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Recent Progress in Reactive Surfactants in Emulsion Polymerisation

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Summary : In the synthesis of latexes for use in waterborne coatings, the benefits of using reactive surfactants are now well known. Improvements are obtained in the stability of the latexes, due to the fact that they are not desorbed from the particle surface. The film properties are also better, chiefly if the films are exposed to humidity, where the water rebound is decreased significantly.

This lecture summarises some recent progress obtained in that field through a European programme, including the participation of 10 academic and industrial laboratories. Four topics are considered.

The first one is dealt with a series of anionic surmers (polymerizable surfactants) prepared upon reacting a polymerisable alcohol with either maleic, or succinic, or sulfosuccinic anhydride. One of these products, resulting from the addition of Hydroxyethylmethacrylate on maleic anhydride is now available commercially. From maleic anhydride one get bifunctional surfmers with 2 polymerisable groups, while the two other anhydride lead to monofunctional surfmers. All these products are engaged in seeded core-shell polymerisations, resulting in film-forming latexes quite stable during and after the polymerisation. However, because they are simply anionic, they do not provide steric stabilization and the latexes flocculate upon addition of strong electrolytes or in freezing tests, except if they are engaged in miniemulsion polymerisations initiated with KPS.

The second topic is concerned with a series of nonionic block copolymer surfmers. A hydrophilic sequence of ethylene oxide units, produced upon ring opening living anionic polymerisation, is followed by a hydrophobic sequence of propyleneoxide, and the living polymer is killed with a polymerisable group attached on a reactive halogen atom. A variety of polymerisable groups have been used : styrenic, methacrylic, vinylic, allylic and maleic. The HLB balance is controlled through the lentgh of the hydrophilic and hydrophobic sequences. The more reactive, associated with an adequate HLB balance allows to prepare core-shell latexes with an excellent steric stabilisation at solid contents up to 40%. It is not the case for the less reactive maleic or allylic, the behaviour of which is close to that of a non reactive surfactant with the same structure.

Transurfs, with an addition-fragmentation mechanism, is the subject of the third topic. A first study was carried out by the group of Eindhoven, who produced a new surfactant on the basis of a MMA dimer condensed on a long chain bromoalcohol and then sulfonated. This transurf was engaged in a MMA emulsion polymerisation, and compared with SDS ; the polymerisation rate was lower and the molecular weight was broader. Optimisation of the incorporation of the transurf was achieved upon using starved feed conditions. We have carried out styrene miniemulsion using controlled RAFT process with a surfactant belonging to the first family reported above together with a RAFT agent. Finally we have used a RAFT agent derived from the nonionic block copolymer surfactants.

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The last topic was done in cooperation with the group of the MPI in Golm, who have studied a family of reactive dienic polymeric surfactants able to be grafted onto the polymer particles from the residual double bonds. These polymeric surfactants are working by an electrostatic stabilization mechanism, being flat onto the particle surface. Our contribution was to add segments of polyethyleneoxide to these polymeric surfactants in order to provide properties of steric, and then electrosteric stabilization.

Introduction

The reason for using reactive surfactants in emulsion polymerisation is to anchor the surfactant molecules onto the surface of the latex particles. Then, when it is achieved, the surfactant cannot migrate in the water phase and continue to stabilize the particles, even after washing. It results a certain number of benefits as indicated in recent reviews devoted to this topic[1-3]

The first kind of benefit which can be expected is an improvement of the stability of the dispersion of particles (latex). Under certain constraints, such as high shear, the classical surfactants, such as SDS (sodium dodecyl sulfate) tend to desorb and no more protect the latex against flocculation. High shearing conditions occur even in the polymerisation reactor if high solid contents latex is to be produced, which is the general trend in the industrial practice. It may occur also when the latex is transported in tubings. Another kind of constraint, very dangerous for the stability of the latex can be met during transportation towards the customers in winter, i.e. freezing conditions. Then, again the surfactants desorb, due to the constraints caused by the formation of ice crystals. Actually it has been demonstrated that reactive surfactants are able to keep the stability of the latexes under such constraints ,as compared with non reactive surfactants having very similar structures [4]. In the case of latexes for coatings, film formation is expected to occur in several steps. During the first step of evaporation, a phase separation takes place, between the organic and the water phases; the surfactants, which are water soluble tend to migrate in the water phase, after desorption from the surface of the particles. The volume of the water phase is rapidly decreasing and tends to be divided in small domains surrounded by the organic phase, in which these domains are almost trapped. A part of the surfactant is able to escape and to migrate towards the surface of the film (both the interface with air and with the substrate supporting the film). It results from that migration process a loss of adhesion on the substrate, which is strongly detrimental for most of the applications. The trend for the formation of a large number of small hydrophilic domains is also detrimental for the applications, even after the film became completely dry. These hydrophilic domains make the material to be sensitive on water when, later on, it is exposed to the humidity. Then, the diffusion of water molecules through the organic material of low Tg cause the swelling of these domains which behave as mechanical defects and tend to reduce the dimentional stability of the material.[4] It was early recognised that the use of reactive surfactants in the synthesis of the latex particles can reduce strongly the sensitivity of the coatings versus exposure to moisture. Recently it was shown that films dipped in water, are able to keep their dimensions when they were prepared from latexes using polymerisable surfactants, at variance with those from latexes using nonreactive surfactants of similar structure and HLB [4].

A possible alternative is to adsorb the surfactant so strongly that it cannot desorb in most of the circumstances encountered in the applications of the latexes. This may happen if the surfactant can have strong enough interactions with the hydrophobic structures of the latex particle surface. Such a situation can be met when using polymeric surfactants[3].

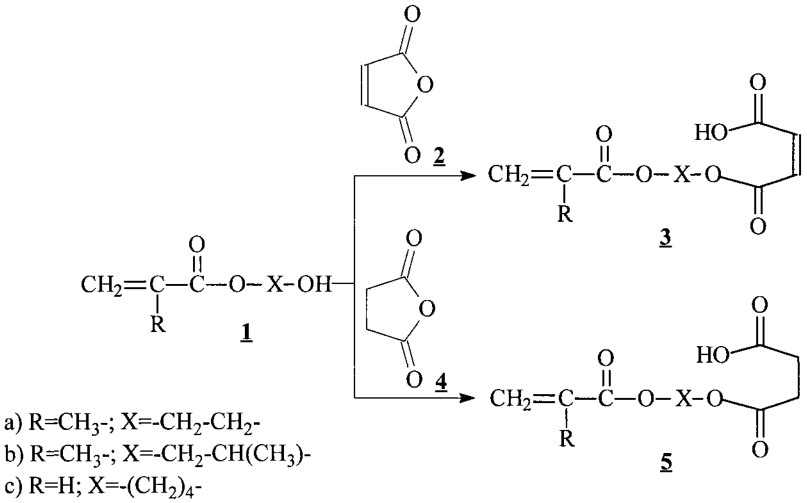
With these ideas in mind a project was proposed to be supported by the European Commission, entitled « Polymerisable and Polymeric surfactants in emulsion polymerisation for waterborne coatings » and was funded in between December 1997 and February 2001. It was following another project on the same kind of topic, executed in the period 1993-1996, who pointed out the interest of simple maleic surfactants. These simple maleic surfactants were exploited by the industrial partners in the last period, and it resulted patented formulations for paints (woodstain finishes), printing inks and metal coatings. In addition a number of new polymerisable and polymeric surfactants were studied by the academic partners of the European project, and this review presents the results obtained in emulsion polymerisations using a selection of these new surfactants.

Four topics are presented : the first one is concerned with a set of polymerisable anionic surfactants , prepared by the Latvian partner of the University of Riga, from alcoholic monomers reacted with various anhydrides [5]. The second one is dealt with nonionic polymerisable surfactants with a block-copolymer structure of oxiranes[6]. The third topic is the work of the group of the University of Eindhoven and is concerned with transurf working with an addition-fragmentation mechanism[7,8], some of them being able to lead to controlled radical polymerisation. The last topic involves polymeric reactive surfactants prepared by the Max Planck Institute für Kolloids in Golm[9].

FIRST PART: ANIONIC POLYMERISABLE SURFACTANTS

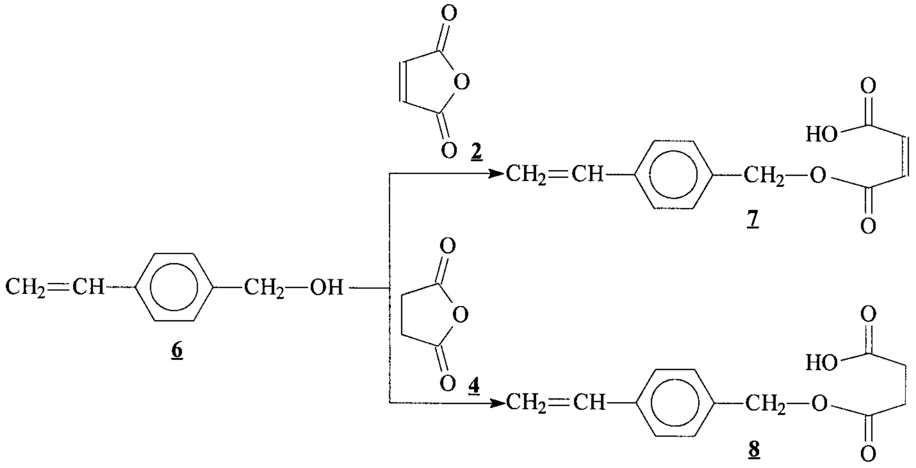
A series of anionic surfactants[5] were prepared upon reacting a polymerisable alcohol ; such as hydroxyethyl methacrylate, hydroxy propylmethacrylate, hydroxybutylacrylate, and vinylbenzylalcohol with either maleic or succinic anhydride, according to schemes 1 and 2. Two of them derived from hydroxyethylmethacrylate are now commercially available (Aldrich). The product of the reaction between vinylbenzylalcool and maleic anhydride can be selectively sulfonated on the maleic double bond, according to the scheme 3, while it has been possible to prepare a sulfonated derivative of the hydroxyethylmethacrylate upon reacting the monomer with sulfosuccinic anhydride, itself prepared from sulfonation of the maleic anhydride followed by dehydratation of the product with acetic anhydride (scheme 4).

Scheme 1

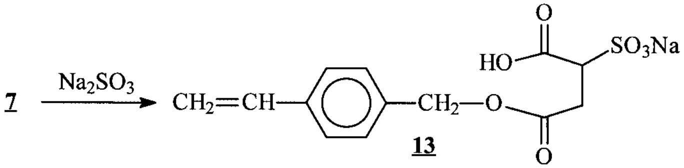


a) $R=CH_3$-; $X=-CH_2-CH_2-$
b) $R=CH_3$-; $X=-CH_2-CH(CH_3)-$
c) R=H; $X=-(CH_2)_4-$

Scheme 2



Scheme 3



All these products were characterized by their NMR spectrum, and , after neutralisation of the carboxylic function, their Critical Micellar Concentration (CMC) was measured as reported in Table 1. Note that the last product MAESS does not show any CMC, being too much hydrophilic ; however it has some surface activity, as it cause a decrease of the surface tension of water, and then has been tested in emulsion polymerisation, as the other surfmers.

Scheme 4

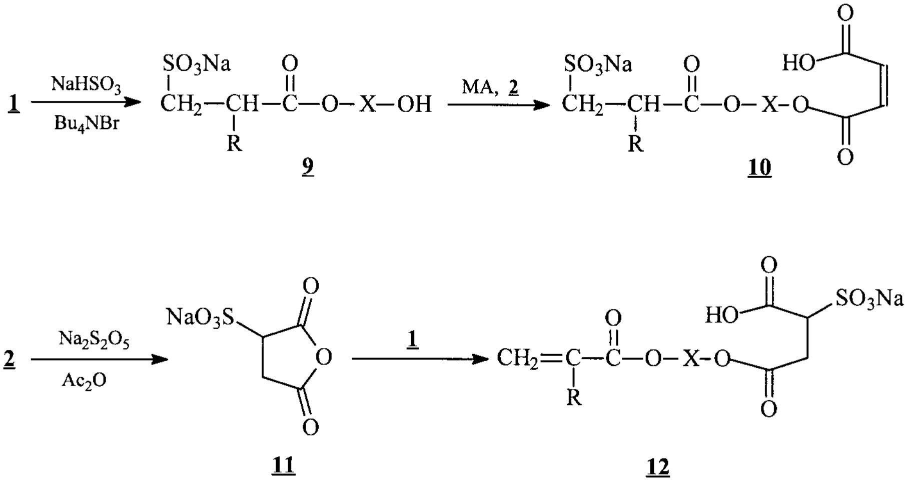


Table 1. New anionic polymerisable surfactants

Name	Formula	CMC m/l	γ mN/m
BAM	$CH_2{=}CHCOO(CH_2)_4OCOCH{=}CHCOOH$	0.040	33
MAPM	$CH_2{=}CH(CH_3)COOCH_2CH(CH_3)OCOCH{=}CHCOOH$	0.035	45
MAEM	$CH_2{=}CH(CH_3)COO(CH_2)_2OCOCH{=}CHCOOH$	0.220	32
VBM	$CH_2{=}CHC_6H_4CH_2OCOCH{=}CHCOOH$	0.008	46
VBS	$CH_2{=}CHC_6H_4CH_2OCOCH_2CH_2COOH$	0.002	45
MAS	$CH_2{=}CH\ (CH_2)_2OCOCH_2CH_2COOH$	0.054	55
BAS	$CH_2{=}CH\ (CH_2)_4OCOCH_2CH_2COOH$	0.016	52
VBSS	$CH_2{=}CHC_6H_4CH_2OCOCH_2CHSO_3COOH$	0.0092	56
MAESS	$CH_2CH_2SO_3\ COO\ CH_2CH_2OCOCH{=}CH\ COOH$		

Batch polymerisations of styrene were carried out using these surfmers. The results are reported in Table 2. All polymerisations reach almost complete conversion after most often less than 150 min. There is only one case where a longer time of 300 min. is needed , which correspond to the surfactant which not displays a CMC. Then it may be concluded that, in this case, the nucleation is more difficult and the final particle size is much larger. In all the other cases the amount of surfactant used in the recipe is much higher than the CMC, and the nucleation is probably a micellar one. The latexes are stable with generally little floc (again except in one case). The particles are essentially monodisperse, which may be surprising in the case where the nucleation is more difficult. The data concerning the surface tension of the final latex show that very little, if any, surfactant is left in the serum , the surface tension being more or less equal to that of pure water. This tends to demonstrate that the polymerisable surfactants are actually incorporated in the polymers. This fact is not surprising because all except one surfactant, have at least one very reactive double bond acrylic, methacrylic or styrenic. The exception is again the sulfonated surfactant which do not show a CMC.

Table 2. Batch polymerisation of styrene

Surfactant	time			Latex Characterisation				
(0.8g)	Min.	Solids %	Dn nm	PDI	Conv. %	Floc %	Np E+16	γ mN/m
MAEM	150	20.4	81	0.07	100	1.2	13	74
BAM	150	20.4	111	0.05	100	1.7	5.3	74
MAPM	180	20.4	100	0.07	100	1.6	7.3	74
VBM	160	20.5	121	0.08	100	2.5	4.1	74
MAES	110	20.4	94	0.05	100	6.2	8.8	72
BAS	130	20.4	112	0.05	100	1.7	5.2	73
VBS	130	19.9	81	0.05	97.3	0.8	13.3	74
MAESS	300	20.4	216	0.06	99.8	2.4	0.72	73
VBSS	150	20.4	108	0.06	100	1.1	5.8	74

A few results about the dependence of particle sizes on the amount of surfactant are reported in Table 3. Obviously the mechanism does not follow the Smity-Ewart theory but the behavior is close to that observed when ionic monomers are used (exponent near 1 instead of 0.6)

Table 3. Effect of the amount of surfactant on the particle size

Latex	MAEM, g/l	phm	Characterisation of latex								t, min
			TS, %	D, nm	PDI	conv., %	coag., %	Np/1 l latex	γ, mN/m	pH	
b1a	2.5	1	19.9	168	0.06	98.4	1.31	7.5E+16	74.6	6.2	130
b1	5.0	2	20.4	81	0.07	100	1.23	6.8E+17	74.7	7.2	100
b1b	7.5	3	20.1	79	0.04	98.3	0.84	7.1E+17	75.1	7.4	140

These surfactants were used to prepare core-shell latexes, with polystyrene core (particle of 95 nm diameter, obtained from styrene polymerisation initiated with KPS and stabilized with SDS. After washing to remove the SDS, these particles were used as a seed for a shell of polybutylmethacrylate. The reactive surfactants were introduced partly at the beginning of a swelling step with a small part of the monomer, and partly as a feed with the major part of the monomer. The targeted final size was 180 nm in diameter with a 20% solid contents. The corresponding data are reported in Table 4.

It can be seen that all the surfactants tried lead to high conversion polymers with small amounts of coagulum and approximately the targeted size and narrow particle size distributions. At variance with the reference latex, prepared using SDS, the surface tension of the final latex are rather high and not far from that of pure water.

More information about the conversion of the surfmer can be obtained upon conductimetric titration of the acid groups. The results reported in Table 5 are rather puzzling, because it appears that only a part of the acid groups of the surfactant is located onto the surface, except in the case of VBSS ; furthermore, it seems that a rather small part of the carboxylates engaged is present onto the particle surface. Then, owing to the fact that not very much surfactant remained in the serum, it must be conclude that a rather large part of these surfmer are buried into the interior of the particles.

Table 4. Results of core-shell polymerisations using reactive anionic surfactants of Table 1

Latex	Surfact. name	NaOH, g	MABu, g	TS, %	Conv., %	D, nm	PDI	Coag., %	γ, mN/m	pH
Maleates										
s1	MAEM	0.140	40	20.3	100	178	0.06	0.46	70.1	5.4
s1a	MAEM	0.140	20/20*	19	92	176	0.07	1.08	69.4	5.5
s2	ABM	0.132	40	20.3	100	177	0.04	0.92	67.2	5.9
s3	MAPM	0.132	40	19.2	93	178	0.07	0.78	68.2	5.9
s4	VBM	0.138	40	19.4	94	174	0.05	4.34	68.1	6.2
Succinates										
s5	MAES	0.139	40	20.3	100	178	0.06	1.03	70.4	6.8
s5a	MAES	0.139	20/20*	20.3	100	166	0.06	0	71.1	6.7
s6	ABS	0.131	40	20.3	100	183	0.04	0.85	65.1	6.8
s7	VBS	0.137	40	19.8	96	175	0.06	0.47	68.1	6.6
Sulfosuccinates										
s8	MAESS	0.2 ($NaHCO_3$)	40	20.2	99	262	0.08	2.81	71.7	7.9
s9	VBSS	-	40	19.8	97	176	0.05	2.85	70.3	5.1
Reference										
S10	SDS	0.218 ($NaHCO_3$)	40	20.0	100	191	0.07	0	47.2	8.5

***Styrene/Butylacrylate mixture (1/1)**

Another puzzling data are those about the crosslinking of these core-shell polymers, which are reported in Table 6. In the case of the maleate surfactants, a crosslinking effect can be expected , because these maleates contain two double bonds, one acrylic or styrenic, which is expected to be reactive, and the second one, maleic is known to have rather low reactivity. On the other hand, the succinate and sulfosuccinate surfmers have only the reactive double bond and are not expected to cause crosslinking. However ; the crosslinking effect can possibly be attributed to transfer reactions onto polymer, and this is known to occur with acrylate monomers [10], as well as for vinyl benzyl derivated monomers [11]. Indeed, it happens for the VB surfmer and also for ABS, and in these two cases, there are not that much differences with the maleates. In other cases, the swelling ratios are very high and the crosslink density is consequently very low.

Table 5. Conductimetric titration of core-shell latexes

Latex	Surfact. name	Amount of surfactant mmol/g pol	$[COO^-]$, μeq/g pol	$[SO_4^{2-}]$, μeq/g pol	Surface located %	Surface coverage COO, %
Maleates						
s1	MAEM	0.075	36.9	6.7	49.2	21.7
s1-30	MAEM	0.079	42.9	6.9	54.3	29.1
s2	ABM	0.070	41.1	8.1	58.7	24.1
s3	MAPM	0.074	45.8	10.4	61.0	27.0
s4	VBM	0.077	51.5	9.0	66.8	29.7
Succinates						
s5	MAES	0.074	52.2	6.2	70.9	30.9
s5-30	MAES	0.078	51.8	5.5	66.5	34.7
s6	ABS	0.069	54.8	8.3	79.4	31.7
s7	VBS	0.075	29.5	-	39.3	17.1
Sulfosuccinates						
s8	MAESS	0.052	40.2	8.2	77.4	34.9
s9	VBSS	0.052	53.9	20.9	100	31.0

Table 6. Gel contents and swelling ratios of core-shell latexes

Latex	Surfactant	Swelling ratio, %	Gel contents, %
Maleates			
s1	MAEM	515	89
s1-30	MAEM	425	90
s2	ABM	559	88
s3	MAPM	413	82
s4	VBM	576	70
Succinates			
s5	MAES	512	18
s5-30	MAES	769	32
s6	ABS	146	22
s7	VBS	190	10
Sulfosuccinates			
s8	MAESS	1285	56
s9	VBSS	534	82

The colloidal stability of these latexes is good enough during and after their synthesis, but the use of these reactive surfactants do not impart the expected improvements of that stability. They do not resist the freeze-thawing test and the addition of electrolytes cause them to flocculate as soon as the salt concentration is higher than 0.1 N. These core-shell latexes are film forming, but surprisingly, except in the case where the shell is composed of a mixture of Styrene and butylacrylate, a rather high temperature (65°C) is needed for getting an homogeneous and non brittle film. We might suppose that at the boundary of the latex particles a high Tg material is formed through copolymerisation of the reactive acid groups containing reactive surfactants with butylmethacrylate; this materials should be able to prevent coalescence unless high enough temperatures are used. A few examples of water rebound are shown in figure 2 as the weight % rebound upon dipping for days a series of films from latexes prepared using hydroxyethylmethacrylate derived surfactants. As compared with the reference film from SDS, both the maleate and the succinate surfmers lead to some improvement (less water rebound), but the sulfosuccinate product give film with more water uptake than the reference. Undoubtedly, this is due to the high hydrophilicity of the corresponding product, which is so water soluble that it do not display any CMC.

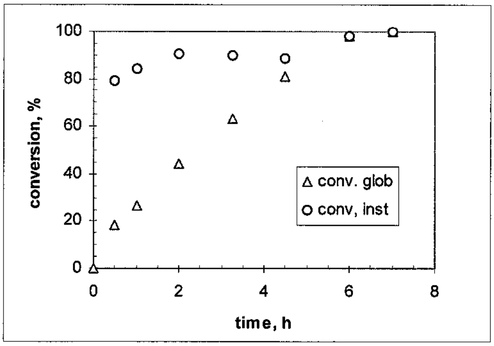


Figure 1 : Example of conversion of the monomer versus time (h)
Core-shell polymerisation of Butylmethacrylate using ABM as surfactant

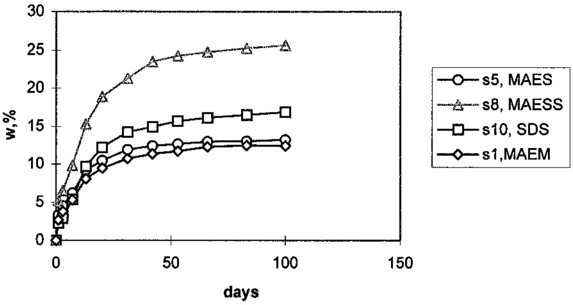


Figure 2 : Water rebound of films (weight %) dipped in pure water for days

Some trials have been carried out in order to prepare miniemulsions using this series of surfmers. Using VBSS as a polymerisable surfactant, showing a CMC close to that of SDS, in the presence of hexadecane, it is rather easy to obtain stable miniemulsions of either styrene or methylmethacrylate, with diameter of droplets in the range 100-250 nm[12]. Upon polymerisation, with either AIBN or KPS, the size of the polymer particles remains near that of the initial droplets with high conversion of the monomers. It appears that 50 to 75% of the surfactant remains fixed onto the surface of the polymer particles, while not much residual surfactant is present in the serum, as shown by surface tension measurements of the final latex. Large differences of latex stability, versus addition of electrolytes or freeze-thawinng test are observed, depending on the initiator used in the copolymerisation. When using KPS, the stability is much better than when AIBN is used. It seems that, in addition to the electrostatic stabilisation due to the anionic sulfonated surfactant, there is a steric stabilisation when KPS initiates the polymerisation. Then there is a rather large difference between the particle diameter as measured by dynamic light scattering and by electron microscopy. This difference show that there is an hydrophilic layer around the particles with a thickness of several nm. Attempts to separate the corresponding polymeric materials were unsuccessful, but the analysis of the serum demonstrates that copolymers of the monomer and the VBSS were present.

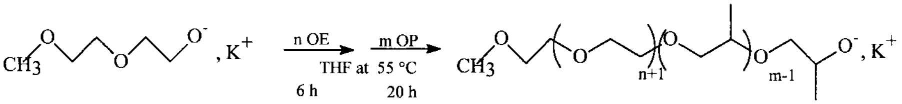
SECOND PART: NONIONIC BLOCKCOPOLYMER POLYMERISABLE SURFACTANTS

A set of block copolymers of propylene oxide-b-ethylene oxide have been prepared through living anionic ring-opening polymerisation of first ethylene oxide (hydrophilic sequence) and then propylene oxide (hydrophobic part)[6]. The initiation of the polymerisation was done using the potassium salt of diethylene glycol monomethylether, while the living chain end has been killed with a reactive chloride derived from a polymerisable moiety. The chemistry of that process is illustrated in the scheme 5 in the case of methacryloyl chloride as the killing agent.

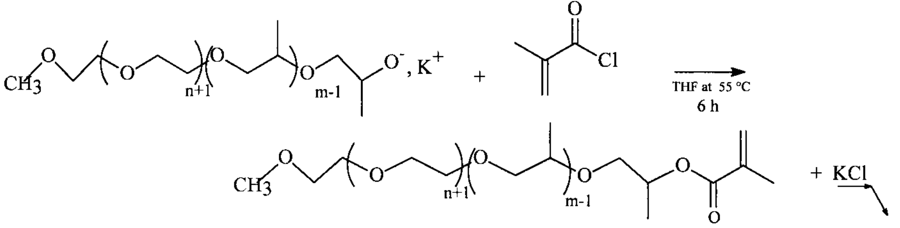
Similar reactions were carried out using allyl chloride and vinylacetochloride, to give instead of a methacrylic derivative, an allylic and a vinylacetate derivatives. Reaction of the living blockcopolymer with isobutyl chloride leads to a non reactive polymeric surfactant. A maleic derivative was also prepared, but in a slightly different way : the living blockcopolymer was first killed with methanol, giving the corresponding alcohol derivative ; after purification , the product was reacted further with Sodium hydride, which was used to open the cycle of maleic anhydride. For that last reaction, the potassium salt was not convenient, giving rise to scission of the ester group.

Scheme 5

Polymerization of ethylene oxide and propylene oxide :



End reaction with methacryloyl chloride :



The length of either the EO or the PO sequence can be varied as we will, so varying the HLB balance. However, previous work in our laboratory[4], using the same kind of technique to prepare a styrenic block copolymer, with a butylene oxide sequence, instead of the propylene oxide one did show that the stability of the latex prepared with that kind of surfactant, was very sensitive to the HLB balance of the surfactant ; the best results were obtained with a sequence of 7 hydrophobic butylene oxide units and 35 units for the hydrophilic sequence. Then, taking into account the change for a propyleneoxide sequence, we choose to have the same HLB, and the length of the hydrophobic sequence was fixed to 10 propyleneoxide units. Characterisation of these surfactants was carried out, by NMR, for their chemical structure, SEC for their molecular weight and by surface tension measurements, for their colloidal properties. Data are reported in Table 7.

The block copolymer reactive surfactants were engaged in the synthesis of core-shell styrene/butylacrylate copolymer latexes. Seeded polymerisations with polystyrene seed with 100 nm. diameter and a shell of 50/50 copolymer of styrene and butyl acrylate, with a final diameter of 250 nm. targeted. The EO-PO surfmer was used only for the shell; a semi batch addition procedure was carried out for both the monomers and the surfmer. Very good results have been obtained as it can be seen in the table 8, where it can be seen that in most cases the targeted size is actually obtained with a very limited amount of floc which increases moderately if the solid contents is increased, or is the HLB balance is a little bit changed.

Table 7. Characterization of the block copolymers surfactants

Surfmer	Yield%	Mn(g/mol	PDI	CMC(mg/l)	CMC mmol/l	γ at CMC mN/m
Non reac.(Iso)	94	2770	1.04	3600	1.56	38.8
Methacrylic	93	2730	1.04	3550	1.54	39.4
Allylic	93	2790	1.04	3650	1.58	40.2
Vinylacetic	94	2820	1.05	3600	1.56	39.6
Maleic	93	2680	1.05	3650	1.58	38.7

Table 8. Results of core-shell styrene-butylacrylate polymerisations Using a series of methacrylic nonionic surfmers

Latex	Surfactant seed/Feed, phm	S.C. %	Floc. %	D particles Nm	PDI	pH	γ mN/m
L 48	NP 30 (0.5/2.5)	32	0.6	234	0.06	6.8	49.8
L 57	Mac-10-37-OMe(1.5/4.5)	33	0.9	278	0.05	6.9	51.3
L 59	Mac-10-37-OMe(1/3)	31	3.2	325	0.06	7.3	50.1
L 60	Mac-10-37-OMe(2/6)	33	0.2	262	0.04	6.7	49.9
L 61	Mac-12-37-OMe(1.5/4.5)	33	0.3	270	0.03	6.4	50.1
L 62	Mac-8-37-OMe(1.5/4.5)	33	1.3	280	0.05	7.1	51.2
L 64	Mac-14-37-OMe(1.5/4.5)	33	0.3	265	0.04	7.1	50.4
L 65	Mac-14-37-OMe(1.5/4.5)	44	1.8	260	0.06	6.5	50.2

If instead of the surfmers, non reactive surfactants with exact analogous structures are used, similar results are obtained , but using 25% less surfactants; This fact suggests that , due to the rather high reactivity of the methacrylic function; some burrying takes place.

The stability of the latexes produced using these surfmers is also excellent, as shown in Table 9; the stability versus the freeze-thawing test is lost when using the nonreactive block copolymer.

Table 9. Stability of the core-shell latexes from methacrylic nonionic surfmers

Latex	Surfactant	Ethanol 1 M	Electrolytes $MgSO_4$ 0.5 M	Freeze -Thaw
L 48	NP 30	Floc	Stable	Floc
L 57	Mac-10-37-OMe	Stable	Stable	Stable
L 61	Mac-12-37-OMe	Stable	Stable	Stable
L 62	Mac-8-37-OMe	Stable	Stable	Stable
L 64	Mac-14-37-OMe	Stable	Stable	Floc

As shown in Table 9, good steric stabilization using the methacrylic block copolymers nonionic surfmers can be achieved, as they lead to good resistance to freezing. Similar surfmers, but with either an allylic or a maleic group did not provide the same excellent stability. In fact, when their serum is recovered after flocculation, the surfmer can be shown to have not reacted(maleic) or poorly reacted (allylic) , and then is not incorporated in the latex particles. Such surfmer have the same behaviour versus the stability than block copolymer surfactants which are not reactive. The vinylic surfmer shows an intermediate behavior. Some typical data are reported in the table 10.

Table 10. Incorporation of the block copolymer surfmers

Surfactant	Amount Phm	Acetone extract %	Oligomer %	Mw	High Pol %	Mw
Iso	1.2 / 3.6	100	-	-	-	164000
Maleic	1.2 / 3.6	100	-	-	-	162000
Allylic	1.4 / 4.2	39	40	45000	21	121000
Vinylic	1.6 / 4.8	33	54	66000	13	145000
Methacryl	1.6 / 4.8	0				174000

With the allylic surfmer, only 21% is incorporated in the polymer, 40% is incorporated as oligomers (or low Mw compounds), and 39% remains free in the serum. The corresponding values for the vinylic surfmer are, respectively 13, 54, and 33%, while in the case of the maleic surfmer or with the nonreactive surfactant almost 100% of the surfactant remains unreacted in the serum and can be extracted with acetone.

In another polymerisation , the vinylic surfmer has been engaged in a copolymerisation where the styrene has been replaced by methylmethacrylate. In that case the latex obtained was fully precipitated in acetone and was shown to be stable versus both electrolytes addition and freeze-thawing tests. The difference from the case of styrene-acrylic latex can be explained by the fact that styrene can be considered as an inhibitor versus the polymerisation of the vinylic monomers , so that this vinylic surfmer can be reacted and incorporated only at the very end of the process, when almost all the styrene has been polymerized. At this moment, because it is known that in the styrene-butylacrylate copolymerisation the styrene is converted at a rate slightly more rapid than the butylacrylate, it remains a part of this second monomer large enough for causing the incorporation of the vinylic surfmer as a copolymer. In that process, incorporation of the vinylic surfmer should take place on the very surface of the latex particles, which is close to the ideal situation.

THIRD PART : TRANSURF WORKING THROUGH AN ADDITION-FRAGMENTATION MECHANISM

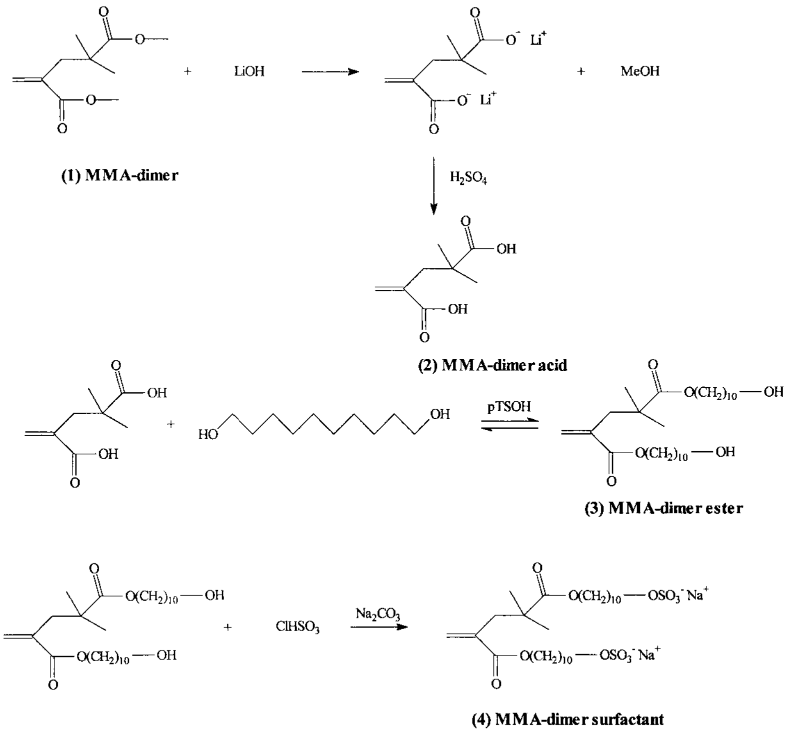
It is probable that the most promising system for controlled radical polymerisation is the so-called RAFT process (Reversible addition-fragmentation transfer), because there is about no limitation concerning the nature of the monomer concerned, at variance with the other systems such as the SFRP (stable free radical polymerisation) or ATRP (atom transfer radical polymerisation). In this part we would like to present data obtained in our European Consortium in that or related line obtained chiefly by the group of EINDHOVEN.

First we will present a study, carried out using a transfer agent working with an addition-fragmentation mechanism which is not reversible and which not lead to controlled radical polymerisation (CRP). It was expected that this transurf should behave better than thiol transurf derivative which are too much reactive and are consumed in the early steps of the process[13].

The synthesis of this transurf agent was carried out according to the scheme 6[7]. Dimer (or trimer) of MMA, are first produced through a radical mechanism in the presence of a powerful Cobalt derivative transfer agent (CoBF), Then, after hydrolysis of the ester groups, with lithine, these carboxylatedimers were esterified by condensation onto a surface-active long alkyl chain sulfate. On the basis of fluorescence and surface tension data, it is surface active. There is further evidence to suggest that there is premicellar aggregation, a possible conformational transition with relatively inefficient packing of the TRANSURF in a micelle. From the surface tension data a flat molecular conformation appears at approximately 1 x 10^{-3} mol dm^{-3} (131 $Å^2$ surface area) which we assume corresponds to low aggregation number of premicellar aggregates. There is evidence to suggest formation of a larger volume of the microdomains in these micelles compared to SDS.

Scheme 6

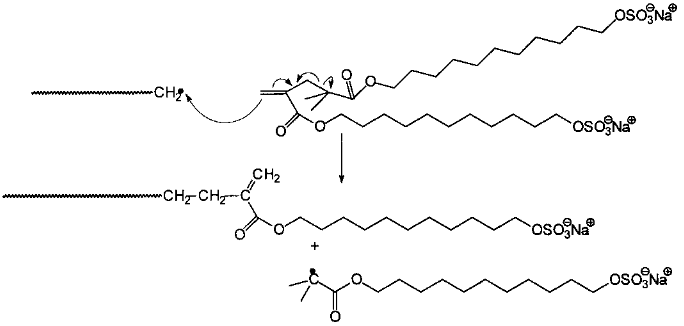
Synthesis of the transurf



This transurf has been used in the ab initio emulsion polymerisation of MMA at 70°C, where it was compared with SDS[8]. It was expected to work through an addition-fragmentation mechanism shown in scheme 7 ; Then, the surface- active alkylsulfate moiety should be located at the end of each polymer molecule. It was found that rate was lowered and average diameter nearly doubled compared to the SDS experiments (control). In addition the molecular weight distribution was very broad but had a lower $\overline{M}n$ than the SDS experiment. Unfortunately due to the formation of many water soluble oligomers the consumption of transurf could not be obtained accurately. However, it was estimated theoretically that only a very small amount of transurf would be consumed and a method to increase the incorporation of transurf into the particles is to keep the ratio of monomer to transurf as loas possible. The best way to achieve this is to carry the experiments out under straved-feed conditions.

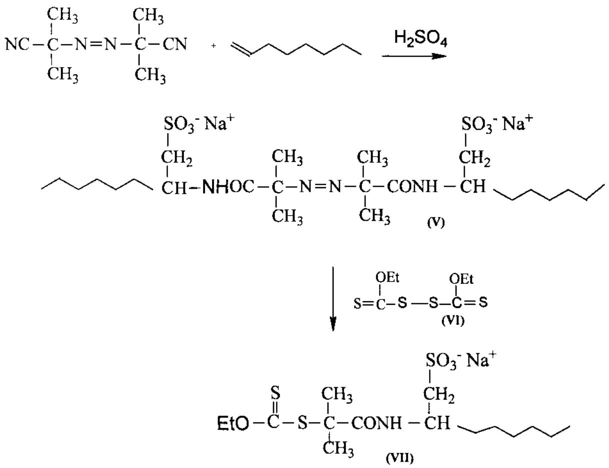
Scheme 7

Addition Fragmentation Mechanism



On the other hand, a few works have been carried out in order to combine reactive surfactants and CRP through the RAFT chemistry. This was done in two ways. The first route was to prepare a surface-active RAFT agent. It has been suggested to name such products SURRaft. Two different compounds have been prepared. One can be used both as a RAFT agent and an INISURF (initiator and surfactant). It was prepared according to scheme 8. The very common initiator AIBN was first modified through the Ritter reaction [14] with a long chain olefin (1-octene or tetradecene or hexadecene) in the presence of Oleum at –5°C. After neutralization with soda, the product was extracted with butanol and reacted with bis(O'-ethylxanthate)at 70°C. The second product was prepared from undecenol according to Scheme 9. First the compound was sulfonated with chlorosulfonic acid in the presence of pyridine. After exchange of the pyridinium salt versus Sodium salt , the product was hydrobrominated and reacted with Potassium xanthate.

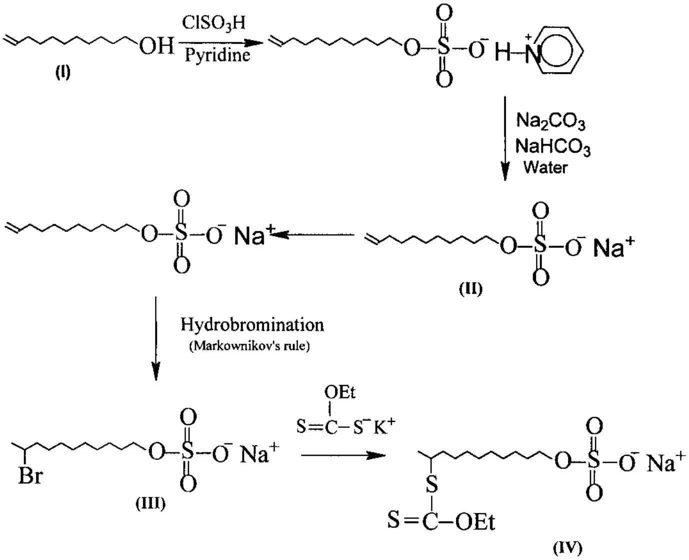
Scheme 8



SUR-RAFT INISURF

Scheme 9

Simple SUR-RAFT Synthesis



These sur raft transfer agents, are currently engaged in emulsions polymerisations, and the corresponding data will be published in a near future, but are not yet available.

The second route to combine reactive surfactants with CRP, is simply to use reactive surfactants in a normal RAFT process carried out in emulsion. A few trials have been done, using some reactive surfactants described in the first part of the present paper. A rather promising result has been obtained as follows : the experiment was carried out in two steps ; in a first step, a RAFT polymerisation of styrene was done in bulk at 70°C in the presence of a $C_6H_5CSSCH_2COOH$ as the raft agent and AIBN as initiator. The controlled polymerisation was obtained, as shown in figure 3, where the molecular weight increases linearly with time and conversion (while the polydispersity is decreasing), and result in a polymer with Mn=2800 and Mw/Mn = 1. In a second step this polymer was introduced as the hydrophobe in a miniemulsion of styrene stabilized by VBS as the surfactant. A variety of initiators have been used , and the results are reported in Table 11. The highest conversions are obtained using the water soluble initiator, but one observes a lack of control of the polymerisation with a broad distribution (Mw/Mn = 2.9). The conversion versus time curves (see figure 4) also show a poor degree of control ; however, it seems that in the case of AIBN, the conversion increases linearly with time at the beginning of the polymerisation, but this feature is lost after about 5 hours and the final distribution is broad.

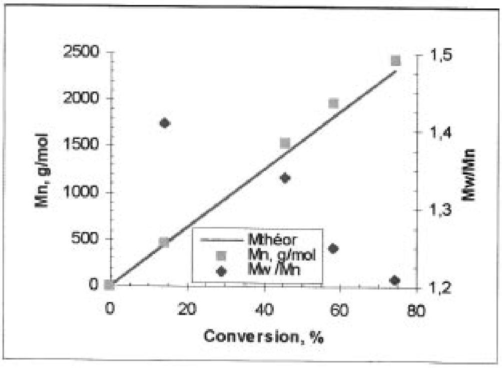


Figure 3 : Controlled RAFT polymerisation of styrene in bulk

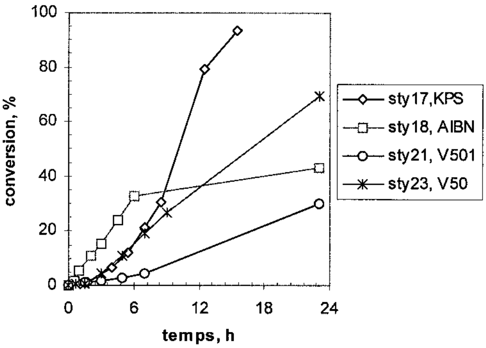


Figure 4 : Kinetics of RAFT miniemulsion polymerisations of styrene in the presence of VBS as reactive surfactant

Table 11. Data of trials for controlled radical polymerisation (RAFT) of styrene in miniemulsion

In the presence of VBS as reactive surfactant

Run	Surfmer g/l	Initiator mg	D,a) nm	PDIb)	$Np*10^{16}/l$	conv., %	Mn, g/mol	M_w/M_n	time, h
Sty17m	VBS 0.45	KPS 10	199	0.15	1.9	93.3	41300	2.9	15.5
Sty18m		AIBN 10	157	0.19	2.1	43.4	69000	9.5	23
Sty21m		V501 10	225	0.07	0.4	29.8	54700	5.2	23
Sty23m		V50 10	215	0.09	1.1	69.3	46200	3.4	23

FOURTH PART : SULFONATER POLYBUTADIENE SURFACTANTS

Polymeric surfactants are expected to be strongly adsorbed onto the surface of latex particles, so that they can be used instead of the reactive surfactant and are expected to confer to the latexes the same benefits than the reactive surfactants. A further step has been raised in the Max Planck group of GOLM; by preparing a reactive polymeric surfactant[9]

Water soluble products were obtained from partial sulfonation of either homopolymers of butadiene and isoprene, or block copolymers of these two monomers with styrene. The degree of sulfonation, as measured by elemental analysis of Sulfur is generally limited (in between 11 and 47%) , at level high enough to assure a good solubility in water, while the values obtained through C13 or H1 NMR measurements are generally higher. The structure of this kind of product is not clear, and many possibilities can be considered for the various units. However, the important features are that the products are surface-active, water soluble and keep enough reactive double bonds able to react through copolymerisation with the main monomers in an emulsion polymerisation. Although polymeric surfactants have been used for a long time in emulsion polymerisation, it is a new fact that a set of reactive polymeric surfactants have been engaged in this process.

A set of products with varying degrees of sulfonation, have been engaged in emulsions polymerisation of styrene and MMA with various initiators. The oil soluble AIBN does not work and the water soluble initiators nonionic VA 086 (azohydroxy) are better than KPS, giving smaller particle size and polydispersity, because a higher ionic strength causes already in a neat solution of the reactive surfactants the formation of globular structures (particle like), so that the surfactant in these globular structures is not available for stabilisation, and it results some agglomeration. After ultrafiltration the latexes displays a high surface tension , close to that of pure water, thus showing that the surfactant does not remain in the water phase.

In a second step, semibatch copolymerisation of butylacrylate with either styrene or MMA were carried out. It result latexes with high solid contents (47 or 48%) with particle size of 179 (MMA) and 158(Sty) nm respectively.

Some polymerisation were carried out in D2O using deuterated styrene in order to determine, from NMR measurements the incorporation of the stabilizer.

Measurements of the charge density before and after cleaning by ultrafiltration show that, while it decreases very much when the latexes have been prepared with SDS as stabilizer, it tends to increase when using the polymeric surfactants ; it means that the sulfonated polybutadienes are well grafted onto the latex particles, and that the washing treatment make accessible new layers of the stabilizer. The stability of these latexes versus electrolyte addition or versus freezing is not improved as compared with the case of SDS. It can be then concluded that the polymeric surfactant stays flat on the particle surface.

In order to get better stabilization, these polymeric surfactants were modified by introducing a nonionic sequence of Polyethylene oxide (PEO)[15]. First block copolymers of polybutadiene-b-PEO have been prepared through living anionic polymerization of butadiene and then ethyleneoxide in THF, which lead to 1,2 butadiene units ; By this way, it was possible to control the length of each sequences. Then the sulfonation of the butadiene sequence was carried out in such conditions that water solubles polymeric surfactants were obtained. It was thus possible to finely tune the properties of the series of surfactants (molecular weight of each sequences and degree of sulfonation (dos). A set of small-scale experiments carried out to choose the best initiator lead to the conclusion that the PEGA200 (Polyoxyethylene glycol-azo) has to be preferred, and that the new surfactants are better than the previous ones. It was further shown that both the structure of the block copolymer and the dos are critical to improve the stability of the latexes. A longer length of the PEO sequence is essential to confer to the polymeric surfactants good properties of steric stabilization, while the dos must be high enough to keep the polymer water soluble.

The properties of steric stabilization have been estimated by measuring the onset of agglomeration upon addition of electrolyte (NaCl solution). These tests allow to see the influence of the structural parameters of the polymeric surfactants. It results that a PEO sequence length of 50 units is needed, while increasing the dos allow to enhance the properties of steric stability.

Some effort have been done to replace the living anionic block copolymerisation, used for introducing the PEO sequence by cheapest methods based on radical polymerisation, of butadiene (ethoxylation of hydroxytelechelic polybutadiene, or radical polymerisation of butadiene with long PEGA initiators) failed to give pure enough products before the step of sulfonation.

Conclusions

In the first part of this review, a set of new anionic surfactants have been described, characterized and used in emulsion and miniemulsion polymerisation. However, except in one case of miniemulsion polymerisation, the results were rather disappointing in terms of colloidal stability. All the reactive surfactants are good stabilizers for the polymerisation process, even those which show no CMC, and, in consequence have poor surface activity , but do not impart to the latexes properties of resistance to addition of electrolytes, freezing or shear. On the other hand, the behaviour of the films from core-shell latexes in the presence of water is conform to the expectation (lower water rebound) except for those showing no CMC, which are too much hydrophilic.

The normal papers describing the contents of the second part will be published in a near future. They involve first the synthesis and characterization of a set of reactive block copolymers of ethylene-oxide as hydrophilic part, and propylene-oxide as the hydrophobic part ; these surfactants have all the same HLB balance optimized after previous data from our laboratory [4], and consequently about the same CMC ; they differ only by the reactive end group located at the end of the hydrophobic sequence. A non reactive reference compound was also prepared. When engaged in seeded(polystyrene with 95 nm in diameter) core-shell (styrene/butylacrylate) emulsion polymerisation, they always allow to prepare the targeted particle size (240 nm) of latex. The amount to be used for that purpose is depending on the reactivity of the polymerisable surfactants. The more reactive they are, the higher the amount needed. Using the methacrylic compound, it is necessary to introduce 125% of the quantity used for the nonreactive surfactant, or for the maleic one. On the other hand the methacrylic product is fully incorporated in the latex particles, and does confer to them an excellent stability versus electrolyte addition and freezing. This is not the case obviously for the nonreactive surfactant, but also, more surprisingly for the maleic compound. This last result is at variance with the data of other groups, who have shown a behaviour of the maleic surfactants close to the optimal, while they have observed poor results for the methacrylic derivatives[14]. Allylic and also vinylic compounds show in our case intermediate behaviour :partial incorporation and lack of resistance to freezing. However vinylic block copolymers show excellent properties in case of use for preparing an all acrylic latex (full incorporation and excellent resistance to stability tests.

The main feature quoted in the third part is related to the use of reactive surfactants in controlled radical surfactants using the RAFT system. Obviously, this topic is still in the infancy. The best way to get CRP, seems to be the use of miniemulsion polymerisation[16,17] and nonionic surfactants. Unfortunately trials to produce miniemulsions of monomers with reactive nonionic surfactants have been unsuccessful up to now. In our group limited success was obtained using a nonionic macromonomer of PEO ; most often the miniemulsions of styrene produced with nonionic reactive surfactants are destabilized upon polymerisation. Trials with VBSS (surfactant described in the first part), although it was observed to give excellent results in simple miniemulsion polymerisation, lead also to destabilization upon polymerization, when a RAFT agent was introduced in the miniemulsion recipe. The use of the SUR Raft agent described just above need specific conditions to get a good control of the emulsion polymerisation. The conclusion is that the field must be studied in details to have a correct idea of its future.

Finely a new domain of research is now open, after the work of the MPIKG described in the last part. Very interesting results have been obtained, with these sulfonated polybutadienes in terms of electrosteric stabilisation of latexes. The use of these fine-tuned structures should be much more exploited in a variety of applications, owing to their wonderful properties , together with their potential cheap cost, when their synthesis will be possible using common methods of polymer chemistry.

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