Copolymerization of dimethylaminoethylacrylate-methyl chloride and acrylamide in inverse emulsion

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The inverse emulsion copolymerization of acrylamide (AM) with dimethylaminoethylacrylate methyl chloride (Q9) using redox initiation with low surfactant concentration in an isoparaffinic solvent has been studied. The kinetics of conversions of inverse-emulsion polymerizations were investigated by HPLC method. It was an interesting way to know rapidly the conversion of each monomer with high reproducibility. In all experiments the monomer concentration was 25% respect the total weight or higher and the experiments were carried out at 50°C.

The effects of initiator concentration, composition of the monomer mixture and monomer concentration on the polymerization conversion and viscosity of copolymers solutions have been examined. For copolymer characterization, the results of viscosity were compared with commercial copolymer viscosities.

The formulations with 3,000 ppm of initiator were the most interesting of all copolymer compositions since they presented very high conversions and their viscosities were higher than those of commercial copolymer solutions. The analysis of monomer concentration was carried out with 3,000 ppm and the conversion and viscosity were higher when the monomer concentration was increased. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Polyacrylamide and acrylamide-based copolymers are important synthetic water-soluble polymers used as coagulants and flocculants in waste water and potable water treatments. Their solutions are also used as pushing fluids in enhanced oil recovery, as drag reduction agents and drilling fluids, as additives in paper making, and as thickeners. These water soluble polymers have a multibillion dollar market value wich is expected to have annual sales growth rates (5–8%) exceeding those of most segments of the chemical and polymer industries [1, 2]. Their molar masses are usually of the order of 10^7 g·mol^{-1} and they are efficiently used in aqueous solid-liquid separations. Concomitant with the high molar mass their solutions show high viscosities, even at polymer concentrations as low as 1–5 wt%, giving rise to difficulties in their synthesis, particularly affecting agitation and heat transfer. The control of polymerizations involving acrylamide monomers is also complicated by the high enthalpy of polymerization ($\Delta H_p = 81.5$ kJ·mol^{-1}) and by a propensity to form covalent crosslinks at high tem-

peratures (over 70°C). To avoid these constraints in the control of high molar mass polyacrylamide homo- and copolymers synthesis, while maintaining a commercially feasible operation (high monomer concentrations). Vanderhoff *et al.* [3] developed a heterophase water-in-oil emulsion polymerization process that they termed "inverse-emulsion". The level of understanding of inverse-emulsion polymerization has been growing continuously over the past 30 years. During the 1980s efforts were dedicated to the clarification of the reaction mechanism, kinetics measurements and reactor modelling of the inverse-emulsion polymerization processes.

Inverse-emulsion polymerization involves the dispersion of an aqueous water-soluble monomer solution in a continuous organic phase. In emulsified droplets stabilization is achieved sterically. The initiating species can be located either in the dispersed water phase (in analogy to suspension polymerization) or in the continuous oil phase (as in classical emulsion polymerization). Further refinements to this process over the last four decades have involved the use of aromatic

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and paraffin continuous phase and various non-ionic emulsifier systems.

The main goal of this work was to evaluate the conditions to obtain stable inverse-emulsions using a minimum emulsifier concentration. For this purpose the influence of different variables like initiator concentration, comonomer composition and monomer concentration on the total conversion, comonomer conversion during the polymerization on the copolymer solutions viscosity was studied. Our experimental design consisted in the variation of variables keeping constant the rest of parameters (emulsifier concentration, EDTA concentration, aqueous/oil ratio and the synthesis temperature). The conversion determination was carried out by a HPLC [4] method.

This paper reports: (i) a method to synthesize cationic copolymers of acrylamide (AM) and dimethylaminoethylacrylate methyl chloride (Q9) by inverse-emulsion polymerization in an isoparaffinic continuous phase, using low surfactant concentration at different compositions and at various monomer and initiator concentrations, (ii) the determination of kinetics of polymerization and conversion of each monomer and (iii) the influence of different parameters in polymerization kinetics and in viscosity of copolymer solutions.

2. Experimental part
2.1. Materials
Reagent-grade water was deionised (Type I water with a resistivity ≥ 0.5 m$\Omega \cdot$cm, Elgastat deionizer, model B114). The acrylamide solution (50% w/w) was purchased from SNF, S.A., and was used without further purification. Certified ACS EDTA (ethylenediamine tetraacetic acid, tetrasodium salt, Quimidroga, S.A.) was used as a quelating agent. The dimethylaminoethylacrylate-methyl chloride (Q9) was obtained from CPS Chemicals as aqueous solutions, 80%, by weight inhibited with approximately 600 ppm of hydroquinone monomethylether. The monomers were used without purification. The aqueous phase was emulsified in Rolling M-245 (Esso Lubricants), a narrow cut off an isoparaffin mixture used as the continuous phase. Sorbitan Monooleate (Span 80, Aldrich Chemical Company, Inc.) was the non-ionic stabilizer. It was used as received. Ammonium persulphate (APS, Panreac) and sodium bisulphite (NaHSO$_3$, Merck) were used as water-soluble initiators. Nitrogen with a purity of 99.99% was purchased from Praxair España, S.L. and was used to eliminate the dissolved oxygen. The inverse emulsion was purged with nitrogen for 60 min before the reaction initiation as well as throughout the polymerization.

2.2. Polymer synthesis
The inverse-emulsion polymerizations were carried out in a 250 mL glass reactor (IKA, model LR-A250) equipped with two mechanical stirrers, a helix stirrer rotated at 100 rpm and an Ultra Turrax T 25 at 8,000 rpm. The reactor was also equipped with an external heating/cooling jacket. The polymerization conversion was analysed by HPLC.

The inverse emulsions were prepared by pouring the oil phase (3% w/w Span 80 in Rolling M-245) in the glass reactor followed by the aqueous solution of monomers, EDTA and APS. The reactor was continuously sparged with nitrogen to remove any residual oxygen, which could consume radicals and interfere with the polymerization process. The system was stirred for 60 min. After the monomer emulsion stabilization aqueous solution of the second component of the dual redox initiator (NaSO$_3$H) was added. The components of the dual redox initiator were in 1:1 mol ratio and its concentration was respect the monomer mixture weight. All experiment had a constant aqueous to organic ratio of 70:30 (w:w). The total weight was 100 g in all samples.

2.3. Conversion determination
The acrylamide conversion to polymer was determined by a HPLC [4] method. The HPLC system [4] consisted of an isocratic Gilson Model 303 HPLC Pump and a CN μ—Bondapak column (7.8 $\times$ 300 mm i.d., Waters) used as stationary phase. A Perkin Elmer LC 290 variable wavelength UV detector was used to measure the monomer absorption at 214 nm. The chromatograms were collected on 486-computer running PL Caliber Version 5.20 software. The mobile phase flow rate was kept at 0,12 L$\cdot$s^{-1}. A 10^{-3} L glass syringe (Hamilton) was used for the injections.

The first step was the selection of a solvent. It had to be a good precipitant of the polymer and good solvent for the monomers. The acetonitrile had the effect of precipitating the polymer and separating the oil and emulsifier while simultaneously solubilizing the monomers. A small quantity of emulsion was withdrawn from the reactor (about 0.005–0.01 g) at different times of polymerization and then precipitated in acetonitrile. Once supernatant was clear, a 2×10^{-5} L aliquot was removed with a glass syringe and injected into the HPLC. Although the injection solvent was pure acetonitrile and mobile phase was an acetonitrile-water mixture, systems peaks were not found to interfere with the chromatogram for either the acrylamide or the quaternary ammonium monomer. Residual monomer concentrations ranging from 0 to 100 ppm for acrylamide and 0–600 ppm for Q9 were determined from the calibration. The calibration curve was prepared daily prior to analysis. In order to know the conversion three aliquots for each sample were injected into the HPLC apparatus and the arithmetic average of the three areas was computed. The conversion values for all runs are given in Table I.

2.4. Copolymer characterization
The viscosity measurements were performed in a Brookfield viscometer model LVDVIII. The Brookfield viscometer was equipped with a small sample adapter for low viscosities (ULA 00). The measurements were performed at 150 rpm rate. All determinations were carried out on 0.005 kg$\cdot$L^{-1} polymer solutions in 0.5 M aqueous NaCl at 25°C. For copolymer characterization, the results of viscosity were compared with commercial copolymer viscosities measured in similar conditions.

TABLE I Formulations and conversions of inverse-emulsion polymerizations of acrylamide with Q9 in 7:3 (w/w) aqueous-oil using APS-NaBiS pair redox as initiator

Monomer concentration (%)	Synthesis temperature (°C)	Initiator concentration (ppm)	Comonomer composition(%)		Time (min)	Runs	Conversion (%)
			AM	Q9			
25	50	500	80	20	180	82c1–180	87
		3,000				82c2–180	97
		5,000				82c3–180	98
25	50	500	60	40	180	64c1–180	90
		3,000				64c2–180	98
		5,000				64c3–180	99
25	50	500	40	60	180	46c1–180	64
		3,000				46c2–180	96
		5,000				46c3–180	99
25	50	500	20	80	180	28c1–180	65
		3,000				28c2–180	97
		5,000				28c3–180	99
25	50	500	0	100	180	010c1–180	46
		3,000				010c2–180	98
		5,000				010c3–180	98
35	50	3,000	40	60	180	46c2–180(35)	99
			20	80		28c2–180(35)	99
40	50	3,000	40	60	180	46c2–180(40)	99
			20	80		28c2–180(40)	99

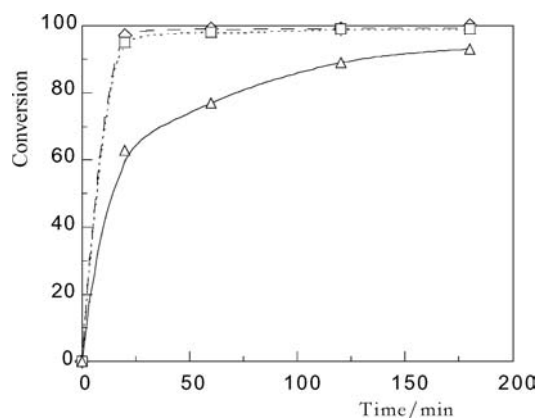*Figure 1* Conversion versus time for 60:40 AM:Q9 at 50°C for (△) 500, (□) 3,000 and (◇) 5,000 ppm of initiator concentration.

3. Results and discussion

The separation of mixtures of acrylamide with Q9 using a CN μ—Bondapak column coated silica stationary phase has been studied by Hunkeler [4]. In the HPLC system used in this work 0.02 M of dibutylamine was necessary for total separation. It was observed that the adsorption, and hence the retention volume, of the cationic monomer was reduced as the dibutylamine concentration was increased. It was necessary to use a minimum concentration of dibutylamine for peak separation (0.02 M).

In relation to the influence of different parameters in conversion, Fig. 1 shows the conversion for AM:Q9 60:40 comonomer composition at 50°C for three initiator concentrations (500, 3,000 and 5,000 ppm of initiator concentration). The rate of polymerization increased as the initiator concentration increased. With an initiator concentration of 500 ppm, the reaction was slow but the other initiator concentrations were very fast and conversions up 95% were obtained. The reactions with 3,000 and 5,000 ppm showed very similar kinetics and final monomer conversion. The monomer conversion

was constant from a polymerization time of 60 min of polymerization but in the case of the formulation with 500 ppm the conversion was increasing up to 180 min. For this reason all polymerizations were carried out in 180 min. In inverse emulsion, when water-soluble initiators are used, most of the authors concluded that the reaction proceeds within the monomer droplets, irrespective of the nature of the organic phase (aromatic or aliphatic). Both monomer and initiator reside in the dispersed droplets and each particle acts as a small batch reactor. The process is essentially a suspension polymerization and therefore the kinetics resembles those for solution polymerization. A square root dependence of the polymerization rate, R_p, on initiator concentration was often observed, in accordance with solution polymerization [5, 7–11]. Similar results were observed for nonionic and cationic inverse emulsion systems [12, 13].

Concerning the conversion of each monomer, the kinetic of dimethylaminoethylacrylate-methyl chloride
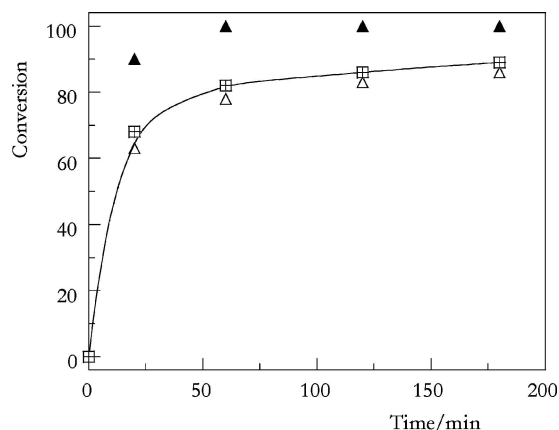

Figure 2 Conversion of each monomer versus time for 500 ppm of initiator concentration and 80:20 AM:Q9 composition: total conversion (⊞), AM (△) and Q9 conversion (▲).
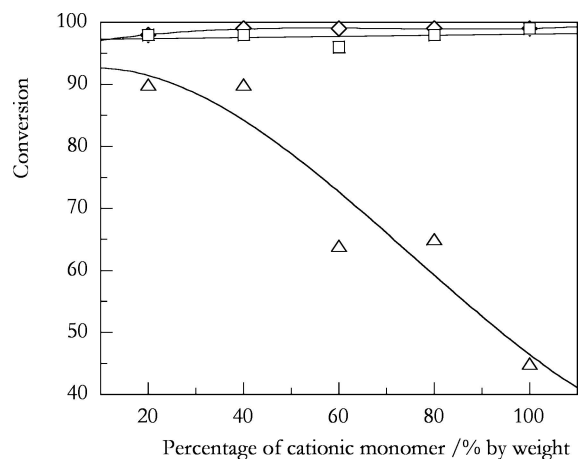
Figure 3 The final conversion as function of comonomer composition for three initiator concentration: (△) 500 ppm, (□) 3,000 ppm and (◇) 5,000 ppm.

was faster than acrylamide's kinetics and the final conversion was higher too for all formulations. Fig. 2 shows the conversion of each monomer versus time for 500 ppm and 80:20 AM:Q9 composition. Clearly dimethylaminoethylacrylate-methyl chloride reacts faster than acrylamide even at low conversions despite the similarities in their reactivity ratios. This behaviour has been previously reported by Hunkeler [4, 14]. This finding can be explained in terms of the monomer partitioning between the aqueous and the continuous phases.

Respect to the influence of comonomer composition, Fig. 3 shows the final conversion as a function of comonomer composition for three different initiator concentrations. For 5000 and 3000 ppm, when the cationic monomer percentage increased, the final conversion maintained constant. The polymerization conversion was fairly insensitive to the comonomer composition. Similar behaviour was observed for other system in inverse emulsion [12]. When the initiator concentration was 500 ppm the conversion was very sensitive to the comonomer composition. Ge *et al.* [12, 13] only analysed formulation until 50% of cationic monomer and there was an important decrease when this percentage was higher than 50%. Fig. 4 shows the final conversion of each comonomer. In formulations with 500 ppm the conversion of acrylamide is lower independently of comonomer mixture composition.

Taking into account these results, the more interesting initiator concentration was 3,000 ppm. In all formulations, the conversion with this concentration was as high as the conversion with 5,000 ppm of initiator concentration. The influence of monomer concentration was analysed only for 3,000 ppm of initiator concentration for the relation 40:60 and 20:80 AM:Q9. Fig. 5 shows the kinetics with 25, 35 and 40% of monomer concentration for 20:80 comonomer composition. In inverse emulsion, when water-soluble initiators are used, most of the authors concluded that the reaction proceeds within the monomer droplets. Both monomer and initiator reside in the dispersed droplets and each particle acts as a small batch reactor. The process is essentially a suspension polymerization and therefore the kinetics resembles those for solution polymeriza-
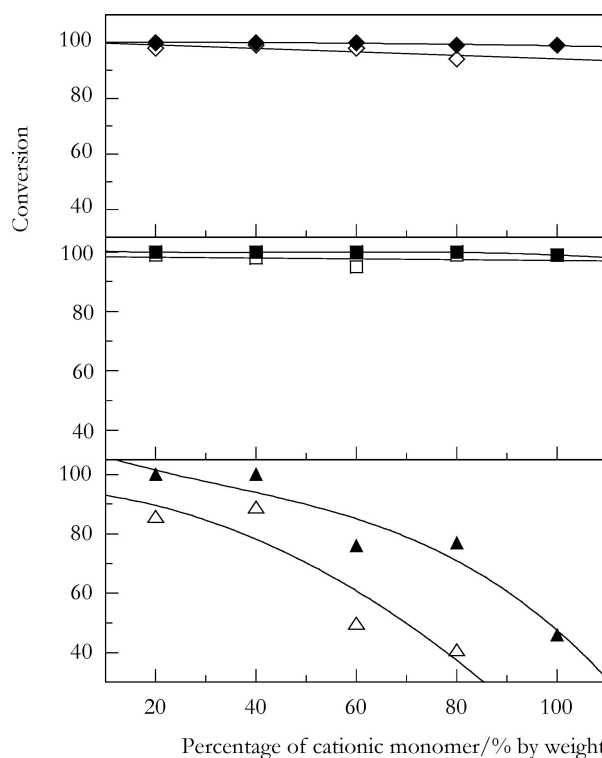

Figure 4 The final conversion of each comonomer for three initiator concentrations: 500 ppm (△) AM and (▲) Q9; 3,000 ppm (□) AM and (■) Q9 and 5,000 ppm (◇) AM and (◆) Q9.
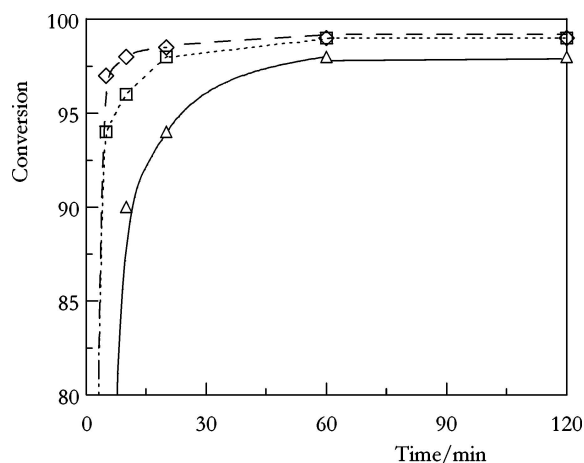

Figure 5 Conversion versus time for 40:60 AM:Q9 comonomer composition with different monomer concentrations (△) 25%, (□) 35% and (◇) 40%.

tion. The reaction order with respect to monomer was found to vary from 1 [7, 10] to 1.7 [8, 9]. Therefore, in emulsion polymerization the influence of monomer concentration in polymerization rate is very important and it is interesting to take a formulation with high monomer concentration for the production of copolymer with flocculant applications. Respect to the final conversion, it doesn't depend on the comonomer composition. Fig. 6 shows the final conversion for different monomer concentration with 40:60 and 20:80 AM:Q9 monomer compositions. This behaviour was clear in Fig. 3 for formulations with 3,000 and 5,000 ppm.

Beginning with the copolymer characterization, in Table II were collected the viscosities of copolymer solutions for different initiator concentrations and the viscosities of commercial copolymer solutions.

TABLE II Viscosities of copolymer solution (0.5%) for different initiator concentrations and copolymer composition

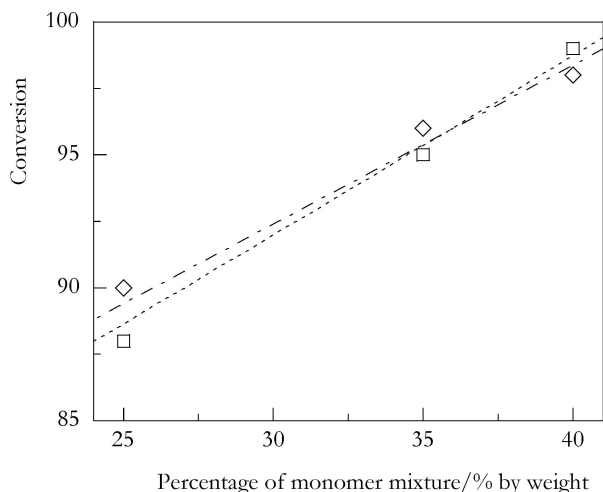| Copolymer composition		Viscosity/Pa.s		
AM	Q9	3,000 ppm	5,000 ppm	Commercial copolymers
20	80	$17 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	$17 \cdot 10^{-3}$
40	60	$28 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$16 \cdot 10^{-3}$
60	40	$21 \cdot 10^{-3}$	$24 \cdot 10^{-3}$	$29 \cdot 10^{-3}$
80	20	$24 \cdot 10^{-3}$	$12 \cdot 10^{-3}$	$25 \cdot 10^{-3}$
100	0	$15 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	–

Figure 6 The final conversion versus monomer concentration for 20:80 (◇) AM:Q9 monomer composition.
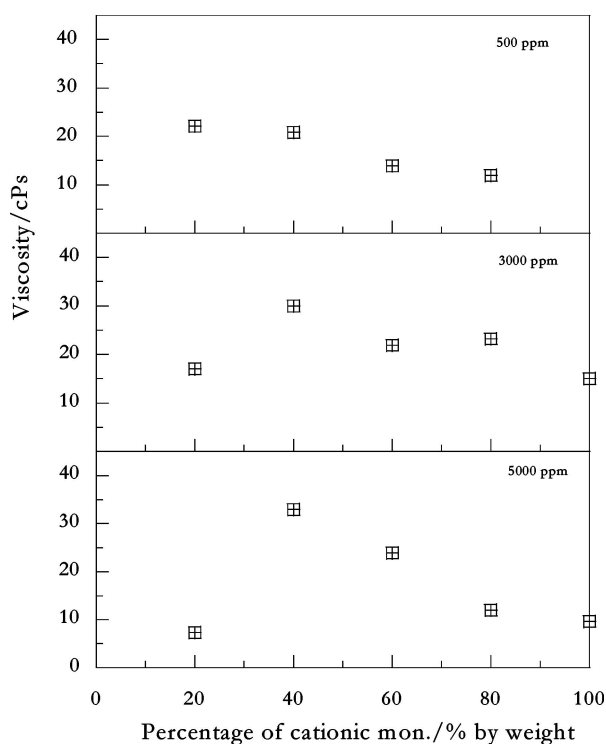

Figure 7 Viscosity as function of cationic comonomer percentage for different initiator concentration.
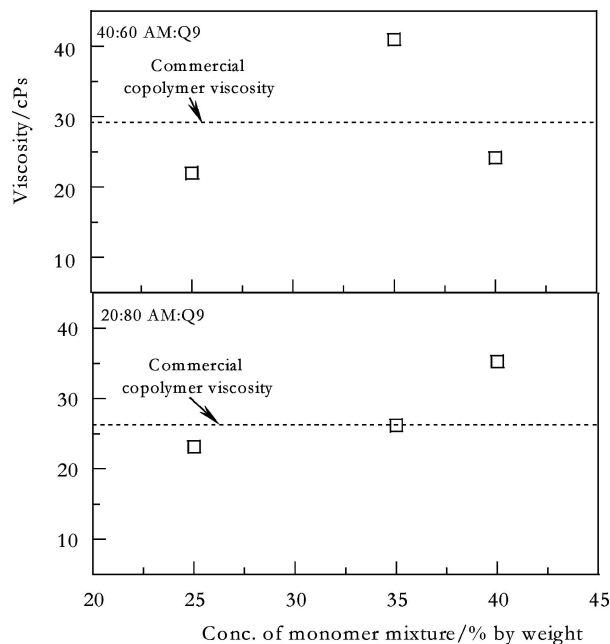

Figure 8 Viscosity as function of monomer concentration for 40:60 and 20:80 AM:Q9 comonomer composition.

Formulation with higher initiator concentration showed lower viscosities. The values of commercial copolymer solutions were similar to the synthesised copolymer solutions using 3,000 ppm initiator concentration. On the other hand, Fig. 7 shows the viscosities as a function of cationic monomer percentage for different initiator concentration. The viscosity decreases while increasing the cationic comonomer concentration after 40% of cationic monomer. This behaviour is similar for all initiator concentrations.

Completing the characterization of copolymers, Fig. 8 shows the viscosities as a function of monomer concentration for 40:60 and 20:80 AM:Q9 comonomer compositions. It can be seen for 20:80 AM:Q9 composition that the viscosity value increases as the monomer concentration increases. However, the increase in the monomer concentration causes an increase in the polymerization heat and gelation, which does not make the polymerization scatter and disappear easily. This causes a rise in the system temperature, which makes the polymerization rate increase sharply. This behaviour was observed in other similar systems [12].

4. Conclusions

Specific features of the inverse emulsion copolymerization of acrylamide with dimethylaminoethylacrylate-methyl chloride using Span 80 as a surfactant with redox initiator have been studied.

The HPLC method has been an interesting way to know rapidly the conversion of each monomer with high reproductibility. The minimum concentration of dibutilamine for peak separation was 0.02 M. The reactivity of cationic comonomer was higher at all initiator concentrations and at different composition of comonomer mixture. This finding can be explained in terms of the monomer partitioning between the aqueous

and the continuous phases. The rate of polymerization increased with the initiator concentration. In inverse emulsion, when water-soluble initiators are used the reaction proceeds within the monomer droplets and the process is essentially a suspension polymerization. The kinetics resemble those for solution polymerization. The kinetics with 3000 and 5,000 ppm were very similar but with 500 ppm the kinetics were lower. The influence of comonomer composition was fairly insensitive to the comonomer composition, for 5,000 and 3,000 ppm. When the initiator concentration was 500 ppm the conversion was very sensitive to the comonomer composition. The conversion increased when the monomer concentration increased. This aspect is very interesting to produce copolymers with flocculants properties in inverse emulsion. With higher polymer concentration the emulsion is more economic because in the same volume the emulsion presents more polymer.

The viscosity decreases with the initiator concentration and the cationic comonomer percentage increases in the formulations as monomer concentration increases.

Acknowledgements

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