Synthesis and evaluation of novel linear and branched polyacrylamides for enhanced oil recovery
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2013

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 6

Branched thermo-responsive polymeric materials: Synthesis and effect of the macromolecular structure on the solution properties

Abstract

A series of comb-like block and random copolymers based on acrylamide (AM) and N-isopropylacrylamide (NIPAM) have been prepared by atom transfer radical polymerization (ATRP). The number of side-arms, the length of the AM and NIPAM blocks as well as the distribution of the two monomers (block or random) were systematically varied. The aqueous solution properties, i.e. the solution viscosity as a function of shear rate and temperature and the critical micelle concentration (CMC) of the different copolymers were evaluated. Particular emphasis is dedicated to the thermo-responsiveness of the aqueous copolymers solutions as measured by rheological behavior. The CMC is a function of the molar ratio between the AM and NIPAM as well as the distribution (block or random). The surface tension of the block copolymers is close to the value for pure poly(NIPAM), while that of the random copolymers is a function of the composition. The block copolymers tend to precipitate from the solution at temperatures above the Lower Critical Solution Temperature (LCST) of poly(NIPAM), indicating the formation of strong aggregates. On the other hand, random copolymers of AM and NIPAM do not precipitate from the solution (up to 80 °C). In addition, depending on the composition, thermo-thickening behavior is observed. Remarkably, the thermo-thickening behavior is only present at low shear rates ($\dot{\gamma} \leq 10$ s$^{-1}$). This, in connection with the ease of the synthesis, makes these copolymers especially interesting for application in Enhanced Oil Recovery (EOR).

6.1. Introduction

Thermoresponsive (or thermosensitive) polymers have been the subject of extensive research in the past decade due to their unique properties.\(^1\) Thermosensitive polymers contain moieties that can undergo major conformational transitions with changes in temperature. Generally speaking, two different types of thermoresponsive polymers are distinguished. The first type is a polymer for which the solubility in a given solvent improves with an increase in temperature (upper critical solution temperature, UCST).\(^2\) The second type displays the exact opposite behavior, with the solubility decreasing with temperature (LCST).\(^3\) Many different application fields have been suggested for thermoresponsive polymers: drug delivery agents,\(^4\)-\(^6\) bioengineering,\(^6\),\(^7\) sensors,\(^8\),\(^9\) drag reduction,\(^10\),\(^11\) and enhanced oil recovery (EOR).\(^12\),\(^13\)

The focus has been mainly on poly(N-isopropylacrylamide) (PNIPAM) because it possesses a sharp\(^1\) (i.e. relatively narrow) LCST window of 31-33 °C (independent of the polymer concentration\(^14\)), which is close to the temperature of the human body. Many efforts have been spent towards the development of drug carriers based on PNIPAM.\(^4\),\(^15\)-\(^18\) Current investigations are mainly focused on manipulating the LCST value. Several molecular properties of the polymer affect the LCST: the molecular weight\(^19\),\(^20\) (or even NIPAM oligomers\(^21\)), the nature of the endgroups\(^21\),\(^22\), and the chemical structure\(^1\),\(^10\) (i.e. incorporation of other, hydrophobic or hydrophilic, monomers). The variety of monomers that have been copolymerized (random, block and graft) with NIPAM is extensive and has been recently reviewed.\(^1\),\(^10\) To elucidate the effect of the different molecular properties on the LCST, control in the polymerization of NIPAM is desirable. The controlled polymerization of NIPAM, i.e. control in the molecular weight and the dispersity index (PDI), has been accomplished by atomic transfer radical polymerization (ATRP)\(^19\),\(^20\),\(^23\)-\(^25\), reversible addition-fragmentation chain transfer (RAFT) polymerization\(^26\),\(^27\) and living anionic polymerization\(^28\),\(^29\).

Attention has mainly been given to the preparation of thermosensitive gels based on NIPAM.\(^30\)-\(^32\) When heated above their LCST, the NIPAM moieties become dehydrated and effectively hydrophobic in nature. This results in association, formation of thermoreversible aggregates and increase in viscosity.\(^1\) Similar behavior is obtained using NIPAM based copolymers. The first reports on this feature were on copolymers of acrylic acid (AA) with NIPAM grafted on the poly(acrylic acid) (PAA) backbone.\(^33\),\(^34\) Acrylamide (AM) and N,N-dimethylacrylamide (DMA) as the hydrophilic block has also been demonstrated to lead to a thermothickening behavior in water.\(^13\),\(^35\) Other moieties such as poly(ethylene oxide) (PEO)\(^36\),\(^37\) and, more recently,
an AM based macromonomer\textsuperscript{38, 39}, as the thermosensitive block have been investigated. The thermoviscosifying effect is observed at shear rates up to $\dot{\gamma} = 800 \text{ s}^{-1}$ indicating strong aggregation. In view of possible applications in EOR, this might lead to the loss of injectivity. Close to the injection well, the shear rates are high (due to the injection of large volumes through small pores), and the temperatures are above the LCST of the polymers. The significant increase in solution viscosity at higher temperatures and shear rates will require high pumping pressure to enable injection of the polymer solution. Ideally, the thermoviscosifying polymer should display a relatively higher solution viscosity (e.g. $\eta > 80 \text{ mPa.s}$) at higher temperatures (e.g. T > 50 °C) but only at low shear rates ($\dot{\gamma} < 30 \text{ s}^{-1}$).

Despite the relevant number of studies already published, a systematic investigation of the copolymer properties (e.g. surface activity and rheological behavior in aqueous solutions) as function of the macromolecular structure has not been yet reported. This is probably related to the difficulties in achieving control over the co-polymerization process. With the advent of synthetic strategies for AM based comb-like homo- and block-copolymers of AM and NIPAM, the effect of the molecular architecture on the solution properties of branched block-copolymers can now be probed.

Although significant progress has been booked in the synthesis of water soluble thermothickening, the synthetic methods comprise multiple steps and are not controlled thus leading to broad molecular weight distributions. In addition, the thermothickening properties arise also at high shear ($\dot{\gamma} > 800 \text{ s}^{-1}$) rates which might be detrimental for application in EOR. Here we report the controlled synthesis of branched terpolymers based on an aliphatic polyketone backbone with a varying number of thermosensitive side chains made of diblock (AM-\textit{b}-NIPAM) or random (AM-\textit{ran}-NIPAM) moieties. The effect of the chemical structure, i.e. random or block, and the molecular architecture (varying number of arms) on the solution properties is presented. To the best our knowledge, this is the first report on a thermoresponsive polymer that displays a thermothickening behavior only at low shear rates ($\dot{\gamma} < 30 \text{ s}^{-1}$), which is crucial for application in EOR.

### 6.2. Experimental section

**Chemicals.** Acrylamide (AM, electrophoresis grade, ≥99%), \textit{N}-isopropylacrylamide (NIPAM, 97%), tris[2-(dimethylamino)ethyl]amine (Me\textsubscript{6}TREN) copper(I) bromide (CuBr, 98%), glacial acetic acid, ethanol, chloroform and diethyl ether were purchased from Sigma Aldrich. CuBr was purified by stirring in glacial acetic acid for at least 5 hours, filtering, and
washing with glacial acetic acid, ethanol and diethyl ether (in that order) and then dried at reduced pressure.  

**Synthesis of the macro-initiator.** The chemical modification of the original PK was performed according to the published method (Scheme 6.1). The reactions were performed in a sealed 250 ml round bottom glass reactor with a reflux condenser, a U-type anchor impeller using an oil bath for heating.

**Scheme 6.1: Synthesis of the macro-initiators**

![Scheme 6.1](image)

The chloropropylamine hydrochloride 14.8 g (0.114 mol) was dissolved in methanol (50 ml) to which an equimolar amount of sodium hydroxide (4.56 g, 0.114 mol) was added. After the polyketone (15 g, 0.114 mol of dicarbonyl units) was preheated to the liquid state at the employed reaction temperature (100 °C), the amine solution 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 a slightly yellowish, low viscosity state, into a highly viscous brown homogeneous paste. The product was dissolved in chloroform and the organic phase was washed afterwards with demineralized water in a separation funnel. The polymer was isolated by evaporating the chloroform at low pressure (100 mbars). The product, a brown powder, was finally freeze dried and stored at -18 °C until further use. The macro-initiator was characterized using elemental analysis, \(^1\)H-NMR spectroscopy (in chloroform), and Gel Permeation Chromatography (GPC).

The conversion of carbonyl groups of the polyketone was determined using the following formula:
\[
x_C^O = \frac{2y}{x+2y} \cdot 100 = \frac{\left( \frac{2N(\text{wt.\%})}{\text{mol}_N} \right)}{\left( \frac{\left( \frac{N(\text{wt.\%})}{\text{mol}_N} \right)}{\bar{n}_C^{n-m}} \right) + \left( \frac{\left( \frac{N(\text{wt.\%})}{\text{mol}_N} \right)}{\bar{n}_C^m} \right)} \cdot 100 \quad (6.1)
\]

\(\bar{n}_C^{n-m} = 3.7\) the average number of carbons in \(n-m\) (see Scheme 6.1)
\(\bar{n}_C^m = 10.4\), the average number of carbons in \(m\) (see Scheme 6.1)
\(\text{mol}_N = \) atomic weight of nitrogen
\(\text{mol}_C = \) atomic weight of carbon

The average number of pyrrole units was determined using the conversion of the carbonyl groups of the polyketone and formula 6.2:

\[
N_{\text{pyrrole units}} = \left( \frac{M_{\text{PK}}}{M_{\text{repeating unit PK}}} \right) \cdot x_C^O \quad (6.2)
\]

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

**Comb polymers preparation.** A 250-ml three-necked flask was charged with the macroinitiator (e.g. entry PK30-\(g_{13}\)-PAM3275, 0.3279 g, 0.117 mmol macroinitiator or 1.521 mmol Cl-groups). Enough acetone (typically 5-10 ml) was added to dissolve the macro-initiator. Demineralized water (400 ml) and acrylamide (100 g, 1400 mmol) were then added to the solution. Subsequently, the mixture was degassed by three freeze-pump-thaw cycles. A nitrogen atmosphere was maintained throughout the remainder of the reaction steps. CuBr (25 mg, 0.174 mmol) was then added to the flask and the mixture stirred for 10 minutes. The flask was then placed in an oil bath at 25 °C. The reaction was started by the addition of the ligand (Me₆TREN, 40 mg, 0.174 mmol) 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.

**Block Copolymerization.** The prepared PK30-\(g\)-PAM (vide supra) was used as macroinitiator for NIPAM polymerization. A round bottomed three-necked flask was charged with the macroinitiator (e.g. entry PK30-\(g_{13}\)-\(b\)-PNIPAM4425, 4.38 g, 0.0186 mmol macroinitiator or 0.242 mmol Cl-groups) and NIPAM (21.03 g, 186 mmol). Double distilled water was
Branched thermosensitive copolymers

added, and the mixture was degassed by three freeze-pump-thaw cycles. Afterwards CuBr (3.5 mg, 0.024 mmol) was added and the solution was stirred for 10 min. The flask was placed in a water bath at 25 °C and the reaction was started by adding Me₆TREN (5.5 mg, 0.024 mmol). All the operations were performed under nitrogen. After the reaction, the mixture was terminated by the addition of demineralized water (80 mL). The polymer was precipitated in a tenfold amount of methanol and dried in an oven at 65 °C. The polymer was re-dissolved in demineralized water and dialyzed (Spectra/Por® Dialysis Membrane, molecular weight cut off = 2 000 g/mol) and subsequently dried in an oven at 65 °C up to constant weight. The codes for the block copolymers are defined as PK30-gₓ-(PAMY-b-PNIPAMZ) with X, Y and Z the designation for the number of arms, number of AM and NIPAM units respectively.

Random Copolymerization. The polyketone macroinitiator was synthesized according to the aforementioned procedure. A three-necked flask is charged with the polyketone macroinitiator (e.g. entry PK30-g₁₃₋ (PAM1405-co-PNIPAM1405), 0.0983g 0.035mmol) and acetone (10 mL). Hereafter, a magnetic stirrer, AM (15 g, 210 mmol) and NIPAM (23.8 g, 210 mmol) dissolved in demineralized water (150 mL) were added and the mixture was degassed by three freeze-pump-thaw cycles. The flask was placed in a thermostated water bath and stirred constantly at 25 °C after which the CuBr (7.6 mg, 0.053 mmol) was added. The reaction was started with the addition of Me₆TREN (12.2 mg, 0.053 mmol). All operations were carried out under nitrogen. After the reaction, the mixture was terminated by the addition of demineralized water (750 mL) and a sample was taken for GC analysis (acrylamide conversion). The polymer solution was dialyzed (Spectra/Por® Dialysis Membrane, molecular weight cut off = 12 000 - 14 000 g/mol) and subsequently dried in an oven at 65 °C up to constant weight. The codes for the block copolymers are defined as PK30-gₓ₋(PAMB-co-PNIPAMC) with A, B and C the designation for the number of arms, number of AM and NIPAM units respectively.

Characterization. The acrylamide conversion was measured by using Gas Chromatography (GC). The samples (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 total molecular weight \( M_{n,tot} \) is calculated by using the acrylamide conversion (monomer-initiator ratio multiplied by the conversion). The span molecular weight \( M_{n,SPAN} \) is calculated using the \( M_{n,tot} \) and is defined as two times the molecular weight of one arm (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 D₂O was used as the solvent. For measurements at higher temperatures, at least 10 minutes was waited before recording the spectrum.

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 series. The columns were operated at 42 °C with a flow-rate 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).

Elemental analysis of the macroinitiators was performed on the EuroEA3000-CHNOS analyzer (EUROVECTOR Instruments and Software). Approximately 2 mg of each sample is weighed and placed in tin sample-cups. The reported values are the average of 2 runs.

Surface tension was measured using the pendant drop method on a LAUDA DROP VOLUME TENSIOMETER TVT 1. A glass micro syringe was attached to a needle with a capillary radius of 1.055 mm. The temperature of the water bath was set to 25 °C and the density difference between air and water was set to 0.997 g/mL. Two sets of three measurements were taken and then averaged. Graphically the critical micelle concentration (CMC) can be obtained from the plot of the surface tension against the concentration by taking the line of best fit in two places and noting the concentration at the intersection (not shown for brevity). ¹⁴²

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. With this, it was ensured that the dynamic measurements were conducted in the linear response region of the samples.
6.3. Results and discussion

6.3.1. Macroinitiators.

The synthesis of the macroinitiators was performed according (Scheme 6.1) to the Paal-Knorr reaction of a halogenated primary amine with aliphatic perfectly alternating polyketones. The carbonyl conversion was determined using elemental analysis. 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 6.1). The resonance of the pyrrole as well as those for the $\alpha$- and $\gamma$-hydrogens (relative to the halogen) all increase with the conversion of the Paal-Knorr reaction. The obtained, chemically modified polyketones are used as macroinitiators in the synthesis of block or random comb-copolymers.

Table 6.1: Properties of the macroinitiator and parent polyketone

<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$_{13}$</td>
<td>62.9 : 7.6 : 4.9</td>
<td>61.14</td>
<td>13</td>
<td>2 072</td>
<td>1.97</td>
</tr>
</tbody>
</table>

$^a$. Number indicates the ethylene content (%) and Cl indicates the halogen present

$^b$. The conversion of the carbonyl groups of the polyketone

$^c$. Average number of pyrrole units per chain

The properties of the macroinitiators are given in Table 6.1. The molecular weight (relative to that of polystyrene) of the macroinitiator decreases as the conversion of the carbonyl groups increases. The decrease is probably due to the decrease in hydrodynamic volume caused by the formation of the pyrrole rings in the backbone of the macroinitiator.
Figure 6.1: $^1$H-NMR spectra of the macroinitiator and the virgin polyketone

6.3.2. Synthesis of PK30-g-(PAM-b-PNIPAM)

The synthesis of the comb graft block-copolymers was performed according to scheme 6.2A by using different molar ratios between the macroinitiator and AM (and NIPAM). First the ATRP of AM was carried out by following a published method.43

Scheme 2: (A) Block copolymerization of AM and NIPAM and (B) Random copolymerization of AM and NIPAM on the polyketone based macroinitiator
Afterwards NIPAM was polymerized as the second block and the NIPAM conversion was determined by $^1$H-NMR (Figure 6.2). A summary of the experimental conditions applied to prepare the different block copolymers as well as their GPC analysis is given in Table 6.2. As can be observed in Table 6.2, different graft block copolymers can be prepared where the average number of grafts, the length of the AM and NIPAM blocks can be systematically varied. The acrylamide conversion is lower for the higher functionalized polyketone macroinitiators. As mentioned before, the theoretical maximum number of side groups that can be obtained is 21.

**Table 6.2:** Synthesis of the different PK30-g-(PAM-b-PNIPAM) block copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[[M]_0:[I]_0:[L]_0:[C]_0]^a$</th>
<th>M/water (wt:vol); $T$; Time (min)</th>
<th>Conv (%) AM$^b$</th>
<th>NIPAM$^c$</th>
<th>$M_n$</th>
<th>DP NIPAM</th>
<th>DP PAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-g$_4$-(PAM7575)</td>
<td>10 005:1:1:1.5</td>
<td>1: 6.0; 25 °C; 1440</td>
<td>-</td>
<td>541 329</td>
<td>7575</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_4$-(PAM7575-b-PNIPAM15)</td>
<td>8 000:1:1:1.5</td>
<td>1:17.4; 25 °C; 1425</td>
<td>-</td>
<td>543 254</td>
<td>7575</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_4$-(PAM7575-b-PNIPAM1690)</td>
<td>3 000:1:1:1.5</td>
<td>1:46.5; 25 °C; 1425</td>
<td>-</td>
<td>732 393</td>
<td>1690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_8$-(PAM7770)</td>
<td>10 025:1:1:1.5</td>
<td>1: 6.0; 25 °C; 1440</td>
<td>-</td>
<td>554 982</td>
<td>7770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_8$-(PAM7770-b-PNIPAM60)</td>
<td>100 000:1:1:1.5</td>
<td>1: 4.2; 25 °C; 1405</td>
<td>-</td>
<td>561 705</td>
<td>7770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_8$-(PAM7770-b-PNIPAM480)</td>
<td>8 000:1:1:1.5</td>
<td>1:18.6; 25 °C; 1440</td>
<td>-</td>
<td>609 368</td>
<td>7770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_13$-(PAM3275)</td>
<td>12 000:1:1:2.5</td>
<td>1: 4.0; 25 °C; 1440</td>
<td>27.3</td>
<td>235 504</td>
<td>3275</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_13$-(PAM3275-b-PNIPAM415)</td>
<td>10 000:1:1:1.5</td>
<td>1:13.3; 25 °C; 1230</td>
<td>-</td>
<td>282 579</td>
<td>415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_13$-(PAM3275-b-PNIPAM4425)</td>
<td>10 000:1:1:1.5</td>
<td>1:10.9; 25 °C; 1425</td>
<td>-</td>
<td>736 146</td>
<td>4425</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_13$-(PAM6140)</td>
<td>12 000:1:1:1.5</td>
<td>1: 6.0; 25 °C; 1405</td>
<td>-</td>
<td>439 326</td>
<td>6140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PK30-g$_13$-(PAM6140-b-PNIPAM205)</td>
<td>4 965:1:1:1.5</td>
<td>1:31.7; 25 °C; 1405</td>
<td>-</td>
<td>462 515</td>
<td>205</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a: AM is the monomer ([M]$_0$) for the homopolymers and NIPAM is the monomer ([M]$_0$) for the block copolymers

*b: The AM conversion was determined by GC

*c: The NIPAM conversion was determined by $^1$H-NMR
The higher the functionalization degree, the more sterically hindered the macroinitiator is. Therefore, the reactivity of the macroinitiator will decrease as the number of halogen atoms increases (due to steric hindrance\textsuperscript{44}), eventually leading to lower AM conversions. The resonance labelled (Figure 6.2) as \textit{a} (\(\delta=3.9\) ppm) represent the hydrogen atom of the CH group of the isopropyl group of the PNIPAM blocks and therefore the size of this resonance (in relation to the resonances labelled \textit{b} and \textit{c}, \(\delta\) in the range 1.2 – 2.5 ppm) corresponds to the amount of NIPAM polymerized on the PK30-\(g_X\)-(PAMY) macroinitiator. The total area of the resonances labelled \textit{b} and \textit{c} correspond to the protons from the backbone of the PK30, PAM and PNIPAM along with the 6 methyl protons of PNIPAM blocks (2× CH\(_3\)). The \(^1\text{H}-\text{NMR}\) data is in agreement with solubility tests, and confirms the preparation of block copolymers with different lengths of the blocks.

\textbf{Figure 6.2}: \(^1\text{H}-\text{NMR}\) spectra of the block copolymers PK30-\(g_X\)-(PAMY-b-PNIPAMZ) and the parent macroinitiators PK30-\(g_X\)-(PAMY)
Branched thermosensitive copolymers

6.3.3. Synthesis of PK30-g-(PAM-co-PNIPAM)

The synthesis of the comb graft random-copolymers was performed according to scheme 6.2B using different molar ratios between the macroinitiator and AM (and NIPAM). Random ATRP of both monomers was conducted in water. The experimental conditions and GPC data are summarized in Table 6.3.

Increasing the [M]₀:[I]₀ yielded, as expected, higher molecular weight copolymers. However the conversion of the monomers is lower indicating mass transfer limitations due to the significant increase in the viscosity of the reaction mixture. The monomer conversion also decreases as the number of arms on the parent macroinitiator increases. This is in line with earlier results on the polymerization of AM on the same macroinitiator in water (Chapter 3). The molar ratio between AM and NIPAM of the copolymers was similar to the molar ratio of the reaction mixture in all the cases, thus suggesting a random distribution of the units. This is in line with an earlier report on the free radical copolymerization of AM and NIPAM. Two samples of the reaction mixture, one taken at low conversion and one at high conversion, displayed the same molar ratio between the two monomeric units suggesting a perfectly random distribution.

Table 6.3: Synthesis of the different PK30-g-(PAM-co-PNIPAM) random copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M]₀[n:m]:[I]₀</th>
<th>M/water (wt:vol), T, Time (min)</th>
<th>Conv (%)</th>
<th>Mₙ, GPC</th>
<th>DP</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-g₄(PAM5015-co-PNIPAM4885)</td>
<td>12 000[1:1]:1</td>
<td>1:4.0;25 °C; 210</td>
<td>83.6</td>
<td>908 999</td>
<td>5 015</td>
<td>4 885</td>
</tr>
<tr>
<td>PK30-g₄(PAM18875-co-PNIPAM19240)</td>
<td>50 000[1:1]:1</td>
<td>1:4.0;25 °C; 210</td>
<td>75.3</td>
<td>5 188 088</td>
<td>18 875</td>
<td>19 240</td>
</tr>
<tr>
<td>PK30-g₄(PAM33395-co-PNIPAM31790)</td>
<td>100 000[1:1]:1</td>
<td>1:4.0;25 °C; 210</td>
<td>68.6</td>
<td>5 970 955</td>
<td>33 395</td>
<td>31 790</td>
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<tr>
<td>PK30-g₅(PAM4400-co-PNIPAM4600)</td>
<td>12 000[1:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
<td>73.4</td>
<td>817 851</td>
<td>4 400</td>
<td>4 460</td>
</tr>
<tr>
<td>PK30-g₅(PAM11125-co-PNIPAM10205)</td>
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<td>1:4.0; 25 °C; 210</td>
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<td>1 945 492</td>
<td>11 125</td>
<td>10 205</td>
</tr>
<tr>
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<td>50 000[1:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
<td>50.3</td>
<td>2 302 870</td>
<td>12 540</td>
<td>12 475</td>
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<tr>
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<td>1:4.0; 25 °C; 185</td>
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<td>3 300 961</td>
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<td>17 510</td>
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<tr>
<td>PK30-g₁₃(PAM1405-co-PNIPAM1405)</td>
<td>12 000[1:1]:1</td>
<td>1:3.9; 25 °C; 210</td>
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<td>1 405</td>
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<td>100 000[2:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
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<td>651 397</td>
<td>5 135</td>
<td>2 530</td>
</tr>
<tr>
<td>PK30-g₁₃(PAM6320-co-PNIPAM6000)</td>
<td>25 000[1:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
<td>50.5</td>
<td>1 127 916</td>
<td>6 320</td>
<td>6 000</td>
</tr>
<tr>
<td>PK30-g₁₃(PAM8375-co-PNIPAM8130)</td>
<td>50 000[1:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
<td>33.5</td>
<td>1 515 267</td>
<td>8 375</td>
<td>8 130</td>
</tr>
<tr>
<td>PK30-g₁₃(PAM9620-co-PNIPAM9620)</td>
<td>75 000[1:1]:1</td>
<td>1:4.0; 25 °C; 210</td>
<td>25.5</td>
<td>1 772 689</td>
<td>9 620</td>
<td>9 620</td>
</tr>
<tr>
<td>PK30-g₁₃(PAM12140-co-PNIPAM11690)</td>
<td>100 000[1:1]:1</td>
<td>1:4.0; 25 °C; 915</td>
<td>24.4</td>
<td>2 183 519</td>
<td>12 140</td>
<td>11 690</td>
</tr>
</tbody>
</table>

a: AM is the monomer ([M]₀) for the homopolymers, n:m is the molar ratio between AM and NIPAM
b: The AM conversion was determined by GC
c. The NIPAM conversion was determined by ¹H-NMR
6.3.4. Solution properties of PK30-g<sub>x</sub>- (PAMY-b-NIPAMZ)

**Solution viscosity as a function of shear.** The viscosity of the polymer dissolved in demineralized water versus shear rate is displayed in Figure 6.3. The polymers used are characterized by different hydrophilic (AM) / hydrophobic (NIPAM) ratios and a different number of arms. All polymers consisted of a comb-like hydrophilic block of AM and a hydrophobic block of NIPAM of different average lengths (and thus different total molecular weight).

*Figure 6.3:* Viscosity vs shear rate of A: PK30-g<sub>4</sub>- (PAMY-b-PNIPAMZ) at a polymer concentration of 5 wt.%, B: PK30-g<sub>8</sub>- (PAMY-b-PNIPAMZ) at a polymer concentration of 4 wt.%, and C: PK30-g<sub>13</sub>- (PAMY-b-PNIPAMZ) at a polymer concentration of 3 wt.%

As can be observed, the addition of a NIPAM block to the branched homopolymer leads to an increase in the solution viscosity and a more pronounced pseudo-plastic behaviour. The increase in solution viscosity is
related to the increased molecular weight of the polymers and the presence of the NIPAM blocks (Chapter 5).

**Solution viscosity as a function of temperature.** The viscosity was measured as a function of the temperature of the solution and the results are displayed in Figure 6.4. All polymers consisted of a hydrophilic block of AM (roughly 525 000 g/mol or 7650 AM units for PK30-\(g_4\) and PK30-\(g_8\), 235 000 g/mol or 3275 AM units for PK30-\(g_{13}\)) and a hydrophobic block of PNIPAM of differing length, resulting in block copolymers with different total molecular weights. The shear rate during the temperature sweep was fixed at a value of 30.0 s\(^{-1}\).

![Graph showing viscosity versus temperature for different samples](image)

**Figure 6.4:** Viscosity (\(\dot{\gamma} = 30\;\text{s}^{-1}\)) versus temperature of A: 5 wt.% PK30-\(g_4\)-(PAM-b-PNIPAM), B: 4 wt.% PK30-\(g_8\)-(PAM-b-PNIPAM), C: 3 wt.% PK30-\(g_{13}\)-(PAM-b-PNIPAM)
To illustrate the effect of NIPAM on the behaviour of the block-copolymers in solution as a function of temperature, the corresponding homopolymers are also displayed. The viscosities of the polymer solutions decrease as the temperature increases (Figure 6.4). The curves for the block copolymers display a sharp drop at a temperature of approximately 32-34 °C, close to the LCST of the NIPAM homopolymer. When the temperature of the polymer solution reaches the LCST, the isopropyl groups of the PNIPAM blocks are dehydrated and aggregation between the PNIPAM blocks arises. Most of the copolymers precipitate out of the solution as the temperature is increased to above 32 °C (Figure 6.5), indicating strong hydrophobic interactions.

**Figure 6.5:** Precipitation of the block copolymers at temperatures above 32 °C and no precipitation of the random copolymers at temperatures up to 80 °C.

The same behaviour is observed for linear block copolymers of AM and NIPAM (Chapter 5). Only entries PK30-\text{g}_4-(PAM7575-b-PNIPAM1690) and PK30-\text{g}_8-(PAM7770-b-PNIPAM60) do not precipitate out of the solution. In these cases, the length of the hydrophilic block appears to be long enough to keep the block copolymer in solution at temperatures above 32 °C. The precipitation of the block copolymers is detrimental for possible application in EOR, as the precipitates will probably block the porous media (reservoir).

The steep increase in solution viscosity of PK30-\text{g}_{13}-(PAM3725-b-PNIPAM4425) is caused by the formation of gel particles (Figure 6.4C, picture) in the rheometer leading to a higher friction and thus a higher apparent viscosity. However, the values for the solution viscosity are not reliable due to the precipitation of the copolymer. To investigate the thermoresponsive character of the NIPAM blocks at a molecular level, $^1$H-NMR spectra were recorded at different temperatures (Figure 6.6). The
resonances (a and c) corresponding to the NIPAM blocks (of the block copolymer) disappear almost completely above 30 °C. This indicates that the NIPAM blocks precipitate out of the solution. Similar results have been obtained for diblock star copolymers of NIPAM and 2-hydroxyethyl methacrylate\textsuperscript{46}, copolymers of NIPAM and vinyl laurate\textsuperscript{47}, miktoarms multihydrophilic star block copolymers based NIPAM, acrylic acid and vinyl pyrrolidone\textsuperscript{48}, and on the homopolymer of NIPAM.\textsuperscript{49} The precipitates correspond to the gel particles observed in the rheometer. The comparison to a random copolymer show that the resonances (a and c) for the random copolymer are still present, even at 75 °C.

\[ \begin{array}{c}
\text{Figure 6.6: } ^1H-NMR \text{ spectra of entries PK30-g}_{13^{\text{a}}}(\text{PAM3275-b-PNIPAM4425}) \text{ and PK30-g}_{13^{\text{c}}}(\text{PAM1405-co-PNIPAM1405}) \text{ at different temperatures} \\
\end{array} \]

6.3.5. Solution properties of PK30-\(g_X^{\text{c}}\)-(PAMY-co-NIPAMZ)

**Solution viscosity as a function of shear.** The solution viscosity as a function of shear rate for some of the random copolymers is displayed in Figure 6.7A. Increasing the amount of NIPAM in the random copolymer leads to a reduction in the solution viscosity (Figure 6.7A). The comparison between the entries PK30-\(g_{13^{\text{a}}\text{c}}^(\text{PAM5135-co-PNIPAM2530})\) and PK30-\(g_{13^{\text{c}}\text{c}}^(\text{PAM6320-co-PNIPAM6000})\) demonstrates that the incorporation rate of NIPAM in the random copolymer has a strong effect on the solution viscosity. The decrease in solution viscosity can be attributed to the reduction in the strength of the hydrogen bonds that arise in the solution. The copolymer with
a 1-1 molar ratio for AM and NIPAM units is an ideal random copolymer, i.e. an alternating distribution of the two monomer units. The proximity of the NIPAM units and the AM units will disrupt the hydrogen bonds. The copolymer with a 2-1 molar ratio will have a lower degree of disruption due to a lower number of NIPAM units. In addition, the effective lengths of the PAM blocks are longer in the latter copolymer and will lead to stronger interactions in solution. This behaviour resembles that of hydrophobic interactions, where longer hydrophobic groups will have stronger interactions.12

Figure 6.7: Viscosity functions of A: different PK30-g13 random copolymers at 20 °C and B: PK30-g13-(PAM1405-co-PNIPAM1405) at different temperatures

The viscosity function of PK30-g13-(PAM1405-co-PNIPAM1405) at different temperatures displays a peculiar behaviour (Figure 6.7B). Increasing the
temperature to 50 °C leads to a reduction of the solution viscosity (at $\dot{\gamma} > 1$ s$^{-1}$), due to the reduced solvent viscosity and lower strength$^{50}$ of the hydrogen bonds. However, at low shear rates ($\dot{\gamma} < 0.5$ s$^{-1}$), the solution viscosity is equal or higher than the values at 20 °C. At higher temperatures and low shear rate ($T = 80$ °C and $\dot{\gamma} \leq 3$ s$^{-1}$), the solution viscosity is significantly higher which points to, weak interactions between the polymer chains. As the shear rate is increased the aggregates are disrupted and the solution viscosity reduces to values lower than those at 50 °C.

**Solution viscosity as a function of temperature.** The viscosity was measured as a function of the temperature of the solution containing the random copolymers and the results are displayed in Figure 6.8.

![Figure 6.8: Viscosity versus temperature of (A): 3 wt.% PK30-g$^{4}$-(PAM5015-co-PNIPAM4885), (B): 3 wt.% PK30-g$^{8}$-(PAM4400-co-PNIPAM4460), (C): 2 wt.% PK30-g$^{13}$-(PAM1405-co-PNIPAM1405) and PK30-g$^{13}$-(PAM3275), and (D): 1 wt.% PK30-g$^{13}$-(PAM9620-co-PNIPAM9620)](image-url)
The random copolymers display peculiar behavior, as an increase in viscosity is observed at higher temperatures at low shear rates ($\dot{\gamma} < 5 \text{ s}^{-1}$). At higher shear rates, this increase can no longer be distinguished. The increase in solution viscosity is attributed to the formation of aggregates due to the hydrophobic character of the NIPAM moieties above the LCST (i.e. $T > 32^\circ C$). Similar to the block copolymers, the solutions were visually inspected for precipitation upon heating (Figure 6.5). As can be observed no precipitation occurs upon heating for 5 minutes till 80 °C. Similar results, i.e. an increase in solution viscosity at higher temperatures, have been reported on copolymers of NIPAM with either AM$^{13}$ or acrylic acid (AA)$^{33, 34}$.

The random copolymer PK30-$g_{13}$-(PAM1405-co-PNIPAM1405) and the homopolymer PK30-$g_{13}$-(PAM3275), both with a similar molecular weight ($M_n \approx 235 000 \text{ g/mol}$) are compared in Figure 6.8C. As can be observed in the figure, the difference in solution viscosity increases as the temperature is increased from 20 to 80 °C. This demonstrates the potential of the random copolymers for application in EOR, especially for reservoirs where the temperature exceeds 70 °C (a limit above which usually the currently used partially hydrolyzed polyacrylamides [HPAM] are not applied).

### 6.3.6. Surface properties

**Critical micelle concentration (CMC).** The surface tension (against air) of the polymer solutions is plotted against the concentration (Figure 6.9) in order to determine the CMCs. S-shaped curves are obtained, in agreement with data on similar systems.$^{51}$ For low polymer concentrations the solutions move towards the surface tension of demineralized water (70.5 mN/m). As the polymer concentration increases, the surface tension reaches a regime where a strong decrease can be observed. Then at a specific concentration, the surface tension stops decreasing with a minimum value near 45 mN/m for the block copolymers. This specific concentration is known as the critical micelle concentration (CMC). The CMC can be determined as the concentration at the intersection of two lines of best fit at two places of the plots in Figure 6.9$^{42}$ (not shown for brevity). As the PNIPAM block length increases the concentration required for micelle formation decreases. This is clearly demonstrated by the comparison between the entries PK30-$g_{13}$- (PAM3275-b-PNIPAM415) and PK30-$g_{13}$-(PAM3275-b-PNIPAM4425). The longer the PNIPAM blocks are, the larger the effect of its lower hydrophilicity will be.$^{52}$ The order of magnitudes $10^{-6}$ and $10^{-7} \text{ M}$ is in line with literature reports for amphiphilic block copolymers.$^{53}$ All the block copolymers display a surface tension close to the value of pure PNIPAM (42 mN/m), albeit with different CMCs. This is in line with the results on linear block copolymers of
AM and NIPAM (Chapter 5). The values of the branched block copolymers is slightly higher than that of the linear block copolymers; this is most probably due to the higher molecular weight of the branched block copolymers (higher molecular weight is known to increase the surface tension\textsuperscript{54}).

![Surface tension vs. Concentration](image)

**Figure 6.9**: Surface tension against the polymer concentration of 5 different block copolymers and 2 different random copolymers (insert)

The random copolymers display a similar behavior, although the final surface tension is higher than that of the block copolymers. Depending on the composition a different final surface tension is obtained. This is in line with earlier results on random copolymers of AM and NIPAM (prepared by free radical polymerization).\textsuperscript{10} The surface tension for the 1-1 (molar ratio) random copolymer PK30-\textsubscript{g13}-(PAM1405-co-PNIPAM1405) is 60.0 mN/m which is higher than that reported\textsuperscript{52} for a linear random copolymer (54.0 mN/m).

### 6.4. Conclusion

Different comb-like block and random copolymers based on acrylamide (AM) and N-isopropylacrylamide (NIPAM) have been prepared by atom transfer radical polymerization (ATRP) in water at room temperature. The
average number of side-arms, AM and NIPAM block lengths, and the type of
distribution of the two monomers (block or random) were varied. The
aqueous solution properties of the different copolymers were investigated.
Particular emphasis is dedicated to the thermo-responsiveness of aqueous
solutions containing the copolymers. The block copolymers tend to
precipitate out of the solution at temperatures above the LCST of PNIPAM,
indicating the formation of strong aggregates. $^1$H-NMR confirmed the
precipitation of the block copolymers, where the resonances corresponding to
the isopropyl groups disappear completely above 32 °C. On the other hand,
random copolymers of AM and NIPAM do not precipitate out of the solution
(the isopropyl resonances were still present at 75 °C and their integral
remained the same). In addition, depending on the composition,
thermothickening behavior is observed. Reducing the amount of NIPAM (from
50 to 25 mol%) in the random copolymer led to a less pronounced
thermothickening behavior. The increase in solution viscosity with
temperature is only present at low shear rates ($\dot{\gamma} \leq 10 \text{ s}^{-1}$).

The CMC is a function of the molar ratio between AM and NIPAM and
their distribution. The surface tension of the block copolymers is close to the
value for pure PNIPAM, while that of the random copolymers is a function of
the composition. The lower surface tension of the solutions might be
beneficial in the recovery of oil. Coupled with the ease of synthesis,
the potential production of polyketones at a commercial scale and the solution
behavior at higher temperatures, the branched random copolymers are
potential candidates for application in EOR.

6.5. Acknowledgements

This work is part of the Research Program of the Dutch Polymer Institute
DPI, Eindhoven, The Netherlands, project #716.

6.6. References

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Branched thermosensitive copolymers

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