Macromol. Symp. ***150,*** *235–240 (2000)*

Reactive Surfactants in Styrene Microemulsion Polymerization

Cédrick Favero[±],Christian Graillat and Alain Guyot*

CNRS-LCPP CPE Lyon, BP 2077, 69616 Villeurbanne, France
[±]ITECH lyon, 181 avenue Jean Jaurès, 69007 Lyon, France

SUMMARY : Polymerization of styrene has been carried out in microemulsion using the sodium salt of the maleic dodecyl hemiester as surfactant and hydroxypropyl methacrylate as cosurfactant. In a limited range of composition, this system forms a transparent microemulsion, leading to small particles ranging between from 15 to 30 nm of diameter. The stability of the system is dependent upon the ionic strength of the media. A model explaining how the limits in solid contents are dependent on the ionic strength is proposed. Fast polymerization with formation of very high molecular weight chains occurs. The cosurfactant is well copolymerized with the styrene, but the surfactant is shown to be only partially incorporated.

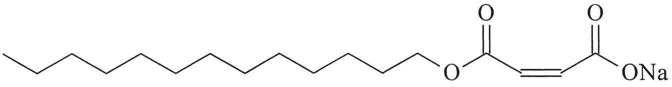
Introduction

One of the main drawbacks of polymerization of oil-soluble monomers in microemulsion to produce small polymer particles at a nanoscale range (10 to 50 nm in diameter) is the need of considerable amount of surfactants and cosurfactants, most often larger than the amount of monomer itself. In order to recover the polymer produced, a very tedious and wasteful process is needed. An obvious solution to such a problem should be to use a polymerizable surfactant which might be incorporated in the final polymer.

Polymerizable surfactants have recently gained a renewal of interest in emulsion polymerization, chiefly those producing film forming polymers for waterborne coatings. Recent reviews have been published in the last few years1-4). Indeed, this technology significantly improves the characteristics of the latexes in term of stability but also in term of the behaviour of the film in the presence of water. However, there are only few reports about the use of polymerizable surfactants to produce nanolatexes. All are quite recent papers. The first to appear 5) was based on a polymerizable product similar to CTAB, namely 11-(acryloyloxy) undecyltrimethylammonium bromide (AUTMAB). The polymerization was carried out with gamma irradiation of transparent mixtures of styrene-water, and polymer particles of 20 nm diameter were obtained. However, a large amount of AUTMAB was

CCC 1022-1360/00/$ 17.50+.50/0

homopolymerized. More recently, the same group of authors[6)] compared the behaviour of AUTMAB with another reactive surfactant in which the polymerizable group is close to the hydrophilic part of the surfactant. In that case, the particle size was not changed, compared to that of the monomer microemulsion, but the particles were linked by water soluble polymers chains, so that the final product is a rather rigid gel. Two other studies use polymerizable cosurfactants. In one case[7)] high solid nanolatexes, made of methyl methacrylate and butyl acrylate with size between 22 and 60 nm and up to 42 % solid contents were based on the use of acrylamide as cosurfactant and sodium disulfonate of diphenyl ether (Dowfax 2 A1) as surfactant. The amount of surfactant was about 9% of the monomers and, for the cosurfactant, the feature was only 1%. The latexes were shown to be stable vs. electrolyte (aluminium sulfate), and also for several cycles of freeze-thaw. These features were attributed to the nature of the surfactant and not due to the use of polymerizable cosurfactant. In another paper[8)], the use of hydroxypropyl methacrylate (HPMA) and similar polymerizable products as cosurfactants was achieved. Polymerization of styrene with 100% conversion was achieved at room temperature using either an oil-soluble photoinitiator or a water-soluble redox system (H_2O_2-ascorbic acid). The resulting latex had a size around 20 nm. The ratio between the monomer and surfactants remains low but, since the cosurfactant becomes incorporated in the latex, there is no need for surfactant removal[9)]. In this paper, was describe a system similar to this lattter one, but the conventional surfactant sodium dodecyl sulfate (SDS) has been replaced by the copolymerizable surfactant HeC12.



HeC12

Experimental part

Materials. All experiments were performed with deionized water. Styrene was distilled in vacuum and stored at –20°C. HEC 12 was prepared according to Zicmanis[10)] from bulk condensation of dodecyl alcohol and maleic anhydride at 80°C. After purification (recrystallisation from heptane), the sodium salt was prepared using an excess of 160% of NaOH and dissolved in hot water (70°C). All the other materials were used as received.

Microemulsion elaboration. O/W microemulsion were prepared by the droplet titration method which consists in adding under gentle magnetic stirring the cosurfactant to a mixture of styrene and HEC 12, up to the point where the heterogeneous mixture became transparent.

In some cases, an homogenous mixture of surfactant and cosurfactant was first prepared and styrene was added up to cloud point. Stability domain of the O/W microemulsion was empirically delimited by this method. A few examples of formulation are reported in table I.

Table I : Formulations for transparent microemulsions(g)

	1	2	3	4	5	6	7	8	9	10	11
Water	81.3	80.6	79.7	80.8	80.1	82.2	81.3	73.8	73.7	65.2	71
NaOH	0.9	0.9	0.9	1.3	1.1	1	0.9	0.8	1.1	0.9	1.4
HEC 12	7.8	7.8	7.8	6.6	8	7.7	6.9	6.3	8.2	8.8	9.9
Sty.	4.1	4.1	4	3.8	5	4.1	4.1	3.7	6.2	6.6	6.9
HPMA	5.5	5.5	5.4	5.4	4.4	3.6	6.1	5.5	9	11.1	9.4

Polymerization. Following the procedure given by Larpent[8], a redox polymerization initiator system was engaged and the polymerization was carried out in a 250 ml reactor equipped with a condenser and a paddle stirrer (300 rpm) under nitrogen at 35°C. Kinetics of polymerization were followed by gravimetry. The main concern was then to be able to stop the polymerization in order to avoid complete conversion upon oven drying for gravimetric measurement. A combination of inhibitors, together with a precipitation process by methanol in the presence of $MgCl_2$ has been usedfor this purpose. After polymerization, the pH and the conductivity was measured as well as the particle size and its distribution by quasielastic light scattering (QELS) with a Malvern Autosizer-low instrument.

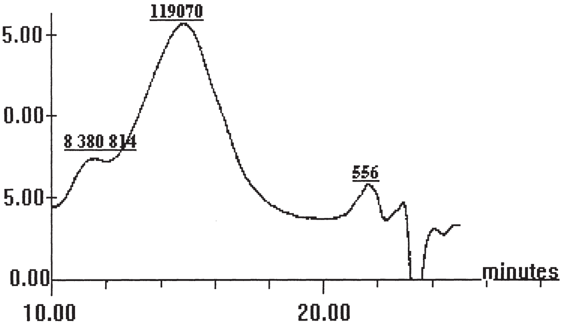


Fig. 1. SEC diagram of the soluble fraction of copolymer (run 4 of tab 2)

Polymer characterization The final polymer is only partially soluble in organic solvent, making GPC analysis difficult. The soluble fraction in THF was analysed by size exclusion chromatography (SEC) using a Waters instrument equiped with refraction index detector (waters 410). It shows a polymodal distribution (fig 1) with a low molecular weight peak corresponding to residual surfactant. The soluble part of the polymer was also analysed by NMR (Bruker 400 MHz) in order to obtain its composition

Results and discussion

The size of the droplets, as measured by QELS, is often in the range 5-15 nm. A set of data obtained upon polymerization is reported in tab 2.

Table 2 : Results of microemulsion polymerisations (corresponding formulation can be found in Tab 1).

run	1	2	3	4	5	6	7	8	9	10	11
H_2O_2	0.42	1.01	1.99	0.19	1.3	1.28	0.6	4.5	1.26	2.96	1.28
Asc ac	0.03	0.1	0.25	0.19	0.11	0.11	0.05	5.41	0.18	4.44	0.2
Dp	30	29	27	21	22	22	34	34	89	_	_
Ip	0.1	0.1	0.1	0.06	0.4	0.4	0.32	0.32	0.4	_	_
aspect	bluish. transparent						bluish		trouble	floculated	
pH	6.2	6.4	6.1	6.3	6.3	6.2	6.4	4	6.7	4	6.9
Conduct. (µS/cm)	260	250	250	260	310	280	250	200	300	400	380

Several runs lead to flocculation. These experiments correspond to serum with the highest conductivity. The reason seems clearly related to the ionic strength of the formulation and the need, for having clear emulsifier solutions, to use a large excess of NaOH for the neutralization of HEC 12. The particle size (Dp in nm.) is larger than the size of the initial droplets and, for the stable polymer microemulsion, remains in the range 15-35 nm in diameter, with rather large polydispersity index (Ip). However, in a few cases, a slightly blue color is observed.

In every case, stable microemulsions are observed only if the solid contents, given by the amount of potentially polymerizable material, is limited. Above 20%, all the experiments lead to flocculation. This fact can be explained by a very simple model assuming an average cubic array for the random organization of the particles, as shown in Fig. 2. In that model, the size of the particle is considered to. include both the spherical polymer particle s and ionic

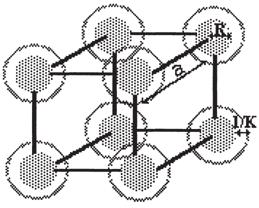


Figure 2 : Model showing packing of particles including the Debye length

double layer. Then the maximum volume fraction of regular particles should be

$$Vf\ \max = \frac{4/3 \times \pi \times R^3}{\left(2 \cdot R + 2/K + a\right)^3} \qquad K = \sqrt{\frac{2.c^{2}.N_a.e.Z}{T.k_b.\varepsilon}}$$

where	R	the radium of the particles	K^{-1}	the Debye length
	c	is the electrolyte concentration	k_b	Boltzman constant
	T	the temperature (Kelvin)	Z	ion valence
	Na	Avogadro Number	e	elementary electric charge
	a	the distance between the boundaries of the particles		

In our conditions, we obtain $K = 3.3.I^{1/2}$ where I, the ionic strenght, is given by $I = ½.\Sigma c_i.Z_i^2$.

The relationship between a (interparticular distance) and Fv is

$$a = \left(\frac{4/3.\pi.R^3}{F_V}\right)^{1/3} - 2.R - 1/1.645.10^9.\sqrt{I}$$

In our system, the ionic strength is about 10^{-1} mol/l. So, with a volume fraction of 0.16, the interparticular distance is reduced to 10 nm, if we consider an average particle size of 25 nm in diameter. This indicates the system, having a double layer around 1 nm thick, is prone to flocculation at this volume fraction,. Flocculated microemulsions have volume fractions larger than 19% (and up to 27%). It can be concluded that adjusted ionic strength and volume fraction are the main conditions to obtain stable microemulsions.

A few experiments have been carried out to follow the polymerization kinetics. (fig. 3). It can be seen that the polymerization are quite rapid and almost finished within a few minutes.

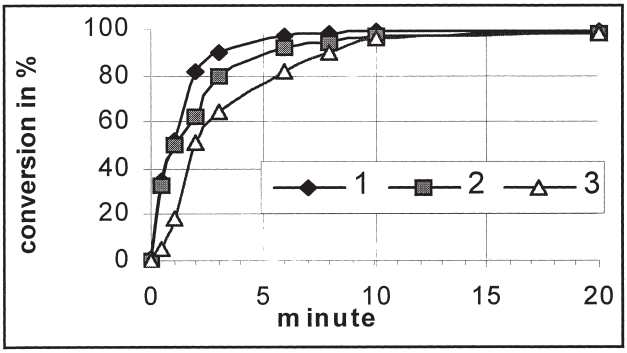


Figure 3 : Kinetics of microemulsion polymerization (run 1,2, 3 of tab 2)

Particle size measurements indicate that coalescence takes place initially between non nucleated particles followed by Ostwald diffusion towards nucleated particles to give a stable final size after 60% conversion. SEC (Fig.1) or the soluble fraction of the polymer is multimodal with a shoulder at a very high molecular weight of more than $8x10^6$ daltons and a mean peak at $1.2x10^5$ daltons. The small peak observed at 550 g/mol corresponds to unreacted surfactant (about 8% of the HEC 12 initially engaged). From the ^{1}H NMR spectrum of the soluble fraction, it was found that the average composition of the copolymer is styrene 38%, HPMA 47% and HEC 12 15%. Before polymerization, the mole percent of the mixture was styrene 37.5%, HPMA 43.5% and HEC 12 19.1%. Therefore, we can conclude that the styrene and the HPMA are completely polymerized, but only a part of the HEC 12 is incorporated in the copolymer.

Conclusions

The use of HEC12 as surfactant and HPMA as cosurfactant allows to carry out microemulsion polymerization of styrene in a limited range of solid contents (less than 17%) and compositions. Both the amount of surfactant and cosurfactant should be higher than the amount of styrene. The stability of the microlatex is very dependent on the ionic strength as shown by a model relating the maximal volume fraction of copolymer particles and ionic strength. The polymerization initiated by a non ionic redox system at 35°C is very rapid and very high molecular weight polymers are produced. Composition analysis of the soluble fraction shows that both the styrene and the HPMA are fully converted, but the conversion of the maleate is only partial.

Acknowledgement : This work is a part of the BRITE BRPR-CT 97 0525

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