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Synthesis and NMR characterization of new poly(ethoxyalkyl) maleates

Surfactants for emulsion polymerization

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Summary.
Polymerizable surfactants derived from maleic anhydride have been synthesized. The hydrophilic part is obtained by a controlled ethylene oxide polymerization according to a new heterogeneous catalytic process. Some maleates derivatives have been obtained and fully characterized by ^1H and ^{13}C NMR. Their cmc were also measured. Some of them have been engaged in styrene emulsion polymerization in which monodisperse latex particles have been produced.

Introduction.

The interest of reactive surfactants containing polymerizable or initiating functions is to provide stabilization under shear-stress or freeze-thawing constraints. An industrial process based on such systems has been described by ICI (1). The use of reactive surfactants with poly(alkyl-oxazoline) structures in both emulsion and dispersion polymerization has also recently been reported by a japanese group (2, 3, 4). However basic knowledge of the relation between the structure of the surfactants and their performances is still lacking. We have developed a special class of surfactants derived from maleic anhydride, namely the ethoxyalkyl maleates, the general structure is

$$CH_3(CH_2)_nOCO\text{-}CH{=}CH\text{-}CO(OCH_2CH_2)_mOH$$

The maleic derivatives are easily copolymerized but cannot produce homopolymer. For that reason, they may avoid the drawback as to produce polymer soluble in the diluent medium (water or water-alcohol mixture) and not to be definitely fixed onto the surface of the polymer particles. This kind of surfactants was already described in 1982 by a russian group (5), with however the number of ethoxy units m limited to the three values 2, 3 and 6 and an experimental pathway rather fastidious.

In our case, commercial fatty alcohols are reacted with maleic anhydride to form the hemiester.The hydrophobic part is the hydrocarbon chain with n between 8 and 16. This hemiester is engaged in the polymerization of ethylene oxide, according to a new heterogeneous catalytic process (6,7), to give the hydrophilic part with $m > 30$. Some maleates derivatives have been obtained and fully characterized by ^1H and ^{13}C NMR. Some of them have been engaged in styrene emulsion polymerization

Experimental.

Monododecyl maleate. Maleic anhydride (49.03 g, 0.50 mole) and 1-dodecanol (95.90 g, 0.51 mole) were stirred in a melted state at 80°C for one hour. Heptane (150 cm^3) was added to the reaction mixture and stirred for some minutes until an homogeneous solution forms. The solution was left at room temperature for three hours, then at 15°C for two hours, with mixing from time to time. The precipitate formed was collected and recrystallized from heptane (150 cm^3) in a similar way. White bright crystals of monododecyl maleate (132.26 g, 93.0 %) were obtained. Other maleates were obtained in a similar way.

Ethylene oxide polymerization. The catalytic system is prepared in Schlenk-type glassware under pure dry argon. Triisobutylaluminium is reacted at room temperature on a suspension of silica (previously dehydrated) in toluene. After reaction, the excess of alkylaluminium is removed and the hemiester (dried on molecular sieves in toluene) added to the medium. The reaction is achieved by heating at 45°C for two hours.
The catalytic suspension is transferred under argon in a flask fitted a pressure sensor, a thermocouple and an addition funnel filled with ethylene oxide. Argon is removed and the reactor heated at 45°C after what the monomer is slowly added. The reaction is always monitored by pressure. After reaction, silica is separated by sedimentation. The solvent is removed yielding the pure surfactant which is characterized by NMR.

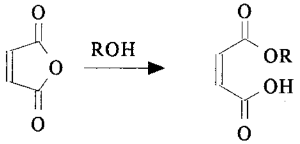
Styrene emulsion polymerization. 1 g of surfactant was dissolved in 450 g water at 70°C. After degassing by nitrogen, 50 g styrene was added and 0.52 g VA 86 (2,2'-azobis [2-methyl-N-(2-hydroxyethyl)-propionamide] from Wako Chemical Industries) a few minutes later.

Measurements. ^1H and ^{13}C NMR spectra were recorded at 330 K on a Bruker AC250 spectrometer at 250 and 62.9 MHz rexpectively. $CDCl_3$ was used as solvent and TMS as internal standard. Melting points were obtained from a Büchi apparatus. The CMC were measured with a Kruss K12 processor tensiometer. The diameter of latex particles was measured by laser diffusion using either a Brookhaven Spectra-Physics apparatus or a Autosizer Lo-C Malvern.

Results and discussion.

Synthesis of the hemiester.

Some syntheses of monoalkyl maleates have been yet reported, for example the reaction of fatty alcohol on the maleic chloride (8). The ring opening of the maleic anhydride by an alcohol gives more easily the hemiester :



Three experimental ways have been used to produce the hemiester. The first way is just by heating an equimolar amount of the reactants for one hour. A rather low temperature must be kept in order to avoid the isomerization into fumarate derivatives. After recrystallization, it gives a very pure product very similar to the common carboxylates soaps. The two other ways are run at room temperature for one day in either toluene or methylene chloride, using triethylamine or dimethylaminopyridine as catalyst. These two latter ways give also pure products, with however a very slight color. The purity of the hemiester was checked by ^{1}H and ^{13}C NMR, and particularly the isomeric purity : no isomerization of the double bond in the fumaric derivative was noted.

The first way is the most versatile to get large quantities of hemiesters and has been applied to several alcohols. The following table reports the yields and the melting points of the various hemiesters.

ROH	n-C_2H_5	n-C_8H_{17}	n-$C_{12}H_{25}$	n-$C_{16}H_{33}$	n-$C_{18}H_{37}$
Yield (%) mp (°C)	96.8 Liquid	61.4 33 - 34	93 58 - 59	94.5 71 - 72	89.3 78 - 79

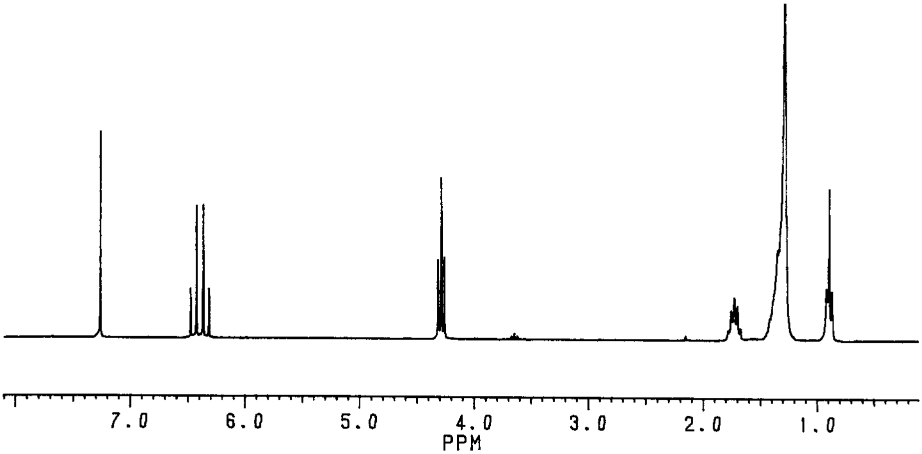


Fig. 1. ^{1}H NMR spectrum of the hemiester.

The ^1H NMR ($CDCl_3$) spectrum is displayed in Fig. 1. The assignments are the following : δ ppm: 0.88 (t, 3H, CH_3); 1.27 (m, 18H, $(CH_2)_9$); 1.72 (m, 2H, CH_2); 4.28 (t, 2H, CH_2O); 6.33 (d, J = 12.8 Hz, 1H, =CH); 6.44 (d, J = 12.8 Hz, 1H, =CH). Both chemical shifts of the olefinic protons at 6.33 and 6.44 ppm and coupling constants ^3J = 12.8 Hz are characteristic of the maleic derivative.

The ^{13}C NMR ($CDCl_3$) are displayed in Fig. 2 with the following assignments : δ ppm :13.86 (C1); 22.53 (C2); 25.70 (C10); 28.23 (C11); 29.05 → 29.50 (C4 →C9); 31.80 (C3); 66.70 (C12); 129.83 and 134.02 (CH=); 165.70 and 166.99 (CO).

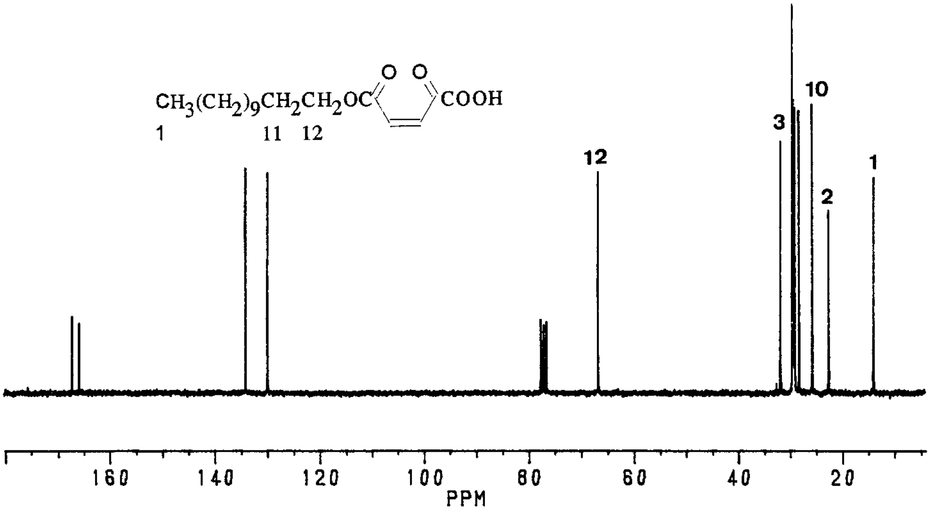
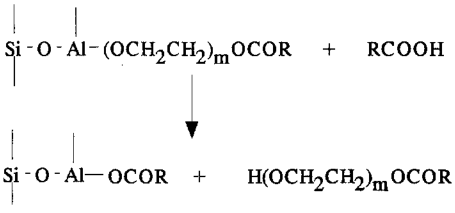


Fig. 2. ^{13}C NMR spectrum of the hemiester.

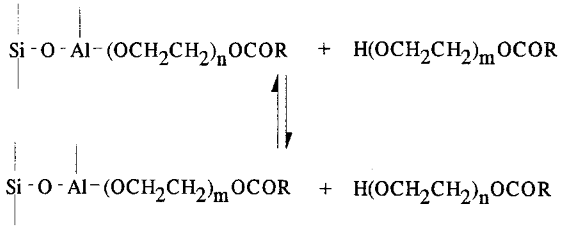
Ethylene oxide polymerization.

Ethylene oxide polymerization has been carried out according to a new heterogeneous catalytic process (6,7). The active centers are aluminium - oxygen bonds linked on a porous silica and the polymerization proceeds by insertion of the monomer inside the Al-O bond. The first active centers are aluminium carboxylate bonds which become aluminium-alcoholates bond after the first ethylene oxide insertion. The hemiester is used in excess, which allows the reaction of the carboxylic group on the aluminium alcoholate. All the starting hemiester molecules are consequently incorporated as chain ends :



$$\text{Si-O-Al-}(OCH_2CH_2)_mOCOR + RCOOH \longrightarrow \text{Si-O-Al-}OCOR + H(OCH_2CH_2)_mOCOR$$

This reaction leads to oligomers carrying an alcohol group as the other chain end. In addition, an exchange reaction takes place between the free alcohols present in the solution and the alcoholate groups bound to the aluminium atoms. A narrow molecular weight distribution is expected if the exchange reaction occurs more frequently than the monomer insertion. The living character of the polymerization was also evidenced, that allows a perfect control of the degree of polymerization.



$$\text{Si-O-Al-(OCH}_2\text{CH}_2)_n\text{OCOR} + \text{H(OCH}_2\text{CH}_2)_m\text{OCOR} \rightleftharpoons \text{Si-O-Al-(OCH}_2\text{CH}_2)_m\text{OCOR} + \text{H(OCH}_2\text{CH}_2)_n\text{OCOR}$$

The reaction proceeds up to 90% in less than four hours. Practically, it is carried out during 12 hours in order to get more than 95% yield. The peaks of the ^1H NMR ($CDCl_3$) spectrum of a crude product (m ≈ 33) after the only evaporation of toluene under vacuum (rotavapor) are assigned as following (Fig. 3) : δ ppm : 0.9 (t, 3H, CH_3); 1.26 (m,18H, $(CH_2)_9$); 1.7 (t, 2H, CH_2 (11); 3.6 (m, (4n + 2)H, CH_2 (PEO chain + b); 4.1 (t, 2H, CH_2 (12)); 4.4 (2H, CH_2 (a)); 6.25 (d, 2H, =CH).

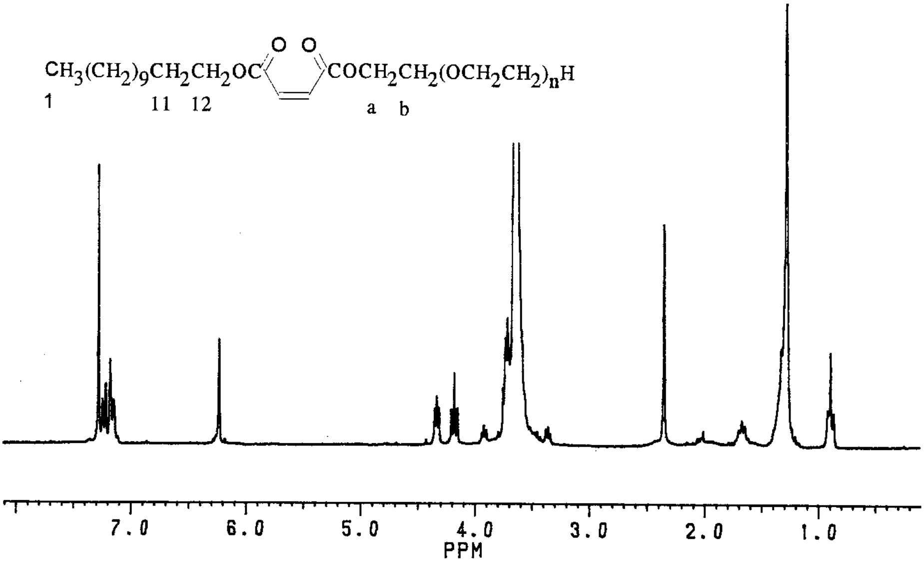


Fig. 3. ^1H NMR spectrum of the polyethoxylation product

The singulet at 2.36 ppm and the massif at 7.2 ppm are assigned to the residual toluene. Both small triplets on both sides of the PEO resonances, separated by about 125 Hz, are due to the ^{13}C satellites. Both olefinic protons are separated by $\Delta\nu \approx 6.9$ Hz and appear as a broadened singulet. The coupling constant can be estimated to ≈ 11.9 Hz.

The value of n agrees with that expected from the initial [OE] / [hemiester] ratio. The quality of the compound obtained without any purification must be highlighted and clearly shows the interest of this process in order to get tailor-made surfactants.

The ^{13}C NMR ($CDCl_3$) are shown in Fig. 4. The assignments are the following : δ ppm : 14.10 (C1); 21.42 (C2); 22.63 (C10); 28.39 (C11); 29.18 → 29.58 (C4 →C9); 31.86 (C3); 61.63 ($CH_2\underline{C}H_2OH$ of the last EO unit); 64.22 ($COO\underline{C}H_2$ of the first EO unit); 65.40 (C12); 68.78 ($COOCH_2\underline{C}H_2$); 70.55 ($\underline{C}H_2\underline{C}H_2O$); 72.56 ($\underline{C}H_2CH_2OH$); 129.51 and 131.13 (CH=); 165.13 and 165.21 (CO). The peaks referred as T are due to the residual toluene.

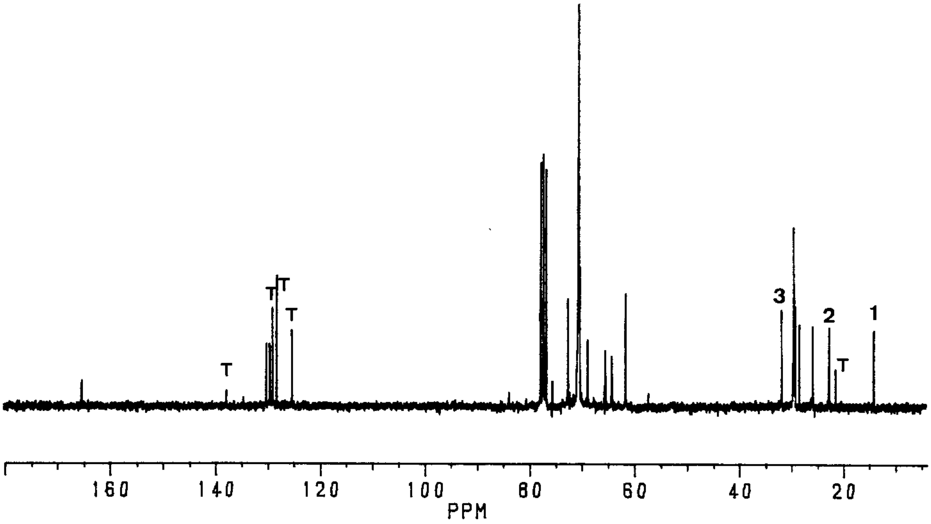


Fig 4 : ^{13}C NMR spectrum of the polyethoxylation product.

Micellar properties.

The critical micellar concentrations of some surfactants with dodecyl group as fatty chain and various PEO chain lengths, namely m = 32 and 41 were measured. The values are 0.03 and 0.13 g/l (1.79 10^{-5} and 6.22 10^{-5} mole/l) respectively, increasing as expected with the PEO chain length. It can be noted the russian team found decreasing cmc values when the chain length increases from 2 to 6 (41.6 10^{-5} down to 13.5 10^{-5} mole/l). The surface tensions are strongly depressed, around 34 mN/m.

Styrene emulsion polymerization.

A few preliminary experiments in styrene emulsion polymerization have been carried out, using two compounds. The diameter of the latex particles increases all along the reaction and monodisperse latex particles of 200 nm (for m = 32) and 300 nm (for m = 41) in diameter have been finally produced. However, upon separation of the latex from its serum, floculation takes place. Some surfactant is recovered after washing of the latex with water. This is not surprising in view of other data of our laboratory showing that a good steric stabilization would need longer chains of PEO. Other experiments are now investigated with other degrees of polymerization.

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