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Styrenic Surfmer in Emulsion Copolymerization of Acrylic Monomers: I. Synthesis and Characterization of Polymerizable Surfactants

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Two procedures to prepare styrenic reactive surfactants are described. The first one, close to a procedure of Ito et al., involves the initiation of anionic polymerization of ethylene oxide by an alkyl silanolate. Once the ethylene oxide is fully consumed, the anion is condensed on a styrenic alkyl bromide. Then the hydroxyl is recovered by a reaction of deprotection. The second one, on the contrary, starts from the hydrophobic end group. This anionic polymerization is initiated by vinyl benzyl alcoholate. Successively butylene oxide and ethylene oxide are polymerized. In the last step, the anion can be used to open the ring of propane sultone and we produce an anionic reactive surfactant, or the living chain can be hydrolyzed to obtain a nonionic surfactant. This second procedure gives good control of both hydrophobicity and hydrophilicity. The physicochemical properties of the corresponding surfactants are measured.

Introduction

The use of reactive surfactants in emulsion polymerization is more and more popular, due to some very interesting improvements in the quality of latexes. The main cause of these improvements is the fact that the reactive surfactants are copolymerized and then the stabilizers are strongly adsorbed onto the particles due to their molecular weight and their hydrophobicity. It results in some cases better stability of the latexes, for instance versus shear flocculation or versus flocculation due to freezing. When the latexes are to be flocculated, as in the rubber industry, the lack of freedom for the surfactants means that they will not remain in the water from the flocculation treatment or the subsequent washing of the flocs. There is then an ecological benefit. However, probably the most interesting feature is for latexes used as binders of pigments or charges in the coating industry. Then the limitation of surfactant mobility avoids too much migration toward the surface, which decreases the adhesive properties of the film upon the substrate to be protected; it also limits the formation of hydrophilic domains inside the film which cause mechanical defects, chiefly when the film is exposed to humidity.

Most of the reactive surfactants studied up to now are polymerizable surfactants which have been reviewed rather recently.[1] Generally they carry the polymerizable group in the hydrophobic part of the surfactant because the main polymerization events are produced in the polymer particles which are most often quite hydrophobic.

The present paper describes some attempts to produce reactive surfactants carrying a styrenic group. Surprisingly there are not very many reports about styrenic polymerizable surfactants. One of the first papers was published by Fitch et al.[2] who prepared SSDSE, styrene sodium dodecyl sulfonate ethers, with a rather tedious and difficult procedure. It was chiefly used to cover a seed latex and to introduce on it a controlled amount of sulfonate charges.

A series of papers has been published by Ito et al.[3] about poly(ethylene oxide) macromomers with either styrenic or methacrylic polymerizable groups. These products however are not surface active but are simply both water and benzene soluble. More recently, Ito et al. published two major improvements. First they used a potassium alcoholate of *tert*-butyldimethylsilyl ether of ethylene glycol as the initiator of the anionic ring opening polymerization of ethylene oxide.[4] After polymerization, the living end was killed with vinyl benzyl chloride (VBC) or a methacryloil chloride. Then the silyl end group was hydrolyzed to restore a hydroxyl group at the end of the macromonomer chain. The second improvement was to increase the hydrophobicity of the macromonomer, thus giving it surface active properties upon killing the living chain end with a styrenic alkyl bromide of controlled chain length.[5]

The anionic polymerization of block copolymers of propylene oxide and butylene oxide, followed by killing with VBC, was used by Schechtman to obtain styrenic surfactants with the styrene group at the end of the hydrphobic propylene oxide chain.[6] They were able to produce a set of surfactants with various HLB. When engaged in emulsion polymerization of styrene, stable latexes with small amounts of coagulum were produced. The incorporation yield of the styrenic group of the

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[1] (a) Holmberg, K. *Prog. Org. Coatings* **1992**, *20*, 325−337. (b) Guyot, A.; Tauer, K. *Adv. Polym. Sci.* **1994**, *211*, 43−65. (c) Guyot, A. In *New Surfactants* Holmberg, K., Ed.; Surface Science Series, Marcel Dekker (in press). (d) Schoonbrood, H. A. S.; Asua, J. M. *Acta Polym.* (in press).

[2] Tsaur, S. L.; Fitch, R. M. *J. Colloid Interface Sci.* **1987**, *115*, 450−462.

[3] (a) Ito, K.; Tsuchida, H.; Hayashi, A.; Kitano, T.; Yamada, E.; Matsumoto, T. *Polymer J.* **1985**, *17*, 7, 827−839. (b) Ito, K.; Tsuchida, H.; Kitano, T. *Polymer Bull.* **1985**, *15*, 425−430. (c) Ito, K.; Yokoyama, S.; Arakawa, F.; Iwashita, T.; Yamasaki, Y. *Polym. Bull.* **1986**, *16*, 337−344. (d) Ito, K.; Tanaka, K.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* **1991**, *24*, 2348−2354.

[4] Ito, K.; Hashimura, K.; Itsuno, S.; Yamada, E. *Macromolecules* **1991**, *24*, 3977−3981.

[5] Chao, D.; Itsuno, S.; Ito, K. *Polymer J.* **1991**, *23*, 9, 1045−1052.

[6] Schechtman, L. A. In *Polymer Solutions, Blends and Interfaces*; Nuda, I., Rubingh, D. N., Eds.; Elsevier: Amsterdam 1992, pp 23−41.

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surfactant in the latex was determined by ^{1}H NMR analysis of the latex and shown to depend on the HLB balance of the surfactant.

A recent patent of PPG Industries[7] covers this kind of block copolymer reactive surfactants; however, examples were given only in the case of allylic polymerizable groups.

More recently, in our laboratory, Filet et al.[8] described another kind of surfactant where VBC is first coupled with hexanediol; the second alcohol group is then used to initiate the ring opening polymerization of ethylene oxide. In the emulsion polymerization of styrene, rather large amounts of coagulum were produced except if the length of the poly(ethylene oxide) sequence is long enough (more than 40 units).

In this paper two kinds of products are described. The first one is rather close to the products described by Ito with some modifications in the procedure. The idea was to initiate the anionic polymerization directly by using a protective group of the hydroxyl function. However, it is shown that there is not good control of the hydrophilicity of the surfactant. Then another method was developed: the styrenic moiety is used to initiate the block copolymerization of butylene oxide and then ethylene oxide, the living chain being free to be functionalized as either a nonionic or an anionic reactive surfactant.

Experimental Section

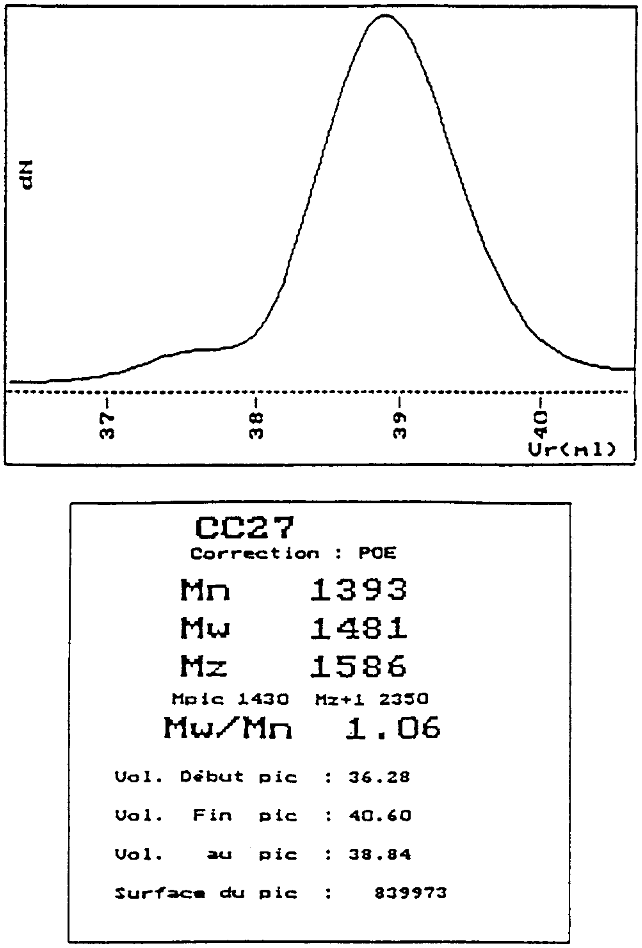
Materials. For the preparation of the halogenated compound, we have used a solution of 0.1 mol l^{-1} dilithium tetrachlorocuprate in THF (Acros), magnesium turnings (Aldrich), 1,5-dibromopentane (97% purity, Aldrich), and diethyl ether (99% purity, Aldrich).

All the materials involved in the anionic polymerization need to be perfectly dry otherwise the living character is lost.

KH, potassium hydride, is received dispersed at 40% w/w in mineral oil (Aldrich). The hydride is washed through dry heptane and kept as pure powder under argon. VBC, vinyl benzyl chloride, is stored on molecular sieves under argon at -30 °C (Aldrich). EO, ethylene oxide, is a gas in a 20 l pressure bottle (Aldrich). The quantity used is purified by condensation at -130 °C (fusion point of ethanol). BO, butylene oxide, is stored on molecular sieves under argon in order to be dry (Aldrich). THF, tetrahydrofuran, is distilled over sodium/benzophenone and stored under argon. ^{t}BuMe$_2$SiOH (*tert*-butyldimethylsilanol), MBA (methyl benzyl alcohol), and PS (propane sultone) are diluted in dry THF and kept on molecular sieves under argon.

Synthesis of 3′- and 4′-(6-Bromohexyl)styrene. Magnesium turnings are washed with heptane and dried. 0.7 mol of magnesium turnings (17.0 g) and 160 mL of ether were added in a 500 mL flask previously dried at 150 °C under argon. A solution of 0.4 mol of VBC (61.0 g) in 100 mL of ether is cautiously added to the flask for 4 h with vigorous agitation and the temperature is kept around 10 °C with an ice bath. The reaction mixture is maintained at room temperature for 1 h. In a second reactor under argon, 0.4 mol of 1,5-dibromopentane (92.0 g), 0.4 mol of Li$_2$CuCl$_4$ (40 mL), and 500 mL of dry THF are strongly agitated when the reaction mixture of the first reactor is added slowly over 1 h. The reaction mixture is kept at room temperature overnight. 12 mL of ethanol are added. The solvents are evaporated as is the excess 1,5-dibromopentane. The final product contains approximately 8% 1,7-distyryl heptane, 3% bis-methylene styrene. The titration is 89% and the global yield is 64%.

Synthesis of VB0,45-OH Starting Potassium *tert*-Butyldimethylsilanolate: SYN24. Under dry atmosphere, 8.8 mmol of *tert*-butyldimethylsilanol (1.38 mL) are neutralized with a potassium naphthalene solution until a green color persists. The reactor is kept at 60 °C and the pressure is reduced. 0.0088 × 45 mol of ethylene oxide (19.8 mL) is added in several times cautiously in order to keep the reactor under vacuum. The consumption of ethylene oxide is followed by a reduction of pressure. After 24 h, polymerization is completed and 9.8 mmol of VBC (1.5 mL) are added. After 24 h at 40 °C, THF is evaporated under reduced pressure and the oligomer is precipitated in petroleum ether. The alcohol is finally deprotected using acidic resins. An 18-g amount is recovered, and after characterization the structure is approximately VB0,51-OH with a rather large polymoleculatity (Ip = 1.24).



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CC27
Correction : POE
Mn    1393
Mw    1481
Mz    1586
Mpic 1430  Mz+1 2350
Mw/Mn   1.06

Vol.  Début  pic  :  36.28
Vol.   Fin   pic  :  40.60
Vol.    au   pic  :  38.84
Surface du pic    :   839973
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Figure 1. Size exclusion chromatogram of VB9,20-SO$_3$K from RUN52.

Synthesis of Vinyl Benzyl Alcohol (VBA). 0.815 mol of potassium acetate (80 g), 0.708 mol of VBC (108 g), 10 mg of hydroquinone, and 250 mL of DMSO are agitated for 48 h at 40 °C. The mixture is extracted with chloroform, the organic phase is washed with water, and then dried with magnesium sulfate. After filtration, the chloroform is evaporated under reduced pressure. For the second step, the product is added to 50 g of NaOH, 50 mL of water, and 300 mL of ethanol, and again to 10 mg hydroquinone. The mixture is boiling for 90 min. The mixture is extracted with chloroform, the organic phase is washed with water, and then dried with magnesium sulfate. After filtration, the chloroform is evaporated under reduced pressure. The product is purified by distillation under 10 mmHg, the boiling point is between 90 and 100 °C. The final product contains less than 5% DMSO.

Synthesis of VB10,17-OCH$_2$CH$_2$CH$_2$SO$_3$K: SYN52. Under a dry atmosphere of argon, 0.017 mol of VBA is added to 0.017 × 0.9 mol of KH (0.61 g) and 0.017 mol of 18-crown-6-ether (4.49 g) in 250 mL THF under hydrogen bubbling. The mixture is heated to 60 °C and 0.017 × 10 mol of butylene oxide (14.6 mL) is added. After 7 h, the end of polymerization is checked by gas chromatography. The reactor is kept at 60 °C and the pressure is reduced. 0.017 × 17 mol of ethylene oxide (14.45 mL) is added in several times cautiously in order to keep the reactor under vacuum. The consumption of ethylene oxide is followed by the decrease of the pressure. For the last step, 0.017 × 0.1 mol of

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(7) Tang, R. H.; Chakrabanti, P. M. U. S. Pat. 5296627, **1994**.

(8) Filet, A.; Guillot, J.; Hamaide, T.; Guyot, A. *Polym. Adv. Technol.* **1995**, *6*, 465–472.

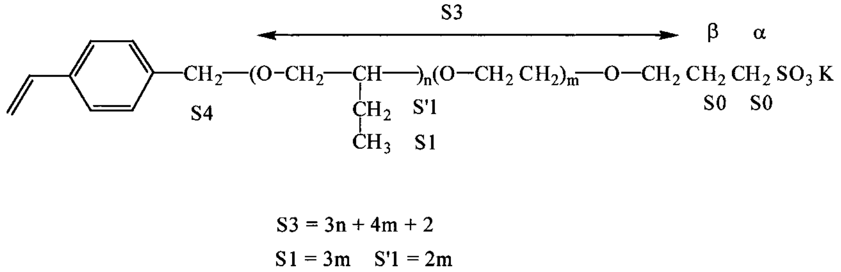
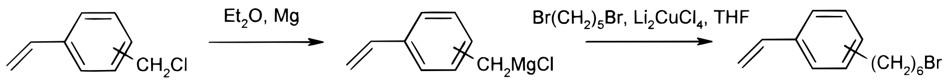


Figure 2. Model structure for the ^{1}H NMR characterization.

Scheme 1 . Preparation of 3′- and 4′-(6-Bromohexyl)styrene



KH (0.068 g), 0.017 × 1.5 mol of propane sultone (3.11 g) are added and the mixture is agitated for 5 h at 40 °C. Most of the THF is then evaporated and the oligomer is isolated by precipitation in ether at −30 °C. The purification is repeated twice and the final product is then dried under strong vacuum. A 26-g amount is recovered, and after characterization, the structure is VB9,20-$OCH_2CH_2CH_2SO_3K$ which is close to expected.

Synthesis of MBn,m−X (X = OH or $OCH_2CH_2CH_2SO_3K$). The procedure is exactly the same as above. The only modification is the replacement of vinyl benzyl alcohol (134 g mol^{-1}) by methyl benzyl alcohol (122 g mol^{-1}).

Cloud Point Procedure. The cloud point is measured by transmission of monochromatic light (600 nm) through a solution of 10 g l^{-1} nonionic surfactant with 0.33 mol l^{-1} of $MgSO_4$. The sample is placed in an oven with a controlled heating rate. The apparatus has been built in our laboratory. The cloud point corresponds to the temperature at which the transmission decays.

Determination of Critical Micellar Concentration (CMC) with Surface Tension. The CMC is determined by surface tension using the method of the plate of Willehmy. The apparatus is a Krüss K12 equipped with a Dosimat Krüss 665 and the temperature is maintained precisely at 20 °C (Lauda cryostat). The platinum plate is cleaned under a flame. The addition is automatic, the sample is agitated 5 min and then the apparatus waits 15 min before the measurement of the surface tension.

Size Exclusion Chromatography. The mobile phase is THF. The SEC apparatus is a Waters 600 equipped with a refractometer Waters 410 and 3 columns, Styragel HR4E, Styragel HR5E, and Eurogel HE145. This selection of columns allows the separation of molecular weights from 10^2 to 10^7 g mol^{-1}. The software is Millenium. The flow rate is 1 mL min^{-1}.

^{1}H NMR Characterization. ^{1}H NMR characterization was made with a Brucker Avance DRX400 apparatus. The solvent used is always deuterated chloroform. These spectra are consistent with the assigned structures. The vinyl group is an AMX type.

3′- and 4′-(6-Bromohexyl)styrene. δ 1.27−1.50 (m, 4H, CH_2 positions 3 and 4), 1.54−1.70 (m, 2H, CH_2 position 5), 1.82 (q, $^3J = 6.5$ Hz, 2H, CH_2 position 2), 2.59 (t, 2H, CH_2 position 6), 3.37 (t, $^3J = 6.5$ Hz, 2H, CH_2 position 1), 5.21 (dd, $^3J_{cis} = 11$ Hz, $^2J_{gem} = 0.8$ Hz, 1H, H_A), 5.69 (dd, $^3J_{trans} = 17.4$ Hz, $^2J_{gem} = 0.9$ Hz, 1H, H_M of compound 4′-), 5.72 (dd, $^3J_{trans} = 17.4$ Hz, $^2J_{gem} = 0.8$ Hz, 1H, H_M of compound 3′-), 6.71 (dd, $^3J_{trans} = 17.4$ Hz, $^3J_{cis} = 11$ Hz, 1H, H_X), 7.03−7.35 (m, 4H, aromatic)

VB0,51-OH from Synthesis SYN24. δ 2.32 (s, 1H, hydroxyl), 3.12−4.16 (m, 102H, H of ethylene oxide), 4.56 (s, 2H, H benzylic), 5.26 (dd, 1H, H_A), 5.75 (dd, 1H, H_M), 6.70 (dd, 1H, H_X), 6.90−7.50 (m, 4H, aromatic)

Vinyl Benzyl Alcohol. δ 1.94 (s, 1H, hydroxyl), 4.560 (s, 2H, H benzylic of compound 4′-), 4.565 (s, 2H, H benzylic of compound 3′-), 5.26 (dd, $^3J_{cis} = 11$ Hz, $^2J_{gem} = 0.6$ Hz, 1H, H_A), 5.73 (dd, $^3J_{trans} = 17.5$ Hz, $^2J_{gem} = 0.6$ Hz, 1H, H_M of compound 4′-), 5.74 (dd, $^3J_{trans} = 17.5$ Hz, $^2J_{gem} = 0.6$ Hz, 1H, H_M of compound 3′-), 6.69 (dd, $^3J_{trans} = 17.5$ Hz, $^3J_{cis} = 11$ Hz, 1H, H_X), 7.19−7.47 (m, 4H, aromatic)

VB9,20-$OCH_2CH_2CH_2SO_3K$ from Synthesis SYN52. (See Figure 2)

δ 0.91 (t, $^3J_{cis} = 7.3$ Hz, S1 = 3 × 9 H, CH_3 of butylene oxide), 1.54 (m, S′1 = 2 × 9 H, CH_2 of butylene oxide), 2.89 (t, $^3J_{cis} = 7.5$ Hz, SO = 2H, $OCH_2CH_2\mathit{CH_2}SO_3K$), 3.14−3.98 (m, S3 = 3 × 9+4 × 20+2 H, ethylene oxide and butylene oxide), 4.56 (s, 2H, H benzylic), 5.25 (dd, 1H, H_A), 5.75 (dd, 1H, H_M), 6.70 (dd, 1H, H_X), 7.20−7.50 (m, 4H, aromatic)

Results and Discussion

The first targeted surfmers do contain a hydrophobic part consisting of a styrenic group associated with an alkyl chain terminated by a labile halogen atom. One of these products does contain only one methylene group and it is the commercial VBC. A second product has a longer chain of 6 methylene groups and is prepared according to the procedure of Tomoi et al.[9] slightly modified. According to that procedure, the Grignard reagent of VBC is first prepared and then condensed onto dibromopentane, according to Scheme 1.

The procedure described using THF as a solvent in the two steps by Tomoi et al. leads to a limited yield of the Grignard reagent due to the formation of 30% of the Würtz product, bismethylene styrene, and also the Schlenk equilibrium producing magnesium chloride and the bismethylene styrene magnesium. A better yield can be obtained replacing the THF with diethyl ether and slowly adding the VBC and setting the final concentration to 1.5 mol l^{-1}.

The second step was carried out using the procedure of Friedman and Shani[10] who used dilithium tetrachlorocuprate in the presence of an excess of dibromopentane. The final product is distilled in the presence of a large amount of radical polymerization inhibitor (hydroquinone). After that step small amounts of bismethylstyrene and 1,7-distyrylheptane remain which cannot react in further steps and which will be extracted during the precipitation of the oligomers.

The hydrophilic part of the surfactant is chiefly a poly(ethylene oxide) chain with two reactive chain ends. One of them is expected to be an alcoholate chain end that must be coupled with the labile halogen atom of the hydrophobic part. The second one should be an OH group able to react to further derivatization. The procedure to prepare such a hydrophilic part was inspired by the work of Ito et al.[3] In this work, Ito et al. used an ethoxylated derivatization of a *tert*-butyldimethylchlorosilane to initiate the anionic polymerization of ethylene oxide. After

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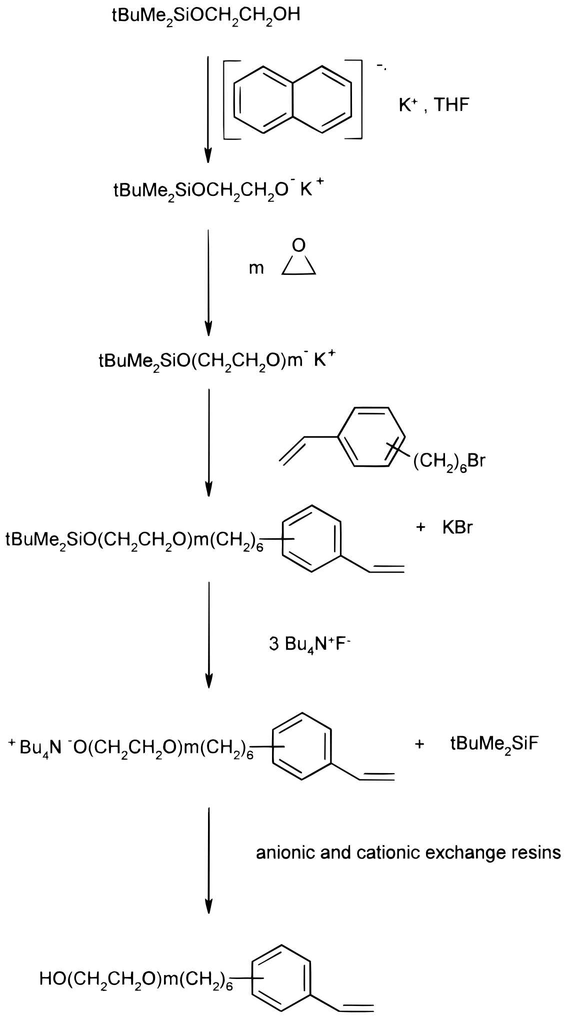
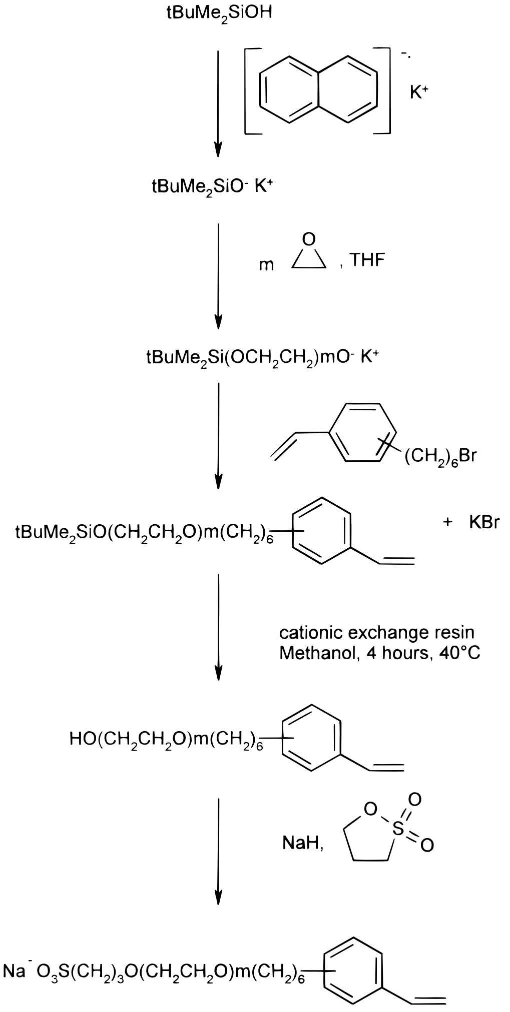
(9) Tomoi, M.; Ogawa, E.; Hosokawa, Y.; Kakuichi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3015−3019.

(10) Friedman, L.; Shani, A. *J. Am. Chem. Soc.* **1974**, *96*, 7101−7103.

Scheme 2. Preparation of H-EO*n*-C*m*-S from Ito et al.



Scheme 3 . Preparation of VB*n*,*m*-OH and VB*n*,*m*-SO$_3$K from *tert*-Butyldimethylsilanol



polymerization the living alcoholate is killed by reaction with a styrenic compound similar to the hydrophobic part described just above, so producing a styrenic end group of the poly(ethylene oxide) chain. Then, upon reaction of the second chain end with $Bu_4N^+F^-$, the OH chain end is deprotected and available for further reaction. The procedure described by Ito is shown in Scheme 2.

The procedure of Ito et al.[3a] requires first the preparation of the monoprotected initiator. This may be done from ethylene glycol according to the procedure described by McDougal et al., by reacting *tert*-butyldimethylchlorosilane with the sodium monoalcoholate of diethylene glycol.[11] However that reaction has a moderate yield of 68% due to the precipitation of the alcoholate on sodium hydride. So we have preferred to use the more direct potassium silanolate of *tert*-butyldimethylsilanol. This compound is preferred over potassium trimethylsilanolate because potassium *tert*-butyldimethylsilanolate is soluble in THF. The simplified route is shown in Scheme 3. Another simplification is to avoid the use of the tertbutylammonium fluoride for the deprotection, which is done more simply by passing the reaction medium on an acidic resin. The reaction can be followed by ^{1}H NMR, upon comparing the signal of the vinylic (or aromatic) protons with those of the ethylene oxide. The characterization is completed by SEC, the calibration of which for poly(ethylene oxide) is based on the Mark Houwink coefficients which are $\alpha = 0.73$ and $K = 1.9 \times 10^{-4}$. A few data are reported in Table 1.

Clearly the targeted structure is not obtained and both measurements show that the length of the poly(ethylene oxide) is longer than expected. Further, the polymolecularity index is rather large. From these results it seems clear that the initiation reaction is not fast enough compared to the propagation reaction. In other words, the silanolate is less reactive than the alcoholate. To try to equilibrate these two reactions of initiation and propagation another set of runs has been carried out in the presence of 1.5 equiv of 18-crown-6-ether at 75 °C for the first step. This modification has a favorable effect (Table 2). Further, in the last run a small amount of ethylene oxide has been introduced. Both modifications result in a narrower polymolecularity index and a better yield (see Table 2).

However it is clear that by that route the control of the hydrophilicity of the surfmer is not really achieved.

So a new route had to be developed. In that route a reverse process has been followed. Instead of introducing the styrenic group by living a chain end, it was decided to initiate the living anionic polymerization of oxirane by a styrenic moiety. This styrenic reactive group of the surfmer needed to be placed at the end of the hydrophobic part of the surfmer in order to force the surfmer to react with the monomer swelling the particles in the emulsion polymerization. Then the polymerization was started with

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[11] McDougal, P. G.; Rico, J. G.; Oh, Y. I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388−3390.

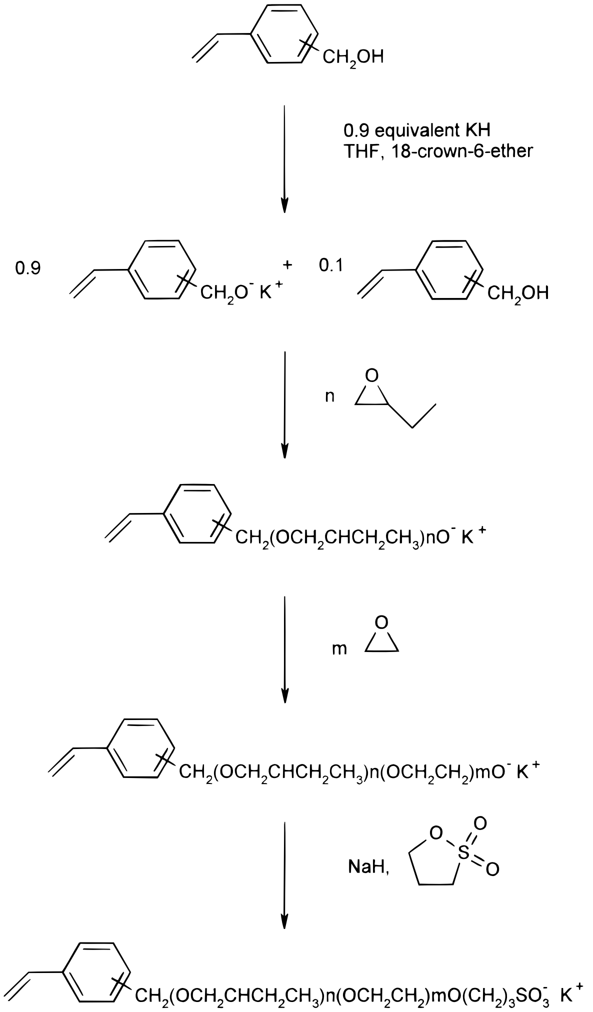
Table 1. Experimental Conditions and Characterization of the First Anionic Polymerizations

run	*n*	*m*	step 2	step 3	SEC	NMR	yield
25	1	40	40 EO, 50 °C, 26 h	1.2 eq., 25 °C, 48 h	m = 59, Ip = 1.18	m = 63	72%
35	6	45	45 EO, 70 °C, 60 h	2 eq., 25 °C, 16 h	m = 66, Ip = 1.38	m = 71	82%
36	6	17	17 EO, 75 °C, 48 h	2 eq., 25 °C, 16 h	m = 48, Ip = 1.27	m = 50	75%

Table 2. Experimental Conditions and Characterization of the Anionic Polymerizations

run	*n*	*m*	step 2	step 3	SEC	NMR	yield
42	1	17	17 EO, 75 °C, 15 h	1.2 eq., 25 °C, 2 h	m = 36, Ip = 1.17	m = 40	55%
45	6	17	17 EO, 75 °C, 6.4 h	1.2 eq., 25 °C, 24 h	m = 32, Ip = 1.27	m = 46	51%
49	6	17	8 EO, 75 °C, 4.3 h	1.2 eq., 25 °C, 62 h	m = 24, Ip = 1.12	m = 28	76%

Scheme 4 . Preparation VB*n*,*m*-SO_3K from VBA



the hydrophobic sequence, using butylene oxide. In that monomer, there is less side reaction (elimination reaction) than in the case of propylene oxide.[12] It may be expected so far that the living character of the polymerization should be kept before starting the hydrophilic sequence of poly(ethylene oxide). After completion of the two monomers engaged in each sequence, the resulting alcoholate is still living. It can be killed to produce an OH chain end for producing a nonionic surfmer, or used to open the cycle of propane sultone to produce an anionic surfactant. Then the synthesis is described by Scheme 4 with vinyl benzyl alcohol as the initiator. However this chemical is not available and it has to be synthesized, which is rather easy from the commercial vinyl benzyl chloride, according to Scheme 5.

Attempts at a direct hydrolysis of vinyl benzyl chloride were not successful because this reaction needs a concentrated solution of soda which itself needs a very polar solvent such as dimethylformamide, DMF, which then causes difficulties for separation from the targeted alcohol because both show about the same boiling points. For these reasons the procedure of Scheme 5 described by Bamford and Lindsay[13] has been used without any problems.

The VBA was then reacted as potassium alcoholate in order to have a good reactivity in opening the ring of butylene oxide. Sodium hydride being not reactive enough, potassium hydride was preferred, but with a nonstoichiometric amount in order to avoid residual hydride which would be able to directly initiate ring opening polymerization. However the acid−base equilibrium between the alcohol and the potassium salt is achieved very rapidly, much quicker than the propagation reaction. Consequently the living character of the polymerization is kept. The temperature was kept under 60 °C in order to avoid any thermal polymerization of the styrenic compound. Then the 18-crown-6 ether was used as catalyst and may accelerate the conversion of butylene oxide.

A nonreactive analogue of the surfmer was prepared by replacing the vinyl benzyl alcohol by a methyl benzyl alcohol (MB) and following the same procedure.

The formation of the potassium alcoholate is checked by a rather strong increase in hydrogen. The first step of polymerization of butylene oxide is completed after 7 h at 60 °C, the completion of the conversion being checked by gas chromatography (GC). Then ethylene oxide is introduced step by step so that the pressure at 60 °C does not pass atmospheric pressure. The consumption of ethylene oxide is followed by pressure measurement and its full conversion is checked by GC. In the final step, a new charge of KH is added, followed by propane sultone at room temperature to produce the anionic surfmer. A part of the product is also simply hydrolyzed with water to produce the nonionic derivative.

The data of various runs are gathered in Table 3, showing for each run the amounts of initiator, butylene oxide, ethylene oxide, and propane sultone or water changed, and finally the yields. The data from SEC and NMR can be found in Table 4. These results show that the experimental structures are close to those targeted, with polymolecularities quite narrow, the largest values never being higher that 1.2. Further the yields are most after close to 100%.

A typical SEC diagram is shown in Figure 1, while Figure 2 displays the corresponding ^{1}H NMR spectrum.

This new synthetic procedure offers a number of important advantages. There is not any consumption of the reactive double bond of the styrenic group, as shown upon comparing the surface area under the vinylic protons and those under the aromatic rings. The whole synthesis is carried out in the same pot, including the two polym-

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(12) *Encyclopedia of Polymer Science and Engineering*; Wiley: New York 1986, Vol. 6, p 237.

(13) Bamford, C. H.; Lindsay, H. *Polymer* **1973**, *14*, 330−332.

Scheme 5 . Preparation of Vinyl Benzyl Alcohol (VBA)

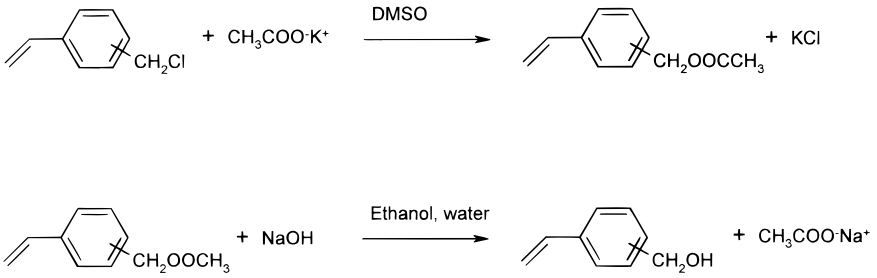

Table 3. Experimental Conditions and Characterization of the Anionic Polymerizations

run	expected structure	KH (g)	18-crown-6-ether (g)	2nd step BO (mL)	3rd step EO (mL)	4th step X	yield
51	VB0,17-OH	0.81	5.96	0	19.2, 4 h	5 mL H_2O	86%
52	VB10,17-SO_3K	0.61	4.49	14.6, 7 h	14.45, 4 h	3.11 g PS[a]	92%
53	VB10,40-OH	1.11	8.18	26.7, 7 h	62.0, 6 h	5 mL H_2O	95%
54	VB10,30-SO_3K	0.97	6.22	24.7, 5 h	43.05, 5 h	5.47 g PS	78%
57	VB6,17-SO_3K	1.97	14.38	28.15, 3 h	46.3, 6 h	9.98 g PS	96%
58	VB6,30-OH	2.66	19.82	38.8, 4 h	112.5, 6 h	5 mL H_2O	84%
58	VB6,30-SO_3K					9.98 g PS	90%
59	MB6,30-OH	1.98	14.52	28.4, 7 h	82.5, 6 h	5 mL H_2O	83%
59	MB6,30-SO_3K					7.31 g PS	88%
60	VB10,30-OH	1.64	11.88	39.82, 4 h	69.45, 6 h	5 mL H_2O	95%
60	VB10,30-SO_3K					5.85 g PS	96%
61	MB10,30-OH	1.49	9.74	31.75, 6 h	61.5, 5 h	5 mL H_2O	98%
61	MB10,30-SO_3K					4.97 g PS	96%

[a] PS Propane sultone.

Table 4. Characterization of the Surfactants

run	expected structure	expected Mn[a]	Mn by SEC	Ip by SEC[b]	*n*, *m* by ^{1}H NMR
51	VB0,17-OH	882	895	1.04	0, 18
52	VB10,17-SO_3K	1762	1393	1.06	9, 20
53	VB10,40-OH	2614	2645	1.09	11, 41
54	VB10,30-SO_3K	2334	2114	1.10	10, 36
57	VB6,17-SO_3K	1474	1200	1.09	6, 17
58	VB6,30-OH	1886	2940	1.10	7, 34
58	VB6,30-SO_3K	2046	1979	1.22	7, 34
59	MB6,30-OH	1874	2621	1.07	6, 33
59	MB6,30-SO_3K	2034	2087	1.17	6, 33
60	VB10,30-OH	2174	3208	1.11	12, 45
60	VB10,30-SO_3K	2334	2734	1.22	12, 45
61	MB10,30-OH	2162	2906	1.08	10, 34
61	MB10,30-SO_3K	2322	2128	1.19	10, 34

[a] Mn: Mean molecular weight in number. [b] Ip: Polymolecularity index.

erization steps and the final functionalization. For that reason the duration of the whole process is limited, and fixed mainly by the first step of butylene oxide polymerization. The yields are high, being limited only by the difficulty of purification when the molecular weight is rather low, because in this case the precipitation of the product in petroleum ether is not immediate. However the main advantage is to have a structure attributable to the living character of both polymerization steps as well as the quantitative character of the final functionalization. Furthermore, the same reaction procedure is able to lead to two products, a nonionic one through hydrolysis, and the anionic surfmer through sulfonation. Finally, this sulfonate group is quite stable versus hydrolysis, which is of further interest for the emulsion polymerization application.

Before applying these surfmers in emulsion polymerization, which will be described in Part II of these series of papers,[14] it is important to determine their physicochemical properties such as their critical micelle concentration (CMC) and cloud points. Obviously it is important not to use these surfactants at polymerization temperature above their cloud points.

The measurement of the cloud points is important only for nonionic surfmers. They are carried out by turbidimetry in water solution containing 0.33 mol l^{-1} of $MgSO_4$. A few data are shown in Table 5 together with the data of CMC.

The CMC are determined by surface tension (γ) measurements. A typical curve showing the break in the plot of γ versus log c (concentration of surfactant) is shown in Figure 3. As shown in Table 5, all the surfactants prepared show a CMC at various concentrations depending on their structure. The only exception is the product containing no butylene oxide sequence which is surface active because the surface tension drops but it is not hydrophobic enough to form micelles. Above the CMC, the surface tension has rather low values, around 37 mN m^{-1} and rather independent on the precise structure (Figure 4).

The value of the CMC itself is largely governed by the hydrophobic part, i.e., the length of the poly(butylene oxide) sequence: the longer that sequence, the smaller the CMC. Consider for instance the comparison of VB11,-41-OH and VB7,34-OH with respective values of 6×10^{-6} and 134×10^{-6} mol l^{-1}. The presence of a terminal sulfonate group increases moderately the CMC (see VB7,-34-OH and VB7,34-SO_3K at 134×10^{-6} and 184×10^{-6} mol l^{-1}). The same is true when the length of the hydrophilic poly(ethylene oxide) sequence is increased (VB6,17-$SO_3$$-$$K^+$ and VB7,34-$SO_3$$-$$K^+$). The change from MB to VB has a very small effect.

Conclusion

The new synthesis of styrenic reactive surfactants described in this paper starting from the vinyl benzyl alcohol as initiator for the living anionic ring opening polymerization of butylene oxide and then of ethylene oxide, is definitely much better than the procedure used

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(14) Soula, O.; Guyot, A. Part II submitted to *J. Polym. Sci., Polym. Chem. Ed.*

Table 5. Critical Micelle Concentrations and Cloud Points of the Various Surfactants Prepared

run	expected structure	determined structure	CMC (10^{-3} g l^{-1})	CMC (10^{-6} mol l^{-1})	γ_{CMC} (mN m^{-1})	cloud point (°C)
51	VB0,17-OH	VB0,18-OH			44	67.6
52	VB10,17-SO_3K	VB9,20-SO_3K	38	21	37.6	
53	VB10,40-OH	VB11,41-OH	16	6	36.9	>100
54	VB10,30-SO_3K	VB10,36-SO_3K	n.d.[a]	n.d.	n.d.	
57	VB6,17-SO_3K	VB6,17-SO_3K	89	62	36.8	
58	VB6,30-OH	VB7,34-OH	288	134	37.9	>100
58	VB6,30-SO_3K	VB7,34-SO_3K	423	184	38.4	
59	MB6,30-OH	MB6,33-OH	349	173	38.1	>100
59	MB6,30-SO_3K	MB6,33-SO_3K	462	213	37.6	
60	VB10,30-OH	VB12,45-OH	12	4	37.9	>100
60	VB10,30-SO_3K	VB12,45-SO_3K	51	16	35.6	
61	MB10,30-OH	MB10,34-OH	9	4	36.6	>100 °C
61	MB10,30-SO_3K	MB10,34-SO_3K	30	12	38.3	

[a] n.d.: not determined.

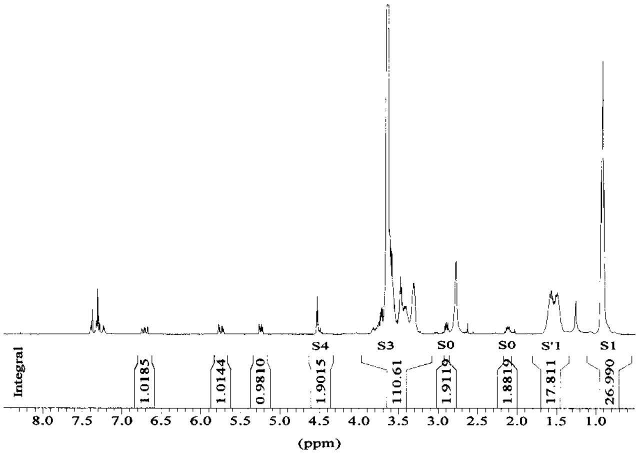

Figure 3. ^{1}H NMR spectrum of VB9,20-SO_3K from RUN52 in $CDCl_3$.

by Ito and Filet. In that synthesis it is possible to easily and precisely control both the hydrophobicity and the hydrophilicity of the surfactants. This preparation is one pot with very high yields and can lead to either nonionic or anionic surfactants.

These surfactants have been engaged in emulsion polymerization of acrylic monomers to produce core−shell latexes with very good stability as described in Part II of the series.[14] The copolymer of these reactive surfactants with the main monomers are strongly adsorbed on the surface of the particles. The analysis of these copolymers and of their conformation at the particle surface can be done using a ^{1}H NMR technique as described in Part III.[15]

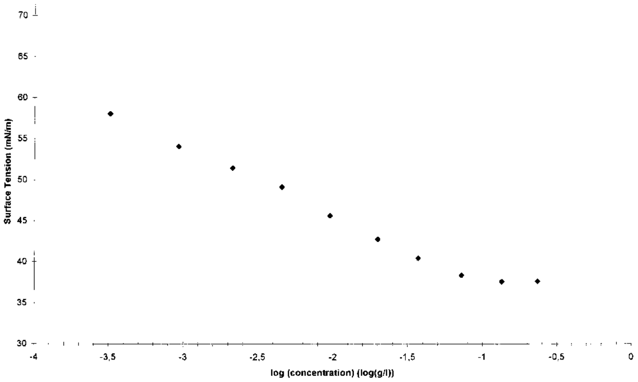

Figure 4. Critical micelle concentration determination of VB6,-17-SO_3K (RUN57) from surface tension versus concentration.

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