Reactive Surfactants in Heterophase Polymerization. 11. Particle Nucleation

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ABSTRACT: The nucleation process in the emulsion polymerizations of styrene, methyl methacrylate, and vinyl acetate stabilized by sodium dodecyl sulfopropyl maleate, a polymerizable surfactant (surfmer), was investigated. A nonpolymerizable surfactant, sodium dodecyl sulfate (SDS), was used as a reference. The results obtained suggested that the presence of the surfmer did not affect the nucleation mechanism (which seems to be micellar for styrene and homogeneous for MMA and VAc). The type of surfactant did not affect the dependence of the number of particles upon surfactant concentration for styrene, but the dependence for the surfmer was lower than that for SDS in the cases of MMA and VAc. This was interpreted in terms of formation of water-soluble oligomers that do not participate in the stabilization of the polymer particles.

Introduction

Although surfactants are needed to provide stabilization of the polymer particles during the emulsion polymerization process, they can have adverse effects afterward. These negative effects are caused by the desorption of the surfactant from the surface of the latex particles. Thus, when the latex is used for coatings, the unbound surfactant can migrate through the film forming aggregates that increase percolation by water. The surfactant can also migrate to the air−film interface affecting gloss or to the film−substrate interface affecting adhesion. If the polymer is recovered via coagulation, the surfactant adversely affects wastewater treatment. A promising way to solve these problems is to use polymerizable surfactants (surfmers) and improvements with respect of the use of nonpolymerizable surfactants have been reported.[1−12] Both the practical importance of the surfmers and the scientific challenge have catalyzed the research of this field. The reader is referred to the available reviews[13−18] for a detailed description of this research.

As in the case of the emulsion polymerization stabilized with nonreactive surfactants, the rate of polymerization of systems using surfmers strongly depends on the number of polymer particles. Therefore, it is interesting to investigate the particle nucleation process in systems using surfmers. One can anticipate that this is going to be a difficult and long task as the nucleation mechanisms in emulsion polymerizations using nonreactive surfactants are still a matter of discussion.[19] Also, it is worth mentioning that the surfmers may affect the polymerization rate by mechanisms different to those involved in the nucleation process. Thus allyl surfmers retarded the emulsion polymerization,[20,21] probably due to degradative chain transfer. On the other hand, Unzué et al.[22] reported that surfmers with crotonate and maleate reactive groups had no effect on the polymerization rate of seeded systems with the same particle size and number.

Chen and Chang[23] studied the emulsion polymerization of styrene in the presence of a surface active comonomer, undecylenic isothionate sodium salt (NaUI), initiated by potassium persulfate. At concentrations of the surfmer below the cmc and constant ionic strength, the number of polymer particles was proportional to the concentration of surfmer and presented a 0.5-order dependence with respect the initiator concentration. The authors, based on the absence of micelles in the system, assumed a homogeneous nucleation mechanisms. The dependence of N_p on the concentration of initiator was explained assuming that the rate of particle nucleation was proportional to the concentration or radicals in the aqueous phase (which was assumed to be proportional to $[\text{initiator}]^{0.5}$), but it is not obvious how this mechanism yielded the observed dependence for the surfmer concentration. These results were compared with those reported by Juang and Krieger[24] for the emulsion polymerization of styrene in the presence of sodium salt of 2-sulfoethyl methacrylate (NaSEM). This compound has a structure similar to the NaUI but with a shorter alkyl chain, and it is not amphifilic. Juang and Krieger's[24] data show that N_p was proportional to [initiator] and to $[\text{NaSEM}]^2$. The effect of the initiator concentration was explained assuming that each particle is formed by aggregation of oligomer chains, each being formed by combination of two oligomeric radicals. The effect of ionic strength on the number of particles was also analyzed by Chern and Chen.[25] It was found that N_p first decreased and then increased as ionic strength increased. The first decrease was explained in terms of the reduction of the electrostatic repulsion among particles as ionic strength increased. Additional increases of the ionic strength led to the formation of micelles, as the cmc decreased with the ionic strength, and particles are formed by micellar nucleation. It was postulated that these particles were more stable than those formed by homogeneous nucleation. It has to be pointed out that this assumption is in conflict with the

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explanation given by Chen and Chang[23] for the dependence of N_p on initiator concentration.

Tsaur and Fitch[26] studied the emulsion polymerization of styrene in the presence of a surface active monomer, sodium sulfodecylstyryl ether (SSDSE), and, in some cases, sodium dodecylsulfonate. Both an anionic water-soluble initiator ($K_2S_2O_8$, KPS) and a nonionic water-soluble photoinitiator (biacetyl) were used, and the experiments were carried out below the cmc. When KPS was used and in the absence of sodium dodecylsulfonate, N_p increased with [SSDSE], the dependence varying from a 2-power at low SSDSE concentrations (from 0.5×10^{-4} to 1×10^{-4} M) to a 0.6-power at higher SSDSE concentrations (from 1×10^{-4} to 5×10^{-4} M). A similar behavior was observed in the presence of 10^{-3} M of sodium dodecylsulfonate with 2.7 and 0.3 power dependences for the same ranges of SSDSE concentrations. In addition, the particle sizes obtained with sodium dodecylsulfonate were substantially smaller than those produced in the absence of sodium dodecylsulfonate. For the nonionic initiator, the sodium dodecylsulfonate did not influence the particle size although it improved the monodispersity of the latex. On the other hand, the observed dependence of N_p upon [SSDSE] is close to one in the presence of sodium dodecylsulfonate ([sodium dodecylsulfonate] = 10^{-3} M) and slightly higher in the absence of sodium dodecylsulfonate. Although no mechanistic explanation of the role of SSDSE was provided, Tsaur and Fitch[26] analyzed the effect of the SDS in terms of the HUFT[27−30] theory. According to this theory, coagulation is often a principal factor in determining the final number of particles in emulsion polymerization. The extent of coagulation depends on the ionic strength of the aqueous medium and the density of stabilizing groups on the particles. During the early stages of emulsion polymerization, coagulation is more likely to occur with ionic initiators than with nonionic ones, because the former significantly contribute to ionic strength. Conventional emulsifiers reduce the extent of coagulation during the nucleation stage, and this led to smaller size particles.

Leary and Lyons[31] discussed the preparation of composite latex particles stabilized by nonionic polymerizable surfactants. One or more preformed polymer (e.g., butylated urea−formaldehyde; epoxy resin; polyester; alkyd) was dissolved in a monomer or mixture of monomers and 2−10% of nonionic surfmer was added. The solution was emulsified using high-speed stirring. The particle size distribution of the resulting emulsion, determined by transmission electron microscopy (after hardening with osmium tetraoxide), consisted of a broad mode of a mean volume average of 325 nm and a multitude of tiny particles on the order of 5−10 nm that were negligible from a volume point of view. Polymerization was initiated using a redox couple consisting of oil-soluble *tert*-butyl perbenzoate and water-soluble sodium erythorbate to generate free radicals at the droplet/water interface. During polymerization, shrinkage, and temperature changes tended to cause instability, but Leary and Lyons[31] reported that these problems might be virtually eliminated by using a polymerizable surfactant with an optimum hydrophilic chain length. It was observed that the small particles disappeared during polymerization and that the particle size distribution remained unchanged and equal to that of the initial emulsion for the whole process. Therefore, it was concluded that most of the monomer droplets (belonging to the main population) were nucleated. No results using nonpolymerizable emulsifier were reported, and hence it is difficult to assess the contribution of the surfmer to the nucleation process.

Guillaume et al.[32] studied the emulsion copolymerization of styrene and butyl acrylate in the presence of sodium acrylamido undecanoate (AUNa), a surface active monomer. The polymerizations were carried out in a batch reactor using sodium 4,4′-azobis-cyanopentanoate as initiator. At low solids content (6.7 wt %) for [AUNa] $< 6 \times 10^{-3}$ M, N_p was proportional to [AUNa], but above this value N_p did not increase further and even decreased for higher concentrations of surfmer. This decrease was attributed to the formation of large amounts of hydrosoluble chains, which caused bridging flocculation. In these reactions, the length of the nucleation period increased with [AUNa], at low surfmer concentrations, nucleation was completed by a 10−20% conversion whereas at high values of [AUNa], nucleation lasted until 50% conversion. At high solids contents (50 wt %), the evolution of N_p vs conversion was characterized by an initial stage in which N_p increased followed by a limited coagulation period, which was more pronounced at high surfmer concentrations, presumably caused by bridging flocculation.

Urquiola et al.[33] studied the emulsion polymerization of vinyl acetate using a polymerizable surfactant, sodium dodecyl alkyl sulfosuccinate (TREM LF-40). They found that, at each initiator concentration, an increase in the surfactant concentration led to a smaller particle size. The dependence of N_p upon TREM LF-40 concentration varied from a 0.4 power at high initiator concentration to a 0.62 power at low initiator concentration. On the other hand, at each surfmer level, the particle size increased with increasing initiator concentration. This effect, which was contrary to what is typically reported, was explained by the increase of the ionic strength with increasing initiator concentration and by the effect of the initiator on the chain length of the oligomers in the aqueous phase. The higher the initiator concentration, the shorter the oligomers (because of extensive bimolecular termination) and hence the lower the probability of particle formation by homogeneous nucleation.

Stahler[34] studied the emulsion polymerization of styrene with several surfmers (sodium sulfopropyldodecyl maleate, sodium sulfopropyltetradecyl maleate, sodium sulfopropyloctadecyl maleate, 2-acryloylamino-2-methylpropanosulfonic acid and sodium sulfopropyldodecyl fumarate), using an oil-soluble initiator, azobisisobutyronitrile. In the polymerization using maleate surfmers, it was found that the nucleation was similar to that using a nonreactive surfmer (SDS). On the other hand, the fumaric surfmer polymerized with S during the nucleation stage forming polyelectrolites that contributed to the colloidal stability of the particles yielding a number of particles higher than that obtained with the maleates.

Ottewill and Satgurunathan[35] studied the effect of adding a 5% of methoxy−poly(ethyleneglycol methacrylate) MeOPEGMA, at different stages of the emulsion polymerization of styrene on the particle size distribution. The MeOPEGMA is not a surfmer but a macromonomer that can provide steric stabilization after reaction with styrene. When no MeOPEGMA was added, a narrow PSD with a number average diameter of 219 nm was obtained. Additions at the beginning of the polymerization gave a bimodal particle size distribution, the dominant population having a number average diameter of 456 nm and with an additional rather broad population of smaller particles of mean diameter of 206 nm. When the MeOPEGMA was added at a conversion of about 10%, the PSD was also bimodal but with two modes corresponding to particle sizes of 231 and 433 nm in approximately similar proportions in number. The population of large particles decreased significantly when the MeOPEGMA was added at about 50% conversion and completely disappeared when the macromonomer was added at conversions beyond 90%. The effect was attributed to the formation of poly(styrene-MeOPEGMA) in the aqueous phase which can cause coagulation by bridging. At high styrene conversions there is no enough styrene in the aqueous phase to form these species, and hence the PSD is not modified.

Chern and Chen[25] studied the emulsion polymerization of butyl acrylate stabilized with sodium dodecyl alkyl sulfosuccinate in a semibatch reactor. They found that above the cmc, the number of latex particles formed was proportional to the concentration of the surfmer in the initial charge to the 0.72−0.80 power. Similar dependence was found for the unreactive sodium dodecyl sulfate.

Chern et al.[36] studied the emulsion copolymerization of methyl methacrylate and butyl acrylate stabilized with a nonionic surfmer. They found that the particle size decreased with the concentration of the surfmer and increased with the initiator concentration (because of the increase in ionic strength). The surfmer gave larger particles but less coagulum than the nonreactive adduct.

Unzué et al.[22] synthesized and screened surfmers with different reactivity in the high solids emulsion copolymerization of styrene−butyl acrylate−acrylic acid. It was reported that very reactive surfmers (sodium 11-methacryloyl undecan-1-sulfate and 11-methacryloyxy undecan-1-ol) gave very unstable latexes with large amounts of coagulum, irrespective of whether they were added continuously or at the end of a reaction carried out with another surfmer. This was ascribed to the formation of polyelectrolytes soluble in the aqueous phase that deprived the particle surface from stabilizing groups and caused bridging flocculation. On the other hand, slow-reactive surfmers such as sodium 11-crotonoyl undecan-1-yl sulfate and the commercial TREM-LF-40 gave relatively stable latexes but a low degree of covalent bonding.[37] A maleate surfmer (sodium sulfopropyl tetradecyl maleate), which is rather reactive with the monomer mixture (mostly with styrene) but does not homopolymerize, also gave stable latexes and a significant degree of incorporation. In polymerizations carried out with this surfmer in a semicontinuous reactor including the 30% of the emulsifier in the initial charge and the rest in the feed, the final number of particles depended upon a 0.7th power of the surfmer concentration.

The scarce data available suggest that the reactivity of the surfmer with the main monomer(s) as well as the polymerization locus plays a critical role in the nucleation of emulsion polymerization systems stabilized with surfmers.

This paper is an attempt to gain more knowledge on this process, by studing the batch emulsion polymerization of three monomers of widely different water solubilities (Table 1) and reactivity ratios (styrene, S, methyl methacrylate, MMA, and vinyl acetate,VAc) stabilized with an anionic surfmer (sodium dodecyl sulfopropyl maleate). S is sparingly soluble in water and copolymerizes reasonably with maleates ($r_{\mathrm{s}} = 8-10$, $r_{\mathrm{maleate}} = 0$[38]), MMA is more water-soluble and almost does not copolymerize with maleates ($r_{\mathrm{MMA}} = 354 \pm 57$, $r_{\mathrm{diethyl\ maleate}} = 0$[38]), and VAc is even more water-soluble and reacts almost alternatingly ($r_{\mathrm{VAc}} = 0.043$, $r_{\mathrm{diethyl\ maleate}} = 0.17$[38]). Sodium dodecyl sulfate (SDS) was used as a reference nonpolymerizable surfactant.

Table 1. Water Solubility of the Monomers

monomer	water solubility (mol/L)
styrene[a]	4.3×10^{-3}
methyl methacrylate[a]	1.5×10^{-1}
vinyl acetate[a]	5×10^{-1}
M12[b]	1.62×10^{-3}
M14[b]	4.4×10^{-4}

[a] 50 °C.[42] [b] 21 °C.[37]

Table 2. Recipe Used in the Bottle Batch Emulsion Polymerizations

component	varying [surfmer]	varying [Initiator]
monomer	6 g	6 g
water	60 g	60 g
potassium persulfate[a]	0.15% (S, MMA) 0.8% (VAc)	0.5−2%
potassium sulfate		variable[b]
sodium bicarbonate[a]	0.15% (S, MMA) 0.8% (VAc)	0.15%
surfactant[a]	M12: 0.1−4% SDS: 0.7−16%	M12: 2.5% SDS: 1.69%
temperature	67 °C	60 °C

[a] Based on monomer. [b] To keep constant ionic strength.

Experimental Section

The following chemicals were used. Styrene (S), methyl methacrylate (MMA) and vinyl acetate (VAc) were distilled and stored at −18 °C until use. Potassium persulfate (KPS), sodium dodecyl sulfate (SDS), potassium sulfate (KS), and sodium bicarbonate (SBC) were of analytical grade and used as received. The surfmer M12 was obtained from K. Stähler, Max Planck Institut für Kolloid und Grenzflächenforschung, and was synthesized according to methods described in the literature.[40] The purity was approximately 92%. The cmc value of the M12 at 2 °C is about 0.7 g/L.[41]

Most of the polymerizations were carried out in glass bottles (100 mL) rotated end-over-end at a speed of 47 rpm at 60 °C. Polymerizations were allowed to proceed for 24 h to ensure high conversion. The concentrations of surfmer and initiator were varied in these reactions (Table 2). In the polymerizations in which the concentration of initiator was varied, potassium sulfate was added to keep the ionic strength constant.

Some polymerizations aiming at studying the kinetics of polymerization of the surfmer were carried out in a 0.5 L jacketed glass reactor. A heat exchanger connected to tap water was placed between the reactor and the water bath to control any sudden heat production and to keep the reactor at the set temperature (60 °C). Samples were withdrawn during the reaction, and the polymerization was short-stopped with a solution of 1% of hydroquinone. The conversion of the main monomer was determined by gravimetry. The recipe used in these reactions is given in Table 3. Samples for determination of the conversion of the surfmers were also taken. Serum replacement[43] was used to separate the serum from the latex particles to determine the free surfmer content. Serum replacement was performed with a UHP-76 of MicroFiltration Systems, flushing distilled water through in discontinuous

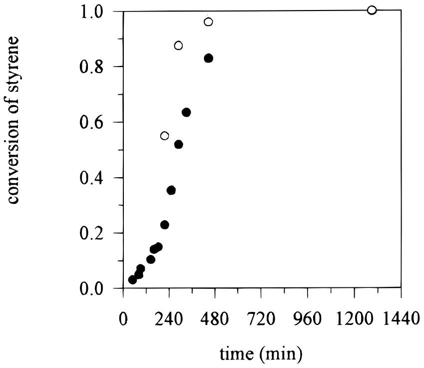

Figure 1. Conversions of styrene (●) and M12 (○). Reaction carried out using the recipe in Table 3.

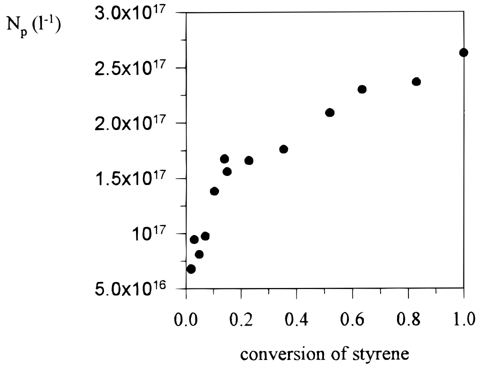

Figure 2. Evolution of the number of polymer particles in the emulsion polymerization of styrene carried out using the recipe given in Table 3.

Table 3. Recipe Used in the Emulsion Polymerizations Carried Out in the Glass Reactor

component	amount (% on monomer basis)
monomer/water ratio	1/10
potassium persulfate	0.15% (S, MMA) 0.8% (VAc)
sodium bicarbonate	0.15% (S, MMA) 0.8% (VAc)
surfactant	M12: 2%
temperature	60 °C

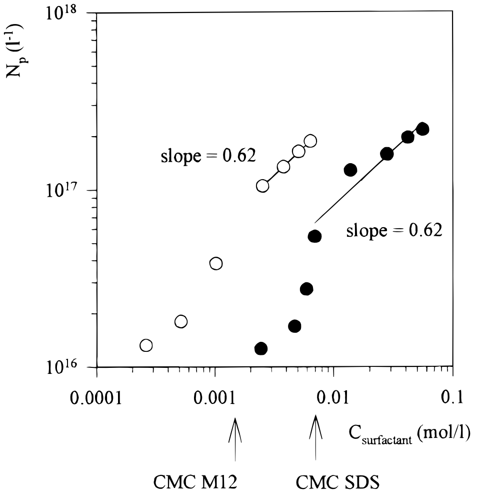

Figure 3. Effect of the surfactant concentration on the number of polymer particles for the emulsion polymerization of styrene: (○) M12; (●) SDS.

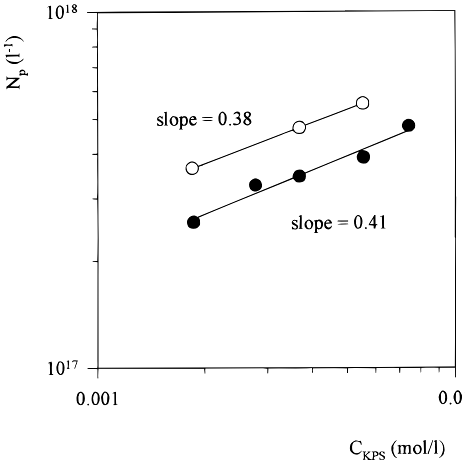

Figure 4. Effect of the initiator concentration on the number of polymer particles for the emulsion polymerization of styrene: (○) M12; (●) SDS.

mode and the affluent was collected for later analysis of the surfmer concentration, by the two-phase titration method.[44]

Particle size was determined with light scattering (LS) with a Coulter N4Plus apparatus. This technique gives an intensity weighted average particle size, $d_{\text{int avg}} = \Sigma(n_iI_id_i)/\Sigma(n_iI_i)$, where I_i is the intensity of light scattered from particles of diameter d_i and n_i is the number of such particles. This value is close to the *z*-average particle size ($d_z = \Sigma(n_id_i^7)/\Sigma(n_id_i^6)$).

Results

Styrene Emulsion Polymerizations. Figure 1 presents the evolution of the conversions of styrene and M12 in the emulsion polymerization carried out using the recipe presented in Table 3 (surfmer concentration above the cmc). It can be seen that M12 copolymerized faster than styrene, even though it is unable to homopolymerize.

Figure 2 presents the evolution of the number of polymer particles during the polymerization. It can be seen that nucleation of new particles was observed during the whole process. A word of warning should be said regarding the slow increase of N_p at high conversions because, due to cubic power relationship between N_p and the actual measurement d_p, N_p is very sensitive to small errors in d_p, and the variations reported at high conversions in Figure 2 are within the experimental error. A long nucleation period (up to 50% conversion) has been reported by Guillaume et al.[32] for the copolymerization of styrene and butyl acrylate in the presence of surfmer (AUNa) concentrations above the cmc, whereas below the cmc a much shorter nucleation period was observed.[25,32] Guyot and Goux[45] reported a continuous nucleation during the whole polymerization in the emulsion polymerization of styrene using monodecyl maleate as a surfmer.

Figure 3 presents the effect of the surfmer and SDS concentrations on the number of polymer particles. It can be seen that an S-shaped curve, probably due to a change of the nucleation mechanism about the cmc value (homogeneous nucleation below the cmc and micellar nucleation above) was obtained. It is interesting to point out that, above the cmc, the slopes of both curves were very close to the 0.6 value predicted by the Smith–Ewart theory of case 2 kinetics.[46]

Figure 4 shows the effect of the initiator concentration on the number of polymer particles for both surfactants in the polymerizations carried out using the recipe in Table 2 (surfactant concentrations above their cmc). It can be seen that N_p presents the same dependence on initiator concentration, 0.4, for both surfactants and that

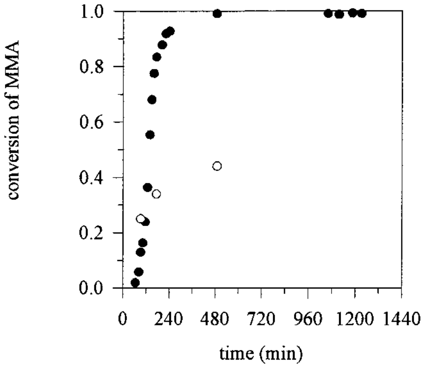

Figure 5. Conversions of methyl methacrylate (●) and M12 (○). The reaction was carried out using the recipe in Table 3.

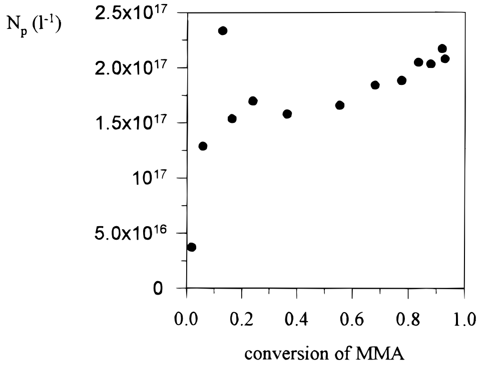

Figure 6. Evolution of the number of particles in the emulsion polymerization of MMA carried out using the recipe in Table 3.

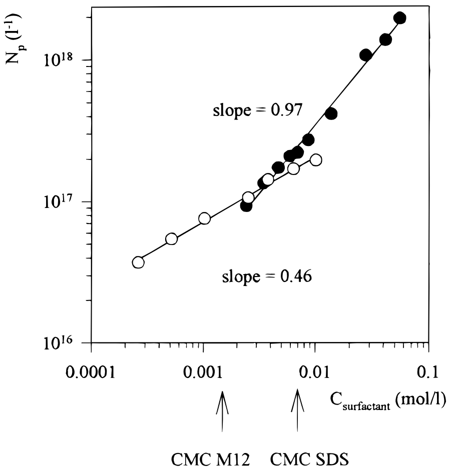

Figure 7. Effect of the surfactant concentration on the number of polymer particles for the emulsion polymerization of MMA: (○) M12; (●) SDS.

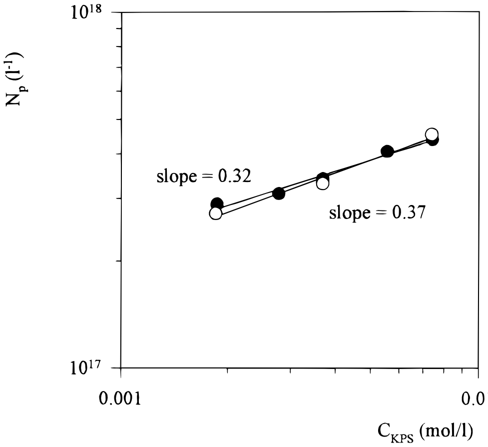

Figure 8. Effect of the initiator concentration on the number of polymer particles for the emulsion polymerization of MMA: (○) M12; (●) SDS.

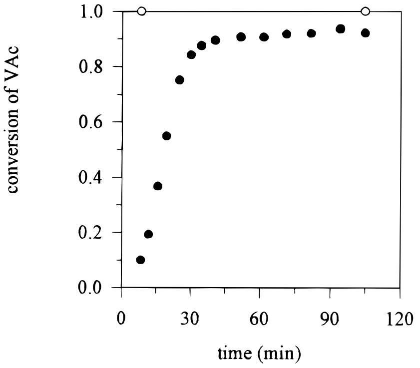

Figure 9. Conversions of vinyl acetate (●) and M12 (○). Polymerization carried out using recipe given in Table 3.

it is the one predicted by the Smith–Ewart theory.[46]

Methyl Methacrylate Emulsion Polymerizations. Figure 5 presents the evolutions of the conversions of MMA and M12 during the emulsion polymerization carried out using the recipe given in Table 3 (surfmer concentration above cmc). It can be seen that, initially, the surfmer reacted as fast as the MMA, but later the opposite was found. The evolution of the number of polymer particles during this polymerization is presented in Figure 6. It can be seen that the nucleation was almost complete when MMA had reached a conversion of 20% of conversion of MMA. The slight increase observed beyond this point, although showing a clear trend, was within the experimental error and should be regarded with caution. Figures 5 and 6 indicate that during the nucleation step, the concentration of M12 in the polymerization loci is substantially higher than the average concentration, and hence it polymerized as fast as MMA. Later, the polymerization locus should change because the MMA is consumed more rapidly.

Figure 7 presents the effect of the M12 and SDS concentrations on the final number of particles. It can be seen that straight lines (in the log–log plot) with no discontinuity about the cmc were observed for both emulsifiers. In addition, the slopes were very different: 0.46 for the M12 and 0.97 for the SDS. The effect of the initiator concentration (for M12 and SDS concentrations above the cmc) on the final number of polymer particles is given in Figure 8. It can be seen that for both emulsifiers N_p showed the same dependence upon the initiator concentration (slope ≅ 0.35), and both produced the same number of particles.

Vinyl Acetate Emulsion Polymerizations. The evolution of the conversions of VAc and M12 in a polymerization carried out using the recipe given in Table 3 ([M12] > cmc) is presented in Figure 9. It can be seen that complete conversion of the M12 was achieved from the very beginning of the process. This was due to the fact that vinyl acetate and maleates react almost alternatingly ($r_{\text{VAc}} = 0.043$, $r_{\text{diethyl maleate}} = 0.17$[38]), and it is in agreement with the results reported for the emulsion polymerization of vinyl esters using M12.[55] Figure 10 shows that the final number of polymer particles resulted from a limited coagulation occurring at about 10–15% VAc conversion.

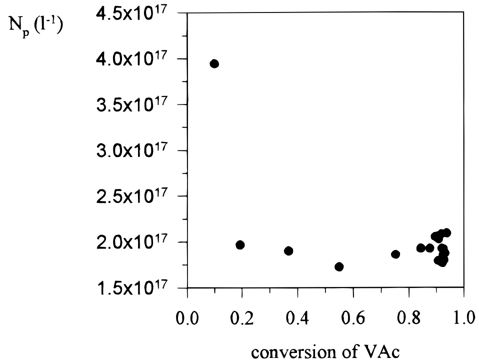

Figure 10. Evolution of the number of polymer particles in the emulsion polymerization of VAc carried out using the recipe given in Table 3.

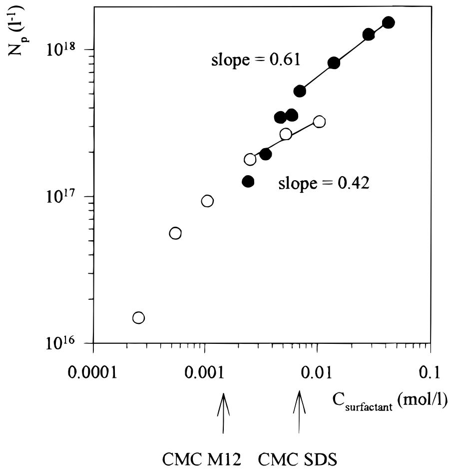

Figure 11. Effect of the surfactant concentration on the final number of polymer particles for the emulsion polymerization of VAc: (○) M12; (●) SDS.

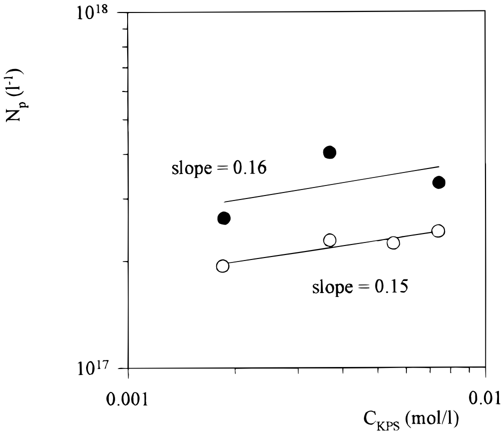

Figure 12. Effect of the initiator concentration on the final number of polymer particles for the emulsion polymerization of VAc: (○) M12; (●) SDS.

The effect of the emulsifier concentrations on the final number of polymer particles is given in Figure 11. It can be seen that for both M12 and SDS there is a slight change in the slope of the log N_p vs log [surfactant] plots at about the cmc, the slopes above the cmcs being smaller. Above the cmc, the dependence of N_p on surfactant concentration was greater for SDS (0.61) than for M12 (0.42). Figure 12 presents the effect of the concentration of initiator on the final number of particles for both surfactants ([surfactant] > cmc). It can be seen that the same dependence (slope $\cong$ 0.15) was found for both surfactants, but the number of polymer particles was higher for SDS than for M12.

Discussion

The shape of the log N_p vs log [surfactant] curve gives us an idea about the nucleation mechanism. S-shaped curves with a strong discontinuity about the cmc obtained for the styrene suggest a change in the nucleation mechanism from homogeneous nucleation below the cmc to micellar nucleation above this value. Below the cmc, the number of polymer particles is mainly controlled by the rate of oligomer precipitation (which is slow because of the low concentration of styrene in the aqueous phase), whereas above the cmc the number of particles is mainly controlled by the amount of surfactant available (as the rate of nucleation by radical entry into micelles is rapid). On the other hand, roughly straight log N_p vs log [surfactant] plots, such as the ones obtained for MMA and VAc, suggest that the same nucleation mechanism (homogeneous nucleation) is operative in the whole range of surfactant concentrations. In this case the rate of nucleation by oligomer precipitation is rapid because of the high concentration of monomer in the aqueous phase, and the number of particles is mainly controlled by the total amount of surfactant available. The fact that for none of the polymerization systems the presence of the surfmer affected the shape of the log N_p vs log [surfactant] curves is a strong indication that the surfmer did not affect the nucleation mechanism. Although, this conclusion is obviously restricted to the systems studied in this work, it has to be pointed out that they cover a wide range of reactivities and water solubilities.

As the nucleation mechanism for styrene is different from that operative for methyl methacrylate and vinyl acetate, the results obtained in the styrene polymerization will be discussed first.

Figure 1 shows that M12 copolymerized faster than styrene even though it is unable to homopolymerize. This is in agreement with the results reported by Schoonbrood et al.[47] for the tetradecyl maleate derivative (M14) and by Roy et al.[48] for M12, and it strongly suggests that the concentration of M12 in the polymerization loci is higher than the average concentration in the system. One can speculate that micelles and the surface of the polymer particles are in fact these polymerization loci. Increasing extents of homopolymerization[49,50] and copolymerization[51,52] of surfmers upon micellization have been reported. However, polymerization in micelles is not likely to be the only polymerization locus for the M12 as a rapid consumption of M14, with respect to styrene, has also been reported for seeded systems.[47]

Preferential polymerization in a region close to the surface of the particles may result from the anchoring of the hydrophilic end-group of the entering radical on the surface of the particle.[53,54] Experimental evidence supporting preferential polymerization of surfmers at the surface of the particles has been reported by Urquiola et al.[33] and Schoonbrood et al.[47,55]

Comparison between Figures 1 and 2 shows that nucleation was faster than M12 polymerization; namely, that most of the particles were nucleated when still there was unreacted M12 in the system. This means that nucleation occurred in the presence of free emulsifier, and hence the presence of the surfmer caused no differences in the nucleation behavior, other than the effect of different cmc (cmc = 0.51 g/L; $cmc_{SDS} = 1.15$ g/L[22]) and specific area ($a_{sM12} = 79$ Å^2; $a_{SSDS} = 42$ Å^2) which resulted in a larger number of particles for M12 (at the same surfactant concentration).

On the other hand, calculations using the specific area of the M12 molecule ($a_s = 79$ Å^2),[34] the conversions of styrene and M12 and the evolution of N_p show that micelles disappeared at about 10−15% conversion of styrene and at about a 40% conversion of M12. This may explain the decrease of the nucleation rate observed in Figure 2 for styrene conversion greater than 20%.

Figure 4 shows that N_p presented the same dependence on the initiator concentration for both emulsifiers and that this dependence was the one predicted by the Smith−Ewart theory.[46] This further supports the hypothesis that the nucleation was mainly micellar and that, as most of the surfmer did not react during nucleation, it behaved as a nonpolymerizable emulsifier. It also means that the part of the M12 that did react during the nucleation stage had no dramatically different effect on particle stability.

Figures 7 and 11 indicate that polymer particles were formed through a homogeneous mechanism in the emulsion polymerizations of MMA and VAc. However, the evolutions of the number of particles were very different. In the emulsion polymerization of MMA, the particles formed during the initial nucleation stage were stable during the process (the number of polymer particles even showed a slight increase after $X_{MMA} = 0.2$, Figure 6), whereas in the emulsion polymerization of VAc a large number of particles was initially formed, but then they suffered a quick limited coagulation in such a way that the final number of polymer particles was attained at a monomer conversion of 20%. This behavior might be due to the different reactivities of the surfmer in these processes, i.e., poorly reactive with MMA (Figure 5) and very reactive with VAc (Figure 9) that led to the formation of water-soluble alternating Vac−M12 copolymer. This is supported by the results obtained by Takahashi and Nagai[56] who used an allylic, cationic surfmer in a polymerization with a comonomer on a preformed seed latex. When diethyl fumarate was used as comonomer, this resulted in the formation of a water-soluble alternating copolymer which caused bridging coagulation. The formation of water-soluble polymers containing surfmer was also observed by Guillaume et al.[32] and by Unzue et al.[22] when a reactive methacrylate surfmer was used. The same could well apply to the present Vac system. However, it should be pointed out that a quick limited coagulation was also observed in the 75/25 VAc−Veova 10 emulsion copolymerization using non polymerizable emulsifiers,[57] i.e., that this behavior might be a feature of the vinyl acetate emulsion polymerization. Figure 5 shows that, initially, the surfmer reacted as fast as the MMA and later, although it reacted slower than the MMA, it reacted quicker than one would expect taking into account the reactivity ratios ($r_{MMA} = 354 \pm 57$; $r_{\text{diethyl maleate}} = 0$[39]). This means that the concentration of surfmer relative to that of MMA in the polymerization loci was higher than the average concentration in the reactor. Preferential polymerization in a region close to the surface of the particle resulting from anchoring of the entering radicals to the surface of the polymer particles may account for the relatively quick polymerization of M12. Following this reasoning, the initial quicker polymerization of M12 can be accounted for by the small size of the polymer particles during the initial stages of the polymerization of the surfmer.

Both MMA and VAc emulsion polymerizations showed a lower dependence of N_p upon [surfactant] for the surfmer than for the nonpolymerizable SDS (Figures 7 and 11). This effect might be due to the formation of water-soluble oligomers resulting from the copolymerization of the main monomer and the surfmer in the aqueous phase. The water-soluble oligomers did not participate in the stabilization of the polymer particles, and hence their net effect was to decrease the amount of surfmer available for stabilization or even to cause destabilization and limited coagulation: the higher the amount of surfmer in the recipe, the higher the amount “lost” in the water-soluble oligomers. This resulted in a lower dependence of N_p upon surfmer concentration.

This effect may also explain the effect of the type of surfactant on the number of particles. At low emulsifier concentrations $N_{p_{M12}} > N_{p_{SDS}}$, which agrees well with the higher specific area for adsorption and lower cmc of the M12. However, at high surfactant concentrations the opposite was found, which might be simply due to the waste of a significant fraction of surfmer by formation of water-soluble oligomers. Loss of surfmer by formation of water-soluble oligomers has been reported by Urquiola et al.[33] for the emulsion polymerization of vinyl acetate in the presence of sodium dodecyl alkyl sulfosuccinate.

Conclusions

In the foregoing, an attempt to investigate the nucleation process in emulsion polymerization systems stabilized with a polymerizable surfactant (surfmer) was presented. Batch emulsion polymerizations of three monomers with widely different water solubilities and reactivity ratios (with the surfmer) were carried out using sodium dodecyl sulfopropyl maleate as a surfmer and potassium persulfate as initiator. A nonpolymerizable surfactant, sodium dodecyl sulfate, was used as a reference. The effects of both the emulsifier concentration and the initiator concentration on the number of polymer particles were determined. The shape of the log N_p vs log [surfmer] curves suggested that the polymer particles were formed by micellar nucleation in the case of styrene and homogeneous nucleation in the cases of methyl methacrylate and vinyl acetate. On the other hand, the shape of these curves was not affected by the type of surfactant (polymerizable vs nonpolymerizable) which is a strong indication that, for the systems studied, the presence of the surfmer did not affect the nucleation mechanism.

The dependence of N_p on [surfactant] and [initiator] in the emulsion polymerization of styrene were equal for both surfactants and equal to those predicted by the Smith−Ewart theory.[46] Although the surfmer is rather reactive with styrene, it was found that nucleation was faster than polymerization. Therefore, to a large extent the surfmer behaved as a conventional surfactant during nucleation and no differences with respect the nonpolymerizable SDS were observed (other than those derived from the effect of different cmc and specific area for adsorption).

It was found that the surfmer reacted faster than the styrene even though it is unable to homopolymerize. This mean that the concentration of M12 relative to that of styrene in the polymerization loci was higher than the average concentration in the reactor. Micelles and the surface of the polymer particles seem to be the main polymerization loci.

Indications that the surface of the particles is the main polymerization locus were also found in the emulsion polymerization of MMA. Both MMA and VAc showed a lower dependence of N_p upon [surfmer] than upon [SDS], which was likely due to the loss of part of the surfmer by formation of water-soluble oligomers that did not participate in the stabilization of the polymer particles or could even have an adverse effect and cause limited coagulation. It appears that the reactivities of the comonomer and the surfmer can be additional factors governing the nucleation process and that a combination of a relatively polar comonomer and a reactive surfmer can adversely affect nucleation and stability.

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