Semicontinuous Emulsion Copolymerization of 3-*O*-Methacryloyl-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (3-MDG) and Butyl Acrylate (BA). Monomer Feed Addition

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ABSTRACT: New polymer colloids based on the saccharide monomer, using of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (3-MDG), were prepared by semicontinuous emulsion polymerization, a widely used industrial process. The copolymerization of 3-MDG and butyl acrylate (BA), by the monomer-addition technique, at 70°C, using sodium persulfate ($Na_2S_2O_8$) as an initiator, was investigated. The influence of some reaction parameters, such as the type and concentration of the surfactants as well as the monomer addition rate (R_m) on the polymerization rate (R_p), the colloidal properties, and the stability of the latexes, was studied. It was found that under starved-feed conditions the polymerization rate and the particle size (D) increased with an increasing rate of monomer addition. The weight-average molecular weight ($\overline{M}_w$) also increased by enhancing R_m and a narrower molecular weight distribution was obtained. Furthermore, the type and the concentration of the surfactants strongly influenced the particle size and its distribution. The effect of the seed stage on the particle size and its distribution was also investigated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2091–2102, 2003

Key words: kinetics (polym.); renewable resources; emulsion polymerization; surfactants

INTRODUCTION

The emulsion polymerization of sugar-based monomers is a new route to develop new polymer colloids for specific applications in many fields, such as paints and coating, water-based adhesives, medicine, pharmaceuticals, and cosmetics. Pichot et al.[1] reported on the surface functionalization of polystyrene latex particles with disaccharide monomers and their use in diagnostics. We have concentrated our attention in the last 10 years on the modification of mono-and disaccharides to introduce them as saccharide monomers to polymer syntheses. We think that, in the near future, carbohydrates, as renewable raw materials, will become an important source for the chemical industry. D-Glucose, with world production over 5 million tons per year, has attracted much attention. In 1945, Yanovsky et al.[2] reported on the preparation of glucose pentamethacrylate and its radical polymerization in chloroform and other solvents using benzoyl peroxide or cobalt naphthenate as an initiator. Fifteen years later, in 1960, Black et al.[3,4] described the preparation and the polymerization of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranose (3-MDG), commonly called 3-methacryloyldiacetonglucose. 3-MDG was polymerized with free-radical and cationic catalyses. At the same time, in 1961, Kimura et al.[5–7] optimized the synthesis of the same sugar monomer and investigated its polymerization using a different method. Lately, 3-MDG has been given more interest by some authors, who have reported in many articles on the optimization of the synthesis of 3-MDG and also on its polymerization using different processes.[8–11] Yaacoub et al. investigated, for the first time, the emulsion homopolymerization of 3-MDG as well as its copolymerization with butyl acrylate (BA) in a batch process.[12–15]

We report in this work on the semicontinuous emulsion copolymerization of the binary system 3-MDG/BA. A semicontinuous process allows one great control over the course of the polymerization, the rate of heat generation, and the properties and the morphology of the polymer colloids. In the semicontinuous process, there are two main classes of feeding the monomer(s) to the reaction vessel: The monomer-addition technique is the simpler of the two classes and involves the metering of neat monomer(s) to the reaction vessel using, usually, a metering pump. The second class is preemulsion addition, which involves the metering of an emulsion prepared from the monomer(s), water, and a part from the surfactant. The main difference between the two classes is the surfactant concentration throughout the polymerization. In

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TABLE I
Recipe of the Semicontinuous Emulsion Polymerization of the Binary System (3-MDG/BA) at 70°C

	Charge (g)	Feed I (g)	Feed II (g)
Water	102	—	18
NaHCO$_3$	0.12	—	—
Surfactant	Variable	—	—
Na$_2$S$_2$O$_8$	0.012	—	0.110
3-MDG	—	17.30	—
BA	—	12.60	—

the case of monomer addition, the surfactant is introduced usually completely at the outset of the polymerization. We used in this work the first type of feeding (monomer addition). The influence of some reaction parameters such as the type and concentration of the surfactants as well as the rate of monomer addition on the kinetic features, the colloidal properties, and the stability of the latexes was studied. A part of this study was also devoted to investigate the influence of the state of the particles formed in the early stage of emulsion polymerization on the particle growth as well as on the particle-size distribution.

EXPERMENTAL

Materials

The sugar monomer (3-MDG) was prepared in our laboratory as described in the literature.[4] BA (Fluka, Germany) was distilled under reduced pressure just before use. All the other materials were used as received. Sodium persulfate, Na$_2$S$_2$O$_8$, and sodium hydrogen carbonate, NaHCO$_3$ (Merck, Germany), were used as an initiator and buffer, respectively. The following ionic surfactants, sodium lauryl sulfate (SDS; Merck), sodium lauryl ether sulfate (SLES; Henkel, Germany), sodium nonyl phenyl poly(ethylene glycol) ether sulfate (NOS10; Wittco, Germany), and the nonionic surfactant nonyl phenyl polyglycol (HV25, Wittco), were used.

Polymerization procedure

Semicontinuous emulsion polymerization was carried out at 70°C according to the recipe in Table I. The monomer ratio of 3-MDG/BA (35/65 mol %) was used in most of the polymerizations in this work, which formed copolymers with a glass transition temperature of ~45°C. The polymerization was carried out in a 250-mL double-wall glass reactor equipped with a glass paddle-type stirrer, nitrogen inlet, and temperature sensor. Two titrating pumps (Perfusor type) were used to feed the monomer mixture and the initiator solution. First, the reactor was charged under a nitrogen atmosphere by deionized, degassed water, the surfactant, and the buffer. The reaction medium

was maintained under constant agitation of 175 rpm at 70°C for 30 min, followed by the addition of 10% of the total amount of the initiator. Directly, the polymerization was started by feeding the reactor. The feed was divided into two streams: The first one was a mixture of both monomers in the required ratio, and the second was a solution of the initiator. The flow rates of these streams were 0.16 and 0.1 g/min, respectively, and were kept constant during the polymerization. Nevertheless, for studying the effect of the monomer-addition rate, the addition time and, consequently, the rate of monomer addition were varied. The rate of monomer addition was low enough to ensure monomer-starved conditions in the reactor. The addition time was 3 h and the polymerization was continued in the batch for a further 30 min. To follow the reaction, at least 10 samples were withdrawn from the reactor during the polymerization. The reactions of the samples were stopped with hydrochinon and they were kept for some minutes in an ice bath.

Characterization of the latexes

Monomer conversion

The conversion was determined gravimetrically as well as by gas chromatography (GC). For total conversion by the gravimetric method, about 0.5 g of the latex sample was weighted in a glass watch and dried under a vacuum for at least 4 h at 50°C. The individual monomer conversion was followed by GC. The apparatus consists of a GC 14-B unit, hydrogen flame-ionization detector (FID), auto sampler AOC-17, and capillary column. The capillary column, with a length of 50 m, 0.32-mm inner diameter, and a layer thickness of 0.5 μm, was filled with Crossbond, 95%–dimethyl, 5%–diphenyl polysiloxane, as the stationary phase. The measurements were carried out by two-step heating program. Nitrogen was used as a carrier gas with a pressure of 100 kPa. The hydrogen and air pressure were 60 and 50 kPa, respectively. For the preparation of the samples, about 1 mL latex was diluted with 1 mL methanol to precipitate the polymer, which had been separated by centrifugation (15,000 rpm), and then toluene, as an internal standard, was added to the solution. Figure 1 shows a typical GC chromatogram of the polymerization system, in the presence of toluene as an internal standard, indicating the retention times of the different components.

Furthermore, two conversions were calculated: a total conversion and an instantaneous conversion. The total conversion was defined as the ratio of the polymer present in the reactor to the total monomer used in the recipe. Instantaneous conversion was defined as the ratio of the polymer present in the reactor to the monomer fed into the reactor at that time. The amounts of the samples withdrawn were taken into
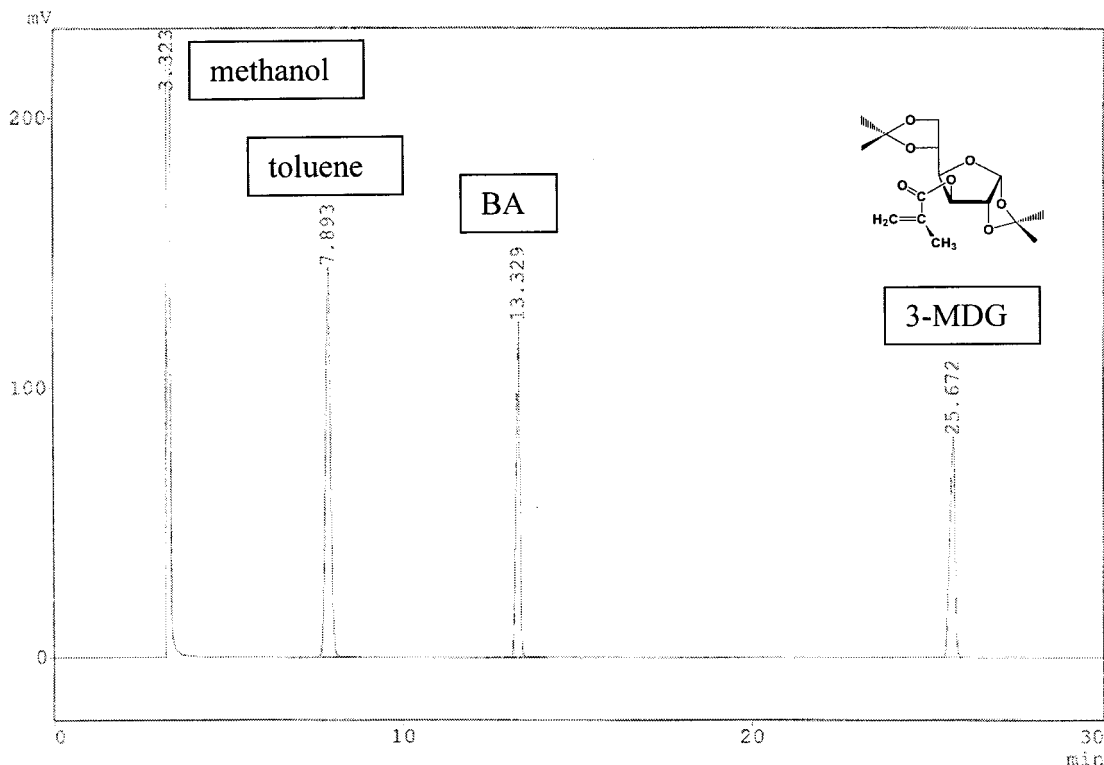
Figure 1 GC chromatogram of 3-MDG/BA in presence of toluene as internal standard. The heating rate of the two steps was 15°C/min. The oven and the column temperatures were 210 and 240°C, respectively.

consideration for the calculation of the overall and instantaneous conversions.

Particle size and particle-size distribution

These were measured by the quasi-elastic light-scattering method (ZetaSizer3, from Malvern Instruments, Ltd.). The total number of particles (N_p) in milliliters latex was calculated by the following eq. (1):

$$N_p = 6 \times 10^{21} TS_t / \pi D^3 \rho \qquad (1)$$

where TS_t is the solid content at time (t) in 1 g latex; ρ, the density of the polymer; and D, the average particle size (nm). The average diameter value obtained by QELS was used for the calculation of N_p and the polydispersity index (PDI).

Transmission electron microscopy (TEM; Philips 300) allows the estimation of the particle sizes and their distributions in the dried state. For the preparation of the samples to be observed, the latexes were highly diluted in an aqueous solution of phosphotungstic acid (1%) as negative staining and mounted onto copper grids, which were coated with carbon. The grids were dried at room temperature and then examined.

Electrophoresis

Experiments were performed with a ZetaSizer3 (from Malvern Instruments, Ltd.) at 25°C. The electrophoretic mobilities (μ) were measured at a constant ionic strength (10^{-3} M NaCl). The measurements were performed three times and were readily reproducible. The electrokinetic potentials or, more frequently, the zeta potentials (ζ) were calculated using either Hückel's eq. (2) or Smoluchowski's eq. (3), depending on the distortion of the applied field by particle and double layer:

$$\text{for } KR \ll 1 \qquad \mu = \frac{v}{E} = \frac{2\varepsilon_r \varepsilon_0 \zeta}{3\eta} \qquad (\mu m\ s^{-1}/V\ cm^{-1})$$

$$(2)$$

$$\text{for } KR \gg 1 \qquad \mu = \frac{v}{E} = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \qquad (\mu m\ s^{-1}/V\ cm^{-1})$$

$$(3)$$

where v is the particle velocity; E, the electrical field; ε_0, the permittivity of the free space; ε_r, the relative permittivity of the medium; η, the viscosity of the medium; K^{-1}, the Debye thickness of the diffuse part of the double layer; and R, the radius of a spherical particle.

TABLE II
Effect of the Monomer-addition Rate in Semicontinuous Process (Versus Batch Process) on the Final Particle Sizes and Their Distributions as Well as on the Average Molecular Weights of the End Polymers and Their Polydispersities (M_w/M_n)

	Batch process	Semicontinuous process			
$R_m \times 10^5$ (g/min)	—	0.44	0.23	0.16	0.12
$R_m \times 10^5$ (mol/s)	—	3.70	1.93	1.33	1.01
$R_p \times 10^5$ (mol/s)	10.23	3.66	1.90	1.31	0.98
D (nm)	72	58.3	52.0	49.5	46.6
$N_p \times 10^{-15}$ (cm^{-3})	1.07	2.03	2.85	3.30	4.08
PDI	0.05	0.068	0.086	0.084	0.068
$\bar{M}_n \times 10^3$ (g/mol)	825	275	153	73	42
$\bar{M}_w \times 10^3$ (g/mol)	1221	429	272	133	86
$\bar{M}_z \times 10^3$ (g/mol)	1810	773	526	308	197
$\bar{M}_w/\bar{M}_n$	1.48	1.56	1.78	1.82	2.05

Copolymer composition

The copolymer compositions were determined from ^{1}H NMR spectra, carried out on a Bruker AM 400 spectrometer. The measurements were performed at room temperature on a polymer solution in CDCl₃, containing tetramethylsilane as an internal standard.

Molecular weights

The weight-average molecular weights ($\overline{M}_w$) were determined by gel permeation chromatography (GPC) on-line with multiangle laser light-scattering (MALLS) and a refractive index detector. The polymers were dissolved in chloroform (3 g/L) and the analyses were performed at 25°C using a GRAM-3000 (10 μm, 300 × 7.5 mm²) column, filled with polyester gel (from PSS Polymer Standards Service GmbH, Germany). Chloroform was used as an eluent with a flow rate of 1 mL/min. The refractive index increment, *dn/dc*, of the 3-MDG/BA copolymer was measured on a light-scattering photometer at 25°C in chloroform and at a wave length of 633 nm. The *dn/dc* of the copolymer (3-MDG/BA; 35/65 mol %) was found to be 0.042 mL/g.

RESULTS AND DISCUSSION

Effect of the monomer-addition rate

In the batch process, the rate of polymerization (R_p) depends on the number of particles (N_p), which depends mainly on the initiator (I) and surfactant (S) concentrations[16]:

$$R_p \propto N_p \propto [I]^{2/5}[S]^{3/5} \qquad (4)$$

In the semicontinuous process, the polymerization rate depends predominately on the addition rate of the monomer. If the monomer-addition rate (R_m) is high enough to maintain the saturation value of the monomer concentration within the latex particles $[M]_p$, the rate of polymerization (R_p) will be independent of the addition rate (flooded region) and, consequently, eq. (4) is applicable in this case. Furthermore, if the monomer-addition rate is low enough, to ensure that the $[M]_p$ is below the saturation value, the polymerization rate approaches a constant value, which, therefore, depends only on the monomer-addition rate (controlled region). In that case, eq. (4) is not applicable.

Four experiments were carried out with different monomer-addition rates, to study the effect of the monomer-addition rate on the polymerization rate, on the colloidal properties (particle sizes and their distributions), as well as on the average molecular weights and their distributions. SDS was used as an anionic surfactant, above its critical micelle concentration (CMC) value, with a concentration of 5 g/L, and all other additives were used as described in Table I. The same amount and composition of the initial monomer mixture (3-MDG/BA; 35/65 mol %) were used, but the addition time was varied as described in Table II. Batch polymerization was carried out with the same formulation as in Table I, to compare the results with the semicontinuous one.

As shown in Figure 2(a), the overall polymerization rate in the batch process is very high (10.23 × 10⁻⁵ mol/s), due to the high reactivity of the sugar monomer. More than 95% total conversion was reached after only 15 min. In semicontinuous reactions, R_p directly depends on R_m. The rate of polymerization was calculated experimentally from the slopes of the nominally linear regions of the total conversion. As can be seen from Table II, the monomer-addition rate (R_m) and the calculated reaction rate (R_p) are relatively the same, which confirmed that all the reactions were carried out under starved-feed conditions. Figure 2(b) shows the evolution of instantaneous conversion versus time. After about 10 min from the start of the
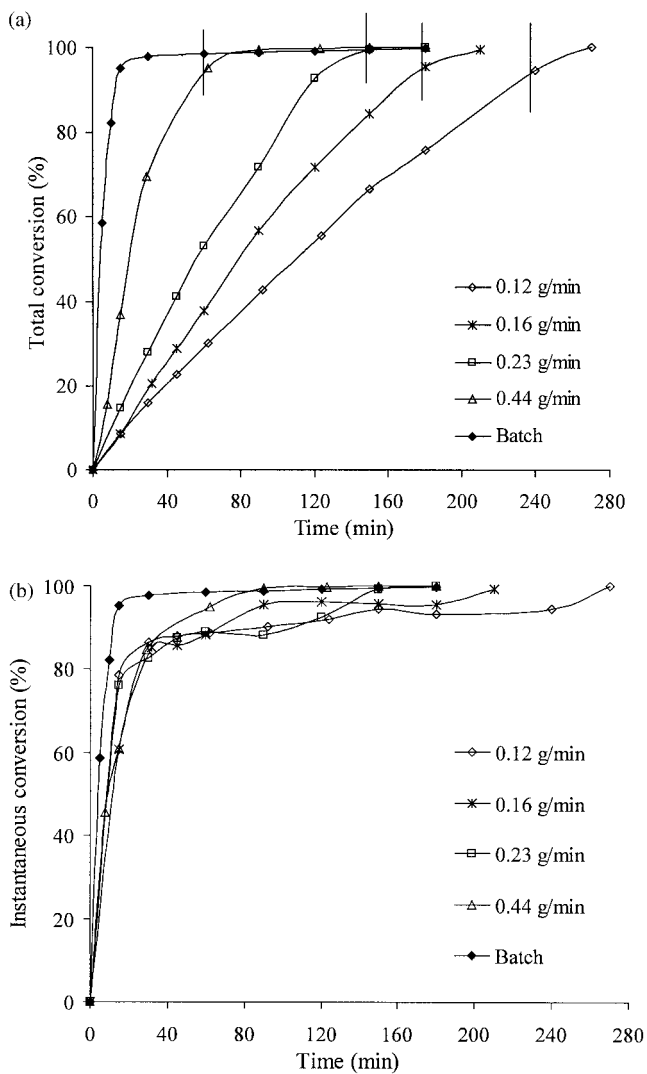
(a)

(b)

Figure 2 Conversion–time curves of batch and semicontinuous emulsion copolymerization of 3-MDG/BA at different rates of monomer addition, according to recipe described in Table I: (a) total conversion (the cross lines indicate the end of feeding); (b) instantaneous conversion.

polymerization, all the instantaneous conversions reached the maximum value (more than 90%).

The effect of the addition rate on the evolution of the particle size (*D*) and the number of particles (N_p) during the polymerization is shown in Figures 3 and 4. It was found that, if the addition rate increases, the particle size also increases and, therefore, the number of particles decreases. In the case of the batch process, the particle size reached, after a short time, its maximum value and remained constant. In the case of the semicontinuous process, the particle sizes increased slowly and continually until the end of the monomer addition. As shown in Table II, a final particle size of 72 nm was obtained in the batch, whereas in the semicontinuous process, the final sizes were smaller and they increased from 46 to 58 nm with an increase of R_m from 0.12 to 0.44 g/min. Nevertheless, the PDI
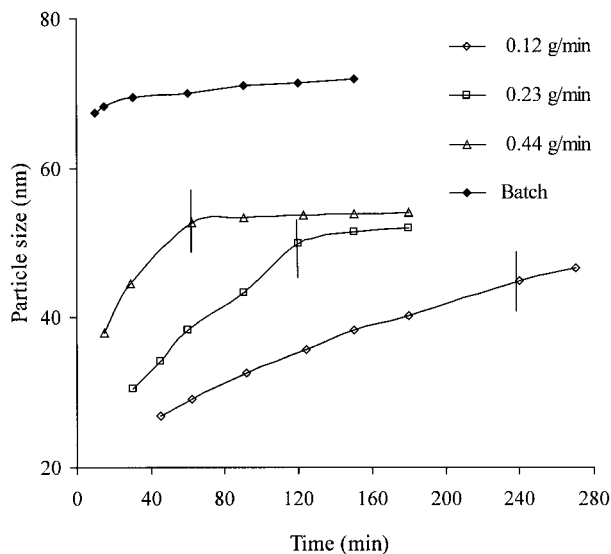

Figure 3 Particle-size evolution against time for semicontinuous copolymerization of 3-MDG/BA at different monomer-addition rates, according to Table II. The cross lines indicate the end of feeding.

of the batch latex is narrower than that of those formed by semicontinuous polymerization using the monomer-addition technique. Moreover, it was found that, under our experimental conditions, the rate of monomer addition has no remarkable influence on the particle-size distribution and the final latexes are polydisperse. As shown in Figure 4, the total number of particles decreases with increasing monomer-addition rates. Sajjadi[17] derived a correlation for particle formation under monomer-starved conditions for hydrophobic monomers such as styrene and found that N_p is inversely proportional to the 0.66[th] order of R_m. In this
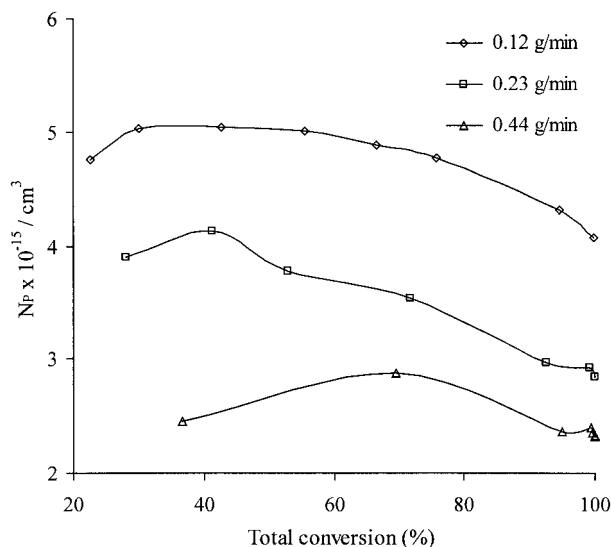

Figure 4 Total number of particles (N_p) against the total conversion for semicontinuous polymerization of 3-MDG/BA at different monomer-addition rates, according to Table II.

work, the proportionality factor was −0.50. Moreover, it can be seen from the curves that, above 45% conversion, the number of particles decreases continuously until the end of the polymerization, which indicates a secondary coagulation. This behavior increased with lowering of the monomer-addition rates. It may be due to the low monomer concentration in the polymer particles and to the huge number of very small particles, which were formed at the beginning of the reaction and stabilized through coagulation.

The rate of monomer addition affected not only the colloidal properties (D, PDI), but also the properties of polymer, such as the average molecular weight. By using the semicontinuous process, it is possible to control the weight-average molecular weight $\overline{M}_w$ and the molecular weight distribution (MWD), characterized by the PDI and defined as the ratio of $\overline{M}_w/\overline{M}_n$. The copolymer formed by the batch process exhibits a higher weight-average molecular weight than that of those formed by the semicontinuous process, as shown in Table II. This could be related to the maximum saturation value of $[M]_p$ in the batch process. Under starved-feed conditions, $\overline{M}_w$ depends on the monomer-addition rate. As the addition rate increases, $[M]_p$ increases, which leads to increase of the $\overline{M}_w$ value. The decrease of $\overline{M}_w$ is due mainly to the lowering of the monomer concentration within the polymer particles and/or to the increase of the chain-transfer reactions to the polymer. A bimodal distribution was obtained in the case of vinyl acetate (VAc)/BA copolymerization,[18] due to the chain transfer to a monomer and a polymer. In our system, all the GPC analyses of the sugar copolymers exhibited a monomodal distribution. The low PDIs indicate, rather, that the termination reactions occurred
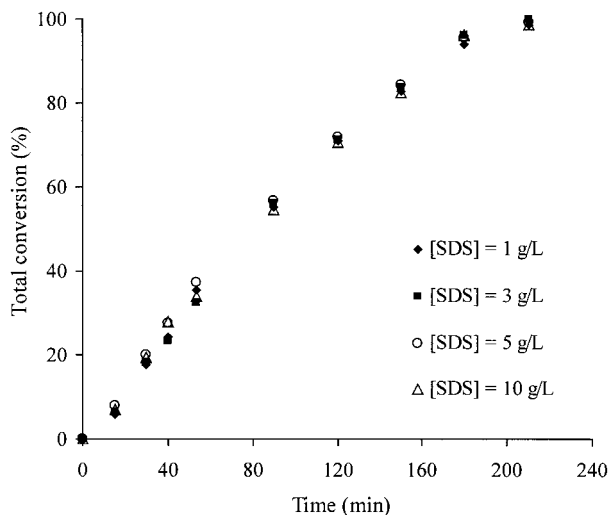

Figure 6 Particle-size evolution against time for semicontinuous copolymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.

through a combination at high R_m and through disproportionation at low R_m.

Effect of the surfactant concentration

One of the most important parameters in emulsion polymerization is the surfactant. The main role of the surfactant is the stabilizing of the monomer droplets in an emulsion form, decreasing the surface tension in the reaction medium and stabilizing the formed latex particles. The CMC is a specific parameter for each surfactant, which controls the particle-formation mechanism. According to the HUFT theory,[19] the particle formation undergoes "homogeneous nucleation" if the surfactant concentration is below the CMC. Polymerization under this mechanism will form particles with a more uniform size (monodisperse). If the surfactant concentration is above the CMC, the particle formation undergoes "micellar nucleation," in which the monomer-swollen micelles are the major loci of the particle nucleation. Oligoradicals generated in the aqueous phase enter into these micelles and form particle nuclei. Polymerization proceeds from the monomer supplied by the monomer droplets by diffusion through the aqueous phase.

To study the effect of the surfactant concentration on the reaction pathway as well as on the colloidal properties, four semicontinuous emulsion polymerization reactions, using surfactant concentrations below and above the CMC, were carried out. We used SDS, which has a CMC of 2.8 g/L, as an anionic surfactant with concentrations of 1, 3, 5, and 10 g/L. The initial monomer composition of 3-MDG/BA was 35/65 mol and the amount of SDS was added at the outset of the reaction (in the charge). All the reactions

Figure 5 Total conversion–time curves of semicontinuous copolymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.
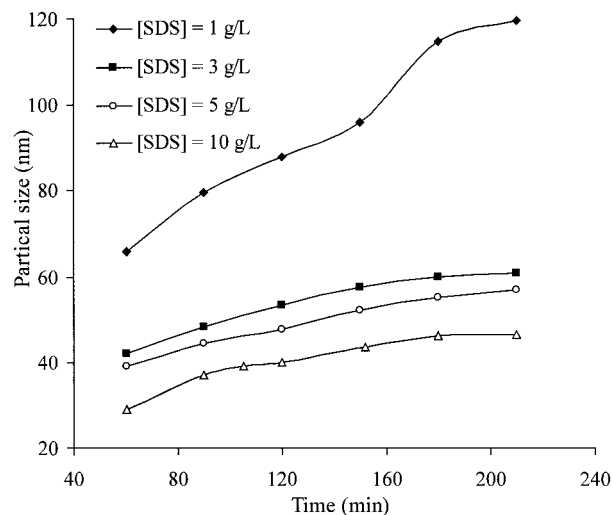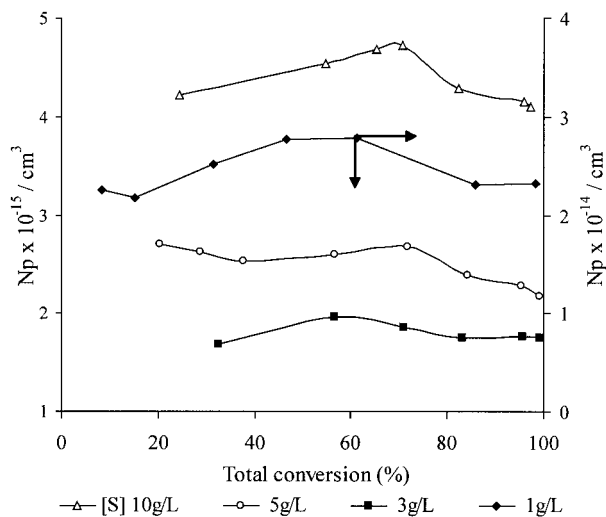
Figure 7 Total number of particles (N_p) against the total conversion curves of semicontinuous polymerization of 3-MDG/BA with different surfactant concentrations. The initial composition of 3-MDG/BA was 35/65 mol.

were carried out under starved-feed conditions, where the addition rate was 0.16 g/min. It was found that the rate of the polymerization is independent of the surfactant concentration (Fig. 5). This behavior is completely different from the case of the batch process, in which the polymerization rate as well as the number of particles is generally proportional to the 0.6[th] power of the surfactant concentration. In the semicontinuous process, the surfactant concentration influences the particle-size evolution and the particle-size distribution. As shown in Figure 6, if the surfactant concentration is above the CMC, the surfactant concentra-

tion has a little effect on the particle size. The high concentration of the surfactant at the outset of the polymerization leads to the formation of a huge number of free micelles, which are able to capture and stabilize the formed oligoradicals in the aqueous phase. If the surfactant concentration is below the CMC, homogeneous nucleation takes place. The primary particles are then stabilized through coagulation by means of Brownian motion, which continued until the resulting polymer particles had enough surface ionic groups, leading to their stabilizations by mutual repulsion forces. The resulting final particle size is bigger than the former one by a factor of 3.

In the semicontinuous processes, particles are formed over the entire duration of the polymerization process,[20] so that the surfactant concentration influences the particle number evolution during the polymerization. Figure 7 shows the evolution of N_p versus the total conversion. The curves can be divided into three regions: The first one is until about 40% conversion and shows an increase of the number of particles. The second one, from 40 to about 70% conversion, shows the stability of the number of particles. The last region, above 70% conversion, shows a decrease in the number of particles, which could be related to a secondary coagulation. This coagulation is relatively high, if the surfactant concentration is below the CMC value. It was also found that the particle-size distribution is clearly affected by the surfactant concentration. Below the CMC, a PDI of 0.04 was obtained, which is smaller than those found above the CMC (PDI = 0.125). We can assume that the increase of the
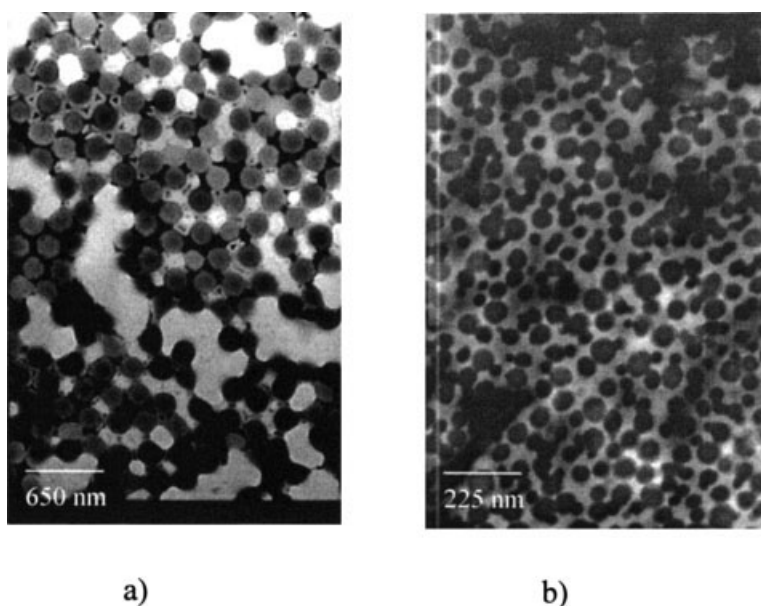

Figure 8 TEM micrographs of two sugar latexes formed at two surfactant concentrations: (a) [SDS] < CMC (1 cm = 630 nm); (b) [SDS] > CMC (1 cm = 225 nm).
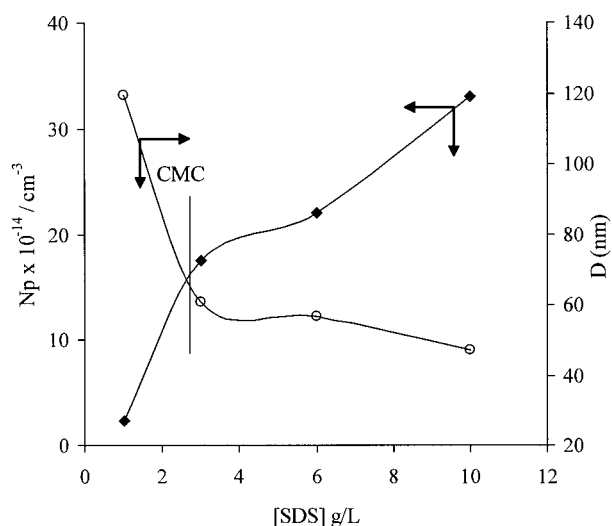
Figure 9 Relationship among [SDS], D, and N_p of the final latexes.

Figure 10 Particle size–time curves of semicontinuous copolymerization of 3-MDG/BA. The concentration of the surfactants SDS, SLES, NOS10, and HV25 was 5 g/L, and all other constituents were maintained as described in Table I.

surfactant concentration leads to a broader particle-size distribution. This is due to the ability of the surfactant to stabilize the newly formed particles in the last period of the reaction. The TEM micrographs of two sugar latexes prepared with different surfactant concentrations show that, below the CMC [Fig. 8(a)], the particles are nearly monodisperse (PDI = 0.04) and, above the CMC [Fig. 8(b)], the particles are polydisperse (PDI = 0.125).

The relationship between the surfactant concentration and the final particle size as well as the final number of particles is illustrated in Figure 9. We can see that N_p increases and, simultaneously, the particle size (D) decreases, with an increasing SDS concentration. The curve of N_p is characteristic for monomers, which have low water solubility. Interestingly, N_p increases more rapidly with an SDS concentration above the CMC, due to the higher solubility of both hydrophobic monomers in the surfactant micelles, in which more favorable interactions with the hydrocarbon core of the micelles take place.

Effect of the type of the surfactant

The type of surfactant has a great influence on the stability and the size of the particles. SDS, SLES, and NOS10, as anionic surfactants, with different chemical structures and molecular weights, as well as HV25 as a nonionic surfactant, were used to investigate their effect on the particle size of the sugar latexes. The polymerizations were carried out at the same surfactant concentration (5 g/L) and under starved conditions with a monomer-addition rate of 0.16 g/min. It was found that the type of surfactant did not influence the reaction rate. The instantaneous conversions reached a maximal value (more than 90%) after 15 min
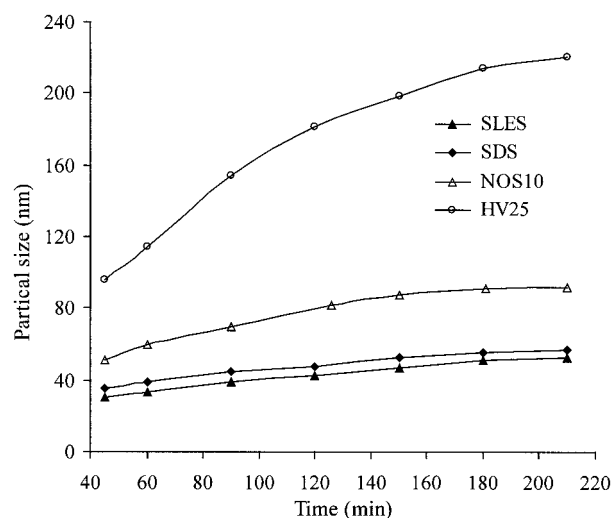
and remained constant. In all cases, a maximum total conversion, more than 99%, was obtained at the end of the reaction. Figure 10 shows the evolution of the particle size throughout the polymerization. By using SDS and SLES, the final particle sizes were relatively the same. NOS10 led to a larger particle size than in the cases of SDS and SLES. The larger particle size was obtained by using HV25. Similar behavior was found by Unzueta and Forcada in the case of seeded semicontinuous emulsion copolymerization of methyl methacrylate (MMA)/BA, using SDS and two nonionic surfactants, such as Brij35 (ICI) and Glytanox1001 (Glyco Iberia, Spain).[21]
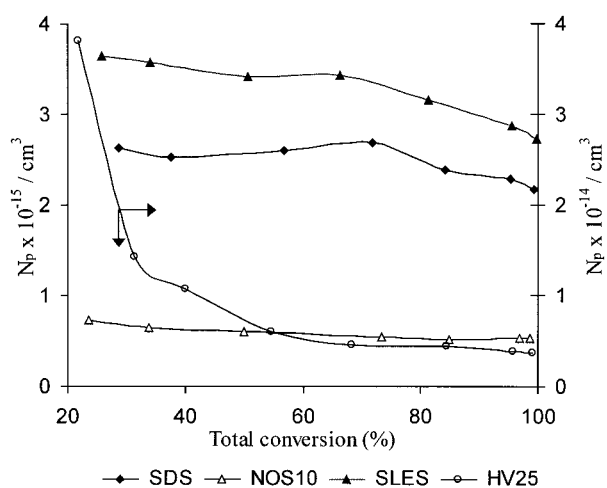

Figure 11 N_p against the total conversion for semicontinuous copolymerization of 3-MDG/BA. The concentration of the surfactants SDS, SLES, NOS10, and HV25 was 5 g/L, and all other constituents were maintained as described in Table I.

By using anionic surfactants, the numbers of particles are relatively stable during the reaction (Fig. 11). But in the case of HV25, in which the polymer particles are stabilized sterically, the number of particles decreased drastically until about 50–60% overall conversion and then remained relatively stable. To understand this behavior, let us first give an example for using HV25 as a nonionic surfactant in the batch emulsion copolymerization of MMA and BA.[22] It was found that the emulsion copolymerization of MMA/BA follows the classical theory of micellar nucleation. In comparison to SDS emulsion copolymerization, a higher polymerization rate, shorter nucleation stage, and complete conversion were obtained by using HV25 at a concentration of 5 g/L. Furthermore, by increasing the initiator concentration, N_p decreases during the steady-state period (phase II), which characterizes a polymerizing system, where the large number of particles, nucleated within a very short duration, are not stabilized enough by the nonionic surfactant to counteract the increase in the ionic strength. It is also conceivable that this high number of original particles may cause the burial of more HV25 surfactant inside themselves.

In this work, similar behaviors were found: In the semicontinuous process, the monomer-addition technique, the surfactant/monomer ratio at the beginning the reaction is very high, which leads to the production of a huge number of particles. During the polymerization, the monomer (polymer)/surfactant ratio increases and then the surfactant is not able to stabilize all of this number of particles, especially when using a nonionic surfactant, which may be buried inside the particles. So, this massive decrease in the particle numbers can be related to the coagulation mechanism,
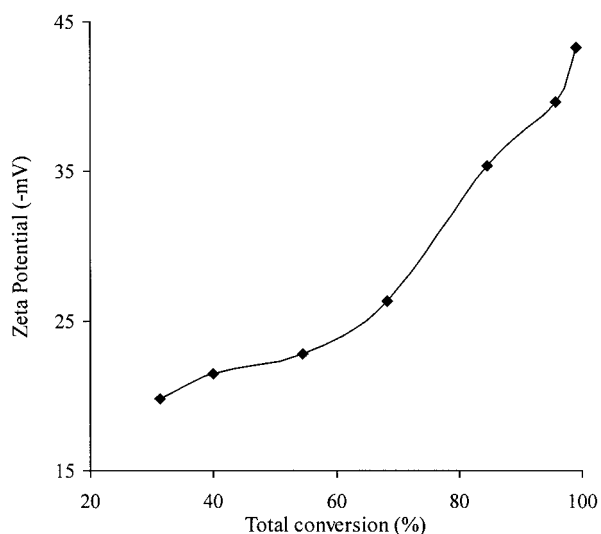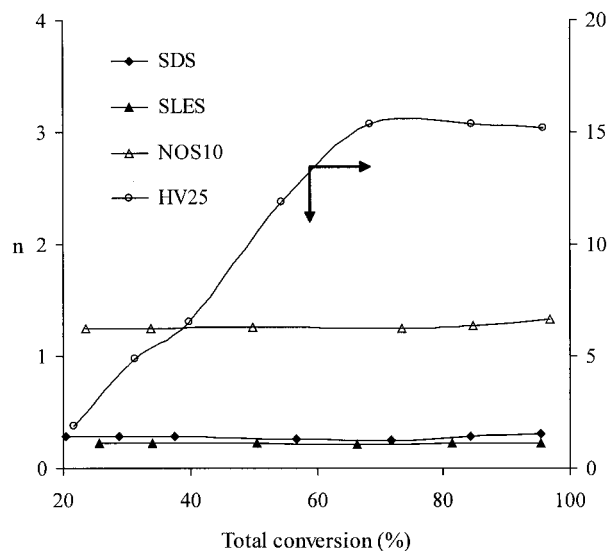

Figure 13 Effect of the type of surfactant on the total average number of radicals per particle ($\overline{n}$) during the polymerization. The initial composition of 3-MDG/BA was 35/65 mol.

by which the charge on the outer surface increased until it reached a state in which the surface charges were able to stabilize the particles. This sharp decrease in the number of particles was also mentioned by Fitch and Tsai[23] for the emulsion polymerization of MMA at a low surfactant concentration and in the total absence of a surfactant. It was suggested that this decrease can only happen by the aggregation of particles by coagulation, in which two charged particles undergo a Brownian collision, stick together, and fuse. As the coagulation progresses and as more oligoradicals are adsorbed, the surface charge density of the resulting particles increases, which, in turn, increases their surface electrical potential, leading to a greater mutual repulsion and reduction in the overall average rate of coagulation. In our case, it seems that the concentration of HV25 used was not high enough to ensure a complete steric stability of the polymer particles, so that coagulation took place and the number of particles decreased tremendously. As the polymerization progressed, the polymer particle surface was more and more charged, arising from the initiator-derived polymer end groups, which contribute to stabilize the particles ionically as well as sterically. As shown in Figure 12, the zeta potential of the particles stabilized with HV25 increases with an increasing total conversion. The increase in the zeta potential was not linear with the conversion. At the beginning of the polymerization, the evolution of the zeta potential was low until 50% of total conversion, then increased obviously to −38 mV at 85%, and, finally, slowly increased to −43 mV at about 99% of total conversion, which is enough to stabilize the polymer particles.

Figure 12 Zeta potential versus the total conversion for semicontinuous copolymerization of 3-MDG/BA; HV25 concentration was 5 g/L.

The average number of radicals per latex particle, which gives an indication of the reaction mechanism, was calculated according to the following eq. (5):

$$\bar{n} = R_p N_A / k_p [M]_p N_p \qquad (5)$$

where $\bar{n}$ is the average number of radicals per latex particle; R_p, the rate of polymerization (mol L^{-1} s^{-1}); k_p, the overall propagation reaction constant (L mol^{-1} s^{-1}); N_A, Avogadro's constant (mol^{-1}); $[M]_p$, the molar concentration of the monomer in the latex particles; and N_p, the total number of the particles per unit volume of the emulsion (L^{-1}). R_p and $[M]_p$ were determined experimentally and k_p was estimated as described in the literature.[24]

The propagation rate constants of 3-MDG and BA are 1265 and 240 L mol^{-1} s^{-1} and their reactivity ratios are 1.94 and 0.54, respectively. Figure 13 shows the variation of the calculated average number of radicals per latex particle versus the overall conversion, depending on the type of surfactant. From the evolution of the $\bar{n}$ values, two different behaviors were observed: (i) By using anionic surfactants, such as SDS and SLES, the average number of radicals per latex particle was approximately 0.3, which means that, in both cases, the polymerization follows the Smith–Ewart theory, case I. In the case of using SDS and SLES (containing two ethylene oxide units), the particle sizes were around 55 nm. With these small sizes, the probability of radical coupling reactions within the polymer particles is very high. The average number of radicals per particle remained approximately 0.3 throughout the polymerization. By using NOS10 (containing 10 units of ethylene oxide with a sulfate end group), the average value of radicals per particle changed and was found to be 1.3.
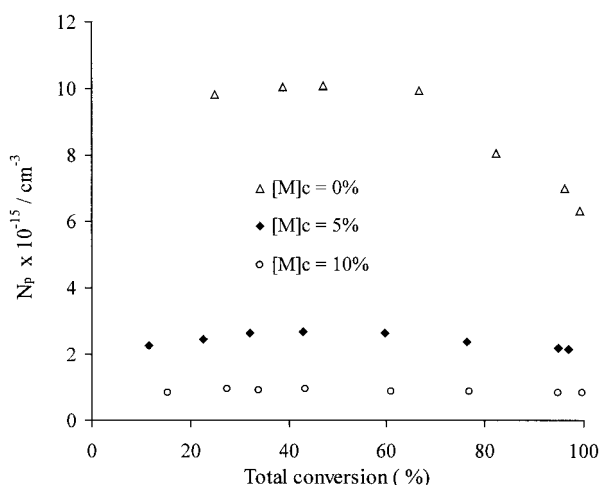

Figure 14 Effect of the precharge on the total number of particles' evolution during semicontinuous copolymerization of 3-MDG/BA. $[M]_c$ refers to the weight percent of the monomer mixture in the precharge, based on the total amount of monomers.

TABLE III
Effect of the Precharge in the Semicontinuous Emulsion Polymerization on the Final Particle Sizes and the PDI

Monomer in the precharge (wt %)	Particle size (nm)		PDI
	Calculated	Found	
0	—	39.7	0.128
5	55.5	56.6	0.097
10	81.0	80.8	0.064

This could be due to a lower surface charge density, leading to a secondary limited coagulation. (ii) By using the nonionic surfactant HV25, containing 25 units of ethylene oxide, the particle sizes are larger than 60 nm and appear to contain more than one radical. The n^- value increased at a conversion interval between 20 and 70% and then remained constant at the end of the polymerization, reaching an average value of 15. This behavior is tightly related to the evolution of D and N_p, indicating that coagulation took place as the polymerization proceeded. So, the evolution of $\bar{n}$ (obviously different from 0.5) indicates that the copolymerization could, rather, follow the Smith–Ewart kinetic, case III.

Effect of seed stage on the particle growth

In the batch process, the particle size can be controlled by varying the concentration of the surfactant and the initiator, since the control of the particle-size distribution is quite difficult. The semicontinuous process offers the opportunity to control both, the particle size and its distribution, at a given surfactant and/or initiator concentration. When semicontinuous processes are performed without adding any monomer at the beginning of the reaction, they commonly suffer from the change of the particle number during the polymerization. So, it was recommended to add about 5–10% of the total monomer at the beginning of the reaction and allow its conversion being completed before starting to add the rest of the monomer(s). This precharge polymerization can be considered as a seed stage. The main aim of this step is to separate the nucleation and the particle-growth phases to enhance the colloidal stability. The time of this stage must be short to exclude the possibility of forming new particles during the polymerization.[25] As shown in Figure 14, without a seed stage, that is, without adding any monomer at the beginning of the reaction, the number of particles decreases at about 60% conversion, which indicates a secondary coagulation. Contrarily, when 5 or 10% of the total monomers was added in the charge, N_p remained constant throughout the polymerization.

Furthermore, the PDI was narrower as the precharge amount increased. The final particle size can be

TABLE IV
Effect of the Initial Monomer Feed Composition in the Semicontinuous Emulsion Polymerization of 3-MDG/BA on the Final Particle Sizes (D), the PDI, the Total Number of Particles (N_p), and the Glass Transition Temperature (T_g)

3-MDG[a] (mol %)	Conversion (wt %)		3-MDG in copolymer[b]		D (nm)	$N_p \times 10^{-15}$ (cm^{-3})	PDI	T_g (°C)
20	40.1	99.7	0.20	0.21	63.5	1.44	0.064	14
35	38.6	99.6	0.35	0.36	63	1.58	0.080	43
50	41.0	99.6	0.50	0.51	61	1.76	0.097	69
65	40.8	99.8	0.66	0.65	58	1.99	0.129	99

[a] An SDS concentration of 5 g/L was used and 10% of the monomers was added at the outset of the polymerization.
[b] The sugar content in copolymer was determined from ^{1}H NMR.

predicted, in the case of the use of the seed stage, according to the following eq. (6)[26]:

$$Dp = Ds[(Ws + W_1)/Ws]^{1/3} \qquad (6)$$

where Dp is projected diameter of the final particle (nm); Ds, the seed particle size (nm); Ws, the seed polymer weight fraction; and W_1, the weight fraction of the polymer to be added on.

The calculated values from the experimental data show that this equation is applicable to our system, as can be seen in Table III.

Effect of the initial monomer composition

The reactivity ratios of 3-MDG and BA determined previously from the batch emulsion polymerization at 70°C were found to be $r_{3\text{-MDG}} = 1.94$ and $r_{BA} = 0.54$, respectively.[14] Copolymers made by batch polymerization exhibit, generally, a high composition drift, due to the difference in the reactivity ratios. The copolymers synthesized by the semicontinuous process under starved-feed conditions have compositions very close to the initial monomer feed compositions, because the monomer mixture completely polymerizes immediately upon entering the reactor. The production of latexes with a homogeneous copolymer composition improved the latex properties such as film formation. We followed the copolymer composition during and after the polymerization. It was found that the copolymer compositions were relatively similar to the initial monomer feed compositions. Furthermore, the variation of the 3-MDG ratio in the initial monomer feed has little influence on the particle size, particle-size distribution, and the number of particles of the final latexes. As can be seen in Table IV, increasing the 3-MDG ratio from 20 to 65% in the feed led to a slight decrease of the particle size from 63.5 to 58 nm and, consequently, increased the total number of particles from 1.44 to 1.99 × 10^{15} per cm^3. The lowering of the particle size by increasing the sugar content may be related to the high density of 3-MDG (1.19 g/L) in comparison to the density of BA (0.89 g/L). It was also found that the polydispersity and the T_g's of the final

latexes increase with an increasing 3-MDG content in the feed. This may be related to the rigidity of the sugar monomer and to the softness of BA. At a low sugar content, due to the low T_g of the copolymer, the newly formed particles are soft and coagulate and, consequently, the particle-size distribution widens. Contrarily, at a high sugar content, the T_g of the copolymer increased and the particles became harder, which hindered the Brownian collision, especially if the T_g was higher than the polymerization temperature. The feeding of the monomer mixtures with the content of more than 70 mol % of 3-MDG was not possible, due to the recrystallization of 3-MDG at room temperature. So, the monomer feed-addition technique could be suitable for the 3-MDG/BA system at a high 3-MDG content, if the temperature of the initial monomer mixture is maintained about 40–45°C.

Effect of solid content on the latex stability

The production of latexes with a solid content over 50% is actually an industrial requirement. The syntheses of sugar latexes with high solid contents were investigated at 70°C using different surfactant types at various concentrations. As shown in Table V, the preparation of sugar latex with about a 40% solid content using SDS as an ionic surfactant was carried out without any amount of coagulum. The coagulum (in weight percent) was determined by filtering a definite amount of latex through a cotton tissue sieve with a 0.24-mm pore size. Then, the coagulum was dried and weighted. It was not possible, by the monomer-addition technique, to prepare coagulum-free latex with a 50% solid content using anionic surfactant solely. Coagulum, 3.8%, was formed at the polymerization conditions reported in Table V. High solid-content sugar latexes (about 50%) were successfully synthesized using an equimolar mixture of an anionic and nonionic surfactant, such as SDS and HV25. At a surfactant concentration of more than 7.6%, based on the monomers, a very low percentage of coagulum (<1%) was observed. Contrarily, using a surfactant

| Solid content | Surfactant | | Conversion (wt %) | Coagulum (wt %) | D (nm) | PDI |
	Type	Concentration[a] (wt %)				
40	SDS	4.4	99.7	<0.5	73	0.190
50	SDS	4.4	99.5	3.8	76	0.183
50	SDS/HV25 (1/1)	1.2	98.9	6.5	128	0.156
50	SDS/HV25 (1/1)	7.6	99.3	<1	72	0.203

[a] Relative to monomers.

concentration of 1.2% based on the monomer, a latex with 6.5% coagulum was obtained. From these results, it can be assumed that increasing the surfactant concentration reduces the coagulum. In all cases, polydisperse latexes were obtained, as seen in Table V (PDI between 0.15 and 0.20).

CONCLUSIONS

Sugar latexes were prepared by semicontinuous emulsion copolymerization of 3-MDG and BA at 70°C, using the monomer feed-addition technique. Three pertinent parameters were found to play an important role on the kinetic behavior and on the colloidal and physical properties of the polymer latexes: (i) the monomer-addition rate, (ii) the type of the surfactant, and (iii) the concentration of the surfactant. The behavior of the sugar methacrylate (3-MDG) in the emulsion polymerization is similar to that of the other hydrophobic alkyl acrylate monomers. It was found that, under starved-feed conditions, the number of particles (N_p), the polymerization rate (R_p), the average molecular weight ($\overline{M}_w$) and the MWD ($\overline{M}_w/\overline{M}_n$) are dependent on the monomer-addition rate (R_m). It was also found that the type and concentration of the surfactant did not show any influence on the polymerization rate. However, their effect on the colloidal properties is marked. N_p remains constant during the entire polymerization, when an ionic surfactant is used. In the case of a nonionic surfactant such as HV25, a lower end number of particles and a greater size were obtained. A typical relationship was found among the surfactant concentration, particle size, and number of particles. At a low SDS concentration (below the CMC), D is high and N_p is small. As the SDS concentration increases, D decreases and N_p increases, following the classical theory of Smith–Ewart for hydrophobic monomers. Furthermore, the use of a seed stage leads to a narrow particle-size distribution and allows the formation of latexes with a defined particle size. It was also found that the increase of 3-MDG in the initial monomer composition enhances the PDI of the latexes and the T_g of the end copolymer. Finally,

high solid content sugar latex was prepared with very low coagulum using a mixture of ionic and nonionic surfactants.

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