Synthesis of Cationic Flocculants by the Inverse Microemulsion Copolymerization of Acrylamide with 60% 2-Acryloxyethyltrimethyl Ammonium Chloride in the Monomer Feed. II. Influence of the Formulation Composition, Hydrophilic-Lipophilic Balance, Starting Polymerization Temperature, and Reaction Time

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ABSTRACT: Acrylamide/2-acryloxyethyltrimethylammonium chloride copolymers in inverse microemulsions, with 60% 2-acryloxyethyltrimethyl ammonium chloride in the monomer feed and a concentration of active matter of 30% (w/w) as flocculants, were obtained by inverse microemulsion copolymerization. Inverse microemulsion formulations of comonomers, interesting from both technical and economical viewpoints, were polymerized by semicontinuous free-radical copolymerization with sodium disulfite as the initiator. The influence of the formulation composition, hydrophilic-lipophilic balance (HLB), starting polymerization temperature, and reaction time on the polymerization and final properties of the products as flocculants was studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 186–197, 2007

Key words: copolymerization; microstructure; polyelectrolytes; radical polymerization; water-soluble polymers

INTRODUCTION

Currently, most commercial flocculants are acrylamide (AM)-based copolymers, and they are marketed in three different forms: solids, dispersions, and emulsions.[1] Emulsion flocculants are easy-to-handle products and allow polymer concentrations above 30% (w/w) with low emulsifier concentrations (< 5% w/w). However, emulsions are thermodynamically unstable and lead to phase separation within a few months. With microemulsions, which are thermodynamically stable, this problem might be avoided, and low-viscosity liquids containing a high concentration of a high-molecular-weight ($\sim 10^7$ g/mol) polymer might be obtained. The main advantage of emulsions over microemulsions is the lower surfactant concentration needed.

Polyelectrolytes can be divided into three different groups according to their ionic character. Most common polyelectrolytes present in the market are anionic and cationic copolymers, the latter having a higher add value and hence being the most interesting from a commercial point of view. Nonionic polymers have few applications in water-treatment processes. Anionic flocculants are mainly used for potable water production or for the flocculation of inorganic dispersions; meanwhile, cationic flocculants are used for sludge flocculation and dewatering in wastewater treatment.

In this work, we studied the most important parameters influencing semicontinuous AM/2-acryloxyethyltrimethylammonium chloride (ADQUAT) inverse microemulsion polymerization. In an earlier work,[2] we studied polymerization initiation with ammonium persulfate and sodium disulfite (DS) as the initiators. In that work, we proved that DS could initiate AM/ADQUAT copolymerization itself, contrary to what was expected. Mukherjee et al.[3] determined that sodium bisulfite (produced by the dissociation of

DS in water) was able to produce radicals by a reaction with vinyl monomers having a methyl group on the double-bond carbon, avoiding radical recombination. In fact, no monomer used in that work had this methyl group contributing to steric hindrance, but the radical that formed was stabilized by resonance through the carbonyl group next to the double bond.

It must be emphasized that this work, in contrast to the systems usually published, is focused on inverse microemulsions having very high monomer concentrations. The goal of this article is to study the influence of the formulation composition, HLB, starting polymerization temperature, and reaction time on the polymerization kinetics and final product properties of flocculants for sludge dewatering.

EXPERIMENTAL

In this article, all percentages given are by weight (wt %). The charge density is expressed as the cationic monomer concentration (wt %) in the initial monomer blend.

Materials

AM (50% aqueous solution; SNF S.A., Andrézieux, France) and ADQUAT (80% aqueous solution; Atochem, Courbevoie, France) were used as received without further purification. The microemulsion aqueous phase (APh) consisted of a mixture of both monomers in demineralized water (conductivity < 10 μS/cm). The disodium salt of ethylenediaminetetraacetic acid (Quimidroga S.A., Barcelona, Spain) was added to complex any metal cation that could inhibit polymerization. The microemulsion oil phase was a 40 : 60 mixture of n-decane and n-tetradecane (Rolling M-245, Quimidroga). Both phases were stabilized by an interface of a nonionic surfactant mixture of sorbitan sesquioleate (Crill 43, Croda, Ltd., Goole, UK; HLB = 3.7) and an ethoxylated C_{13} secondary alcohol (Softanol 90, Quimidroga, Barcelona, Spain; HLB = 13.3). DS (synthesis-grade; Panreac, Spain) was used as the initiator.

Formulation

Before the polymerization studies, suitable formulations from both technical and economical viewpoints were determined. To this end, pseudo-ternary-phase diagrams for different HLB values were obtained. The results and methods have been presented before.[2] As the conclusion of that study, the following formulation was selected: 60% APh, 30% oil phase, and 10% surfactant blend (HLB = 9.5). This formulation gives a cationic copolymer concentration of 30% with 60% cationic monomer. We made the selection, taking into account conditions of industrial interest: a high solid concentration, a low surfactant system (SS) concentra-

tion, and easy inversion of the microemulsion when put in contact with water or sludge slurry.

All stable microemulsions published by Escudero et al.[2] had bicontinuous microstructures rather than globular microstructures. This microstructure did not remain throughout the polymerization process but was modified during polymerization, producing a final globular microemulsion. This was related to visual microemulsion evolution during polymerization (which coincided with Candau et al.'s description[4]). The initial system was a transparent, water-like-viscosity liquid that turned cloudy and viscous during the earlier stages of reaction; usually some time later, the system became a clear, low-viscosity liquid similar to the primary microemulsion.

Polymer synthesis

APh was prepared via weighing, and its pH was adjusted by the addition of a dilute solution of HNO_3. The oil and surfactants were weighed together and mixed with APh in a 250-mL stirred jacket reactor. Separately, a diluted solution of DS was prepared. The pH of the DS solution had to be adjusted with a dilute solution of HNO_3.

Before reaction initiation, the microemulsion temperature was adjusted to its initial value; afterwards, the reaction mixture was purged with nitrogen for 15 min at a constant flow (4 mL/min at 25°C and 1 bar). The polymerization of the microemulsion systems was initiated by the addition of a diluted SD aqueous solution to a vigorously stirred inverse microemulsion. A nitrogen purge (4 mL/min at 25°C and 1 bar) was maintained throughout the reaction, and a DS aqueous solution was continuously added at a constant flow with a Methrom Dosino 700 dosing unit. (Methrom AG, Herisau, Switzerland). The reaction mixture was cooled by water kept at a constant temperature. As the copolymerization was strongly exothermic under these experimental conditions and for this setup, the cooling did not allow isothermal reactions. Therefore, the reaction was considered to be finished when the temperature went back to its initial value. Then, both the DS solution addition and nitrogen purge were stopped.

Inverse microemulsions of cationic copolymers were considered stable if no phase separation was observed after centrifugation for 30 min at 5000 rpm.

The general reaction conditions, unless otherwise stated, were as follows: the initial polymerization temperature was 30°C, the specific flow rate of addition (Q_{sp}) of the DS aqueous solution was 111.1 mL/kg of APh/h with an SD concentration of 0.5%, and the total mass of the inverse microemulsion was 150 g.

Freeze-fracture electron microscopy

The samples were frozen with liquid propane (−188°C) in a Leica EM CPC instrument (Leira Microsystems,

Wetzlar, Germany) and stored in liquid nitrogen ($-196°C$) until they were processed by cryofracturing. The sandwiches that were produced were cryofractured with a BalTec Baf 060 instrument (Bal-Tec AG, Balzers, Liechtenstein). The prepared samples were observed with a JEOL 1010 transmission electron microscope (JEOL Europe S.A.S., Croissysur Seine, France) with a CCD SIS Megaview III camera (Olympus SIS GmbH, Munster, Germany). Transmission electron microscopy observations were performed in a high void (10^{-8} mbar) and at a low temperature ($-150°C$) conditions.

Viscosity measurements

A solution of 4.5 g of the cationic copolymer/L was directly prepared by the addition of a microemulsion, drop by drop, over vigorously agitated deionized water. The solution was kept agitated for 15 min to allow complete phase inversion, so the cationic copolymer became dissolved in water. Afterwards, the viscosity was measured with a Brookfield LVDV-II (Brookfield Viscometers Ltd., Harlow, UK) with an LV-1 spindle at 30 rpm and $25°C$. The viscosity was expressed as the relative viscosity with respect to a commercial emulsion of cationic polyacrylamide (trade name C1596, Cytec Corp., Madrid, Spain) with the same charge density as our copolymers. The C1596 copolymer had a weight-average molecular weight (M_w) of 6.1×10^6 g/mol and a radius of gyration (R_g) of 156 nm, both measured by light scattering. The light scattering method is described next.

Light scattering

M_w and R_g were determined by laser light scattering (LLS) with an Amtec photogoniodiffusometer (model 9863) (Amtec, Nice, France) equipped with an Inova 90C series model I90C-4 argon laser (wavelength = 514 nm, 100 mW) (Laser Coherent Auburn Group, Auburn, CA) and a sample cell that could be thermostated to $\pm 0.5°C$ by circulating water. As a reference, benzene was used. The refractive-index increment of the cationic copolymer dissolved in a $0.05M$ NaCl aqueous solution was determined with a Brice–Phoenix model BP-2000V differential refractometer (Phoenix Precision Instrument Co., Phoenix, AZ) equipped with a helium–neon laser. The measurement procedure was as follows. The copolymer was precipitated from the microemulsion in acetonitrile (ACN) under vigorous stirring; the solid was 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 Soxhlet extraction for 3 h with acetone as the solvent. Afterwards, the solid was removed and oven-dried at a temperature corresponding to the acetone boiling point. The water content of the copolymer was determined by thermogravimetry (scanning first from 30 to $150°C$ at $10°C$/min and then at a constant temperature of $150°C$ for 10 min under a nitrogen flow rate of 200 mL/min) just before the samples were prepared for LLS measurements. With the knowledge of the copolymer water content, a 0.5 g/L stock copolymer solution in $0.05M$ NaCl was prepared. After complete dissolution (2 days), the stock solution was diluted with an aqueous solution of 0.05 M NaCl to obtain four samples with concentrations ranging from 0.10 to 0.5 mg/L. These solutions were centrifuged at 10,500 rpm for 4 h to remove dust, after which they were transferred to precleaned glass vials. After the vials were sealed, M_w was determined by the extrapolation of the LLS data at $25°C$ and 514 nm according to the classical Zimm plot procedure with BI-ZPW static light scattering software (Brookhaven Instruments Corp., Holtsville, NY). For each copolymer sample, three independent measurements were carried out, the reported M_w value being the average value.

AM conversion

An aqueous polymer solution (1 g of microemulsion/L) was prepared. It was agitated for 5 min to allow both the polymer and unreacted monomers to dissolve. Then, the solution was vigorously stirred with a high-speed mixer at 8000 rpm for 1 min. Afterwards, the solution was allowed to settle for 5 min to allow occluded bubbles to be removed. Finally, the final solution was prepared by the dilution of 5 g of the solution up to 100 mL with deionized water.

A 100-µL sample was filtered through a 25-µm pore filter and injected into a Waters Corp. (United States) E600 high-pressure liquid chromatograph fitted with two columns in series [Novapack C18 followed by a Fast Fruit Juice column (both from Waters S.A.S., Saint-Quentin, France) placed inside an oven thermostated at $55°C$] and a Waters FID E600 detector set to a wavelength of 200.4 nm. The flow rate of the mobile phase (ultrapure water adjusted to pH 3.5 with H_2SO_4) was 0.5 mL/min. The running time was 30 min.

This method did not allow the determination of the ADQUAT conversion at a high conversion level. Therefore, the AM conversion was assumed to be similar to the global conversion. As the reactivity ratios for AM and the cationic monomer were 0.61 and 0.475, respectively,[5] and the initial monomer blend concentrations were 0.4 and 0.6, respectively, the monomer blend composition was not strongly modified during the reaction. Chromatography studies on 80% cationic charge density systems (not presented here, as they are beyond the scope of this work), performed with the same monomers, showed that the polymer charge den-

sity remained nearly constant during the reaction. It increased slightly in the first polymerization step and stayed nearly constant up to high conversion levels. When total conversion was achieved, the charge density was the same as that described in the initial blend; when it was not, the density was slightly higher.

Flocculation tests

A solution of 1 g of the microemulsion/L was prepared by the addition of the microemulsion to stirred water. After 15 min, the solution was ready to be used. Parallel to the sample preparation, sludge preparation was also carried out. The sludge had to be fresh; otherwise, unrealistic results might have been obtained. It had to be at room temperature and homogenized. Much care had to be taken during homogenization to avoid promoting aerobic digestion of the sludge.

Comparative flocculation tests were carried out with anaerobically digested sludge (pH = 7.4, solid concentration = 3.21%) obtained from Vitoria Municipal Water Treatment (Vitoria, Spain). This method determined the amount of the polymer, related to the sludge volume, needed to produce flocs strong enough to resist imposed shear and having good dewatering capacity. To do this, a certain volume of the copolymer solution was added to 100 mL of homogenized sludge. The mixture was stirred at 1000 rpm for 10 s with a Triton WRC stirrer timer type 131 (Dunmow, UK). If after stirring the initial sludge was clearly separated into a compact, solid aggregate and a clear supernatant, the dose was high enough and could be lowered. If not, the dose had to be increased until clear separation was observed.

RESULTS AND DISCUSSION

Initiation temperature

The temperature is an important factor in microemulsion polymerizations for several reasons. It has an important effect on both the polymerization rate and molecular weight and also on the polymer structure as branching reactions take place at temperatures higher than 70°C.[6] The relative reactivity ratios of the monomers can be modified, and consequently, the monomer distribution in the copolymer can be modified, which in turn can modify the flocculant properties. It might also affect the inverse microemulsion microstructure as polyoxyethylene-type nonionic surfactant solubility changes with the temperature.

The copolymerization of AM and ADQUAT is a very exothermic reaction. Therefore, taking into account the high monomer concentration in the microemulsion and the experimental setup of this study,
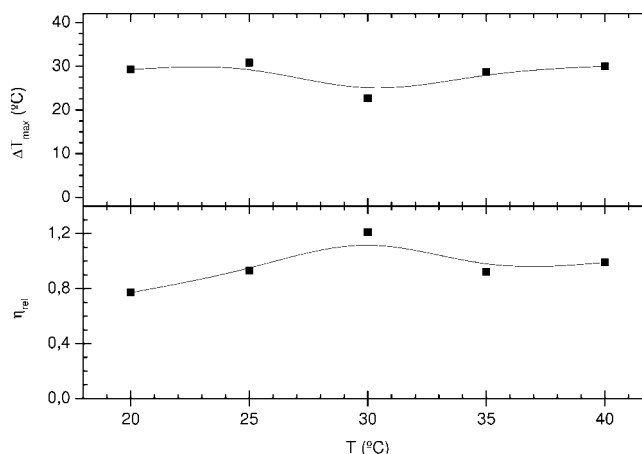
Figure 1 Variation of the relative viscosity (η_{rel}) and thermal jump (ΔT_{max}) as a function of the initiation temperature (general reaction conditions: HLB = 9.5, initiation temperature = 35°C, SD concentration = 0.5 wt %, Q_{sp} = 111.11 mL/kg of APh/h).

we could not keep a constant temperature during the copolymerization. Consequently, the influence of temperature was studied through changes in the initial copolymerization temperature.

As can be seen in Figure 1, there is nearly no effect of the initiation temperature on the increase in the temperature (i.e., the thermal jump, or the difference between the peak temperature of the copolymerization and the initial one). On the other hand, the relative viscosity reaches a maximum at 30°C. These results may be coupled with the visual observation of the reaction evolution. For reactions beginning at 30°C, the system behaves as usual (as described by Candau et al.[4] for a bicontinuous microemulsion polymerization). The transparent and waterlike-viscosity microemulsion turns into a viscous and turbid system in the early stages of copolymerization; later, it goes back to a transparent and low-viscosity state. Candau et al. described this transition as microstructural changes, that is, from a bicontinuous microstructure to an inverse, globular microstructure. For reactions having initiation temperatures of 35 and 40°C, no significant changes in the viscosity or transparency have been observed (a phase transition does not seem to take place). However, for temperatures below 30°C, a strong change in the rheology behavior, during the early stages of polymerization, has been observed. The usual bicontinuous, transparent, and low-viscosity microemulsion turns into a highly viscous, non-Newtonian system (the Weissenberg effect can be clearly observed; see Fig. 2) and later turns back into a transparent, low-viscosity system, which usually contains polymer coagulum (a kind of gel 1 mm in diameter) but seems to be stable. These systems are not really stable and easily undergo phase separation
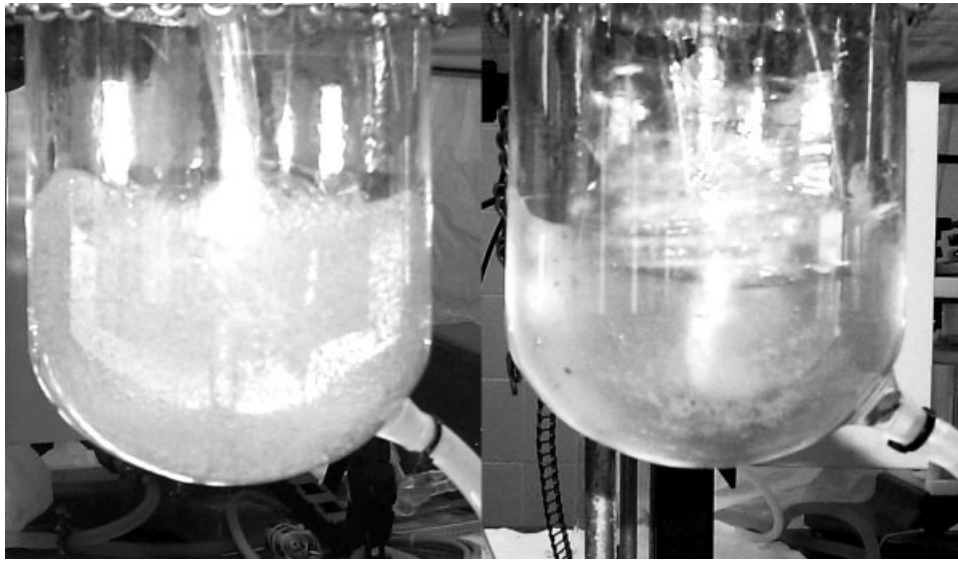
Figure 2 Copolymerization reactor photographs. On the right, the system shows a clear Weissenberg effect, which is related to the system suffering a strong phase transition. On the left, the system reacts in a common way, without producing any strong rheology modification.

in the 6 months after the manufacturing date or immediately if they are centrifuged.

This phase behavior must be related to the temperature; the temperature might have a strong influence on the phase behavior, especially if ethoxylated, nonionic surfactants are used. However, although the initial microstructure is stable in the temperature range studied (no significant change in the microemulsion conductivity before copolymerization has been observed between 20 and 40°C), once copolymerization has started, the composition of the system continuously changes until the reaction is completed. Consequently, during copolymerization, the system might become unstable at lower temperatures, as has been observed in these experiments, and suffer a phase transition. Whether the final microstructure is globular or a lyotropic, liquid-crystal phase (probably a lamellar phase) depends on the interface curvature and consequently on the thermodynamic equilibrium, which is a function of the polymerization development. As the reaction medium changes, all transfer (heat and mass) and physical properties are strongly modified, and this may provoke strong differences in the final product properties. This microstructure transition implies a rheological change that strongly modifies the mass and heat-transfer capacity. Polymer coagulum gels observed in the final products of reactions initiated at 20 and 25°C can be produced either during the phase transition or during the non-Newtonian reaction state. Some polymer is rejected to the oil phase during these stages, giving rise to coagulum formation by precipitation.

In light of these effects, the results obtained for initiation temperatures of 20 and 25°C cannot be easily explained and might be related to polymerization me-

dium changes occurred during the reaction. For 30°C, the thermal jump and relative viscosity achieve a minimum and a maximum, respectively, and the reaction time is shorter than that for lower temperatures. For higher temperatures, the thermal jump slightly increases and the reaction time decreases, probably because of the higher initiation and polymerization rates, which increase the number of growing chains. This might explain why the relative viscosity decreases when the temperature increases from 30 to 35°C. No significant change in either the thermal jump or relative viscosity is observed when the initiation temperature is increased from 35 to 40°C, probably because the initiation rate stays nearly constant.

Comparative flocculation tests were conducted for reactions beginning at 25, 30, 35, and 40°C. From these, it can be concluded that the maximum dewatering quality is obtained at 30 and 35°C (the optimum dose is 280 ppm). There is not, however, a big dewatering quality difference between the 30, 35, and 40°C samples. The results were slightly worse for systems initiated at 40°C. Solid aggregation of the flocculated sludge was weaker when the product of the polymerization initiated at 40°C was used. Much worse results were obtained for the reactions initiated at 25°C. Flocculation results at 280 ppm for the product obtained at 25°C were not satisfactory, and the product dose was increased over 320 ppm to achieve acceptable results. This last sludge dewatering result could be related to reaction medium modification during copolymerization, which was manifested as a great rheology behavior change, as described previously. This modification may have a strong influence on the structure of the flocculants obtained and hence on their sludge dewatering qual-

ity. Generally, good dewatering quality products are high-molecular-weight polymers with a low poly-dispersity; meanwhile, both oligomers and highly branched or crosslinked polymers decrease the dewatering capacity of cationic flocculants (there are few exceptions for special sludges that need polymers with some structuration degree[7,8]). Comparing results for systems initiated at 35 and 25°C, we see that both the thermal jump and relative viscosity are similar, but the dewatering system quality for these systems is rather different. Possible causes for this could be polymer loss, leading to a decrease in the active matter in the systems initiated at 25°C because of coagulum formation and/or production of a crosslinked polymer. It is apparent that the lower the polymer concentration is in the microemulsion, the lower the dewatering quality is (this is discussed later). Moreover, highly crosslinked polymers prevent highly viscous aqueous solutions from being achieved because crosslinking prevents chain expansion. From a sludge dewatering standpoint, the negative results are as follows: on the one hand, the lengths of the polymer chains in solution are lower than those for uncrosslinked polymers of similar molecular weight, and so the flocculation mechanisms[9–11] due to adsorption and bridge formation are unfavorable affected; on the other hand, an excessively crosslinked polymer leads to masking, in comparison to an uncrosslinked or slightly crosslinked polymer, of the cationic charges responsible for the flocculation mechanism related to charge neutralization.

In our opinion, the very poor dewatering quality of copolymers obtained at 25°C is due to both strong crosslinking and coagulum formation. The latter leads to a reduction of active matter. As the viscous, transitory reaction medium must induce hot spot production, this is expected to produce crosslinked polymers. As the temperature increases up to 30°C, coagulum formation disappears, and the temperature is still low enough to obtain long, linear polymer chains. Therefore, both the relative viscosity and dewatering capacity of the copolymers increase. However, above 30°C, the number of growing polymer chains increases dramatically in such a way that the average molecular weight decreases and, consequently, the relative viscosity and dewatering capacity of the copolymers also decrease. Finally, above 35°C and up to 40°C, a slight decrease in the relative viscosity and dewatering capacity of the copolymers compared with those obtained at 35°C may be related to both the increased number of growing polymer chains and the formation of undesirable crosslinked copolymers. It is worthwhile to remember that at 40°C, the initial copolymerization temperature is 40°C, but the peak temperature during polymerization is 70°C, the temperature at which crosslinking reactions are promoted.[6]

HLB influence

The HLB value of the SS in the microemulsion partially determines the microemulsion structure[12] and also the capacity for making soluble the polymer in the APh of the inverse microemulsion. Likewise, the HLB value determines the macroemulsion–microemulsion limit interface position and therefore the minimum surfactant concentration needed to achieve a stable microemulsion. The HLB is also related to the maximum concentration of the copolymer that can be achieved in the inverse microemulsion and to the self-inverting capacity of the microemulsion in contact with the sludge slurry. This property is absolutely necessary to allow the copolymer to act as a flocculant. Flocculants are prepared in solution before being added to sludge to be treated. Consequently, to promote microemulsion phase inversion and allow the concentrated polymer solution (APh) to be diluted in water, a highly hydrophilic surfactant is necessary. The relationship between the HLB and formulation composition before polymerization has been discussed in an earlier work.[2] Now we discuss this relationship during polymerization.

Several polymerization reactions have been carried out for HLB values ranging from 8.9 to 10.0. Above 9.5, the system becomes unstable during the reaction, and a phase transition occurs. It is well known that flocculants marketed in inverse emulsions need to be inverted by dilution in excess water just before application, usually with the addition of a high HLB (> 13) inverting surfactant or surfactant mixture, which is added at the end of the polymerization.[13] Likewise, the cosurfactant properties of ionic monomers are well established.[12,14] Because of the high cationic monomer concentration, the real inverse microemulsion HLB is much higher than 9.5 and close to the HLB of inverting surfactants. This may explain the phase transition of systems having HLB values over 9.5.

Effects other than stability effects have not been observed. Both the maximum temperatures of polymerization and the relative viscosity of the copolymers are almost constant in the range of experimental polymerization conditions used (see Fig. 3). Likewise, flocculation tests show that apparently there is no significant influence of HLB on the flocculant properties of the cationic copolymers. The optimum flocculation dose is 400 ppm for samples having HLB values of 9.0, 9.25, and 9.5 (all stable products); however, the solid compaction of sludge flocculated with the sample with an HLB value of 9.0 is slightly smaller than that of the flocculating test with a product with a higher HLB value.

Further studies to elucidate the HLB influence on the flocculant performance have been undertaken for AM/ADQUAT copolymers with 40 and 80% cationic
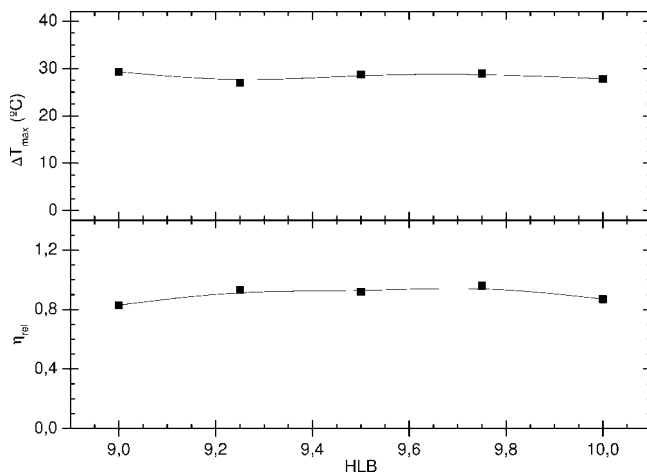
Figure 3 Variation of the relative viscosity (η_{rel}) and thermal jump (ΔT_{max}) as a function of HLB (general reaction conditions: initiation temperature = 35°C, SD concentration = 0.5 wt %, Q_{sp} = 66.67 mL/kg of APh/h).

charges, and they will be presented in other publications. Preliminary results for both charge densities show a clear relationship between the HLB of an inverse microemulsion and the flocculant performance[15] that is the opposite of the results of this study. In all cases, because of the high concentration of the monomers inside the microemulsion droplets, the macromolecular chains grow in a very collapsed state.[16] Micelles have a lower size than R_g of the polymers; that is, for AM/ADQUAT copolymer inverse microemulsions with a 40% cationic charge and a 30% copolymer concentration,[17] the average particle sizes for three samples with molecular weights ranging from 5.48 to 9.30 × 10^{6} g/mol are about 88 nm, much lower than the copolymer R_g value (from 146.5 to 227.2 nm). This may promote a certain degree of uncontrolled structuring (intramolecular and intermolecular hydrogen bonding, branching by chain transfer, and crosslinking), which in turn affects the polymer properties.[18] Then, as HLB influences the microemulsion structure, the droplet size should be a function of HLB and therefore so are the polymer molecular weight and its distribution and the polymer structuring degree. Consequently, the relative viscosity of the polymers and their flocculant performance, which are related to the molecular weight and polymer structuring, should be affected by HLB.

Hernández-Barajas and Hunkeler[18] found that for the polymerization of AM in an inverse microemulsion with V-70 as the initiator, the rate of polymerization, molecular weight, and R_g were independent of HLB for HLB values of 7.8–8.2. We think their results were due to the very narrow HLB window studied. Therefore, the results obtained for this case could be anomalous because the range of the experimental conditions was too short and/or the characterization methods were not sensitive enough. In other

words, the conditions for measuring the relative viscosity and sludge characteristics employed in this work are such that flocculation is not strongly affected by the flocculant molecular weight. In fact, it is well known that the nature and structure of the flocculant needed for dewatering specific waste-activated sludge depend on the characteristics of this.[7,19,20]

APh pH

To study the aqueous pH effect on polymerization, several experiments were conducted, with the APh pH varied from 3.0 to 6.8. The results are given in Figure 4. At pH 6.8, the thermal jump is very low, indicating a very slow copolymerization. The relative viscosity of the cationic copolymer is also very low for the same reason. As the pH decreases, the reaction rate increases until pH 4.6, which in turn leads to much higher conversions and therefore to an increase in the relative viscosity. Below this pH value, the reaction rate is constant, and the relative viscosity increases slowly. The dependence of the polymerization rate on the pH must be related to the equilibrium sulfite ion/bisulfite ion/sulfurous acid and the redox reaction between the initiator and monomers, which obviously must be influenced by the pH.

Flocculation studies show that from 3.0 to 4.6, the pH of the polymerization has no influence on the sludge dewatering capacity. No significant difference has been observed in flocculation tests for samples obtained at pH values of 3.05, 4.64, 4.84, and 5.61. The optimum dose is 220 ppm for all of them, and no clear difference in the separation quality at this dose has been observed: all treated samples had the same solid aggregation and compaction and supernatant clearness.
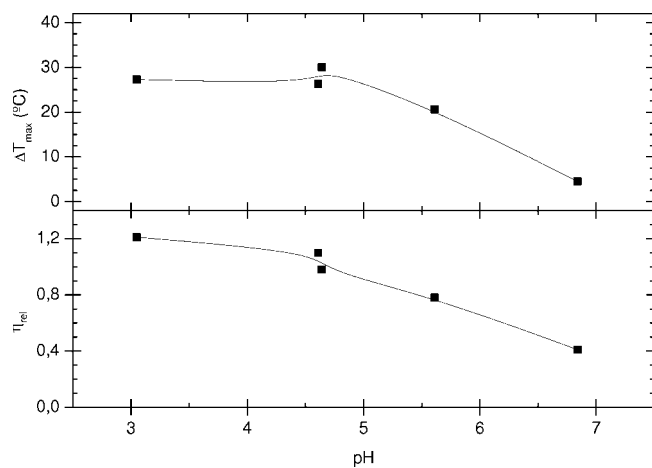
Figure 4 Variation of the relative viscosity (η_{rel}) and thermal jump (ΔT_{max}) as a function of the APh pH (general reaction conditions: HLB = 9.5, initiation temperature = 35°C, SD concentration = 0.5 wt %, Q_{sp} = 66.67 mL/kg of APh/h).

TABLE I
Stability of the Polymer Inverse Microemulsion as a Function of the Formulation Composition

Reaction	APh (wt %)	SS (wt %)	APh/SS (w/w)	ΔT_{max} (°C)[a]	η_{rel}[b]	Stability	Remarks
R60-1	60.0	12.0	5.0	27.1	0.94	Stable	
R65-1	65.0	12.0	5.4	26.6	1.14	Stable	Slightly viscous
R70-1	70.0	12.0	5.8	23.8	0.82	Stable	Gel
R65-2	65.0	11.0	5.9	33.5	1.06	Stable	Gel
R60-2	60.0	10.0	6.0	22.7	1.21	Stable	
R65-3	65.0	10.5	6.2	32.8	1.12	Stable	
R60-3	60.0	9.5	6.3	28.2	0.92	No	Unstable upon polymerization
R70-2	70.0	11.0	6.4	26.9	1.11	Stable	Gel
R65-4	65.0	10.0	6.5	17.3	1.08	No	Unstable upon polymerization
R60-4	60.0	9.0	6.7	26.6	0.95	No	Unstable upon polymerization
R70-3	70.0	10.0	7.0	19.7	1.01	Stable	Gel
R60-5	60.0	8.5	7.1	26.3	0.93	No	Unstable upon polymerization
R60-6	60.0	8.0	7.5	25.3	1.02	No	Unstable upon polymerization
R65-5	65.0	8.0	8.1	27.8	0.89	No	Unstable upon polymerization

The general reaction conditions were as follows: HLB = 9.5, initiation temperature = 35°C, DS concentration = 0.5 wt %, and Q_{sp} = 66.67 mL/kg of APh/h. The samples were considered stable if no phase separation after centrifugation for 30 min at 5000 rpm was observed.
[a] Thermal jump.
[b] Relative viscosity.

Formulation composition

From an industrial standpoint, formulations with high polymer contents and low surfactant concentrations are desired. To study the effect of this kind of formulation on the polymer properties, several reactions have been carried out. The results are presented in Tables I and II. As expected, the formulations become unstable when the surfactant concentration decreases and when the APh/SS weight ratio increases. For systems having an HLB value of 9.5 (the stability limiting value observed under studied conditions in an HLB influence study), above a 6.2 APh/SS weight ratio, the inverse microemulsion becomes unstable during copolymerization. Exceptions to this rule are those systems with less than 24% (w/w) oil phase. In this particular case, before polymerization, the viscosity of these systems is rela-

tively low, but in the earlier stages of polymerization, their viscosity increases drastically, giving rise to a clear gel. It is because of this enormous viscosity that the system cannot undergo evolution and remains a clear and stable gel for years. However, these highly viscous systems might have suffered a phase transition to a rather viscous microstructure, probably a lyotropic microstructure, which is stable. However, if the HLB value is slightly reduced, the stability is enhanced, and formulations having much higher APh/SS weight ratios can be obtained (see Table II). The same has already been observed[2] in primary microemulsions: if HLB is reduced from 9.5 to 9.0, formulations containing higher APh proportions can be obtained. Even though no phase separation was observed after centrifugation testing, the results given in Table II should be considered carefully as these formulations might be miniemulsions.

TABLE II
Formulation Improvement: Flocculation Results

Reaction	APh (wt %)	SS (wt %)	APh/SS (w/w)	ΔT_{max} (°C)[a]	Flocculation dose at t = 30 min (ppm)[b]	
					Product	Polymer
R70-4	70.0	6.0	11.7	16.5	229	109
R70-4	70.0	5.0	14.0	16.1	299	142
R65-6	65.0	4.2	15.5	17.5	360	159
R70-4	70.0	4.2	16.7	24.0	280	133
R73-1	72.9	4.2	17.4	24.6	260	129

The general reaction conditions were as follows: HLB = 9.2, initiation temperature = 35°C, DS concentration = 0.1 wt %, Q_{sp} = 55.33 mL/kg of APh/h, and APh pH = 3.5. All samples were considered stable. No phase separation was observed after centrifugation for 30 min at 5000 rpm.
[a] Thermal jump.
[b] The dose of the flocculant necessary to obtain a clear separation and a compact solid. It is expressed as parts per million of the product (the liquid quantity) and the polymer (the product dose is corrected by the polymer contained in each sample; the full conversion is considered).

No general relationship can be supposed for either the thermal jump or relative viscosity. The thermal jump seems to be related to the monomer content and not to the surfactant content. However, an important data dispersion has been observed, and consequently, these results can be considered only trends. The viscosity for the stable systems is almost constant, although it was expected to increase with the APh/SS weight ratio. This may be related to the measurement conditions. The viscosity is measured 15 min after solution preparation. This can be enough for normal systems, but structured polymer chains may need longer times to evolve to an expanded configuration.

Comparative flocculation test results for the samples described in Table II are presented in Figure 5 for three different solution lifetimes (the time that elapsed from solution preparation, i.e., $t = 30$, 150, or 520 min). The flocculation product yield is related to the polymer content (total conversion is supposed) and expressed as the required polymer dose (mg of polymer/L of sludge slurry). In this way, we can study the reaction medium effect on the chain structure by means of the polymer flocculation properties. Unexpectedly, the best results correspond to the lowest studied APh/SS weight ratio value; over this APh/SS weight ratio, the required dose increases to achieve a maximum and decreases later to reach a plateau. It can also be observed in Figure 5 that the required polymer dose decreases during the first 150 min to increase strongly later (up to $t = 525$ min). This improvement in the flocculation yield may be explained by polymer chain expansion during this period, leading to a more expanded polymer chain configuration that is better adapted to the bridge formation flocculation mechanism. When chains are expanded (at $t = 150$ min), differences between the sample flocculation capacities are quite softened; therefore, the sample preparation may mask some information on the product flocculation capacity. As guessed before, polymer chains in a highly collapsed state take some time to evolve to an expanded structure. If the polymer is used before the final expansion, just a part of the chain will be active, and so the chains will be less adapted to the bridge formation mechanism, decreasing its yield. Polymer chains growing in a highly collapsed state may have rather nonlinear structures, including crosslinking that will limit chain expansion. Therefore, the higher the chain structuring is, the more limited its capacity will be to be expanded, and consequently, the lower its yield will be under standard test conditions. A reduction of the flocculation yield observed before 150 min can be related to polymer hydrolysis. It is well known that this kind of copolymer suffers hydrolysis[21,22] if the pH is over 6.0. Ester group hydrolysis (see Fig. 6) produces ampholytic polymers with a smaller cationic charge density and
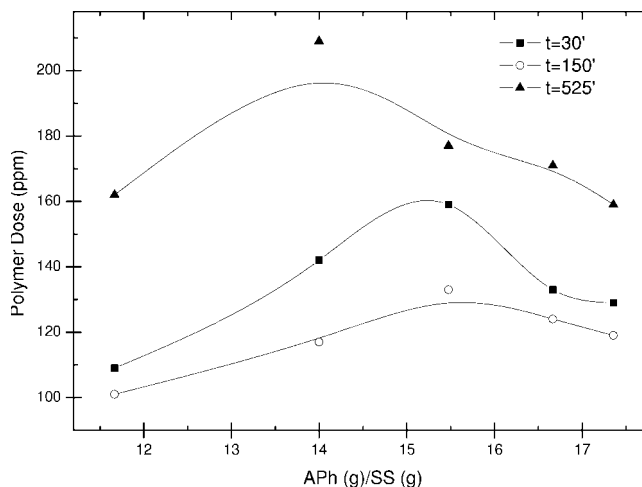
Figure 5 Comparative flocculation results as a function of the APh/SS ratio realized at different lifetimes (the times that elapsed from the polymer solution preparation; general reaction conditions: HLB = 9.0, initiation temperature = 35°C, DS concentration = 0.1 wt %, Q_{sp} = 55.33 mL/kg of APh/h).

lower solubility, which is negative for flocculation. Amide groups also suffer hydrolysis, but it is much slower than ester group hydrolysis under neutral or alkaline conditions.[21] The flocculation yield of samples having APh/SS values of 15.5 or greater decreases slowly, so it can be concluded that they are much less susceptible to hydrolysis than samples having APh/SS weight ratios below 15.5. Hydrolysis can be reduced by hindered structures such as chains in a collapsed state. It can be assumed that for lower APh/SS weight ratios, the system is less structured, so it evolves faster to an expanded configuration and consequently is more affected by hydrolysis. Over these values, there is no big difference in the sample behavior, but no reasonable explanation can be given for the maximum observed at an APh/SS weight ratio of 15.5. We can assume that all polymers studied in this flocculation test were synthesized in a highly collapsed state, which favors a higher degree of branching and crosslinking for copolymers obtained at a higher monomer concentration, and consequently, the dewatering quality is lowered because of the decreased polymer capability to expand in solution. It must be considered that the higher the monomer concentration is, the more viscous the reaction medium (the microemulsion) becomes, and consequently, heat exchange will be more difficult. This heat-transfer limitation can promote the appearance of hot spots and hence promote interimidization reactions, which take place over 70°C,[6] and therefore crosslinking. This crosslinking reaction has several effects on the dewatering quality of products: it limits the expansion of the chain and hence the flocculation capacity thereof, but it also makes some cationic charge highly hindered and consequently decreases
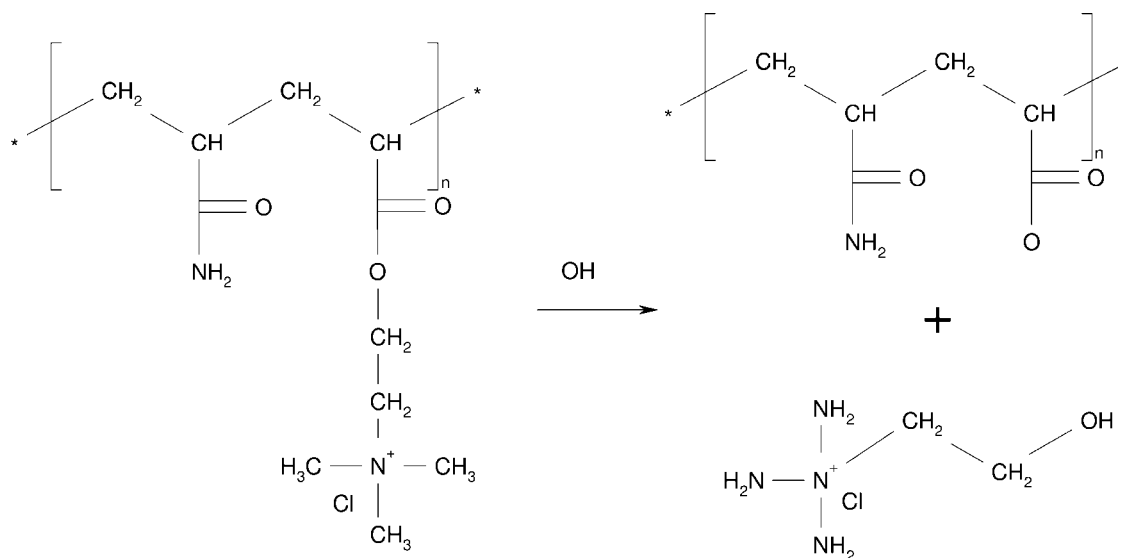
Figure 6 Ester group hydrolysis mechanism.[22]

the effective cationic charge density available for sludge dewatering.

Similar results have been obtained for 40[17] and 80%[15] cationic charge density systems. Therefore, an explanation for these results may be related to the copolymer microstructure, which in turn may be related to the droplet size of the microemulsions. A polyacrylamide of an average molecular weight of 10^7 g/mol has an R_g value higher than 200 nm, which is greater than the mean diameter of a micelle in a polymer microemulsion, which is about 100 nm.[13] The results for 40 and 80% cationic charge density systems are given next. The micelle size measurements of the AM/ADQUAT copolymer inverse microemulsions with an 80% cationic charge and a 42% copolymer concentration, carried out by freeze-fracture electronic microscopy, showed a droplet size range of 90–125 nm for molecular weights greater than 3×10^6 g/mol and an R_g value of about 250 nm.[15] For AM/ADQUAT copolymer inverse microemulsions with a 40% cationic charge and a 30% copolymer concentration,[17] the average particle size for three samples with molecular weights ranging from 5.48 to 9.30×10^6 g/mol was about 88 nm, much lower than the copolymer R_g (from 146.5 to 227.2 nm).

Initiator addition time

Up to now, it has been supposed in this study that copolymerization takes place as long as the temperature is above the initiation temperature. This reaction time could be excessive, and during the end part of the reaction, initiator addition might lead only to oligomer formation, which is useless for flocculation, or finish chain growth, preventing a molecular weight increase because of termination by chain combination. Neither mechanism improves polymer

flocculation performance, so it is necessary to know how the initiator addition time influences the polymer properties.

For this study, the same reaction (HLB = 9.5, SD concentration = 0.5 wt %, Q_{sp} = 66.67 mL/kg of APh/h) was repeated five times, with just the initiator addition time changed. All reactions were initiated under the same conditions. The initiator addition was continued until a prefixed reaction time. The shortest initiator addition time was the one needed to achieve the maximum reaction temperature. The results are presented in Figure 7. Initiator addition was stopped at 6.50, 7.25, 8.00, 9.25, and 11.00 min, and the temperatures when the initiator addition was stopped for each reaction were 58.7, 45.0, 39.9,
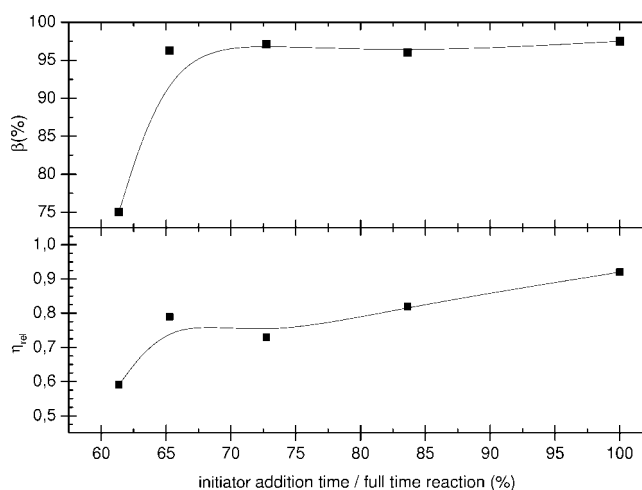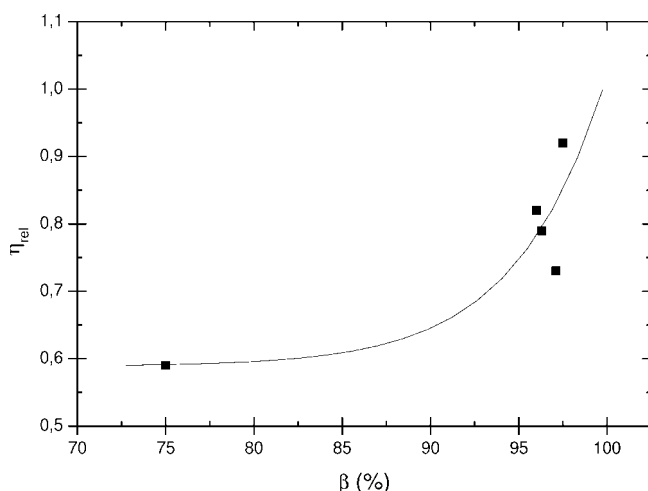

Figure 7 Variation of the relative viscosity (η_{rel}) and the conversion (β) as a function of the DS addition time (general reaction conditions: HLB = 9.5, initiation temperature = 35°C, DS concentration = 0.5 wt %, Q_{sp} = 66.67 mL/kg of APh/h).

38.1, and 35.0°C, respectively. Except for initiator addition, all standard reaction conditions, (stirring, cooling, nitrogen purging, etc.) were kept constant until the reaction temperature got back to the initial temperature (35°C). Consequently, all reactions had reaction times shorter than 11.00 min.

As expected, the thermal jump stayed constant for all reactions (thermal jump = 22.7 ± 1.8°C), accounting for reaction repeatability. However, the reaction for which initiator addition was stopped at the maximum temperature reached a slightly lower thermal jump than the rest of the reactions. If we compare the first two reactions (in terms of the initiator addition time), we can observe strong differences in the AM conversions and relative viscosities. The slight difference between the two thermal jump values does not account for these strong differences. As for higher initiator addition times, the conversion stays nearly constant or increases quite slowly; it can be concluded that most conversion is obtained in the reaction time until the maximum temperature is reached.

As can be observed in Figure 7, the conversion hardly attains values over 96% even when much longer reaction times are used. Conversions over 96% cannot be directly related to a higher reaction time as they can also be related to small differences in the thermal jump between reaction repetitions.

It has been also observed that the conversion is 76% when the temperature maximum is reached. If a plot is made correlating the copolymer relative viscosity to the conversion degree (Fig. 8), a dramatic increase in the viscosity for a conversion degree of 90–100% is produced, probably because of termination reactions by combination or long-chain branching. At high conversions, chains should be instead collapsed, and so it is quite probable that this kind of reaction takes place.

For the nonisothermal (as in our case, though for a microemulsion) inverse macroemulsion polymerization of AM, Hunkeler and Hernández-Barajas[13] found that between 95 and 100% conversion degrees, the molecular weight increases strongly. They also justified this molecular weight increase at high levels of conversion as due to either long-chain branching or intramolecular association.[12]

CONCLUSIONS

Flocculants having 60% cationic monomer have been obtained by means of inverse microemulsion copolymerization. By polymerizing, under carefully controlled conditions, a formulation comprising an aqueous solution of AM and ADQUAT as the APh, a mixture of an ethoxylated C_{13} secondary alcohol (Softanol 90) and sorbitan sesquioleate (Crill 43) as a surfactant blend, and a mixture of decane and tetradecane as a continuous oil phase, we can obtain flocculants in inverse microemulsions having a cationic copolymer concentration higher than 30% with an SS concentration as low as 5% that show very good sludge dewatering properties.

The initial reaction temperature and pH of the APh have a strong influence on the initiation reaction and therefore on the copolymer properties. Apparently, in the range studied, HLB has no influence on the flocculant performance but may allow an increase in the APh/SS weight ratio and hence the active matter content. However, formulation studies have demonstrated that increasing the monomer content, under the studied conditions, does not provide better dewatering properties to the final product. At high APh/SS weight ratios, polymer chains grow in a strongly collapsed state. This collapsed state promotes crosslinking and long-chain branching, especially at high conversion levels, as indicated by viscosity measurements, and is, in most cases, negative for the dewatering properties of the polymers.

Figure 8 Variation of the relative viscosity (η_{rel}) for the copolymer versus the conversion (β; general reaction conditions: HLB = 9.5, initiation temperature = 35°C, SD concentration = 0.5 wt %, Q_{sp} = 66.67 mL/kg of APh/h).

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