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Semicontinuous emulsion copolymerization of methyl methacrylate and n-butyl acrylate: 2. Effect of mixed emulsifiers in unseeded polymerization

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The unseeded semicontinuous emulsion copolymerization of methyl methacrylate and n-butyl acrylate using mixed surfactant systems (anionic SLS (sodium lauryl sulfate) and non-ionic Brij35) in a wide range of concentrations and at different SLS/Brij35 ratios (1/0, 1/1, 1/3, 1/9, 0/1) was studied. Two different kinetic behaviours led to reactor 'starved' conditions with single anionic or with mixed surfactant systems above a critical concentration, and reactor 'flooded' conditions with single non-ionic or with mixed surfactant systems at the lowest concentration. The use of mixed surfactant systems, compared to the use of SLS alone, led to a competitive effect between decrease in particle number due to the addition of Brij35 and increase in particle number due to the increase of the total concentration of emulsifier. Moreover, narrower particle-size distributions (*PSD*s) with larger average particle sizes were obtained with mixed surfactant systems than those obtained with single anionic systems. The *PSD*s at the early stages of reaction lost the positive skewness obtained in soapless emulsion copolymerization with the addition of emulsifier, SLS being more effective than Brij35. High total concentration of emulsifier led to broad *PSD*s.

(Keywords: emulsion copolymerization; mixed emulsifiers; particle size distribution)

INTRODUCTION

Many studies have been carried out on the stabilization effect of emulsifiers in emulsion copolymerization in batch reactors[1-5]. The operational flexibility of semicontinuous reactors requires that the effect of the emulsifier system in semicontinuous operation conditions be studied. In these reactors, the kinetics of the process must be controlled by adjusting the operating conditions, above all, the reactant feeds. In addition, the effect of the emulsifier system on the kinetic behaviour of the process can determine the production conditions. The effect of the emulsifier system on the colloidal properties of the latex (colloidal stability, rheological properties, etc.) is fundamental to ensure problem-free production of good latexes.

The effect of the concentration and type of the surfactant system using mixtures of non-ionic and anionic emulsifiers in seeded semicontinuous emulsion copolymerization was studied in a previous paper[6]. The aim of this work is to study the effect of the concentration and type of the surfactant system on kinetic features (conversion, copolymer composition) and colloidal characteristics (mean particle diameter and particle-size distribution) in unseeded semicontinuous emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BuA). Unseeded semicontinuous emulsion copolymerization reactions were carried out in order to study the effect of the nature and concentration of the surfactant system on the nucleation process and on the growth and coagulation of polymer particles.

EXPERIMENTAL

Methyl methacrylate (MMA) and butyl acrylate (BuA) monomers were distilled under reduced nitrogen pressure. All other materials were used as received. Potassium persulfate ($K_2S_2O_8$, Merck) and sodium dihydrogenphosphate ($NaH_2PO_4 \cdot H_2O$, Merck) were used as initiator and buffer, respectively. The surfactants used were sodium lauryl sulfate (SLS, Merck) and polyethylene oxide lauryl ether (Brij35, ICI). Deionized water was used throughout.

Polymerizations were carried out in a 1 litre glass reactor fitted with a reflux condenser, stainless-steel stirrer, sampling device, nitrogen inlet and a feed inlet tube.

The semicontinuous emulsion copolymerizations were carried out using the recipes given in *Table 1*. The initial charge in the reactor was the surfactant or mixed surfactant system (25 wt% of the total surfactant amount in the recipe), buffer and initiator (42 wt% of the total initiator amount in the recipe) and water. The

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Table 1 Recipe used for the semicontinuous emulsion copolymerizations (the ratio of emulsifier in the initial charge and in stream 1 was 25/75 in all the runs)

Reactant	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
DDI water	97	450	
MMA			132
BuA	–	–	168
$K_2S_2O_8$	0.126	0.174	
$NaH_2PO_4 \cdot H_2O$	0.126	0.174	
Emulsifier	Variable	Variable	

Table 2 Anionic/non-ionic weight ratios and SLS amount in the initial charge

	Initial amount of SLS (g)			
SLS/Brij35	1.125	0.388	0.097	0.039
1/0	E27	E39	E44	E49
1/1	E34	E41	E46	E51
1/3	E37	E42	E47	E52
1/9	E38	E43	E48	E53
0/1	E32	E40	E45	E50
Soapless	E54			

feed was divided into two streams. The first was a solution of initiator, surfactant or surfactant system and buffer in water, and the second was a mixture of both monomers in the required ratio. The monomer and aqueous feeds were calculated to finish the addition in 5.5 h. Subsequently, the polymerization was continued in batch for 1 h.

Twenty-one runs were carried out to investigate the effect of the type and amount of surfactant on the overall polymerization features and colloidal characteristics, namely average particle diameters and particle-size distributions. Run E54 was a soapless emulsion copolymerization carried out using the recipe shown in *Table 1*.

In *Table 2* the experimental conditions used to carry out the different runs are shown. The runs were designed in order to establish the effect of the addition of the non-ionic emulsifier to a recipe with a constant amount of anionic emulsifier. This was made at different anionic emulsifier concentrations and non-ionic emulsifier added was proportional to those amounts. The runs shown in *Table 2* were divided into four amount levels of SLS in the initial charge (1.125, 0.388, 0.097 and 0.039 g) and, at each level, five SLS/Brij35 weight ratios (1/0, 1/1, 1/3, 1/9, 0/1). In all runs the amount of emulsifier in the feed was proportional to the emulsifier in the initial charge, both in quantity (the emulsifier of the initial charge was always 25% of the total emulsifier used in each run) and in composition (the same SLS/Brij35 ratio).

In *Table 3*, the runs carried out using different SLS/Brij35 ratios and at different concentrations, both in the initial charge and in the feed, are shown. In this table, the run number, the amount of SLS, Brij35 and the total emulsifier in the initial charge in grams, SLS/Brij35 ratio, final overall conversion (X_T), reaction time (t, min) (feeding time was 330 min in all the runs), particle volume-average diameter measured using TEM (d_v, nm), total particle number (N_p) and polydispersity index (*PDI*) are listed for each run. The methods and calculations used to obtain the experimental data were described in a previous paper[6].

Table 3 Emulsifier amount in the initial charge, SLS/Brij35 ratio, overall conversion (X_T), reaction time (t), volume-average diameter (d_v), particle number (N_p) and polydispersity index (*PDI*) obtained

	Emulsifier amount (g)								
Run	SLS	Brij35	Total	SLS/Brij35	X_T (%)	t (min)	d_v (TEM) (nm)	N_p (TEM)	*PDI*
E27	1.125	0.0	1.125	1/0	99	390	112	3.5×10^{17}	1.200
E34	1.125	1.125	2.250	1/1	98	390	137	1.9×10^{17}	1.190
E37	1.125	3.375	4.500	1/3	100	390	93	6.3×10^{17}	1.280
E38	1.125	10.125	11.25	1/9	99	390	84	8.4×10^{17}	1.376
E32	0.0	1.125	1.125	0/1	64	390	357	7.2×10^{15}	1.016
E39	0.388	0.0	0.388	1/0	100	390	117	3.2×10^{17}	1.163
E41	0.388	0.388	0.776	1/1	99	390	138	1.9×10^{17}	1.235
E42	0.388	1.164	1.552	1/3	99	390	140	1.8×10^{17}	1.184
E43	0.388	3.492	3.880	1/9	97	390	87	7.4×10^{17}	1.092
E40	0.0	0.388	0.388	0/1	65	300	588	1.6×10^{15}	1.025
E44	0.097	0.0	0.097	1/0	99	390	384	8.8×10^{15}	1.032
E46	0.097	0.097	0.194	1/1	81	390	293	1.6×10^{16}	1.055
E47	0.097	0.291	0.388	1/3	95	390	305	1.7×10^{16}	1.025
E48	0.097	0.873	0.970	1/9	95	390	257	2.8×10^{16}	1.097
E45	0.0	0.097	0.097	0/1	43	390	365	4.5×10^{15}	1.021
E49	0.039	0.0	0.039	1/0	82	585	579	2.1×10^{15}	1.020
E51	0.039	0.039	0.078	1/1	55	450	432	3.4×10^{15}	1.013
E52	0.039	0.117	0.156	1/3	33	450	321	5.0×10^{15}	1.024
E53	0.039	0.351	0.390	1/9	72	328	305	1.3×10^{16}	1.076
E50	0.0	0.039	0.039	0/1	42	450	527	1.4×10^{15}	1.016

RESULTS AND DISCUSSION

Kinetic features

In *Figures 1* and *2*, the evolution of the instantaneous conversion with time for the reactions carried out at SLS/Brij35 ratios of 1/0 and 0/1, respectively, in both the initial charge and in the feed are shown.

Instantaneous conversion is defined as the ratio of the polymer present in the reactor to the monomer fed into the reactor up to that time. Overall conversion is defined as the ratio of the polymer present in the reactor to the total monomer used in the recipe.

In each figure, the effect of the total emulsifier amount for the different SLS/Brij35 ratios is shown. The results obtained show that the kinetic behaviour of the system is strongly influenced by the nature and amount of the emulsifier used in the recipe.

In *Figure 1*, where SLS/Brij35 = 1/0, a reduction in the polymerization rate with a decrease in the amount of SLS is observed. Moreover, the lower the emulsifier amount, the later monomer-starved conditions were achieved and, in the case of the lowest emulsifier amount, the later the reaction started.

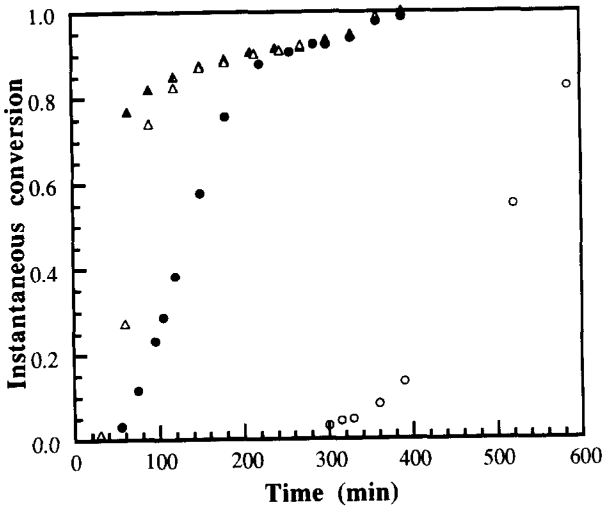

Figure 1 Time evolution of the instantaneous conversion for the reactions carried out with SLS/Brij35 ratio = 1/0. Legend (run, amount in grams of SLS, Brij35 and total amount in the initial charge): (▲) E27, 1.125, 0.0, 1.125; (△) E39, 0.388, 0.0, 0.388; (●) E44, 0.097, 0.0, 0.097; (○) E49, 0.039, 0.0, 0.039

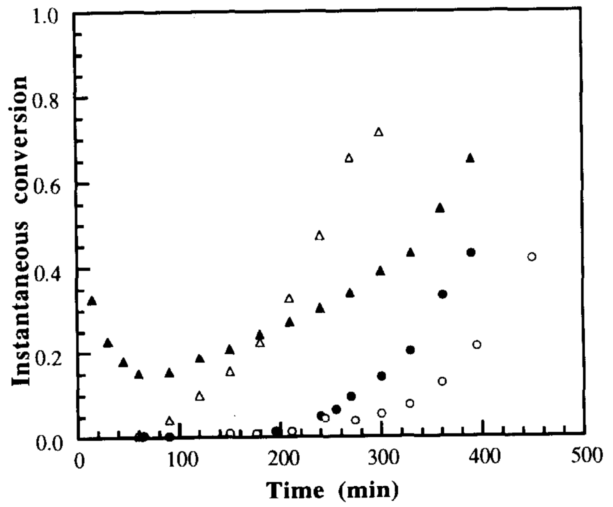

Figure 2 Time evolution of the instantaneous conversion for the reactions carried out with SLS/Brij35 ratio = 0/1. Legend (run, amount in grams of SLS, Brij35 and total amount in the initial charge): (▲) E32, 0.0, 1.125, 1.125; (△) E40, 0.0, 0.388, 0.388; (●) E45, 0.0, 0.097, 0.097; (○) E50, 0.0, 0.039, 0.039

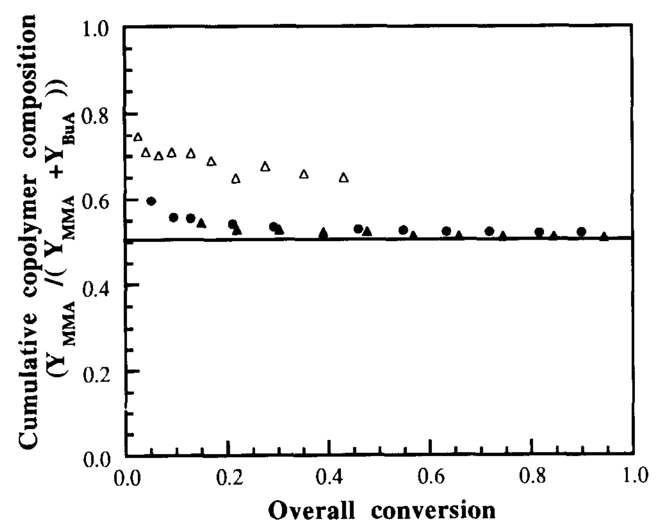

Figure 3 Cumulative copolymer composition with overall conversion, for the reactions carried out with SLS/Brij35 = 1/0, 0/1 and 1/1. Legend (run, amount in grams of SLS, Brij35 and total amount in the initial charge): (▲) E27, 1.125, 0.0, 1.125; (△) E32, 0.0, 0.125, 1.125; (●) E44, 1.125, 1.125, 2.250

In *Figure 2*, SLS/Brij35 = 0/1, the kinetic evolution of the reactions carried out using non-ionic Brij35 alone reveal a high monomer concentration in the reactor during the process and reaction conditions far from monomer-starved conditions. As a consequence, the instantaneous conversion and polymerization rate were lower than in the case of starved conditions. In this figure, processes had high inhibition periods, these being greater with the lower amounts of emulsifier.

The evolution of the instantaneous conversion in reactions carried out with mixtures of SLS and Brij35 followed the same behaviour as shown in *Figure 1*. In these cases, the effect of the emulsifier on the reaction kinetics is controlled by the total amount of emulsifier, but not by the SLS/Brij35 ratio.

The kinetic behaviour shown in *Figures 1* and *2* has a direct effect on the copolymer composition obtained. In *Figure 3* the evolution of the cumulative copolymer composition for the reactions carried out with SLS/Brij35 ratios of 1/0, 0/1 and 1/1 and at initial emulsifier levels of 1.125, 1.125 and 2.25 g (runs E27, E32 and E34) is shown. The cumulative composition of the latex produced in conditions far from monomer-starved conditions (run E32) was not homogeneous with time and did not fit the desired composition (MMA/BuA = 50/50 molar). On the other hand, the copolymerization under starved conditions ensured that the desired homogeneous copolymer composition with time was achieved (runs E27 and E34). Hence, the small deviations measured at the beginning of the reaction were a consequence of the initial inhibition period, when some monomer accumulated in the reactor. These results indicate that the effect of emulsifier on the kinetic behaviour of the process had a direct effect on the copolymer composition.

The data shown in *Figures 1* and *2* indicate the

Table 4 Values of the parameters used in the calculations of n

Parameter[a]	Units	Value	Ref.
K_{pAA}	$cm^3 mol^{-1} s^{-1}$	9.20×10^5	15
K_{pBB}	$cm^3 mol^{-1} s^{-1}$	2.47×10^5	16
r_A		2.64	17
r_B		0.315	17
$[MMA]_w/[MMA]_p$		2.32×10^{-2}	18
$[MMA]_w/[MMA]_o$		1.69×10^{-2}	18
$[BuA]_w/[BuA]_p$		2.18×10^{-3}	18
$[BuA]_w/[BuA]_o$		1.42×10^{-3}	18

[a] A = MMA, B = BuA; w = water, p = particles, o = droplets

existence of two main but different trends. The first, namely 'starved state', is characterized by moderate inhibition periods at the beginning of the reactions and a sharp increase in polymerization rate to achieve the 'steady state'[7] of about 0.8–0.9 instantaneous conversion. The average particle diameters in this case are between 100 and 200 nm, or smaller in the case of runs more concentrated in emulsifier. The reactions carried out with single anionic emulsifier with initial amount higher than 0.097 g and with mixed systems of anionic and non-ionic emulsifiers (except the cases of the lowest concentrations for the ratios 1/1 and 1/3) showed these 'starved' conditions (see *Table 3*).

The second behaviour, namely 'flooded state', is characterized by large inhibition periods, often close to the total feeding time, high monomer concentration in the reactor and low polymerization rates. In this case, copolymer composition is far from the composition of the feed, and average particle diameters are greater than in the 'starved' reactions (from 300 to 600 nm). Reactions carried out using non-ionic emulsifier alone or mixed emulsifier systems at the lowest concentration limit showed this behaviour (see *Table 3*). The 'flooded' state is characterized by a polymerization rate lower than monomer feeding rate[8].

In order to define the kinetic behaviour of both cases, namely 'starved' and 'flooded' cases, the polymerization rate and the average radical number per particle ($\bar{n}$) were calculated using the method described by Masa *et al.*[9]. In *Table 4* the kinetic parameters used in the calculations are summarized. The average radical number per particle ($\bar{n}$) can be calculated from the polymerization rate using this expression:

$$n = \frac{R_p}{\Delta_p N_p} \qquad (1)$$

Here R_p is the polymerization rate (mol min^{-1}), N_p is the total particle number in the reactor and Δ_p is calculated as follows:

$$\Delta_p = (k_{pAA} P_A^p + k_{pBA} P_B^p)[A]_p + (k_{pBB} P_B^p + k_{pAB} P_A^p)[B]_p \qquad (2)$$

where $[A]_p$ and $[B]_p$ are the concentrations of monomers in the particles, k_{pij} are the propagation constants and P_i^p are probability constants defined by Forcada *et al.*[10].

The polymerization rate, in a semicontinuous reactor, is calculated as:

$$R_p = (Ft + M_0)\frac{dX_i}{dt} + FX_i \qquad (3)$$

where F is the feed rate (mol min^{-1}), t is the time (min), M_0 is the initial monomer charged in the reactor (mol) and X_i is the instantaneous conversion.

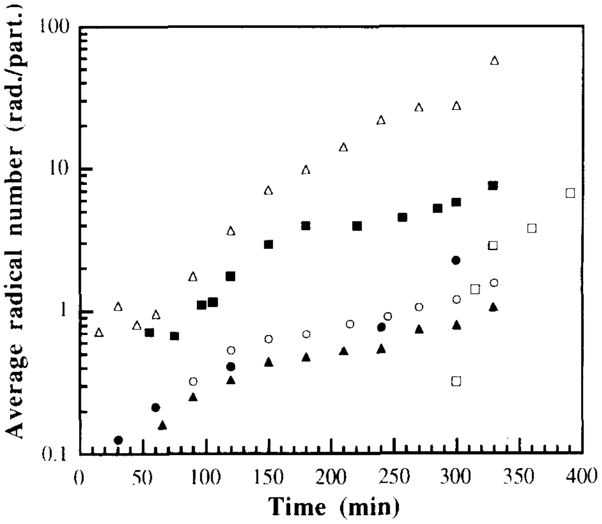

Figure 4 Time evolution of the average radical number per particle ($\bar{n}$). Legend (run, SLS/Brij35 and SLS amount in the initial charge in grams): (▲) E37, 1/0, 1.125; (△) E32, 0/1, 1.125; (●) E34, 1/1, 1.125; (○) E39, 1/0, 0.388; (■) E44, 1/0, 0.097; (□) E49, 1/0, 0.039

The monomer concentrations in the different phases were calculated from the partition constants, using the values listed in *Table 4*.

In *Figure 4*, the evolution of $\bar{n}$ for reactions with both types of kinetics, 'starved' (runs E27, E34, E39 and E44) and 'flooded' (runs E32 and E49), is shown. In the 'starved' cases, the average number of radicals per particle increases slightly during the reaction, starting from a value below 0.5 and achieving an end value greater than 1. However, in the 'flooded' cases, $\bar{n}$ increases sharply during the reaction from values greater than 1 to tens. This is clearly Smith–Ewart case III kinetics ($\bar{n} \gg 0.5$). Run E44 showed an intermediate behaviour between both cases, with an average radical number per particle higher than that obtained in 'starved' runs. In run E44 it must be taken into account that this reaction achieved monomer-starved conditions later than the other 'starved' runs, and, from this point of view, this run had an intermediate kinetic behaviour between 'starved' and 'flooded' runs. The average radical number was lower in reactions carried out in 'starved' conditions than that obtained in 'flooded' conditions due to the larger size and lower total number of particles in the 'flooded' reactions.

In *Figure 5* the evolution of the product of the average radical number per particle and the total number of particles ($\bar{n}N_p$) is shown. The total radical number in particles was higher in runs carried out under 'starved' conditions, the highest being run E39 (SLS/Brij35 = 1/0 and an initial amount of SLS of 0.388 g), than in runs carried out under 'flooded' conditions. This result could indicate that aqueous-phase termination was not negligible in the kinetic behaviour of the process and had a greater effect in 'flooded' reactions (diminishing the total number of radicals in particles).

In *Figure 6*, the evolution of the polymerization rate for the runs E27 and E39 (starved conditions) and E32 and E49 (flooded conditions) compared with the monomer feed rate ($Q_m = 0.008$ mol min^{-1}) is shown. Under starved conditions, the polymerization rate equals the feed rate, while under flooded conditions it is lower.

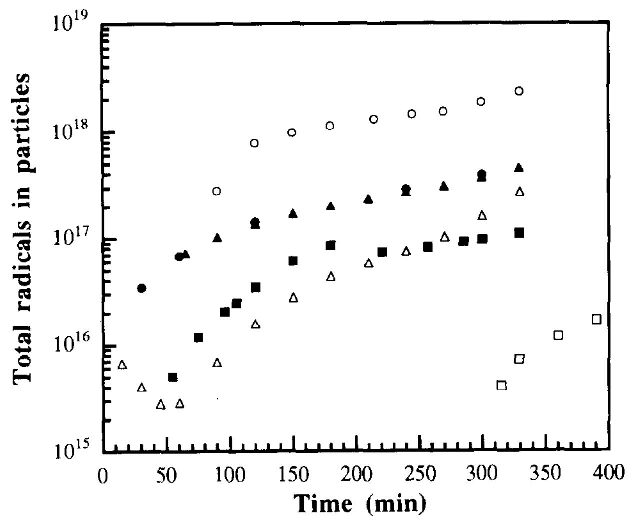

Figure 5 Time evolution of the total number of radicals in particles ($\bar{n}N_p$). Legend (run, SLS/Brij35 and SLS amount in the initial charge in grams): (▲) E27, 1/0, 1.125; (△) E32, 0/1, 1.125; (●) E34, 1/1, 1.125; (○)E39, 1/0, 0.388; (■) E44, 1/0, 0.097; (□) E49, 1/0, 0.039

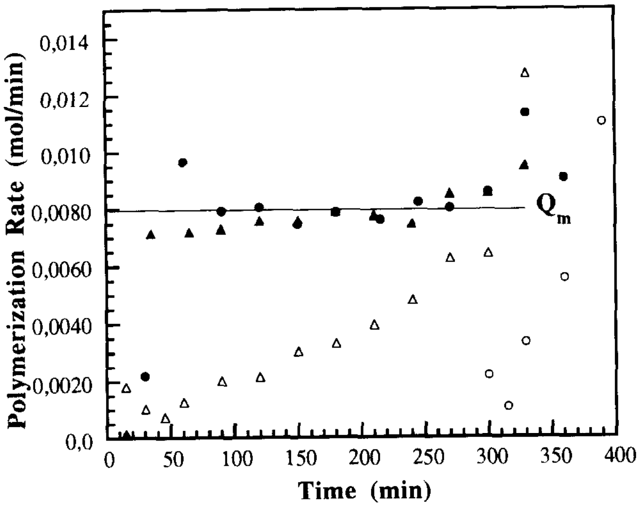

Figure 6 Polymerization rate compared with monomer feed rate Q_m for various runs: (▲) E27, (△) E32, (●) E39, (○) E49

Colloidal features

The runs were designed in order to establish the effect of the addition of the non-ionic emulsifier to a recipe with constant anionic emulsifier level. This was carried out at different anionic emulsifier concentrations and the mass of non-ionic emulsifier added was proportional to that amount. The runs, shown in *Table 3*, were divided into four amounts of SLS in the initial charge (1.125, 0.388, 0.097 and 0.039 g) and, at each level, five SLS/Brij35 weight ratios (1/0, 1/1, 1/3, 1/9, 0/1) were used. In these runs, the general trend was that the increase in the total emulsifier amount at any SLS/Brij35 ratio led to a decrease in average diameter and subsequent increase in particle number in the reactor (see *Table 3*).

In the reactions carried out with the initial amount of SLS of 1.125 g, the increase of the emulsifier amount from run E27 to E34 (decrease in the SLS/Brij35 ratio from 1/0 to 1/1) led to an increase in the average particle diameter obtained, although at higher Brij35 amounts (runs E37 and E38) the increase in emulsifier mass led to the expected decrease in average diameter. On the other hand, the substitution of the anionic emulsifier by the non-ionic one (runs E27 and E32) produced larger particles and a decrease in particle number close to two orders of magnitude. The polydispersity index (*PDI*) was lowest at the SLS/Brij35 ratio of 0/1. Moreover, in the runs with anionic emulsifier in the recipe, the lowest *PDI* was obtained in run E34, in which particle diameter increased with emulsifier amount. The higher the total emulsifier amount, the larger was the *PDI*.

In the series of reactions carried out with an initial amount of SLS of 0.388 g, an increase in the particle average diameter was found again with increasing total amount of emulsifier (decreasing the SLS/Brij35 ratio). The SLS/Brij35 ratio range at which this non-expected behaviour took place covered from 1/1 to 1/3 runs (runs E41 and E42). In this case, the polydispersity index was the highest in this range. In run E40, in which non-ionic emulsifier was used alone, the largest particle average diameters were obtained and the particle number was two orders of magnitude lower than in the runs with SLS in the recipe.

In the third series of reactions shown in *Table 3* the initial amount of SLS was 0.097 g. Average particle diameters obtained in this series were larger than those obtained at higher concentrations of SLS in the initial charge. Under these conditions, the increase of the total emulsifier amount (decrease of the SLS/Brij35 ratio) led to the expected decrease in particle size and increase in total particle number. The polydispersity index was greatest at the highest emulsifier level (lower SLS/Brij35 ratio) but, however, did not decrease monotonically with emulsifier concentration. The particle number produced in the reactions carried out using Brij35 alone is the lowest, but its value is closer to the number of particles obtained using single anionic emulsifier than to that found in runs carried out at higher SLS amounts.

Table 3 shows the results of the series of reactions in which the initial amount of SLS was 0.039 g. In the case of using single anionic or non-ionic emulsifiers (runs E49 and E50) average particle diameters were higher and showed less variation than those obtained at higher SLS concentrations. The total particle number was lowest when non-ionic emulsifier was used alone. In mixed surfactant systems, the particle number increased with the addition of Brij35 (decrease of SLS/Brij35 ratio) due to the increase in the total quantity of emulsifier. Polydispersity indices were low (in both single and mixed emulsifier systems) and increased with emulsifier concentration from 1.013 to 1.076.

In *Figure 7*, the total particle number obtained *versus* the SLS amount used in the initial charge for the different SLS/Brij35 ratios is shown. In the runs carried out with 1/0, 1/1 and 1/9 ratios, particle numbers depended strongly on emulsifier concentration at SLS amounts lower than 0.388 g and N_p was constant at higher concentrations. In the case of the SLS/Brij35 ratio of 1/3, the number of particles did not achieve a constant value over the concentration range studied.

In *Figure 8* the total particle numbers obtained at the end of each run as a function of the weight fraction of the non-ionic emulsifier in the emulsifier mixture, for different initial amounts of SLS, are shown. In the reactions carried out at lower SLS amount in the initial charge (0.039 and 0.097 g), the effect of the increase of the total emulsifier amount was more important than the

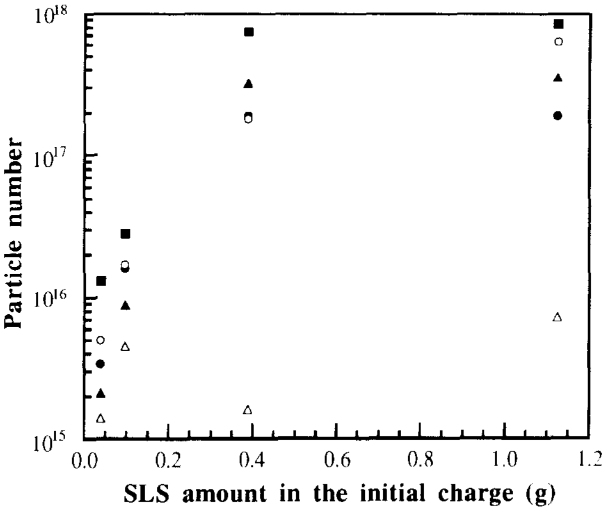

Figure 7 Total particle number *versus* the amount of SLS in the initial charge for the different SLS/Brij35 ratios: (▲) 1/0, (●) 1/1, (○) 1/3, (■) 1/9, (△) 0/1

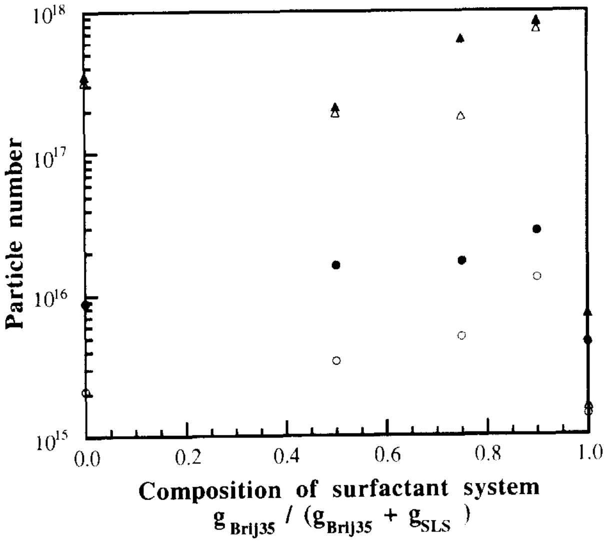

Figure 8 Total particle number *versus* the composition of the surfactant system for the different initial SLS amounts (g): (▲) 1.125, (△) 0.388, (●) 0.097, (○) 0.039

effect of the addition of non-ionic emulsifier (increase of the Brij35 fraction in the surfactant system) and, subsequently, the total particle number increased with increasing non-ionic emulsifier in the recipe. On the other hand, in the reactions carried out at higher SLS amounts in the initial charge (0.388 and 1.125 g), at low fractions of Brij35 in the surfactant system, the effect of the addition of the non-ionic emulsifier was more important than the effect of the increase of total emulsifier concentration and, hence, particle number decreased in the range of Brij35 fraction between 0.5 and 0.75. At higher Brij35 proportions in the mixture, 0.9, the effect of the increase of the total amount of emulsifier led to an increase in the total number of particles. The particle number produced in the reactions carried out using only Brij35 was the lowest in all the cases. These reactions, carried out with a single emulsifier system of Brij35, showed a kinetic behaviour drastically different from the runs that included SLS in their recipe, as indicated above, and this was also confirmed in the study of the colloidal features of each run.

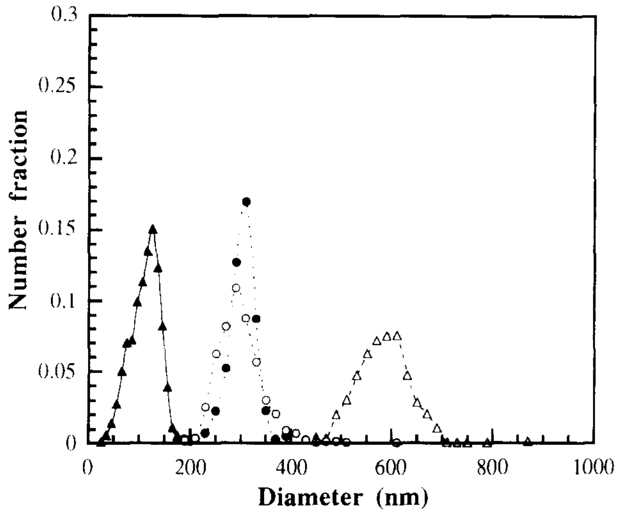

Figure 9 *PSD*s measured at the end of the reaction in runs carried out with an emulsifier total amount in the initial charge of 0.388 g for the different SLS/Brij35 ratios. Legend (run, SLS/Brij35): (▲) E39, 1/0; (●) E47, 1/3; (○) E53, 1/9; (△) E40, 0/1

In order to establish the effect of the emulsifier mixture composition on the *PSD* obtained and, subsequently, on the average particle size and on the *PDI*, runs carried out at the same total emulsifier amount of 0.388 g in the initial charge are compared. These runs are E39, E40, E47 and E53 (see *Table 3*). The substitution of part of the anionic emulsifier by the non-ionic one led to an increase in the average particle size and subsequent decrease in particle number. The *PDI* was lowest at SLS/Brij35 = 1/3 and 0/1. In *Figure 9* the *PSD*s obtained at the end of this set of reactions are shown. In this figure, a narrower *PSD* in the case of the use of mixed surfactants (the narrowest at SLS/Brij35 = 1/3) is observed. The relatively high value of *PDI* for run E53 (SLS/Brij35 = 1/9) compared to the *PDI* obtained in run E47 (SLS/Brij35 = 1/3) (*Table 3*) is due to the contribution of the tail of large particles, while the main part of the distribution is clearly narrower than the latext obtained in run E40 (SLS/Brij35 = 0/1).

Nucleation of particles and PSD *evolution*

In the HUFT model[11,12], particle nucleation in emulsion polymerization is considered a dynamic process based on the precipitation of precursor particles from growing oligoradicals in the aqueous phase. The growth of these precursors by propagation or coagulation and their competitive capture by particles lead to the experimentally observed nucleation process. Recently, Giannetti[13] has modelled the evolution of the *PSD* as a function of the mechanism involved in the nucleation process.

The effect of the emulsifier system on the processes involved in particle nucleation is an important factor in determining the number of particles nucleated and their size in the final product. In this work, the evolution of particle-size distribution (*PSD*) at early stages of the reaction was studied in order to clarify the effect of the amount and the nature of the emulsifier system in the nucleation of polymer particles.

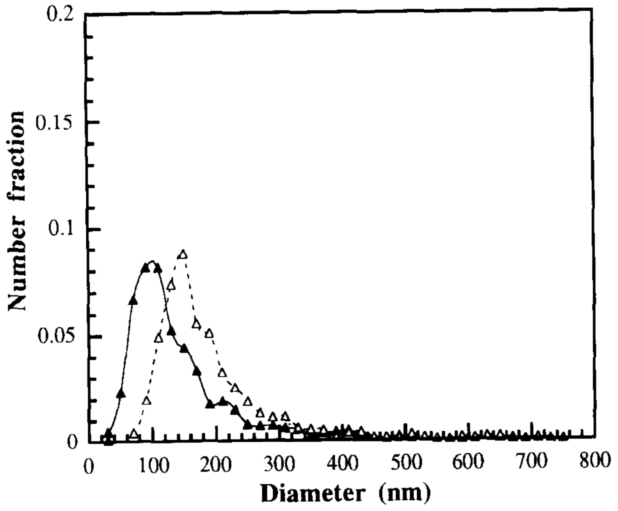

Figure 10 *PSD*s at low conversion in the soapless semicontinuous emulsion copolymerization of MMA and BuA (E54). Overall conversion (%): (▲) 0.8, (△) 1.7

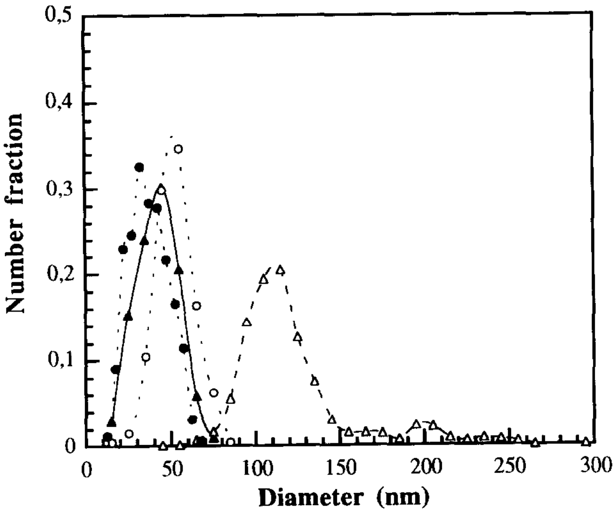

Figure 11 *PSD*s at low conversions for runs carried out with an emulsifier total amount in the initial charge of 0.388 g for the different SLS/Brij35 ratios. Legend (run, SLS/Brij35, overall conversion (%)): (▲) E39, 1/0, 4.8; (●) E47, 1/3, 0.9; (○) E53, 1/9, 0.9; (△) E40, 0/1, 1/1

The study of the effect of the emulsifier system in the early stages of emulsion copolymerization is difficult to carry out, owing to both the coupling of many dynamic processes such as nucleation, growth and coagulation, and the experimental limitations in sampling at comparable low conversions and for measuring the *PSD*s by TEM in samples with particles smaller than 50 nm.

One reference run (E54) was carried out using the recipe shown in *Table 1* and without emulsifier, namely, soapless emulsion copolymerization. The kinetic features of this run were a very slow polymerization rate and a low conversion during reaction time and an apparent long induction period (close to the total feed time). Moreover, it was observed that particle nucleation started earlier than the apparent inhibition time and instantaneous conversion remained very low during monomer addition due to the low polymerization rate. After 570 min of reaction 28% overall conversion was achieved and the average particle diameter measured by TEM was 557 nm (*PDI* = 1.092).

In *Figure 10* the *PSD*s obtained by TEM in two samples of 0.8% and 1.7% overall conversions of run E54 are shown. Both distributions had long tails at large diameters, namely, positive skewness, and were highly polydisperse. Total particle number calculated from the volume-average diameter increased from 4×10^{14} to 5.1×10^{14} when conversion changed from 0.8% to 1.7%. These *PSD*s were the result of a large nucleation period with an increasing particle nucleation rate with time. In this way, the tail of large particles corresponds to the small fraction of particles that nucleated at the beginning of the process, while the main part of the distribution at small sizes appeared at the end of the nucleation process, when the nucleation rate was the highest. These experimental results have usually been used as evidence of the coagulative nucleation mechanism described by Feeney *et al.*[14].

The evolution of the *PSD* in the early stages of the reaction was measured by TEM for all the reactions. Two samples were studied for each run, the first at very low conversion (close to 1%) and the second at close to 10%. In this way, it was possible to study the evolution of the *PSD* at the beginning of the reaction, while nucleation takes place.

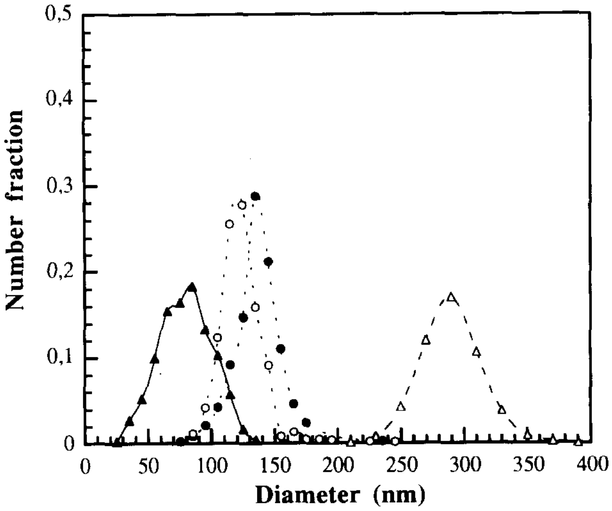

Figure 12 *PSD*s at low conversions for runs carried out with an emulsifier total amount in the initial charge of 0.388 g for the different SLS/Brij35 ratios. Legend (run, SLS/Brij35, overall conversion (%)): (▲) E39, 1/0, 20; (●) E47, 1/3, 10; (○) E53, 1/9, 9.2; (△) E40, 0/1, 12.1

In *Figure 11*, the *PSD*s measured at the beginning of the reaction for the runs carried out with the same total amount of emulsifier, 0.388 g in the initial charge, and at different SLS/Brij35 ratios (runs E39, E40, E47 and E53) are shown. The *PSD* obtained with non-ionic Brij35 alone (run E40) had the largest particle diameters and a long tail at large sizes. The *PSD*s obtained with anionic emulsifier alone or with mixtures were smaller and very similar. In *Figure 12* the evolution of these distributions at conversions close to 10% is shown. The *PSD* of the run carried out with single non-ionic emulsifier (run E40) has lost the positive skewness, while the *PSD*s obtained with mixture surfactant systems (E47 and E53) are clearly more monodisperse than the single ones.

These results indicate that the presence of anionic emulsifier in the recipe leads to a faster nucleation period of a more abundant population of particles. The long tail of large particles observed when the non-ionic emulsifier is used alone indicates a long nucleation period with unstable precursor particles, according to the coagulative nucleation theory[14]. The growth of the *PSD* in these runs was both by propagation and by coagulation.

The positive skewness observed in soapless polymerization (*Figure 10*) and reactions with non-ionic emulsifier alone is also observed in reactions carried out with SLS alone at lower concentrations (below the c.m.c.) in the initial charge (run E49). The increase in the emulsifier concentration in the recipe reduced the extent of the tail at large diameters observed in the *PSD*s at low conversions, SLS being more effective than Brij35.

In mixed or pure anionic systems, the initial *PSD*s evolved to Gaussian-like distributions when a critical emulsifier amount was reached. However, when the emulsifier amount was too high (run E38 in *Table 3*), the *PSD*s became positively skewed and close to bimodal, due to very long nucleation periods.

From the study of the evolution of *PSD* in the early stages of unseeded emulsion copolymerization, the important role of the emulsifier system in the particle nucleation process was evident. This role implied a direct effect on the total number of particles due to the stabilization effect and the micellar nucleation mechanism, and also had a direct effect on the nucleation kinetics, reducing nucleation time and controlling the broadness of the *PSD* obtained just after nucleation. The anionic SLS was more effective in achieving a rapid nucleation, without significant tails, than the non-ionic Brij35. Moreover, the use of Brij35 alone at high concentrations produced high initial numbers of particles with coagulative processes controlling particle growth during the early stages of the reaction. On the other hand, at the highest concentration of mixed surfactant system, the extent of the nucleation period became significant with reaction time and led to a broader *PSD*, close to bimodality, with an increasing particle number with time.

CONCLUSIONS

Semicontinuous operation in emulsion copolymerization was determined by the nature and concentration of the emulsifier system used. Monomer-'starved' conditions were achieved using recipes that included SLS in the emulsifier system at total concentration of emulsifier above a critical value. Brij35 used alone produced larger particle sizes and lower polymerization rates.

Two competitive effects were found when Brij35 was added to SLS in the surfactant system: increase of particle number due to the increase of the total emulsifier concentration prevailing at low SLS concentration, and decrease in particle number due to the effect of addition of Brij35 prevailing at high SLS concentration and SLS/Brij35 ratios between 1/1 and 1/3.

The effect of the surfactant system on the broadness of the *PSD* was more complex, both in the final latex and during the early stages of reaction, when nucleation takes place. Narrower *PSD*s with larger average particle sizes were obtained at the end of the reaction when mixed surfactant systems were used compared to those obtained with single anionic systems. *PSD*s at low conversions were positively skewed in soapless or low emulsifier concentrations, narrower and Gaussian-like at intermediate concentrations and broader at high concentrations.

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