S0032-3861(96)00506-X

Polymer Vol. 38 No. 2, pp. 437–447, 1997

0032-3861/97/$17.00 + 0.00

Inverse-emulsion polymerization of acrylamide using block copolymeric surfactants: mechanism, kinetics and modelling

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(Received 25 January 1996)

A comprehensive experimental investigation of the inverse-emulsion polymerization of acrylamide was carried out using an oil soluble initiator and a block copolymeric surfactant whose hydrophobic moiety is poly(12-hydroxystearic acid) and whose hydrophilic moiety is polyethylene oxide. It was found that the initial polymerization rate was first order with respect to molar monomer concentration, first order with respect to molar initiator concentration, and zeroth order with respect to molar emulsifier concentration. Based on these experimental findings, a mechanism was proposed which includes initiation, propagation, transfer to monomer and termination. The elementary reaction scheme also includes transfer to impurities which are found in the surfactant. The kinetic model developed from the proposed mechanism is found to be in good agreement with the experimental conversion and weight-average molecular weight data. Compared with sorbitan esters of fatty acids, the copolymeric surfactant provides higher polymerization rates and very high and linear molecular weights. These are comparable to those obtained by solution polymerization, however the total monomer level in the recipe can be substantially greater. Furthermore, stable inverse-laticies can be produced at emulsifier levels as low as 2 wt%. Copyright © 1996 Elsevier Science Ltd.

(Keywords: acrylamide; block copolymeric surfactant; inverse-emulsion; inverse-microsuspension polymerization; water soluble polymers)

INTRODUCTION

Polyacrylamide and acrylamide based copolymers are important synthetic water soluble polymers which are used as coagulants and flocculants in waste water and potable water treatment applications. They are also employed as pushing fluids in enhanced oil recovery, as drag reduction agents and drilling fluids, as additives in paper making, and as thickening agents. These water soluble polymers have a multi-billion dollar market value with projected annual sales growth rates (5–8%) exceeding those of most segments of the chemical and polymer industries[1,2].

Acrylamide has the largest $k_p/k_t^{1/2}$ of any commercial olefinic monomer, and the corresponding kinetics permit the synthesis of water soluble polymers with molecular weights exceeding 10 000 000 Daltons. The high enthalpy of polymerization for acrylamide ($\Delta H_p = 19.5\,\mathrm{kcal\,mol^{-1}}$) along with extreme solution viscosities generated by the high molecular weights leads to problems in large scale reactor operation including non-uniform mixing and heat transfer limitations. This renders the solution polymerization process unattractive. These difficulties are generally overcome by polymerizing the acrylic monomer(s) in a heterophase water-in-oil (w/o) polymerization process such as inverse-suspension (emulsion) polymerization[3]. In this process, an aqueous solution of the monomer(s) is emulsified under agitation in a continuous aliphatic oil phase. Steric stabilizers are employed and the polymerization is initiated using, in general, oil soluble initiators at temperatures in the range of 35–50°C. This process allows for polymerizations at high solid concentrations, low viscosities and with good temperature control.

The level of understanding of inverse-emulsion polymerization has continued to grow over the past 30 years. During the 1980s, efforts were dedicated to the elucidation of the reaction mechanism, kinetic measurements and reactor modelling of the inverse-emulsion polymerization processes. The kinetic behaviour of inverse-emulsion polymerization is complex and is specific to a given monomer-emulsifier-initator-continuous phase set. Unfortunately, all the kinetic studies have emphasized the use of sorbitan esters of fatty acids such as sorbitan monoleate which presents a degradative chain transfer reaction resulting in branched homopolymers and lower polymerization rates. In addition, the stability of the final emulsions is poor.

Industrially, these disadvantages seem to be overcome with the use of certain triblock polymeric (ABA) surfactants such as linear block copolymers of polyester–polyethylene oxide–polyester prepared by reacting condensed 12-hydroxystearic with polyethylene oxide[4] as is outlined in the US Patent 4,203,877. Steric stabilization using these polymers is achieved when the polyethylene oxide chain is anchored to the interface and the

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poly(12-hydroxystearic acid) end is free to move in the continuous phase. The stabilization is enhanced relative to the low molecular weight fatty acid ester derivatives due to the inherent advantages of triblock surfactants as well as the larger extended length of the poly(12-hydroxystearic acid), 115 Å, compared with 20–22 Å for C_{18} sorbitan esters[8]. There are few papers dealing with the use of these emulsifiers in inverse-emulsion polymerization and the information presented is rather qualitative and incomplete[8-10]. The objectives of this investigation are: (i) to carry out a comprehensive kinetic investigation of the inverse-emulsion polymerization of acrylamide using these block copolymeric surfactants; (ii) to extend the kinetic models available[11,12] using the experimental data obtained in part (i) to be able to predict conversion and molecular weight as a function of the reaction time; (iii) to characterize the final products obtained by inverse-emulsion polymerization using these block copolymeric surfactants and sorbitan monooleate.

EXPERIMENTAL

Materials

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

Isopar-M (Exxon, supplied by ChemCentral, Nashville, TN), a narrow cut of an isoparaffinic mixture, was chosen as the continuous phase. Hypermer B239 (a linear block copolymer of polyester–polyethylene oxide–polyester prepared by reacting condensed 12-hydroxystearic with polyethylene oxide) and peroxide-free sorbitan monooleate (G-946), gifts from ICI Americas (Wilmington, DE), were used as nonionic stabilizers. The HB239, 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 monooleate was purified by repeated washing with acetone to remove any soluble impurities. The surfactant 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 filtered using a 0.45 mm Metricel membrane filter (Fisher Scientific, Norcross, GA) prior to polymerization.

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

The water used was Type I reagent grade water with a resistivity of at least 18 cm obtained through a megohms/series of deionization and organic scavenger cartridges (Continental Water Systems Corporation, San Antonio, TX).

Polymer synthesis

Syntheses were performed in a 5 L stainless steel reactor equipped with an external heating/cooling jacket. The reactor was computer controlled using an error-squared proportional–integral–derivative (PID) 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 would 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. Further details of the polymerization procedure have been reported elsewhere[13].

Conversion

The determination of conversion of acrylamide monomer to polymer was carried out by following a novel phase-inversion micellar mobile phase method[14]. Briefly, this procedure begins with the inversion of the inverse-emulsion (water-in-oil) into a direct emulsion (oil-in-water) using Tergitol TMN-10 (Union Carbide Chemicals and Plastics Co., Inc., Danbury, CT) as an inverting surfactant and deionized water under strong agitation. The monomer is separated from the polymer by size exclusion chromatography (s.e.c.) using a micellar mobile phase. The high pressure liquid chromatography (h.p.l.c.) system consisted of a Rheodyne 7725i injector (Cotati, CA) and a Waters HPLC 510 pump (Waters, Millford, MA). A Shodex OHPAK SB-800P column (JM Science, Buffalo, NY) was used as the stationary phase with a 25×10^{-3} M sodium dodecyl sulfate (SDS) in highly deionized water as the mobile phase. An ultraviolet (u.v.) detector (Hitachi L-4000H, Tokyo, Japan), operating at a wavelength of 214 nm, was used to measure the monomer absorption. The peak heights were used to construct a calibration table and for the analysis of the unknown samples. Samples from a given experiment were always analysed together within a 10-h period. Chromatograms were collected on either a HP Vectra 286 or a 486 computer running Viscotek GPC PRO Version 4.01 software (Houston, TX).

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 (2W) 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.

Molecular weights

Static light scattering experiments were also performed on the same Brookhaven system using a laser intensity of 20 mW. Polyacrylamide aliquots were withdrawn from the reactor and precipitated immediately in Certified ACS acetone (Fisher Scientific, Norcross, GA). These were then dried to constant weight under vacuum for 12 h at 25°C. A stock polyacrylamide solution (1000 ppm) was prepared directly in 1.0 M NaCl. Following complete dissolution (several days) the stock solution (approximately 1 mg mL^{-1}) was filtered twice through 0.65 μm Nucleopore cylindrical pore membranes (Fisher Scientific, Norcross, GA). The stock solution was then diluted with aqueous sodium chloride in a laminar flow hood and placed in 30 mL polypropylene centrifuge tubes. These were centrifuged at 21 000 *g* for 4.0 h using a Marathon 21 K centrifuge (Fisher Scientific, Norcross, GA). The centrifuge tubes were then returned to the laminar flow hood and the solutions were transferred to precleaned 20 mL scintillation glass vials. Following the sealing of the vials, the samples were taken to the analytical room for analysis. The samples were analysed within 1 h of being removed from the centrifuge, and in all cases the molecular weight estimates were based on four independent angular scans of each sample. The sodium chloride solvent was recirculated for a period of 24 h through a nylon filter (0.2 μm). This provided virtually dust free solvent. Zimm plots ($Kc/R(q)$ *versus* $\sin^2(q) + kc$, where K is a pre-determined optical constant, c the mass concentration, $R(q)$ an experimentally measured 'Rayleigh Factor' and k an arbitrary constant) were constructed and the weight-average molecular weight was obtained by linear extrapolation to both zero concentration and zero angle. The laser was aligned so that the product of the intensity and the sine of the measurement angle (θ) varied by less than 2% over the angular range 20–165°.

Partitioning studies

A set of partitioning studies was performed to determine the equilibrium partition coefficient of acrylamide between the aqueous and organic phases. The aqueous phase consisted of a 0.5 mol L^{-1} acrylamide solution prepared with highly deionized water. The organic phase contained 0.13% weight 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 12 h. 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. H.p.l.c. was used to measure the amount of acrylamide solubilized by the organic phase. The HPLC system was the same as previously reported in this paper with the exception of a Hitachi L6000 isocratic pump (Hitachi Instruments, Tokyo, Japan). A stainless steel filter and a CN precolumn (Waters, Millford, MA) were connected in-line between the pump and the column. The CN column used was housed in Waters Radial Pak RCM system, operating at a nominal pressure of 180 kg cm^{-2}. The column had an 8 mm i.d. and was packed with 10 μm particles (mean pore size 125 Å), with a 6% carbon load bonded to a μ-porasil (silica) substrate. The mobile phase consisted of acetonitrile/water (50/50 vol%) with 0.01 M dibutylamine with the pH adjusted to 3.0 with phosphoric acid (85 wt%, Fisher Scientific, Norcross, GA). The flowrate was set at 2.0 mL min^{-1}. Details of the h.p.l.c. method have been reported elsewhere[15].

Experimental conditions

Inverse-emulsion polymerizations of acrylamide were carried out isothermally over the temperature range 42–52°C. The surfactant was used in levels up to 6 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 polymerization are listed in *Table 1*.

RESULTS AND DISCUSSION

Preliminary observations

Figure 1 shows the experimental conversion vs time data for two inverse-emulsion polymerizations of acrylamide at 47°C and 440 RPM using the copolymeric surfactant (Hypermer B239) and sorbitan monooleate (SMO), respectively. The shape of the curves is as expected[11] with the maximum rate at low conversion and the reaction rate decreasing with time. In addition to the constant polymerization rate observed until 50–60%, a mild gel-effect, which is not visually evident, is also characteristic of these acrylamide polymerizations[11]. Polymerization rates with SMO are lower than those obtained with HB239. This is a consequence of the transfer activity of sorbitan esters of fatty acids[11] and the inert nature of the Hypermer B239 which will be discussed in the section on kinetic modelling.

A further indication of the inert nature of Hypermer B239 is reported in *Figure 2*, where the weight-average molecular weight of the precipitated homopolymers is plotted as a function of the Hypermer B239 molar concentration. Clearly, the weight-average molecular weight is independent of emulsifier concentration indicating a lack of any chain transfer activity to the HB239. If the initial polymerization rate is plotted against the molar concentration of Hypermer B239, a straight line is obtained with a slope of 0.0 indicating a purely physical role for the emulsifier. This value contrasts with the value of −0.2 obtained with SMO for similar inverse-emulsion polymerization studies where the emulsifier has a secondary chemical role in the reaction mechanism and with the value of 0.45 obtained with SMO in toluene where inverse-micelles are present[11,16,17]†.

The dependence of the initial polymerization rate on monomer concentration is found to vary to the 1.0 power and is similar to the findings in other studies of heterophase polymerization of acrylamide, both in inverse-macroemulsion and inverse-microemulsion[11,17–19]. *Figure 3* shows the initial polymerization rate plotted against the molar concentration of initiator. A 1.0 order dependence is observed which is an indication of the presence of unimolecular termination that is competing with the traditional bimolecular reaction (disproportionation). This behaviour is also characteristic of heterophase water-in-oil polymerizations with oil soluble initiators[11]. Since AIBN and water do not show any transfer activity[20], the impurities of the Hypermer B239 emulsifier such as xylene are believed to be responsible for this transfer activity‡. As support for this hypothesis, we refer to the work of Candau who has shown, for inverse-microemulsion polymerization of acrylamide in aromatic continuous phases, that toluene can act as a unimolecular terminating agent[21].

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† Generally, negative dependencies of the polymerization rate on the surfactant concentration are characteristic of a reactive interface, while positive dependencies are attributed to the role of the surfactant in particle nucleation

‡ Clearly the Hypermer B239 surfactant is not the radically active species in contrast to the case of inverse-suspension polymerizations with fatty acid esters of sorbitan[11] where the emulsifier is reactive

Table 1 Experimental conditions for the inverse-emulsion polymerization of acrylamide using HB239

Run	Weight of AIBN (g)	Weight of acrylamide (g)	Weight of water (g)	Weight of Isopar-M (g)	Weight of surfactant (g)	Temperature (°C)	Agitation rate (RPM)
1	0.20	350	650	960	40	47	440
2	0.45	350	650	960	40	47	440
3	0.70	350	650	960	40	47	440
4	0.95	350	650	960	40	47	440
5	0.70	275	725	960	40	47	440
6	0.70	200	800	960	40	47	440
7	0.70	350	650	880	120	47	440
8	0.70	350	650	920	80	47	440
9	0.45	350	650	960	40	52	440
10	0.70	350	650	960	40	47	440
11	0.70	350	650	960	40	42	440

Based on these experimental observations, a mechanism for the homopolymerization of acrylamide in inverse-emulsion using block copolymeric surfactants has been elucidated and will be presented in the following section.

Mechanism

Reactions in the oil phase:

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^{\bullet}_{\mathrm{in,O}} \qquad (1)$$

$$\mathrm{R}^{\bullet}_{\mathrm{in,O}} + \mathrm{HC} \xrightarrow{k_4} \text{inert products} \qquad (2)$$

$$\mathrm{R}^{\bullet}_{\mathrm{in,O}} + \mathrm{M_O} \xrightarrow{k_p} \mathrm{R}^{\bullet}_{1,\mathrm{O}} \qquad (3)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{O}} + \mathrm{M_O} \xrightarrow{k_p} \mathrm{R}^{\bullet}_{r+1,\mathrm{O}} \qquad (4)$$

where $\mathrm{R}^{\bullet}_{\mathrm{in,O}}$, HC, $\mathrm{M_O}$ and $\mathrm{R}^{\bullet}_{r,\mathrm{O}}$ are the symbols for primary radicals, hydrocarbon, monomer and macroradicals in the organic phase, k_4 is a kinetic constant and k_p is the propagation constant for acrylamide. I and k_d represent the initiator and its dissociation constant, respectively.

Transfer between phases:

$$\mathrm{R}^{\bullet}_{\mathrm{in,O}} \xrightarrow{k_r} \mathrm{R}^{\bullet}_{\mathrm{in,W}} \qquad (5)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{O}} \xrightarrow{k_{rr}} \mathrm{R}^{\bullet}_{r,\mathrm{W}} \qquad (6)$$

$$\mathrm{M_O} \overset{\Phi_m}{\rightleftarrows} \mathrm{M_W} \qquad (7)$$

where the subscript 'w' denotes a water phase concentration, $k_{r,r}$ is the mass transfer constant of an oligoradical of length r which will tend to k_r at small chain lengths[11]. Φ_m is the equilibrium partition coefficient of monomer between the aqueous and organic phase.

Reactions in the water phase:

$$\mathrm{R}^{\bullet}_{\mathrm{in,W}} + \mathrm{M_w} \xrightarrow{k_p} \mathrm{R}^{\bullet}_{1,\mathrm{W}} \qquad (8)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{W}} + \mathrm{M_w} \xrightarrow{k_p} \mathrm{R}^{\bullet}_{r+1,\mathrm{W}} \qquad (9)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{W}} + \mathrm{M_w} \xrightarrow{k_{fm}} \mathrm{P}_r + \mathrm{R}^{\bullet}_{1,\mathrm{W}} \qquad (10)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{W}} + \mathrm{HC_{imp}} \xrightarrow{k_5} \mathrm{P}_r + \text{inert products} \qquad (11)$$

$$\mathrm{R}^{\bullet}_{r,\mathrm{W}} + \mathrm{R}^{\bullet}_{s,\mathrm{W}} \xrightarrow{k_{td}} \mathrm{P}_r + \mathrm{P}_s \qquad (12)$$

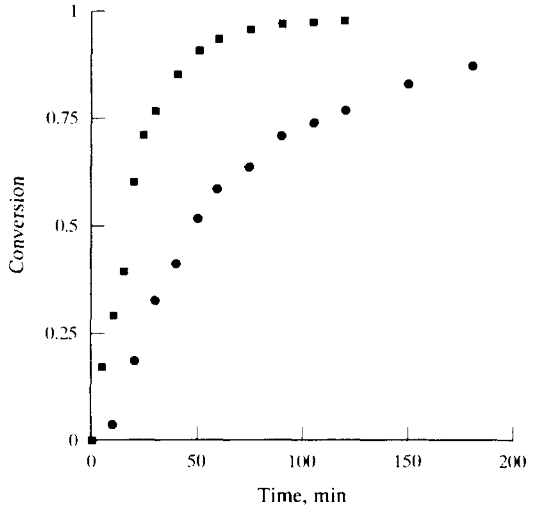

Figure 1 Experimental conversion vs time data for the inverse-emulsion polymerization of acrylamide using HB239 (■) and SMO (●) at 2 wt% (based on the total weight of emulsion). Experimental conditions: $T = 47°\mathrm{C}$, $[\mathrm{AIBN}] = 3.33 \times 10^{-3}\,\mathrm{mol}\,L_O^{-1}$, $[\mathrm{M}] = 4.93\,\mathrm{mol}\,L_w^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

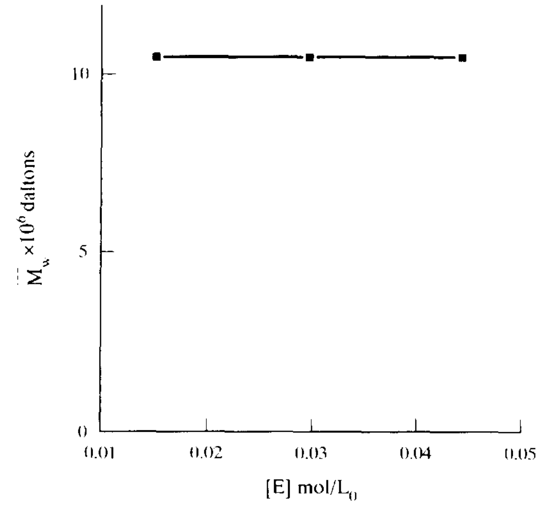

Figure 2 Weight-average molecular weight ($\bar{M}_W$) of polyacrylamide vs the molar concentration of HB239. Experimental conditions: $T = 47°\mathrm{C}$, $[\mathrm{AIBN}] = 3.33 \times 10^{-3}\,\mathrm{mol}\,L_O^{-1}$, $[\mathrm{M}] = 4.93\,\mathrm{mol}\,L_W^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

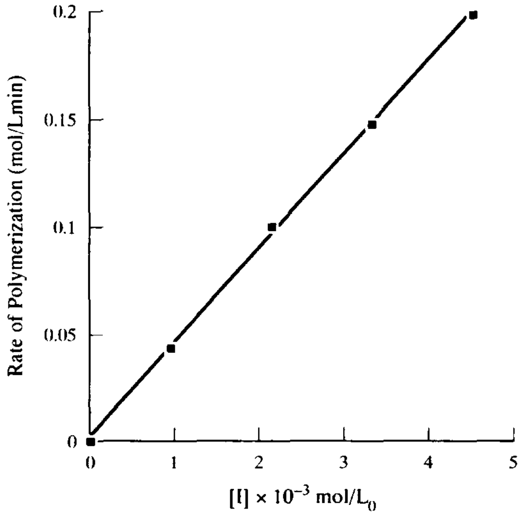

Figure 3 Rate of polymerization vs the first power of AIBN concentration. Experimental conditions: $T = 47°C$, $[M] = 4.93\,mol\,L_W^{-1}$, $[E] = 0.015\,mol\,L_O^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

where HC_{imp} represents hydrocarbon phase impurities which have transferred to the aqueous phase or the aqueous portion of the W/O interface. k_{fm} is the transfer to monomer constant, k_5 is a kinetic constant and k_{td} is the termination by disproportionation constant. P_r and P_s are dead polymer chains of length r and s, respectively.

KINETIC MODEL

Initiation

If we apply the stationary state hypothesis to primary radicals in the oil and water phases, the following equations are obtained:

$$\frac{d[R^{\bullet}_{in,O}]}{dt} \approx 0 = 2k_d[I] - k_p[R^{\bullet}_{in,O}][M_O] - k_4[R^{\bullet}_{in,O}][HC] - \frac{k_r}{V_O}\left(\frac{[R^{\bullet}_{in,O}]}{\Phi_r} - [R^{\bullet}_{in,W}]\right) \tag{13}$$

$$\frac{d[R^{\bullet}_{in,W}]}{dt} \approx 0 = \frac{k_r}{V_W}\left(\frac{[R^{\bullet}_{in,O}]}{\Phi_r} - [R^{\bullet}_{in,W}]\right) - k_p[R^{\bullet}_{in,O}][M_W] \tag{14}$$

where V_O and V_W are the volume of the oil and water phases and Φ_r is the partition coefficient of primary radicals between the organic and aqueous phases.

From equilibrium partitioning measurements, we can express the concentration of monomer in the oil phase as:

$$[M_O] = \Phi_m[M_W]$$

Adding equation (13) and $\frac{V_W}{V_O} \times$ equation (14), and rearranging, we obtain:

$$[R^{\bullet}_{in,O}] = \frac{2k_d[I] - k_p[M_W][R^{\bullet}_{in,W}]\frac{V_W}{V_O}}{k_p\Phi_m[M_W] + k_4[HC]} \tag{15}$$

Substituting equation (15) into equation (14) and solving for $[R^{\bullet}_{in,W}]$, one obtains:

$$[R^{\bullet}_{in,W}] = 2k_d[I]\frac{Y}{\delta} \tag{16}$$

where:

$$Y = \frac{k_r}{V_W\Phi_r}\left(\frac{1}{k_p[M_W] + \frac{k_r}{V_W}}\right)\left(\frac{1}{k_p\Phi_m[M_W] + k_4[HC]}\right) \tag{17}$$

$$\delta = 1 + \frac{k_r}{V_W\Phi_r}\left(\frac{1}{k_p[M_W] + \frac{k_r}{V_W}}\right)\left(\frac{k_p[M_W]\frac{V_W}{V_O}}{k_p\Phi_m[M_W] + k_4[HC]}\right) \tag{18}$$

Assuming that the main source of initiation is the diffusion of primary radicals into polymer particles, we may write:

$$R_I = k_p[M_W][R^{\bullet}_{in,W}] = 2k_d[I]\left(\frac{k_p[M_W]Y}{\delta}\right) \tag{19}$$

We can equivalently express the rate of initiation as:

$$R_I = 2fk_d[I] \tag{20}$$

Comparing equations (19) and (20), we obtain an expression for the efficiency of initiation, f:

$$f = \frac{k_p[M_W]Y}{\delta} \tag{21}$$

which can be simplified to give:

$$f = \frac{1}{1 + \frac{V_O\Phi_r}{k_r}\left(1 + \frac{k_r}{k_p[M_W]V_W}\right)(k_p\Phi_m[M_W] + k_4[HC])} \times \cdot \frac{V_O}{V_W} \tag{22}$$

$k_p[M]$ is large and k_r is of the order of 10^{0-3}, so therefore:

$$1 + \frac{k_r}{k_p[M_W]V_W} \approx 1$$

Defining the overall mass transfer constant (k_r) as:

$$k_r = k_r^* \cdot A_t$$

and

$$A_t = a_{sp} \cdot V_O$$

where A_t is the total interfacial area and a_{sp} is the specific interfacial are per litre of oil. The expression for the efficiency of initiation can now be reduced to:

$$f = \frac{1}{1 + \frac{\Phi}{k_r^*}\left(\frac{k_p\Phi_m[M_W]}{a_{sp}} + \frac{k_4[HC]}{a_{sp}}\right)} \cdot \frac{V_O}{V_W} \tag{23}$$

This expression can be further simplified for conditions where f is not a function of conversion to the equation that we will use in our kinetic model:

$$f = \frac{1}{1 + \frac{\Phi_r}{k_r^*}\left(\frac{k_4[HC]}{a_{sp}}\right)} \cdot \frac{V_O}{V_W} \tag{24}$$

Rate of polymerization

Applying the stationary state hypothesis to macroradicals $[R^\bullet]$, we obtain:

$$\frac{d[R^\bullet]}{dt} \approx 0 = R_I - k_{td}[R^\bullet]^2 - k_5[HC_{imp}][R^\bullet] \quad (25)$$

where

$$[R^\bullet] = \sum_{r=1}^{\infty}[R_p^\bullet]$$

Two cases can be examined:

Case 1: (Unimolecular termination dominates)

$$k_5[R^\bullet][HC_{imp}] \gg k_{td}[R^\bullet]^2$$

which yields:

$$R_p = \frac{2fk_dk_p[I][M]}{k_5[HC_{imp}]} \quad (26)$$

In this case, the rate of polymerization is proportional to the initiator and monomer concentration to the first order as many researchers have found for the inverse-emulsion polymerizations of acrylamide[11,17], and we report herein.

Case 2: (Bimolecular termination dominates)

$$k_5[R^\bullet][HC_{imp}] \ll k_{td}[R^\bullet]^2$$

$$R_p = \left[\frac{2fk_d[I]}{k_{td}}\right]^{\frac{1}{2}} \cdot k_p[M] \quad (27)$$

which is the classical free radical polymerization equation. At high conversions termination and the reaction will be diffusion controlled. This has been modelled using the following empirical equations, as is standard for acrylamide polymerizations[11,22].

$$k_{td} = k_{td}^{o}/(\exp(Aw_p))^2 \quad (28)$$

where $A = a_0 + a_1T$, w_p is the weight fraction of polymer in the aqueous phase, T is the temperature in degrees Kelvin and a_0 and a_1 are empirical constants.

Molecular weights

Using the method of moments, the following equations have been derived for the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$)[11]:

$$\bar{M}_n = M_m\frac{Q_1}{Q_O} \quad (29)$$

$$\bar{M}_w = M_m\frac{Q_2}{Q_1} \quad (30)$$

where M_m is the molecular weight of the monomer and Q_i is the ith moment of the distribution of polymer molecules. These moments may be found by solving the following equations:

$$\frac{dQ_O}{dt} = Y_OX \quad (31)$$

$$\frac{dQ_1}{dt} = Y_1X \quad (32)$$

$$\frac{dQ_2}{dt} = Y_2X \quad (33)$$

where $X = k_{fm}M + k_{td}Y_O$, and Y_i are the moments of the macroradical distribution for molecules. The zeroth, first and second moments of the macroradical distribution are given by[11]:

$$Y_0: \ 0 = R_I - k_{td}(Y_{OT})^2 \quad (34)$$

$$Y_1 = \frac{R_I + k_{fm}MY_O + k_pMY_O}{X} \quad (35)$$

$$Y_2 = \frac{R_I + 2k_pMY_1 + k_{fm}MY_O}{X} \quad (36)$$

Effect of emulsifier type on the rate of polymerization

As was discussed earlier, the low rates of polymerization of acrylamide in inverse-emulsion with sorbitan monooleate have been explained in terms of the emulsifier's chain transfer activity[11]. Sorbitan monooleate has an unsaturated carbon in the middle of its hydrophilic tail and five labile hydroxy functional groups on its surfactant head. These radically active functional groups can react with primary radicals in the continuous phase, lowering the polymerization rate and increasing the molecular weight[11]. Since our partitioning experiments show that the amount of acrylamide present both in the bulk organic phase and in the emulsifier boundary layer are similar using the HB239 and SMO (≈ 1–2% acrylamide by weight), the high polymerization rate observed with HB239 is due to two factors: (1) the lack of unsaturation or reactive functional groups in the molecule of Hypermer B239; (2) the presence of xylene in the HB239 (≈ 5% by weight)[23] which may enhance the solubilization of AIBN in the interfacial layer[24]. The solubilization of AIBN in xylenes is significant since the initiator efficiency is higher if the initiator molecules are partly located in the emulsifier sheath because the heterophase diffusion of the initiator (oil to water), which normally scavenges radicals due to organically soluble impurities, is eliminated. This causes an increase in both the initiation and polymerization rates. The effect on the initiation efficiency is explained kinetically through equation (24). By combining our observations with a prior investigation[11], we may write:

$$R_{p,HB239} > R_{p,SMS} > R_{p,SMO}$$

It should be noted that the polymerization rate is greatest for the HB239 due to a lack of labile hydroxy or other radically active species which lower the initiator efficiency. Sorbitan monostearate (SMS) is intermediate in its radical reactivity due to the presence of 5 hydroxy groups, while sorbitan monooleate, as stated earlier, also contains an unsaturated carbon in the liphophilic moiety.

Parameter estimation

In order to apply the kinetic model to specific inverse-emulsion polymerizations of acrylamide, several rate, mass transfer and partition coefficients are needed. In the absence of available literature values these must be estimated from experimental data. These parameters have been determined by non-linear weighted least squares regression using Marquardt's procedure to minimize the sum of squares of the residuals. The total residual is comprised of two independent measurements, conversion and weight average molecular weight, which are weighted by the reciprocal of their variances as follows:

$$\mathrm{Min}\sum_{i=1}^{n}\left[\left|\left(\frac{X_{i,\mathrm{p}}-X_{i,\mathrm{d}}}{\sigma_{\mathrm{x},i}^{2}}\right)\right|+\left|\frac{\mathrm{MW}_{i,\mathrm{p}}-\mathrm{MW}_{i,\mathrm{d}}}{\sigma_{\mathrm{MW},i}^{2}}\right|\right]^{2} \quad (37)$$

where n is the number of repetitions, $X_{i,\mathrm{p}}$ and $X_{i,\mathrm{d}}$ are the predicted and measured conversion. $\mathrm{MW}_{i,\mathrm{p}}$ and $\mathrm{MW}_{i,\mathrm{d}}$ are the model and experimental weight average molecular weights. $\sigma_{\mathrm{x},i}^{2}$ and $\sigma_{\mathrm{MW},i}^{2}$ are the variance of the ith conversion and molecular weight measurements.

The conclusions from the parameter estimation are given below:

(1) The individual parameters values for Φ_{r} and $\mathrm{k}_{\mathrm{r}}^{*}$ in equation (24) are indeterminate since this would require experimentation into the partitioning and mass transfer of primary radicals between the oil and water phases. While such research is certainly warranted, it would be extremely non-trivial to perform on reactive intermediates. The exact value of [HC] is also unknown since Isopar-M is a mixture of high boiling point straight chain alkanes with some aromatics. For this reason, these parameters were fitted as a group of constants, as they appear in the kinetic model:

$$\frac{\Phi_{\mathrm{r}}}{\mathrm{k}_{\mathrm{r}}^{*}}\left(\frac{k_{4}[\mathrm{HC}]}{a_{\mathrm{sp}}}\right) \quad (38)$$

The regressed value of this grouped parameter is 0.2972 at 47°C which renders f, the efficiency of initiation, close to unity (0.96–1.0). This indicates that the rate of transfer of primary radicals from the oil to the aqueous phase is very efficient as postulated previously.

(2) k_5 and $[\mathrm{HC}_{\mathrm{imp}}]$ in equation (26) were fitted as a single parameter. The temperature dependence of this lumped parameter follows the Arrhenius equation with a relatively moderate positive activation energy as shown in *Table 2*. A low positive activation energy is typical of termination reactions.

Kinetic model predictions

Conversion–time data. The kinetic model can predict the conversion *versus* time behaviour very well over the range of initiator concentrations studied as indicated in *Figure 4*. At lower initiator levels and high conversions, small deviations are observed. These deviations can be explained in terms of initiator starvation conditions, or a shift from unimolecular to bimolecular termination as was observed for inverse-microsuspension polymerizations of acrylamide with fatty acid esters of sorbitan as stabilizers[11].

Molecular weight. The estimates of the weight average-molecular weight ($\bar{M}_{\mathrm{w}}$) agree reasonably well with the experimental values of $\bar{M}_{\mathrm{w}}$, as reported in *Figure 5*. The unimolecular termination due to transfer to monomer is the $\bar{M}_{\mathrm{w}}$ controlling reaction[22]. Moreover, the model predictions of the weight average-molecular weight ($\bar{M}_{\mathrm{w}}$) as a function of initiator level are very good, as is illustrated in *Figure 6*. It is interesting to note that the values of $\bar{M}_{\mathrm{w}}$ for the polymers produced by inverse-emulsion polymerization using HB239 are quite large and similar in value to those reported by Kim for poly(acrylamide)s produced by solution polymerization[22]. Furthermore, the radius of gyration, $\langle \bar{r}^{2}\rangle^{1/2}$, of our polymers is ≈ 210–230 nm, and similar in value to those reported by Kulicke for polyacrylamides obtained in solution polymerization[29]. Therefore, when the block copolymeric surfactant HB239 is used in the inverse-emulsion polymerization of acrylamide, the particles behave like isolated micro-batch reactors following a solution-like mechanism. Similar behaviour has also been reported in the literature using water-soluble initiators. However, the weight average molecular weight of the resulting polymers was found to be lower due to a transfer reaction to the hydrophilic part of the emulsifier[30]. The average particle diameter of the inverse laticies produced herein was found to be invariant of the initiator concentration with values in the range of 230 nm as shown in *Figure 7*.

Effect of reagent concentrations. The model predictions of the conversion *versus* time data at various levels of both the monomer and emulsifier are excellent, as is indicated in *Figures 8* and *9*, respectively. A first order dependence in molar monomer concentration is predicted. As indicated before, this has also been observed by Baade[16] and Baade and Reichert[31]. Both the reaction rate and weight-average molecular weight (*Figure 2*) are independent of the emulsifier concentration ($R_{\mathrm{p}} \propto [\mathrm{E}]^{0}$) revealing that the emulsifier is playing a purely physical role in these polymerizations. This is not surprising given the absence of unsaturated or labile groups on either the polyethylene oxide or poly(12-hydroxystearic acid). In addition, the average particle diameter of the particles obtained with increasing levels of HB239 decreases slightly as indicated in *Figure 10*. Therefore, it is expected that the radical capture efficiency and the polymerization rate are essentially independent of the stabilizer level since the interfacial area is essentially unchanged. In any case, the mild decrease in the particle size with increasing emulsifier levels is likely the result of a

Table 2 Summary of the main parameter values

Parameter	Value	Units	Source
k_{d}	$9.48 \times 10^{16} \exp(-30800/RT)$	min^{-1}	ref. 25
k_{p}	$9.9 \times 10^{7} \exp(-2743/RT)$	$\mathrm{L\,mol^{-1}\,min^{-1}}$	refs 26–28
$k_{\mathrm{t}}^{1/2}$	$9.192 \times 10^{4} \exp(-741/RT)$	$\mathrm{L\,mol^{-1}\,min^{-1}}$	refs 26–28
k_{fm}	$5.73 \times 10^{8} \exp(-10438/RT)$	$\mathrm{L\,mol^{-1}\,min^{-1}}$	ref. 22
$k_5\,[\mathrm{HC}_{\mathrm{imp}}]$	$7.562 \times 10^{4} \exp(-2760/RT)$	min^{-1}	This work
A	$11.22 - 1.67 \times 10^{2}\,T$	Dimensionless	This work and ref. 22

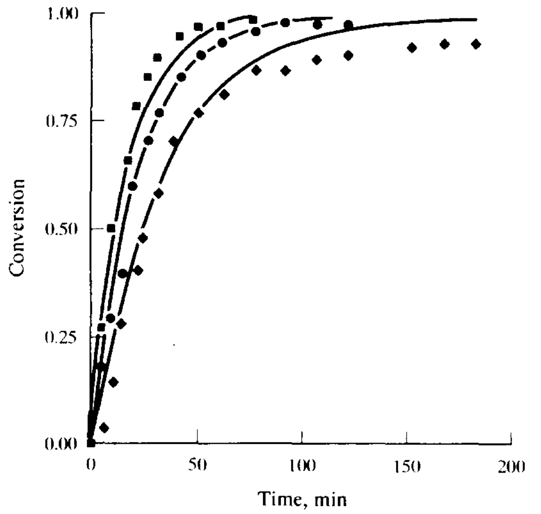

Figure 4 Experimental and predicted conversion (——) vs time data for the inverse-emulsion polymerization of acrylamide at various molar initiator concentrations: 4.52 × 10^{-3} mol L_O^{-1} (■), 3.33 × 10^{-3} mol L_O^{-1} (●) and 2.14 × 10^{-3} mol L_O^{-1} (◆). Other conditions: $T = 47°C$, [M] = 4.93 mol L_W^{-1}, [E] = 0.015 mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

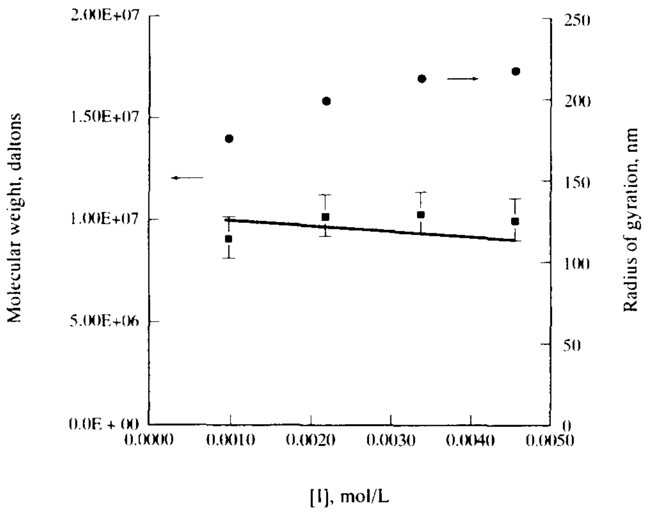

Figure 6 Experimental (■) and predicted weight-average molecular weight ($\bar{M}_W$) (——) and radius of gyration (●) as a function of molar initiator concentration for the inverse-emulsion polymerization of acrylamide. Experimental conditions: $T = 47°C$, [M] = 4.93 mol L_W^{-1}, [E] = 0.015 mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

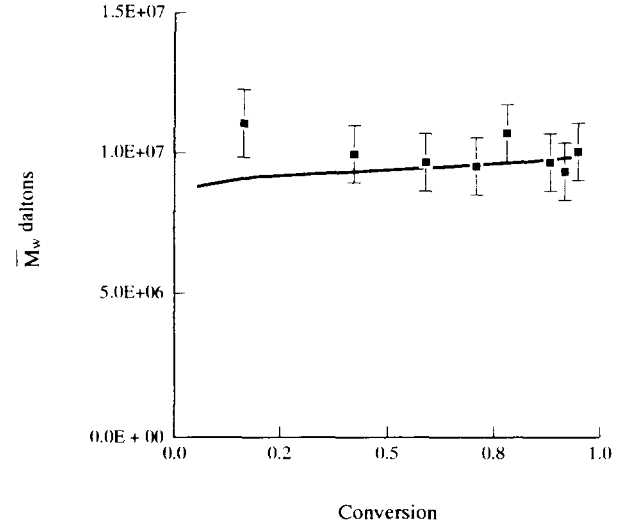

Figure 5 Experimental (■) and predicted weight-average molecular weight ($\bar{M}_W$) (—) as a function of conversion for the inverse-emulsion polymerization of acrylamide. Experimental conditions: $T = 47°C$, [M] = 4.93 mol L_W^{-1}, [AIBN] = 3.33 × 10^{-3} mol L_O^{-1}, [E] = 0.015 mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

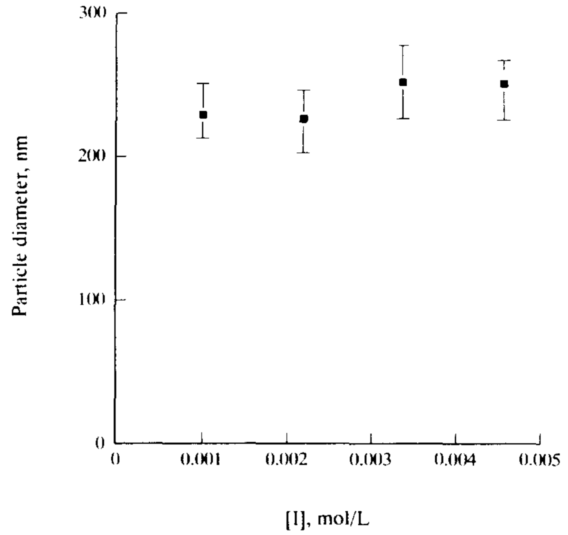

Figure 7 Experimental particle diameter as a function of molar initiator concentration for the inverse-emulsion polymerization of acrylamide. Experimental conditions: $T = 47°C$, [M] = 4.93 mol L_W, [E] = 0.015 mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

reduction in the interfacial tension which will influence the Weber number and the droplet break-up/coalescence mechanism. Both the particle diameter and weight-average molecular weight of the homopolymers are found to be invariant of the monomer concentration.

Temperature effects. The model also gives reasonable predictions of the conversion and weight-average molecular weight at temperatures between 42 and 52°C as shown in *Figures 11* and *12*, respectively. At lower temperatures, limiting conversions are observed. This behaviour has also been found in the inverse-emulsion polymerization of acrylamide initiated with potassium persulfate[32] and has been attributed to initiator depletion. The activation energy, corrected for constant interfacial area, calculated from the initial polymerization rates plotted in *Figure 11*, is 24.36 kJ mol^{-1} which is in excellent agreement with the reported value of 25–26 kJ mol^{-1} for the polymerization of acrylamide reported by other workers[24,31]. Again, the values of $\bar{M}_w$ for the homopolymers produced by inverse-emulsion polymerization using HB239 as a function of temperature are very high and similar in value to those produced by solution polymerization. This is a further indication that these polymerizations occur through a suspension-like mechanism.

Polymer and latex properties. *Table 3* presents a comparison of the final properties of the polyacrylamides and laticies obtained in inverse-emulsion with HB239 and

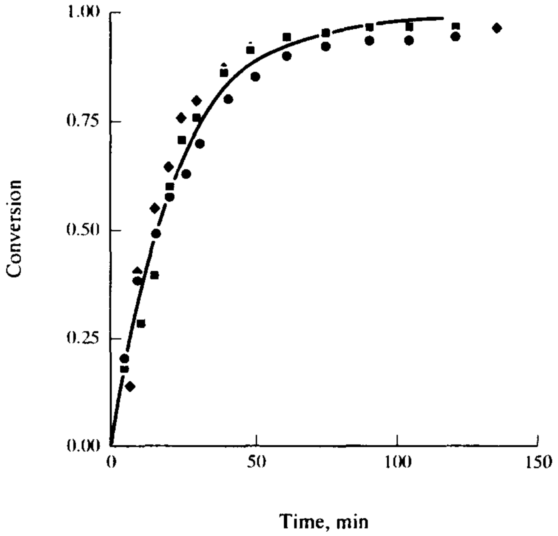

Figure 8 Experimental and predicted conversion (—) vs time behaviour for the inverse-emulsion polymerization of acrylamide using various monomer concentrations: 4.93 mol L_W^{-1} (■), 3.87 mol L_W^{-1} (●) and 2.82 mol L_W^{-1} (◆). Experimental conditions: $T = 47°C$, $[AIBN] = 3.33 \times 10^{-3}$ mol L_O^{-1}, $[E] = 0.015$ mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

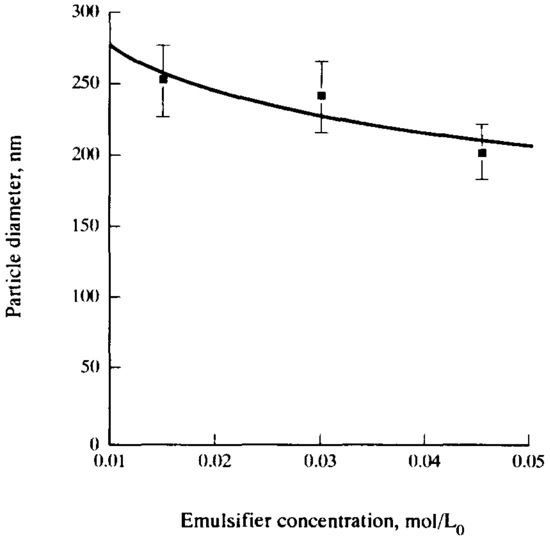

Figure 10 Experimental particle size vs molar emulsifier concentration for the inverse-emulsion polymerization of acrylamide using various levels of emulsifier. Experimental conditions: $T = 47°C$, $[M] = 4.93$ mol L_W^{-1}, $[AIBN] = 3.33 \times 10^{-3}$ mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM. The continuous line represents a power model fit

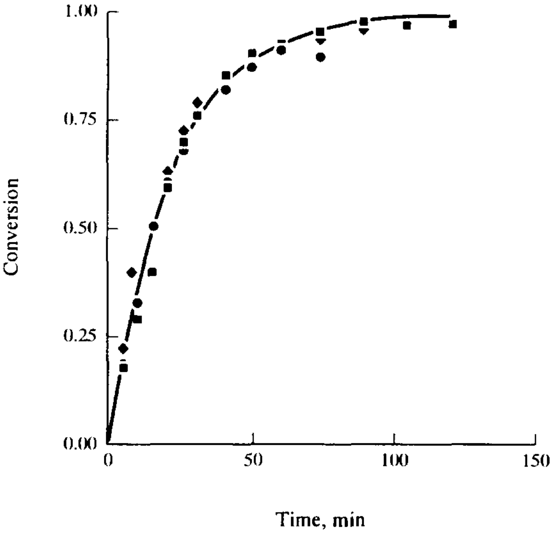

Figure 9 Experimental and predicted conversion (——) vs time behaviour for the inverse-emulsion polymerization of acrylamide using various levels of emulsifier: 0.045 mol L_O^{-1} (■), 0.030 mol L_O^{-1} (●) and 0.015 mol L_O^{-1} (◆). Experimental conditions: $T = 47°C$, $[M] = 4.93$ mol L_W^{-1}, $[AIBN] = 3.33 \times 10^{-3}$ mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

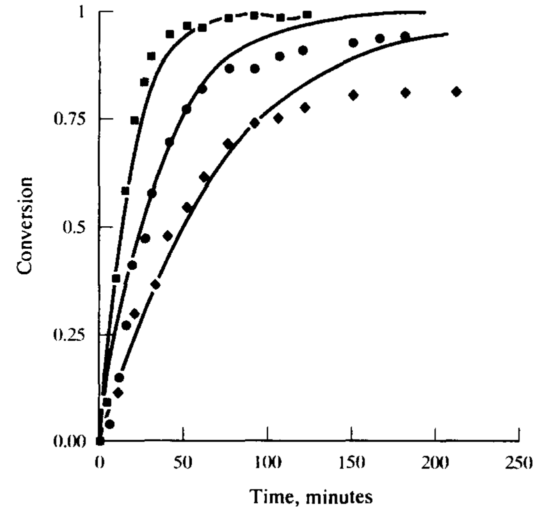

Figure 11 Experimental and predicted conversion (——) vs time behaviour for the inverse-emulsion polymerization of acrylamide at 52°C (■), 47°C (●) and 42°C (◆). Experimental conditions: $[M] = 4.93$ mol L_W^{-1}, $[AIBN] = 2.14 \times 10^{-3}$ mol L_O^{-1}, $[E] = 0.015$ mol L_O^{-1}, $\Phi_{W/O} = 0.78$ and 440 RPM

SMO synthesized under identical conditions. Both the weight-average molecular weight and radius of gyration are essentially equal in value, when one considers the experimental errors involved in the light scattering measurements (±10%). Similar values of weight-average molecular weight have been reported by Baade[16] and Baade and Reichert[31] for the inverse-emulsion polymerization of acrylamide using sorbitan monooleate (intrinsic viscosity measurements) and Kim and Hamielec[22] for the solution polymerization of acrylamide using potassium persulfate as initiator (low angle laser light scattering measurements). For the same experimental conditions, the average particle diameter for the latex obtained with sorbitan monooleate is smaller than obtained with HB239 (163 *versus* 228 nm) which indicates that sorbitan monoleate produces a more rigid or tightly packed interfacial film than HB239. Latices with the same range of particle size have been reported by Pichot for the inverse-emulsion polymerization of acrylamide using sorbitan sesquiolate[24]. The particle size distribution is broad as indicated in *Figures 13* and *14* for the inverse-latices obtained with HB239 and sorbitan monooleate, respectively. This is expected for particles produced by a break-up/coalescence mechanism. Despite the small particles, the inverse-emulsions produced with sorbitan monoleate are not very stable. Three days after production, the amount of oil separated from the bulk emulsion reaches almost 20%. The laticies

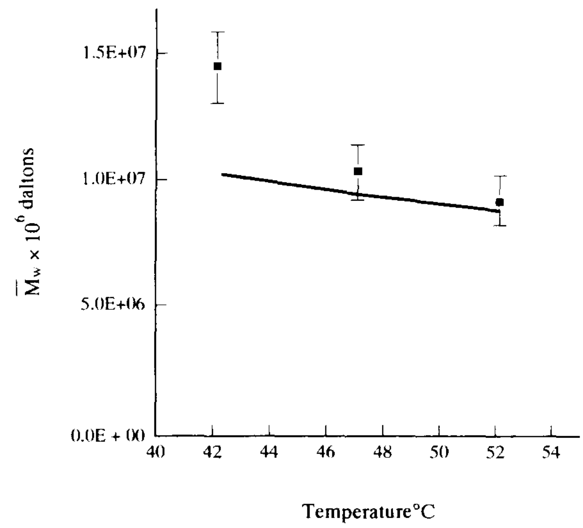

Figure 12 Experimental and predicted weight-average molecular weight ($\bar{M}_W$) behaviour for the inverse-emulsion polymerization of acrylamide at various temperatures. Experimental conditions: $[M] = 4.93\,\mathrm{mol}\,L_W^{-1}$, $[AIBN] = 2.14 \times 10^{-3}\,\mathrm{mol}\,L_o^{-1}$, $[E] = 0.015\,\mathrm{mol}\,L_O^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

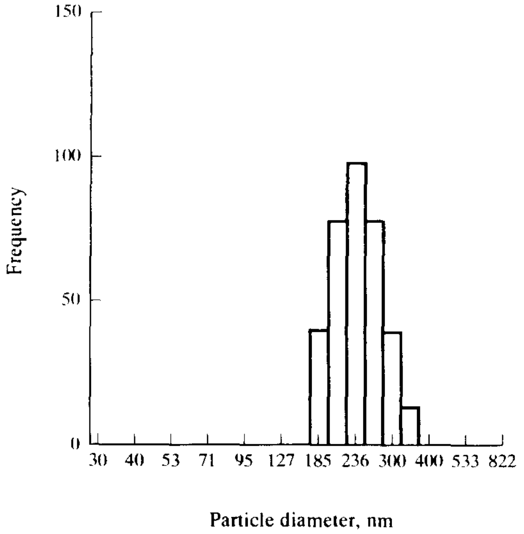

Figure 13 Frequency vs particle diameter for a particle size distribution of a latex obtained by inverse-emulsion polymerization of acrylamide with the block copolymeric surfactant (HB239) at 2 wt% (based on the total weight of emulsion). Experimental conditions: $T = 47°C$, $[AIBN] = 3.33 \times 10^{-3}\,\mathrm{mol}\,L_O^{-1}$, $[M] = 4.93\,\mathrm{mol}\,L_W^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

Table 3 Comparison of the properties of polyacrylamide obtained by inverse-emulsion polymerization using Hypermer B239 and sorbitan monooleate. Experimental conditions: $T = 47°C$, $[AIBN] = 3.33 \times 10^{-3}\,\mathrm{mol}\,L_O^{-1}$, $[M] = 4.93\,\mathrm{mol}\,L_W^{-1}$, 2 wt% surfactant (based on the total weight of emulsion), $\Phi_{W/O} = 0.78$ and 440 RPM

Surfactant	Weight-average molecular weight	Radius of gyration (nm)	Particle diameter (nm)
Hypermer B239	10.5×10^6	205	256
Sorbitan monooleate	10.3×10^6	198	163

obtained with HB239, on the other hand, show higher stability with no signs of oil separation after 1 month. This is true even at emulsifier levels as low as 2 wt%. Similar stability results have been reported by others[7 9]. As mentioned earlier, this stability has been explained in terms of the extended hydrophobe moiety of the HB239 which is five times larger than that of the sorbitan esters of fatty acids[7] and the inherent advantage of triblock *versus* diblock stabilizers.

CONCLUSION

The rate of polymerization of acrylamide in inverse-emulsion polymerization is higher when the block copolymeric surfactant HB239 is utilized in comparison with sorbitan monoleate.

The initial rate of polymerization of an inverse-emulsion polymerization of acrylamide using HB239 is found to be: (i) first order with respect to the initiator which suggests that unimolecular termination dominates; (ii) first order with respect to the monomer which implies standard free radical initiation and propagation steps; (iii) zeroth order with respect to the emulsifier suggesting a purely physical role of the emulsifier. It is believed that the impurities present in the block copolymeric surfactant are responsible for the unimolecular termination.

A kinetic model has been proposed for the inverse-emulsion polymerization of acrylamide using block copolymeric surfactants based on the above experimental observations and was found to predict very well conversion and molecular weight well at various levels of initiator, monomer, emulsifier and temperature.

The values of weight-average molecular weight of the

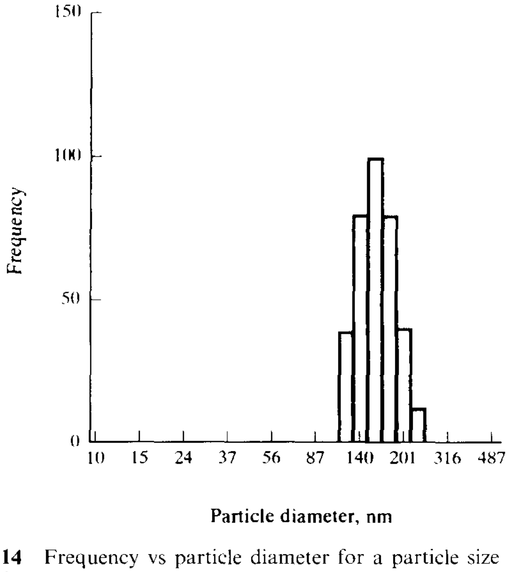

Figure 14 Frequency vs particle diameter for a particle size distribution of a latex obtained by inverse-emulsion polymerization of acrylamide with sorbitan monooleate at 2 wt% (based on the total weight of emulsion). Experimental conditions: $T = 47°C$, $[AIBN] = 3.33 \times 10^{-3}\,\mathrm{mol}\,L_O^{-1}$, $[M] = 4.93\,\mathrm{mol}\,L_W^{-1}$, $\Phi_{W/O} = 0.78$ and 440 RPM

polyacrylamides obtained with both the block copolymeric surfactant HB239 and sorbitan monooleate are very high. In addition, both the weight-average molecular weight and the radius of gyration of these polymers are similar in value to those obtained with solution polymerization. From an industrial point of view, the advantages of using the block copolymeric surfactant HB239 in an inverse-emulsion polymerization of acrylamide are the superior stability of the final latex and the higher productivities due to the larger polymerization rates relative to sorbitan monooleate.

REFERENCES

1 Goin, J. 'Water Soluble Polymers', CEH Marketing Research Report 582.0000 D-E, August 1991, SRI International, Menlo Park, CA
2 Peaff, G. *Chem. Eng. News* 1994, 14 Nov.
3 Hunkeler, D. J., Candau, F., Pichot, C., Hamielec, A. E., Xie, T. Y., Barton, J., Vaskova, V., Guillot, J., Dimonie, M. V. and Reichert, K. H. *Adv. Polym. Sci.* 1994, **112,** 115
4 O'Conner, M. N., Barker, L. J. and Ryles, G. US Patent 5,298,555, 1994
5 Robinson, P. M. and Jenkins, M. R. US Patent 5,200,448, 1993
6 Yang, H. W., Pacansky, T. J. US Patent 4,918,123, 1990
7 Robinson, P. M., Rakowitz, D. H. and Nowakowski, L. J. US Patent 4,339,371, 1982
8 Bognolo, G. in 'Industrial Applications of Surfactants' (Ed. D. R. Karsa), The Royal Society of Chemistry, Cambridge, 1990
9 Schofield, J. D. in 'Recent Developments in the Technology of Surfactants' (Ed. M. R. Porter), Elsevier, New York, 1990
10 Kruger, G. in 'Industrial Applications of Surfactants (Ed. D. R. Karsa), The Royal Society of Chemistry, Cambridge, 1991
11 Hunkeler, D. J., Hamielec, A. E. and Baade, W. *Polymer* 1989, **30,** 127
12 Hunkeler, D. J. and Hamielec, A. E. *Polymer* 1991, **32,** 14
13 Hernandez-Barajas, J. and Hunkeler, D. J. *Polym. Adv.Technol.* 1994, **6,** 509
14 Hernandez-Barajas, J., Hunkeler, D. J. and Petro, M. *J. Appl. Polym. Sci.*, in press
15 Hunkeler, D. J., Ni, H., Hernandez-Barajas, J. and Petro, M. *Int. J. Polym. Anal. Char.* (in press)
16 Baade, W. PhD Thesis, Technical University of Berlin, Berlin, Germany, 1986
17 Baade, W. and Reichert, K. H. *Makromol. Chem., Rapid Commun*, 1986, **7,** 235
18 Vanderhoff, J. W., Disteffano, F. V., El-Aaser, M. S., O'Leary, R., Schoffer, O. M. and Visioli, D. L. *J. Dispersion Sci. Technol.* 1984, **5,** 323
19 Candau, F. and Leong, Y. S. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23,** 193
20 Loeng, Y. S. and Candau, F. IUPAC Symposium, Strasbourg, 1981
21 Carver, M. T., Dreyer, U., Knoesel, R. and Candau, F. *J. Polym. Sci. Part A: Polym. Chem.* 1989, **27,** 2161
22 Kim, C. J. and Hamielec, A. E. *Polymer* 1984, **25,** 845
23 Material Safety Data Sheet, Hypermer 239, ICI Americas, Wilmington, DE, 1991
24 Graillat, C., Pichot, C., Guyot, A. and El-Aasser, M. S. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24,** 427
25 Azo Polymerization Initiators, Wako Chemical Industries Ltd, Osaka, Japan, 1993
26 Currie, D. J., Dainton, F. S. and Watt, W. S. *Polymer* 1965, **451** 6
27 Ishige, T. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1973, **17,** 1479
28 Dainton, F. S. and Tordoff, M. *Trans Faraday Soc.* 1953, **53,** 499
29 Kulicke, W. M., Kotter, M. and Grujer, M. *Adv. Polym. Sci.* 1989, **1,** 89
30 Dimone, M. V., Boghina, C. M., Marinescu, N. N., Marinescu, M. M., Cincu, C. I. and Oprescu, C. G. *Eur. Polym. J.* 1982, **18,** 639
31 Baade, W. and Reichert, K. H. *Eur. Polym. J.* 1984, **20,** 505
32 Hunkeler, D. J. *Macromolecules* 1991, **24,** 2160