Chapter 4

Control over the viscoelasticity of aqueous polyacrylamide solutions by tailoring the polymer architecture

Abstract

The controlled synthesis of high molecular weight comb-like polyacrylamide (PAM) has been accomplished using atomic transfer radical polymerization (ATRP) of acrylamide (AM) in water at room temperature. The number and length (molecular weight) of the arms was varied. In addition, the overall molecular weight of the macromolecule was also varied (i.e. macromolecules with equal number of longer arms). Halogen-functionalized aliphatic polyketones acted as macronitiators in the polymerization. The obtained branched polymers were used in water solutions to study the effect of the molecular architecture on the rheological properties. For comparison purposes, linear PAM was synthesized using the same procedure. The intrinsic viscosities and light scattering data suggest that the 13- and 17-arm PAMs are more extended compared to the linear, 4- and 8-arm analogues. The comparison of linear, 4-, 8-, 12-, 13- and 17-arm PAM in semi-dilute solutions demonstrated that the 13- and the 17-arm have the highest solution viscosity at equal molecular weight. Depending on the PAM molecular weight and concentration, a significant (as much as 5-fold) increase in solution viscosity (at a shear rate of 10 s⁻¹) is observed. The elastic response of aqueous solutions containing the polymers critically depended on the molecular architecture. Both the 4- and 8-arm polymers displayed a larger phase angle value compared to the linear analogue. The 13- and 17-arm PAMs displayed a lower phase angle than the linear one. Ultimately, the rheological properties are dependent on the number of arms present. The combination of a higher hydrodynamic volume and higher
entanglement density leads to an improved thickening efficiency (for number of arms \( N \geq 13 \)). The improved thickening efficiency of the branched \( N \geq 13 \) PAMs makes these polymers highly interesting for application in Enhanced Oil Recovery.

4.1. Introduction

Polyacrylamide (PAM) is a versatile industrial polymer that finds use in wastewater treatment, cosmetics and enhanced oil recovery (EOR)\(^1\). In particular, the main purpose of using PAM (mostly in water solution) resides in the corresponding improvement of the rheological properties. Indeed, in most applications, an enhancement of the solution viscosity is required. However, in EOR, it has been concluded that, at equal viscosity, the viscoelasticity of the solution plays a crucial role in ensuring a high oil recovery\(^2\)-\(^7\). Such rheological behavior arises from the extremely high molecular weight (typically \(M_w \approx 2 \cdot 10^7 \text{ g/mol}\)) and the ionic character of the water soluble polymer employed. The presence of electric charges along the backbone results (in deionized water) in the stretching of the polymer chains/coils and ultimately in larger viscosity values. In this context, the use of partially hydrolyzed PAM (HPAM) represents the most popular choice. The importance of the solution elastic response has been supposedly demonstrated\(^2\)-\(^7\) by comparing a water solution of HPAM and one of glycerin in flow experiments specifically designed to simulate oil recovery processes. However, such comparison might be not completely correct since HPAM is a high molecular weight polyelectrolyte while glycerin a small molecule. Such difference in structure of the used chemicals as well as of the corresponding water solution might indeed result in differences also in other properties (e.g. surface tension between oil and water), thus hindering a direct correlation of the observed effect and the supposed cause, in this case the elastic behavior of the water solution. A better comparison would be between polymeric solutions where the viscoelasticity is systematically changed. However, for water soluble PAM a systematic change in the elastic response without affecting other properties (i.e. molecular weight and dispersity) is difficult. One approach can be the controlled synthesis of PAM. However, the monomer itself (acrylamide) represents a difficult candidate to polymerize in a controlled fashion.\(^8\)

Controlled synthesis of branched PAM has only limitedly been reported in literature. In the past, high conversion and high temperature in conventional free radical polymerization was demonstrated to lead to uncontrolled branched polyacrylamide.\(^9\)-\(^14\) By increasing the reaction temperature (from room temperature to 90 °C) and the conversion level of acrylamide, more branches could be obtained.\(^10\) The properties of the uncontrolled branched PAM were evaluated with respect to their ability to perform as flocculants, and it was concluded that linear PAM performed better than the uncontrolled branched PAM. This was attributed to the inherent lower hydrodynamic volume of the branched PAM.\(^13\), \(^14\) Nevertheless, given the uncontrolled
nature of the polymerization procedure, a mixture of products is synthesized with no well-defined structure. Controlled radical polymerization for the preparation of hyperbranched PAM has been recently reported.\textsuperscript{15} The hyperbranched PAMs were synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. Although the polymerization is a controlled one, the branching occurs randomly.\textsuperscript{15} Therefore the control in architecture of the PAM is limited and no correlation between molecular architecture and rheological properties can be obtained.

Recently controlled synthesis of PAM has been reported in water-ethanol mixtures\textsuperscript{16} and, by our group, in water.\textsuperscript{17} In a water-ethanol mixture, linear PAM (with molecular weights up to \textasciitilde350 000 g/mol and dispersities as low as 1.10) could be synthesized.\textsuperscript{16} The molecular weights of PAM reached values >150 000 g/mol (with dispersities as low as 1.39) in water using the same catalyst/initiation system.\textsuperscript{17} With the accomplishment of atomic transfer radical polymerization (ATRP) of acrylamide, the controlled preparation of branched PAM can be envisaged. This enables the systematic study of the structure-property relationships of PAM (with different topologies) in water solutions. The aim of this work is to prepare in a controlled fashion branched PAM with varying numbers (and molecular weight) of arms and to investigate the effect of the architecture on the rheological properties of the corresponding water solutions. To the best of our knowledge, this represents an absolute novelty, in terms of synthetic strategy as well as structure-property relationship, of the present chapter.

4.2. Experimental section

\textbf{Chemicals.} Acrylamide (AM) (electrophoresis grade, \textasciitilde99\%), PAM (M\textsubscript{w} = 5-6\texttimes10\textsuperscript{6} g/mol), tris[2-(dimethylamino)ethyl]amine (Me\textsubscript{6}TREN), 2,2-bipyridine (bpy), copper(I) chloride (CuCl, 98\%), copper(I) bromide (CuBr, 98\%), methyl 2-chloropropionate MeClPr, 97\%), 3-chloropropylamine hydrochloride (98\%), and sodium hydroxide (pellets) were purchased from Sigma Aldrich. CuCl and CuBr were purified by stirring in glacial acetic acid (Aldrich), washing with glacial acetic acid, ethanol and diethyl ether (in that order) and then dried under vacuum. All solvents were reagent grade and used without further purification. The alternating polyketones with 30 mol\% ethylene content (PK30, M\textsubscript{n} = 2800 g/mol, PDI = 1.74) was synthesized according to a published procedure.\textsuperscript{18, 19}

\textbf{Macroinitiators.} The PK30 functionalization was performed according (Scheme 4.1) to the published method.\textsuperscript{20} 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.

**Scheme 4.1: Synthesis of the macro-initiators**

For the preparation of PK30-Cl\textsubscript{12} (taken here as representative 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, 0.076 mol of di-carbonyl 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 functionalization degree) or a brown powder (high functionalization degree), was finally freeze dried and stored at -18 °C until further use. Some properties of the macro-initiators are given in Table 4.1. The macro-initiators were characterized using elemental analysis and \textsuperscript{1}H-NMR spectroscopy (in chloroform). The conversion of carbonyl groups of the polyketone was determined using the following formula:

\[
x_{CO} = \frac{2y}{x+2y} \cdot 100 = \frac{\left(\frac{2(N\text{(wt.\%)}_{\text{mol}_N})}{\text{mol}_N}\right)}{\left(\frac{C(\text{wt.\%})}{\text{mol}_C}\right) + \left(\frac{N(\text{wt.\%})}{\text{mol}_N}\right) + \left(\frac{N\text{(wt.\%)}_{\text{mol}_N}}{n_{C}^{m-n}}\right)} + \left(\frac{2(N\text{(wt.\%)}_{\text{mol}_N})}{\text{mol}_N}\right)} \cdot 100 \quad (4.1)
\]

\(n_{C}^{m-n} = 3.7,\) the average number of carbons in \(n-m\) (see Scheme 4.1)  
\(n_{C}^{m} = 10.4,\) the average number of carbons in \(m\) (see Scheme 4.1)  
\(\text{mol}_N =\) molecular weight of nitrogen  
\(\text{mol}_C =\) molecular weight of carbon
The average number of pyrrole units was determined using the conversion of the carbonyl groups of the polyketone and formula 4.2:

\[
N_{\text{pyrrole units}} = \left( \frac{M_{PK}}{M_{\text{repeating unit PK}}} \right) \cdot x_{CO} \tag{4.2}
\]

\[M_{PK} = \text{the average molecular weight of the parent (unmodified) polyketone}\]
\[M_{\text{repeating unit PK}} = \text{the average molecular weight of the repeating unit of polyketone}\]

**Comb polymerization.** A 250-mL three-necked flask was charged with the macro-initiator. Sufficient acetone (typically 5-10 ml) was added to dissolve the macro-initiator. Demineralized water and acrylamide 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. CuX \((X=\text{Cl, Br})\) 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 \((\text{Me}_6\text{TREN})\) using a syringe. After the pre-set reaction time, the mixture was exposed to air and the polymer was precipitated in a tenfold amount of methanol. For the higher molecular weight polymers the solution was first diluted with demineralized water before being precipitated. The polymer was isolated by filtration and subsequently dried in an oven at 65 °C.

As mentioned before, for the comb-shaped PAMs, the length and number of arms was varied (Figure 4.1).

![Figure 4.1: Schematic overview of the different architectures of the comb-shaped PAMs](image)

**Figure 4.1:** Schematic overview of the different architectures of the comb-shaped PAMs
Characterization. The acrylamide conversion was measured by using Gas Chromatography (GC). Several different samples directly taken from the reaction mixtures were dissolved in acetone (polymer precipitates) and injected on a Hewlett Packard 5890 GC with an Elite-Wax ETR column. The overall molecular weight ($M_{n,overall}$) is calculated using the acrylamide conversion (monomer-initiator ratio multiplied by the conversion value). The span molecular weight ($M_{n,SPAN}$) is calculated using the $M_{n,overall}$ and is defined as two times the molecular weight of one arm (star PAM) or two times the molecular weight of one arm plus the molecular weight of the macro-initiator (comb PAM).

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. For analysis chloroform was used as the solvent.

The particle sizes of the different polymers were measured using a Brookhaven ZetaPALS zeta potential and particle size analyzer. Dilute (polymer concentration < 0.1 wt. %) aqueous solutions were prepared and filtered prior to the measurement. The laser angle for the measurements was set at 90 ° and a total of 10 runs were performed for each sample (the reported value is the average).

The macroinitiators were analyzed by GPC using THF (used as received) as the eluent with toluene as a flow marker. The analysis was performed on a Hewlett Packard 1100 system equipped with three PL-gel 3 μm MIXED-E columns in serie. The columns were operated at 42 °C with a flowrate of 1 ml/min, and a GBC LC 1240 RI detector was used at 35 °C. The apparent molecular weights and dispersities were determined using polystyrene standards and WinGPC software (PSS).

Cryo-Transmission Electron Microscopy (cryo-TEM). A drop of the polymer solution was placed on a glow discharged holey carbon-coated grid. After blotting away the excess of solution, the grids were rapidly plunged into liquid ethane. The frozen specimen were mounted in a Gatan (model 626) cryo-stage and examined in a Philips CM 120 cryo-electron microscope operating at 120 kV. Micrographs were recorded under low-dose conditions.

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.

The viscosity function of the different polymeric solutions was modeled using the Carreau-Yasuda model^{21, 22} (equation 4.3).

\[
\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda \cdot \gamma)^a\right]^{\frac{n-1}{a}}
\]  

(4.3)

where \(\eta\) is the viscosity, \(\eta_0\) is the zero shear rate viscosity, \(\eta_\infty\) is the viscosity at infinite shear rate, \(1/\lambda\) is the critical shear rate for the onset of shear thinning, \(n-1\) is the power law slope and \(a\) represents the width between \(\eta_0\) and the power law region.

### 4.3. Results and discussion

**Macroinitiators.** The synthesis of the macroinitiators was performed according to the Paal-Knorr reaction (Scheme 4.1) of a halogenated primary amine with aliphatic perfectly alternating polyketones. The carbonyl conversion was determined using elemental analysis (Table 4.1).

**Table 4.1: 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_{CO}) (%)(^{b})</th>
<th>Pyrrole units(^c)</th>
<th>(M_n,GPC)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30 (virgin)</td>
<td>67.0 : 8.4 : 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(_{12})</td>
<td>64.2 : 7.8 : 4.6</td>
<td>55.10</td>
<td>12</td>
<td>2 093</td>
<td>1.76</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>
<tr>
<td>PK30-Cl(_{17})</td>
<td>73.7 : 7.9 : 6.1</td>
<td>81.27</td>
<td>17</td>
<td>2 117</td>
<td>2.18</td>
</tr>
</tbody>
</table>

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

\(\(b\) Carbonyl groups conversion as define by equation (4.1)\)

\(\(c\) Average number of pyrrole units per chain as defined by equation (4.2)\)

Resonance peaks corresponding to the pyrrole units were observed with \(^1\)H-NMR spectroscopy at \(\delta\) 5.68 ppm while the \(\alpha-, \beta-, \) and \(\gamma\)-hydrogens (relative to the halogen) were detected at \(\delta\) 3.51, 1.95, and 3.86 ppm respectively (Figure 4.2). The formation of the pyrrole units was also previously demonstrated using model compounds.\(^{20}\) As can be observed in Figure 4.2,
the resonance of the pyrrole, $\alpha$- and $\gamma$-hydrogens (relative to the halogen) all increase in magnitude with the conversion of the Paal–Knorr reaction.

The obtained, chemically modified polyketones are used as macro-initiators in the ATRP of acrylamide for the preparation of comb-polymers with different number of side chains.

**Figure 4.2:** H-NMR spectra of virgin polyketone and the macroinitiators at different conversion levels of the Paal–Knorr reaction

**Comb polymerization.** The synthesis of the comb-shaped PAM was performed according to Scheme 4.2. The ratio between the (macro)initiator and the monomer was varied in order to synthesize comb-shaped and linear PAM with different molecular weights. Table 4.2 lists the results for the different polymers prepared. The reaction of all the halogen sites on the macroinitiator has already been demonstrated (*Chapter 3*).

As can be observed in Table 4.2, high molecular weight branched PAM can be synthesized. An increase in the monomer:macroinitiator ratio leads to higher average molecular weights. The conversion of acrylamide is suppressed when a low amount of the co-solvent (acetone) is used. Similar results were reported for the ATRP of acrylamide in water-ethanol mixtures, where an optimum exists (30:70, ethanol-water) for the controlled polymerization. In addition, the viscosity of the reaction mixtures increases rapidly during the polymerization from water to gel-like solid within 15
minutes. Therefore, from that point on, mass transfer limitations might play a role in the low conversion of acrylamide.

**Scheme 4.2: Synthesis of the comb PAMs**

![Scheme 4.2](image)

The dispersities of entries 1, 4, 7 and 10 (PDI < 2.5) could be directly determined by GPC. The molecular weights of the rest of the entries fall outside the measurable range of the GPC and are therefore difficult to measure. However, as will be evident later (Figure 4.9 and 4.10), the dispersities of the higher molecular PAMs are also relatively low. Indeed, the slopes of $G'$ and $G''$ in the terminal zone (on a double logarithmic scale) are 2 and 1 respectively, which is in line with other narrow-distributed polymers.²³

**Table 4.2: Characteristics of the (co)polymers**

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Entry</th>
<th>$[M]_0:[I]_0:[CuCl]_0: [Me₆TREN]_0$</th>
<th>M/s1/s2 ($)</th>
<th>T; Time (min)</th>
<th>Conv. (%)</th>
<th>$M_n, overall$</th>
<th>$M_n, SPAN$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>1</td>
<td>14 399:1:1.5:1.5:1.5</td>
<td>1:6:0</td>
<td>25 °C;15</td>
<td>50.8</td>
<td>519 928</td>
<td>519 928</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>50 942:1:1.5:1.5:1.5</td>
<td>1:6:0</td>
<td>25 °C;25</td>
<td>42.1</td>
<td>1 524 432</td>
<td>1 524 423</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>57 654:1:1.5:1.5:1.5</td>
<td>1:6:0</td>
<td>25 °C;60</td>
<td>62.0</td>
<td>2 540 789</td>
<td>2 540 789</td>
</tr>
<tr>
<td>4-arm</td>
<td>4</td>
<td>14 894:1:3.0:3.0:3.0</td>
<td>1:4:1/5</td>
<td>25 °C;60</td>
<td>69.9</td>
<td>743 019</td>
<td>374 307</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37 707:1:1.5:1.5:1.5</td>
<td>1:4:1/10:25 °C;60</td>
<td>65.4</td>
<td>1 613 401</td>
<td>809 498</td>
<td></td>
</tr>
<tr>
<td>8-arm</td>
<td>6</td>
<td>10 037:1:3.0:3.0:3.0</td>
<td>1:4:1/10:25 °C;60</td>
<td>48.8</td>
<td>1 730 784</td>
<td>435 493</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>49 822:1:3.0:3.0:3.0</td>
<td>1:4:1/10:25 °C;60</td>
<td>88.1</td>
<td>631 116</td>
<td>160 576</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>12 019:1:1.5:1.5:1.5</td>
<td>1:6:1/3</td>
<td>25 °C;60</td>
<td>68.8</td>
<td>587 766</td>
<td>100 758</td>
</tr>
<tr>
<td></td>
<td>9ᵇ</td>
<td>47 610:1:1.5:1.5:1.5</td>
<td>1:6:1/5</td>
<td>25 °C;60</td>
<td>35.7</td>
<td>1 208 130</td>
<td>204 152</td>
</tr>
<tr>
<td>13-arm</td>
<td>10</td>
<td>100 050:1:3.0:3.0:3.0</td>
<td>1:4:1/20:25 °C;60</td>
<td>23.8</td>
<td>1 692 550</td>
<td>263 189</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>149 634:1:3.0:3.0:3.0</td>
<td>4:15:1/20:25 °C;60</td>
<td>23.6</td>
<td>2 510 092</td>
<td>388 965</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>150 084:1:2.0:2.0:2.0</td>
<td>1:4:1/40:25 °C;60</td>
<td>32.8</td>
<td>3 499 094</td>
<td>541 119</td>
<td></td>
</tr>
<tr>
<td>17-arm</td>
<td>13</td>
<td>149 859:1:3.0:3.0:3.0</td>
<td>2:15:1/20:25 °C;60</td>
<td>14.8</td>
<td>1 576 493</td>
<td>188 267</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>150 174:1:1.5:1.5:1.5</td>
<td>1:2:1:20:25 °C;60</td>
<td>23.8</td>
<td>2 540 500</td>
<td>301 679</td>
<td></td>
</tr>
</tbody>
</table>

a. M/s1/s2 = Monomer / solvent 1 / solvent 2 = Acrylamide / water / acetone
b. 12-arm
The experimental conditions can be designed in such a way that branched PAM with similar molecular weights but different number of arms (i.e. shorter armlength) and relatively low dispersities can be prepared using ATRP in water (and water-acetone mixtures). This allows the investigation of the effect of the number of arms on the rheological properties of these polymers in water solutions.

**Cryo-TEM, semi-dilute solutions.** Aqueous solutions of the branched polymers were investigated using cryo-TEM. A typical cryo-TEM picture (of the branched PAMs) is displayed in Figure 4.3.

![Cryo-TEM image](image)

**Figure 4.3:** Cryo-TEM image (scale bar is 100 nm) of branched PAM, entry 10 ([p] = 0.5 wt.%)

The darker spheres with a diameter of on average approximately 5 nm are assumed to be the polyketone backbone of the branched PAMs (not present in the cryo-TEM picture of the linear analogue, not shown for brevity). The average area (in nm²) available for each arm can be computed by dividing the surface area of the central backbone (based on a sphere with a diameter of 5 nm) with the number of arms. The surface area available per arm significantly decreases as the number of arms increases. The decrease in surface area will lead to an increase in the steric hindrance for the polymeric arms close to the backbone.

With this, it can be envisaged that if a high number of arms are present the polymeric arms will be more extended (especially close to the backbone) compared to a polymer with a lower number of arms. More evidence to support this hypothesis is provided by the higher values of intrinsic viscosity.
for the polymers with a high \( N \geq 13 \) number of arms (as will be evident in the following section). A similar behavior has been observed for PAM grafted dextran.\(^{24}\)

**Intrinsic viscosity, effect of the number of arms (at equal overall molecular weight).** The intrinsic viscosity can be used to investigate the dilute solution properties of the architecturally different polymers. The intrinsic viscosity of entries 2, 5, 7, 10, and 13 were determined using Martin’s\(^{25}\) equation:

\[
\text{log} \left( \frac{\eta_{sp}}{c} \right) = \text{log} [\eta] + k \cdot [\eta] \cdot c
\]  

(4.3)

where \( \eta_{sp} \) is the specific viscosity, \( k \) is the slope of the viscosity-concentration-plot, \( c \) is the polymer concentration and \([\eta]\) is the intrinsic viscosity. The intrinsic viscosity is obtained by extrapolating the plot of the specific viscosity over concentration as a function of the concentration to \( c = 0 \) (Figure 4.4).

As can be observed in Figure 4.4, the intrinsic viscosity is a function of the degree of branching. The intrinsic viscosities of the linear, 4- and 8-arm are the same within the experimental error. Remarkably, the intrinsic viscosities of the 13- and 17-arm PAMs are significantly higher than the values found for the 8- and 4-arm PAMs. This is strong evidence that the highly branched PAMs \( (N \geq 13) \) are more extended in solution compared to the PAMs with a low degree of branching \( (N \leq 8) \).

**Figure 4.4:** (A) Reduced viscosity as a function of the concentration using Martin’s equation for entries 2, 5, 7, 10, and 13
Figure 4.4, continued: (B) Intrinsic viscosity for entries 2, 5, 7, 10, and 13

Solution viscosity, effect of the number of arms (at equal polymer volume fraction and overall molecular weight). The rheological comparison between the branched PAM polymers is conveniently carried out at equal polymer volume fraction ($\varphi_s = c/c^*$), with $c$ being the polymer concentration and $c^*$ the critical overlap concentration. This can be defined as\textsuperscript{26-28}:

$$c^* = \frac{3M}{4\pi R_h^3 N_{av}} = \frac{3M\rho^3}{4\pi R_g^3 N_{av}}$$  \hspace{1cm} (4.4)$$

with $M = \text{molecular weight}$, $R_h = \text{hydrodynamic radius}$, $R_g = \text{radius of gyration}$, $N_{av} = \text{Avogadro constant}$.

The radius of gyration ($R_g$) of the comb polymers is estimated (Table 4.3) using the model developed by Daoud and Cotton\textsuperscript{29} for star shaped polymers (equation 4.5).

$$R_g \sim D_p^{3/5} \cdot v^{1/5} \cdot N^{1/5} \cdot l$$  \hspace{1cm} (4.5)$$

with $D_p = \text{number of monomer units}$, $v = \text{monomer excluded volume parameter}$, $N = \text{number of arms}$, and $l = \text{length of each monomeric unit}$.

For the linear polymer, used in the comparisons, the $R_g$ is found in literature\textsuperscript{30, 31} for a similar size (molecular weight) PAM.
In order to carry out the measurements well above the overlap concentration, and maintain an equal excluded volume, the comparison of the architecturally different polymers is carried out at 5 times the $c^*$. Higher values are not tested given the difficulty in measuring the viscosity accurately for the highly branched PAMs (gelation).

As mentioned before, the comparison between the architecturally different polymers are performed at equal polymer volume fraction in order to investigate the effect the branching has on the solution properties of PAM. The zero shear rate viscosity ($\eta_0$) is determined by oscillation experiments using equation 4.6:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}$$

with $G''$ = loss modulus, $\omega$ = frequency. The $\eta_0$ is plotted against the molecular architecture in Figure 4.5, at a polymer concentration of $5 \cdot c^*$. As can be observed, the results suggest that the number of arms does affect in that a higher $\eta_0$ is obtained with more arms.

The viscoelasticity of the architecturally different polymers at equal excluded volume ($5 \cdot c^*$) was evaluated through oscillation measurements (Figure 4.6). For low number of arms (4 & 8), a lower elastic response, compared to a linear PAM, is observed. The elastic response is higher (compared to a linear analogue) when the number of arms is high, i.e. 13 & 17. According to literature for polymer melts, $\eta_0$ is exponentially dependent on the molecular weight of the arms and the effect of the number of arms becomes saturated above 4 arms. It is also predicted by a model for comb shaped polymers in the melt that the highest $\eta_0$ are obtained with comb polymer having low number of long arms. However, the results in aqueous solution (Figure 4.5 & 4.6) are not in agreement with these predictions. The discrepancy might lie in the difference in concentration regime (melt vs. semi-dilute), and the fact that associations (Chapter 3) can

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Table 4.3: Properties of the different (co)polymers

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Entry</th>
<th>$R_g, \text{ est} ,(\text{nm})$</th>
<th>$R_h, \text{ DLS} ,(\text{nm})$</th>
<th>$C_{\text{ext}} ,(\text{wt} %.)$</th>
<th>$5 \cdot C_{\text{ext}} ,(\text{wt} %.)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>2</td>
<td>88$^a$</td>
<td>48</td>
<td>0.09</td>
<td>0.45</td>
</tr>
<tr>
<td>4-arm</td>
<td>5</td>
<td>72</td>
<td>36</td>
<td>0.17</td>
<td>0.85</td>
</tr>
<tr>
<td>8-arm</td>
<td>8</td>
<td>57</td>
<td>51</td>
<td>0.36</td>
<td>1.80</td>
</tr>
<tr>
<td>13-arm</td>
<td>10</td>
<td>61</td>
<td>60</td>
<td>0.44</td>
<td>2.20</td>
</tr>
<tr>
<td>17-arm</td>
<td>14</td>
<td>40</td>
<td>71</td>
<td>0.96</td>
<td>4.80</td>
</tr>
</tbody>
</table>

$a.$ Taken from literature$^{30}$
arise in the aqueous solution due to the hydrophobic backbone. In addition, unlike in the melt, in water solution hydrogen bonding (between the solvent and polymer) might play a significant role in rheological properties.

![Graph showing viscosity as a function of molecular architecture](image)

**Figure 4.5**: $\eta_0$ as a function of the molecular architecture at $M_{n,overall} \approx 1.6$ MDa and a polymer concentration of $5\cdot c^*$

![Graph showing G' and G''](image)

**Figure 4.6**: The $G'$ and $G''$ (A) and the phase angle (B) as a function of the frequency for the different polymers at a polymer concentration of $5\cdot c^*$

**Solution viscosity, effect of the number of arms (at equal concentration and overall molecular weight)**. The effect of the number of arms on the solution viscosity has been evaluated. The solution viscosity (at $\dot{\gamma} = 10$ s$^{-1}$) as a function of concentration has been measured, while maintaining the overall molecular weight constant (Figure 4.7).
Figure 4.7: Viscosity (measure at $\dot{\gamma} = 10$ s$^{-1}$) as a function of concentration for different overall molecular weights (A, 0.6 MDa, B, 1.6 MDa and C, 2.6 MDa)

As can be observed, the solution viscosity of the 13- and 17-arm branched PAM is systematically the highest at all molecular weights. The PAM polymers can also be compared as a function of shear rate. In Figure 4.8A, such a comparison is made where the concentration of the polymer is kept constant but the number of arms is varied.

The viscosity function in Figure 4.8A is modeled using the the “Carreau-Yasuda” model\textsuperscript{21, 22} in order to evaluate the relaxation time ($\lambda$). In the melt, the molecular weight\textsuperscript{35, 36}, dispersity index\textsuperscript{35, 36}, and polymer concentration\textsuperscript{22} (in solution) are parameters that influence $\lambda$. As can be observed in Figure 4.8B, the molecular architecture has a pronounced effect on the relaxation time ($\lambda$) in that a higher number of branches leads to a higher $\lambda$.

An increase in the relaxation time also affects the extent of shear thinning behavior. As can be observed in Figure 4.8A, a solution containing PAM with 13 or 17 arms display the most pronounced shear thinning behavior.
The onset of non-Newtonian behavior (in this case shear thinning) is also affected by branching. As can be observed in Figure 4.8A, the critical shear rate for the onset of shear thinning is lower for the 17 and 13-arm PAMs compared to their linear analogue. This is confirmed by the value of $1/\lambda$ (not shown for brevity) and in line with earlier studies on branched polyisoprenes$^{37}$ and polybutadienes$^{38, 39}$, which concluded that the critical shear rate for the onset of non-Newtonian behavior is reduced upon branching.

Figure 4.8: A; Viscosity function for PAMs (entries 2, 5, 7, 10 and 13; polymer concentration of 3.85 wt.%), lines correspond to fits of the “Carreau-Yasuda” model and B; the relaxation time for entries 2, 5, 7, 10 and 13
The fact that the 13- and the 17-arm PAM display the highest solution viscosity deviates from experimental observations on polyisoprenes in the melt, where the highest viscosity is obtained for polymers with low number of arms.\textsuperscript{33} Theoretical models, for combs\textsuperscript{34} and stars\textsuperscript{32} polymers, also predict the highest viscosity for polymers with few arms in the melt. In the entangled regime, the reptation of a star-chain is hindered by the arms. The built-up stress relaxes through arm retraction, which is a much slower process compared to linear-chain reptations.\textsuperscript{32, 34} For star polyisoprenes, the effect of the number of arms (above \( N > 4 \)) saturates and the molecular weight of the arms determines the viscosity.\textsuperscript{33} However, recently it has been demonstrated that comb like polyethylenes have \( \eta_0 \) much higher than their linear and long chain branched analogues.\textsuperscript{40} Nevertheless, these measurements are performed in the melt and thus the highest possible “concentration” is measured. In semi-dilute solutions the number of arms does have an effect on the solution viscosity, in that the increase in the number of arms means an increase in the segment density and thus higher viscosity (provided that the comparison is made above the entanglement critical concentration). However, if a higher solution viscosity is required, the increase in segment density has to overcome the negative effect that the reduction in hydrodynamic volume (due to branching\textsuperscript{27}) has on the solution viscosity.

**Viscoelasticity, effect of the number of arms (at equal concentration and overall molecular weight).** The effect of the number of arms on the viscoelasticity of a water solution was probed by oscillation experiments. The results are displayed in Figure 4.9, where the polymer concentrations of the solutions were kept constant for each comparison. Viscoelastic fluids display at low frequencies (i.e. in the terminal zone) a \( G'' \) that is directly proportional to the frequency (\( \omega \)) with a slope of 1 and \( G' \) proportional to \( \omega^2 \) (a slope of 2).\textsuperscript{23} As can be observed in the Figure 4.9, all samples display this behavior at low frequencies. The comparison at equal polymer concentration demonstrates that the 13- and 17-arm PAM display a more pronounced elastic response (lower phase angle) irrespective of the molecular weight. However, the results can be masked by the difference in viscosity; therefore the comparison is also made at equal \( \eta_0 \) (at different concentration).
Figure 4.9: A1, G’ and G” of the PAMs with $M_{\text{tot}} = 0.6$ MDa and A2 their respective phase angles (polymer concentration = 5.66 wt.%). B1, G’ and G” of the PAMs with $M_{\text{tot}} = 1.6$ MDa and B2 their respective phase angles (polymer concentration = 2.91 wt.%). C1, G’ and G” of the PAMs with $M_{\text{tot}} = 2.6$ MDa and C2 their respective phase angles (polymer concentration = 1.96 wt.%)

Viscoelasticity, effect of the number of arms (at equal $\eta_0$ and overall molecular weight). The results of the comparison between the different
PAMs at equal $\eta_0$ are displayed in Figure 4.10. The comparison at equal $\eta_0$ reveals that the 13- and 17-arm PAMs display lower phase angles at low frequencies irrespective of the molecular weight.

**Figure 4.10:** A1, $G'$ and $G''$ of the PAMs with $M_{tot} = 0.6$ MDa and A2 their respective phase angles (equal $\eta_0$). B1, $G'$ and $G''$ of the PAMs with $M_{tot} = 1.6$ MDa and B2 their respective phase angles (equal $\eta_0$). C1, $G'$ and $G''$ of the PAMs with $M_{tot} = 2.6$ MDa and C2 their respective phase angles (equal $\eta_0$)
As the frequency is increased ($M_{n,overall} = 0.6$ MDa) to above 10 rad/s, the phase angles of the 4- and 8-arm PAM decreases to lower values than that of the linear and 12-arm. Given the different concentration required to reach the same viscosity, the number of polymeric chains in the solution also differs. For the 4- and 8-arm PAM a concentration of 3.85 and 4.76 wt.% (respectively) is required. Compared to the linear and 12-arm PAM (polymer concentration of 2.91 and 1.96 wt.% respectively), more polymeric chains are present in the 4 and 8-arm solutions. In addition, the length of the arms of the 4- and 8-arm PAMs are longer than that of the 12-arm. The combination of longer arms (a higher arm molecular weight leads to a more pronounced elastic behavior in the melt\(^1\)) and higher number of polymeric chains in solution (an increase in the concentration leads to a more pronounced elastic behavior for polystyrene in chlorinated diphenyl\(^23, 42\)) might explain the more pronounced elastic behavior of the solutions containing 4- and 8-arms. Another explanation might be that more arms leads to more steric hindrance and therefore less hydrophobic associations between the hydrophobic polyketone backbones. The 4- and 8-arms PAM supposedly display more hydrophobic associations, given the less steric hindrance, and more/stronger hydrophobic associations are known to lead to a more pronounced elastic response.\(^43\)\(^-\)\(^46\) Nevertheless, further studies (currently being carried out) are required to fully elucidate the mechanism behind the observed behavior.

**Viscoelasticity, effect of the length of the arms (at equal concentration and equal number of arms).** The effect of the length of the arms on the viscoelasticity of a water solution was investigated by oscillation experiments. The results for the 13-arm PAM are displayed in Figure 4.11. As can be observed in Figure 4.11, the increase in length of the arms leads to an increase in both the loss and storage modulus. The transition from the terminal to the plateau zone is shifted to lower frequencies as the arm length increases (i.e. also the $M_{n,overall}$). In addition the plateau zone becomes longer as the arm length is increased. Both these effects are in line with results on low dispersity polystyrene (in the melt).\(^23\) In the melt constraints, due to entanglement, cause an increase in the terminal relaxation time and increases with molecular weight.\(^23\) In the 13-arm PAM case, the constraints arise due to its high molecular weight and architecture. Therefore the terminal relaxation time increases with increasing arm length. One might speculate that it should increase more rapidly compared to a linear polymer (given the higher relaxation time in the melt for branched polymers\(^34\)). This is in line with the higher solution viscosity of the 13-arm branched PAM compared to its linear analogue. The phase angle decreases as the arm
length increases. The disentanglement of the overlapping chains becomes progressively more difficult as the length of the arms increase. Therefore, in essence, a stiffer solution is obtained as the length of the arms increase.

The dependence of the $\eta_0$ in solution on length of the arms is displayed in Figure 4.11D. As can be observed, the $\eta_0$ increases exponentially (relatively good fit) with the increase in the length of the arms. This matches the theory in the melt where the same exponential dependency of the $\eta_0$ on the arm molecular weight is observed\textsuperscript{33}.

**Figure 4.11**: The loss (A) and storage (B) modulus, the phase angle (C) as a function of the frequency of the 13-arm PAM with different length of the arms (polymer concentration = 2.91 wt.%), and the $\eta_0$ as a function of the DP\textsubscript{arm} (D)

**Schematic model.** With the available data on linear and branched PAMs a conceptual model can be devised (Figure 4.12) for the branched PAMs in dilute and semi-dilute solutions. The hydrodynamic radius of the branched PAMs depends on the number of arms. At low number of arms ($N \leq 8$) the
hydrodynamic volume is slightly lower compared to that of a linear analogue. This is in line with the general view of the more compactness of branched polymers compared to their linear analogues, which leads to lower $\eta_0$ for the branched polymers in dilute solutions. However, for a relatively high number of arms ($N \geq 13$), the low amount of space available for each arm will lead to an extended configuration for the arms close to the backbone and possibly in solution.

Figure 4.12: Schematic model of the branched PAMs

Increasing the concentration of the polymer to above the critical overlap concentration leads to entanglements. When entangled at equal polymer concentration, the branched PAMs with a higher number of arms ($N \geq 13$)
have a higher entanglement density compared to PAMs with few arms \((N \leq 8)\). The increase in entanglement density leads to a higher solution viscosity. In addition, above the critical overlap concentration, the rheology of a star-like (compared to a linear analogue) polymeric solution is governed by the arm retraction, where the arms explore new configurations through retraction and extension into new directions.\(^{32}\) As this is a much slower process\(^{32}\) compared to the reptation of linear chains\(^{48-51}\), an exponential dependence of the \(\eta_0\) on the arm molecular weight is observed in the melt.\(^{32}\)

For the 13- and 17-arm PAM, the combination of a higher hydrodynamic volume (due to stretching) and a higher entanglement density leads to an increase thickening efficiency compared to their linear analogue. In addition, an increase in entanglement density, leads to a more pronounced shear thinning behavior. This is in line with the results in Figure 4.8A.

### 4.4. Conclusion

The controlled synthesis of branched high molecular weight polyacrylamides (PAM) with equal overall molecular weight or with equal arm lengths, through ATRP in water (and acetone as a co-solvent), has been accomplished. Branched PAMs of 4, 8, 12, 13 and 17 arms have been synthesized. The effect of the molecular architecture (i.e. number of arms) on the rheological properties in semi-dilute water solutions (solution viscosity and viscoelasticity) was investigated. The 13-arm and 17-arm PAM displayed a higher solution viscosity compared to the linear, 4-arm, and 8-arm analogues irrespective of the molecular weight. The comparison between the 13-arm PAM and a linear analogue displays an as much as 5-fold increase in solution viscosity (at a shear rate of 10 s\(^{-1}\)). Furthermore, a more pronounced shear thinning is observed for the 13 and 17-arm PAMs. The elastic response of the 13- and 17-arm PAM in solution is more pronounced compared to their linear analogue. The 4- and 8-arm though, display a lower elastic response compared to their linear analogues. The rheological properties of the branched PAMs are dependent on the number of arms and their length. In semi-dilute aqueous solutions, the combination of a higher hydrodynamic volume and higher entanglement density leads to an improved thickening efficiency (for \(N \geq 13\)) of the branched PAMs. The manipulation of the rheological properties of PAM in water through smart architectural design opens new ways in designing PAM-based materials for new applications where control in the rheological properties is crucial. The increased thickening efficiency of the branched PAMs makes these water soluble polymers highly attractive for applications in EOR.
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4.6. References

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