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Non-ionic thiol-ended surfactants

Synthesis and NMR characterization

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Summary.

Non ionic thiol-ended surfactants have been prepared either by esterification of thioglycolic acid with poly(ethylene oxide) methyl ether or by anionic coordinated polymerisation of ethylene oxide in the presence of bromo-11-undecanol as transfer agent followed by reaction with thiourea and subsequent hydrolysis. The surfactants have been characterized by ^{1}H NMR, as well as the possible by-products. The transfer constants are in the range 16-19 and decrease with the chain length.

Introduction.

Surfactants are widely used in emulsion polymerization in order to control the particle size and to stabilize the latex at high solid contents. Usually only physically adsorbed on the surface of the particles, they can be desorbed in case of high shear stress or freeze-thawing cycles. In addition, the coalescence of films formed from the latexes may be more or less hindered, owing to the migration of the surfactants toward the more hydrophilic domains, causing water rebound.

The idea was then to synthesize reactive surfactants able to take part to the radical polymerization process in such a way they are grafted through a covalent bond to the polymer chain. These molecules may be a comonomer, an initiator or a transfer agent. Recent papers have discussed the problems and interests of these products [1]. We have recently focused our attention on the first kind of molecules in order to make latexes without charge. For this aim, we synthesized non ionic surfactant comonomers derived from maleates and styrene, the hydrophylic part being obtained upon polymerization of ethylene oxide [2,3] using a new heterogeneous catalytic process [4].

This paper is dealing with the synthesis and NMR characterization of new non ionic surfactants carrying thiol groups acting as transfer agents usually called "Transurfs". Only one paper reported the synthesis of ionic surfactant with thiol group and its use in polystyrene latex synthesis[5]. The structures of the transurfs which are investigated here are the following :

I : $CH_3\text{-}(CH_2CH_2O)_m\text{-}COOCH_2\text{-}SH$
II : $HO\text{-}(CH_2CH_2O)_m\text{-}C_nH_{2n}\text{-}SH$

The synthesis of the first transurf has been carried out by esterification of the thioglycolic acid with PEO methyl ether[6] while the second one was obtained by polymerization of ethylene oxide in the presence of bromo-11-undecanol followed by reaction with thiourea and subsequent hydrolysis.

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Experimental.

Toluene was stored on molecular sieves (3 Å) and kept under argon. Chemicals were purchased from Aldrich and used as received. The bromo-11 undecanol was previously dissolved in toluene and stored on molecular sieves (3 Å) under argon. Ethylene oxide was purchased from Fluka and used after distillation. NMR spectra were made on a Bruker AC250 spectrometer operating at 50 MHz. Deuterochloroform was used as solvent and TMS as internal standard.

Transurf I : $CH_3\text{-}(CH_2CH_2O)_m\text{-}COOCH_2\text{-}SH$.

Poly(ethylene glycol) methyl ether (5.15 10^{-3} mole) and thioglycolic acid (5 10^{-2} mole) are dissolved in 150 mL of toluene. Residual water is removed by azeotropic distillation of 20 mL of toluene and the solution is refluxed overnight. After removing the solvent under vacuum, the residue is purified by dissolution in chloroform and precipitation in cold ether. The thiol is finally dried under vacuum at room temperature and characterized by ^1H NMR.

Transurf II : $HO\text{-}(CH_2CH_2O)_m\text{-}C_nH_{2n}\text{-}SH$.

The ethylene oxide polymerization is carried out according to procedure described elsewhere [2,3] using bromo-11 undecanol as transfer agent . After polymerization, the brominated derivative (3 10^{-3} mole) and thiourea (15 10^{-3} mole) are dissolved in 70 mL of ethanol and refluxed for 24 hours under nitrogen. A solution of soda (15 10^{-3} mol in 65 mL water) is then added and the mixture is refluxed for additional 15 minutes. The solution is then washed with 25 mL of H_2SO_4 2.5M, and extracted with 4x25 mL $CHCl_3$. The organic phase is washed with 4x20 mL of water and dried on $MgSO_4$. The thiol is recovered by evaporation of the solvent and characterized by ^1H NMR. Yields are generally over 90%.

When working with higher molecular weight derivatives, the alcoholic solution is allowed to reflux for 48 hours in order to reduce the amount of disulfide.

If necessary, the reduction of disulfide is carried out as followed : the disulfide is refluxed in 10 mL ethanol under nitrogen with 0.4 g zinc powder and aqueous HCl (2.8 mL HCl 35% in 10 mL water) is droped by an addition funnel during 30 minutes. After 4.5 hours reflux, the solution is extracted with 3x10 mL $CHCl_3$. The organic phase is washed first with 2x5 mL of a solution of saturated $NaHCO_3$ in water and then 3x5 mL water and finally dried on $MgSO_4$. The solvent is removed by evaporation and the product dried under vacuum.

Results and discussion.

Poly(ethylene oxide) derivatives are usually obtained from the parent PEO using classical organic reactions such as etherification or esterification reactions [7] for exemple. Nevertheless, although generally easy to carry out, the purification steps may be sometimes fastidious, particularly in case of surfactants. An alternative way to get polyether chains consists in polymerizing ethylene oxide anionically with a suitable transfer agent (a protic compound). This procedure allows to choose the chain lengths and recovering the product needs only stripping the solvent. The problem stands in the reaction conditions (basic medium, high pressure and temperature) which may lead to undesirable by-products. We used a new heterogeneous catalytic process in order to overcome these drawbacks and to recover functionalized polyethers in high yield without further purifications [4]. The first transurf was made according to the first procedure, while the other one was synthesized by ethylene oxide polymerization.

Transurf I : $CH_3\text{-}(CH_2CH_2O)_m\text{-}COOCH_2\text{-}SH$.

This hydrosoluble transurf has been synthesized by esterification of the thioglycolic acid with PEO ,[6]. Other attempts to get thiols from halogenated precursors such as chlorinated or brominated PEO gave poor yields. The parent PEO was a monomethylether in order to avoid the diester.

$$CH_3(OCH_2CH_2)_nOH + HOOCCH_2SH \rightleftharpoons CH_3(OCH_2CH_2)_nOCOCH_2SH$$

^1H NMR was used to characterize the products and to determine the yield of esterification (Figure 1). The assignments are reported in the figure.

The yield of the esterification is easily determined by NMR, looking at the area of the peaks resonance at 3.4 (I_4 : OCH_3) and 4.3 ppm (I_3 : $COOCH_2$). Note that the area of the ^{13}C satellites resonance must sometimes be taken into account. If x and y are the molar fractions of the ester and the free alcohol respectively and p the intensity of the proton, then

$$x + y = 100$$
$$I_4 = 3(x+y)p$$
$$I_3 = 2xp$$

The yield can also be found with the peak area of the polyether chain. That leads nevertheless to an higher uncertainty because of the relative areas of these peaks. Yields are always around 75 and 90%.

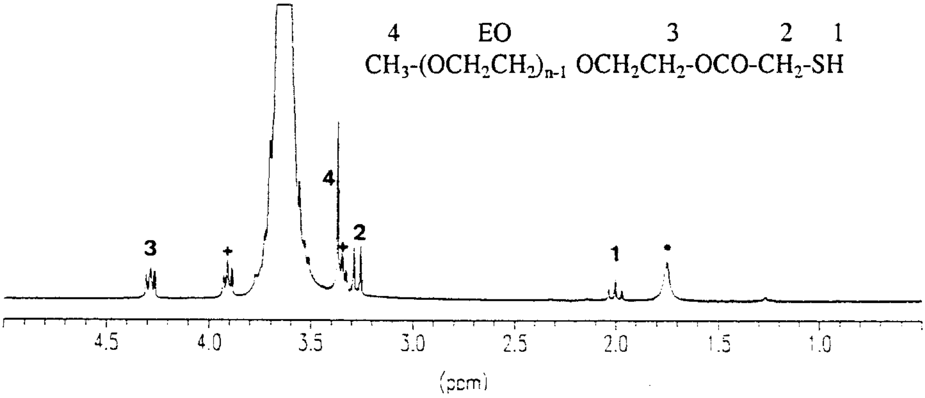


Figure 1. 1H NMR spectrum of Transurf I.
Small triplets (+) on both sides of the PEO resonances are due to the ^{13}C satellites.
* is water.

Oxidative coupling of the thiols may occur to give disulfides R-S-S-R with R = $CH_3\text{-}(OCH_2CH_2)_m\text{-}OCOCH_2\text{-}$ or $\text{-}CH_2COOH$. In that case, the disulfides cannot be removed and the transurfs must be used as they are. The percent of thiol with respect to disulfide is calculated from NMR intensities. If I_1 is the peak area assigned to $CH_2S\underline{H}$ at 2.1 ppm and I_3 that of the ester $\text{-}CH_2OCO$ at 4.3 ppm, then

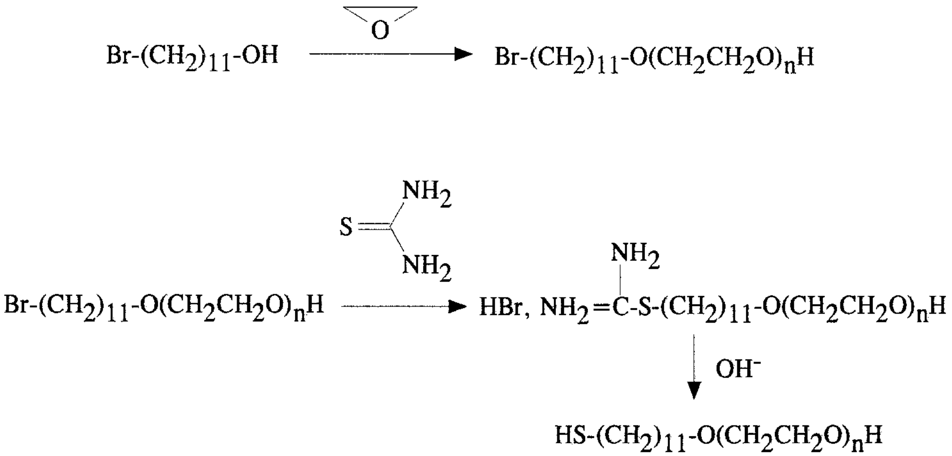
$$x + y = 100$$
$$I_1 = xp$$
$$I_3 = 2(x+y)p$$

Transurf II : HO-$(CH_2CH_2O)_m\text{-}C_nH_{2n}\text{-}SH$.

The alkyl moiety between the thiol function and the polyether chain allows to increase the hydrophobic character of the molecule and to expect a better incorporation of the transurf in the latexes particles.

The polyether chain was made by ethylene oxide polymerization using the heterogeneous catalytic procedure developed in our laboratory. The active centers are aluminium alcoholates grafted on porous silica. The polymerization is carried out in the presence of a protic compound as transfer agent in order to promote exchange reactions between the alcoholates bound on the active centers and the free alcohols in the medium, that allows to get a catalytic mode. This polymerization displays a living-like character, that is the degree of polymerization is a linear function of the ethylene oxide conversion. In our case, the transfer agent must be difunctional, the first functionality being an alcohol group and the second one with no mobile hydrogen, able to be easily transformed in thiol. We then chose bromo-11-undecanol. The brominated derivative was submitted to a nucleophilic substitution of the bromine atom by thiourea and finally, a basic hydrolysis.

An alternative pathway was investigated, namely using undecenol-11 as transfer agent, followed by addition of thioacetic acid on the double bond and hydrolysis [8,9]. The yields were always low (< 60%) and we gave up this procedure.



$$Br\text{-}(CH_2)_{11}\text{-}OH \longrightarrow Br\text{-}(CH_2)_{11}\text{-}O(CH_2CH_2O)_nH$$

$$Br\text{-}(CH_2)_{11}\text{-}O(CH_2CH_2O)_nH \xrightarrow{S=C(NH_2)_2} HBr,\ NH_2{=}\overset{NH_2}{\overset{|}{C}}\text{-}S\text{-}(CH_2)_{11}\text{-}O(CH_2CH_2O)_nH \xrightarrow{OH^-} HS\text{-}(CH_2)_{11}\text{-}O(CH_2CH_2O)_nH$$

Brominated derivatives and transurfs were analyzed by ^1H NMR (Figure 2). The NMR assignments are given in the figure.

Chain lengths can be estimated from the conversion since we are faced to a living-like polymerization (DP = Conversion.$[EO]_0$/[bromoundecanol] with $[EO]_0$ the initial amount of ethylene oxide) and correlated by NMR results, keeping in mind that the values in case of high molecular weight can be subject to a more or less uncertainty owing to the relative areas of the resonance peaks. Brominated derivatives with chain lengths from 10 to 90 have been obtained by ethylene oxide polymerization and then submitted to reaction with thiourea without further purification.

The thiols are then obtained by a basic hydrolysis and characterized by ^1H NMR. The $^{11}C\underline{H}_2Br$ resonance peak is replaced by the $^{11}C\underline{H}_2SH$ peak (doublet of triplets) at 2.5 ppm and the methylenic protons $^{10}CH_2$ are shifted to 1.6 ppm to give a quadruplet overlapping with that of $^2CH_2$.

Some by-products may occur during the hydrolysis, particularly disulfide by oxidation of the thiols, which are to be subsequently reduced. The hydrolysis time must be then the smallest as possible. The disulfide is characterized in the NMR spectrum by the presence of a triplet ($-CH_2C\underline{H}_2S-$) at 2.7 ppm.

$$2\ HS(CH_2)_{11}(OCH_2CH_2)_nOH \xrightarrow{OH^-} HO(CH_2CH_2O)_n(CH_2)_{11}S\text{-}S(CH_2)_{11}(OCH_2CH_2)_nOH$$

The presence of sulfide can also be noticed, due to the nucleophilic substitution of the bromine atom by the thiolate anion if the reaction of the brominated derivative with thiourea does not go to completion :

$$R\text{-}SH \xrightarrow{OH^-} R\text{-}S^- \xrightarrow{CH_3(CH_2)_{10}Br} R\text{-}S\text{-}(CH_2)_{10}CH_3$$

The transfer constants C_{tr} of the transurfs have been determined in the emulsion polymerization of styrene[10] using a new method developed by Gilbert *et al*[11] who analyzed the first part of the GPC signal which is due to the highest molecular weights. The C_{tr} values are in the range 16 - 19, which is in a good agreement with the usual values found for thiols in the literature (C_{tr} = 20.75 for $C_{12}H_{25}SH$) and tends to decrease with the chain length. Both transurf I [12] and II [13] have been used for steric stabilization of polystyrene colloïds.

Acknowledgments. The authors are indebted to Mrs. C. Monnet who contributed to the ^1H NMR characterization.

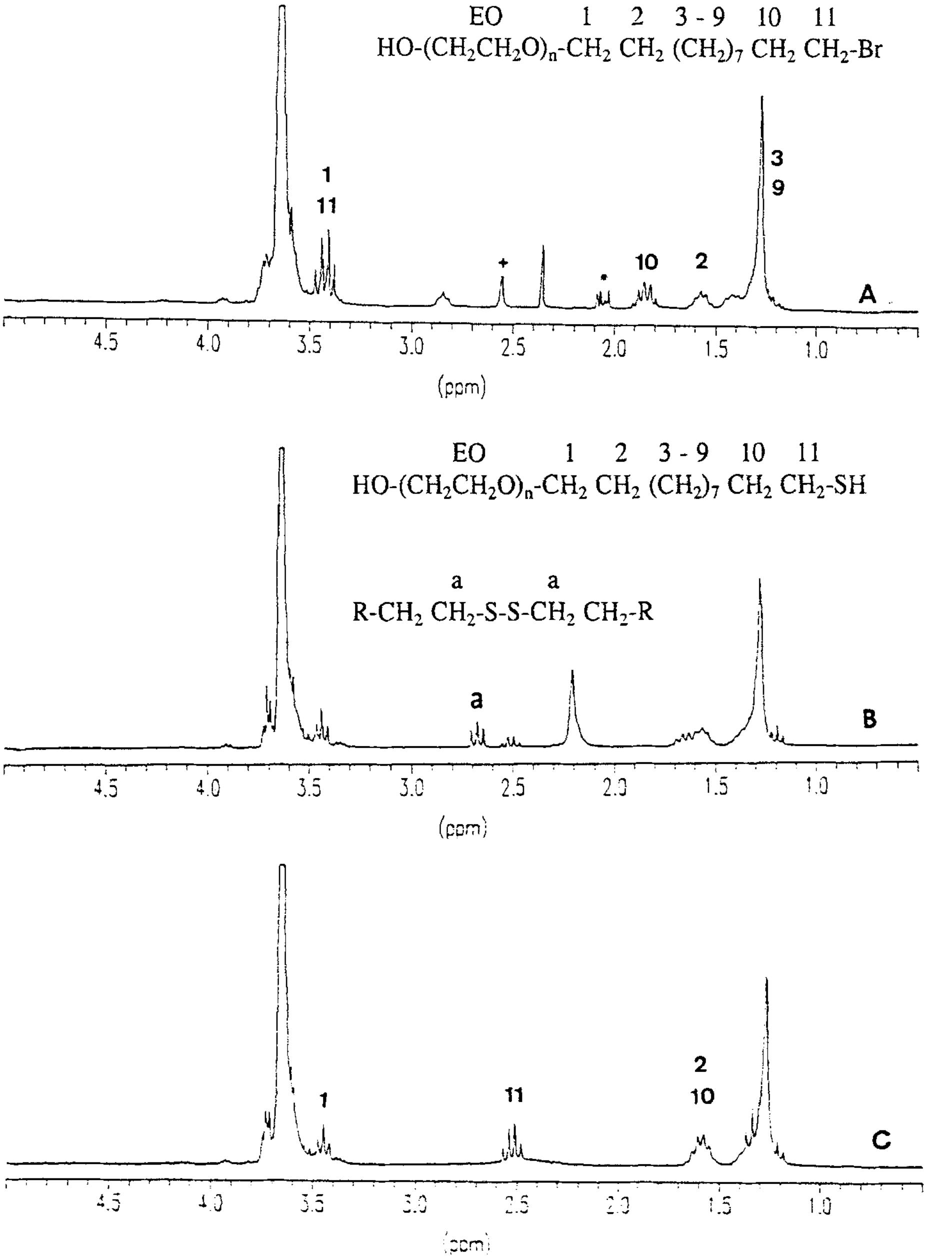


Figure 2. Monitoring of the Transurf II synthesis by ^{1}H NMR.
A : crude brominated derivative; * is some impurity due to the catalytic system and + is water. The singulet at 2.3 ppm is due to residual toluene. B : Mixture of sulfide and disulfide. C : Transurf II.

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