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Thermoresponsive comb polymers as thickeners for high temperature aqueous fluids

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Comb (co)polymers containing 17 check query responsearms of N,N-dimethylacrylamide (DMA) and N-isopropylacrylamide (NIPAM) were prepared at 0 °C in water with atom transfer radical polymerization (ATRP). The ratio between both monomers was varied and its effect on the solution properties as function of temperature was studied. Polymers containing ≤51% DMA are found to precipitate from the solution at their LCST, suggesting strong interaction between chains, while at higher DMA content the precipitation is preceded by thermothickening behaviour. The latter was only present at low shear rates (γ < 30 s⁻¹), rendering the copolymers interesting candidates for applications using viscous aqueous fluids at high temperatures such as in the oil industry.

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1. Introduction

Stimuli-responsive polymers can undergo large transformations in physical properties upon a small change in their physical or chemical environment, with temperature being the most widely studied stimulus [1], including reports on the thermal responsive-ness of poly(N-isopropylacrylamide) (PNIPAM) dating from 1967 [2]. Changes in solubility are displayed at either a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST), whereby solubility decreases or increases respectively, with increasing temperature. In that respect, Houdret et al. investigated thermoresponsive behaviour of associating polymers [3]. PNIMAM or dodecyl arms were grafted onto a poly(sodium acrylate) backbone and studied in the semidilute regime. The latter two copolymers display opposite rheological behaviour with respect to temperature, namely thermothickening and thermosthinning. Applications for thermoresponsive polymers range from rheological control additives in the oil industry (e.g. enhanced oil recovery, drilling, fracturing, cementing), drug release, gene therapy, and bioseparation to actuators and sensors [4–8].

Previous research indicated the advantages of co-polymerizing NIPAM with acrylamide (AM), especially in random copolymers, with respect to thermothickening behaviour [9]. By tailoring the monomer ratio, it was possible to obtain a pronounced increase in solution viscosity around 70–80 °C (50 mol% NIPAM). The latter effect was obtained at low shear rates, i.e. usually found deep in an oil field, while at higher shear rates, the thermothickening effect was found to diminish.

With respect to application in the oil industry, polymers have to withstand harsh conditions present in reservoirs, for prolonged times ranging up to several years. A well-known disadvantage of using AM is the hydrolysis of the amide linkage in situ. The latter introduces negative moieties along the backbone, eventually leading to precipitation of the polymer in presence of divalent ions and a subsequent loss of solution viscosity.

Introduction of N,N-dimethylacrylamide (DMA) on the other hand is known to improve the thermal and hydrolytic stability of the copolymer [10,11], rendering it an interesting alternative for AM in thermoresponsive applications that require demanding conditions.

Xu et al. recently synthesized linear diblock copolymers, containing a block of DMA and NIPAM (random) and a block of β-lactide [12]. The possibility of tailoring the LCST by playing with the ratio between DMA and NIPAM was clearly illustrated. Because of the envisioned application of the copolymers, namely drug delivery, rheological characteristics were not provided.

Fan et al. grafted NIPAM and DMA copolymer arms (M N = 4000–11,000) randomly on a backbone of acrylic acid, by reaction of amines with carboxylic acids [13]. Viscosity of aqueous solutions (2 wt.%) was found to increase by a factor 15 when increasing temperature from 40 to 65 °C, up to 800 mPa.s. However, the thermothickening effect is not only present at low shear rates and the molecular weights of the graft copolymers

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were not listed. The phenomenon was found to be apparent at high shear rates (344 s⁻¹) as well, rendering the copolymer less attractive for oil industry applications. Moreover, presence of salts was found to increase the thixotrophic effect.

Previous research has indicated the advantages of using a branched (comb) structure over a linear structure [14–16]. ATRP was applied on a macro-initiator with an average number of arms ranging from 4 to 17, in the copolymerization of AM and NIPAM. It was demonstrated for the homopolymers of AM that higher solution viscosities are obtained for the branched polymers with an average number of arms ≥12 compared to linear analogues. The latter effect was attributed to the combination of a larger hydrodynamic volume, because of stretching of the arms, and an increased entanglement density because of the higher number of arms [15]. Moreover, applying ATRP offers additional control over the reaction, making it possible to tailor the macroscopic properties of the polymer to the designated application.

While ample literature is available on thermo-responsive copolymers, limited research focusses on the application of these copolymers in the oil industry. To the best of our knowledge, employing a one step synthetic approach in the copolymerization of comb-polymers containing DMA and NIPAM with respect to the oil industry has not been displayed before. Ideally, copolymers of DMA and NIPAM display a relatively low viscosity at high shear rates. In that respect, copolymer solutions should be suitable for injection into the oil well with low energy consumption in absence of plugging. Under reservoir conditions, namely low shear rates and high temperature, an increase in solution viscosity is desirable. In the current work, such copolymers containing DMA and NIPAM are presented. Because of their superior resistance against hydrolysis, the viscosifying effect of the latter copolymers is stable over time, rendering them interesting candidates for application in the oil industry. The present research focusses on the effect of the chemical composition on the solution properties, with respect to their application in the oil industry.

2. Experimental

2.1. Chemicals

N,N-Dimethylacrylamide (DMA, 99%), N-isopropylacrylamide (NIPAM, 97%), acrylamide (AM, electrophoresis grade, ≥99%), Tris[2-(dimethylamino)ethyl]amine (Me₂TREN), copper(I)bromide (CuBr, 98%), copper(II)bromide (CuBr₂, 99%), glacial acetic acid, ethanol, chloroform and diethyl ether were purchased from Sigma–Aldrich. Purification of CuBr was performed by stirring with glacial acetic acid for at least 5 h, filtering and washing with glacial acetic acid, ethanol and diethyl ether and subsequently drying the product in vacuo. A polyethylene backbone modified with chloropropylamine hydrochloride to afford chloride groups was used as macro initiator for ATRP [16]. Functionalized polyethylene was applied as macro initiator because of its versatility in tailoring the number of initiating sites [15], its ease of synthesis [16], its suitability in the polymerization of multiple amide monomers [9,14–16], and the carbon linkage of the arms to the backbone, which makes the polymer less susceptible to hydrolysis of arms. Properties of the macro initiator are listed in Table 1.

2.2. Polymerization

The macro-initiator was added to a 250 ml three-necked flask equipped with a stirring magnet and dissolved in 10 ml acetone. NIPAM and DMA were dissolved in demineralized water and added to the initiator. The reaction mixture was degassed by application of three freeze–pump–thaw cycles and put under nitrogen atmosphere. The flask was put in an ice bath, CuBr and CuBr₂ were subsequently added to the flask and the mixture was left to stir for 10 min. Hereafter, the (co)polymerization was initiated by the addition of the ligand (Me₂TREN) through a syringe. After a pre-set reaction time of 3 h, the mixture was exposed to air and demineralized water was added to the flask to quench the reaction and reduce the viscosity. The (co)polymer was dialyzed against de-mineralized water (M₁₀ cutoff 12–14 kDa) and subsequently dried in an oven at 70 °C. The codes for the copolymers are defined as DMAy-co-NIPAMz, whereby y and z designate the corresponding number of DMA and NIPAM monomers incorporated into the copolymer.

2.3. Characterization

Conversion of DMA was measured using gas chromatography (GC). Samples of reaction mixtures were dissolved in acetone with 1000 ppm pentadecane (reference) and injected on a Hewlett-Packard 5890 GC equipped with an Elite-Wax ETR column. NIPAM conversion was determined using ¹H NMR. Spectra were recorded using a Varian Mercury Plus spectrometer operating at 400 MHz, for 64 scans, with a delay time of 1 s and D₂O as solvent.

Polymer samples were dissolved in milli-Q water containing 0.05 M sodium nitrate and subjected to gel permeation chromatography (GPC). An Agilent 1200 system was equipped with Polymer Standard Service (PSS) columns (100 Å, 1000 Å, and 300 Å, 8 mm × 300 mm) and an aqueous 0.05 M sodium nitrate solution was used as the eluent. Column temperature was maintained at 30 °C and detection (co)polymers was conducted with a refractive index (RI) detector, operated at 30 °C. AM-based calibration and WinGPC software (GPC) were used to calculate the apparent molecular weight and polydispersity (PDI) of the samples. GPC was selected despite predicted problems regarding the solubility and branched nature of the samples, to get an estimation of the molecular weight.

Cloud point measurements were performed on a Jasco V-630 UV-Vis spectrophotometer equipped with a temperature controlled six-position sample holder. The transmittance of (co)polymer solutions of 2 wt.% were recorded at 500 nm, with a heating rate of 0.5 °C/min from 25 to 80 °C against a reference sample containing demineralized water. The cloud point was designated as the temperature at which the first turbidity in the solution was obtained.

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 1750 s⁻¹ and at each step the equilibrium shear force was recorded in order to construct flow curves. Shear rate as a function of temperature was measured by increasing the temperature from 20 to 80 °C in discrete steps of 1 °C, after waiting for equilibrium at each step.

Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Elemental composition (C:H:N, wt.%)</th>
<th>Xₜₜₜ (%)</th>
<th>Average number of pyrrole units</th>
<th>MₙGPC (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30 (virgin)</td>
<td>67.6:8:4.0</td>
<td>–</td>
<td>0</td>
<td>2800</td>
<td>1.74</td>
</tr>
<tr>
<td>PK30-C117</td>
<td>73.7:7.9:6.1</td>
<td>81.3</td>
<td>47</td>
<td>2120</td>
<td>2.18</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Polymerization

Aqueous (co)polymerization of NIPAM and DMA was conducted according to the scheme outlined in Fig. 1, yielding graft copolymers consisting of 17 arms with different compositions. Experimental ratios as well as conversions are listed in Table 2. After 3 h, the latter was found to vary between 50 and 98%, the lower values ascribed to oxidation of the catalyst (Cu(I)). Reactivity of both monomers was found to be comparable, with DMA displaying a slightly higher average conversion compared to NIPAM. Bauri et al. recently investigated the reactivity ratios of NIPAM and DMA [17]. The reactivity ratios of NIPAM and DMA were calculated as \( r_{\text{NIPAM}} = 0.838 \) and \( r_{\text{DMA}} = 1.105 \), indicating a slightly higher rate of incorporation of DMA. The authors polymerized up to low molecular weight \( (M_{\text{theo}} < 16,000 \text{ g/mol}) \) in DMF at 70 °C by RAFT polymerization. Correspondingly, the present work identifies a slightly higher (average) rate of incorporation of DMA. Similar copolymerizations with AM and NIPAM displayed a perfectly random distribution [9], moreover, composition was found to be very near to the feed ratio in the radical copolymerization of DMA and NIPAM [13]. Monomer ratios were checked with \(^1\text{H} \) NMR (displayed in Fig. 2) and were found to have good correspondence with experimental ratios. Moreover, monomer conversion was not found to be influenced by the exact ratio between the monomers applied.

3.2. Lower critical solution temperature

Due to its chemical nature, hydrophilicity of PNIPAM deteriorates at its LCST around 32 °C [18]. However, by copolymerizing with a hydrophilic monomer, it is possible to tailor the LCST of the copolymer. In Fig. 3, cloud point measurements for graft (co)polymers with different fractions of NIPAM and DMA are displayed. As shown, LCST is found to increase with decreasing the NIPAM fraction, corresponding with incorporating more hydrophilic monomer in the copolymer. Similar results were obtained for random copolymers of DMA and NIPAM with an additional block of poly lactic acid (PLA) [12].

![Fig. 1. ATRP (co)polymerization of NIPAM and DMA with 17-arm macro-initiator.](image1)

![Fig. 2. 1H NMR spectra of graft (co)polymers of DMA and NIPAM containing different monomer ratios.](image2)
Table 2
ATRP of graft copolymers of DMA and NIPAM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PK30-g17 (DMA5260)</th>
<th>DMA</th>
<th>NIPAM</th>
<th>CuBr/CuBr₂</th>
<th>Mₜ₀/TREN</th>
<th>Conv (%) DMA</th>
<th>Conv (%) NIPAM</th>
<th>M₁: L</th>
<th>Mₜ₀,conv (g/mol)</th>
<th>Mₜ₀,GPC (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-g17-(DMA3765-co-NIPAM385)</td>
<td>1</td>
<td>6.205</td>
<td>1.69/0.35</td>
<td>1.36</td>
<td>85.8</td>
<td>69.4d</td>
<td>49.7</td>
<td>0.13</td>
<td>542.291</td>
<td>330.300</td>
<td>2.91</td>
</tr>
<tr>
<td>PK30-g17-(DMA4555-co-NIPAM1530)</td>
<td>1</td>
<td>4.695</td>
<td>1.560</td>
<td>1.85/0.29</td>
<td>1.49</td>
<td>97.0</td>
<td>97.8</td>
<td>0.14</td>
<td>527.243</td>
<td>290.800</td>
<td>3.00</td>
</tr>
<tr>
<td>PK30-g17-(DMA2015-co-NIPAM1290)</td>
<td>1</td>
<td>3.920</td>
<td>2.350</td>
<td>1.55/0.32</td>
<td>2.65</td>
<td>51.4</td>
<td>51.0</td>
<td>0.14</td>
<td>348.562</td>
<td>345.900</td>
<td>2.81</td>
</tr>
<tr>
<td>PK30-g17-(DMA2765-co-NIPAM2705)</td>
<td>1</td>
<td>3.125</td>
<td>3.115</td>
<td>0.90/0.32</td>
<td>1.59</td>
<td>48.5</td>
<td>47.8</td>
<td>0.14</td>
<td>582.573</td>
<td>235.800</td>
<td>3.51</td>
</tr>
<tr>
<td>PK30-g17-(DMA1835-co-NIPAM2645)</td>
<td>1</td>
<td>2.355</td>
<td>3.945</td>
<td>1.81/0.29</td>
<td>3.09</td>
<td>77.9</td>
<td>67.0</td>
<td>0.14</td>
<td>483.728</td>
<td>162.900</td>
<td>5.06</td>
</tr>
<tr>
<td>PK30-g17-(DMA1455-co-NIPAM4570)</td>
<td>1</td>
<td>1.570</td>
<td>4.685</td>
<td>1.55/0.29</td>
<td>1.49</td>
<td>92.8</td>
<td>97.5</td>
<td>0.14</td>
<td>564.129</td>
<td>122.700</td>
<td>5.48</td>
</tr>
<tr>
<td>PK30-g17-(DMA665-co-NIPAM3720)</td>
<td>1</td>
<td>740</td>
<td>5535</td>
<td>1.52/0.29</td>
<td>1.57</td>
<td>89.5</td>
<td>67.2</td>
<td>0.14</td>
<td>489.751</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PK30-g17-(NIPAM4400)</td>
<td>1</td>
<td>6.205</td>
<td>1.54/0.29</td>
<td>2.97</td>
<td>-</td>
<td>70.9</td>
<td>70.9</td>
<td>0.11</td>
<td>500.634</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a Measured with GC.

b Determined by 1H NMR.

c Calculated based on ratio l:M.

d Measured gravimetrically.

e Not possible to measure with GPC.

However, also displayed the largest hydrodynamic volume in GPC measurements. Polymers with a NIPAM fraction of 85% and higher, did not yield interpretable peaks with refractive index measurements. The latter might be related to the LCST of these copolymers being in close vicinity to the temperature at which the GPC is operated. Contrarily, the other (co)polymers showed clear peaks in GPC measurements. In previous research, solution viscosity of comb copolymers of NIPAM and AM was found to increase with AM content [9]. The latter is attributed to the pronouncedly higher solution viscosity of the AM homopolymer. In the present work, differences in solution viscosity among the different (co)polymers are attributed to a combination of differences in the molecular weight of the (co)polymers and a higher viscosifying effect of NIPAM compared to DMA. Generally, (co)polymers with higher experimental molecular weights were found to display higher solution viscosities. However, a high NIPAM fraction in the copolymer was found to compensate for a pronouncedly lower molecular weight, as displayed in copolymer PK30-g17-(DMA1835-co-NIPAM2645) and PK30-g17-(DMA1455-co-NIPAM4570). Similarly, a higher intrinsic viscosity of PNIPAM, compared to poly(N,N-dimethylacrylamide) (PDMA) was reported in literature for measurements in methanol [19]. Deviations of the experimental molecular weight (measured by GPC) from the theoretical molecular weight might originate from the synthetic procedure. The initiator, namely, is hydrophobic in nature and is solubilized by dissolution in a cosolvent (acetone) before adding the remaining solvent (water). In case of marginal solubility of the initiator, it is possible for some of the latter to precipitate out of solution and not participate in the further reaction, leading to an underestimation of the initiator to monomer ratio, and a discrepancy between the theoretical and actual molecular weight. Moreover, deviation of the measured molecular weight from the theoretical molecular weight might be attributed to different interactions between the (co)polymers and the GPC columns. Especially copolymers containing a large fraction of NIPAM, display relatively low number average molecular weights. The GPC is calibrated with polyacrylamide standards, rendering interpretations of the measured molecular weights challenging. In order to be more conclusive on the exact nature of the differences in viscosifying effect, more accurate molecular weight analyses are required.

In Fig. 5, the viscosity as a function of the shear rate at different temperatures of copolymer PK30-g17-(DMA4555-co-NIPAM1530) is displayed. As shown, viscosity is found to decrease over the whole range of measured shear rates when increasing the temperature from 20 to 50 °C. However, increasing the temperature to 80 °C yields remarkable results. At low shear rates (γ ≤ 1 s⁻¹), viscosity is found to be higher at 80 °C than at 20 °C. Contrarily, at higher shear rates, viscosity was found to decrease significantly with increasing temperature. The latter indicates that weak
interactions between copolymer chains are present in the mixture at low shear rates; however, when the shear rate is increased, this interactive effect diminishes and solvent viscosity combined with weaker H-bonding [20] becomes governing for the solution viscosity [21]. Similar results were obtained with graft copolymers of AM and NIPAM, however, these copolymers contained a larger monomeric fraction of NIPAM (50 mol%) [9]. Industries like oil production can benefit from the obtained effect, as less work is required during injecting, while in the field a desirable increase in solution viscosity is obtained.

3.4. Solution properties as function of temperature

Comb (co)polymers with different monomeric compositions were subjected to viscosity measurements as a function of temperature. As shown in Figs. 6 and 7, viscosity of aqueous solutions was found to increase at a certain temperature, near the LCST of the copolymer. However, the degree to which the thickening behaviour was observed was found to increase with increasing the DMA ratio, i.e. at higher DMA content (≥61 mol%) precipitation was preceded by a marked increase in solution viscosity. According to literature, the LCST of a (linear) DMA homopolymer was determined to be 216 °C [22]. Correspondingly, the viscosity of an aqueous solution of PK30-g17-(DMA5260) was not found to increase in the measured temperature range ($\gamma = 1 \text{ s}^{-1}$).

At a low shear rate ($\gamma = 1 \text{ s}^{-1}$), the thermostickening effect was found to be especially pronounced for copolymers containing NIPAM, although, at a shear rate of 10 s$^{-1}$ the former was still present. In Figs. 8 and 9, the viscosity versus temperature for two
different copolymer solutions at several shear rates are displayed. 
As can be seen, at low shear rates \( (\gamma \leq 30 \text{s}^{-1}) \) the thermosthickening effect is present, however, at higher shear rates \( (\gamma > 50 \text{s}^{-1}) \), it diminishes. The latter is beneficial from an application point of view, as shear rates during injection of \( \text{(co)polymer} \) solutions into oil wells are relatively high \( \text{[23]} \), while in the permeable rock formations low shear rates become apparent due to low linear velocities.

In order to confirm solubility of the copolymer samples, visual inspections were undertaken. In Fig. 10, a photograph of two samples with LCSTs of 90 and 52 °C respectively are shown. At 20 °C, both solutions are clear and confirm dissolution of the copolymer. However, after heating to 80 °C, the copolymer with a LCST of 52 °C clearly precipitates out of solution, while the polymer with a LCST of 90 °C is still nearly dissolved. The latter copolymer, however, precipitates when heating the solution to a temperature of 90 °C or higher (not shown for brevity).

In order to explain the difference between copolymers of NIPAM and AM versus NIPAM and DMA, solubility parameters were calculated according to Hoftyzer–Van Krevelen \( \text{[24]} \). As shown in Table 3, the solubility parameter \( (\delta) \) of PDMA and PNIPAM are pronouncedly lower than that of PAM, the latter being very comparable to the value of water. A calculated solubility parameter of a polymer near the solubility parameter of a solvent is an indication for solubility. However, as the difference between the two values increases, solubility is expected to decrease, especially at \( \delta_{\text{polymer}} - \delta_{\text{solvent}} > 5 \sqrt{\text{Mj/m}^3} \) \( \text{[24]} \). Compared to similar comb copolymers containing NIPAM and AM, less NIPAM was found to be required in order to obtain an LCST at lower temperature. Moreover, thermosthickening behaviour was displayed already at lower NIPAM content in the copolymer. Both effects are ascribed to the lower degree of hydrophilicity of DMA compared to AM. The latter is indeed confirmed by calculating the solubility parameter, displaying higher hydrophilicity of PAM compared to PDMA.

Table 3
Solubility parameter calculated according to Van Krevelen \( \text{[24]} \).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \delta \sqrt{\text{Mj/m}^3} )</th>
<th>( (\delta_{\text{polymer}} - \delta_{\text{solvent}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td>23</td>
<td>-6.4</td>
</tr>
<tr>
<td>PDMA</td>
<td>19.9</td>
<td>-3.5</td>
</tr>
<tr>
<td>PNIPAM</td>
<td>16.6</td>
<td>-6.8</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>23.4</td>
<td>-</td>
</tr>
</tbody>
</table>

4. Conclusion

ATRP in water was employed at 0 °C to grow arms consisting of NIPAM and DMA from an initiator with 17 reactive groups, leading to comb \( \text{(co)polymer} \)s with arms of different composition with theoretical molecular weights ranging from 349,000 to 664,000g/mol. Solubility of \( \text{(co)polymer} \)s was determined by UV–Vis spectrophotometry and visual inspection, and aqueous solutions were subjected to rheological measurements. Polymers containing up to 49% NIPAM were found to display a clear LCST and precipitate out of solution. A smaller NIPAM share, however, led to thermosthickening behaviour, followed by precipitation. Compared to equivalent copolymers consisting of NIPAM and AM, a smaller share of NIPAM is required to obtain a viscosifying effect at higher temperatures, because of the lower hydrophilicity of DMA. A copolymer containing 25% NIPAM displayed remarkable results, as it offers thermosthickening behaviour at elevated temperatures \( (T > 65 \text{s}^{-1}) \) and low shear rates \( (\gamma < 30 \text{s}^{-1}) \), while this effect was found to vanish with increasing the shear rate. Finally, substituting AM with DMA in the comb \( \text{(co)polymer} \) offers a pronounced increase in hydrolytic stability, rendering the \( \text{(co)polymer} \) a promising candidate for application in the oil industry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at: http://dx.doi.org/10.1016/j.mtcomm.2016.12.001.

References


