by the formation of a cake on the face of the core. However, Dehghanpour et al. attributed higher recoveries to the formation of
Figure 21: Oil recovery from sandstone cores with entry 10 [10] and entry 16 [16]

Figure 22: Oil recovery from sandstone cores with entry 2 [2] and entry 9 [9]

an "internal cake" (frictional pressure drop\textsuperscript{48}) which ultimately improves volumetric or macroscopic sweep efficiency during the polymer flood in porous media.\textsuperscript{49} The former research concluded that fluids with higher elasticity exhibit a higher pressure drop, similar to linear HPAM entry 16. In their observations, however, the polymer solution which displayed a higher pressure drop recovered more oil. Similar observations were reported by Urbissinova et al, who experienced improved EOR with highly elastic polymers compared to low elastic polymers, even though shear viscosities were identical.\textsuperscript{50} A third explanation for the higher pressure drop is an increased thickness in the adsorbed polymer layer throughout the core for the
7.4 Conclusions

In the present study star-like branched polyacrylamides (SB-PAMs) with molecular weights ranging from 1.3 to 12 MDa were compared with linear polyacrylamides (PAMs) on their performance in enhanced oil recovery (EOR). The former polymers were found to afford higher solution viscosity than the latter, at comparable molecular weight. Moreover, intrinsic viscosity was found to increase with the amount of crosslinker in the core of the polymer, as well as arm length of the polymer. The latter trend, however, was limited when aiming at very high molecular weight, because of loss of control originating from the high ratio between core and monomer. Flow-cell experiments demonstrated the effect of branching on oil recovery from dead ends. The SB-PAMs displayed superior performance and required lower concentrations than a linear reference polymer. Where the linear reference polymer managed to recover 15% of the oil, 17 to 47% was reported for the branched polymers. Interestingly, no correlation between elastic response and oil recovery was found in these experiments. In core-flood experiments, SB-PAMs were set in direct comparison to a linear PAM and a high molecular weight linear HPAM. The SB-PAMs displayed the highest oil recoveries and the lowest pressure drops over the sandstone cores. However, a lower polymer concentration was required for the HPAM, due to its high molecular weight. The SB-PAMs passed the filtration experiments and good salt and shear resistance was recorded, while the solution viscosity of HPAM was found to decrease after a phase of shearing and addition of salt. Therefore, the currently evaluated polymers are especially of interest for the application in medium permeable and high salinity reservoirs. The results demonstrate the usefulness of the introduction of branching in the topology of the polymer, when envisioning the application in EOR.

7.5 Acknowledgement

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Thermoresponsive Comb Polymers as Thickeners for High Temperature Aqueous Fluids