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Application of a non-ionic amphiphilic maleic diester as polymerizable surfactant in free-radical emulsion polymerization

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Summary

A non ionic amphiphilic maleic diester with a poly(ethylene oxide) hydrophilic chain was used as a copolymerizable surfactant in batch free-radical emulsion polymerizations of styrene and n-butylacrylate. A good stability during the polymerization process was observed together with a high incorporation of the surfactant.

Introduction

The surfactants which are obviously needed during the emulsion polymerization processes can be thereafter the source of many problems for the application. To overcome these negative aspects essentially related to their mobility in the final polymer, surfactants can be covalently bound to the particles surface through incorporation into the polymer chains. This is based on three reactions taking place in conventional free-radical polymerization : initiation, chain transfer or propagation. It respectively corresponds to the use of surface-active initiators (*inisurfs*), surface-active transfer agents (*transurfs*) or surface-active comonomers (*surfmers*) (1,2). Concerning the *surfmers* which have been the most widely applied and studied species, many conventional polymerizable groups have been used such as substituted styrenes and acrylic or methacrylic esters (2,3,4). However, owing to their high reactivity, early incorporation might occur and lead to the loss of the surfactant which can be buried inside the particles during their growth. In contrast, a too low reactivity of the *surfmers* (such as crotonic ester) (3,4) can be the cause of incomplete conversion and poor covalent incorporation. Therefore, polymerizable groups with intermediate reactivity should be used and the reactivity ratios for copolymerization of the *surfmer* with the main monomer have been reported to be of major importance (5). Actually, the *surfmer* should be unable to homopolymerize ($r_{surfmer} \approx 0$) and the reactivity ratio of the comonomer should be comprised between 0.5 and 10 (5). The use of the non-homopolymerizable maleate group was proposed (1,2,6-9) and shown to be well suited since good incorporation of the corresponding *surfmers* was generally observed. The maleate based *surfmers* were usually anionic or cationic ones (1-13). To our knowledge, the use of a non ionic amphiphilic maleic diester *surfmer* as the only stabilizer in emulsion polymerization has been reported only once (6) and very few

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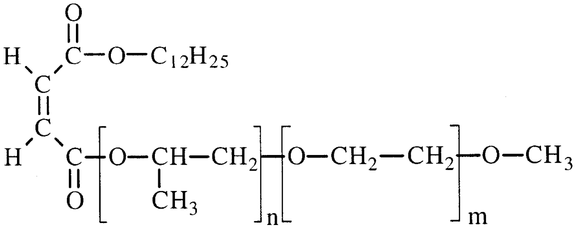
details were provided. A second paper from the same group will appear very soon (7). A more extensive study was performed in styrene dispersion polymerization (in water/ethanol mixture) and it was shown that those compounds were less efficient than the corresponding non amphiphilic hydrosoluble macromonomers (14,15).

In the present work, we wish to report on the use of a non ionic amphiphilic maleic diester *surfmer* in batch emulsion polymerization of styrene and n-butylacrylate. The *surfmer* (Sinnoester CPM1) was provided by Sidobre-Sinnova and has the following structure. Polymerization kinetics and the evolution with time of the number of particles were studied together with the incorporation of the *surfmer* during polymerization and at final stage.

Sinnoester CPM1

(n = 2.3 ; m = 17)



Experimental

Analytical techniques

Proton NMR analyses were performed in deuterated solvents such as chloroform ($CDCl_3$) and dimethylsulfoxide (d6-DMSO) in 5 mm diameter tubes at room temperature using a 200 MHz AC200 Bruker spectrometer. Chemical shift scale was calibrated on the basis of the solvent peak (7.25 ppm for $CHCl_3$ and 2.49 ppm for DMSO). Critical micelle concentration (CMC) was determined at 25 °C by surface tension measurements using a Kruss digital tensiometer (K10T). Latex particles diameter were measured by dynamic light scattering using a Zetasizer4 from Malvern.

Materials

Styrene (St) and n-butylacrylate (BA) were distilled under reduced pressure before use. The initiator, potassium persulfate ($K_2S_2O_8$, 99+ % from Aldrich) was used as received.

Emulsion polymerization procedure and latex characterization

Batch emulsion polymerizations were carried out at 70 °C using a conventional 250 mL thermostated reactor. Typical recipe is described just below (for the experiments L2 and L3, the respective amounts of water, monomer and *surfmer* were varied, as mentioned in Tab.I). Deionized water (180 mL), the polymerizable surfactant (0.400 g : 2 wt.% with respect to monomer) and monomer (20 g : τ = 10 % polymer content at final conversion) were introduced into the reactor and the mixture was bubbled with nitrogen. After stabilization of the temperature at 70 °C, an aqueous solution of the initiator ($K_2S_2O_8$, 0.270 g : 5.55 10^{-3} mol.L^{-1} in the latex aqueous phase) was added which corresponded to time zero of the reaction. Samples were periodically withdrawn in order to follow monomer (St or BA) conversion by gravimetry and to measure particles diameter. The particle concentration (number of particles per mL of latex) was calculated according to the classical equation :

$$N_p = \frac{6.\tau}{\pi.D_p^3.d_p}$$

with τ : polymer content ($g.mL^{-1}$)
D_p : particles diameter (cm)
d_p : polymer density ($g.mL^{-1}$)

Final characteristics of the latexes are summarized in Tab.1.

Tab.1 Final characteristics of the latexes prepared in the presence of **Sinnoester CPM1**

n°	Monomer (wt.% in the latex)	*Surfmer* (wt.% with respect to monomer)	Final polymer content ($g.mL^{-1}$)	Final D_p (nm)	Final N_p ($10^{13}.mL^{-1}$)	Stationary rate of polymerization[a] (R_p) ($mol.L^{-1}.s^{-1}$)	A[b]
L1	St (10 %)	2 %	0.093	184	2.95	$1.3\ 10^{-4}$	350
L2	St (10 %)	1 %	0.067[c]	280	0.80	$5.0\ 10^{-5}$	340
L3	St (20 %)	3 %	0.195	269	1.92	$1.3\ 10^{-4}$	170
L4	BA (10 %)	2 %	0.092	235	1.40	$3.2\ 10^{-4}$	290

[a] R_p is measured in the linear part of the conversion versus time plots
[b] Calculated stabilized surface area per *surfmer* molecule, assuming quantitative incorporation on the surface (Å^2/molecule)
[c] Incomplete conversion (67 %)

After complete polymerization, the latexes were centrifuged (20000 rpm during 1 hour, Beckman J2-MC centrifuge) in order to separate the serum from the polymer ; the procedure was repeated a second time after replacement of the serum with deionized water. The overall serum was collected, dried, resolubilized in d6-DMSO and analyzed by ^{1}H NMR spectroscopy. This allowed one to determine the nature of the water-soluble non volatile species (at this stage no quantitative analysis was performed). The polymer was also dried, thoroughly washed with hot methanol (soxhlet extraction, during 5 to 10 hours), solubilized in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy in order to quantify the amount of incorporated stabilizer. This analysis was possible for polystyrene in which the aromatic protons and the protons of the poly(ethylene oxide) chains are well separated. For n-butylacrylate however, this could not be performed with accuracy. The same procedure (centrifugation and washing with methanol) was applied at two reaction times before complete styrene conversion (30 min and 1 hour) in order to determine the conversion of the maleate group upon analysis of the washed polystyrenes. Conversion of the *surfmer* at a given time was calculated on the basis of the amount which was incorporated into the polystyrene, taking into account the conversion of styrene at this time.

Results and discussion

Characterization of the surfmer

The maleate-based surfmer was analyzed by proton NMR spectroscopy in d6-DMSO (Fig.1). No isomerization of the maleate group into fumarate could be detected. Critical micelle concentration was measured at 25 °C after purification. For this purpose, the *surfmer* was dissolved in diethyl ether ; the solution was filtered in order to remove the insoluble hydrophilic byproducts and dried overnight under vacuum at 30 °C. The measured CMC was 5.5 10^{-5} mol.L^{-1} ; it is very close to that reported by Hamaide et al. for *surfmers* with similar structure (6).

To check the possible occurrence of hydrolysis of the ester groups during emulsion polymerization, a *surfmer* aqueous solution at pH = 4 was heated at 70 °C during 6 hours and samples were withdrawn at regular time intervals. The solutions were dried and the products were analyzed by size exclusion chromatography in THF eluent. Hydrolysis would be detected by an increase of the peak corresponding to the liberated lauryl chain (either with an hydroxy or with a maleate end-group). Since no significant change could be observed in the chromatograms, it was concluded that, under conditions similar to those of a polymerization, hydrolysis could be neglected.

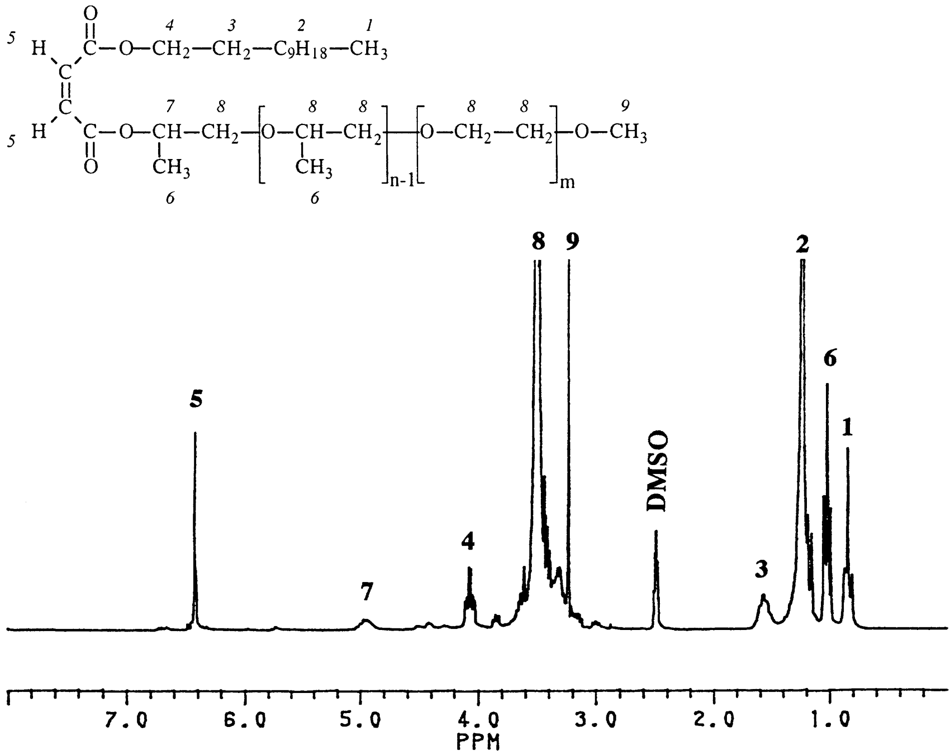


Fig.1 ^1H NMR spectrum of the purified **Sinnoester CPM1** in d6-DMSO solution.

Emulsion polymerization of styrene

Batch emulsion polymerizations of styrene were performed at 70 °C in the presence of the the non ionic amphiphilic maleic diester polymerizable surfactant. Potassium persulfate was chosen as a radical initiator. In that case, particles surface was not completely free of charges and thus both electrostatic and steric stabilization should take place. The combination of both types of stabilization is often used in the industry (for instance use of mixtures of anionic and non ionic surfactants) in order to reach small particle size together with improved shear, freeze-thaw and electrolyte stabilities. Stable latexes were obtained since no significant amount of coagulum was recovered. Monomer conversion and number of particles per volume unit versus time are plotted in Fig.2. Except for latex L2 for which the amount of polymerizable surfactant was reduced by a factor 2, the polymerizations were completed within 4 hours. The number of particles per volume unit increased with time during approximately 30 minutes and then it stabilized. This is the indication of a well defined nucleation period and of a good stability during the polymerization. At this stage, a linear increase of conversion with time was observed indicating that conventional interval II was reached. For 10 % solid content and 2 wt.% of added *surfmer* with respect to monomer (latex L1), the final particle diameter was 184 nm (Tab.1). Final particle size was significantly larger when either *surfmer* concentration was decreased (280 nm for latex L2) or when monomer content was increased (269 nm for latex L3). The effect of *surfmer* initial concentration is illustrated in Fig.2 and in Tab.1. As expected, a decrease by a factor 2 of the initial concentration of surfactant leads to a decrease of the final number of particles together with a decrease of the stationary rate of polymerization R_p. For latex L2 however, the value of R_p was somewhat larger than it could be expected on the simple basis of the decrease of N_p owing to a larger average number of radicals per particle (2.2 for latex L2 instead of 1.2 for latex L1) explained by larger particles volume.

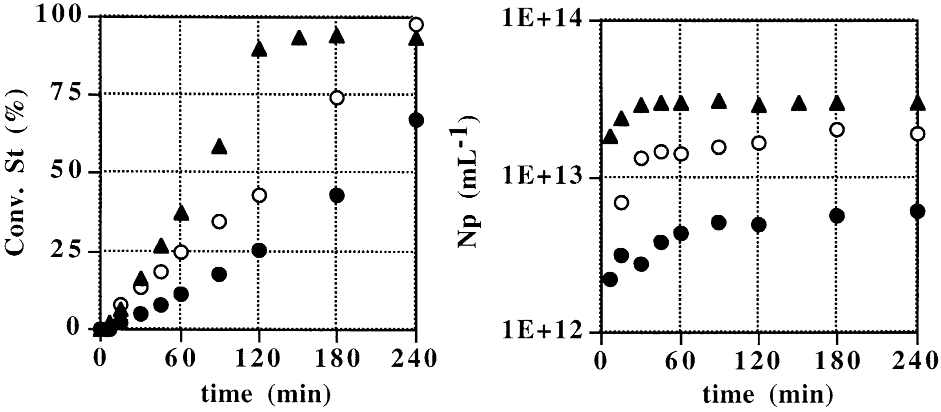


Fig.2. Emulsion polymerization of styrene in the presence of the polymerizable surfactant **Sinnoester CPM1** : ▲ L1 ; ● L2 ; O L3.

Proton NMR analyses of the final serum after centrifugation systematically showed that no *surfmer* was remaining. This result indicates that either complete incorporation occurred or that centrifugation was unable to eliminate the physically adsorbed species. For latex L1, the recovered polystyrene was then washed with hot methanol in order to remove the adsorbed species and it was analyzed by proton NMR spectroscopy in CDCl3 solution. The amount of incorporated *surfmer* was 1.2 - 1.3 wt.% with respect to polystyrene (2 wt.% were introduced which means that 60 % to 70 % of the surfactant was incorporated). Using the same procedure, conversion of the *surfmer* was determined at two reaction times before complete conversion of styrene and it was compared with that of styrene (see experimental part). Results are reported in Tab.2 where it appears that *surfmer* conversion is close to that of styrene. The methanol solutions obtained after extraction were dried and the residues were also analyzed by proton NMR in d6-DMSO solvent. They appeared to be composed of unreacted *surfmer* (for the intermediate times 30 min and 60 min) and of styrene oligomers which probably contained also *surfmer* units. Thus, owing to the probable presence of polymerized *surfmer* in the methanol extracts, it is possible that the calculated *surfmer* conversions are slightly underestimated.

Tab.2 Styrene and *surfmer* conversion for latex based on the recipe of L1

Time (min)	Styrene conversion	*Surfmer* conversion
30	25 %	29 %
60	49 %	43 %

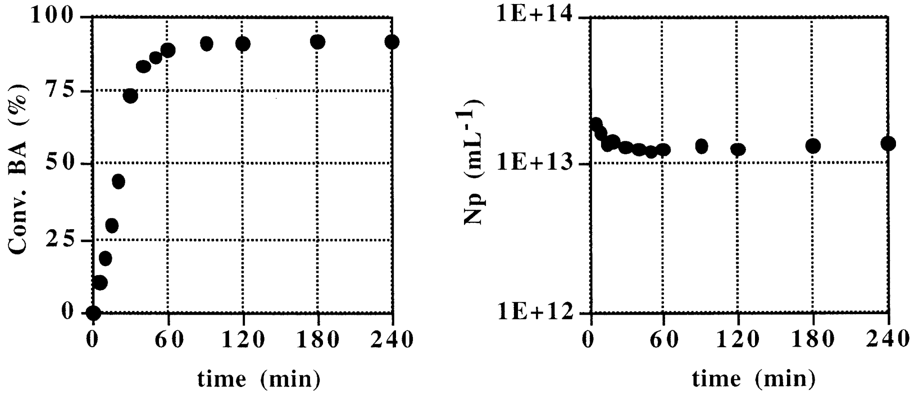


Fig.3. Emulsion polymerization of n-butylacrylate in the presence of **Sinnoester CPM1** at 2 wt.% with respect to monomer (Latex L4) .

Emulsion polymerization of n-butylacrylate

Sinnoester CPM1 was also used to stabilize poly(n-butylacrylate) latexes. Conversion and number of particles versus time are plotted in Fig.3. In contrast to styrene polymerization, N_p decreased during the first 30 minutes and then reached a constant value. This situation indicates that limited flocculation occurred during the early stages of the polymerization owing to the formation of a large number of precursor particles with insufficient stability.

Discussion

Homopolymerization of maleic diesters is very unfavorable, thus hydrosoluble or surface active homopolymer should not be formed, neither in the water phase nor in the micelles. Moreover, owing to the low concentration of styrene and n-butylacrylate in the water phase (approximately 0.003 mol.L^{-1} for St and 0.016 mol.L^{-1} for BA (16)), to the even lower concentration of *surfmer* (CMC = 5.5 10^{-5} mol.L^{-1}) and to the reactivity ratios (R_{St} = 5 and $R_m \approx 0$ for styrene and diethyl maleate respectively (17) ; R_{BA} > 10 and $R_m \approx 0$ for BA and diethyl maleate respectively (5)) it is very unlikely that copolymerization occurs in the aqueous phase before styrene or n-butylacrylate oligomers reach the critical length at which they should enter micelles or existing particles. Copolymerization most probably occurs at the particle/water interface where local concentration of the *surfmer* is high. This reaction takes place when the oligoradicals enter the micelles or the existing particles. It explains that, despite the values of the reactivity ratios, the observed consumption rate of the *surfmer* is close to that of styrene. A similar observation was previously reported for anionic maleic diester *surfmers* which were shown to be converted even faster than styrene in batch emulsion polymerization (9).

The efficiency of the *surfmer* was calculated for all the experiments in term of the apparent stabilized surface area per added surfactant molecule (see Tab.1). This value does not represent the surface area really occupied by a single molecule since the surface incorporation has not been directly measured. However, it enables to compare the stabilizing efficiency according to the experimental conditions : the higher the surface area, the better the efficiency. The parameter which affects it the more seems to be the monomer content (see Tab.1). When it was increased from 10 % (latexes L1 and L2) to 20 % (latex L3), the surface area decreased from 340 - 350 Å^2 to 170 Å^2. Nature of the monomer appears to have also a significant effect : under similar experimental conditions the *surfmer* stabilized a smaller interface for poly(n-butylacrylate) than for polystyrene. These results can be explained by the partial solubility of the non ionic surfactants in the organic phase (18) leading to a loss of part of the available *surfmer* inside the particles. This phenomenon is enhanced when the monomer/water ratio is increased or when more polar monomer is used.

Conclusion

A non ionic amphiphilic maleic diester with a poly(ethylene oxide) hydrophilic chain was used as a copolymerizable surfactant in batch free-radical emulsion polymerization of styrene and n-butylacrylate. Good stability during the polymerization process was observed since the number of particles remained constant throughout the polymerization. High incorporation of the surfactant was also found together with good stabilizing efficiency. An increase of the hydrophilic chain length would however improve the efficiency and reduce the solubility in the organic phase.

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