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Semicontinuous emulsion copolymerization of methyl methacrylate and n-butyl acrylate: 1. Effect of mixed emulsifiers in seeded polymerization

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In the seeded semicontinuous emulsion copolymerization of methyl methacrylate and n-butyl acrylate, the use of mixed surfactant systems (anionic sodium lauryl sulfate and non-ionic Brij 35 and Glytanox 1001) leads to a decrease in the total particle number in the reactor during the reaction. Moreover, the decrease in the particle number is higher when the emulsifier used is non-ionic. The kinetic behaviour of the process is not influenced by the nature or amount of the emulsifier. The study of the evolution of particle size distribution shows that the distribution becomes broader during the reaction in all the cases studied. The total particle area decreases when the amount of non-ionic emulsifier in the recipe is increased.

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

INTRODUCTION

Semicontinuous emulsion copolymerization offers a great degree of operational flexibility which permits both polymer quality (copolymer composition, particle size distribution) and the reactor temperature to be controlled.

The evolution of the latex particle size distribution (PSD) in emulsion polymerization is governed by the nucleation, growth and coalescence of the latex particles. Although the influence of operating strategies on particle growth is well understood, the influence on particle nucleation and coalescence is much less clear. The emulsifier or emulsifier system used in emulsion polymerization, owing to its ability to play the role of both nucleation promoter and colloidal stabilizing agent, has a direct effect in the PSD evolution during polymerization.

Many studies have been carried out to analyse the effect of the nature and type of the emulsifier in emulsion polymerization. Emelie *et al.*[1,2] studied the batch emulsion copolymerization of methyl methacrylate (MMA) and n-butyl acrylate (BuA) using anionic (sodium lauryl sulfate) and non-ionic (polyethylene oxide ethers) emulsifiers. Chu and Piirma[3] studied the stabilization effect of mixed surfactant systems in the batch emulsion polymerization of styrene, work continued later by Chu and co-workers using MMA[4] and BuA[5]. Lee and Mallinson[6] studied the effect of mixed surfactants (anionic SDS and non-anionic AOT) in the emulsion polymerization of vinyl acetate.

Moreover, the use of anionic and non-ionic mixed surfactant systems may be a powerful tool to ensure the production of monodisperse latexes. Woods *et al.*[7] synthesized monodisperse latexes of different mean diameter using different emulsifier concentrations with optimum anionic/non-ionic ratios. Feeney *et al.*[8] explained the role of certain surfactants in obtaining monodisperse latexes as being due to the influence of the emulsifier on the reaction kinetics.

The aim of this work was 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 seeded semicontinuous emulsion copolymerization of MMA and BuA. A seed was used to ensure that all reactions had the same initial number of particles and, in this way, to study the effect of the nature and concentration of the emulsifier system on the growth of particles starting from the same initial particle number. Future work will focus on the effect of the emulsifier system on the nucleation process during non-seeded semicontinuous copolymerization.

EXPERIMENTAL

MMA and BuA monomers were distilled under reduced nitrogen pressure. All the other materials were used as received. Potassium persulfate ($K_2S_2O_8$, Merck) and sodium dihydrogen phosphate ($NaH_2PO_4.H_2O$, Merck) were used as initiator and buffer, respectively. The surfactants used were sodium lauryl sulfate (SLS, Merck), polyethylene oxide lauryl ether (Brij 35, ICI) and polyethylene oxide sorbitan monolaurate (Glytanox 1001, Glyco Iberica). Deionized water was used throughout.

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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 seed was prepared at 80°C by means of batch emulsion copolymerization of MMA and BuA using the recipe given in *Table 1*. After polymerization, the seed was kept overnight at 90°C to decompose the initiator. The volume average diameter of the seed used in all the polymerizations was 38 nm, calculated from its PSD.

The seeded semicontinuous emulsion copolymerizations were carried out using the recipes given in *Table 2*. The emulsifier concentration was 1.5 wt% of total monomer for each emulsifier. The anionic/non-ionic weight ratios used were 1/0, 0/1 and 1/1. The initial reactor charge was the seed, surfactant or mixed surfactant system, buffer, initiator and double deionized water. The amount of seed was 76 g. The amounts of the other materials in the initial charge were: surfactant, 1.125 g (2.25 g if a mixed surfactant system was used); buffer and initiator, 0.126 g each; water, 32 g. The ratio between the amount of emulsifier in the initial charge and in the feed was 25/75.

The 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 flow rates of these streams were 1.37 ml min^{-1} and 1.0 ml min^{-1}, respectively, and were kept constant and low enough to ensure monomer 'starved' conditions in the reactor and, thus, homogeneous copolymer compositions (50/50 molar) were obtained during the reaction. 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.

Five polymerizations 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.

Three polymerizations were carried out using an initial charge and a feed including only one surfactant, either anionic (SLS) or non-ionic (Brij 35 or Glytanox 1001). The remaining two polymerizations included two mixtures of anionic (SLS) and non-ionic (Brij 35 or Glytanox 1001) in a weight ratio of 50/50. In all cases the solids content of the latexes was 36 wt%.

Table 1 Recipe used to obtain the seed

Reactive	Weight (g)
Double deionized water	760
MMA	51
BuA	63
$K_2S_2O_8$	2.1
$NaH_2PO_4.H_2O$	2.1
SLS	20.1

Table 2 Recipe used for the semicontinuous emulsion copolymerizations

Reactive	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Seed	76	–	–
Double deionized water	32	450	–
MMA	–	–	132
BuA	–	–	168
$K_2S_2O_8$	0.126	0.174	–
$NaH_2PO_4.H_2O$	0.126	0.174	–
Emulsifier	Variable	Variable	–

Samples were withdrawn during the process and the polymerization was quenched with hydroquinone. The conversion was determined gravimetrically. Two conversions were defined: overall and instantaneous conversion. Overall conversion was defined as the ratio of the polymer present in the reactor to the total monomer used in the recipe (including the monomer used to produce the seed). Instantaneous conversion was defined as the ratio of the polymer present in the reactor to the monomer fed into the reactor at that time (including the monomer used to produce the seed).

The copolymer composition was determined by ^{1}H n.m.r. and by measuring the residual monomer using gas chromatography (g.c.). In order to carry out these measurements, the latex samples were diluted in water prior to injection. A precolumn filled with glass wool was used to retain the copolymer and to avoid the clogging of the column. The average particle sizes were measured by dynamic light scattering (d.l.s., 4700 Malvern) and transmission electron microscopy (TEM, H-7000 FA Hitachi). The PSDs were obtained by TEM on representative samples of more than 1000 particles. The latex samples were diluted in an aqueous solution of phosphotungstic acid (PTA, Merck) (negative staining), placed on copper grids covered with formvar (polyvinyl formal, Polaron) and dried by means of a u.v. light source in order to harden the MMA–BuA copolymer particles and to avoid film formation while drying, and particle deformation and shrinkage under the electron beam.

Number ($\bar{d}_n$), volume ($\bar{d}_v$) and weight ($\bar{d}_w$) average diameters were calculated from the PSD, defined as follows:

$$\bar{d}_n = \frac{\sum_i n_i d_i}{\sum_i n_i} \tag{1}$$

$$\bar{d}_v = \left(\frac{\sum_i n_i d_i^3}{\sum_i n_i} \right)^{1/3} \tag{2}$$

$$\bar{d}_w = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \tag{3}$$

where n_i is the number of particles of diameter d_i.

The polydispersity index (PDI) is defined as:

$$\mathrm{PDI} = \frac{\bar{d}_w}{\bar{d}_n} \tag{4}$$

The total number of particles (N_p) was calculated from TEM measurements as follows:

$$N_p = \frac{(M_s + M_T)X_T}{\frac{4}{3}\pi\rho_{cop}\left(\frac{\bar{d}_v}{2}\right)^3} \tag{5}$$

where M_s is the weight (g) of polymer of the seed, M_T is the weight (g) of monomer added to the reactor up to the end of the reaction, X_T is the overall conversion, ρ_{cop} is the density of the copolymer and $\bar{d}_v$ is the volume average diameter obtained by TEM.

Table 3 shows calculated number and volume average diameters and polydispersity indexes of the synthesized latexes obtained by TEM and the average diameters measured by d.l.s.

RESULTS AND DISCUSSION

Polymerization features

Figures 1 and *2* show the effect of the type of emulsifier in the feed and initial charge on the time evolution of the overall and instantaneous conversions for the reactions using SLS, Brij 35 and Glytanox 1001 and mixtures of SLS/Brij 35 and SLS/Glytanox 1001.

Figures 1 and *2* show that neither the type nor the amount of surfactant had a significant effect on the polymerization rate. *Figure 2* shows that a significant amount of monomer was accumulated in the reactor at the beginning of the reaction owing to an induction period (the small size of the seed implies low polymer weight in the initial charge and subsequent large decrease of instantaneous conversion when monomer feeding starts). This effect is more evident in the runs made with SLS alone or with a mixture of SLS and Glytanox 1001. This means that for a long time from the start of the reaction, greater when the induction time is longer, the copolymerizations did not proceed under starved

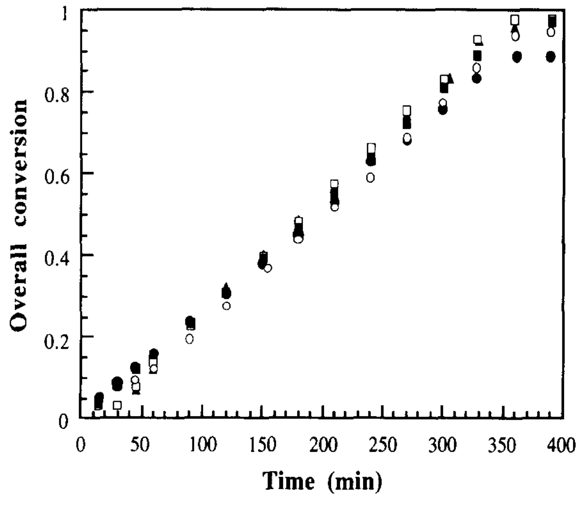

Figure 1 Time evolution of the overall conversion for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

Table 3 Number and volume average diameters and polydispersity index (PDI) obtained by TEM and average diameters obtained by d.l.s. of the final latexes

Run	$\bar{d}_n$ (nm)	$\bar{d}_v$ (nm)	PDI	$\bar{d}_{dls}$ (nm)
SLS	133	136	1.06	102
Glytanox 1001	159	164	1.08	126
Brij 35	180	183	1.05	136
SLS + Glytanox 1001	144	148	1.08	114
SLS + Brij 35	131	138	1.14	137

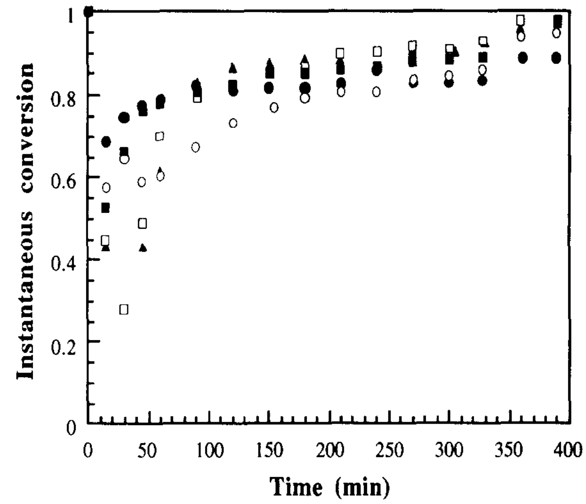

Figure 2 Time evolution of the instantaneous conversion for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

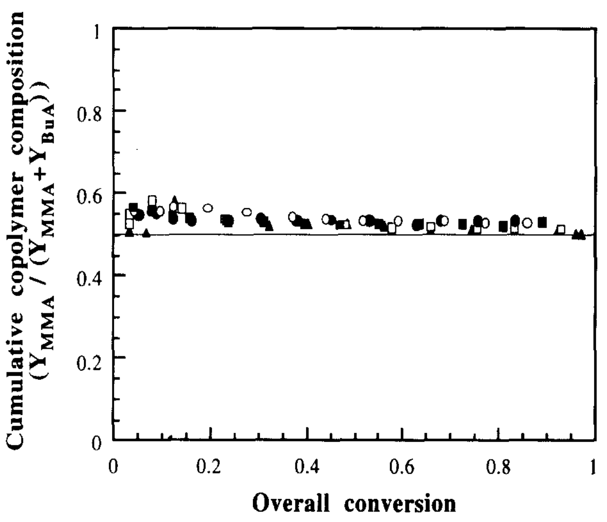

Figure 3 Evolution of the cumulative copolymer composition for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

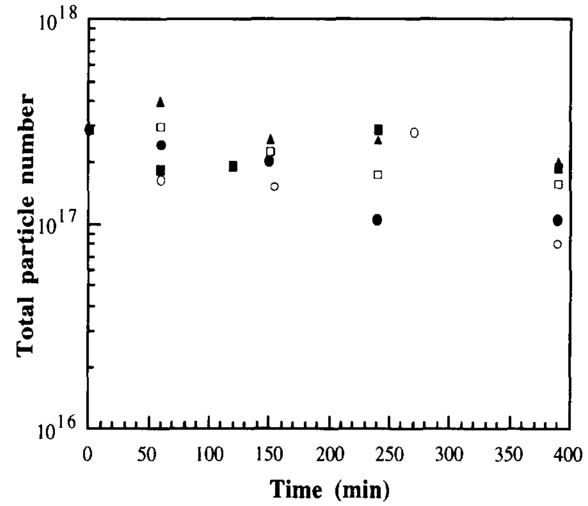

Figure 4 Time evolution of the total number of particles calculated from TEM measurements for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

Table 4 Values of the parameters used in the calculations of $\bar{n}$

$K_{pAA}{}^{a}$, $K_{pBB}{}^{b}$ (cm^3 mol^{-1} s^{-1})	9.20×10^5	2.47×10^5
$r_A{}^{c}$, $r_B{}^{c}$	2.64	0.315
$[MMA]_w/[MMA]_p{}^{d}$, $[MMA]_w/[MMA]_o{}^{d}$	2.32×10^{-2}	1.69×10^{-2}
$[BuA]_w/[BuA]_p{}^{d}$, $[BuA]_w/[BuA]_o{}^{d}$	2.18×10^{-3}	1.42×10^{-3}

A, MMA; B, BuA; w, water; p, particles; o, droplets
[a] Ref. 12
[b] Ref. 13
[c] Ref. 14
[d] Ref. 15

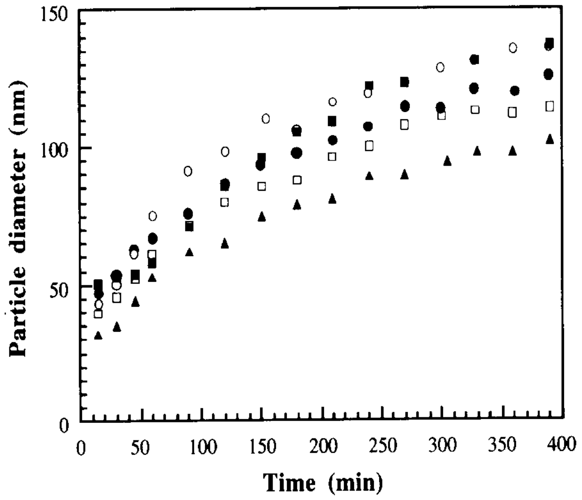

Figure 5 Time evolution of the average particle diameters measured by d.l.s. for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

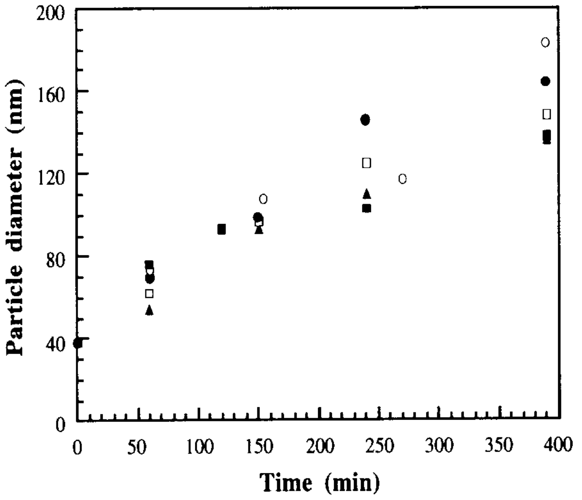

Figure 6 Time evolution of the volume average particle diameters measured by TEM for the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

conditions. Examining the cumulative copolymer composition evolution shown in *Figure 3*, the less reactive monomer (BuA) accumulated in the reactor at the beginning of the reactions and, in this way, the copolymer composition obtained is different from the monomer ratio in the feed.

In order to analyse these results, the time evolutions of the total number of particles (N_p) calculated from TEM measurements are presented in *Figure 4*, which shows that the total number of polymer particles did not remain constant and equal to the initial particle number of the seed. In addition, the number of particles decreased during the reaction in all cases and this effect was clearer when the emulsifier used was non-ionic.

In a semicontinuous emulsion polymerization the polymerization rate would be insensitive to N_p if the polymerization rate was controlled by the monomer addition rate (starved conditions) and/or if the system kinetics were independent of N_p. If the polymerization proceeds according to Smith–Ewart case III ($\bar{n} \gg 0.5$) or case I kinetics ($\bar{n} \ll 0.5$) the polymerization rate is insensitive to N_p. In order to differentiate between these kinetics, the average number of radicals per particle ($\bar{n}$) was calculated[9] using the parameters given in *Table 4*. It was found that the calculated value of $\bar{n}$ ranged from 1 to 6 for all the reactions. This result suggests that the insensibility of the polymerization rate to surfactant type and concentration is due to the fact that the seeded polymerizations proceeded according to Smith–Ewart case III kinetics.

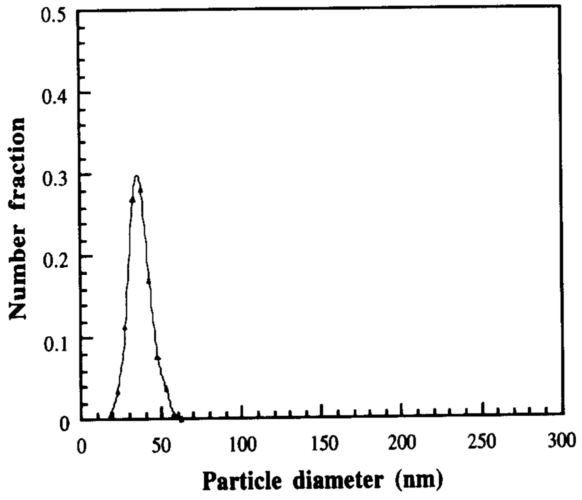

Figure 7 PSD of the seed ($\bar{d}_v$ = 38 nm, PDI = 1.09)

Colloidal features: particle average diameter and particle size distribution

The time evolution of the average diameter measured by d.l.s. and volume average diameters obtained by TEM for the different copolymerizations are shown in *Figures 5* and *6*. It can be seen that the copolymerization using SLS gives the smaller diameter throughout the reaction and that when using non-ionic emulsifiers alone (Brij 35 or Glytanox 1001) the diameters are the largest. When

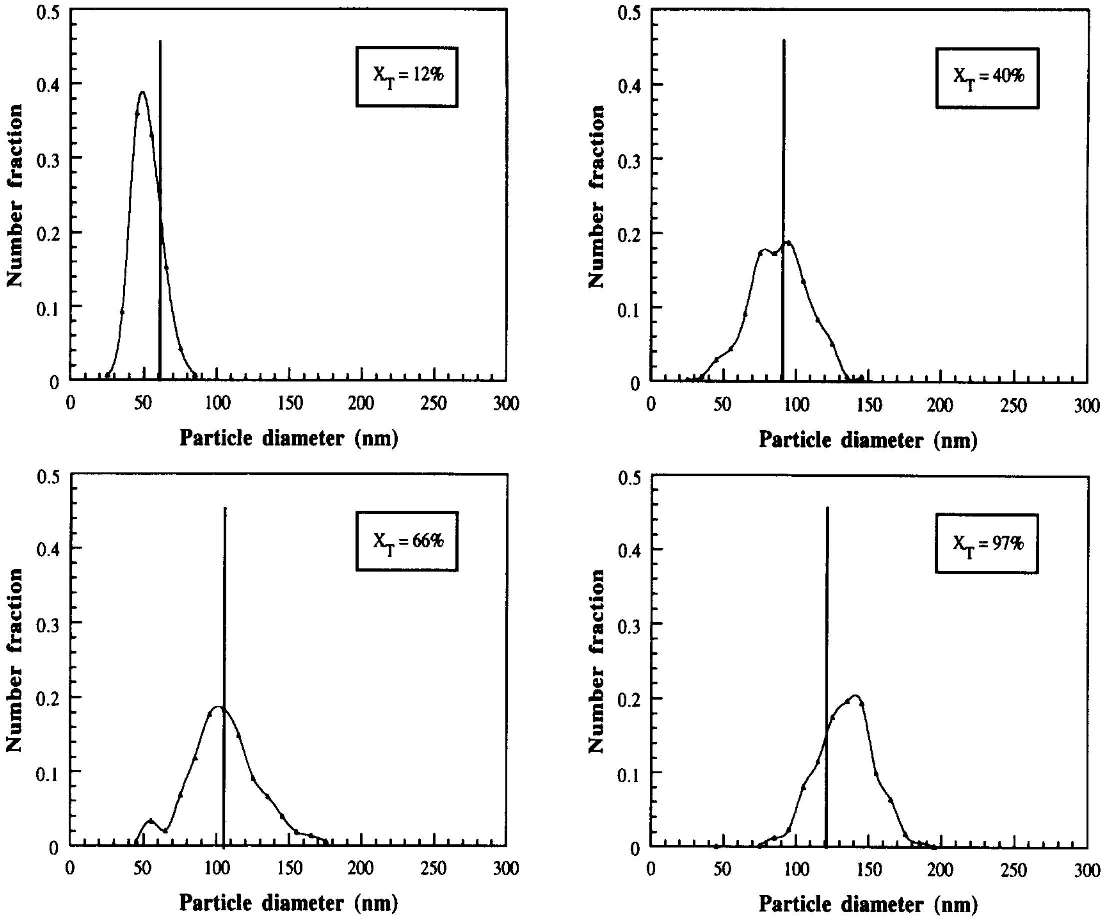

Figure 8 Evolution of PSD with overall conversion in the reaction carried out using SLS

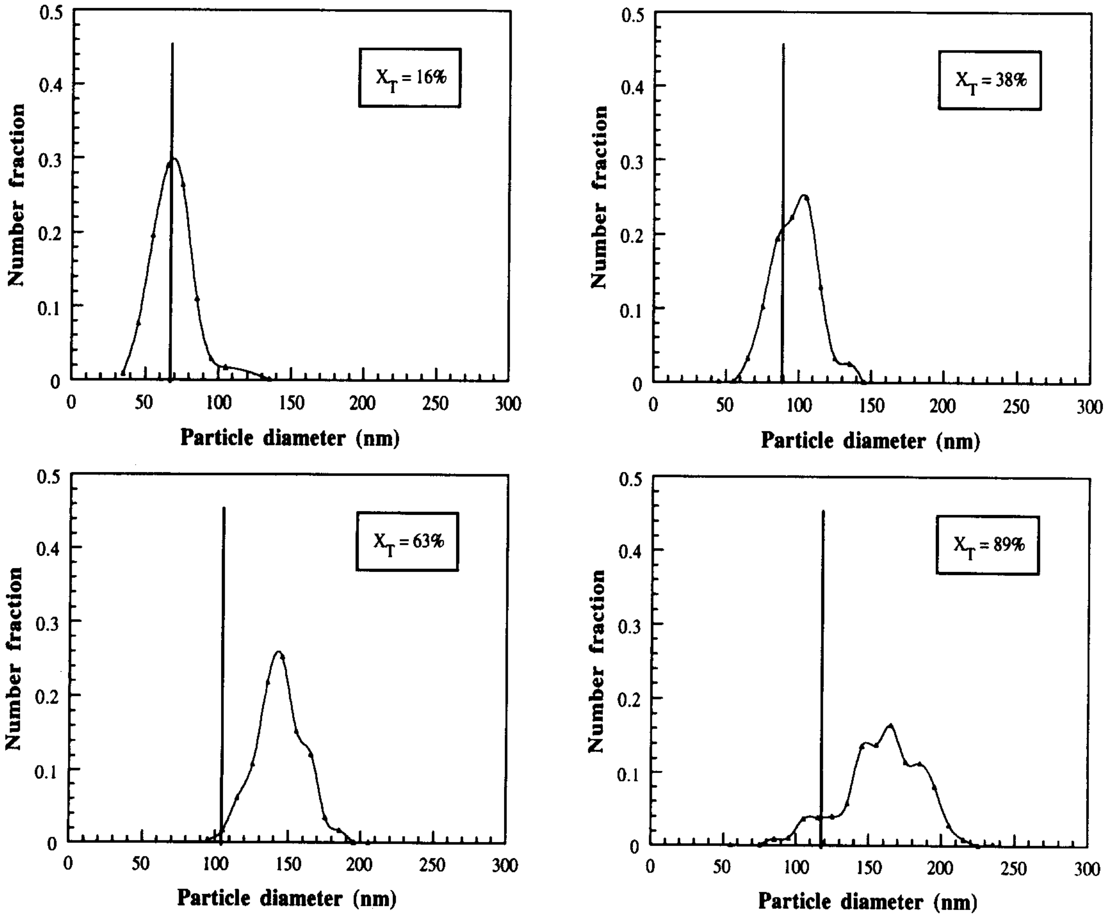

Figure 9 Evolution of PSD with overall conversion in the reaction carried out using Glytanox 1001

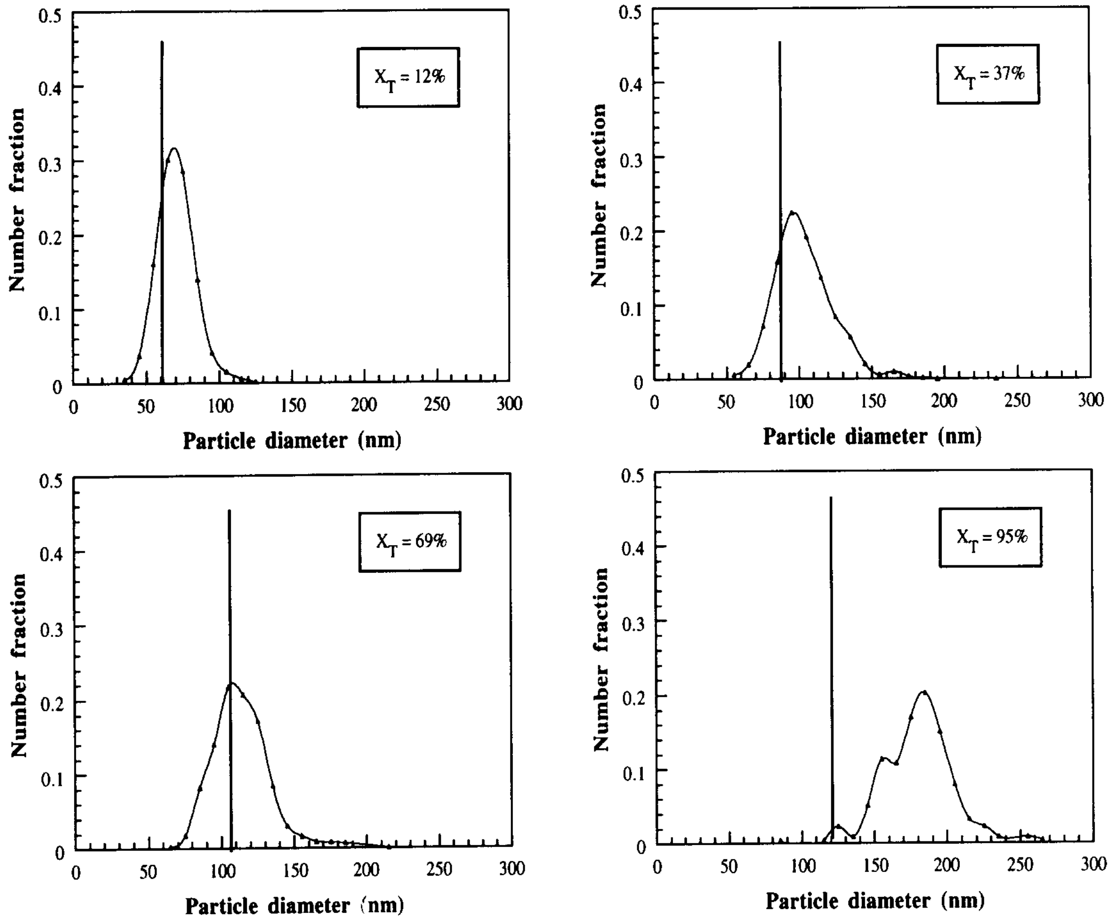

Figure 10 Evolution of PSD with overall conversion in the reaction carried out using Brij 35

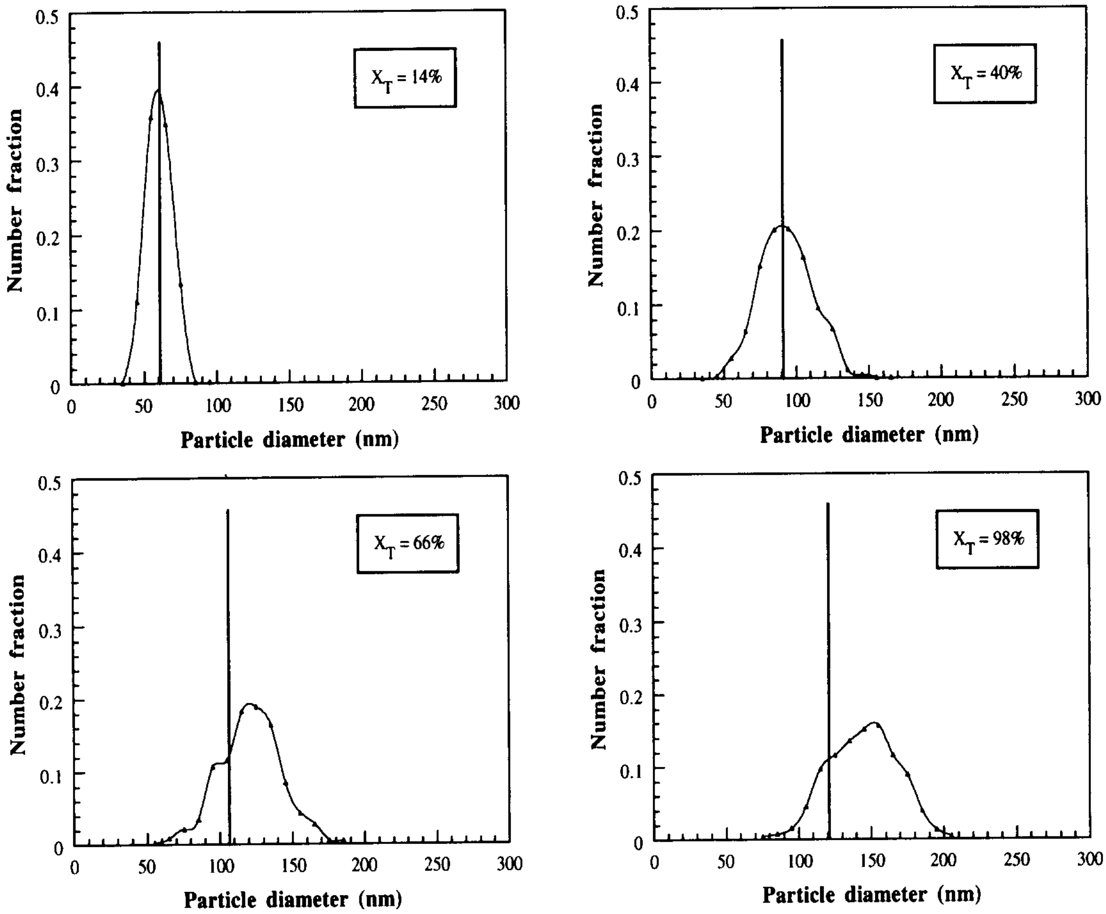

Figure 11 Evolution of PSD with overall conversion in the reaction carried out using SLS and Glytanox 1001

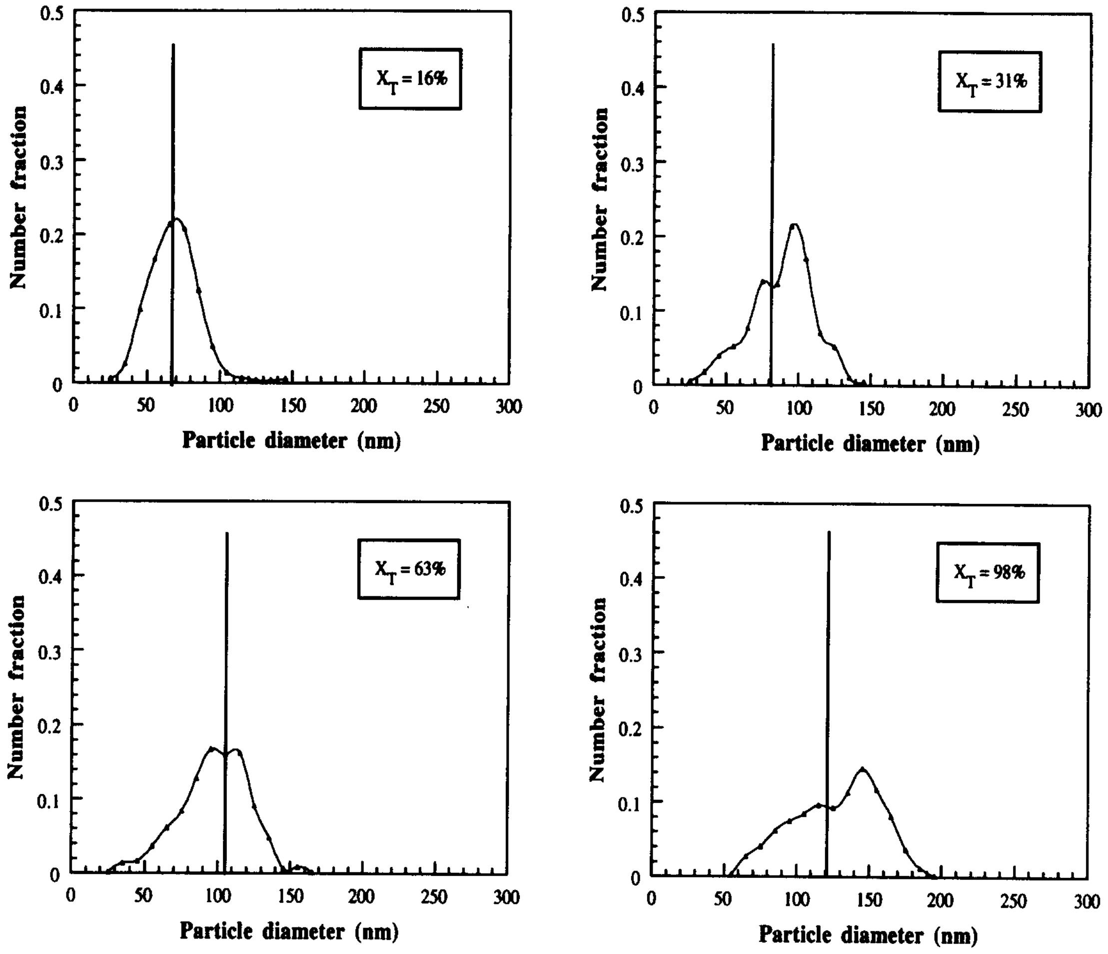

Figure 12 Evolution of PSD with overall conversion in the reaction carried out using SLS and Brij 35

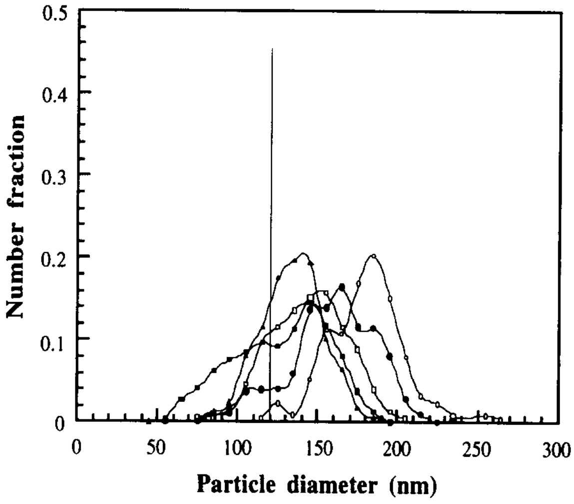

Figure 13 PSD obtained at the end of the seeded copolymerizations. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

using a mixture of anionic and non-ionic emulsifiers, the total emulsifier amount is higher but the obtained diameter values are in between the former ones.

These results suggest that the type of emulsifier influences the particle diameter evolution obtained more than the amount of emulsifier, at least in the concentration range studied. Furthermore, the inclusion of a non-ionic emulsifier in the recipe leads to an increase in particle growth by coagulation, which is competitive with growth by polymerization.

In *Figure 7* the PSD of the seed used in this work is presented.

In order to find evidence of coagulation, *Figures 8* to *12* represent the evolution of PSDs obtained by TEM in the different reactions. It can be seen that all the distributions become broader with time. In each distribution, the vertical line indicates the expected volume average diameter at the same overall conversion if the total particle number had remained constant at the initial particle number of the seed. The displacement of the mean part of the distribution to larger sizes than that of the theoretical growing seed, indicates that particle coagulation takes place during the reaction. This deviation of the mean part of the PSD to higher diameters is very clear when the emulsifier used is non-ionic (*Figures 9* and *10*), and when the emulsifier used is SLS this effect only appears at very high conversions (*Figure 8*).

In *Figure 13* the PSDs obtained at the end of each reaction are presented, in which the vertical line indicates the expected volume average diameter that would be obtained if the total particle number had remained constant. Comparison of the PSDs of the latexes obtained using anionic (SLS) and non-ionic emulsifiers (Glytanox 1001 and Brij 35) showed that the distributions were more polydisperse, with a tail at large diameters, in the case of non-ionic emulsifiers. Furthermore, the distributions

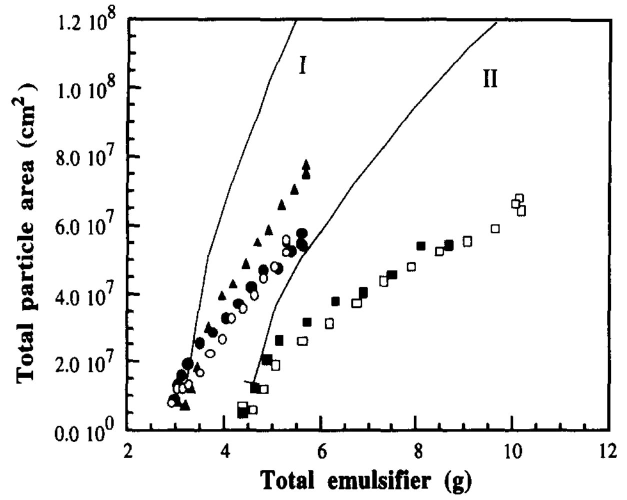

Figure 14 Total area of particles *versus* emulsifier amount in the reactor for the copolymerization reactions. (▲) SLS; (●) Glytanox 1001; (○) Brij 35; (□) SLS + Glytanox 1001; (■) SLS + Brij 35

obtained with the mixtures of emulsifiers are the broadest and have a small diameter tail.

In *Figure 14* the evolution of the total area of the particles *versus* the total amount of emulsifier present in the reactor at the same time is shown (note that the emulsifier amount in the reactor is a linear function of time). The continuous lines indicate the evolution of the particle total area that would be expected if particle number had remained constant (line I for reactions with SLS, Glytanox 1001 and Brij 35, and line II for reactions with SLS + Glytanox 1001 and SLS + Brij 35). In this figure the total particle area grows linearly with the amount of emulsifier. The increase in the amount of emulsifier in the runs carried out with mixed surfactant systems does not lead to an increase in the total particle area compared with the run carried out with SLS alone. On the other hand, both the total area and the slope are lower than theoretical evolution and this effect is enhanced when non-ionic emulsifier is included in the recipe.

Usually, seeded emulsion polymerizations have been carried out in kinetic and morphological studies with the assumption that total particle number remains constant throughout the reaction. However, many workers have reported that the presence of emulsifier in seeded polymerization can lead to an increase in particle number, namely, secondary nucleation. Recently, Urquiola *et al.*[10] found an increase in particle number at the beginning of the reaction in seeded semicontinuous emulsion copolymerization using Aerosol MA as emulsifier. Vandezande and Rudin[11], using mixed surfactant systems, reported that an increase in the amount of emulsifier increases particle nucleation in seeded copolymerization.

In this work, the addition of emulsifiers to the seed shows a more complex behaviour, with a decrease in the initial particle number as the prevailing tendency, an effect enhanced by the non-ionic emulsifiers. These results suggest that the use of mixed surfactant systems can lead to a destabilizing effect in seeded copolymerization and, consequently, a broader PSD and a lower particle number in the final product are achieved.

CONCLUSIONS

The use of a non-ionic emulsifier, with or without an anionic one, to stabilize the growing seed in semicontinuous seeded emulsion polymerization caused the colloidal destabilization of the system and led to a broader particle size distribution with larger particle sizes compared to those predicted theoretically. The decrease of total particle number was reduced when anionic emulsifier (SLS), with or without a non-ionic one, was used. PSDs exhibited tails at large sizes when the emulsifier used was non-ionic and at small sizes when mixed emulsifiers were used.

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