Synthesis of cationic flocculants based on acrylamide and [2-(acryloyloxy)ethyl]trimethylammonium chloride copolymers by semicontinuous inverse microemulsion polymerization. Part II: influence of initiator addition conditions, initial temperature, pH and comonomer concentration on flocculating performance

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Abstract: The influence of initiator concentration, specific flow rate of initiator addition ($Q_{sp}$), initial copolymerization temperature ($T_i$), aqueous phase pH and total comonomer concentration (TCC) on flocculating performance of latex particles of acrylamide and [2-(acryloyloxy)ethyl]trimethylammonium chloride copolymers with a cationic charge density of 40%, obtained by inverse microemulsion copolymerization by using a surfactant blend of Arlacel 83 and Softanol 90 as emulsifier and Rolling M-245, a mixture of n-decane and n-tetradecane in about 40/60 weight ratio, as oil phase, has been studied for high TCC, ranging from 28 to 34.5% (w/w). Comonomer inverse microemulsion copolymerizations were carried out in the semicontinuous mode by adding continuously an aqueous solution of sodium metabisulfite as initiator into stirred inverse comonomer microemulsions. Initiator concentration has a strong influence on viscosity, viscometric structuring degree (VSI) and average weight molar mass ($M_w$) of copolymers in the range from 5 to 25 g/L. Both viscosity and $M_w$ decrease with increasing initiator concentration. Best flocculating performance is obtained from 10 to 20 g/L, values at
which VSI shows a minimum. Under the experimental conditions used, $Q_v$ (153 to 310 mL/h/kg of comonomer), $T_i$ (25 to 35°C) and aqueous phase pH (2.5 to 4.5) have almost no influence on both viscosity and VSI and, hence, on flocculating performance. On the contrary, TCC has a slight influence on copolymer viscosity but a strong one on VSI which increases dramatically with TCC, being the worst flocculating performance obtained at the highest TCC studied (34.5% (w/w)). Flocculating performance results are explained in terms of copolymer structuring degree and collapsed state of copolymer chains inside latex particles as well as in terms of the composition drift with conversion.

**Introduction**

Polyacrylamide and its copolymers with anionic and quaternary ammonium monomers are worldwide used in applications such as paper making (finest retention), flocculation of municipal and industrial waste water, and enhanced oil recovery [1-3]. Most common marketed acrylamide-based flocculants are anionic and cationic copolymers, the latter being the most interesting from the commercial point of view, due to their higher added value. Nonionic polymers have little application in water treatment processes. Anionic flocculants are mainly used for potable water production or for flocculation of inorganic dispersions while cationic flocculants are used for sludge flocculation and dewatering in waste water treatment.

They are mainly supplied either in a solid state or as an inverse emulsion [4]. In the first case, the main problem is the time used to prepare the flocculant solution just prior to the application because such solution must be prepared daily in order to avoid copolymer degradation. In the second one, in spite of the fact that inverse emulsion latex particles are easy to handle and can be obtained with polymer concentrations above 30% (w/w) with emulsifier concentrations below 4% (w/w) (based on total weight of the emulsion), they lack thermodynamic stability resulting in phase separation.

To overcome this problem, during the 1980s a new polymerization method was used to obtain flocculants: inverse microemulsion polymerization [5]. Microemulsions are transparent, homogeneous mixtures of water, or an aqueous solution of chemicals, and oil stabilized by a fairly large amount of surfactant or, in most cases, surfactant mixture. Inverse microemulsions can adopt a large variety of structural organizations, ranging from small globules of uniform size ($\sim 10^{-2}$ μm), in the oil-rich region, to bicontinuous structures with randomly connected oil and water domains in the phase inversion region. The inverse microemulsion copolymerization of acrylamide (AM) and ionic monomers allows the preparation of stable, clear or milky, low viscosity microlatex particles of a high molar mass ($\sim 10^7$ g/mol) useful as flocculants. However, to achieve this goal, a higher concentration of surfactant mixture must be used in comparison with inverse emulsions in order to stabilize the system. The surfactant concentration in an inverse emulsion is ranged between 2 and 4% (w/w), considerably lower than the one in an inverse microemulsion, generally $> 10\%$ (w/w) although lower concentrations are needed if a heterophase water-in-oil polymerization process is used [6], by means of which starting from an inverse emulsion of monomers an inverse microemulsion is obtained after polymerization.

Up to now, most inverse microemulsion polymerization work related to
products useful as flocculants has been devoted to both acrylamide (AM) homopolymerization [6, 7-11] and acrylamide copolymerization with alkaline metal acrylates and methacrylates, such as sodium acrylate [12] and 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) [13], or cationic monomers, basically quaternary ammonium acrylates and methacrylates, meanly (2-(methacryloyloxy)ethyl)trimethylammonium chloride (MADQUAT) [14-16]. Also, ampholytic terpolymers based on acrylamide, MADQUAT and NaAMPS have been obtained by inverse microemulsion polymerization [17, 18].

Due to its relative reactivity, similar to AM [19, 20], [2-(acryloyloxy)ethyl]trimethylammonium chloride (Q9) is often copolymerized with AM for manufacturing commercial cationic flocculants. Despite this, there is no systematic study either about copolymerization of both monomers in inverse microemulsion or about flocculating properties of copolymers thus obtained. Criteria for selecting a comonomer inverse microemulsion formulation of AM and Q9 were discussed in an earlier paper [21] and a specific comonomer formulation with a cationic charge density (Q9 concentration by weight based on total amount of comonomers) of 40% (w/w) was chosen for semicontinuous copolymerization studies (see experimental part) using sodium metabisulfite (SMB) as initiator. In this paper, we report the influence of some inverse microemulsion copolymerization variables, namely initiator concentration, specific flow rate of initiator addition (Qsp), initial temperature (T_i), aqueous phase pH and total comonomer concentration (TCC) on flocculating performance of copolymers obtained, correlating the flocculating yield with both viscosity (molecular weight) and structuring degree of copolymers. In a forthcoming paper, influence of HLB and emulsifier concentration will be addressed. Products are under patent [22].

**Results and discussion**

*System evolution during copolymerization*

Before copolymerization the system was a true inverse microemulsion as it was visually observed by the transparency of dispersions as well as by their stability after centrifuging at 5,000 rpm for 30 min. No phase separation was observed. Just after beginning the copolymerization, the evolution is similar to other acrylamide inverse microemulsion copolymerizations reported in the literature: the transparent and water-like viscosity microemulsion turns into a viscous and turbid macroemulsion at the early stages of copolymerization and later returns to a transparent and low viscosity system with inverse microemulsion structure. Candau et al. [5, 9, 23] describe this transition as due to microstructure changes from a bicontinuous microstructure to an inverse globular one.

*Influence of initiator concentration*

Experimental conditions and results obtained in copolymerizations carried out to study the influence of this variable from 2.5 g/L to 25 g/L are given in Tab. 1.
For the selected $Q_{sp}$, below 5 g/L the initial monomer microemulsion does not evolve into a stable copolymer microemulsion and gel formation (self-inversion) occurs during copolymerization (run R1). Thermal jumps ($\Delta T$; difference between copolymerization peak temperature and initial one) are ranged between 59 ºC and 64ºC for runs R3 to R6, and peak temperature is achieved in less than 1 min. However, for run R2 peak temperature is 57 ºC and is attained in 1.5 min, showing that the lower the initiator concentration the lower the reaction rate. Then, an explanation of the observed self-inversion for run R1 must be related to its low initiator concentration (2.5 g/L) and, hence, to its low reaction rate, as well as to the system evolution during copolymerization described in the above section.

Tab. 1. Influence of initiator concentration. Copolymerization conditions: $T_{initial}$ = 30 ºC; specific flow rate of initiator addition = 307.7 mL/h*kg of comonomers; aqueous phase pH = 4.05; initiator solution pH = 3.5; monomer concentration = 32.2 % (w/w). Surfactant blend HLB = 8.3. Meaning of symbols is given in experimental part.

<table>
<thead>
<tr>
<th>Run #</th>
<th>[SMB] (g/L)</th>
<th>BV (cP)</th>
<th>SV (cP)</th>
<th>VSI</th>
<th>Residual AM (ppm)</th>
<th>$C_{AM}$ (%)</th>
<th>$M_w*10^6$ (g/mol)</th>
<th>$R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>2.5</td>
<td>Self-inversion (unstable)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>5</td>
<td>171.4</td>
<td>23.6</td>
<td>7.3</td>
<td>475</td>
<td>99.75</td>
<td>6.14</td>
<td>175.6</td>
</tr>
<tr>
<td>R3</td>
<td>10</td>
<td>155.2</td>
<td>23.8</td>
<td>6.5</td>
<td>583</td>
<td>99.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>15</td>
<td>137.0</td>
<td>22.6</td>
<td>6.1</td>
<td>478</td>
<td>99.75</td>
<td>5.48</td>
<td>146.5</td>
</tr>
<tr>
<td>R5</td>
<td>20</td>
<td>132.6</td>
<td>21.6</td>
<td>6.1</td>
<td>378</td>
<td>99.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R6</td>
<td>25</td>
<td>125.4</td>
<td>19.0*</td>
<td>6.5</td>
<td>453</td>
<td>99.76</td>
<td>5.04</td>
<td>148.6</td>
</tr>
</tbody>
</table>

* Value out of recommended viscometer measurement range. Viscosity accuracy lower than one for the rest of samples.

The transformation of the monomer microemulsion in a viscous, turbid macroemulsion at the early stages of copolymerization may be related to the comonomers consumption. Taking into account that both AM and Q9 behave as cosurfactants [7-9,14], the depletion of comonomer concentration results in a reduced microemulsion domain and, therefore, the system evolves to a macroemulsion which will only turn back to an inverse clear microemulsion if another factor counteracts the loss of monomer cosurfactant action. According to Hernández-Barajas and Hunkele [6] this factor is the temperature rise produced during polymerization which enlarges the inverse microemulsion domain in the phase diagram. They concluded that at low rates of reaction the heat generated is insufficient to move the phase boundary and the system cannot evolve to an inverse microemulsion. Then, phase separation or gel formation occurs, such as in our case for reaction R1. However, the later explanation cannot justify why the system remains as a stable microemulsion for runs R-2 to R-6 just after copolymerization has been completed and temperature returns to room temperature. At this point, with almost zero comonomer concentration, inverse microemulsion domain in the phase diagram would be shortened again leading to phase separation. As this does
not happen we must conclude that cationic copolymer has a cosurfactant character.

BV and average weight molar mass ($M_w$) variation with SMB concentration are plotted in Fig. 1. As it can be seen, BV, $M_w$ and $R_g$ (Tab. 1) decrease with SMB concentration. These results are in agreement with predictions of free radical polymerization theory. On the other hand, a good correlation between BV and $M_w$ can be observed in Fig. 1, indicating that under the experimental conditions used there is no appreciable modification of copolymer microstructure with initiator concentration.

Copolymer flocculating performances as measured by CST test are given in Fig. 2. As shown, copolymers with highest BV and $M_w$ (R2) show the lowest flocculation yield. The other copolymers show similar results although the best are obtained for copolymers R3 y R4.

![Graph showing BV and Mw variations as a function of SMB concentration](image)

**Fig. 1.** Bulk viscosity (BV) and molar mass ($M_w$) variations as a function of SMB concentration for reactions given in Tab. 1.

Generally accepted flocculation theory states that the higher the molecular weight of a flocculant the higher its flocculating performance due to the increased probability for bridge formation between particles [24] which is not in agreement with the results given in Fig. 2. The reason may be due to the fact that in CST tests mixing times higher than those needed for agglomeration of formed flocs (ball formation) were used. Consequently, CST tests measure not only the flocculating performance (formation of flocs and sludge dewatering speed) but also the shear strength of already formed and agglomerated flocs and, hence, their physical stability. Therefore, flocculating performance is not only controlled by copolymer $M_w$ but also by copolymer microstructure as it has been pointed out by others authors [24, 25].
In this work, the copolymer structuring degree (which is related to the degree of branching and/or crosslinking) has been related to the relationship \( \frac{BV}{SV} \) [26] and from now it will be referred to as viscometric structuring degree (VSI). The higher the VSI the higher the structuring degree. The relationship between VSI and structuring degree has been also clearly demonstrated by Ochoa et al. [27] for cationic floculants based on acrylamide and [2-(acryloyloxy)ethyl] trimethylammonium chloride copolymers with a cationic charge density of 80%, a similar system to the one reported in this paper and whose synthesis was likewise carried out by semicontinuous inverse microemulsion copolymerization using the same surfactant blend and organic solvent than the ones used here. For this system, the addition to the aqueous phase of increasing amounts of a crosslinking agent (MBA: N,N’-methylenbisacrylamide) from 10 ppm to 125 ppm (based on the total amount of comonomers) resulted in a dramatic increase in VSI from 4.9 (0 ppm) to 70.4 (123 ppm) with increasing values with MBA concentration: 12.5 (10 ppm), 25.3 (30 ppm) and 52.3 (62 ppm).

As it can be seen from Tab. 1, VSI decreases with SMB. VSI is maximum for run R2 ([SMB] = 5 g/L) and its minimum value is reached at a SMB concentration ranged from 10 to 15 g/L, concentration range in which highest flocculating performance is achieved.

At low initiator concentration (run R2) both \( M_w \) and VSI are higher than for higher initiator concentrations. The copolymer R2 is more structured which may be due to the longer chain length which implies that during copolymerization copolymer chain has been growing in a highly collapsed state. In this situation, the formation of both inter and intramolecular hydrogen bonding as well as long chain branching [6] are favored which in turn result in an enhanced shield of the cationic charge density available for flocculation and also in a less expanded conformation of the copolymer in the inverted solution to be dosed into the sludge. Consequently, flocculating performance decreases. The collapsed state of copolymer inside latex particles in microemulsion can be deduced by the fact that, for instance, a polyacrylamide with \( M_w \) of \( 10^7 \) g/mol has a radius of gyration \( (R_g) \) above 200 nm, much higher than the average diameter of a micelle in a polymer microemulsion which is...
about 100 nm [28]. In fact, we measured the size of latex particles for run R4 by transmission electronic microscopy (see Fig. 3) following the method given in the Experimental Part and we found that their average diameter was 87.4 nm, all diameters ranging from 73.6 to 99.3 nm, much lower than \( R_g \) for sample R4 (146 nm).

On the other hand, the higher collapsed state of polymer chains in inverse microemulsion compared to solution or inverse emulsion polymerizations could result in reactions with the unsaturated groups of the oleate portion of one of the surfactants (Arlacel 83) in the emulsifier blend [29-31], reactions which are part of a long chain branching cascade leading to a more structured polymer.

![Fig. 3. TEM image for run 4 (HLB 8.26). Bar indicates 200 nm.](image)

For SMB concentrations ranging from 15 to 20 g/L, \( M_w \) decreases. Polymer chains grow in a less collapsed state than in the reaction R2 and, hence, VSI also decreases. Consequently, the flocculating performance improves slightly. For SMB concentrations above 25 g/L the decrease of \( M_w \) is the prevalent factor and flocculating performance decreases again.

Finally, residual acrylamide concentrations in copolymer inverse microemulsions are also given in Tab. 1. All of them are below 600 ppm and consequently acrylamide conversions \( (C_{AM}) \) are higher than 99.6%. The same results were obtained for the rest of reactions reported in this paper. Therefore, from now \( C_{AM} \) will not be specified. Taking into account that Q9 reactivity is higher than AM one, Q9 conversions have been assumed to be 100% for all reactions.
**Influence of specific flow rate of initiator addition (Q_{sp})**

Experimental conditions and results obtained in copolymerizations carried out to study the influence of this variable from 150 to 310 mL/h/kg of comonomers for a SMB concentration of 15 g/L are given in Tab. 2.

**Tab. 2.** Influence of specific flow rate of initiator addition (Q_{sp}). Copolymerization conditions: initiator aqueous solution concentration = 15 g/L; T_{initial} = 30 °C; aqueous phase pH = 4.05; initiator solution pH = 3.5; monomer concentration = 32.2 % (w/w). Surfactant blend HLB = 8.3. ΔT = thermal jump. t_{Tpeak} = reaction time to reach the copolymerization peak temperature.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Q_{sp} (mL/h/kg of comonomers)</th>
<th>ΔT (°C)</th>
<th>t_{Tpeak} (s)</th>
<th>BV (cP)</th>
<th>SV (cP)</th>
<th>VSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>R7</td>
<td>153.8</td>
<td>55.9</td>
<td>90</td>
<td>147.2</td>
<td>23.8</td>
<td>6.2</td>
</tr>
<tr>
<td>R8</td>
<td>205.1</td>
<td>56.0</td>
<td>75</td>
<td>145.2</td>
<td>23.6</td>
<td>6.2</td>
</tr>
<tr>
<td>R9</td>
<td>256.4</td>
<td>56.3</td>
<td>75</td>
<td>139.0</td>
<td>22.4</td>
<td>6.2</td>
</tr>
<tr>
<td>R4</td>
<td>307.7</td>
<td>62.3</td>
<td>50</td>
<td>137.0</td>
<td>22.6</td>
<td>6.1</td>
</tr>
</tbody>
</table>

As it can be seen from Tab. 2, in the range studied Q_{sp} has a very slight influence on BV and no one on VSI. Accordingly, the flocculating performance of the copolymers should be similar as it was showed by CST tests (not reported because all samples shared the same CST curve). The only effect of this variable was related to the copolymerization rate which increases with Q_{sp} as measured by t_{Tpeak}.

**Influence of initial copolymerization temperature (T_i)**

Experimental conditions and results obtained in copolymerizations carried out to study the influence of this variable from 25 to 35 °C for a Q_{sp} of 307.7 mL/h/kg of comonomers and for a SMB concentration of 15 g/L are given in Tab. 3. In all cases ΔT was ranged from 55.6 °C to 58.2 °C and t_{Tpeak} was equal to 75 s, indicating that in the range studied copolymerization rate was independent on T_i.

**Tab. 3.** Influence of T_i. Copolymerization conditions: initiator aqueous solution concentration = 15 g/L; Q_{sp} = 307.7 mL/h/kg of comonomers; aqueous phase pH = 4.05; initiator solution pH = 3.5; monomer concentration = 32.2 % (w/w). Surfactant blend HLB = 8.3. T_{peak}: peak temperature during copolymerization.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T_i (°C)</th>
<th>T_{peak} (°C)</th>
<th>BV (cP)</th>
<th>SV (cP)</th>
<th>VSI</th>
<th>M_w*10^5 (g/mol)</th>
<th>Rg (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R10</td>
<td>25</td>
<td>83.2</td>
<td>168.8</td>
<td>24.4</td>
<td>6.9</td>
<td>6.03</td>
<td>157.2</td>
</tr>
<tr>
<td>R2</td>
<td>30</td>
<td>87.9</td>
<td>171.4</td>
<td>23.6</td>
<td>7.3</td>
<td>6.14</td>
<td>175.6</td>
</tr>
<tr>
<td>R11</td>
<td>35</td>
<td>90.6</td>
<td>177.4</td>
<td>24.2</td>
<td>7.3</td>
<td>7.49</td>
<td>186.9</td>
</tr>
</tbody>
</table>

In the range studied both BV and M_w increase very slightly with T_i, which are anomalous results according to the radical polymerization theory that predicts an opposite variation. One possible explanation is that the higher the T_i the
higher the peak temperature during copolymerization and, therefore, the average copolymerization temperature increase with $T_i$. Consequently, taking into account that polyacrylamides are known to branch at temperatures above 70-75°C (intermolecular imidization) [32] the slight increase in both BV and $M_w$ may be related to an increase in the structuring degree with $T_i$, assumption which is in agreement with the also slight increase in VSI with $T_i$.

CST tests (not shown) indicated that flocculating performances were very similar for all the copolymers, results in accordance with the slight differences in BV, $M_w$ and VSI thereof.

Influence of aqueous phase pH

Experimental conditions and results obtained in copolymerizations carried out to study the influence of this variable from 2.5 to 4.5 at $T_i$ 30ºC for a $Q_{sp}$ of 307.7 mL/h/kg of comonomers and for a SMB concentration of 15 g/L are given in Table 4. In the range studied pH has almost no influence on both BV and VSI (VSI at pH 4.50 is higher than the others but at this pH SV measurement had a higher experimental error due to be out of recommended viscometer measurement range). This behaviour was likewise reflected on flocculating performances (CST curves not shown because there is no difference between them) of the copolymers which were practically independent on aqueous phase pH.

The only pH effect observed was a strong viscosity increase of the latex at pH 4.5 which could be due to a modification of the surface composition of latex particles resulting in stronger interparticle attractive interactions. This modification in particle surface composition could be caused by an increase of Softanol 90 solubility in the aqueous pool of microemulsion at pH 4.5. Then, its concentration in the interface (in the latex particle surface) between the dispersed water phase and the continuous oil phase would decrease and the interface would become enriched in the oil soluble surfactant (Arlacel 83).

Tab. 4. Influence of aqueous phase pH. Copolymerization conditions: initiator aqueous solution concentration = 15 g/L; $Q_{sp}$ = 307.7 mL/h/kg of comonomers; initiator solution pH = 3.5; monomer concentration = 32.2 % (w/w); $T_i$ = 30ºC Surfactant blend HLB = 8.3. $\Delta T$ = thermal jump. $t_{Tpeak}$ = reaction time to reach the copolymerization peak temperature.

<table>
<thead>
<tr>
<th>Run #</th>
<th>pH</th>
<th>$\Delta T$ (ºC)</th>
<th>$t_{Tpeak}$ (s)</th>
<th>BV (cP)</th>
<th>SV (cP)</th>
<th>VSI</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>R12</td>
<td>2.49</td>
<td>62.6</td>
<td>60</td>
<td>144.0</td>
<td>22.2</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>R13</td>
<td>3.50</td>
<td>64.5</td>
<td>50</td>
<td>137.6</td>
<td>21.8</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>4.00</td>
<td>62.5</td>
<td>50</td>
<td>137.0</td>
<td>22.6</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>R14</td>
<td>4.50</td>
<td>64.1</td>
<td>45</td>
<td>144.6</td>
<td>16.4*</td>
<td>8.8</td>
<td>Thick latex</td>
</tr>
</tbody>
</table>

* Value out of recommended viscometer measurement range. Viscosity accuracy lower than one for the rest of samples.

Particle surfaces enriched in the oil soluble surfactant would allow latex particles to become in close vicinity each other, thereby establishing strong hydrogen bonding interactions between the OH groups of the Arlacel 83.
sorbitan moieties from different particles, which ultimately would result in an increase of latex viscosity. However, with the available data no experimental evidence of this assumption can be given.

**Influence of total comonomer concentration (TCC)**

From an industrial standpoint, it is very desirable to increase the active matter concentration of inverse microemulsions. Experimental conditions and results obtained in copolymerizations carried out to study the influence of this variable from 28.5% (w/w) to 34.5% (w/w) at 35°C for a \( Q_{sp} \) of 151.9 mL/h/kg of aqueous phase and for a SMB concentration of 15 g/L are given in Tab. 5. Viscometric and flocculating performance results were compared to C1594 (marketed in Spain by Acideka S.A. and manufactured by Cytec Technology Corp. USA), a commercial cationic flocculant of the same cationic charge as the ones herein reported but manufactured by inverse emulsion copolymerization of AM and Q9 instead of inverse microemulsion copolymerization.

**Tab. 5.** Influence of TCC. Copolymerization conditions: initiator aqueous solution concentration = 15 g/L; \( Q_{sp} \) = 151.9 mL/h/kg of aqueous phase; aqueous phase pH = 4.05; initiator solution pH = 3.5; surfactant blend HLB = 8.3; \( T_i \) = 30°C.

<table>
<thead>
<tr>
<th>Run #</th>
<th>TCC (% (w/w))</th>
<th>( \Delta T ) (°C)</th>
<th>( t_{Peak} ) (s)</th>
<th>BV (cP)</th>
<th>SV (cP)</th>
<th>VSI</th>
<th>( M_w \times 10^6 ) (g/mol)</th>
<th>Rg (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1594</td>
<td>34.5</td>
<td>-</td>
<td>-</td>
<td>91.6</td>
<td>22.0</td>
<td>4.2</td>
<td>8.24</td>
<td>196</td>
</tr>
<tr>
<td>R16</td>
<td>28.0</td>
<td>54.8</td>
<td>60</td>
<td>136.8</td>
<td>32.0</td>
<td>4.3</td>
<td>6.71</td>
<td>180</td>
</tr>
<tr>
<td>R15</td>
<td>30.0</td>
<td>58.6</td>
<td>60</td>
<td>133.2</td>
<td>23.2</td>
<td>5.7</td>
<td>6.71</td>
<td>180</td>
</tr>
<tr>
<td>R4</td>
<td>32.2</td>
<td>62.3</td>
<td>50</td>
<td>137.0</td>
<td>22.6</td>
<td>6.1</td>
<td>5.48</td>
<td>146</td>
</tr>
<tr>
<td>R14</td>
<td>34.5</td>
<td>66.7</td>
<td>50</td>
<td>141.8</td>
<td>21.4</td>
<td>6.6</td>
<td>7.46</td>
<td>190</td>
</tr>
</tbody>
</table>

Active matter modifications in microemulsion formulations before copolymerization were carried out by changing the water percentage in aqueous phase; percentages of both surfactant blend (10.9 % (w/w)) and organic solvent (23.8% (w/w)) in inverse microemulsion were kept constant. In these runs \( Q_{sp} \) was constant with respect to aqueous phase but not with respect to total comonomer content. Based on this last parameter, it was changed from 307.7 mL/h/kg of comonomers for a TCC of 34.5% (w/w) to 354.2 mL/h/kg of comonomers for a TCC of 28% (w/w). Nevertheless, as it is shown above, within this \( Q_{sp} \) range, copolymer properties do not depend on this variable. SMB concentration, which was kept constant, is the key variable.

\( M_w \) variation with TCC follows an apparently anomalous pattern. It decreases with TCC up to 32.2% (w/w) and then undergoes a dramatic increase at TCC 34.5%. At first, this behaviour is controversial; \( M_w \) should increase with TCC because \( Q_{sp} \) has been kept constant with relation to aqueous phase and, consequently, the comonomer/initiator mole ratio increases with TCC. However, the observed \( M_w \) variation with TCC could be due to the fact that at lower TCC copolymer chains grow in a less collapsed state as it is shown by
the strong decrease in VSI as TCC decreases (Fig. 4). In this less collapsed state, $M_w$ increases because terminations by transfer to comonomers are lower. Above a TCC of 32%, the situation undergoes a dramatic change and the copolymer collapsing degree is so high that transfer to copolymer chains, which results in branching and/or crosslinking, as well as inter and intramolecular associations by hydrogen bonding, are the predominant reactions, resulting in increasing $M_w$ and VSI values.

![Graph showing VSI variation as a function of TCC](image)

**Fig. 4.** Variation of VSI as a function of total comonomer concentration (TCC) for runs given in Tab. 5.

The strong variation of both $M_w$ and VSI is reflected on flocculating performance as it can be seen in Fig. 5 where a comparison is also made with commercial product C1594. Flocculating performances are unaffected by TCC up to 32.2% (w/w) and are equal to the one obtained for C1594. However, at TCC of 34.5% (w/w) a respectable decrease in flocculating performance is observed. Taking into account that for runs R4, R15 and R16 CST curves are similar, independently on their strong $M_w$ differences and that, in spite of its high molecular weight, flocculating performance for sample R14 is much lower than the one for the remaining samples, we must conclude that, in this molecular weight interval, flocculating performance is controlled by copolymer structuring degree as expressed by VSI. Effectively, above a critical value, the higher structuring degree at TCC of 34.5% (w/w) results in an enhanced shield of the cationic charge and, therefore, in a reduction of the available cationic charge for flocculation and, hence, in a reduction of flocculating performance. Additionally, above a critical VSI a reduction in the swollen capacity of the copolymer in aqueous solution during the inversion operation prior to application is produced as a consequence of copolymer crosslinking and inter and intramolecular hydrogen bonding between different and the same copolymer chains, respectively. The lowered copolymer swollen capacity (macromolecular chain less expanded in aqueous solution) leads to lowering the flocculating power because of reduced copolymer surface available for particle adsorption.
Fig. 5. TCC influence on copolymer flocculating performance. Capillary suction time (CST) versus active matter dose (ppm) for lattices given in Tab. 5. Numbers in legends are related to TCC in % (w/w). Experimental error for CST measurements lower than 2%.

Finally, another factor must be considered. The strong differences in $M_w$ for samples in Tab. 5 should result in a strong variation of BV. However, this is not the case and BV is almost constant with TCC. The typical correlation between BV and $M_w$ (the higher the $M_w$ the higher the BV) which can be deduced from Fig. 1 is not observed. This result is at first anomalous but could be explained by differences in composition polydispersity between copolymers of different runs as a consequence of a composition drift during copolymerization due to differences in comonomer reactivities. Since conversion is very close to 100%, average compositions for all copolymers herein obtained are obviously the same (Q9:AM 40:60 (w/w)). However, differences in composition polydispersities between copolymers of the same average composition would involve the coexistence of polyelectrolytes with different cationic charge inside the same microlatex and, therefore, with different viscometric behaviour. Then, BV variation will not be only related to $M_w$ but also to composition polydispersity. Lacik et al. [33] demonstrated the strong influence of compositional heterogeneity due to the composition drift during polymerization on rheological properties of water-soluble polymers.

Composition drift with conversion for the system studied in this paper was shown for run R4. Q9 percentage in copolymer was measured at different reaction times (15 s, 45 s and 10 min) by analysing the chlorine concentration in a sample of isolated copolymer according to the method described in experimental part.

Reaction rate was very high and a 60% conversion was attained in 15 s. A strong average copolymer composition drift from 57% of Q9 at a conversion of 60% to 40% at the end of reaction was produced. This means that Q9 reactivity is much higher than AM one and, therefore, copolymer composition
at low conversions could be very close to 100% of Q9. Consequently, in the earlier steps of copolymerization polyQ9 homopolymers are the only species formed and copolymers with different and decreasing Q9 compositions are obtained as copolymerization proceeds. Even, at the end of copolymerization, uncharged polyAM homopolymers could be obtained, which are not useful for sludge dewatering. Of course, the relative distribution (composition polydispersity) of these different charged macromolecules may vary as the experimental copolymerization conditions change from run to run, which can influence on both BV and flocculating performance. In fact, for charged monomers the reactivity is a function of pH, ionic strength and monomer concentration [34] and consequently, severe composition drifts with conversion have been reported [35-36].

More studies related to our system are necessary to distinguish the influence of composition drift on both viscometric behaviour and flocculating performance.

**Experimental part**

**Materials**

50% (w/w) Acrylamide aqueous solution (from SNF S.A., France), and [2-(acryloyloxy)ethyl]trimethylammonium chloride (Q9; 80% (w/w) aqueous solution from Atochem, France) were used as received. To obtain the aqueous phase of desired concentration the above solutions were diluted in demineralized water (conductivity below 10 μS/cm).

Organic solvent for oil phase was Rolling M-245, a mixture of n-decane and n-tetradecane in a weight ratio of about 40/60, supplied by Shell Co.

Emulsifier was a blend of two nonionic surfactants: Arlacel 83, a sorbitan sesquioleate, HLB 3.7, supplied by ICI; and Softanol 90, a C11-C13 secondary ethoxylated fatty alcohol, HLB 13.3, supplied by INEOS Oxide.

Nitrogen (Technical grade B-50) was supplied by Air Liquide.

Sodium metabisulfite (SMB) (Synthesis grade, from Panreac, Spain) was used as initiator.

Disodium salt of EDTA (from Quimidroga S.A., Spain) was added in order to complex any metal cation that could inhibit polymerization.

All chemicals were used as received from suppliers without further purification.

**Copolymerization procedure**

Inverse microemulsion formulation for copolymerization was selected according to rules given in [21] and, unless otherwise specified, consisted of 65% (w/w) of an aqueous phase comprised by AM (30% (w/w)), Q9 (20% (w/w)), Na2EDTA (0,1% (w/w) and water (49,9% (w/w)); 11% (w/w) of emulsifier with a HLB of 8.3; and 24% (w/w) of Rolling M-245 as oil phase. pH of aqueous phase was adjusted with 10% (w/w) aqueous nitric acid.

Reactions were carried out in a 0.5 L, five necks, jacketed reactor fitted with a
thermometer and a mechanical stirrer (Heidolph RZR 2021 at 300 rpm). Semicontinuous free radical copolymerizations were carried out by continuously adding an aqueous SMB solution to the above inverse microemulsion of comonomers, which was previously thermostatted at the desired initial temperature and purged with nitrogen for 15 minutes at constant flow (3 L/min at 25°C and 1 bar). Nitrogen purge was kept during the reaction time. Copolymerization is strongly exothermic and reaction was considered to be finished when temperature returned to its initial value (about 10 min after starting initiator addition). Reaction was very quick and peak temperature was reached in less than 1 min. SMB aqueous solution was added at constant flow using a Methrom Dosino 700 dosing unit. Active matter concentrations were calculated by taking into account the amount of SMB solution added. Inverse cationic copolymer microemulsions were considered stable if after centrifuging at 5000 rpm for 30 min no phase separation was observed.

Acrylamide conversion ($C_{AM}$) was measured by HPLC according to the method described by Vers [37]. A 2 g/l copolymer microemulsion solution in water was inverted by stirring for 15 min to allow both copolymer and unreacted monomers to dissolve. Then, the solution was vigorously stirred using a high speed mixer at 8000 rpm for 1 min. Afterwards, solution was kept standing for 10 minutes to allow to remove bubbles occluded. Then, the final solution was prepared by diluting 5g of solution up to 100 ml using demineralised water. 100μl of the sample were filtered through a 25 μm pore filter and injected into a Water E600 HPLC chromatograph fitted with two columns in series (Novapack C18 followed by a Fast Fruit Juice column (both from Waters Corp., USA) placed inside an oven at 55°C) and a UV Waters E600 detector set at 200.4 nm. The mobile phase (ultrapure water adjusted at pH 3.5 with H$_2$SO$_4$) flow rate was 0.5 ml/min. Running time was 30 min.

In the present article, we will consider $C_M$ as global one. As reactivity ratios for AM and cationic monomer are respectively $r_1=0.61$ and $r_2 = 0.47$ [19], comonomer blend will become richer in AM as conversion increases. Then, conversion values here given are slightly lower than the total real ones.

**Copolymer characterization**

Copolymer bulk viscosities (BV) were obtained by measuring the viscosity of a 0.5 g/L aqueous solution of copolymer in demineralized water Type I. Copolymer aqueous solutions were prepared by inverting copolymer inverse microemulsions in demineralized water Type I for 30 min. Measurements were carried out using a Brookfield LVDVII+ with an ULA spindle at 3 rpm and 25°C.

Standard viscosities (SV) were measured in the same way and at the same conditions that BV, with the exception that a concentrated NaCl solution was added to the inverted copolymer microemulsions 30 min after inverting so that final NaCl concentration was 0.005 M. Then, stirring was continued for 10 min and SV was subsequently measured. Ionic strength increase provided by NaCl produces a dramatic decrease of viscosity. The BV/SV ratio is an index of the structuring degree of the copolymer [26] and in this paper it will be referred to as viscometric structuring index (VSI). The higher the VSI the higher the copolymer structuring degree is.
Average weight molar masses ($M_w$) and radii of gyration ($R_g$) were determined by Laser Light Scattering (LLS) with an AMTEC photogoniodiffusometer, Model 9863 equipped with an argon laser INNOVA 90C Series, Model 190C-4 ($\lambda = 514$ nm, 100 mW), and a sample cell which can be thermostated to $\pm 0.5 \, ^\circ$C by circulating water. As reference, benzene was used. The refractive index increment of cationic copolymer (dn/dc) dissolved in a 0.05 M NaCl aqueous solution was determined with a Brice-Phoenix differential refractometer Model BP-2000V equipped with a helium-neon laser. The measurement procedure was as follows: copolymer was precipitated out from microemulsion in acetonitrile (ACN) under vigorous stirring; solids were filtered off and washed with ACN. The washed solid was redispersed in ACN under stirring for 10 min. Then, it was filtered off and subsequently subjected to soxhlett extraction for 3 h using acetone as solvent. Afterwards, the solid was removed and oven dried at a temperature corresponding to the acetone boiling point. Water content of copolymer was determined by thermogravimetry (scanning first from 30ºC to 150ºC at 10 ºC/min, and then at constant temperature of 150ºC for 10 min, under a nitrogen flow rate of 200 mL/min) just before preparing samples for LLS measurements. By knowing the copolymer water content a 0.5 g/L stock copolymer solution in NaCl 0.05 M was prepared. Following complete dissolution (2 days), the stock solution was diluted with an aqueous solution of NaCl 0.05 M in order to obtain four samples of concentrations ranged from 0.10 to 0.5 mg/L. These solutions were centrifuged at 10500 rpm for 4 h to remove dust, after which they were transferred to precleaned glass vials. After sealing the vials, $M_w$ was determined by extrapolation of the LLS data at 25ºC and 514 nm according to the classical Zimm-plot procedure by using a I-ZPW Static Light Scattering software. For each copolymer sample three independent measurements were carried out, the $M_w$ reported being the average value.

Average size of latex particles for Run 4 was measured by transmission electronic microscopy (TEM). Samples were frozen using liquid propane (-188ºC) in a LEICA EM CPC equipment and stored in liquid nitrogen (-196ºC) up to processing by cryofracture. Sandwiches produced were cryofractured using BalTec Baf 060 equipment. Prepared samples were observed using a Jeol 1010 transmission electron microscope with a CCD SIS Megaview III camera. TEM micrographs were taken in high vacuum ($10^{-8}$ mbar) at -150ºC.

Copolymer composition of Q9 versus conversion for run R4 was measured by analyzing at several times the chlorine concentration of a solid sample of copolymer by means of an EOX analyzer EUROGLAS ECS 1600. Samples were taken from the reactor in three points: 15 s, 45 s (peak temperature) and at the end of copolymerization when temperature was again the initial one (about 10 min). Copolymers were precipitated out from microemulsion by adding acetone. Then, they were thoroughly washed out with acetone and dried at 80ºC to constant weight. The Q9 percentage in copolymer was calculated by means of equation (1):

$$Q9(\%) = (Cl_m/Cl_t)*0.4*100$$

(1)

Where $Cl_m$ is the measured chlorine percentage and $Cl_t$ is the theoretical one, corresponding to a Q9 percentage in the comonomer feed of 40% (w/w). The
accuracy of the method was assessed by analyzing the Q9 concentration in C1594, a commercial cationic flocculant (marketed in Spain by Acideka S.A. and manufactured by Cytec Technology Corp. USA) of the same cationic charge as the ones reported here (40% w/w) but manufactured by inverse emulsion copolymerization of AM and Q9 instead of inverse microemulsion copolymerization. Three determinations were carried out. Average Q9 content was 39.8 ± 0.6 % (w/w) in good agreement with the theoretical one.

Flocculation tests

Flocculation performance of cationic copolymers was analyzed by measuring the capillary suction time (CST) by means of a Capillary Suction Timer Type 304B from Triton Electronics Ltd. The test [38] is performed by treating the sludge with a dose of flocculant and then placing the sludge in an upright metallic cylinder, or sludge reservoir, resting on a standard filter paper (CST paper 7x8 cm, Triton Electronics Ltd). The capillary suction of the paper extracts liquid from the sludge wetting the paper. The time required for the filtrate to flow 1 cm radially is recorded as the CST. The lower the CST the higher the polymer flocculating performance is.

For each test series, 100 g of fresh, homogenized and tempered sludge were poured on a precipitation glass. Then, a specific dose of copolymer solution was quickly added by means of a syringe. The mixture was stirred at 1000 rpm for 60 s by using a Triton WRC Stirrer Timer Type 131 (Triton Electronics Ltd.). Afterwards, an aliquot was poured on the sludge reservoir of the CST equipment and the CST was recorded. For flocculant dosage, a diluted solution of 1 g/L of microemulsion was prepared directly by inverting copolymer microemulsion as it was synthesized over stirred water at room temperature. After 15 minutes, the solution was ready to be used.

Sludge used in flocculation tests was an anaerobic digested sludge obtained from Vitoria Municipal Water Treatment (Spain). Sludge pH was 7.4 and solid concentration 3.21% (w/w).

Conclusions

The results reported here for semicontinuous inverse microemulsion copolymerization of Q9 and AM at 40:60 Q9:AM feed ratio by using a surfactant blend of Arlacel 83 and Softanol 90 as emulsifier and Rolling M-245 as oil phase, can be summarized as follows:

1. Initiator (sodium metabisulphite) concentration has a strong influence on viscosity, viscometric structuring degree and average weight molar mass of copolymers in the range from 5 to 25 g/L. Both viscosity and $M_w$ decrease with increasing initiator concentrations. Best flocculating performance is obtained from 10 to 20 g/L, values at which viscometric structuring degree presents a minimum.
2. In the range studied, $Q_{sp}$ (153 to 310 mL/h/kg of comonomer), $T_i$ (25 to 35°C) and aqueous phase pH (2.5 to 4.5) have almost no influence on either viscosity or VSI and, hence, on flocculating performance.
3. Total comonomer concentration has a slight influence on copolymer viscosity but a strong one on viscometric structuring degree, which
increases dramatically with total comonomer concentration from 28\% (w/w) to 34.5 \% (w/w), concentration at which the worst flocculating performance is obtained.

Flocculating performance results can be explained in terms of copolymer structuring degree and collapsed state of copolymer chains inside emulsifier micelles. Radii of gyration of copolymers are much higher than mean diameters of microlatex particles. Therefore, the macromolecular chains grow in a collapsed state. Under certain experimental conditions, this collapsed state may favor an excessive structuring degree (branching and/or crosslinking) of copolymers by intra and intermolecular hydrogen bonds, reactions with the unsaturated groups of the oleate portion of one of surfactants (Arlacel 83) and transfer to polymer. Finally, the excessive structuring degree leads to both increasing the cationic charge shield and decreasing the expanding capacity of the copolymer in aqueous solution and, hence, a decrease in copolymer flocculating performance is produced.

Likewise, a strong composition drift with conversion has been observed. At the beginning of copolymerization macromolecular chains were enriched in Q9 while at the end of reaction they were enriched in AM. This results in a composition polydispersity which may be a function of experimental conditions and account for some “anomalous” viscometric results. Likewise, composition polydispersity may influence on flocculating performance because this is related to cationic charge of copolymer for a given sludge. More studies are needed for elucidating the influence of composition polydispersity on both viscometric behaviour and dewatering efficiency.

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