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Synthesis of new alkyl maleates ammonium derivatives and their uses in emulsion polymerization

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Abstract The synthesis of several ammonium derivatives of maleic acid diesters are reported. The starting material is the hemiester of maleic acid, easily obtained from ring opening of the maleic anhydride. The hemiester is submitted to functionalization with an aminated compound, followed by quaternarization with the convenient alkylation reagent. Products crystallize easily and yields are generally high. They have been fully characterized by ^1H and ^{13}C NMR and the CMC have

been measured. Some of them have been engaged in emulsion polymerization with styrene or methyl methacrylate. Maleates functionalized with quaternary ammonium salts yield polystyrene particle sizes around 30 nm with a narrow size distribution without adding any additional emulsifier.

Key words Alkyl maleates ammonium derivatives – surfactants – ^1H NMR – CMC – emulsion polymerization

Introduction

Maleates are widely investigated compounds since they are easily prepared from maleic anhydride (MA) which is a cheap and quite available substance. Salts of maleic acid hemiesters (MHE) have proved to be efficient anionic surfactants. The best way to synthesize the MHE is the reaction of MA with alcohols [1, 2].

The maleic acid diesters (MDE) may become surfactants provided their molecules contain one or more hydrophilic groups. The most promising combination for surfactant features in the maleic acid diester molecule might be hydrophobic sufficiently long *n*-alkane chain (C_8 – C_{18}) in one ester group and hydrophilic neutral or ionogenic short-chain group in another MDE group. Furthermore, maleate derivatives are versatile monomers, since they can only copolymerize with another comonomer without giving homopolymer chains (reactivity ratio = 0). Only single maleate units are conse-

quently observed in the macromolecular chains. In emulsion polymerization, these units are covalently incorporated in polymer chains and might be used to control the hydrophilic–hydrophobic balance of the latexes. Then, such MDE are a new class of polymerizable surfactants for the improvement of surface characteristics.

Sodium and other salts of MHE have proved to serve the above purposes [3]. Prepared from MA and fatty alcohols, they have entered copolymerization reactions with styrene molecules, latexes formed in this way having substantially different surface characteristics by comparison with polystyrene latexes.

We have already described the synthesis of nonionic reactive surfactants based on the ethylene oxide polymerization in the presence of monoalkyl maleates [2]. This work deals with the preparation and characterization of *N,N*-dialkylamino-alkyldiesters from MHE and their subsequent conversion into ammonium salts and sulfobetaines. Some preliminary results on emulsion

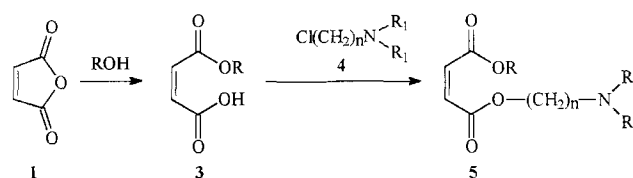
copolymerization with styrene or methyl methacrylate will also be reported.

Results and discussion

The syntheses require to first obtain the hemiester. Some syntheses of monoalkyl maleates have been yet reported, for example, the reaction of fatty alcohol on the maleic chloride [4]. We previously found that the ring opening of the maleic anhydride by an alcohol more easily gives the hemiester [2]. Among several experimental paths, the best way consists of heating an equimolar amount of the reactants for 1 h. A rather low temperature must be kept in order to avoid the isomerization into fumarate derivatives. After recrystallization, it gives a very pure product similar to the common carboxylate soaps. The purity of the hemiester was checked by ^1H and ^{13}C NMR, and particularly the isomeric purity: no isomerization of the double bond in the fumaric derivative was noted. This way is quite versatile and has been applied to several alcohols. The synthesis and NMR characterization of the monododecyl maleate is reported in the experimental section in order to illustrate a very simple way to get large quantities of hemiesters.

Carboxylic group of MHE easily loses proton in basic medium to give the carboxylate anion which can be alkylated by ω -aminoalkyl halides, both in polar aprotic solvent and in water-organic solvent mixture in the presence of a phase-transfer catalyst such as 18-crown-6 or $\text{Bu}_4\text{N}^+\text{Cl}^-$. Then MHE (3) forms the corresponding ω -aminoalkylmaleates (5) with both 2-(N,N-dialkylamino)ethyl chloride (4, $n = 2$) and 3-(N,N-dialkylamino)propyl chloride (4, $n = 3$) according to Scheme 1. The MDE (5) contains slightly hydrophilic tertiary amino groups at the end of a short alkyl chain (Table 1). Their melting points are low and they are usually recovered as slightly yellow oils with a limited solubility in water. This solubility increases in acidic medium because of the N-protonation.

Aminoalkyl maleates (5) enter N-alkylation reactions with both alkyl halides (6) and 1,3-propane sultone (8). Tertiary amines convert into the corresponding quater-



Scheme 1

nary ammonium salts (7) in reactions with alkyl halides (ethyl iodide or allyl bromide) by heating in polar aprotic solvent medium (Table 2). The reactions are quite sensitive to overheating which may cause deamination, the scale of this side reaction depending on the reaction temperature and time. Therefore, it is better not to exceed 70°C in these reactions.

Quaternary ammonium salts (7) which can be used as cationic polymerizable surfactants are white or slightly yellow (especially iodides) substances with a noticeable solubility in water which considerably exceeds that of the corresponding tertiary amines. The solubility decreases with increasing the length of the n -alkane chain in MDE of another ester group.

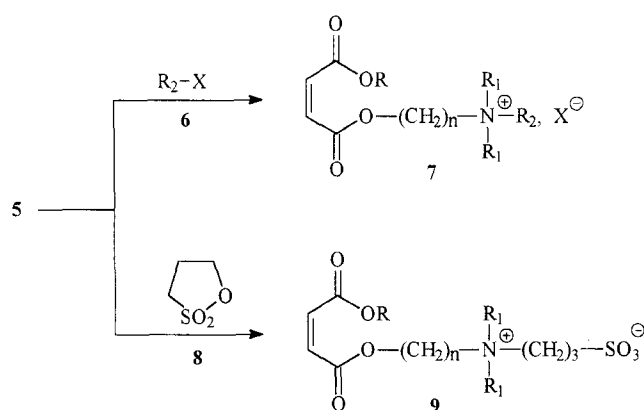
Alkylation of tertiary amines (5) by 1,3-propane sultone (8) leads to the corresponding sulfobetaines (9) which are polymerizable surfactants with zwitterionic hydrophilic groups. They are white crystalline substances, slightly hygroscopic and with much higher water solubility than the above amines or quaternary ammonium salts.

MDE isomerize into fumaric acid diesters under heating or in presence of strong acids [5]. The last esters are unable to enter radical polymerization. To meet the needs of polymerizable surfactants, careful control of the above-mentioned reactions' stereoselectivity is necessary, ^1H NMR spectroscopy being the best method for it. Resonance signals of $\text{CH}=\text{CH}$ double bonds of maleates at 6.4 ppm are far enough from those of fumarates at 6.9 ppm. The proton coupling constants J also are quite different for both isomers, namely <15 Hz for maleates and >16 Hz for fumarates. Polymerizable surfactants of this paper are all maleates according to NMR data (experimental part). Some NMR assignments have been made according to ref. [6].

Table 1 Characterization of some ω -aminoalkyl maleates 5

Reference	Formula	R	Yield (%)	%N Calc	%N Found	cmc ^(*) (mmol/L)
5a	$\text{C}_{18}\text{H}_{33}\text{NO}_4$	$n\text{-C}_8\text{H}_{17}$	87	4.28	4.51	6.46
5b	$\text{C}_{20}\text{H}_{37}\text{NO}_4$	$n\text{-C}_{10}\text{H}_{21}$	90	3.94	3.32	0.93
5c	$\text{C}_{22}\text{H}_{41}\text{NO}_4$	$n\text{-C}_{12}\text{H}_{25}$	90	3.65	3.75	0.28
5d	$\text{C}_{26}\text{H}_{49}\text{NO}_4$	$n\text{-C}_{16}\text{H}_{33}$	98	3.19	3.20	0.02
5e	$\text{C}_{27}\text{H}_{51}\text{NO}_4$	$n\text{-C}_{17}\text{H}_{35}$	90	3.09	3.26	0.01

(*) cmc values for protonated forms (5, HCl).



Scheme 2

Synthesized neutral, cationic and zwitterionic maleates are efficient surfactants. Their surface tension values are in the 11–26 mN/m range and depend substantially on the alkyl chain length. Critical micelle concentrations (CMC) of the polymerizable surfactants are even more dependent on the alkyl chain length, and zwitterionic maleates (9) seem to be the most powerful surfactants among the investigated compounds. A paper devoted to the characterization of surface activity will follow soon [7].

O-Alkylation of MHE leads to nonionic surfactants and subsequent N-alkylation allows to convert them into cationic or zwitterionic polymerizable surfactants. The latter maintain cis-configuration at the $CH=CH$ double bond. It allows to incorporate surfactant molecules into polymer chains.

A few preliminary experiments in copolymerization of maleates with styrene or methyl methacrylate have been carried out in order to appreciate their further potentials. Two quaternary ammonium salts (7) and a sulfobetaine (9b) have been used (Table 3).

In some cases, dodecyl trimethyl ammonium bromide (DTAB) has been added as a cationic emulsifier.

The main interesting feature is the very low particle sizes around 30 nm with a narrow sizes distribution ob-

Table 3 Alkyl maleates ammonium derivatives used in emulsion polymerization

Kind of maleate	R	n	R ₁	R ₂	X ⁻
Quaternary ammonium salt 7c	C ₁₂ H ₂₅	2	C ₂ H ₅	C ₂ H ₅	I ⁻
Quaternary ammonium salt 7g	C ₁₆ H ₃₃	2	CH ₃	CH ₂ -CH=CH ₂	Br ⁻
Sulfobetaine 9	C ₁₂ H ₂₅	2	C ₂ H ₅	-	-

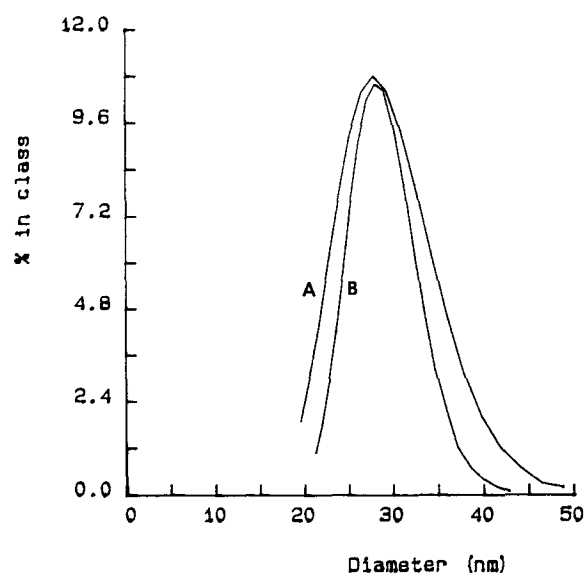


Fig. 1 Particles size distributions of polystyrene latex with quaternary ammonium salt maleates 7c and 7g. A: 7c with DTAB; B: 7g without DTAB

tained from polymerization of styrene with the quaternary ammonium salts (Fig. 1). It is noteworthy that styrene polymerizations with the same amount of DTAB, but without maleate, lead to particle sizes around 105 nm. Styrene polymerizations have also been carried out without DTAB. The same particle sizes are obtained in that case, which shows the only maleate can stabilize the particles. The monomer conversion is complete and no

Table 2 Characterization of some 2-(N,N,N-trialkyl) ammonioethyl-alkyl maleates halides 7

Ref	Formula	R	R ₁	R ₂ X	Yield%	m.p. °C	%N calc	%N found	%X calc	%X found	cmc (mmol/L)
7a	C ₂₀ H ₃₈ NO ₄ I	C ₈ H ₁₇	C ₂ H ₅	C ₂ H ₅ I	77	oil	2.90	3.24	26.25	26.17	9.12
7b	C ₂₂ H ₄₂ NO ₄ I	C ₁₀ H ₂₁	C ₂ H ₅	C ₂ H ₅ I	63	oil	2.74	2.54	24.81	24.64	2.63
7c	C ₂₄ H ₄₆ NO ₄ I	C ₁₂ H ₂₅	C ₂ H ₅	C ₂ H ₅ I	61	73–75	2.60	2.65	23.52	23.92	0.18
7d	C ₂₈ H ₅₄ NO ₄ I	C ₁₆ H ₃₃	C ₂ H ₅	C ₂ H ₅ I	68	76–80	2.35	2.27	21.31	20.89	0.05
7e	C ₂₉ H ₅₆ NO ₄ I	C ₁₇ H ₃₅	C ₂ H ₅	C ₂ H ₅ I	90	75–78	2.30	2.31	20.82	20.88	0.02
7f	C ₂₉ H ₅₄ NO ₄ Br	C ₁₆ H ₃₃	C ₂ H ₅	allyl-Br	56	68–70	2.50	2.26	14.25	14.00	0.07
7g	C ₂₇ H ₅₀ NO ₄ Br	C ₁₆ H ₃₃	CH ₃	allyl-Br	48	-	2.63	2.44	15.00	15.21	-

coagulum is observed. Some latex has been washed on ion-exchange resins in order to get rid of the free charges and a coulometric analysis has shown that it has twice as many charges as those measured on latex obtained with the only DTAB as emulsifier (7.7 $\mu\text{eq N}^+/\text{g}$ polymer).

Using methyl methacrylate instead of styrene gives the same particle sizes but a broader size distribution is observed, which may be due to the more marked hydrophilicity of the monomer. Conversely, larger particle size around 150 nm with narrow size distribution are obtained using sulfobetaine functionalized maleates. Nevertheless, some flocculation can occur in a large scale.

Experimental part

We describe here some typical experimental procedures related to the synthesis of the surfactants described in the above part. The ^1H and ^{13}C NMR spectra have been recorded on a Bruker AC 250 spectrometer at 250 MHz and 62.9 MHz respectively. The assignments have been made by reference with model compounds and according to some spectra collected in the Aldrich Library [8]. Some ^1H NMR spectra are reported in order to complete and illustrate the chemical shifts tables.

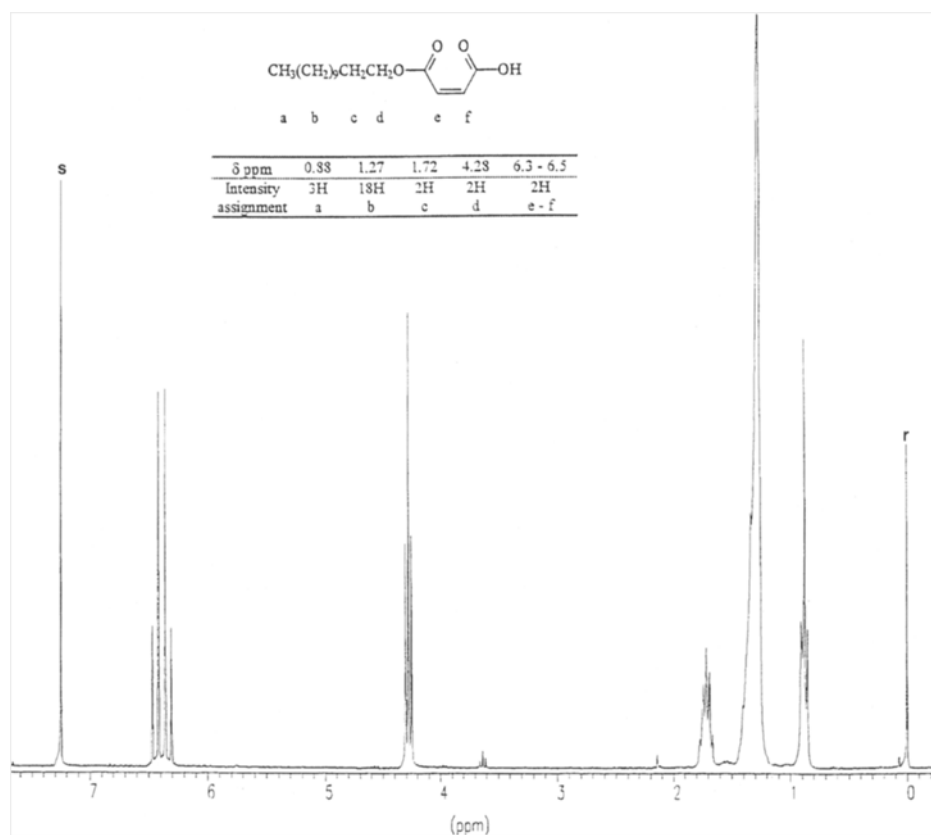
The surface tension measurements and the interfacial tension measurements at the water-dodecane interface were measured with a KSV Du Nouy tensiometer.

Monododecyl maleate (3c)

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 1 h. Heptane (150 mL) was added to the reaction mixture and stirred for some minutes until the formation of a homogeneous solution. The solution was left at room temperature for 3 h, then at 15 °C for 2 h, with mixing from time to time. The precipitate formed was collected and recrystallized from heptane in a similar way. White bright crystals of mono-dodecylmaleate (132.26 g, 93.0%) were obtained with m.p. 58–59 °C. Figure 2 displays the ^1H NMR spectrum. The chemical shifts of the olefinic protons at 6.33 and 6.44 ppm and coupling constants $^3J_{\text{H-H}} = 12.8$ Hz are characteristic of the maleic derivative.

Monooctyl-(3a), decyl-(3b), hexadecyl-(3d), heptadecyl-(3e) and octadecyl-(3f) maleate was obtained in a similar way with yield 90–95%. The ^1H NMR spectra are quite identical, except the intensity of the resonance peak related to the protons Hb. Below are reported the

Fig. 2 ^1H NMR of monododecyl maleate in CDCl_3



^{13}C NMR chemical shifts (the carbon atoms of the alkyl chain are numbered from 1 to 12 from the methyl group).

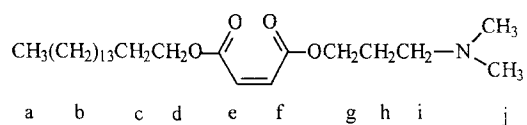
^{13}C NMR (CDCl_3), δ ppm: 13.86 (C1); 22.53 (C2); 25.70 (C10); 28.23 (C11); 29.05 \rightarrow 29.50 (C4 \rightarrow C9); 31.80 (C3); 66.70 (C12); 129.83 and 134.02 (CH=); 165.70 and 166.99 (CO).

2-(N,N-Diethyl)aminoethyl-hexadecyl maleate (5d)

Monohexadecylmaleate (13.62 g; 0.04 mol) was dissolved in chloroform (100 mL). Solution of potassium carbonate (11.06 g; 0.08 mol) and 18-crown-6 (1.05 g; 0.004 mol) in water was added drop by drop to the stirred chloroform solution at room temperature, then the mixture stirred at 50°C for 0.4 h. Solution of 2-(N,N-diethyl)aminoethyl chloride hydrochloride (13.77 g; 0.08 mol) in water (50 mL) was added drop by drop to the above water-chloroform solution at 50°C , the mixture being stirred at this temperature for another 22 h, then cooled to room temperature. Layers were separated, chloroform solution was carefully filtered and evaporated in vacuo. Yellow oil of **5d** (17.23 g; 98%) was collected and used without further purification.

$\text{C}_{26}\text{H}_{49}\text{NO}_4$. Calc%: N: 3.19; Found: N: 3.20.

Other aminoalkyl maleates (**5**) were obtained in a similar way, their characteristics being presented in Table 1. As an example, the chemical shifts of 3-(N,N-Dimethyl)amino-propyl-hexadecyl maleate are reported below. With respect to the above hemiester, both ethylenic protons become chemically equivalent so that the resonance signal is a singlet.



δ ppm (CDCl_3)	0.88	1.27	1.72	1.97	2.40	2.61	4.2–4.3	6.2
Intensity assignment	3H a	26H b	2H c	2H h	6H j	2H i	2H d-g	2H e-f

2-(N,N,N-Triethyl) ammonioethyl-heptadecyl maleate iodide (7e). (method A)

A solution of 2-(N,N-diethyl) aminoethyl-heptadecyl maleate (31.75 g; 0.07 mole) and ethyl iodide (17.4 mL; 0.21 mole) in dry acetone (10 mL) was stirred at 50°C for 96 h, then cooled at 5°C for 12 h. Yellow crystals were

separated and carefully washed twice with t-butylmethyl ether. Light yellow crystals of **7e** (38.41 g; 90%) were obtained with m.p. $75\text{--}78^\circ\text{C}$ (decomp) which should be stored in vacuo or in inert atmosphere.

$\text{C}_{29}\text{H}_{56}\text{INO}_4$. Calc%: N: 2.30; I: 20.82;

Found: N: 2.31; I: 20.88.

Other iodides **7** were prepared in a similar way and their characteristics are presented in Table 2.

2-(N,N,N-Triethyl) ammonioethyl-dodecyl maleate iodide (7c). (method B)

Monododecyl maleate (17.07 g, 0.06 mole), 2-(N,N-diethylamino)ethyl chloride, hydrochloride (10.32 g, 0.06 mole) and potassium hydrocarbonate (15.03 g, 0.15 mole) in acetone 99% (200 mL) were stirred at room temperature for 18 h, then at 60°C for 24 h. Reaction mixture was filtered immediately, precipitate was washed with hot acetone (50°C , 2×50 mL). The joint filtrate was evaporated in vacuo until no liquid distilled off.

The residue was dissolved in acetone (99%, 50 mL), ethyl iodide (10 mL, 0.125 mole) was added and the mixture was stirred at 60°C for 24 h. The viscous solution was evaporated in vacuo. The residue was dissolved in ethyl acetate and left to crystallize at 4°C overnight. The precipitate was filtered under argon atmosphere and recrystallized from ethyl acetate for the second time. 20.71 g (64%) of slightly hygroscopic ammonium iodide (**6c**) were recovered with m.p. $73\text{--}75^\circ\text{C}$.

$\text{C}_{24}\text{H}_{46}\text{INO}_4$. Calc%: N: 2.60; I: 23.52.

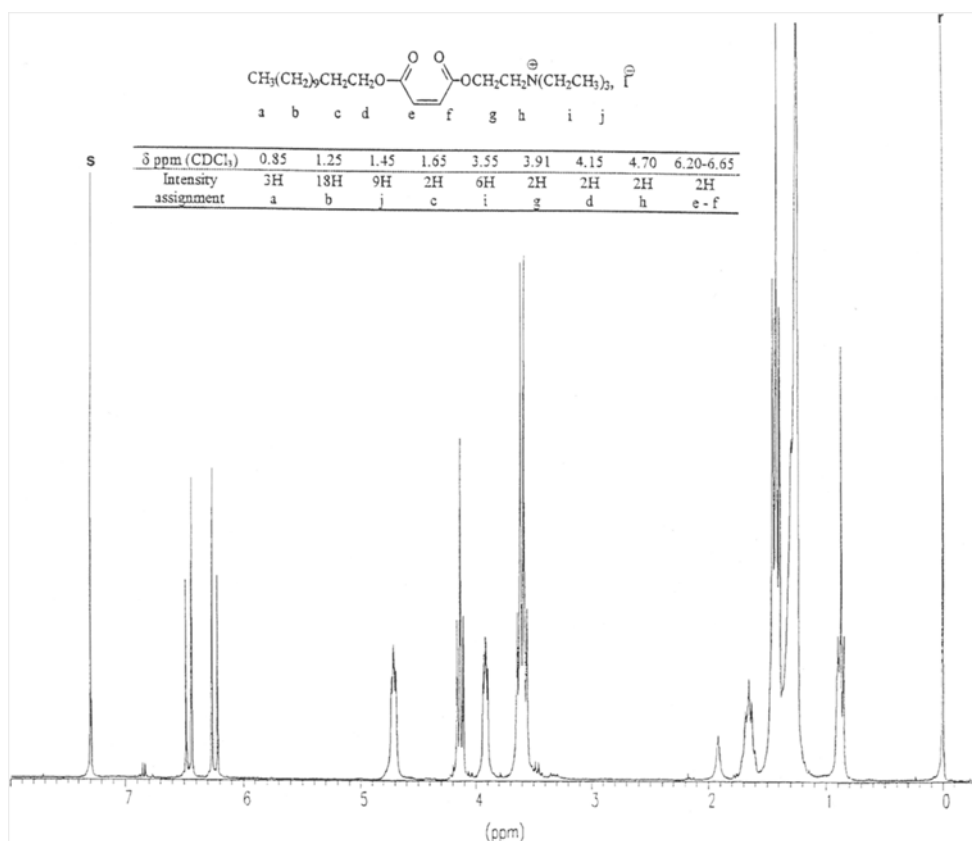
Found: N: 2.65; I: 23.92.

Figure 3 displays the ^1H NMR spectrum. The ethylenic protons are no longer chemically equivalent. The coupling constant $^3J_{\text{H-H}}$ value ($^3J_{\text{H-H}} = 11.9$ Hz) is always characteristic of the maleic derivative, which clearly shows that no isomerization occurs during this step.

2-(N-Allyl-N,N-dimethylammonio) ethyl-hexadecyl maleate bromide (7g)

Monoheptadecyl maleate (20.43 g, 0.06 mole), 2-(N,N-dimethylamino) ethyl chloride hydrochloride (10.32 g, 0.072 mole) and potassium hydrocarbonate (15.03 g, 0.15 mole) in acetone 99% (200 mL) were stirred at room temperature for 18 h, then at 60°C for 24 h. The reaction mixture was filtered immediately and the precipitate (KCl) was washed with hot acetone (2×50 mL). The filtrate was evaporated in vacuo until no liquid distilled off.

Fig. 3 ^1H NMR of 2-(N,N,N-Triethyl ammonio ethyl-dodecyl maleate iodide **7c**



The residue was dissolved in 1,4-dioxane (50 mL), allyl bromide (8.47 g, 6.06 mL, 0.07 mole), was added and the mixture was stirred at 70 °C for 24 h. The viscous solution was evaporated in vacuo. The residue was dissolved in dry ethyl acetate (40 mL) and allowed to crystallize at 4 °C for 12 h. The precipitate was filtered under argon and recrystallized from ethyl acetate for the second time. 18 g (67%) of very hygroscopic ammonium bromide were obtained and characterized by NMR.

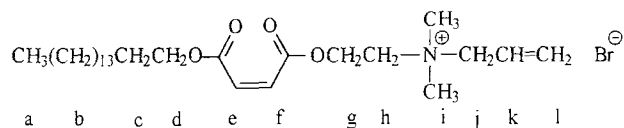
$\text{C}_{29}\text{H}_{56}\text{NO}_4\text{Br}$. Calc%: N: 2.50; Br: 14.25.

Found: N: 2.21; Br: 13.96.

2-(N-allyl-N,N-diethylammonio) ethyl-hexadecyl maleate bromide (**7f**) was obtained in a similar way. The NMR spectrum is shown in Fig. 4.

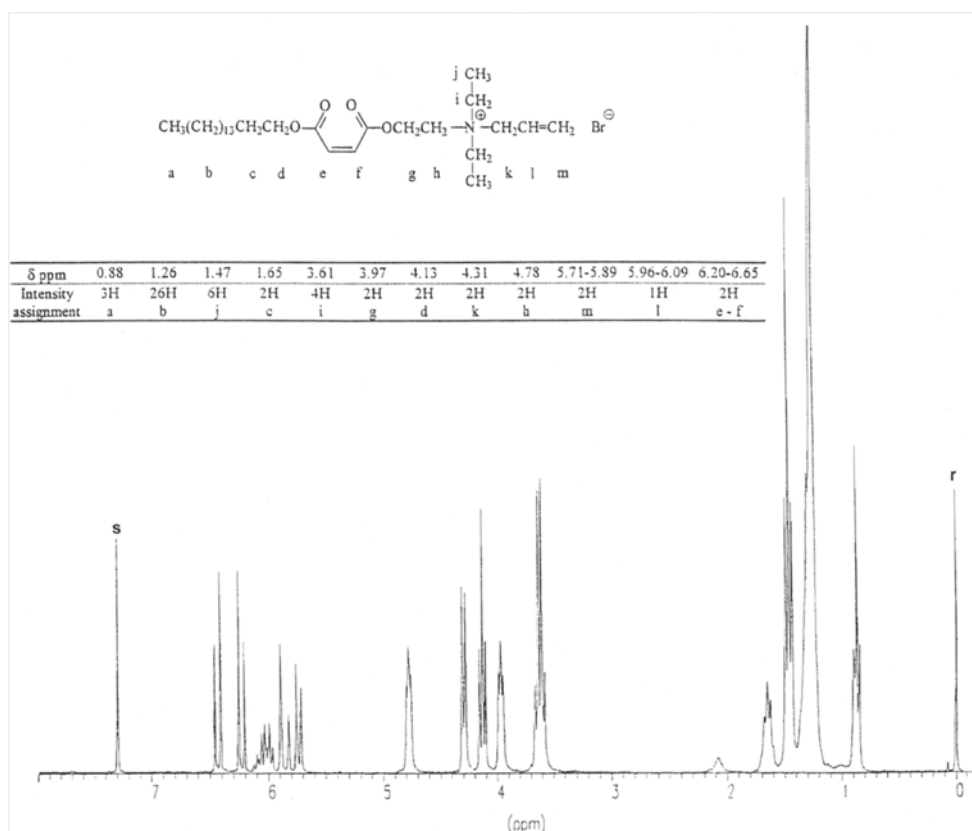
2-[N,N-Diethyl-N-(3-sulfopropyl)ammonio] ethyl hexadecyl maleate (**9a**)

Mono-hexadecyl maleate (20.43 g, 0.06 mole), 2-(N,N-diethylamino)ethyl chloride hydrochloride (10.32 g, 0.06 mole) and potassium hydrocarbonate (15.03 g, 0.15 mole) in acetone 99% (200 mL) were stirred at room temperature for 18 h, then at 60 °C for 24 h. Reaction



δ ppm (CDCl ₃)	0.85	1.25	1.65	3.40	4.15	4.50	4.80	5.60-6.10	6.20-6.65
Intensity	3H	26H	2H	6H	4H	2H	2H	3H	2H
assignment	a	b	c	i	d-g	j	h	k-l	e-f

Fig. 4 ^1H NMR of 2-(N-allyl-N,N-diethyl) ammonio ethylhexadecyl maleate bromide **7g**

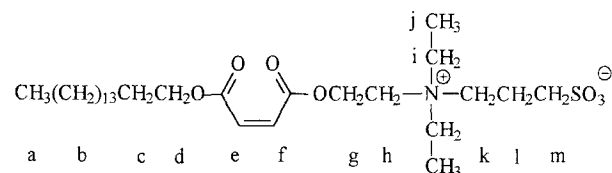


mixture was washed with hot acetone (50 °C, 2 × 50 mL), the filtrate was evaporated in vacuo. The residue was dissolved in a small amount of DMF (10 mL); 1,3-propane sultone (7.33 g, 0.06 mole) was added and the reaction mixture was stirred at 95 °C for 24 h.

Ethyl acetate (240 mL) was added to the reaction mixture and the mixture was stirred at 70 °C for 30 min. After 18 h at room temperature, ethyl acetate solution was decanted from the residue and the last treated with hot acetone (300 mL). The product obtained was dissolved in methanol (100 mL) and the solution was treated with charcoal and silica. Dry diethyl ether (400 mL) was added drop by drop to yellow methanol solution. The precipitate was collected in inert atmosphere and dried in vacuo.

$\text{C}_{29}\text{H}_{55}\text{NO}_7\text{S}$. Calc%: N: 2.49; S: 5.71.

Found: N: 2.30; S: 5.54. CMC: 0.004 mmol/l.



δ ppm (DMSO)	0.85	1.25	1.60	1.95	3.40-3.60	4.15	4.50	6.5
Intensity	3H	32H	2H	2H	10H	2H	2H	2H
assignment	a	b + j	c	l	h-i-k-m	d	g	e-f

3-(N,N-Dimethyl-N-sulfopropyl)ammonio] propyl hexadecyl maleate (9b)

Hexadecyl maleate (13.62 g; 0.04 mol) was dissolved in chloroform (80 mL). Solution of potassium hydroxide (6.72 g; 0.12 mol) and tetrabutyl ammonium chloride (0.5 g) in water (80 mL) was added to stirred chloroform solution at room temperature, stirring being continued for 1 h. Solution of 3-dimethylaminopropyl chloride hydrochloride (12.62 g; 0.08 mol) in water (40 mL) was added and the mixture was stirred overnight at room temperature, then at 60 °C for 24 h. Layers were separated. The chloroform solution was evaporated in vacuo to give a yellow oil. 1,3-propane sultone (2.44 g; 0.03 mol) in 2-butanone (30 mL) was added to the above oil, and the mixture obtained was stirred at 80 °C for 96 h. The solution was cooled, a precipitate formed, which was separated

and immediately recrystallized from 2-butanone. Product was dried in vacuo at room temperature. White crystals of sulfobetaine **9b** (9.42 g; 43%) were obtained.

$C_{30}H_{57}NO_7S$. Calc%: N: 2.56; S: 5.85.

Found: N: 2.60; S: 5.72.

3-[N,N-Dimethyl-N-sulfopropyl]ammonio] propyl octodecyl maleate (**9c**) is obtained in a similar way.

Emulsion copolymerizations

3 g maleate was dissolved in 150 g water at 70°C. After degassing by nitrogen, 13 g distilled monomer and 0.15 g V50 (2-2'-azobis (2-amidino propane) hydrochloride from Wako Chemical Industries) were added. The particle sizes measurements were performed by using a Autosizer Lo-C Malvern apparatus.

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