Styrenic Surfmers in Emulsion Polymerization of Acrylic Monomers. 3. Surface Analysis

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ABSTRACT: Styrenic block-copolymer polymerizable surfactants, when engaged in emulsion polymerization of core−shell acrylic latexes, are forming copolymers containing a large majority of monomer units. These copolymers can be extracted, and analyzed, after extensive washing of the particles by ultrafiltration. Owing to the restricted mobility of the polymer inside the particles**,** direct ^{1}H NMR analysis, in normal water—with water suppression—of the latex itself, in its initial serum, gives selective detection of the water-solvated species and allows to estimate both the amount of surfmer remaining at the surface of the particle and their conformation, thus allowing to determine what part of it participates in the steric and electrosteric stabilization.

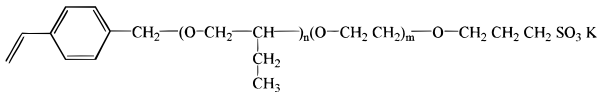
Introduction

The paint industry is a huge consumer of latex from emulsion polymerization. The surfactants essential to the stability of the latex weaken the film properties upon aging. The surfactants tend to migrate toward the interfaces of the films or to segregate inside the film. The film loses adhesion and becomes water sensitive. When using a reactive surfactant in emulsion polymerization, whatever it is, i.e., inisurf, transurf, or surfmer, the main criterion of the success of its use is its strong incorporation at the very surface of the latex particles by copolymerization with the main monomers. Its derivatives must not be buried inside the particles or lost in the serum surrounding the particles as either nonreacted surfactants or water-soluble species.

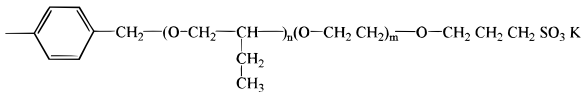
The actual incorporation of these surfactants at the surface of the particles can be estimated after a careful characterization of these particles, first separated from the serum, for instance, by centrifugation, dialysis, or finally ultrafiltration. It is also necessary to wash thoroughly the particles in order to eliminate the surfactant that is simply adsorbed onto the surface of the particles. When the surfactants do contain a hydrophilic poly(ethylene oxide) sequence, a useful technique is to estimate from the ^{1}H NMR analysis of the latex, after dissolving the whole polymer in a suitable deuterated solvent, the number of protons belonging to that hydrophilic sequence compared to the number of protons of a typical group of the main monomer unit. This technique has been applied for instance in the case of another styrenic nonionic surfactant used to produce polystyrene latexes by Filet et al.,[1] Charleux et al.,[2] or also Lacroix Desmazes et al.[3] in the dispersion polymerization of styrene stabilized with methacrylic or maleic macromonomers of poly(ethylene oxide) and again by Schechtman for styrene emulsion polymerization with nonionic styrenic surfactants of the block-copolymer of propylene oxide and ethylene oxide.[4] In such case the possible error introduced by the styrenic nature of the surfactant is quite negligible because the contribution of this styrenic group compared with the signal of the main monomer unit is very small. Since the hydrophilic sequences represent an extremely low part of the whole polymer, of course the accuracy of this kind of measurement is not very good, although a rather long poly(ethylene oxide) sequence in the surfactant is an excellent and sensitive ^{1}H NMR probe (important number of equivalent protons giving an intense singlet resonance at $\delta = 3.6$ ppm).

Scheme 1. Stabilizers Structures

VBn,m-SO_3K



MBn,m-SO_3K



In part 1 of that series, the synthesis of a family of reactive surfactants (Scheme 1) has been described.[5] A successive living anionic ring-opening polymerization of butylene oxide (BO), and then ethylene oxide (EO), was initiated from the potassium vinyl benzylic (VB) alcoholate. After complete consumption of each monomer in the successive steps, the still living chain end can be neutralized, and in that case a styrene nonionic surfactant is produced, which is very similar to those used by Schechtman except that the hydrophobic sequence carrying the styrenic group at its chain end is here butylene oxide instead of propylene oxide. The living chain end can also be used to open the ring of propane sultone, so producing an anionic surfactant.

Part 2 of that series[6] presents the use of these surfactants [compared with nonreactive analogues where the vinylbenzyl (VB) group is replaced by a methylbenzyl (MB) chain end] in emulsion polymerization of core−

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shell latex with a poly(methyl methacrylate) (PMMA) core and a shell formed with a copolymer (50/50 in weight) of methyl methacrylate (MMA) and butyl acrylate (BA). It was shown that very stable latexes can be produced, able to resist the most severe stability tests such as addition of concentrated electrolyte solution, addition of ethanol, freeze−thawing test, and finally shear tests. The best results were obtained with those surfactants showing the largest cmc, thus suggesting that the copolymerization of the water-soluble molecules of the surfactant with the main monomers has a strong effect on the stability of the particles. However, due to the semibatch protocol used in the synthesis of the shell, these polymers are not fully soluble. Indeed, the starved conditions of introduction of the monomer mixture allows transfer reaction to the polymer to take place as shown by Lovell et al.[7] for the polymer and copolymer of butyl acrylate. This transfer reaction causes crosslinkage of the polymer, and it is insoluble in the usual organic solvents used for NMR purposes. Then the method used by previous authors[1−3] was not possible, and another method to estimate the incorporation of the surfactant on the surface of the particle had to be carried out.

Another NMR technique may be used to study the hydrophilic structures of latexes, which consists of analyzing directly the latex itself. The first report about such technique was published by Fitch and Jelinski[8] and also McDonald.[9] In our group a similar technique has been applied by Bonardi et al.[10,11] and reviewed recently by Llauro et al.[12] However, in all cases the latexes were characterized by their ^{13}C NMR spectrum, which makes difficult a quantitative analysis and is not at all a sensitive method.

In direct latex observation, highly mobile hydrophilic polymer structures give detectable signal resonances, whatever they are, completely free in water or at the water−particle interface. In the second case, of course, a broadening of the resonances is expected. On the contrary, the hydrophobic polymer chains chemically anchored or strongly adsorbed at the surface are expected to have a low reorientational mobility, thus producing resonances that spread over the entire spectral range and consequently have a nearly null intensity. As for the polymer inside the particles, it has been shown that the NMR signals are closely linked to both the polymer T_g and the temperature of the NMR observation.[8−12] With particles having a sufficiently high T_g, it is possible to have a selective view of the water-solvated species.

Concerning ^1H NMR analysis, it combines sensitivity and quantitativity, but the presence of huge quantities of normal water puts obstacles on its use for direct latex analysis. Of course, after separation of the serum, the latex can be smoothly dried and redispersed in deuterated water. For instance, by this way it was possible to characterize the grafting of a poly(vinyl alcohol) macromonomer onto a polystyrene seed.[2] For biological and biochemical applications ^1H NMR spectra usually have to be recorded in normal water, with the addition of only 10% deuterated water to provide the necessary lock signal. Higher D_2O content would cause the exchangeable NH protons to disappear. For suppressing the huge water signal a multitude of techniques have been proposed[13−15] which are now available on most spectrometers.[16] To our knowledge, these techniques have not yet been applied to the analysis of latexes, which is done in the present paper.

Table 1. Characteristics of the Latexes Washed by Ultrafiltration

latex	surfactant (1−3 phm)[a]	coagulum (%)	diameter (nm)	surface tension (mN m^{-1})
E52	VB6,17-SO_3K	0.7	274	49.4
E57	VB12,45-SO_3K	4.1	234	49.1
E62	VB7,34-OH	2.3	277	47.1
E71	MB6,33-SO_3K	0.7	274	49.4

[a] phm = quantity of surfactant as a percentage of expected mass of polymer.

Table 2. Ultrafiltration on Latex E52 Prepared with VB6,17-SO_3K

vol of serum collected (L)	0	0.5	1.5	2.5	3.5	4.5
replacement function	0	2.7	8.5	13.8	19.4	25
surf. tension (mN m^{-1})	52.3	56.3	65.8	66.7	62.7	72.6

Results and Discussion

A few latexes have been washed thoroughly by ultrafiltration. Their characteristics from core−shell are reported in Table 1.

It can be observed that their surface tension is rather small, showing that their serum does contain a significant amount of surface-active compounds. In Tables 2−4 are reported the data of surface tension carried out immediately after the last filtration, depending on the replacement function.

It can be seen for the latex E52 and E57 that the washing process can be considered as finished after a replacement function of 25 and 40, respectively (cf. Experimental Section). However, if the surface tension measurement is carried out again after a few days, it drops to 66.3 and 58.6 mN m^{-1} after respectively 6 and 3 days. These results show that the extraction procedure was not really finished, because some surface-active moieties are released from the particles. The latex is out of equilibrium: the distribution of the stabilizers between the serum and the surface of the particles is under kinetic control. The desorption is very slow. In other words, these species are probably strongly adsorbed onto the particles and weakly soluble in water.

In the case of E62, the washing process was continued much beyond, up to a replacement function of about 200. The surface tension remains rather low and increases very slowly. In the meantime, as shown by the particle size measurement carried out by QELS, the latex seems to remain stable. This experiment reveals how slow is the desorption of the stabilizers when using a nonionic surfmer for the emulsion polymerization or in other words how strongly are adsorbed the stabilizers. These results show that desorption of surfmers can occur despite their ability to copolymerize.

For the latex E71, produced with a nonreactive surfactant MB6,33-SO_3K, the latex does not remain stable when the replacement function is greater than 12. We see here the great advantage in using a reactive surfactant.

After having obtained 2 L of ultrafiltrate from E52, i.e. a replacement factor of about 10 and a residual surface tension of about 66 mN m^{-1}, that serum has been concentrated. Upon cooling, some polymer is separated by precipitation, and one obtains 18 mg of dry polymer. Its molecular weight is measured by SEC as M_n = 64 000 and M_w = 400 000. The composition of that polymer can be estimated from ^1H NMR analysis after dissolution in deuterated toluene or chloroform. The ^1H NMR spectrum of ultrafiltrate residues from E52 is shown in Figure 1; it shows three main resonance

Table 3. Ultrafiltration on Latex E57 Prepared with VB12,45-SO_3K

vol of serum collected (L)	0	1	2	3	4	5	6	7	13
replacement function	0	5.7	11.4	17.1	22.8	28.5	34.3	40	74.2
surf. tension (mN m^{-1})	51.8	55.6	59.8	61.0	62.8	64.3	70.3	71.9	71.6

Table 4. Ultrafiltration on Latex E62 Prepared with VB7,34-OH

vol of serum collected (L)	0	6.2	11.2	14.2	16.2	19.7	23.2	26.7	42.3
replacement function	0	3.9	17.8	30.5	35.4	42.0	50.2	58.7	188
surf. tension (mN m^{-1})	48.8	49.9	51.0	53.7	51.6	52.9	53.6	54.8	63.2

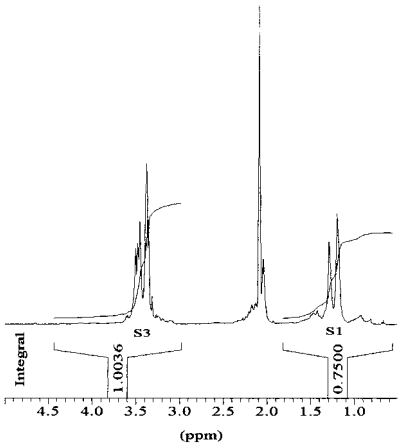

Figure 1. ^{1}H NMR spectrum in toluene-d_6 of ultrafiltrate residues from E52 latex made with VB6,17-SO_3K.

regions. At low field the area S_3 corresponds to all CH_2−O, CH−O, and CH_2−SO_3K from the surfmer (except the benzylic protons which are at lower field) and to CH_3−O from MMA units; at high field the area S_1 corresponds to CH_3−CH_2− from butylene oxide groups of the VB surfmer and CH_3−C from MMA. The intermediate area is unusable, because it is polluted by the CHD_2− multiplet (centered at $\delta = 2.10$) of residual protonated toluene-d_6. As VB6,17-SO_3K has been used to produce E52 latex, these S_3 and S_1 areas represent respectively [90VB+3MMA] and [30VB+3MMA], which allow to calculate the composition of the polymer extracted from the latex; a value of 50 MMA units for one VB surfmer is found (MMA/VB = $[3S_1-S_3]/[S_3-S_1]$). In that spectrum of Figure 1 there is no trace of butyl acrylate units (which should have its OCH_2 resonance at about 4 ppm). So, from this analysis of the first volumes of exchanged serum we can conclude that the surfmer is copolymerized with the monomer present in the water phase and then chiefly with methyl methacrylate. These hydrophilic compounds, containing chiefly the surfmer and MMA units, are progressively desorbed.

The spectrum of polymer extracted upon washing the latex E62 between the replacement function of 151 and 188 is shown in Figure 2. In that case there is clearly the presence of butyl acrylate units (CH_3 at $\delta = 0.9$ and O−CH_2 at $\delta = 4$ ppm) while there are also MMA units (O−CH_3 at $\delta = 3.65$ ppm). The molecular weight of that polymer is much higher, $M_n = 503\,000$, $M_w = 1\,240\,000$. From the ^{1}H spectrum the MMA/BA composition is found to be 4−5 MMA units for 10 BA units [from A_3 and A_1 values]. Then, the observed A_2 value rules out the presence of a significant amount of VB molecules in the polymer extracted, since this area should include 155 protons by mole of VB surfmer. It is not surprising to not detect any more stabilizers after such an intensive washing. Moreover, it is clear that this copolymer is much more hydrophobic and of higher molecular weight than the previous sample from E52. This polymer could come from very small particles gone to the serum.

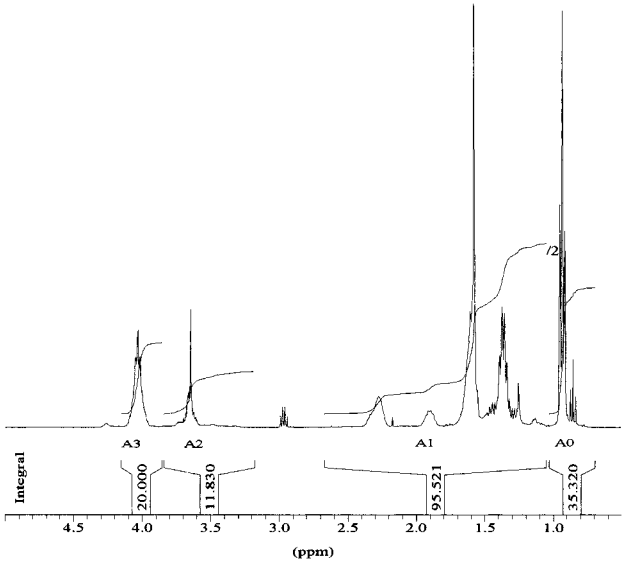

Figure 2. ^{1}H NMR spectrum in $CDCl_3$ of ultrafiltrate residues from E62 latex made with VB7,34-OH.

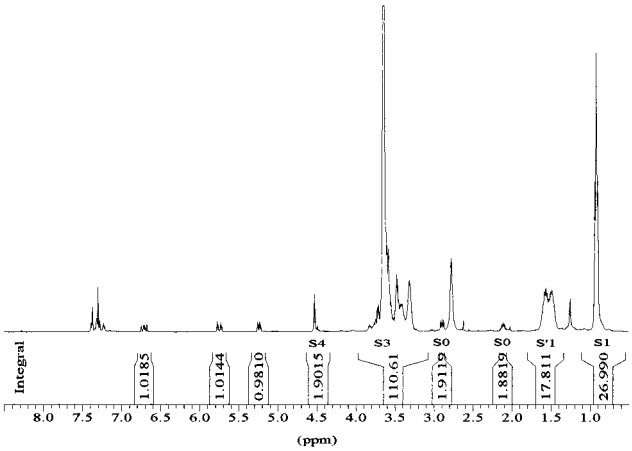

Figure 3. ^{1}H NMR spectrum in $CDCl_3$ of VB9,20-SO_3K surfmer.

In an effort to determine how the surfmer units are linked to the particles, ^{1}H NMR direct observation of the latexes (in normal water, with water resonance suppression, cf. Experimental Section) has been applied.

For this type of analysis some preliminary conditions must be fulfilled: (a) the inside of the particles is not detected (sufficiently high T_g and consequently not enough mobility to give some proton resonances that could prevent the spectral analysis); (b) both hydrophobic and hydrophilic constitutive sequences of the surfmer itself are completely detected when free in water solution.

It was first checked that both the spectra of the surfmer VB9,20-SO_3K in $CDCl_3$ (Figure 3) and in water (Figure 4) are the exact reflection of the complete surfmer structure (Scheme 1), so that there is no

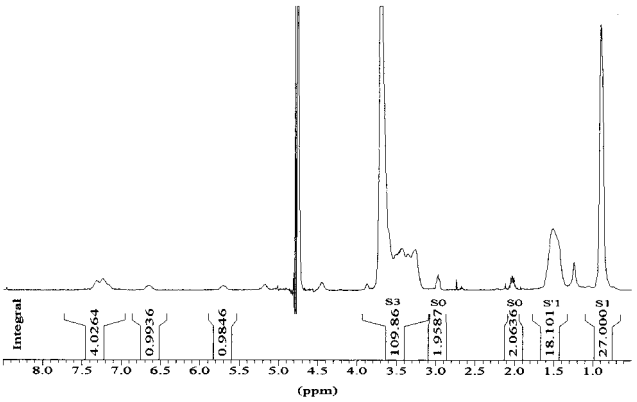

Figure 4. ^{1}H NMR spectrum in water of VB9,20-SO_3K surfmer.

problem due to the possible organization of the surfmer as micelles. Of course, some broadening of the resonances from the hydrophobic part of the surfmer is observed in water (Figure 4), but relative areas are the same.

As we have just seen in the previous paragraph, the surfmer is copolymerized with a rather large number of hydrophobic monomer units so that, even if the resulting copolymers can be extracted after extensive serum replacement, they are strongly adsorbed on the surface of the particles, and only the more hydrophilic parts of these molecules are sufficiently solvated by water to have enough mobility and then be observable by NMR. That means that only the poly(ethylene oxide) sequence and the sulfonate chain end are expected to be observed in the NMR spectrum of the latex. Moreover, the adsorption of a butylene oxide sequence may induce the undetectability of some adjacent ethylene oxide units. It happens for two apparent reasons: (i) the ethylene oxide units close to the butylene oxide sequence are less mobile, and (ii) some ethylene oxide can be adsorbed onto the particles. Indeed, an ethylene oxide unit without hydrogen bound to water is hydrophobic.

To be able to obtain quantitative results, it was very useful to have an internal probe for ^{1}H NMR that is not liable to be adsorbed on the particle: a chemical function or group of the surfactant. Fortunately, the anionic surfactants contain such a probe. If there is no probe, which is the case of the nonionic surfactants, an additional calibration substance could permit to evaluate for example the number of EO units per area of particles. Attempts to have such calibration are described in the Appendix. These calibrations have been evaluated with latexes prepared with surfactants containing a NMR probe (anionic surfmers). The surfactants recovered in the water phase are overestimated with no explanation, but it tends to prove that there is no or very small quantities of surfactants buried inside the particles.

For the anionic surfactants, the probe is constituted by protons of the methylene unit in the α-position to the sulfonate. It is assumed that the area under the $-CH_2-SO_3K$ methylenic protons corresponds to the total number of surfmers in the water phase (and not buried in the particle), whatever is its form, grafted, strongly adsorbed at the surface of the particles, or completely free in water. Then the molar quantity of surfmer, which corresponds to the total BO units detected, is considered as the maximum surfmer amount that can be completely free in water. The corresponding

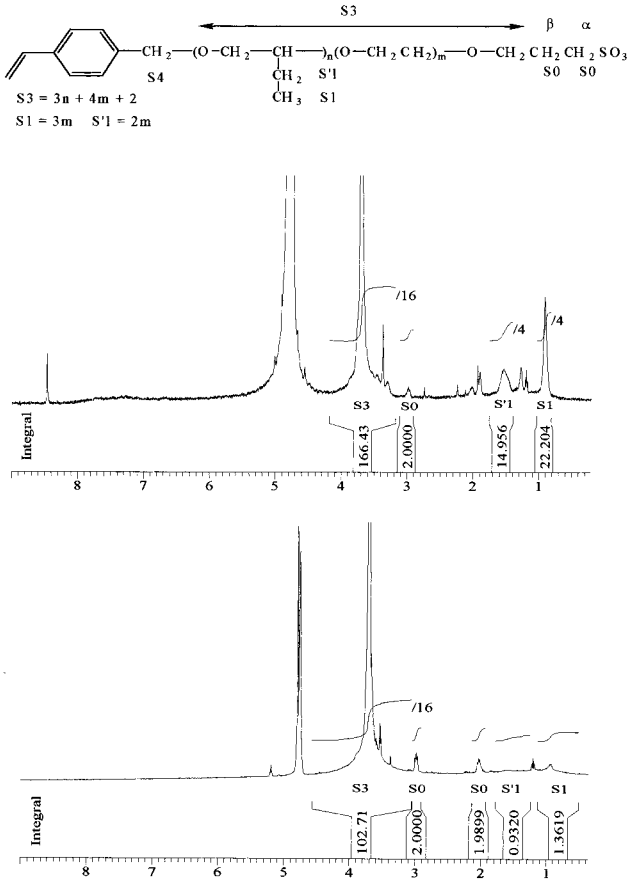

Figure 5. ^{1}H NMR spectrum (with water resonance suppression): (top) after addition of VB10,36-SO_3K to a washed E47 latex in normal water; (bottom) ^{1}H NMR spectrum of latex E50 made with VB10,36-SO_3K in normal water.

numbers of EO units and terminal groups are then subtracted from the related observed resonances. What is left over is the minimum amount of surfmer adsorbed at the surface.

Its EO mobile part is easily deduced from the spectum, and it is found to consist of the whole or only a part of the EO sequence of the surfmer. An example is given below.

The spectrum of the surfmer VB-10,36-SO_3K just adsorbed onto a latex made from SDS (E47)—but free of SDS—is shown in Figure 5 (top). The resonance from the methylene group near the sulfonate group is clearly detected at 2.980 ppm. At high field, broadening of the CH_3-CH_2- resonances from butylene oxide units (δ = 0.905 and 1.530 ppm, S_1 and S'_1, respectively) is noticeable, compared with the spectrum of the surfmer alone in water, thus indicating a restricted mobility. For 1 mol of surfmer [So = 2] the respective areas S_3 [4m′ + 3n′ + 2], S'_1 [2n′], and S_1 [3n′] allow to calculate that about 74% of the BO units and 100% of the EO units are detected. If the total BO units detected are considered as the maximum amount of hydrophobic sequence completely free in water, then about 26% of the surfmer is adsorbed on the particles and its EO sequence is completely free in water.

When looking at the spectrum of the latex made from the same surfmer (Figure 5, bottom) compared to the previous one, the ratio $2S_1/3So$ is much lower (0.4 instead of 7.4 and 10 for the surfmer itself, free in water). That means that the hydrophobic BO sequence is rather strongly adsorbed onto the surface of the

Table 5. Analysis by ^{1}H NMR in Water

latex	surfactant (1−3 phm)[a]	mobile EO units	% free in water	% onto the particles
E50	VB10,36-SO_3K 1−3	25	4.2	95.8
E52	VB6,17-SO_3K 1−3	8	12.6	87.4
E57	VB12,45-SO_3K 1−3	11	5.2	94.8
E61	VB6,17-SO_3K 1.3−3.9	14	4.8	95.2
E59	MB10,34-SO_3K 1−3	12	9.4	90.6
E60	VB7,34-SO_3K 1−3	12	5.7	94.3
E64[b]	VB7,34-SO_3K 1−3	12	4.4	95.6
E65	VB7,34-SO_3K 0.5−1.5	10	4.6	95.4
E56	MB6,33-SO_3K 1−3	8	14.8	85.2
E66[c]	VB7,34-SO_3K 1−3	15	6.6	93.4
E68[c]	VB7,34-SO_3K 1−3	13	4.8	95.2

[a] phm = quantity of surfactant as a percentage of expected mass of polymer. [b] 40% solid contents instead of 25%. [c] Emulsion copolymerization composed of MMA/BA/AA 50/49/1 (AA = acrylic acid).

particles and that the maximum amount of the surfmer present in the water phase is around 4%. Moreover, the S_3 area is very low, indicating that the EO sequence itself is not entirely free in water. Whereas the surfmer alone gives $S_3 = 174$, the surfmer simply adsorbed on a latex previously washed gives $S_3 = 166.5$ (Figure 5, top), and a much lower value is obtained ($S_3 = 102$) with the latex made from the same surfmer. Taking into account the contribution to this area of BO and EO units corresponding to the maximum amount of free surfmer (0.04 mol), then the residual area corresponds to 24 EO for 0.96 mol of surfmer. So it may be estimated that only 70% of EO sequence length of the surfmer is sufficiently mobile to be detected, whereas when the surfmer is just adsorbed on the latex (Figure 4), the whole EO sequence is observed.

This last comparison needs to be completed with another comparison between the latex E60 prepared with VB7,34-SO_3K and the latex E56 prepared with an analogue nonreactive surfactant (see Table 5). With MB6,33-SO_3K in E56, the mobile length is surprisingly shorter, 8 units instead of 12, and the distribution of the surfactant is as expected less in favor of the surface of the particles, 15% in the water phase instead of 5%.

From these two comparisons, it appears that the shortening of the EO mobile sequence is induced by the process of polymerization and not by the ability of the surfmer to be covalently bound. If the surfactant is used for the emulsion polymerization, part of its structure is swallowed up by the particles. It occurs for several reasons: (i) The particles are growing from 120 to 240 nm in diameter. (ii) During emulsion polymerization, the particles are very soft because the polymer is solvated by the monomers so its T_g is extremely low and the temperature of polymerization is 70 °C. (iii) The EO units are hydrophilic only if they can form a hydrogen bound with water; otherwise, they are hydrophobic and compatible with the polymer.

Despite the capacity of the particles to swallow up the stabilizers, they do not completely disappear inside the particles. The anionic end group constitutes a driving force which extracts the compound from the soft growing particle.

The second conclusion of these comparisons is that the distribution of the surfmer is the result of both the emulsion process and its capability to copolymerize.

Quantitative treatment of the ^{1}H NMR spectrum of the latex directly observed in its serum gives (i) the percentage of surfmer in the water phase and (ii) the length of the poly(ethylene oxide) sequence which is mobile and does impart steric stabilization to the latex.

The corresponding data are reported in Table 5. Some conclusions are the following: (1) when using nonreactive surfactants (E59 and E56), the proportion of surfactant moieties in the water phase is larger (10 and 15% instead of around 5%); (2) the length of the mobile sequence of poly(ethylene oxide) is always much smaller than that of the original structure, often around one-third. Going from 25 to 40% solid contents (E60 and E64) does not change the figure. But the use of some acrylic acid (E66 and E68), which is more hydrophilic than the other acrylic monomers, seems to cause the mobile sequence to be slightly longer.

Conclusions

Styrenic polymerizable surfactants, either ionic or nonionic, when engaged in emulsion polymerization of acrylic monomers, are producing—either in water phase or when they are adsorbed onto the surface of the particles—copolymer with the main monomers and chiefly with the more hydrophilic monomer (MMA). These copolymers containing a large amount of the main monomer units are very strongly adsorbed onto the surface of the particles, but always in equilibrium with the water phase, because after thorough washing of the particle by ultrafiltration a part of them can desorb from the surface of the particles, thus decreasing the surface tension of the new serum. From this extraction procedure, the molecular weight and the structure of these copolymers can be estimated.

It seems that the copolymers extracted along the ultrafiltration are varying in composition. The more water-soluble copolymers are recovered at the beginning of the ultrafiltration, mainly composed of MMA−VB, and more hydrophobic copolymers are extracted with an extensive washing of the particles. These hydrophobic copolymers, in which no surfmer structure could be detected, could come from very small particles gone to the serum.

Even if the surfmers copolymerized can be desorbed from the particles, these stabilizers are incomparably more strongly adsorbed than the nonreactive surfactants. Then a latex prepared with a surfmer can support an extensive washing without aggregation whereas a latex prepared with an analogue nonreactive surfactant is rapidly flocculated. This great advantage of the surfmers over the surfactants appears also clearly in part 2[6] with the stability tests applied to the latexes.

Direct ^{1}H NMR analysis of the latex itself, in normal water—with water resonance suppression—is shown to be a selective and sensitive detection method of the very low ponderal amounts of mobile, water-solvated species. For example, in the case of E50, the protons detected correspond to as low as 240 μg of surfmer free in the water phase and 11.52 mg of surfmer grafted onto the particles for 150 mg of solid contents. The analysis needs a latex volume of about 0.5 mL. The analysis has been conducted successfully with a latex up to a solid content of 40%. There is not the disagreement of the dilution whereas the distribution of the stabilizers is controlled by concentrations.

The selectivity and sensitivity of the method are the consequence of the restricted mobility of both the polymer inside the particles (absence of solvent, no residual monomer and sufficiently high T_g's) and the surfmer sequences which are strongly adsorbed onto the particles. Both species do not give any ^{1}H NMR signal although representing the major part of the material.

Here, after a total conversion of the monomers, the T_g are between 5 and 10 °C.

The quantitative analysis of the NMR data gives the following results: it can be estimated that about 5% of the surfmer units remains in the serum, most probably as copolymers, while only a part (between $^1/_3$ and $^2/_3$) of the hydrophilic poly(ethylene oxide) sequence is mobile enough to participate to the steric and electrosteric stabilization of the particles. It can be estimated also that not any surfmer remains buried into the particles. About nonreactive surfactants, the quantity free in water is about 10−15%. The reduced mobility of the EO sequence is essentially due to the emulsion polymerization process. The soft growing particles have a tendency to partly phagocyte the hydrophilic part of the stabilizers. A nonreactive surfactant is more distributed in the water phase than an analogue surfmer. This analysis is an opportunity to get an image of the chemical structures responsible for the stabilization.

Experimental Section

Materials. The synthesis of the reactive surfactants has been fully described in part 1 of this series. The syntheses of the core−shell acrylic latexes were described in part 2, together with the stability tests and some properties of the films prepared from coalescence of the latexes.

The chemicals used for ^{1}H NMR calibration experiments described in the Appendix, i.e., trimethylsilyltetradeuteriopropionic acid, sodium salt (Eurisotop), and tetramethylammonium chloride (Aldrich) were used as received.

Separation and Analysis of the Copolymer of Styrenic Surfactants. The latexes were thoroughly washed by ultrafiltration (apparatus Waters-Minitan) through membranes able to retain the particles but not the molecules dissolved in water. Then the serum can be replaced continuously by pure water, and the liquid after filtration can be analyzed by conductimetry or surface tension measurement. The extraction procedure is considered as finished when the conductivity is less than 10 μS and when the surface tension is higher than 71 mN m^{-1}.

To follow the ultrafiltration advancement, we use what we call a replacement function. This parameter is defined as the ratio of the volume of extracted serum over the volume of ultrafiltrated latex at a solid content of 1%.

The liquid from the filtration process is then concentrated, using rotary evaporation, and precipitation generally takes place. After redissolution in tetrahydrofuran (THF), it can be analyzed by size exclusion chromatography (SEC) to estimate the molecular weight and their distribution.

The dissolution of the precipitate in deuterated toluene or in chloroform makes possible NMR analysis using a Brucker A400 apparatus.

Proton NMR Analysis in Normal Water. These direct analyses of latex in normal water were carried out with a Bruker Avance DRX400 apparatus, working at 400 MHz for ^{1}H. A 5 mm inverse probe head, optimized on ^{1}H nucleus, was used. To provide the necessary lock signal for field/frequency stabilization, a small quantity of deuterated water (about 10%) is added to the latex itself or, preferably, is introduced in an internal coaxial tube.

In a view to obtain quantitative results, a defined amount of a water-soluble compound is added for calibration of the ^{1}H resonances (cf. above: paragraph Materials and Appendix).

The magnet is well shimmed on the water sample, so as to have a reasonable line shape; the line width must be sufficiently narrow to provide, afterward, a good suppression of the solvent signal. The presaturation method is used for suppression of the huge water signal: a selective irradiation (duration $D_1 = 1.5$ s) at the water resonance frequency is applied before the 90° pulse; acquisition time is equal to 2.7 s.

Appendix

Trials for Internal Calibration of the Water-Soluble Surfmer. To estimate the amount of water-soluble products from the surfmer in the serum, two kinds of internal calibration standards have been tried.

The first one was the sodium salt of deuterated trimethylsilylpropionic acid (TSP-d_4), $\delta = 0$ ppm. The latex E52 was titrated. However, it turns out that a significant part of the internal standard was adsorbed onto the particles because of the hydrophobicity of the trimethylsilyl group, thus not being detected by ^{1}H NMR. Then the titration of the surfmer in the serum is strongly overestimated (5.6 times the total amount of VB6,17-SO_3K engaged in the latex).

The second product tested was tetramethylammonium chloride, which shows 12 equivalent protons (singlet at 3.20 ppm). This area is compared with the resonance of the CH_2 in the α-position to the sulfonate group. Much better results have been observed, but the amount of SO_3 group so titrated remains 1.27 times larger than the total amount of VB6,17-SO_3K engaged in the latex.

To avoid any adsorption of the calibration of the standard onto the surface of the particles, a third trial has been carried out using an internal coaxial tube containing a deuterated water solution of tetramethylammonium chloride. By this method, the amount of SO_3 group remains 1.23 times larger than the total amount of VB6,17-SO_3K engaged in the latex.

As a conclusion, it is necessary to use a fully water-soluble compound like tetramethylammonium chloride as a reference, and there is no advantage in using a coaxial tube except that the sample is not modified at all.

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