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Synthesis of cationic flocculants in continuous reactors

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ABSTRACT

The synthesis of cationic flocculants by inverse microemulsion copolymerization of acrylamide and [2-(acryloyloxy)ethyl]-trimethylammonium chloride in continuous reactors (single CSTR and two CSTRs in series) was investigated. It was found that the particular microstructure of the polymers strongly depended on the process. The polymer synthesized in two CSTRs in series presented the best performance as flocculant because it contained both short (polymer produced in the second reactor) and branched long (polymer produced in the first reactor) polymer chains.

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1. Introduction

Polyelectrolytes are currently used as flocculating agents in solid–liquid separation processes where suspended colloidal particles are difficult to sediment. Applications include water treatment, mineral processing and paper making [1]. The main use of polyelectrolytes is in waste water treatment processes where flocculation of the colloidal particles is generally carried out by the addition of oppositely charged polyelectrolytes [2]. Because most of the dispersed solids are negatively charged, cationic polyelectrolytes produced by copolymerization of acrylamide and cationic acrylates are commonly used as flocculants [1–3]. The destabilization of the suspension usually takes place through two mechanisms: charge-neutralization and particle-bridging flocculation. Therefore, in order to accelerate flocculation and to enhance its efficiency, these polymers should have a high molecular weight and a certain ionic charge along the polymer backbone. The high molecular weight promotes "particle bridging flocculation" whereas the cationic charge provides "charge neutralization" [4].

In order to obtain the high molecular weight polymer required for an efficient flocculation, the synthesis of the polymeric flocculant is usually performed in either inverse emulsion or inverse microemulsion polymerization [5,6]. In those systems, the polymerization takes place in the dispersed phase consisting of an aqueous solution of monomers and polymer. The compartmentalization of the system reduces bimolecular termination of the radicals allowing the formation of high molecular weight polymers. The main drawback of the inverse microemulsion polymerization is the larger amount of emulsifier required. Nevertheless, it presents some important advantages over the inverse emulsion polymerization. The smaller droplet size achieved in inverse microemulsion polymerization allows a greater compartmentalization of the system, which results in higher molecular weights than those obtained through inverse emulsion polymerization [7]. Moreover, the products synthesized by inverse microemulsion polymerization are self-inverting and present superior stability than those obtained by inverse emulsion.

In practice, inverse microemulsion polymerization is mainly carried out in jacketed stirred tank reactors working in semibatch mode. The flexibility of the process to produce different products in the same reactor, the ability to fine-tune the product properties and the relative easiness to control the heat generated are the reasons for the success of the semibatch process. However, in large stirred tank reactors in which the heat removal capacity is limited, the process time required to control the reactor temperature is very long. This long process time together with the time spent in cleaning, filling, heating, cooling and discharging the semicontinuous reactor strongly reduces the productivity. The current scenario of strong competition and margin reductions is pushing polymer producers to achieve an efficient production of high quality materials in a safe and consistent way [8]. A way to improve efficiency is through process intensification by replacing semicontinuous reactors with

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continuous systems. Inverse microemulsion polymerization in a continuous stirred tank reactor [9] (CSTR), in a conical reactor [10] and in a Taylor–Couette reactor [11] has already been reported. However, it is well known that in polymerization reactions, the polymer characteristics and hence the product properties strongly depend on the reactor type [12]. Therefore in the feasibility of the production process not only the consistency, safety and efficiency of the process must be taken into account, but also the quality of the final product must be considered.

In this work, the synthesis of cationic flocculants by inverse microemulsion copolymerization of acrylamide (Am) and [2-(acryloyloxy)ethyl]-trimethylammonium chloride (Adamquat) in continuous stirred tank reactors was investigated. The effect of the reactor type (semibatch, one CSTR and two CSTRs in series) on the polymer microstructure was discussed and related with the flocculating efficiency of the products obtained in the different operation modes.

2. Experimental

2.1. Materials

Technical monomers, acrylamide (Am, 50 wt% aqueous solution) and [2-(acryloyloxy)ethyl]-trimethylammonium chloride (Adamquat; 80 wt% aqueous solution), both supplied by SHF Floeger, were used. Ethylenediaminetetraacetic acid tetrasodium salt hydrate (EDTA, chelating agent which suppresses the effect of the inhibitors contained in the monomers) was supplied by Dow Chemical and used without further purification. Isopar M supplied by Proquibasa was used as the continuous organic phase. A mixture of Crill 43 (Sorbitan sesquioleate, HLB 3.7 supplied by Croda, Inc.) and Softanol 90 (C11-C13 secondary ethoxylated fatty alcohol, HLB 13.3 supplied by Quimidroga) was used as the surfactant system, sodium metabisulfite (SMB) as initiator and 2-propanol as chain transfer agent. SMB has been used before as the sole initiator in the homopolymerization of [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT) [13] and in copolymerization of Am/Adamquat in inverse microemulsion [14]. Deionized water was used throughout the work.

The polymerizable inverse microemulsion was prepared by mixing under agitation the aqueous and the oil phases previously prepared. The aqueous phase contained the monomers, deionized water and EDTA, and was adjusted to a pH 4 to avoid hydrolysis of acrylamide. The oil phase contained Isopar M and the surfactant system. The whole microemulsion included 31.8 wt% of Isopar M, 8.6 wt% of Am, 34.3 wt% of Adamquat, 0.8 wt% of an aqueous solution of EDTA (16 $g\,L^{-1}$), 2.9 wt% of Crill 43 and 4.4 wt% of Softanol 90. The total monomer content (solids content) was 42.9 wt%.

One CSTR and two CSTRs in series were used as continuous reactors. For the sake of comparison of the product performance, a reaction with the same formulation was carried out in a semicontinuous reactor. It was found that the oxygen dissolved in the microemulsion, which was fed into the reaction medium, made the process highly irreproducible. On the other hand, when the oxygen contained in the microemulsion was removed achieving very low oxygen concentrations, the microemulsion polymerized in the feeding tank. In order to improve the reproducibility of the process, a control system based on the alternative purging with air and nitrogen (depending on the value measured by an oxygen sensor, Hach Lange), was implemented in the microemulsion feeding tank. This allowed controlling the concentration of oxygen in the microemulsion between 0.2 and 0.05 ppm, which led to smoother operations. However, because of the concentration of oxygen could only be controlled within a range and the initiation of the polymerization was very sensitive to this concentration, complete reproducibility could not be achieved.

2.2. Semicontinuous reactor

The experimental set-up includes a 0.6 L jacketed reactor equipped with a combination of a six-blade turbine impeller in the lower part of the reactor and a two pitched blades (45°) in the upper part at 400 rpm. The initial charge of the reactor comprised 100 g of a product previously synthesized in batch with the same microemulsion formulation and fully converted. The temperature was set to 35 °C and then the microemulsion and an aqueous solution of initiator (SMB, 0.33 $g\,L^{-1}$) were fed for 60 min via separate streams at 6.7 $g\,min^{-1}$ and 0.342 $g\,min^{-1}$, respectively. The reaction was carried out under nitrogen atmosphere and once the feeding was stopped, the reactor was kept at 35 °C for 60 min.

2.3. Continuous reactors (CSTR and two CSTRs in series)

Continuous microemulsion polymerizations were carried out in one and two 0.3 L jacketed reactors equipped with the same type of impeller as for semicontinuous reactor rotating at 400 rpm. The operation started with the reactor completely filled with a previously polymerized and fully converted latex in order to reduce the time required to achieve the steady state [15]. For both reactor systems, the microemulsion was fed at 27.6 $g\,min^{-1}$. For the single CSTR, the initiator solution (SMB, 3 $g\,L^{-1}$) was fed in a separate stream at 0.15 $g\,min^{-1}$, namely, 4.5×10^{-4} $g\,min^{-1}$ of initiator. For the two CSTRs in series, the initiator solution was fed to both reactors in two separate streams, both of them at 0.15 $g\,min^{-1}$. In this case, the concentration of the initiator solution was varied (3 or 1.5 $g\,L^{-1}$) to change the initiator fed to each reactor (4.5×10^{-4} or 2.25×10^{-4} $g\,min^{-1}$). The mean residence time (τ) defined as the ratio between the reactor volume and flow rate was 10 min for the single CSTR and 20 min for the whole system of two CSTRs in series, namely, 10 min for each reactor.

Four reactions were carried out in the single CSTR, three of them for different temperatures (35, 55 and 70 °C) and one with a chain transfer agent (CTA, 2-propanol) at 35 °C. In the later case, the CTA (0.7 wt%) was included in the microemulsion feed.

Three reactions have been carried out in the train of two CSTRs in series at 35 °C and changing the initiator fed in each reactor. Table 2 summarizes the reactions carried out in the train of two CSTRs in series together with the main results obtained.

2.4. Polymer characterization

Monomer conversion and copolymer composition were calculated by of a mass balance using the free monomer content of the samples determined by HPLC (HP 1100). Particle size was determined by dynamic light scattering of samples diluted in an surfactant saturated organic phase (Malvern Zetasizer Nano ZT). In the polymerization of acrylates, the determination of long chain branching by ^{13}C NMR is not possible because of the number of long branches is much smaller than that of the short branches [16] produced by backbiting. Therefore, the formation of branches was inferred from the viscosity of aqueous solutions of the copolymer, which is related to the average molecular weight. For the viscosity measurements, the microemulsion was inverted in water to form a solution of polymer in water (0.5 $g\,L^{-1}$ water), and the viscosity of the solution was measured at room temperature in a Brookfield DVII using the UL adapter (spindle 00) at 2.5 rpm.

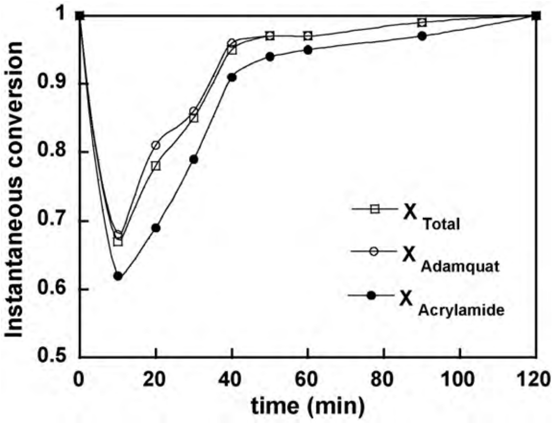

Fig. 1. Evolution of the instantaneous (total and partial) monomer conversions in the semicontinuous microemulsion polymerization.

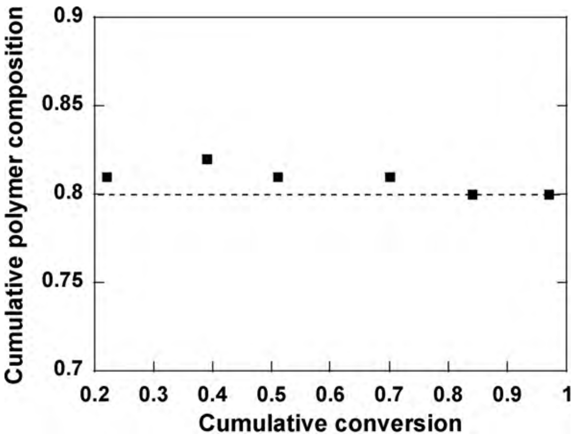

Fig. 2. Cumulative copolymer composition vs. cumulative conversion in the semicontinuous microemulsion polymerization.

2.5. Flocculation efficiency

The efficiency of the copolymers as flocculants was assessed in a Turbiscan Lab$^{\text{expert}}$ apparatus. An aqueous solution of the copolymer was added to a 0.38 wt% aqueous dispersion of colloidal silica placed in a cylindrical glass cell, which was scanned with a light source and the transmitted light measured. Upon addition of the flocculant, the dispersion became opaque (presumably because of the formation of flocs), and then sedimentation of the flocs occurred leading to the formation of two separate regions: a clear phase at the upper part, which in most cases was basically devoid of particles, and a silica rich opaque phase at the bottom. The efficiency was characterized by the settling rate, the clarity of the upper phase, and the density of the sediment.

3. Results and discussion

Fig. 1 presents the evolution of the instantaneous conversions (total, X_{Total} and for each monomer, $X_{\text{Acrylamide}}$, X_{Adamquat}) in the semicontinuous process. It can be seen that a complete conversion was achieved at the end of the process, although the polymerization was not carried out under starved conditions. Adamquat reacted faster than acrylamide indicating that the cationic monomer was more reactive. This agrees with what was observed in the inverse microemulsion copolymerization of these monomers in a Taylor–Couette reactor [11], but the opposite trend was observed in solution polymerization [17]. It seems that the inverse microemulsion system used can be the reason for this result.

Fig. 2 shows the cumulative copolymer composition evolution (defined as the weight fraction of Adamquat in the copolymer, Y_{Adamquat}). It can be seen that the final polymer weight composition in Adamquat was 0.8 that was the same than the feeding microemulsion. A value slightly higher than 0.8 was observed at the beginning of the reaction because the operation did not proceed under starved conditions.

The evolution of the viscosity is presented in Fig. 3. The viscosity, and hence the molecular weight, was almost constant during the whole process (≈128 mPa s). It has been already reported that in the copolymerization of acrylamide and Adamquat, substantial intermolecular chain transfer to polymer takes place due to the fact that both monomers contain abstractable hydrogens and their corresponding radicals are efficient for hydrogen abstraction [18–20]. This implies that a branched polymer architecture was obtained. Since the viscosity showed not significant changes during the process, the molecular weights and long chain branching levels should also remain constant. The intermolecular chain transfer depends not only on the polymer concentration but also on the time that the polymer spends in the reactor in the presence of radicals. In the semicontinuous operation, the monomer microemulsion and the initiator were fed during 60 min. Therefore, the polymer was continuously formed in the reactor. As the instantaneous conversion was high, the polymer concentration was also high and one would expect a substantial chain transfer to polymer with the subsequent formation of long branches. However, Fig. 3 indicates that the polymer architecture was not substantially modified during a significative part of the process (for a cumulative conversion greater that 0.5, i.e., for times greater than 30 min). Two effects can explain this result. Firstly, the change in polymer concentration was modest (the instantaneous conversions were always higher than 0.8) and secondly, the average time that the polymer remained in the reactor in the presence of radicals was not too high, because although Fig. 1 shows that the polymer remained in the reactor for a long time, no initiator was fed after 60 min.

The product obtained was a stable dispersion of polymer particles (polymer dissolved in water) in Isopar M. The final particle diameter obtained in the semicontinuous process was of 163 nm.

Four reactions changing the reaction temperature (35, 55 and 70 °C) and the microemulsion formulation (including a chain transfer agent at 35 °C) were carried out in a single CSTR. In all the experiments, the mean residence time (τ) was 10 min. As an example, Fig. 4 shows the evolution of the conversions (total and that of each monomer) and the polymer weight composition for the experiment carried out at 55 °C. It can be seen that with the start-

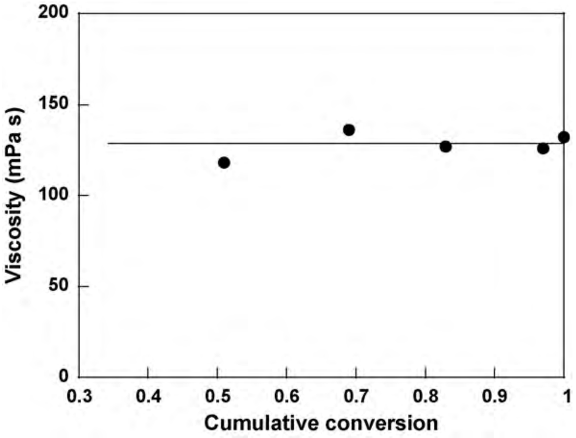

Fig. 3. Evolution of the viscosity of the aqueous solution of the copolymer during the semicontinuous reaction.

Table 1
Main results of the reactions carried out in a single CSTR.

Run	Temperature (°C)	X_{Adamquat}	$X_{\text{Acrylamide}}$	X_{Total}	Y_{Adamquat}	dp (nm)	μ (mPa s)
CSTR-1	35	0.97	0.92	0.96	0.81	152	112
CSTR-2	55	0.96	0.91	0.95	0.81	167	98
CSTR-3	70	0.97	0.91	0.96	0.81	152	64
CSTR–CTA	35	0.96	0.91	0.95	0.81	149	24

up procedure used in this work, the steady state was reached in only two residence times. Moreover, the control of the oxygen dissolved in the feeding tank allowed achieving a quite stable operation and provided good consistency in the synthesized product. As in the semicontinuous operation, Adamquat reacted faster than acrylamide, and the conversion was very high for the two monomers. Consequently, the polymer composition was almost the same (0.81) than that of the microemulsion composition (0.8). A holding tank maintained at 35 °C and under nitrogen atmosphere was placed at the reactor exit to collect the product. For emulsion copolymerization of 2-ethyl hexyl acrylate/methyl methacrylate carried out in CSTRs and initiated by a redox pair, the conversion and polymer architecture dramatically changed in the holding tank [12]. However, for the reactions carried out in this work, no change in the polymer properties was observed in the holding tank, indicating that the initiator was almost completely consumed in the reactor.

The same trends were observed for the rest of the reactions made in a single CSTR. Table 1 summarizes the main results obtained for these reactions. Over the entire range of temperatures used, phase separation was not observed in the reactor and stable latexes were obtained in all cases. In this table, the run CSTR–CTA represents the reaction carried out including the chain transfer agent in the formulation.

Table 1 shows that monomer conversion was affected by neither the temperature nor the chain transfer agent. SMB is able to initiate the polymerization by means of the reaction of the bisulfite anions with the monomers resulting in two radicals, one monomeric radical and one sulfite radical. The polymerization takes place if the monomeric radical is sufficiently stable to prevent the recombination of the two radicals allowing the propagation of sulfite radical [14,21]. The fact that no further reaction occurred in the holding tank indicates that these reactions were very fast, even at low temperature. This might result in a very small increase in the production of radicals when the temperature increased. On the other hand, the rate of termination of radicals in the reaction medium should increase with temperature due to the increase in the termination rate constant. The available results suggest that these effects were compensated by the increase in the propagation rate constant resulting in a similar polymerization rate. Moreover, the high conversion achieved in the reactor makes the conversion very insensitive to major changes in operating conditions [22]. On the other hand, the fact that the conversion was not affected by the chain transfer agent means that the radicals produced by chain transfer to CTA were efficient for starting polymerization [23].

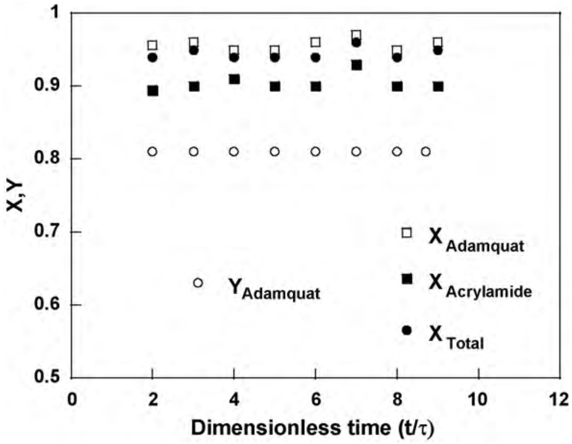

Fig. 4. Evolution of conversions and polymer composition for the reaction carried out in a single CSTR at 55 °C.

Particle diameter (dp) was not affected by the polymerization conditions nor by the polymerization process (the particle diameter in the semicontinuous operation was 163 nm). This indicates that the particle diameter was controlled by the surfactant concentration in the microemulsion formulation rather than by the operating conditions or the process type.

The viscosity (μ) of the aqueous solution of the polymer, and hence the molecular weight and branching, changed dramatically with the temperature and also with the CTA content. These results indicate that chain growth termination took place mainly by chain transfer reactions to the monomer or to the chain transfer agent. These processes resulted in a decrease of the kinetic chain length, which would decrease both the length of the polymer backbone and that of the branches. The total number of branches is proportional to the concentrations of polymer and radicals. Therefore, CTA had no effect on the total number of branches, and the viscosity reduction with respect to run CSTR-1 was due to the shorter length of both polymer backbone and branches. The effect of temperature on the number of branches is difficult to assess because of two counteracting effects. On one hand, the lack of effect of temperature on monomer conversion indicates that the radical concentration decreased with temperature, but on the other hand, the rate coefficient for chain transfer to polymer increases with temperature [24]. Nevertheless, the results in Table 1 indicate that the decrease in kinetic chain length was the main reason for the decrease of the viscosity of the aqueous solution of the polymer with the temperature increase.

Comparison of the viscosity (molecular weight) of the aqueous solution of the polymer produced at 35 °C in run CSTR-1 (Table 1) with that of the semicontinuous process at the same temperature (Fig. 3) shows that a lower viscosity was achieved in the single CSTR. It is not likely that this difference was due to the differences in conversion (polymer concentration in the reactor) because the differences were very small. More likely it was due to the different time spent by the polymer in the reactor in the presence of radicals [25]. In the semicontinuous process, the feeding time was 60 min, whereas in the single CSTR the average residence time was only 10 min. Therefore, the level of branching was greater for the flocculant produced in the semicontinuous reactor.

The initiator fed in each reactor was varied in the reactions carried out in the train of two CSTRs in series at 35 °C and 20 min of residence time (10 min for each reactor). As an example, Fig. 5 shows the evolution of the total conversion attained in each reactor (X_{T1}, X_{T2}) in run 2CSTR-3. The mean residence time considered to normalize the time was 10 min, i.e., the average residence time for each reactor. It can be seen that the operation proceeded smoothly and that the steady state was quickly reached. The conversion at the exit of the system was almost complete. Fig. 6 shows the evolution of the copolymer weight composition for the polymer produced in

Table 2
Main results of the reactions carried out in two CSTRs in series.

Run	Initiator feed rate (g min^{-1})		X_{T1}	X_{T2}	$Y_{Adamquat1}$	$Y_{Adamquat2}$	dp (nm)	μ_1 (mPa s)	μ_2 (mPa s)
	First reactor	Second reactor							
2CSTR-1	2.25×10^{-4}	2.25×10^{-4}	0.80	0.98	0.83	0.68	153	85	120
2CSTR-2	4.5×10^{-4}	2.25×10^{-4}	0.90	0.99	0.81	0.68	140	103	117
2CSTR-3	2.25×10^{-4}	4.5×10^{-4}	0.86	0.99	0.82	0.66	156	114	125

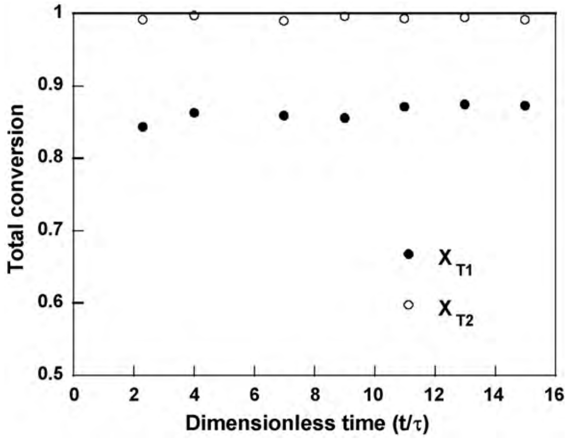

Fig. 5. Evolution of the conversion in each of the two CSTRs in series for the reaction carried out at a initiator feeding rate of 2.25×10^{-4} g min^{-1} in the first reactor and 4.5×10^{-4} g min^{-1} in the second reactor.

each reactor ($Y_{Adamquat1}$, $Y_{Adamquat2}$) for run 2CSTR-3. It can be seen that in the first reactor, the copolymer composition was slightly higher than 0.8 and that in the second reactor was clearly lower than 0.8. This was due to the fact that the Adamquat is more reactive than acrylamide and hence the polymer produced in the first reactor was richer in Adamquat. Consequently, the monomer composition that entered the second reactor was richer in acrylamide, and hence the polymer produced was richer in acrylamide. Because the final conversion was almost complete, the final average copolymer composition was near 0.8, but the polymer was composed by two parts of different composition, although the polymer fraction produced in the first reactor was greater.

The results of the reactions carried out in the train of two CSTRs in series are summarized in Table 2. It can be seen that almost complete conversion was achieved in the second reactor in all cases. The differences in monomer conversion in the first reactor between runs 2CSTR-1 and 2CSTR-3 illustrate the effect of the variations in the oxygen contained in the feeding tank. The weight composition of the copolymer produced in each reactor was almost the same for the three reactions carried out, namely the final product was a mixture of two polymers of different composition.

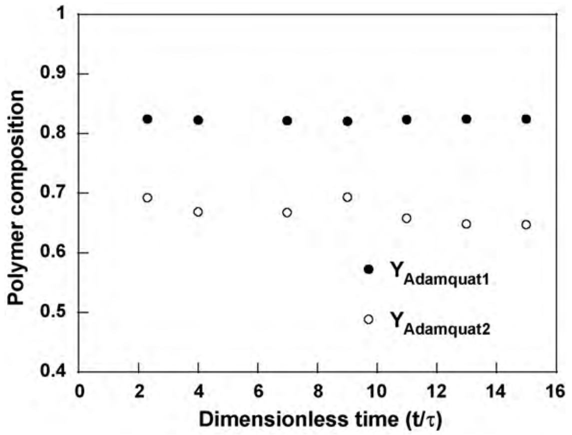

Fig. 6. Evolution of the polymer composition in each of the two CSTRs in series for the reaction carried out at a initiator feeding rate of 2.25×10^{-4} g min^{-1} in the first reactor and 4.5×10^{-4} g min^{-1} in the second reactor.

A small effect of the initiator feed rate on the particle diameter was found. For all the reactions carried out in this work only slight changes in particle diameter were observed, indicating that particle size was mainly determined by the surfactant concentration in the microemulsion formulation.

The effect of the initiator feed rate on the molecular weight was the result of the interplay between chain transfer to polymer and the termination events controlling the kinetic chain length. In the first reactor, an increase of the initiator concentration led to an increase of the monomer conversion, which in turn favored the increase of the molecular weight because of the higher chain transfer to polymer. However, the increase of the initiator concentration accelerated the termination reactions leading to a shorter kinetic length. These counteracting effects explain the relatively high viscosity obtained in the first reactor in run 2CSTR-3 as compared to those obtained in runs 2CSTR1 and 2CSTR2.

The final product was the result of the polymer formed in the first reactor and at least partially modified in the second reactor through chain transfer to polymer reactions and the polymer formed in the second reactor, which represented the smaller fraction, and that was richer in acrylamide and had a different molecular weight. The differences in molecular weight resulted from the differences in the kinetic chain length (caused by the overall monomer concentration, the comonomer ratio [17] and the initiator concentration) and the extent of the chain transfer to polymer suffered by the polymer (higher for the polymer formed in the first reactor). The final product was therefore a mixture of two polymers with different composition and different molecular weight and branching level, although Table 2 shows that the final average viscosity was similar for the three reactions.

The differences in molecular weight and branching of the polymers synthesized by different processes affect their performance as flocculants. The flocculation efficiency was characterized by three parameters, the settling rate, the clarity of the supernatant and the sediment compactness. The flocculation experiments were carried out using an aqueous dispersion of silica (210 nm, 0.38 wt%) to which a small dose of flocculant (11 ppm) was added. The aim of using a small dose of flocculant was to enhance the differences between flocculants. The fraction of particles removed from the upper phase (PC) was quantified by the transmitted light measured. Using a calibration curve (transmitted light vs. silica concentration), the wt% of the initial particles in the supernatant was calculated. The compactness of the sediment was then calculated by the following expression:

$$h_i \rho_i = h_u \rho_u + h_s \rho_s \tag{1}$$

where h_i, h_u and h_s are the initial, upper phase and sediment heights and ρ_i, ρ_u and ρ_s their corresponding silica weight percentages. Since h_i and ρ_i are known, and h_u, h_s and ρ_u can be measured (ρ_u from the transmitted light calibration curve), Eq. (1) allows calculating ρ_s (the compactness of the sediment). On the other hand, the settling rate was determined by the displacement of the sedi-

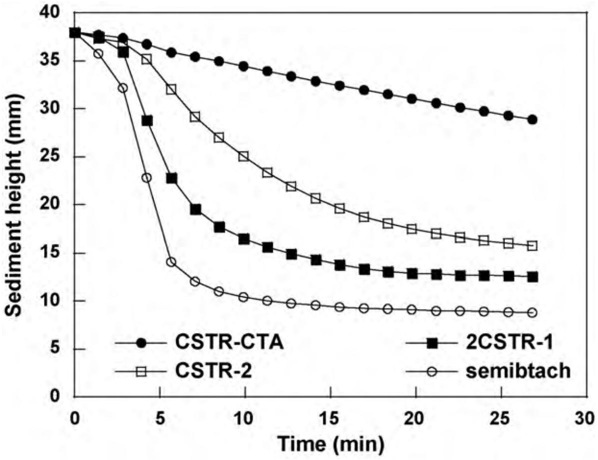

Fig. 7. Evolution of the sediment height for the flocculants synthesized in different processes.

ment front separating the clear supernatant (upper phase) and the sediment.

Fig. 7 compares the sedimentation rates (slope of the curves) of some representative flocculants produced in a single CSTR (CSTR-2 and CSTR–CTA) and in two CSTRs in series (2CSTR-1) with that of the flocculant produced in the traditional semicontinuous process. Table 3 completes this comparison with the results of the percentage of particles cleared in the upper phase (PC), the final height of the sediment (h_s) and the compactness of the sediment (ρ_s). It can be seen that the sedimentation rate (Rs) increased with the viscosity (molecular weight) of the flocculant, namely, $Rs_{semicontinuous} > Rs_{2CSTR\text{-}1} > Rs_{CSTR\text{-}2} > Rs_{CSTR\text{–}CTA}$. On the other hand, low molecular weights (CSTR–CTA) allowed the complete removal of the silica particles from the upper phase, whereas the highly branched polymer produced in semibatch was not able to clean the supernatant.

Flocculation involves charge neutralization and particle bridging. Short and mobile polyelectrolyte chains would likely be more efficient in charge neutralization, whereas long and branched chains would enhance particle bridging flocculation and faster sedimentation. The results in Fig. 7 and Table 3 suggest that the flocculant formed in the semicontinuous reactor was too big and branched and hence it was not efficient neutralizing the charges on the silica particles. Consequently, many silica particles remained dispersed, whereas the few large flocs formed by particle bridging underwent a fast sedimentation.

The flocculant CSTR–CTA showed the opposite behavior. Because of its low molecular weight, it was able to efficiently neutralize the charges on the silica particles causing their sedimentation and yielding a clear upper phase. However, its efficiency for particle bridging was low, and hence only small flocs that sedimented slowly were formed.

Fig. 7 and Table 3 show that the flocculant formed in Two CSTRs in series (2CSTR-1) presented the best performance as flocculant, likely because it contained two different polymers: a branched high molecular weight polymer formed in the first reactor and a polymer of lower molecular weight formed in the second one. This balance between high and low molecular weights results in a good clarity in the supernatant together with a fast sedimentation rate and a high compactness of the sediment.

Table 3
Flocculation results for the flocculants synthesized in different processes.

Run	μ_{final} (mPa s)	PC (%)	h_s (mm)	ρ_s (wt%)
CSTR-2	98	98	16	0.89
CSTR–CTA	24	100	29	0.49
2CSTR-1	120	98	12	1.18
Semibatch	130	2	9	0.40

4. Conclusions

The synthesis of cationic flocculants by inverse microemulsion copolymerization of acrylamide and [2-(acryloyloxy)ethyl]-trimethylammonium chloride in continuous reactors (single CSTR and two CSTRs in series) was investigated. Continuous reactors represent a way of improving the efficiency of the traditional semicontinuous processes. The process proceeded smoothly provided that the oxygen content of the feed was controlled. The microstructure of the polymer was strongly affected by the occurrence of chain transfer to polymer, which led to the formation of a branched polymer. The level of branching depends on both the polymer concentration and the time that the polymer remains in the reactor in the presence of radicals. Therefore, the microstructure of the polymer strongly depended on the process. Thus, the molecular weight and, presumably, the level of branches of the polymer produced in a single CSTR was lower than those of the polymer produced in the traditional semicontinuous process, because the time spent by the polymer in the CSTR was shorter than that in the semicontinuous reactor. In addition, the polymer produced in two CSTRs in series consisted of a blend of two different polymers: a branched high molecular weight polymer formed in the first reactor and a polymer of lower molecular weight formed in the second reactor.

The performance of the polymers as flocculants for a silica dispersion was studied finding that the microstructure of the polymer critically affected its efficiency. Low molecular weight polymers (as those obtained using a chain transfer agent) were very efficient in neutralizing the charges of the silica, but formed small flocs, which sedimented slowly. Branched high molecular weight polymers (e.g., those produced in the semicontinuous process) were very efficient in forming large flocs through particle bridging that sediment fast, but they were not efficient neutralizing the charges of the silica particles. Therefore, many silica particles remained dispersed in the upper phase. The polymer synthesized in two CSTRs in series presented the best performance as flocculant because it contained both, short (polymer produced in the second reactor) and branched long (polymer produced in the first reactor) polymer chains.

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