Polymer Vol. 38 No. 2, pp. 449–458, 1997
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0032-3861/97/$17.00+0.00

S0032-3861(96)00511-3

Inverse-emulsion copolymerization of acrylamide and quaternary ammonium cationic monomers with block copolymeric surfactants: copolymer composition control using batch and semi-batch techniques

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(Received 25 January 1996)

An experimental investigation of the inverse-emulsion copolymerization of acrylamide and quaternary ammonium cationic monomers (dimethylaminoethylacrylate, DMAEA and dimethylaminoethylmethacrylate, DMAEM) has been carried out using both a block copolymeric surfactant (HB246) whose hydrophilic moiety is polyethylene oxide and whose hydrophobic moiety is poly(12 hydroxy stearic acid) and sorbitan monoleate (SMO). Our results indicate that the choice of surfactant influences strongly the quality of the copolymers produced. For example, more uniform copolymers of acrylamide and DMAEA can be synthesized using the block copolymeric surfactant (HB246) at faster production rates in comparison with sorbitan monoleate (SMO) when utilizing batch reactors. However, a composition drift is observed in the inverse-emulsion copolymerization of acrylamide and DMAEM using HB246. A possible explanation for this behaviour is either a reduced reactivity ratio (r_2) or propagation constant (k_{22}). However, physical effects such as a possible lower interfacial acrylamide concentration are not to be ruled out. It is also shown, for the first time, that copolymers of acrylamide and DMAEM of more uniform composition can be produced by implementing simple semi-batch policies with non time-varying feedrates. It is believed that these cationic copolymers would have a higher flocculation efficiency both in municipal and in industrial water treatment due to their more uniform distribution of the positive charge along the polyacrylamide backbone. Copyright © 1996 Elsevier Science Ltd.

(Keywords: acrylamide; batch and semi-batch polymerizations; block copolymeric surfactant; h.p.l.c.; inverse-emulsion; sorbitan monooleate; quarternary ammonium monomers)

INTRODUCTION

Acrylamide based polymers are part of a multibillion-dollar water soluble industry which has projected average annual rate growth rates of 5–8%[1]. Generally, these polymers are classified into nonionic, anionic and cationic species according to the nature of their covalently bound ionic groups. Cationic homopolymers and acrylamide based copolymers are applied for fines retention in paper making, as flocculants and biocides in water treatment, as stabilizers for emulsion polymerization, in cosmetics and pharmaceuticals, and in general wherever aqueous solid-liquid separations are required.

Homopolymers obtained from cationic quaternary ammonium monomers derived from acrylic and methacrylic acid as well as their copolymers with acrylamide have attained significant commercial importance because of their supermolecular polyelectrolyte structure[2]. These are applied as nontoxic flocculants and are more efficient than either of the respective nonionic and cationic homopolymers[3]. They also offer advantages over inorganic flocculants such as alum, including smaller dosage requirements, less floc generation and a reduction of the ash produced during incineration.

Acrylamide based copolymers of high molecular weight can be obtained by solution polymerization in aqueous media. However, solution polymerization is limited to relatively low monomer concentrations because of the high viscosity of the final copolymer solution. These difficulties are overcome using heterophase water-in-oil (inverse-emulsion) polymerizations[4]. This process involves the dispersion of an aqueous monomer(s) solution in an aliphatic continuous phase. Nonionic steric stabilizers are blended to achieve an overall HLB (hydrophilic–liphophilic balance) of between 4 and 9 in order to prevent particle coalescence. The polymerizations take place in batch reactors under inert atmospheres using chemical initiators. Temperatures in the range between 25–55°C are employed with continuous vigorous agitation. Often temperature profiles which increase with conversion are utilized.

There has been considerable progress in the field of inverse-emulsion polymerization since the pioneering work of Vanderhoff[4]. Significant efforts were dedicated

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*To whom correspondence should be addressed. Present address: Department of Chemistry (IGC-1), Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland toward the elucidation of the mechanism, kinetics and reactor modelling of the inverse-emulsion homo- and copolymerization processes during the 1980s. The first general mechanism for any type of inverse-macroemulsion polymerization was proposed in 1987 by Hunkeler[5]. This was subsequently expanded and developed into a kinetic model for homopolymers of acrylamide[6] and copolymers of acrylamide and quaternary ammonium cationic monomers[7]. However, for the case of cationic copolymers, these kinetic models are limited by the availability of good values of reactivity ratios for the monomers involved. Reactivity ratios for any monomer pair are generally obtained by solution copolymerization at low conversions and dilute concentrations. However, different values of reactivity ratios for water soluble monomer pairs have been reported for the same system[8–11]. Furthermore, notable differences have also been observed between the reactivity ratios obtained by solution and water-in-oil heterophase polymerization processes[8,12,13]. It is now believed that the reactivity ratios are complex functions of monomer concentration, pH, the ionic strength of the reaction mixture and the extent of the reaction[8,11]. Moreover, the studies of the inverse-emulsion copolymerization of acrylamide and cationic monomers have been limited to the use of only sorbitan esters of fatty acids as stabilizers which impart very poor stability to the final latex. The studies comparing nonionic stabilizers on the inverse-emulsion copolymerization of acrylamide and cationic monomers are nonexistent. In addition, the use of semi-batch inverse-emulsion copolymerization processes to produce uniform water soluble copolymers is confined only to the patent literature.

This paper reports a comparison of the inverse-emulsion copolymerization of acrylamide and quaternary ammonium dimethylaminoethyl methacrylate (DMAEM) and dimethylaminoethyl acrylate (DMAEA) using either a block copolymeric surfactant [based on polyethylene oxide and poly(12-hydroxystearic acid)] or sorbitan monooleate and a series of semi-batch inverse-emulsion copolymerization studies with acrylamide and DMAEM. Our objective is to synthesize copolymers with more uniform microstructures. It is believed that more homogeneous copolymers with respect to charge density would perform better in applications such as municipal and industrial water treatment.

EXPERIMENTAL

Materials

White crystals of acrylamide (Cytec Industries Inc., Charlotte, NC) were purified by recrystallization with Certified ACS-grade chloroform (Fisher Scientific, Norcross, GA), dried in vacuum to constant weight and stored in silica gel desiccators.

Dimethylaminoethyl acrylate (DMAEA) and dimethylamintoethyl methacrylate (DMAEM) both quaternized with methyl chloride were obtained from CPS Chemicals (West Memphis, AR) as aqueous solutions (75 wt% for DMAEM and 80 wt% for DMAEA) inhibited with approximately 600 ppm of hydroquinone monomethylether. The faster reacting DMAEM was also stabilized with 10 ppm of cupric ions to chelate the monomers. The quaternized cationic monomers were purified by repeated extraction with acetone. This procedure removed simultaneously water, cupric ions and hydroquinone monomethylether as well as precipitating the monomer[14]. Following several vigorous extractions (five were required for DMAEM while six were needed for DMAEA), the quaternary ammonium monomer precipitated out as a powder. It was then dried in a vacuum oven at room temperature and stored at 5°C in a freezer.

Isopar-M (Exxon, supplied by ChemCentral, Nashville, TN), a narrow cut of an isoparafinic mixture, was chosen as the continuous phase. Hypermer B246 (a linear block copolymer of polyester-polyethylene oxide-polyester prepared by reacting condensed 12-hydroxystearic acid with polyethylene oxide) and peroxide free-sorbitan monooleate (G-946), gifts from ICI Americas (Willmington, DE), were used as nonionic stabilizers. The HB246, while it contains aromatic impurities, was found to have no radical generating species as evidenced by a lack of any polymerization reaction in the absence of chemical initiators. Sorbitan monoleate was purified by repeated washing with acetone to remove any soluble impurities. It was then kept under vacuum at 50°C for 5 days to strip any other volatile components and decompose any species which could initiate the reaction. The oil phase mixture was prepared by heating the solid HB246 in Isopar-M under strong agitation prior to polymer synthesis.

Azobisisobutyronitrile (AIBN, Kodak, Rochester, NY) was used as an initiator and was purified by recrystallization with Certified-ACS methanol (Fisher Scientific, Norcross, GA), dried in vacuum and stored at 5°C in a freezer.

Certified ACS EDTA (ethylenediamine tetraacetic acid, disodium salt dihydrate) (Fisher Scientific, Norcross, GA) was used as a chelating agent in the copolymerizations with unpurified monomers.

The water used was Type 1 reagent grade water with a resistivity $\geq 18\,\mathrm{M\Omega}$-cm obtained through a series of deionization and organic scavenger cartridges (Continental Water Systems Corporation, San Antonio, TX).

Polymer synthesis

All copolymers were synthesized by inverse-emulsion polymerization using a 5-litre stainless steel reactor equipped with an external heating/cooling jacket. The reactor was computer controlled using an error-squared PID (proportional-integral-derivative) controller to within ±0.5°C throughout the reaction by varying the chilled water-to-steam ratio entering the cooling jacket. The reactor was sparged continually with purified 99.99% nitrogen (AL Compressed Gas, Nashville, TN) to remove any residual oxygen which could consume radicals and interfere with the polymerization. The initiator, in solution with Certified ACS acetone (Fisher Scientific, Norcross, GA) was injected through a septum cap placed at the top of the reactor to start the polymerization. Samples were withdrawn periodically at fixed time intervals by means of a bottom flush valve. The semi-batch polymerization reactions were performed adding initially 50 wt% of the aqueous phase and 100 wt% of the continuous organic phase into the reactor and feeding the remainder of the aqueous phase continuously using a B-100-S Eldex metering pump immediately after the injection of the initiator. The aqueous phase was pumped from a quick-opening 1-litre stainless steel reservoir equipped with a dip tube to sparge nitrogen and several openings in the top plate. The aqueous phase in this reservoir was sparged with nitrogen for 30 min prior to feeding the reactor and then fed continuously at a rate up to 3.0 ml min^{-1} using pure acrylamide and mixtures of acrylamide/DMAEM of several molar ratios. Details of the polymerization procedure are reported elsewhere[15].

Determination of monomer and polymer composition

Conversion and polymer compositions were inferred from h.p.l.c. measurements[16]. The h.p.l.c. system consisted of a Hitachi L6000 isocratic pump (Hitachi Instruments, Tokyo, Japan), a Hitachi L4000H variable wavelength u.v. detector operating at 214 nm, and a Rheodyne 7725i injector (Cotati, CA). The mobile phase consisted of acetonitrile–water (50/50 vol%) with 0.01 M dibutylamine (Kodak, Rochester, NY) adjusted to a pH of 3.0 with phosphoric acid (85 wt%, Fisher Scientific, Norcross, GA). The dibutylamine was used to suppress undesired interactions of the cationic monomer with the sorbent surface and thereby influence the retention volume and peak separation. For all analyses the mobile phase flow rate was kept at 2.0 ml min^{-1}. A stainless steel filter and a CN precolumn (Waters, Millford, MA) were connected in-line between the pump and the column. The column used was a CN column housed in a Waters Radial RCM housing, operating at a nominal pressure of 180 kg cm^{-2}. The CN column had an 8 mm ID and was packed with 10 μm particles (mean pore size 125 Å), with a 6% carbon load bonded to a μ-porasil (silica) substrate. Chromatograms were collected on a 486 computer running Viscotek GPC PRO Version 4.01 software (Houston, Texas). Residual monomer concentrations were determined following the following procedure: a small sample of the inverse-latex was weighed (nominally 0.0200 g) in an analytical balance to four decimal places in a pre-sterilized 20 ml glass scintillation vial. Ten ml of Certified-ACS acetonitrile (Fisher Scientific, Norcross, GA) were then added to the vial and the contents were agitated vigorously for at least 6 h with a magnetic stirrer. The precipitated copolymer was separated from the supernatant liquid by centrifugation at 2000 rpm using an IEC centrifuge or filtration with a 0.45 μm nylon membrane filter (Scientific Resources, Inc., North Brunswick, NJ). A 100 μl aliquot was removed with a glass syringe (Hamilton Co., Reno, NV) and injected into the h.p.l.c. system. Although the injection solvent was pure acetonitrile and the mobile phase was an acetonitrile–water mixture, system peaks were not found to interfere with the chromatogram for either the acrylamide or the quaternary ammonium monomers. In all cases the reaction mixtures contained less than 100 ppm of acrylamide and 500 ppm of the quaternary ammonium monomers since these were the corresponding limits for Beer's law. Residual monomer concentrations were determined from calibration curves between 0 and 500 ppm for the DMAEA and DMAEM and 0 and 100 ppm for the acrylamide. These were prepared each day prior to analysis and duplicated at the end of the analysis. Samples from a given experiment were always analysed together within a 10 h period.

Partitioning studies

Partitioning studies were performed to determine the equilibrium partition coefficient of acrylamide, DMAEA and DMAEM between the aqueous and organic phases. The aqueous phase consisted of a nominal 0.5 mol l^{-1} monomer solution prepared with highly deionized water. The organic phase contained 0.13 wt% surfactant. Emulsions were prepared using an organic phase to aqueous phase ratio of 1/1 (volume). The emulsions were agitated vigorously for 6 h to ensure equilibrium. The phases were then decanted for periods of up to one week. The aqueous phase was carefully extracted from the bottom and filtered with a 0.2 μm nylon filter to remove all traces of surfactant. In all cases the aqueous phase was clear. The h.p.l.c. method described earlier in this paper was used to measure the amount of monomer solubilized by the organic phase.

Particle size

The determination of the average particle size was carried out by dynamic light scattering. The system consisted of a Lexel Argon-ion laser (2 W) operating at 15 mW and a Brookhaven BI-DS Goniometer (Brookhaven Instruments Corporation, Holtsville, NY). Data were acquired for up to 60 s with a 486 PC containing a Brookhaven BI9000 card. Diameters were then inferred using the Stokes–Einstein relationship from measurements of a mean diffusion coefficient. Measurements were performed at 25°C with disposable presterilized 20 ml glass stationary cells (Fisher Scientific, Norcross, GA). The inverse-emulsions were dispersed with filtered pure Isopar-K (Exxon, supplied by ChemCentral, Nashville, TN) to a volume fraction of 0.5 to 2% of the dispersed phase.

Experimental conditions

Inverse-emulsion copolymerizations of acrylamide with DMAEA or DMAEM were carried out isothermally over the temperature range of 45–50°C. The surfactant level was 4 wt% based on the total amount of emulsion. In order to reduce the heat generation rate, equal weights of aqueous and oil phases were used in the recipe. The specific experimental conditions for each batch polymerization are listed in *Table 1*. *Table 2* shows the conditions for each semi-batch polymerization.

RESULTS AND DISCUSSION

Batch reactor studies

Acrylamide–DMAEA system. The individual experimental values of conversion vs. time for the inverse-emulsion copolymerization of acrylamide and DMAEA at $f_{10} = 0.89$ and 50°C using sorbitan monoleate (SMO) and the block copolymeric surfactant (HB236) are shown in *Figures 1* and *2*, respectively. When SMO is employed, the DMAEA reacts faster than acrylamide. This behaviour contrasts significantly with what is observed when the block copolymeric surfactant is employed. In this case, the individual polymerization rates for each monomer are virtually equal in value over the whole range of conversion. The total copolymerization rate for these two polymerizations is shown in *Figure 3*. A constant initial copolymerization rate is observed until 50–60% conversion accompanied by a mild gel-effect. In addition, the total copolymerization rate with SMO is significantly lower than that obtained

Table 1 Experimental conditions for the batch inverse-emulsion copolymerization of acrylamide and cationic monomers[a]

Run	Acrylamide mass, g	Cationic monomer mass, g DMAEA	Cationic monomer mass, g DMAEM	Water mass, g	Isopar-M mass, g	Surfactant mass, g HB246	Surfactant mass, g SMO	AIBN mass, g	Temp. °C
1	262.5	87.5		350.0	644.0		56.0	0.50	50
2	262.5	87.5		350.0	644.0	56.0		0.50	50
3	210.0	140.0		350.0	644.0	56.0		0.25	45
4	262.5		94.9	342.6	644.0	56.0		0.50	50
5	262.5		126.5	311.0	644.0	56.0		0.50	50
6	262.5		94.9	342.6	644.0		56.0	0.50	50
7	262.5		126.5	311.0	644.0	28.0	28.0	0.50	50

[a] Other experimental conditions: (1) the agitation rate was 440 rpm in all runs; (2) runs 6 and 7 used unpurified monomers. 0.25 g of EDTA as a chelating agent was utilized in these runs

Table 2 Experimental conditions for the semi-batch inverse-emulsion copolymerization of acrylamide and DMAEM[a]

Run	AAM, g	DMAEA, g	Water, g	ISOPAR-M, g	HB246, g	Added f_{10}	Flow rate, ml min^{-1}
8	131.25	63.25	155.50	644.0	56.0	0.89	3.0
9	131.25	63.25	155.50	644.0	56.0	1.0	2.0
10	131.25	63.25	155.50	644.0	56.0	1.0	3.0

[a] Other experimental conditions: (1) the agitation rate was 440 rpm in all runs; (2) unpurified monomers were utilized with 0.25 g of EDTA; (3) 50 wt% of the aqueous phase was mixed with the total organic phase at the beginning of the polymerization

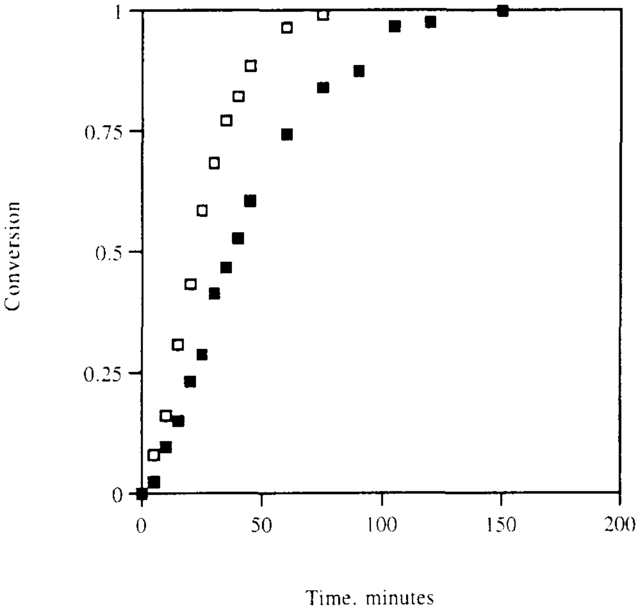

Figure 1 Individual conversion vs. time for an inverse-emulsion copolymerization of AAM (■)/DMAEA (□) at 50°C using SMO. Experimental conditions: [Monomer] = 5.92 mol/L_w, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{w/o}$ = 0.74

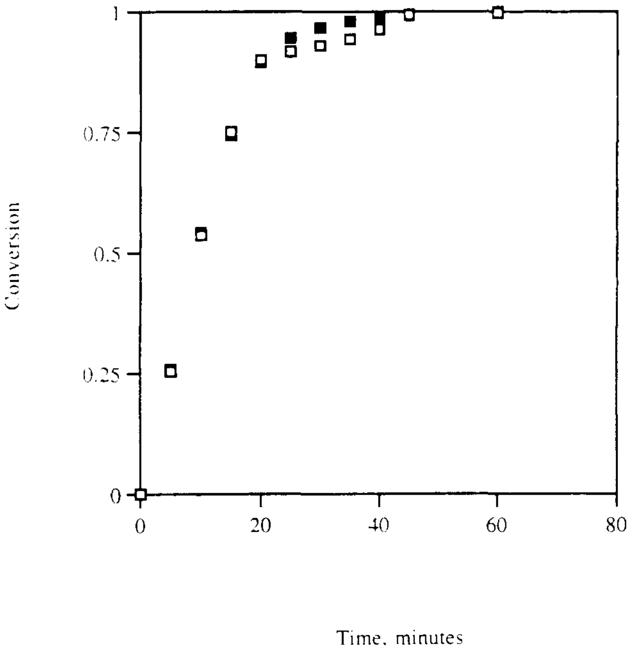

Figure 2 Conversion vs. time for an inverse-emulsion copolymerization of AAM (■)/DMAEA (□) at 50°C using HB246. Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74

with HB246, as it is found with a similar block copolymeric surfactant for the inverse-emulsion homopolymerization of acrylamide[17]. The low total copolymerization rate observed with SMO can be attributed to the transfer activity of sorbitan esters of fatty acids[6,7]. Sorbitan monoleate has an unsaturated carbon in the middle of its hydrophilic tail and five labile hydroxy functional groups on the hydrophilic moiety. These radically active functional groups can react with primary radicals in the continuous phase lowering the polymerization rate[6,7]. *Table 3* shows the results of our partitioning experiments. Clearly, the amount of acrylamide and DMAEA present in the organic phase is similar using the HB246 and SMO and the kinetic differences cannot be due to different comonomer oil phase concentrations when alternate surfactants are employed. Therefore, the high overall copolymerization rate observed with HB246 appears to be due to two factors: (1) the lack of unsaturation or reactive functional groups in

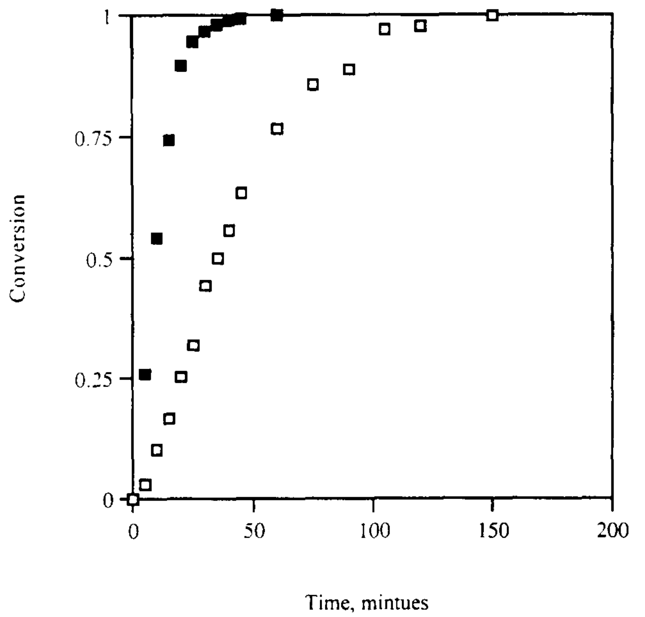

Figure 3 Total conversion vs. time for an AAM/DMAEA inverse-emulsion copolymerization at 50°C using HB246 (■) and SMO (□). Experimental conditions: $[\mathrm{M}] = 5.93\,\mathrm{mol}/L_\mathrm{W}$, $[\mathrm{AIBN}] = 3.22\,\mathrm{mmol}/L_0$, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{\mathrm{W/O}} = 0.74$

Table 3 Monomer partitioning between the aqueous and organic phases percent weight of monomer present in the organic phase

Monomer	HB246	SMO
Acrylamide	0.087	1.45
DMAEA	1.82	2.62
DMEAM	0.6	2.60

the molecule of HB246; and (2) the presence of xylene in the HB246 ($\approx 5\%$ by weight)[18] which may enhance the solubilization of AIBN in the interfacial layer[17]. A higher interfacial AIBN concentration would increase the initiator efficiency since the initiator molecules are partly located in the emulsifier sheath. The initiator heterophase diffusion (from the oil to the aqueous phase), which normally scavenges radicals due to organically soluble impurities, is, therefore, eliminated. This causes an increase in both the initiation and copolymerization rates[17].

The monomer composition drift vs. total conversion for the inverse-emulsion copolymerization of acrylamide and DMAEA ($f_{10} = 0.89$ and 50°C) is shown in *Figure 4* for the respective reactions with SMO and HB246. Severe compositional heterogeneities are observed with SMO, even at low conversions, despite the reported similarities in the reactivity ratios for these monomers[7]. This drift in monomer composition with conversion has been previously reported for the same system in inverse-emulsion and is also typical for the solution copolymerization of this monomer pair[7]. However, in the case of the block copolymeric surfactant, very homogeneous and uniform copolymers can be produced up to 90% total conversion for moderate charge density copolymers ($f_{10} = 0.89$) and 50°C. Relatively uniform copolymers are also obtained for the inverse-emulsion copolymerization of AAM and DMAEA for higher charge density copolymers ($f_{10} = 0.75$) and 45°C as indicated in *Figure 5*.

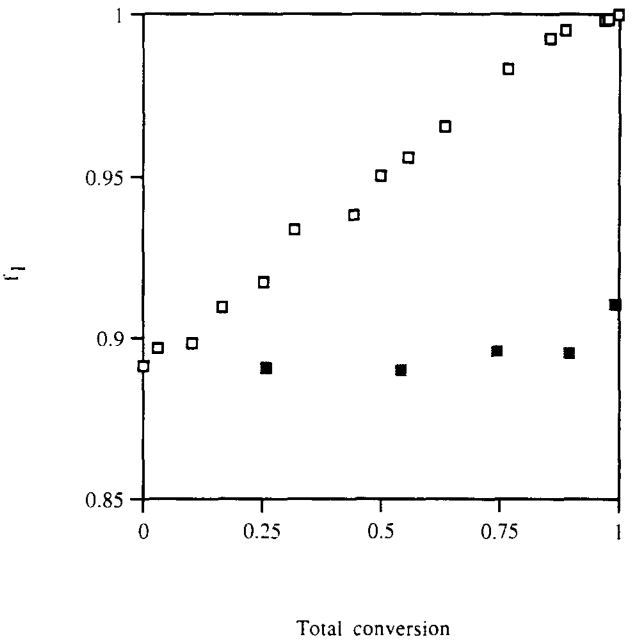

Figure 4 Composition drift for the AAM/DMAEA inverse-emulsion copolymerization at 50°C using SMO (□) and HB246 (■). Experimental conditions: $[\mathrm{Monomer}] = 5.92\,\mathrm{mol}/L_\mathrm{W}$, $[\mathrm{AIBN}] = 3.22\,\mathrm{mmol}/L_0$, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{\mathrm{W/O}} = 0.74$

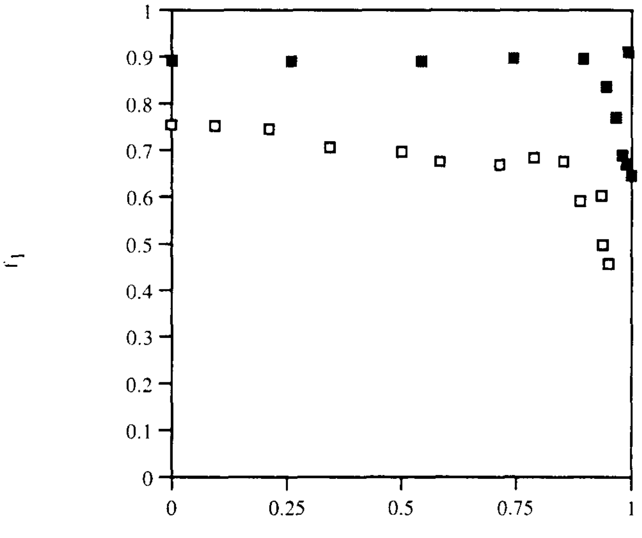

Figure 5 Composition drift for the AAM/DMAEA inverse-emulsion copolymerization at 45°C HB246 at two initial monomer compositions ($f_{10} = 0.89$ (■) and 0.75 (□). Experimental conditions: $[\mathrm{Monomer}] = 5.92\,\mathrm{mol}/L_\mathrm{W}$, $[\mathrm{AIBN}] = 3.22\,\mathrm{mmol}/L_0$, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{\mathrm{W/O}} = 0.74$

Deviations from the solution copolymerization behaviour have been reported for monomer systems other than acrylamide–DMAEA using water-in-oil heterophase copolymerizations such as the inverse-emulsion polymerization of acrylamide–DMAEM[8], the inverse-microemulsion polymerization of acrylamide and acrylic acid[9] and the inverse-microemulsion copolymerization of sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS) and 2-methacrylooxyethyltrimethylammonium chloride (MADQUAT)[13]. Our deviations from the solution copolymerization behaviour for two systems (acrylamide–DMAEA and acrylamide–DMAEM) can be correlated in terms of a reduced reactivity ratio (r_2) or a reduced propagation constant (k_{22}) for the cationic monomer in the presence of an organic phase. By combining these observations with those of a prior investigation[8], we may write

$$r_{1,\mathrm{Solution}} \approx r_{1,\mathrm{Inv-Emul}}$$

$$k_{11,\mathrm{Solution}} \approx k_{11,\mathrm{Inv-Emul}}$$

$$r_{2,\mathrm{Solution}} > r_{2,\mathrm{Inv-Emul,SMO}} > r_{2,\mathrm{Inv-Emul,HB246}}$$

$$k_{22,\mathrm{Solution}} > k_{22,\mathrm{Inv-Emul,SMO}} > k_{22,\mathrm{Inv-Emul,H_B246}}$$

These results seem to imply that the reaction between a charged monomer and a charged macroradical is the most sensitive of the four propagation steps to the presence of either organic phase or emulsifier. This seems reasonable since such a reaction would be influenced by the properties of the reacting medium including the dielectric constant, which are very sensitive to trace impurity levels. The elucidation of the effect of the emulsifier on the copolymerization kinetics warrants further investigation.

Acrylamide–DMAEM system. The individual experimental values of conversion vs. time for the inverse-emulsion copolymerization of acrylamide and DMAEM ($f_{10} = 0.89$ and 50°C) using SMO and HB246 are reported in *Figures 6* and *7*, respectively. The shape of the curves is as expected with linear polymerization rates observed until 50–60% and a gel effect which is more apparent for the case of the individual polymerization rate of acrylamide using SMO (*Figure 6*). Again, when SMO is employed, the DMAEM monomer reacts faster than acrylamide as one can expect from the reactivity ratios[7]. However, when the HB246 is used, the individual polymerization rates for each monomer are similar in value up to 45% total conversion. After this point, the acrylamide reacts faster than the DMAEM. The total copolymerization rate for the acrylamide–DMAEM system is reported in *Figure 8*. The total copolymerization rate is higher when the HB246 is utilized in comparison to SMO giving further indication of a purely physical role played by the block copolymeric surfactant as postulated earlier.

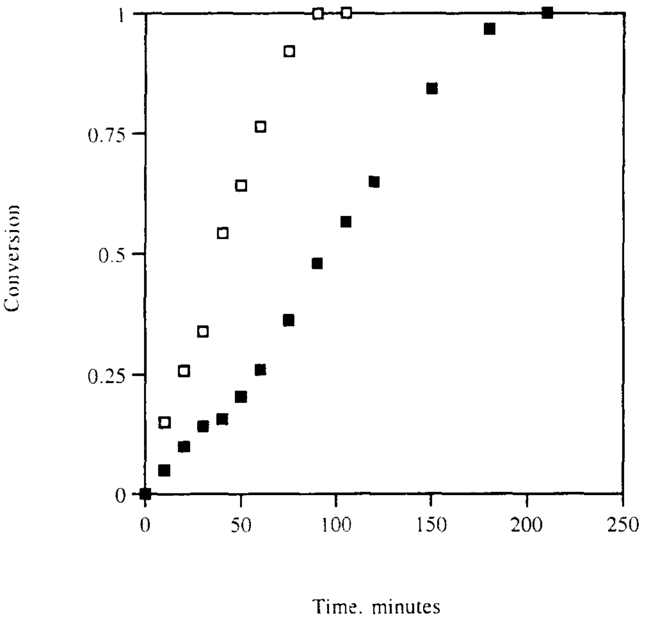

Figure 6 Individual conversion vs. time for an inverse-emulsion copolymerization of AAM (■)/DMAEM (□) at 50°C using SMO. Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_O, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{W/O} = 0.74$

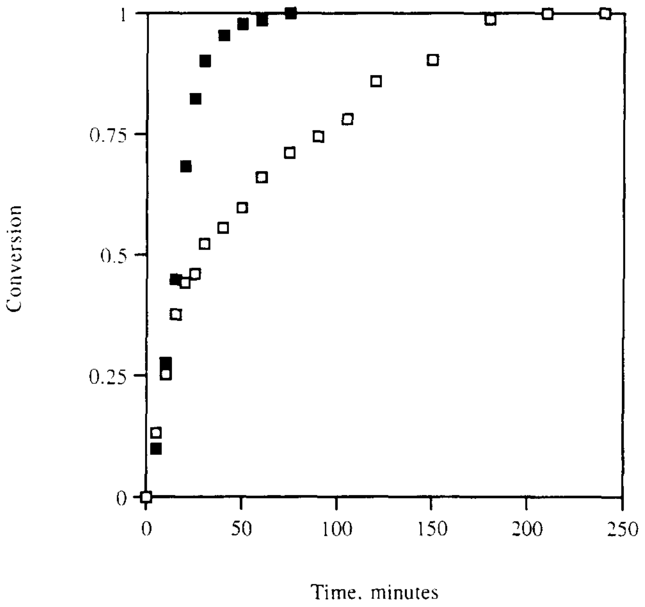

Figure 7 Individual conversion vs. time for an inverse-emulsion copolymerization of AAM (■)/DMAEM (□) at 50°C using HB246. Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_O, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{W/O} = 0.74$

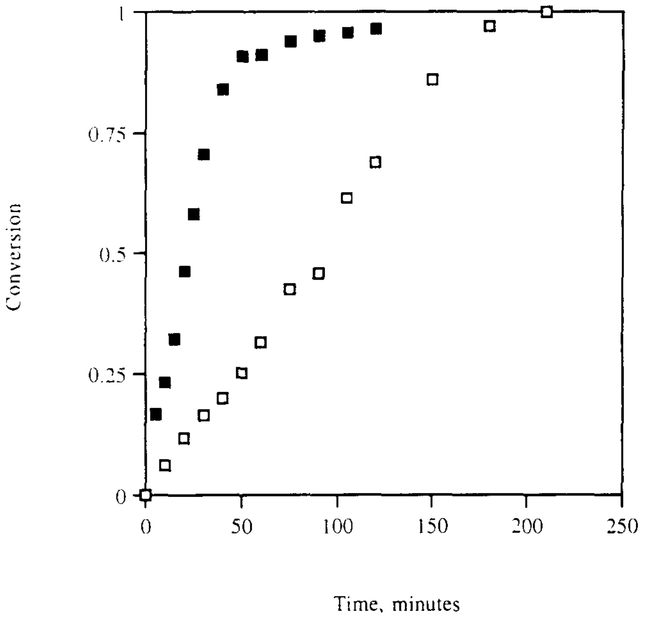

Figure 8 Total conversion vs. time for an AAM/DMAEM inverse-emulsion copolymerization at 50°C using HB246 (■) and SMO (□). Experimental conditions: [M] = 5.93 mol/L_W, [AIBN] = 3.22 mmol/L_O, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{W/O} = 0.74$

Figure 9 shows the average copolymer composition ($\bar{F}_1$) and the comonomer composition drift vs. total

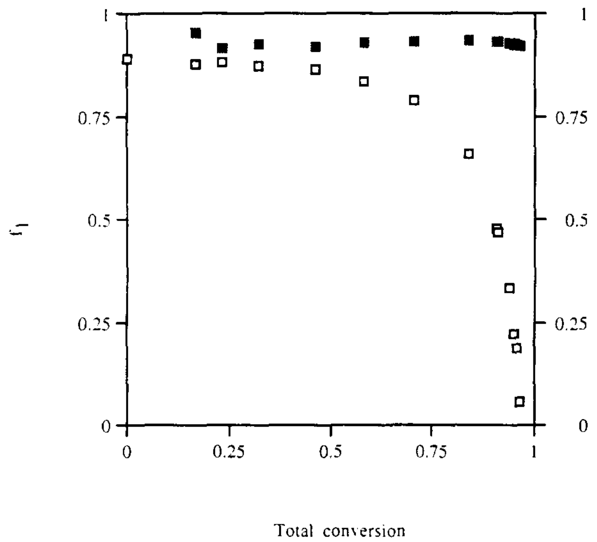

Figure 9 Composition drift (□) and average copolymer composition ($\bar{F}_1$) (■) as a function of conversion for the AAM/DMAEM inverse-emulsion copolymerization at 50°C using the copolymeric surfactant (HB246). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74

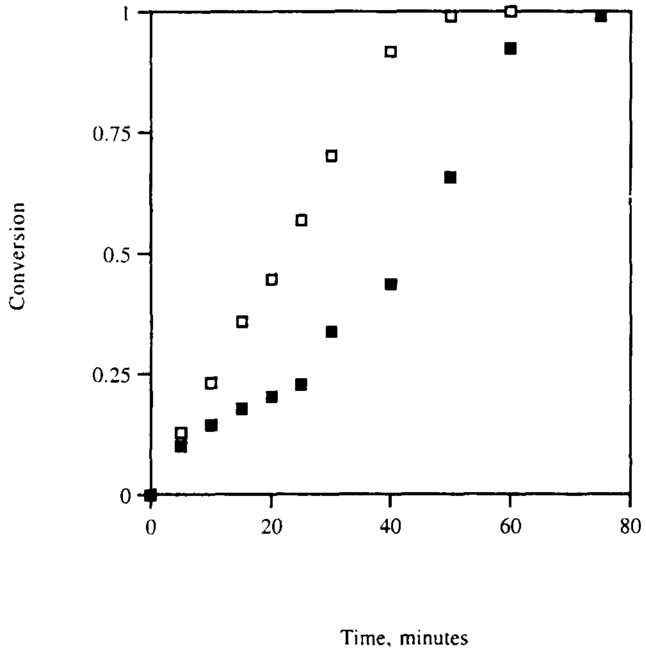

Figure 10 Individual conversion vs. time for an inverse-emulsion copolymerization of AAM (■)/DMAEM (□) at 50°C using a blend of HB246 and SMO (50/50 wt%). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74

conversion for this system at f_{10} = 0.89 and 50°C using the block copolymeric surfactant. Clearly, compositional heterogeneities are observed after intermediate conversions yielding a blocky distribution of nonionic groups along the polymer backbone. This trend in the experimental data is opposite to what is observed when acrylamide/DMAEM are copolymerized in solution[7]. This deviation from the solution copolymerization behaviour for the acrylamide–DMAEM system can be again explained in terms of a lower reactivity ratio (r_2) or a reduced propagation constant (k_{22}) for the quaternary ammonium monomer in the presence of an organic medium, as was also the case for the more hydrophilic DMAEA.

Figure 10 reports the individual values of conversion vs. time behaviour for the inverse-emulsion copolymerization of acrylamide and DMAEM using a blend of SMO and HB246 (50/50 wt%) at f_{10} = 0.89 and 50°C. Based on the preceding results* one might expect the acrylamide and DMAEM to have similar reactivities in a blend of SMO and HB246. Furthermore, it is a common industrial practice to use blends of two or more nonionic stabilizers in the inverse-emulsion homo- and copolymerization of acrylamide based polymers and copolymers to reduce costs and/or improve the stability of the final latex[20–26]. Surprisingly, DMAEM reacts faster than acrylamide in a SMO/HB246 blend. In addition, a very strong gel effect is observed for the individual polymerization rate of acrylamide. This behaviour is similar to the one observed when only SMO is employed in the inverse-emulsion copolymerization of these two monomers, reported in *Figure 6*, indicating a negligible kinetic role effect of the block copolymeric surfactant when blended with SMO.

Based on the preceding discussion, it is also possible that the copolymer composition behaviour observed in inverse-emulsion copolymerization can be explained in terms of arrangements at the interface. It was reported in a previous investigation that sorbitan monoleate produces a more rigid or tightly packed interfacial film compared to the block copolymeric surfactant. It has also been shown that acrylamide acts as a co-surfactant in emulsifier systems which include fatty acid esters of sorbitan and polyoxyethylene derivatives of these fatty

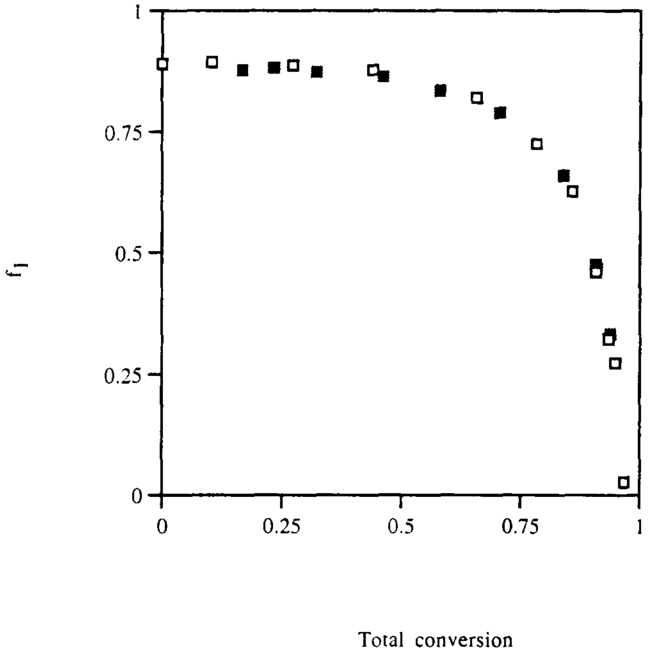

Figure 11 Composition drift as a function of total conversion for the inverse-emulsion copolymerization AAM/DMAEM at 50°C using the copolymeric surfactant (HB246), purified monomers (■) and unpurified monomers (□). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74

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* DMAEM is the faster reacting monomer in SMO inverse-emulsions and the slower reacting when HB246 is utilized

acid esters[27]. These surfactants are very similar in their composition to HB246, and it is therefore a reasonable assumption that acrylamide also will have a high surface activity with the triblock copolymeric HB246. This would explain the lower individual polymerization rates of acrylamide observed when only SMO is used as a surfactant since acrylamide would be excluded from the reactive interface relative to HB246. When blends of SMO and HB246 are utilized, SMO seems to be more efficient in covering the interface than HB246 and apparently displaces the bulkier HB246 to the continuous oil phase. Therefore, the concentration of interfacial acrylamide is lower, reducing the individual polymerization rate of acrylamide.

Figure 11 reports a comparison of the monomer composition drift vs. total conversion for purified and unpurified acrylamide and DMAEM at $f_{10} = 0.89$ and 50°C. The monomer composition drift curves for both systems overlaid demonstrating that the effect of impurities is negligible and that the repeatability of the polymer synthesis is excellent.

Semi-batch reactor studies

The compositional heterogeneities observed in the inverse-emulsion copolymerization of acrylamide and DMAEM can be circumvented with semi-batch feed strategies. There are many semi-batch feed policies that have been developed to maintain a constant copolymer composition during polymerization[19]. For example, all the slower reacting monomer and some of the faster monomer can be added to the reactor at time zero to provide the desired monomer ratio (N_{10}/N_{20}) and polymer composition. The faster monomer can then be fed to the reactor at a feed rate which maintain N_1/N_2 constant. In order to maintain a constant polymer composition, this feed rate will vary with reaction time which presents logistical problems in large-scale production. Another feed policy is to maintain $[M_1]$ and $[M_2]$ constant during the polymerization. Under 'monomer starved' conditions, the composition of the polymer produced is the same as the composition of the monomers being fed. Using this feed policy, the monomers can be premixed and fed at any convenient rate including, a time-invariant one. The feed rate would be based on the ability to remove heat from the reactor. That is to say, the maximum feed flow rate is governed by the reactor cooling capacity. In this paper, the later feed policy was used to control copolymer composition due to its simplicity and therefore greater probability of application.

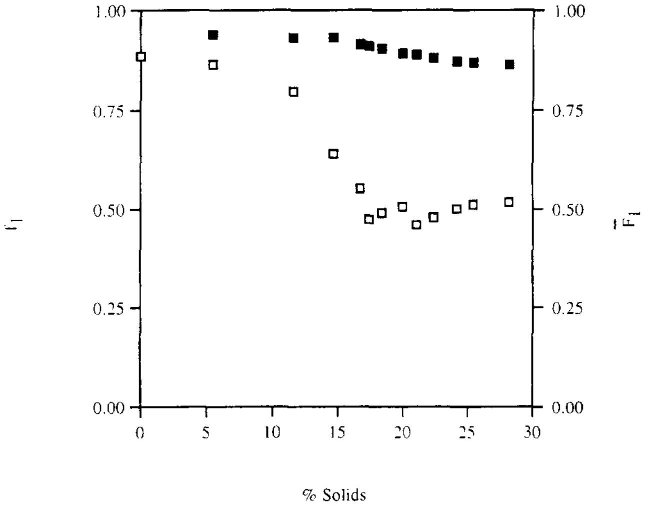

Figure 12 Composition drift (□) and average copolymer composition ($\bar{F}_1$) (■) as a function of % solids for the semi-batch inverse-emulsion copolymerization AAM/DMAEM at 50°C using the copolymeric surfactant (HB246). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 3.22 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), $f_{10} = 0.89$ and $\Phi_{W/O} = 0.74$. Fifty wt% of the monomer was added initially. Monomers at $f_{10} = 0.89$ and 3.0 mL min^{-1} were added continuously

Figure 12 shows the composition drift and the average copolymer composition ($\bar{F}_1$) as a function of the percent solids for a semi-batch inverse-emulsion copolymerization of acrylamide and DMAEM at 50°C and 3.2 mmol/L_0. Initially, 50 wt% of the aqueous phase with a molar composition of acrylamide ($f_{10} = 0.89$) was mixed with the total continuous phase. The remainder of the aqueous phase (of the same composition) was added continuously at a rate of 3.0 mL min^{-1}. Clearly, a composition drift is observed which then levels off. Nevertheless, the compositional heterogeneity is less than the observed for batch polymerizations (*Figure 9*). It is obvious that the acrylamide was consumed at a much faster rate than was supplied resulting in the composition drift at intermediate stages of the copolymerization.

The composition drift and the average copolymer composition ($\bar{F}_1$) as a function of percent solids for a second semi-batch inverse-emulsion copolymerization of acrylamide and DMAEM at 50°C and [AIBN] = 1.92 mol/L_0 are shown in *Figure 13*. Again, 50 wt% of the aqueous phase of the desired acrylamide molar composition in the final copolymer ($f_{10} = 0.89$) was initially mixed with the total continuous phase. Subsequently, an aqueous solution of 50 wt% pure acrylamide ($f_{10} = 1.0$) was fed continuously at 2.0 mL min^{-1}. A more uniform product has been prepared in comparison with the batch product (*Figure 9*) with a mild composition drift at the beginning of the polymerization. The composition drift also seems to be corrected due to the addition of the faster monomer (acrylamide).

Figure 14 illustrates the composition drift and the average copolymer composition ($\bar{F}_1$) as a function of percent solids for a third semi-batch inverse-emulsion copolymerization of acrylamide and DMAEM at 50°C and [AIBN] = 1.92 mol/L_0. Fifty wt% of the aqueous phase of the desired acrylamide molar composition in the final copolymer ($f_{10} = 0.89$) was initially mixed with the total oil phase. Then, an aqueous solution of 50 wt% pure acrylamide ($f_{10} = 1.0$) was fed continuously at a rate of 3.0 mL min^{-1}. Obviously, a more uniform product has been prepared in comparison with the previous polymerizations (*Figures 12* and *13*) with a mild composition drift at the beginning of the polymerization which seems to be corrected due to the addition of acrylamide. The small dip in f_1 between 10 and 25% solids could be corrected using a time-varying feedrate, where the acrylamide flow is increased with time. However, this complication may not be warranted, since it would require on-line estimation of the reaction conversion or solids level. It is our preference to demonstrate the utility of a constant feed policy and a simplified technology.

These polymerizations are, to our knowledge, the first synthesis of relatively uniform copolymers of acrylamide–DMAEM using semi-batch feed policies. The

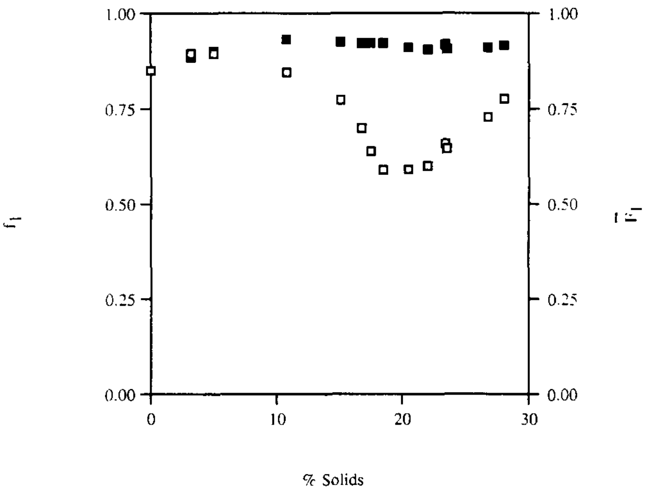

Figure 13 Composition drift (□) and average copolymer composition $(\bar{F}_1)$ (■) as a function of percent solids for the semi-batch inverse-emulsion copolymerization AAM/DMAEM at 50°C using the copolymeric surfactant (HB246). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 1.92 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74. Fifty wt% of the monomer was added initially. Monomers at f_{10} = 1.0 and 2.0 mL min^{-1} were added continuously

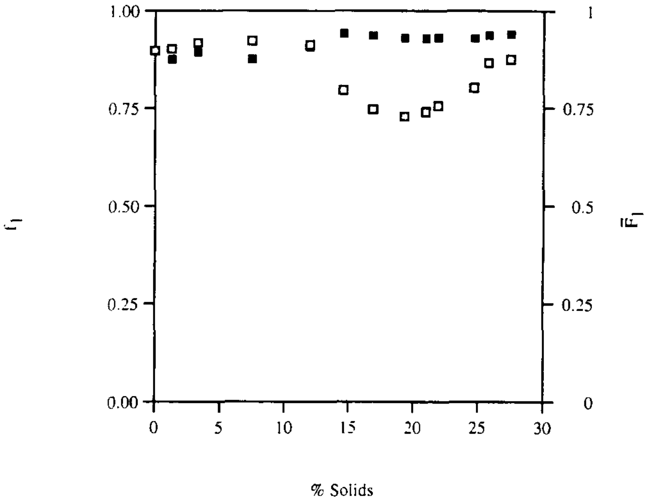

Figure 14 Composition drift (□) and average copolymer composition $(\bar{F}_1)$ (■) as a function of percent solids for the semi-batch inverse-emulsion copolymerization AAM/DMAEM at 50°C using the copolymeric surfactant (HB246). Experimental conditions: [Monomer] = 5.92 mol/L_W, [AIBN] = 1.92 mmol/L_0, 4 wt% surfactant (based on the total weight of emulsion), f_{10} = 0.89 and $\Phi_{W/O}$ = 0.74. Fifty wt% of the monomer was added initially. Monomers at f_{10} = 1.0 and 3.0 mL min^{-1} were added continuously

advantage of the block copolymeric surfactant is that it increases the reactivity of the more expensive DMAEM relative to acrylamide allowing for the production of more economical and more uniform copolymers of acrylamide–DMAEM in inverse-emulsion. It is expected that these copolymers would also be more efficient in flocculation processes both in waste water and in industrial water treatment due to their more uniform distribution of the positive charges along the polyacrylamide backbone.

CONCLUSIONS

The inverse-emulsion copolymerization of acrylamide and DMAEA using a block copolymeric surfactant based on polyethylene oxide and poly(12-hydroxystearic acid) allows for the formation of copolymers of very uniform composition using a batch reactor at higher production rates in comparison with sorbitan monoleate. However, composition drifts are observed in the inverse-emulsion copolymerization of acrylamide and DMAEM using these block copolymeric surfactants in a batch reactor. This is likely due to either a lower reactivity ratio (r_2) or propagation constant (k_{22}) in the presence of an organic phase. Physical factors such as a lower interfacial concentration of acrylamide may also be responsible for this behaviour.

Semi-batch techniques have been implemented using inverse-emulsion processes with a block copolymeric surfactant to circumvent the composition drift observed with an AAM/DMAEM system. A feed policy which maintains the molar concentration of both acrylamide and DMAEM in the reactor was used in this study. Acrylamide, the faster reacting monomer, was fed continuously with reaction time. These semi-batch feed policies are very attractive with this monomer pair system and the block copolymeric surfactant since the relative reactivity of DMAEM, the more expensive monomer, is also increased. Uniform water soluble copolymers of acrylamide and DMAEM can therefore, be synthesized using semi-batch policies with *non* time-varying feedrates.

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