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ORIGINAL CONTRIBUTION

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Novel nonionic polymerisable surfactants based on sulfoxides. 1. Monomer synthesis and general surfactant behaviour

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Abstract The synthesis, surface activity, and micellisation of a series of new nonionic polymerisable surfactants, often referred to as surfmers, are described. These monomers bear terminal vinyl groups or acrylic esters, and the nonionic sulfoxide moiety. Compared to many other nonionic hydrophilic fragments, the sulfoxide group behaves as a strongly hydrophilic fragment of small volume, that can balance up to an acryloyloxyundecyl hydrophobic chain. The incorporation of the polar acrylate moiety at the end of the hydrophobic chain seems to confer surfactant properties similar to the ones of bola amphiphiles to the monomers.

Key words Polymerisable surfactants · Alkyl sulfoxides · Monomer synthesis · Surfmers

Introduction

Much work has been devoted in the past 2 decades to polymerisable surfactants (frequently referred to as "surfmers"), often in the context of reactive emulsifiers for emulsion polymerisation and related processes [1–3]. Also, polymerisable surfactants have served as chemically well defined building blocks for the construction of the so-called "polysoaps" [1, 4, 5]. Polysoaps present a special class of micellar polymers which can be visualised as a necklace of laterally linked, individual surfactant fragments. The surfactant fragments can be anchored to the polymer backbone at different positions: via the hydrophilic head group (the so-called "head type"), via the end of the hydrophobic chain (the so-called "chain-end type"), or via a position in the midst of the hydrophobic chain (the so-called "mid type"). These different geometries give rise to strongly differing properties even for isomeric polymers [1, 5, 6]. As polymerisable surfactants are typically hygroscopic, free-radical polymerisation is the method of choice and, therefore, most known compounds bear a vinyl or a vinylidene moiety as the polymerisable group [1]. The high density of substituents on the backbone of such polymers results in severe steric crowding [7, 8], and thus generally, water-soluble homopolymers are only obtained from polymerisable surfactants of the "chain-end type" [1, 5–8].

Surfactants and polysoaps are classified according to the nature of their hydrophilic group in three subclasses; namely, ionic ones, zwitterionic ones, and nonionic ones. Although ionic, in particular anionic, polymerisable surfactants and the corresponding polymers have found the most practical interest so far [1, 2], they are much less suited for model studies than the other classes. This is a consequence of the inherent problems in the investigation of polyelectrolytes. In the past we therefore focused on uncharged polymerisable surfactants and the corresponding micellar polymers, namely such bearing zwitterionic groups [5, 7, 8]. These polymers enabled us to perform a series of fundamental studies, so some basic relationships between the polymer geometry and the polarity of backbones, and key properties such as surface activity, solubilisation capacity, and emulsifying power could be established.

Although zwitterionic polysoaps proved to be suited for fundamental studies, they are not ideal candidates. Often, they are difficult to synthesise in pure form, and their solubility is low. Also, polyzwitterions are still sensitive to small amounts of added salts [9, 10], though the effects observed differ from the ones observed for polyelectrolytes. In fact following similar reasoning, nonionic polymerisable surfactants have attracted interest for fundamental studies since the early days [6, 11, 12], because their solubilites are often high and the sensitivity to added salts is low. Moreover, the "classical" nonionic groups are oligo(ethylene oxide)s which can be easily prepared even on an industrial scale; however, such polymerisable surfactants present their own drawbacks. Oligo(ethylene oxide)s are rather weakly hydrophilic groups only, and thus very voluminous: about two $-\mathrm{O{-}CH_2{-}CH_2}-$ fragments are needed to balance three $-\mathrm{CH_2}-$ groups [13, 14] in order to obtain water-soluble products. The ratio of the hydrophilic volume to hydrophobic volume is therefore at least 2:1, and is often much higher. Moreover, oligo(ethylene oxide) surfactants suffer from limited solubility at elevated temperatures owing to the occurrence of a lower critical solution temperature [13]. Also, long oligo(ethylene oxide) fragments are usually mixtures, rendering the discussion of experimental results in fundamental studies difficult. Additionally, the micellar polymers obtained tend to become insoluble with time, presumably owing to cross-linking by attack of oxygen on the numerous $-\mathrm{CH_2{-}O}-$ groups.

Still, studies on alternative nonionic surfactants are rare. They mainly comprise oligomers of oxazolines [15, 16], which share many problems with their poly(ethylene oxide) analogues, or derivatised sugars [17]. The latter are generally complicated to synthesise in pure form, and suffer from limited solubility in water in many cases owing to strong hydrogen bonding [18–20]. Moreover, they still present a rather unfavourable ratio of the hydrophilic volume to the hydrophobic volume, as normally about one $-\mathrm{CHOH}-$ fragment is required for two $-\mathrm{CH_2}-$ groups in order to obtain water-soluble products [13, 17].

Though often neglected, there are a variety of very small, nonionic hydrophilic groups, such as aminoxides, sulfoxides, phosphinoxides, and arsineoxides [21, 22]. The latter two groups are difficult to prepare when bearing additional functional fragments, but the first two groups are well accessible by various methods. Yet, amine oxides tend to inhibit free-radical polymerisation. Therefore, we explored the sulfoxide group as a small nonionic polar group for its use as an alternative head group for polymerisable surfactants. As the sulfoxide group is much more hydrophilic than a single ethylene oxide group [23], the head group can be much smaller than in oligo(ethylene oxide) surfactants. This is also true in comparison with the newly emerging nonionic surfactants based on sugars (see earlier). For example, an octyl chain is balanced by one sulfoxide group only, whereas this hydrophobic group typically requires six ethylene oxide units or one hexose unit [24]. Also, owing to the uncharged character, we expected strongly improved solubilities of sulfoxides compared to zwitterionic analogues in most solvents. Additional aspects, such as the potential chirality of the unsymmetrically substituted sulfoxide group, might offer some additional future perspectives.

Experimental

Methods

Elemental analysis was done at the University College of London. NMR spectra were recorded with Gemini 200 and 300 spectrometers (Varian). IR spectra were recorded with a FTS 135 IR Fourier transform spectrometer (BioRad). Surface tensions were measured with a manual tensiometer (Krüss 8501, De Noüy) at 21 ± 1 °C. Monomer solutions were equilibrated for 24 h before the measurements. Differential scanning calorimetry was performed with a PerkinElmer DSC7, applying heating and cooling rates of 2 °C/min.

Materials

The water used for all the experiments was purified by an Elgastat water purification system (resistance 18 MΩ). "Flash" column chromatography was performed on silicagel (Merck 230–400 mesh), or if stated explicitly, on $\mathrm{Al_2O_3}$ (Acros, basic, 150 mesh). A small amount of the inhibitor di-*t*-butyl-*p*-cresol was added to all the reaction mixtures containing polymerisable components, but not to the final products.

*Dodecyl methyl sulfoxide (**1**)*

Dimethyl sulfate (11.00 g, 0.087 mol) was slowly added to *n*-dodecanthiol (19.22 g, 0.095 mol) and KOH (5.43 g, 0.092 mol) in 20 ml ethanol under a nitrogen atmosphere. The mixture was stirred for 72 h, producing a white precipitate. After addition of 100 ml water, the aqueous phase was extracted three times with $\mathrm{CH_2Cl_2}$. The organic phases were combined, washed with 100 ml water, dried with sodium sulfate, and evaporated. Yield: 14.2 g (71%) dodecyl methyl thioether as a colourless liquid. $n^{20} = 1.4583$.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, δ): 2.45 (t, 2H, $-\mathrm{CH_2{-}S}-$), 2.05 (s, 3H, $-\mathrm{S{-}CH_3}$), 1.55 (m, 2H, $-\mathrm{CH_2{-}C{-}S}-$), 1.40–1.15 [m, 18H, $-(\mathrm{CH_2})_9-$], 0.85 (t, 3H, $\mathrm{CH_3}-$).

^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$, δ): 34.0 ($\mathrm{CH_3{-}CH_2{-}}\mathit{C}\mathrm{H_2}-$, $\mathit{C}\mathrm{H_2{-}S}-$), 32.0 ($-\mathit{C}\mathrm{H_2{-}C{-}S}-$), 30.3, 30.0 [$-(\mathit{C}\mathrm{H_2})_6$], 28.9 ($-\mathit{C}\mathrm{H_2{-}C{-}C{-}S}-$), 23.0 ($\mathrm{CH_3{-}}\mathit{C}\mathrm{H_2}-$), 15.6 ($-\mathrm{S{-}}\mathit{C}\mathrm{H_3}$), 14.0 ($\mathit{C}\mathrm{H_3}-$).

A solution of magnesium monoperoxyphthalate (1.52 g, 3.07 mmol) hexahydrate and of a few milligrams tetrahexylammonium chloride in 10 ml water was added to dodecyl methyl thioether (1.00 g, 4.62 mmol) in 10 ml $\mathrm{CH_2Cl_2}$. After 6 h of stirring at 40 °C, the organic phase was separated, washed twice with 10 ml water, dried over sodium sulfate, and evaporated. The crude dodecyl methyl sulfoxide was recrystallised from water and purified by flash chromatography (eluant: ethyl acetate) to remove traces of sulfone formed. Yield: 0.25 g (23%) as a colourless crystals. m.p.: 62 °C.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, δ): 2.70 [m; 2H, $-\mathrm{CH_2{-}S(=O)}-$], 2.54 [s; 3H, $-\mathrm{S(=O){-}CH_3}$], 1.70 (m; 2H, $-\mathrm{CH_2{-}C{-}S(=O)}-$), 1.40–1.15 [m; 18H, $-(\mathrm{CH_2})_9-$], 0.85 (t; 3H, $\mathrm{CH_3}-$).

^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$, δ): 54.9 [$-\mathit{C}\mathrm{H_2{-}S(=O)}-$], 38.6 [$-\mathrm{S(=O){-}}\mathit{C}\mathrm{H_3}$], 31.9 ($\mathrm{CH_3{-}C{-}}\mathit{C}\mathrm{H_2}-$), 29.9, 29.3, 29.2 [$-(\mathit{C}\mathrm{H_2})_7-$, $-\mathit{C}\mathrm{H_2{-}C{-}S(=O)}-$], 28.8 ($-\mathit{C}\mathrm{H_2{-}C{-}C{-}S}-$), 22.5 ($\mathrm{CH_3{-}}\mathit{C}\mathrm{H_2}-$), 14.1 ($\mathit{C}\mathrm{H_3}-$).

11-Dodecenyl methyl sulfoxide (**2**)

Tosyl chloride (25.2 g, 132.1 mmol) was slowly added to 10-undecenol (15.0 g, 88.1 mmol) in 200 ml dry pyridine and stirred for 2 h at room temperature until no more alcohol was detected by thin-layer chromatography (TLC). The mixture was then shed on 400 g crushed ice and extracted twice with 300 ml diethyl ether. The combined ether phases were extracted twice with 200 ml acidified water (pH 5) and once with 200 ml neutral water. Drying the ether phase with sodium sulfate and removal of the solvent gave of a mixture (23.4 g, 94.1%) of 10-undecenyltosylate and 10-undecenylchloride (69 mol% tosylate and 31 mol% chloride according to ^{1}H NMR).

^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.7, 7.3 (d, 1.4 + 1.4H, aryl), 5.8 (m; 1H, =CH–), 5.1–4.8 (m; 2H, CH_2=), 4.0 (t, 1.4H, –CH_2–O–tosyl), 3.5 (t, 0.6H, –CH_2–Cl), 2.4 (s; 2.1H, aryl–CH_3), 2.0 (m; 2H, =C–CH_2–), 1.8–1.5 (m; 4H, –CH_2–C–Cl, –CH_2–C–O–tosyl), 1.10–1.40 [m; 12H, –$(CH_2)_6$–].

A solution of sodium methylsulphinyl methide (200 ml, 0.84 M) in dimethyl sulfoxide (DMSO) [25–27] was added dropwise under vigorous stirring to 23.4 g of the mixture of 11-tosylundecene and 11-chloroundecene in 40 ml dry diethyl ether cooled to 20 °C. After 3 h, the mixture was shed on 400 ml brine and extracted four times with 250 ml diethyl ether. The brownish solid which formed slowly at the water–ether interface was isolated. The combined ether phases were dried with sodium sulfate and evaporated to give a yellow oil to which 100 ml petroleum ether was added. The mixture cooled to 4 °C for 24 h yielded more precipitate. The combined precipitates of crude dodecenyl methyl sulfoxide were recrystallised four times from petroleum ether/ethanol (95:5 v/v). Yield: 7.3 g (38%) colourless crystals. m.p.: 39 °C.

^{1}H NMR (200 MHz, C_6D_6, δ): 5.78 (m; 1H, =CH–), 5.15–4.97 (m; 2H, CH_2=), 2.70 [m; 2H, –CH_2–S(=O)–], 2.54 [s; 3H, –S(=O)–CH_3], 1.85–2.25 (m; 2H, =C–CH_2–), 1.40–1.60 [m; 4H, =C–C–CH_2–, –CH_2–C—S(=O)–], 1.10–1.40 [m; 12 H, –$(CH_2)_6$–].

^{13}C NMR (50 MHz, $CDCl_3$, δ): 139.69 (=*C*H–), 114.68 (*C*H_2=), 55.40 [–*C*H_2–S(=O)–], 39.12 [–S(=O)–*C*H_3], 34.33 (=C–*C*H_2–), 30.01, 29.96, 29.88, 29.75, 29.65, 29.49, and 29.37 [–$(CH_2)_7$–], 23.12 [–*C*H_2—C—(S=O)–].

8-Acryloyloxyoctyl methyl sulfoxide (**3**)

1,8-Dibromooctane (26.0 g, 95.6 mmol) in 150 ml water and potassium thiolate (4.53 g, 52.6 mmol) in 200 ml tetrahydrofuran (THF) and 30 ml water were mixed and refluxed for 1 night, when the ^{1}H NMR spectra indicated 52% of total conversion of the bromide groups. After filtration and concentration, 200 ml diethyl ether was added, the ether phase was extracted three times with 200 ml water, then dried with sodium sulfate, and the solvent removed. The crude 8-bromooctyl methyl sulfide was purified by flash chromatography on silica gel (eluant: petroleum ether/diethyl ether 9:1 v/v). Yield: 8.3 g (36%) colourless liquid.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 3.37 (t, 2H, Br–CH_2–), 2.45 (t, 2H, –CH_2–S–), 2.05 (s, 3H, –S–CH_3), 1.78–1.15 [m, 12H, –$(CH_2)_6$–].

A mixture of cesium acrylate (7.37 g, 31.4 mmol) and 8-bromooctyl methyl sulfide (5.00 g, 20.9 mmol) in 75 ml dimethylformamide (DMF) was stirred overnight. The mixture was shed on 200 ml diethyl ether, extracted nine times with 200 ml water, and the solvent evaporated to obtain pure 8-acryloyloxyoctyl methyl sulfide. Yield: 4.7 g (98%) colourless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.35 (dd, 1H, CH=C–COO–cis), 6.07 (dd, 1 H, =CH–), 5.76 (dd, 1H, HC=C–COO– trans), 4.10 (t, 2H, –COO–CH_2–), 2.40 (t, 2H, –CH_2–S–), 2.04 (s, 3H, –S–CH_2), 1.7–1.2 [m, 12H, –$(CH_2)_6$–].

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 166.69 (–*C*OO–), 130.83 (*C*H_2=), 129.15 (=*C*H–), 65.05 (–COO–*C*H_2–), 34.70 (–*C*H_2—S-), 29.57, 29.13, and 29.05 [–COO–C–*C*H_2–, (–*C*H_2–)$_4$], 26.32 (COO–C–C–*C*H_2–), 15.94 (–S–*C*H_3).

8-Acryloyloxyoctyl methyl sulfide (4.50 g, 19.5 mmol) and $NaIO_4$ (4.60 g, 21.5 mmol) were stirred in 80 ml methanol for 24 h. After filtration on celite and on Al_2O_3 and removal of the solvent, the residual oil was dissolved in 3 ml $CHCl_3$ and purified by flash chromatography (eluant: ethyl acetate). Yield: 5.0 g (84%) colourless powder.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 6.38 (dd, 1H, CH=C–COO–cis), 6.07 (dd, 1H, =CH–), 5.85 (dd, 1H, HC=C–COO– trans), 4.13 (t, 2H, –COO–CH_2–), 2.76–2.6 [m, 2H, –CH_2–(S=O)–], 2.54 [s, 3H, –(S=O)–CH_3], 1.82–1.20 [m, 12H, –$(CH_2)_6$–].

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 166.02 (–*C*OO–), 130.33 (*C*H_2=), 128.42 (=*C*H–), 64.34 (–COO–*C*H_2–), 54.44 [–*C*H_2–(S=O)–], 38.41 [–(S=O)–*C*H_3], 28.89, 28.76, 28.48, and 28.36 [–COO–C–*C*H_2, –(*C*H_2)$_4$–], 25.63 [–COO–C–C–*C*H_2–], 22.34 [–*C*H_2–C–(S=O)–].

Elemental analysis ($C_{12}H_{22}O_3S$, $M_r = 246.36$): Calcd (%): C:,58.50; H, 9.00; S, 13.01. Found (%): C, 57.44; H, 8.90; S, 12.65.

Mass spectrum (EI 70 eV, *m*/*z*): 229.2 (100%, M–OH^+), 246.2 (5%, M^+); (FAB, *m*/*z*): 247.0 [100%, $(M+H)^+$].

11-Acryloyloxyundecyl methyl sulfoxide (**4**)

A mixture of 11-bromoundecanol (10.0 g, 40.0 mmol) in 100 ml THF and potassium methyl thiolate (22 g, 212 mmol) in water was refluxed for 2 h until all the bromide was consumed according to ^{1}H NMR. The mixture was concentrated under reduced pressure and shed on 100 ml diethyl ether. The ether phase was extracted three times with 100 ml water, and the solvent was evaporated to give 7.8 g (95%) pure 11-hydroxyundecyl methyl sulfide as a colourless powder.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 3.63 (t, 2H, –O–CH_2–), 2.48 (t, 2H, –CH_2–S–), 2.09 (s, 3H, –S–CH_3), 1.58–1.19 [m, 18H, –$(CH_2)_9$–].

Acryloyl chloride (2.15 g, 23.8 mmol) in 20 ml dry diethyl ether was added dropwise under vigorous stirring to solution of 11-hydroxyundecyl methyl sulfide (4.00 g, 18.3 mmol) and triethyl amine (2.8 g, 28 mmol) in 100 ml dry diethyl ether cooled to 0 °C. The white-yellowish mixture stirred overnight at room temperature was filtered, and the filtrate was extracted three times with 100 ml water and three times with 100 ml 0.5 M aqueous $NaHCO_3$. The compact precipitate of triethyl amine hydrochloride was dissolved in 100 ml water and extracted with 100 ml diethyl ether, which was washed identically. The ether phases were combined and dried with sodium sulfate. After removal of the solvent, the crude 11-acryloyloxyundecyl methyl sulfide was purified by flash chromatography on silica gel (eluant: diethyl ether/ethanol 10;1 v/v). Yield: 3.9 g (91%) colourless liquid.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 6.39 (dd, 1H, HC=C–COO–cis), 6.10 (dd, 1H, =CH–), 5.80 (dd, 1H, HC=C–COO– trans), 4.13 (t, 2H, –COO–CH_2–), 2.47 (t, 2H, –CH_2–S–), 2.08 (s, 3H, –S–CH_3), 1.68–1.16 [m, 18H, –$(CH_2)_9$–].

Sodium metaperiodate (3.42 g, 16 mmol) was added to a solution of 11-acryloyloxyundecyl methyl sulfide (3.87 g, 14.5 mmol) in 50 ml methanol which was cooled to 0 °C. The reaction medium was stirred at room temperature overnight. After filtration on celite and on Al_2O_3, and after removal of the solvent, the crude 11-acryloyloxyundecyl methyl sulfoxide was purified by flash chromatography (eluant: diethyl ether/ethanol 10:1 v/v). Yield: 3.8 g (93%) colourless powder.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.36 (dd, 1H, CH=C–COO–cis), 6.08 (dd, 1H, =CH–), 5.78 (dd, 1H, CH=C–COO trans), 4.12 (t, 2H, –COO–CH_2–), 2.77–2.57 [m, 2H, –CH_2-(S=O)–], 2.55 [s, 3H, –(S=O)–CH_3], 1.74–1.2 [m, 18H, –$(CH_2)_9$–].

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 167.09 (–*C*OO–), 131.15 (*C*H_2=), 129.32 (=*C*H–), 65.25 (–COO–*C*H_2–), 55.31 [–*C*H_2–(S=O)–], 39.07 [–(SO)–*C*H_3], 29.92, 29.80, 29.69, 29.28, and 29.10 [–COO–C–*C*H_2–, –(*C*H_2)$_6$–], 26.39 (–COO–C–C–*C*H_2–), 23.05. [–*C*H_2–C–(S=O)–].

Elemental analysis ($C_{15}H_{28}O_3S$, $M_r = 288.45$): Calcd (%): C, 62.46; H, 9.78; S, 11.11. Found (%): C, 62.54; H, 10.05; S, 11.16.

Mass spectrum (EI 70 eV, *m*/*z*): 271.2 (100%, M–OH$^+$), 288.0 (2%, M^+); (FAB): 289.1 [100%, $(M+H)^+$].

*12-Acryloyloxydodecyl methyl sulfoxide (**5**)*

3,4-Dihydropyran (21.1 g, 251 mmol) in 100 ml dry diethyl ether was slowly added to a solution of 11-bromo-1-undecanol (34.9 g, 139 mmol) and of dry *p*-toluene sulfonic acid (2.69 g, 15.6 mmol) in 70 ml dry diethyl ether under an argon atmosphere, while stirring vigorously. After 4 h, the mixture was extracted four times with 400 ml water buffered to pH 7. The organic phase was separated, dried with sodium sulfate, and evaporated. Purification by flash chromatography (eluant: petroleum ether/diethyl ether 8:1 v/v) gave 11-bromo-1-(2-tetrahydropyranoyl) undecane as a colourless powder in quantitative yield.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 4.54 (dd, 1H, –O–CH–O), 3.84–3.33 (m, 4H, –O–CH_2– tetrahydropyranoyl, –CH_2–O– chain), 3.38 (t, 2H, Br–CH_2–), 1.86–1.25 [m, 26H, Br–C–$(CH_2)_{10}$, –$(CH_2)_3$– tetrahydropyranoyl].

A 0.75 M solution of sodium methylsulphinyl methide (100 ml) in DMSO [25–27] was added dropwise to a solution of 11-bromo-1-(2-tetrahydropyranoyl) undecane (12.0 g, 35.7 mmol) in 40 ml dry diethyl ether under an argon atmosphere and the mixture was stirred overnight. After filtration, the precipitate was shed on 200 ml brine, the resulting solution was extracted four times with 200 ml diethyl ether, the combined ether phases were dried with sodium sulfate, and evaporated. The brownish crude 12-(2-tetrahydropyranoyl)dodecyl methyl sulfoxide was purified by flash chromatography on Al_2O_3 using diethyl ether/chloroform (4:1 v/v) as the starting eluant, gradually increasing the chloroform content to 6:1 v/v. Yield: 10.5 g colourless powder (88%).

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 4.53 (m, 1H, –O–CH–O–), 3.71–3.31 (m, 4H, –O–CH_2– THP, –CH_2–O– chain), 2.67–2.56 [m, 2H, –CH_2–(S = O)–], 2.52 [s, 3H, –(S = O)–CH_3], 1.74–1.23 [m, 26H, –$(CH_2)_{10}$–, –$(CH_2)_3$– THP].

12-(2-Tetrahydropyranoyl)dodecyl methyl sulfoxide (10.0 g, 30.1 mmol) was refluxed in methanol for 1 h with *p*-toluene sulfonic acid (1 g, 6 mmol). After removal of the solvent, the crude 12-hydroxydodecyl methyl sulfoxide was recrystallised from diethyl ether/CH_2Cl_2 (85:15 v/v). Yield: 7.4 g (quantitative) colourless powder.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 3.63 (t, $J = 6.5$ Hz, 2H, –O—CH_2–), 2.75–2.56 [m, 2H, –CH_2–(S = O)–], 2.56 [s, 3H, –(S = O)–CH_3], 1.78–1.27 [m, 20H, –$(CH_2)_{10}$–].

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 63.52 (–O–*C*H_2–), 55.25 [–*C*H_2–(S = O)–], 38.99 [–(S = O)–*C*H_2], 33.32 (–O–C–*C*H_2–), 30.08, 30.00, 29.99, 29.93, 29.82, 29.70, and 29.29 [–(*C*H_2)$_7$–], 26.27 (O–C–C–*C*H_2–), 23.08 [–*C*H_2–C–(S = O)–].

A solution of acrylic acid (1.84 g, 24.0 mmol) in 10 ml dry CH_2Cl_2 was dropped slowly into a mixture of 12-hydroxydodecyl methyl sulfoxide (2.00 g, 8.05 mmol), dicyclohexyl carbodiimide (DCC) (5.0 g, 24 mmol) and a small amount of *N*,*N*-dimethylaminopyridine (DMAP) in 50 ml dry CH_2Cl_2, cooled to 0 °C. After the addition, the mixture was stirred for 48 h at room temperature. The precipitated urea which was formed was filtered off, and the crude 12-acryloyloxydodecyl methyl sulfoxide was purified by flash chromatography (eluant: $CHCl_3$). Yield: quantitative, white powder.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 6.40 (dd, 1H, CH = C–COO– cis), 6.10 (dd, 1H, = CH–), 5.80 (dd, 1H, CH = C–COO– trans), 4.13 (t, 2H, –COO–CH_2–), 2.75–2.63 [m, 2H, –CH_2–(S = O)–], 2.6 [s, 3H, –(S = O)–CH_3], 1.79–1.19 [m, 20H, –$(CH_2)_{10}$–].

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 166.9 (–*C*OO–), 131.0 (*C*H_2 =), 129.2 (= *C*H–), 65.2 (–O–*C*H_2–), 55.3 [–*C*H_2–(S = O)–], 39.1 [–(S = O)–*C*H_3], 29.9, 29.8, 29.7, 29.6, 29.2, and 29.0 [–COO–C–*C*H_2–, –(*C*H_2)$_7$–], 26.3 (–COO–C–C–*C*H_2–), 23.0 [–*C*H_2–C–(S = O)–].

Elemental analysis ($C_{16}H_{30}O_3S$, $M_r = 302.47$): Calcd (%): C, 63.53; H, 10.00; S, 10.60. Found (%): C, 63.16; H, 10.10; S, 10.60.

Mass spectrum (EI 70 eV, *m*/*z*): 285.2 (100%, M–OH$^+$); (FAB, *m*/*z*): 303.1 [100%, $(M+H)^+$].

*2-Acryloyloxydodecyl methyl sulfoxide (**6**)*

Potassium thiolate (14.0 g, 162.8 mmol) and 1,2-epoxydodecane (20.0 g, 108.5 mmol) in 200 ml THF and 180 ml water were refluxed for 1 night. After filtration and evaporation of the solvent, the residue was diluted with 200 ml diethyl ether. The ether phase was extracted three times with 200 ml water, dried with sodium sulfate, and evaporated to give pure 2-hydroxydodecyl methyl sulfide. Yield: 25 g (quantitative).

^{1}H NMR (CD_3OD, 200 MHz, δ): 3.37 [m, 1H, –CH(O)–], 2.49 (dd, 2H, –CH_2–S–), 2.01 (s, 3H, –S–CH_3), 1.5–1.2 [m, 18H, –$(CH_2)_9$–], 0.80 (t, 3H, CH_3–).

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 69.22 [–*C*H(OH)–], 42.81 (–*C*H_2–S–), 36.78 [–*C*H_2–CH(OH)–], 32.46 (CH_3–C–*C*H_2–), 30.22, 30.15, and 29.89 [–(*C*H_2)$_5$–], 26.33 [–*C*H_2–C–CH(OH)–], 23.23 (CH_3–*C*H_2–), 16.07 (–S–*C*H_3), 14.65 (*C*H_3–).

The general procedure for synthesis and purification of acrylates described earlier was applied to of 2-hydroxydodecyl methyl sulfide (25.0 g, 108 mmol) and acryloyl chloride (12.7 g, 140 mmol) to give pure 2-acryloyloxydodecyl methyl sulfide. Yield 30.2 g (quantitative).

^{1}H NMR (CD_3OD, 200 MHz, δ): 6.39 (dd, 1H, CH = C–COO– cis), 6.1 (dd, 1H, = CH–), 5.81 (dd, 1H, CH = C-COO- trans), 5.05 [m, 1H, –CH(OOC)–], 2.66 (d, 2H, –CH_2–S–), 2.11 (s, 3H, –S–CH_3), 1.8–1.5 [m, 2H, –CH_2–C–C(OOC)–] 1.5–1.1 [m, 18H, –$(CH_2)_9$–], 0.82 (t, 3H, CH_3–).

The general procedure of oxidation as described previously with $NaIO_4$ (16.5 g, 77.1 mmol) was applied to 2-acryloyloxydodecyl methyl sulfide (20.0 g, 69.8 mmol) in 200 ml 2-propanol. After removal of the solvant, 2-acryloyloxydodecyl methyl sulfoxide was purified by flash chromatography (eluant: ethyl acetate). Yield: 18.1 g (86%).

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.43 (dd, 1H, CH = C–COO– cis), 6.10 (dd, 1H, = CH–), 5.92–5.83 (dd, 1H, HC = C–COO– trans), 5.34 (43%) and 5.19 (57%) [m, 1H, –CH(OOC)–, two diastereomers], 3.18 (43%) and 3.13 (57%) [d, –CH_2–(S = O)–, two diastereomers], 2.67 (57%) and 2.63 (43%) [s, –(S = O)–CH_3, two diastereomers], 1.9–1.6 [m, 2H, –CH_2–C–C(OOC)–], 1.45–1.10 [m, 16H, –CH_2)$_8$–], 0.87 (t, 3H, CH_3–).

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 165.74 and 165.54 (–*C*OO–), 131.95 and 131.75 (*C*H_2 =), 128.45 and 128.35 (= *C*H–), 69.60 and 69.18 (–*C*H–O–), 60.19 and 59.47 [–*C*H_2–(SO)–], 39.91 and 39.49 [–(S = O)–*C*H_3], 34.62 and 34.37 (–*C*H_2–C–CO–), 32.18 (CH_3–C–*C*H_2–), 29.84, 29.78, 29.70, 29.59, and 29.50 [–(*C*H_2)$_5$–], 25.45 and 25.22 (–*C*H_2–C–CO–), 22.96 [CH_3–(*C*H_2)–], 14.42 (*C*H_3–).

Elemental analysis ($C_{16}H_{30}O_3S$, $M_r = 302.47$): Calcd (%): C, 63.54; H, 10.00; S, 10.60. Found (%): C, 63.29; H, 10.17; S, 10.89.

Mass spectrum (EI 70 eV, *m*/*z*): 285.2 (100%, M–OH$^+$), 302.2 (12%, M^+); (FAB, *m*/*z*): 303.1 [100%, $(M+H)^+$].

*N-n-Dodecanoyl-S-oxo-thiomorpholine (**7**)*

n-Decanoylchloride (5.50 g, 29.1 mmol) was cautiously added to a mixture of thiomorpholine (3.00 g, 29.1 mmol) and dry pyridine (3.0 g, 38 mmol) while cooling with ice, and the mixture was reacted for 3 h. Then, 10 ml 2 M HCl was added slowly. The aqueous phase was extracted twice with diethyl ether, dried over Na_2SO_4, and evaporated. The residue containing some decanoic acid was dissolved in 25 ml dry ethanol containing 0.28 g (53 mmol) NaOH. After evaporation, the residue was extracted with dry diethyl ether, yielding 5.51 g (74%) *N*-*n*-dodecanoylthiomorpholine as slightly orange, waxy crystals. m.p.: 29–30 °C.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 3.90–3.65 (m; 4H, –CON–CH_2– trans and cis r), 2.60–2.50 (m; 4H, –CH_2–S– trans and cis), 2.25 (t; 2H, –CH_2–CON<), 1.59 (m; 2H, CH_2–C–CON<), 1.40–1.15 [m; 12H, –$(CH_2)_6$–], 0.83 (t; 3H, CH_3–).

^{13}C NMR (50 MHz, $CDCl_3$, δ): 171.0 (>C=O), 48.2, 44.0 (–CON–CH_2– trans and cis), 33.4 (–CH_2–CON<), 31.7 (CH_3–CH_2–CH_2–), 29.3 and 29.1 [–$(CH_2)_4$], 27.8 and 27.3 (CH_2–S– trans and cis), 25.2 (CH_3–CH_2–), 22.5 (–CH_2–C–CON<), 14.0 (CH_3–).

A solution of magnesium monoperoxyphthalate (1.28 g, 2.59 mmol) in 10 ml methanol was slowly added to –*n*-dodecanoylthiomorpholine (1.00 g, 3.89 mmol) dissolved in 10 ml methanol. After 24 h of stirring at 30 °C, the organic phase was separated from the white precipitate and evaporated to dryness. The raw product was purified by flash chromatography on silica gel (eluant: ethyl acetate) to yield 0.65 g (61%) *N*-*n*-dodecanoyl-*S*-oxo-thiomorpholine as a colourless powder. m.p.: 97–98 °C.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.55–4.40, 4.21–4.10, and 3.80–3.60 (m; 1H + 1H + 2H, –CON–CH_2– trans and cis, axial and equatorial positions), 2.90–2.50 [m; 4H, –CH_2–S(=O)– trans and cis, axial and equatorial positions], 2.33 (m; 2H, –CH_2–CON<), 1.60 (m; 2H, –CH_2–C–CON<), 1.40–1.15 [m; 12H, –$(CH_2)_6$–], 0.83 (t; 3H, CH_3–).

^{13}C NMR (50 MHz, $CDCl_3$ δ): 171.0 (>C=O), 45.8 and 45.6 [–CH_2–S(=O)– cis and trans], 36.8 and 32.7 (–CON–CH_2– cis and trans), 33.1 (–CH_2–CON<), 31.8 (CH_3–CH_2–CH_2–), 29.3 and 29.2 [–$(CH_2)_4$], 25.1 (CH_3–CH_2–), 22.6 (–CH_2–C–CON<), 14.0 (CH_3–).

Elemental analysis ($C_{14}H_{27}O_2S$, $M_r = 273.43$): Calcd (%): C, 61.44; H, 9.95; N, 5.12; S, 11.72. Found (%): C, 63.10; H, 9.37; N, 5.01; S, 11.09.

N-10-Undecenoyl-S-oxo-thiomorpholine (**8**)

As described previously, 10-undecenoylchloride (5.89 g, 29.1 mmol) was reacted with thiomorpholine (3.00 g, 29.1 mmol) in the presence of dry pyridine (3.0 g, 38 mmol). The crude *N*-10-undecenoylthiomorpholine was filtered over silica gel (eluant: diethyl ether). Yield: 6.84 g (87%) brownish liquid, $n^{18} = 1.5109$.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 5.80–5.55 (m; 1H, =CH–), 4.90–4.75 (m; 2H, CH_2=C–), 3.80–3.58 (m; 4H, –CON–CH_2– trans and cis), 2.60–2.40 (m; 4H, –CH_2–S– trans and cis), 2.15 (t; 2H, –CH_2–CON<), 1.95 (m; 2H, =C–CH_2–), 1.50 (m; 2H, –CH_2–C–CON<), 1.40–1.15 [m; 10H, –$(CH_2)_5$–].

^{13}C NMR (50 MHz, $CDCl_3$, δ): 171.0 (>C=O), 139.0 (=CH–C–), 114.0 (CH_2=), 48.0 and 43.8 (–CON–CH_2– trans and cis), 33.5 (=C–CH_2–, –CH_2–CON<), 28.9 and 28.6 [–$(CH_2)_5$–], 27.6 and 27.1 (–CH_2–S– trans and cis), 24.9 (–CH_2–C–CON<).

As described earlier, *N*-10-undecenoylthiomorpholine (2.00 g, 7.42 mmol) was oxidised by of magnesium monoperoxyphthalate (2.44 g, 4.10 mmol). The crude *N*-10-undecenoyl-*S*-oxo-thiomorpholine was recrystallised from diethyl ether. Yield: 0.70 g (33%) colourless powder. m.p.: 86 °C.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 5.75 (m; 1H, =CH–), 4.80–4.00 (m; 2H, CH_2=C–), 4.52–4.37, 4.15–4.10, and 3.80–3.60 (m; 1H + 1H + 2H, –CON–CH_2– trans and cis, axial and equatorial positions), 2.85–2.52 [m; 4H, –CH_2–S(=O)– trans and cis, axial and equatorial positions], 2.30 (m; 2H, –CH_2–CON<), 1.98 (m; 2H, =C–CH_2–), 1.60 (m; 2H, –CH_2–C–CON<), 1.15–1.40 [m; 10H, –$(CH_2)_5$–].

^{13}C NMR (50 MHz, $CDCl_3$, δ): 171.0 (>C=O), 139.0 (=CH–C–), 114.0 (CH_2=), 45.8 and 45.7 [–CH_2—S(=O)– cis and trans], 36.8 and 32.7 (–CON–CH_2– cis and trans), 33.7 and 33.1 (=C–CH_2–, –CH_2–CON<), 29.3 and 28.8 [–$(CH_2)_5$–], 25.1 (–CH_2–C–CON<).

Elemental analysis ($C_{15}H_{27}O_2S$, $M_r = 285.43$): Calcd (%): C, 63.11; H, 9.93; N, 4.90; S, 11.23. Found (%): C, 62.76; H, 9.71; N, 4.78; S, 11.20.

MS (FAB): $m/z = 305.2$ ($M + Na^+$).

N-8-Acryloyloxyoctanoyl-S-oxo-thiomorpholine (**9**)

N-8-bromooctanoyl thiomorpholine was prepared in analogy to its undecanoyl homologue (described later) from of 8-bromooctanoic acid (5.00 g, 22.4 mmol), of thiomorpholine(2.54 g, 24.6 mmol), and DCC (5.55 g, 26.9 mmol). Purification by flash chromatography (eluant: diethyl ether/petroleum ether 3/2 v/v). Yield: 6.42 g (93%) colourless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 3.83 [m, 2H, –CON$(CH_2)_2$ cis], 3.69 [m, 2H, –CON$(CH_2)_2$ trans], 3.38 [t, 2H, Br–CH_2–)], 2.65–2.50 [m, 4H, –$(CH_2)_2$S], 2.28 (t, 2H, –CH_2–CON<), 1.9–1.7 (m, 2H, Br–C–CH_2–), 1.7–1.5 (m, 2H, –CH_2–C–CON<), 1.5–1.2 [m, 6H, –$(CH_2)_3$–].

N-8-acryloylooxyctanoyl thiomorpholine was made in analogy to its undecanoyl homologue from of *N*-8-bromooctanoyl thiomorpholine (6.43 g, 20.8 mmol) and of cesium acrylate (6.88 g, 33.6 mmol). Yield: 6.12 g (98%) colourless liquid.

^{1}H NMR ($CDCl_3$, 200 MHz, δ): 6.41 (dd, 1H, CH=C–COO–cis), 6.12 (dd, 1H, =CH–), 5.82 (dd, 1H, HC=C–COO– trans), 4.15 (t, 3H, –COO-CH_2–), 3.85 (m, 2H [–CON$(CH_2)_2$– cis–], 3.74 [m, 2H, –CON$(CH_2)_2$– trans], 2.64–2.50 [m, 4H, (–$CH_2)_2$S], 2.31 (t, 2H, –CH_2–CON<), 1.70–1.50 (m, 4H, –COO–C–CH_2–, –CH_2–C–CON<), 1.5–1.2 [m, 6H, –$(CH_2)_3$–].

^{13}C NMR ($CDCl_3$, 50 MHz, δ): 171.77 (–CON<), 166.53 (–COO–), 130.75 (CH_2=), 128.97 (=CH–), 64.84 (–COO–CH_2–), 48.58 and 44.47 [–CON$(CH_2)_2$ trans and cis], 33.60 (–CH_2–CON<), 29.57 29.32, 28.84, 28.22, 27.68, 26.07, and 25.43 [–CH_2–S–CH_2– and –$(CH_2)_5$–].

N-8-acryloyloxyoctanoyl thiomorpholine (3.70 g, 12.3 mmol) was oxidised by $NaIO_4$ (2.64 g, 12.3 mmol) to give *N*-8-acryloyloctanoyl-*S*-oxo-thiomorpholine, as described for **3**. Purification by flash chromatography (eluants: diethyl ether followed by chloroform/2-propanol 9:1 v/v). Yield 3.51 g (90%) colourless liquid.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.40 (dd, 1H, CH=C–COO–cis), 6.12 (dd, 1H, =CH–), 5.82 (dd, 1H, CH=C–COO– trans), 4.47, 4.2–3.95, 3.85–3.6 [m, 1H + 3H + 2H, –COO–CH_2–, –CON$(CH_2)_2$– cis and trans, axial and equatorial positions], 2.85–2.50 [m, 4H, (–$CH_2)_2$SO cis and trans, axial and equatorial positions], 2.31 (m, 2H, –CH_2–CON<), 1.70–1.45 (m, 4H, –COO–C–CH_2–, –CH_2–C–CON<), 1.50–1.20 [m, 6H, –$(CH_2)_3$–].

^{13}C NMR ($CDCl_3$, 75 MHz, δ): 171.89 (–CON<), 166.60 [–(COO)–], 130.90 (CH_2=), 128.92 (=CH–), 64.86 (–COO–CH_2–), 46.11 and 45.88 [–CH_2–(SO)–CH_2–], 37.15 [(–CON–CH_2)– cis], 33.34 (–CH_2–CON<), 33.08 (–CON–CH_2– trans), 29.56 (–COO–C–CH_2–), 29.33 (–COO–C–C–C–CH_2–), 28.85 (–CH_2–C–C–C–CON<), 26.09 (–COO–C–C–CH_2–), 25.34 (–CH_2–C–CON<).

Elemental analysis ($C_{15}H_{25}NO_4S$, $M_r = 315.43$): Calcd (%): C, 57.12; H, 7.99, N, 4.44; S, 10.16. Found (%): C, 56.79; H, 7.98; N, 4.39; S, 10.25.

Mass spectrum (EI 70 eV, *m*/*z*): 119 (100%), 315.2 (20%, M^+); (FAB, *m*/*z*): 316.0 [100%, $(M+H)^+$].

N-11-Acryloyloxyundecanoyl-S-oxo-thiomorpholine (**10**)

11-Bromo undecanoic acid (10.0 g, 37.7 mmol) and a catalytic amount of DMAP in 30 ml dry CH_2Cl_2 were added to a 0 °C solution of thiomorpholine (3.89 g, 37.7 mmol) and DCC (8.56 g, 41.5 mmol) in 40 ml dry CH_2Cl_2. After stirring the mixture for 1 day at room temperature, the precipitated urea was filtered off, the filtrate was concentrated, and filtered once again. After evaporation, the crude *N*-11-bromoundecanoyl thiomorpholine was purified by flash chromatography (eluant: ethyl acetate). Yield: 13.0 g (98%) colourless powder.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 3.87 (t, 2H, –CON–CH_2– cis), 3.72 (t, 2H, –CON–CH_2– trans), 3.41 (t, 2H, Br–CH_2–), 2.7–2.5 [m, 4H, –$(CH_2)_2$S], 2.29 (t, 2H, –CH_2–CON<), 1.80–1.15 [m, 16H, –$(CH_2)_8$–C–CON<].

^{13}C NMR (CDCl$_2$, 75 MHz, δ): 172.23 (–*C*ON<), 48.71 and 44.58 [–CON(*C*H$_2$)$_2$– trans and cis], 34.54 (Br–*C*H$_2$–), 33.87 (–*C*H$_2$–CON<), 33.21 (Br–C–*C*H$_2$–), 29.83, 29.77, 29.74, 29.72, 29.12, and 28.53 [–(*C*H$_2$)$_6$–], 28.35 and 27.82 (–*C*H$_2$–S–*C*H$_2$– trans and cis), 25.66 (–*C*H$_2$–C–CON<).

N-11-bromoundecanoyl thiomorpholine (3.50 g, 10 mmol) and cesium acrylate (2.40 g, 11.8 mmol) in 50 ml dry DMF were stirred overnight at room temperature. After filtration and dilution by 100 ml CHCl$_3$, the solution was extracted eight times with 100 ml water, dried with sodium sulfate, and the solvent evaporated to give pure *N*-11-acryloylundecanoyl thiomorpholine. Yield: 3.4 g (quantitative) colourless viscous liquid.

^{1}H NMR (CDCl$_3$, 200 MHz, δ): 6.38 (dd, 1H, HC=C–COO– cis), 6.09 (dd, 1H, =CH–), 5.79 (dd, 1H, CH=C–COO– trans), 4.12 (t, 3H, –COO–CH$_2$–), 3.85 (m, 2H (–CON–CH$_2$– cis), 3.72 (m, 2H, –CON–CH$_2$– trans), 2.65–2.53 [m, 4H, (–CH$_2$)$_2$S], 2.28 (t, 2H, –CH$_2$–CON<), 1.8–1.5 (m, 4H, –COO–C–CH$_2$–, –CH$_2$–C–CON–), 1.5–1.2 [m, 12H, –(CH$_2$)$_6$–].

^{13}C NMR (CDCl$_3$, 50 MHz, δ): 171.99 (–*C*ON<), 166.63 [(–*C*OO)–], 130.68 (*C*H$_2$=), 129.14 (=*C*H–), 65.06 (–COO–*C*H$_2$–), 48.75 and 44.63 (–CON–*C*H$_2$– trans and cis), 33.85 (–*C*H$_2$–CON<), 29.84, 29.79, and 29.05 [–COO–C–*C*H$_2$–, –(*C*H$_2$)$_5$–], 28.39 and 27.85 (–*C*H$_2$–S–*C*H$_2$–), 26.33 (–COO–C-C–*C*H$_2$–), 25.73 (–*C*H$_2$–C–CON<).

N-11-acryloyloxyundecanoyl thiomorpholine (2.0 g, 5.8 mmol), magnesium monoperphthalate hexahydrate (1.6 g, 3.2 mmol), and a small amount of hydroquinone in 50 ml of 2-propanol were stirred for 1 day, the temperature being allowed to rise gradually from 0 °C to ambient temperature. After filtration and evaporation of the solvent, the crude *N*-11-acryloyloxyundecanoyl-*S*-oxo-thiomorpholine was purified by flash chromatography (eluant: ethyl acetate/ethanol 9:1 v/v). Yield: quantitative, colourless powder.

^{1}H NMR (CDCl$_3$, 300 MHz, δ): 6.40 (dd, 1H, CH=C–COO– cis), 6.12 (dd, 1H, C=CH–), 5.82 (dd 1H, CH=C–COO– trans), 4.49, 4.20–4.05, and 3.85–3.70 [m, 1H + 3H + 2H, –COO–CH$_2$– and –CON(CH$_2$)$_2$– cis and trans, axial and equatorial positions], 2.90–2.80, 2.75–2.60 [m, 2H + 2H, –CH$_2$–(S=O)–CH$_2$– cis and trans, axial and equatorial positions], 2.45–2.25 (m, 2H, –CH$_2$–CON<), 1.75–1.55 (m, 4H, –COO–C–CH$_2$—, –CH$_2$–C–CON<), 1.4–1.2 [m, 12H, –(CH$_2$)$_6$–].

^{13}C NMR (CDCl$_3$, 75 MHz, δ): 172.50 [–(*C*ON)–], 167.15 [–(*C*OO)–], 131.20 (*C*H$_2$=), 129.32 (=*C*H–), 65.29 (–COO–*C*H$_2$–), 46.40 and 46.16 [–*C*H$_2$–(S=O)–*C*H$_2$–], 37.37 and 33.28 [–CON(*C*H$_2$–)$_2$ trans and cis], 33.69 (–*C*H$_2$–CON<), 29.96, 29.40, and 29.07 [–COO–C–*C*H$_2$–, –(*C*H$_2$)$_5$–], 26.42 (–COO–C–C–*C*H$_2$–), 25.69 (–*C*H$_2$–C–CON<).

Elemental analysis (C$_{18}$H$_{31}$NO$_4$S, $M_r = 357.51$): Calcd (%): C, 60.47; H, 8.74; N, 3.92; S, 8.97. Found (%): C, 60.54; H, 8.87; N, 3.81; S, 8.99.

Mass spectrum (EI 70 eV, *m*/*z*): 119 (100%), 357.2 (24%, M^+); (FAB, *m*/*z*): 358.1 [100%, $(M+H)^+$].

*2-(10′-Undecen-1′-yl-sulfinyl) ethanol (**11**)*

Tosyl chloride (23.5 g, 123 mmol) was cautiously added to 11-hydroxyundecene (15.0 g, 88.1 mmol) in 200 ml dry pyridine, and the mixture was stirred at room temperature until no more alcohol was detected by TLC (approximately 2 h). The reaction mixture was shed on 400 g crushed ice and extracted with 400 ml diethyl ether. The ether phase was extracted four times with 200 ml water and twice with 200 ml 0.5 M aqueous NaHCO$_3$. After drying with sodium sulfate, the solvent was removed to give pure 11-tosylundecene. Yield: 28.5 g (quantitative).

^{1}H NMR (CDCl$_3$, 200 MHz, δ): 7.78 and 7.33 (d + d 2H + 2H, CH aryl), 5.80 (m, 1H, =CH–), 5.06–4.85 (m, 2H, CH$_2$=), 4.00 (t, 2H, –CH$_2$–O–tosyl), 2.44 (s, 3H, aryl–CH$_3$), 2.02 (m, 2H, –CH$_2$–C=), 1.7–1.5 (m, 2H, –CH$_2$–C–O–tosyl), 1.5–1.1 [m, 12H, –(CH$_2$)$_6$–].

Mercaptoethanol (2.60 g, 33.3 mmol) and (1.9 g, 33.8 mmol) KOH were stirred in 50 ml methanol for 2 h. After removal of the solvent, the thiolate salt formed was added to 11-tosylundecene (9.00 g, 27.7 mmol) in 50 ml THF and 20 ml water. The mixture was refluxed for 5 h, cooled to room temperature, and shed on 200 ml diethyl ether. The ether phase was extracted four times with 200 ml 0.5 M aqueous NaOH, dried with sodium sulfate, and the solvent evaporated to give pure 10-undecenyl 2-hydroxyethyl sulfide. Yield: 6.23 g (quantitative) white powder.

^{1}H NMR (CDCl$_3$, 200 MHz, δ): 5.78 (m, 1H, =CH–), 5.07–4.85 (m, 2H, CH$_2$=), 3.70 (t, 2H, –CH$_2$–O–), 2.72 (t, 2H, –S–CH$_2$–C–O), 2.5 (t, 2H, –CH$_2$–S-), 2.05 (m, 2H, =C–CH$_2$–), 1.61 (m, 2H, –S–C–CH$_2$–), 1.5–1.1 (m, 12H, –(CH$_2$)$_6$–).

^{13}C NMR (CDCl$_3$, 50 MHz, δ): 139.5 (=*C*H–), 114.6 (*C*H$_2$=), 61.05 (–*C*H$_2$–O), 35.60 (–S–*C*H$_2$–C–O), 34.21 (=C–*C*H$_2$–), 32.35 (–*C*H$_2$–S–), 30.26, 29.90, 29.86, 29.66, 29.53, 29.37, and 29.29 [–(*C*H$_2$)$_7$–].

10-Undecenyl 2-hydroxyethyl sulfide 5.00 g, 21.7 mmol) in 50 ml 2-propanol was oxidised by NaIO$_4$ as described for **3**. After removal of the solvent, 2-(10′-undecen-1′-yl-sulfinyl) ethanol was purified by flash chromatography (eluant: ethyl acetate/ethanol 9:1 v/v). Yield: 4.84 g (90.5%) white powder.

^{1}H NMR (CDCl$_3$, 200 MHz, δ): 5.78 (m, 1H, =CH–, 5.01 (m, 2H, CH$_2$=), 3.7 (t, 2H, –CH$_2$–O–), 2.72 [t, 2H, –(S=O)–CH$_2$–C–O], 2.5 [t, 2H, –CH$_2$–(S=O)–], 2.15–1.90 (m, 2H, =C–CH$_2$–), 1.85–1.65 [m, 2H, –(S=O)–C–CH$_2$–], 1.60–1.1 [m, 16H, –(CH$_2$)$_8$–].

^{13}C NMR (CDCl$_3$, 50 MHz, δ): 139.52 (=*C*H–), 114.66 (*C*H$_2$=), 56.24, 54.83 and 53.17 [–*C*H$_2$–O–, –(S=O)–*C*H$_2$–C–O, –*C*H$_2$–(S=O)–], 34.21 (=C–*C*H$_2$–), 29.80, 29.75, 29.63, 29.50, 29.35, 29.27, and 29.14 [–(*C*H$_2$)$_7$–].

Elemental analysis (C$_{13}$H$_{26}$O$_2$S, $M_r = 246.41$): Calcd (%): C, 63.37; H, 10.64; S, 13.01. Found (%): C, 62.51; H, 10.62; S, 13.28.

Mass spectrum (EI 70 eV, *m*/*z*): 229.2 (100%, M–OH$^+$), 246.1 (2%, M^+); (FAB, *m*/*z*): 247.1 [100%, $(M+H)^+$].

Results and discussion

Synthesis of the amphiphiles

Typically, the sulfoxides studied (Fig. 1) were prepared in a three-to-four-step synthesis, employing simple

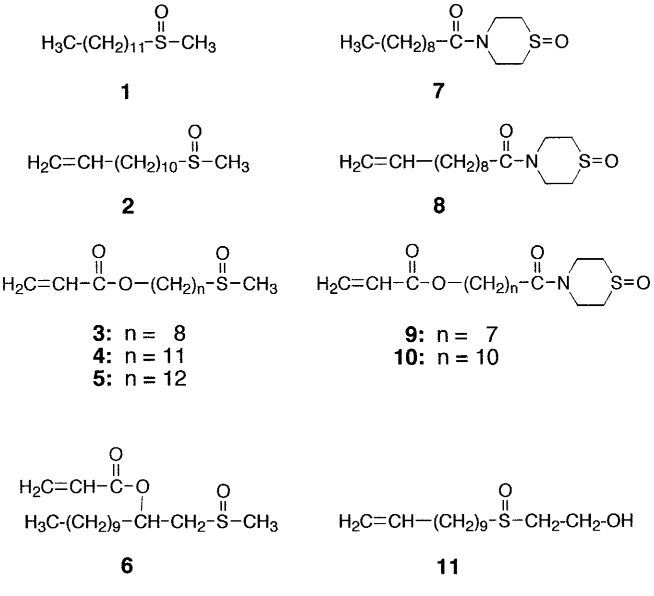
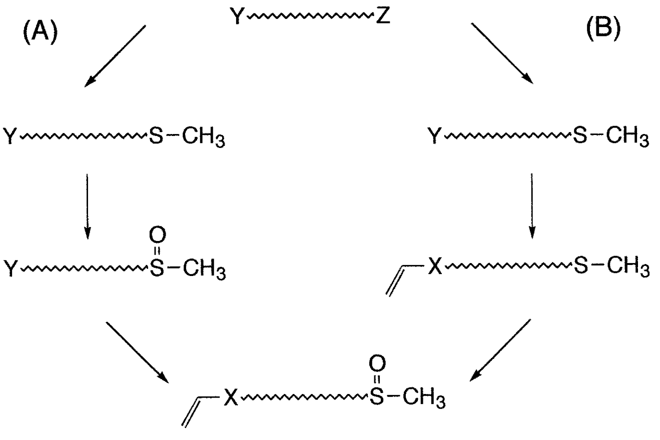


Fig. 1 Sulfoxide surfactants synthesised and studied

starting compounds of high purity. Surfactants **1** and **7** served as references. The acrylates **3**–**6**, **9**, and **10** are easily subjected to free-radical polymerisation. Surfactant monomers with terminal olefin groups, such as **2**, **8**, and **11**, can be employed in copolymerisations, for example, with SO_2 [28]. Two general strategies were applied to synthesise such polymerisable surfactants with sulfoxide groups, incorporating either the sulfoxide moiety before fixing the polymerisable group, or vice versa (Scheme 1). The first strategy facilitates handling and storage of the intermediates, as the sensitive polymerisable group is only incorporated in the last step of the synthesis. In addition, this strategy can reduce the number of necessary reaction steps, by avoiding the oxidation step when employing DMSO as the starting compound. Still, the second strategy proved to be more practical – at least for the synthesis of model compounds, because it enabled us to obtain the surfactants in the very pure grades needed to perform reliable surface tension studies. In contrast, the first path generally resulted in small amounts of side products which were difficult to separate. In particular, the separation of ω-acryloyloxyalkyl methyl sulfoxides from the corresponding ω-hydroxyalkyl methyl sulfoxides, or from the ω-bromoalkyl methyl sulfoxides, respectively, proved to be extremely difficult. All attempts, however, to drive the conversion of the intermediates to completion by using a large excess of reagent, and/or by raising the reaction temperature, induced side reactions on the sulfoxide group. In fact, sulfoxides are known to be sensitive to alkylating as well as acylating agents [29].



Scheme 1 Synthetic strategies to polymerisable sulfoxide surfactants

Also, we explored various methods to oxidise the sulfide to the sulfoxide group. Again, the possibility to purify the compounds satisfactorily turned out to be the decisive factor, and not the highest possible yields. Magnesium monoperoxyphthalate as an oxidising agent was rather efficient for the selective oxidation; however, occasionally, this method resulted in spontaneous polymerisation during the reaction and the workup, which may be related to a slow decomposition of the peroxide. The recently described oxidation by $Bi(NO_3)_3$/$BiBr_3$ [30] gave high yields, in particular when bubbling air through the reaction mixture, but unfortunately led to some tenacious by-products. For our purpose, particularly good results were obtained when using sodium metaperiodate in methanol.

The molecular characterisation by NMR spectroscopy revealed some pecularities for the thiomorpholine derivatives **7**–**10** which produce rather complex ^1H NMR spectra (Fig. 2). Owing to the slow rotation around the CO–N bond of the amide group, each $-CH_2-$ group of the ring gives rise to a separate signal. Analogously, the ^{13}C NMR spectra show a separate signal for each carbon

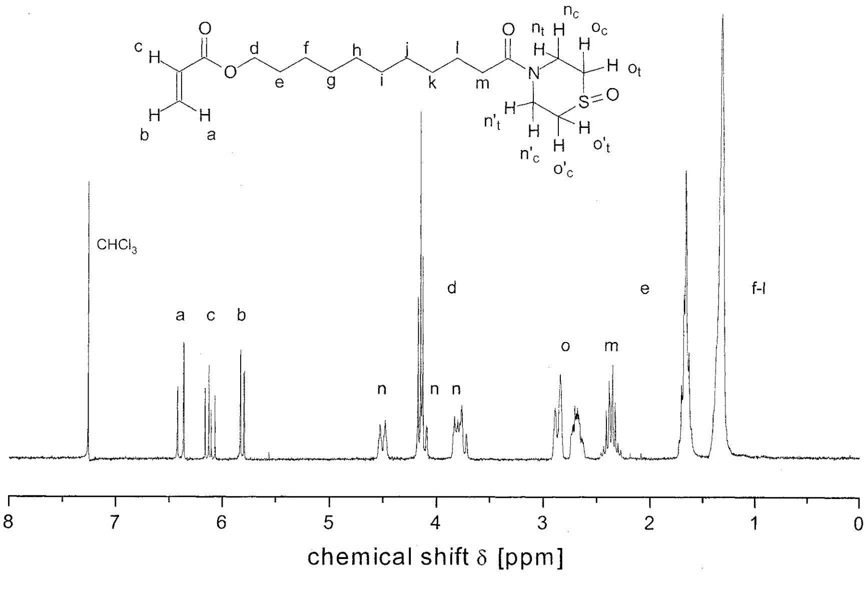


Fig. 2 ^1H NMR of monomer **10** in $CDCl_3$

atom of the heterocycle. Furthermore, after oxidation of the sulfide to the sulfoxide group, the two protons of the heterocyclic –CH_2– groups are no longer equivalent, but are in cis and trans positions, respectively, versus the S = O bond. In consequence, each of the eight protons of the heterocyle produces an individual signal. Whilst this behaviour is easily understood, the complex multiplet at 2.35 ppm shown by the aliphatic –CH_2- group next to the carbonyl moiety, after oxidation of the sulfide to the sulfoxide group, came to a surprise. We hypothesise that the strong dipole moments of the C = O and the S = O bonds favour a boat conformation of the ring, thus creating slightly different environments for these two protons.

Monomer **6** has two stereocentres, namely the carbon of the secondary ester group and the sulfur of the sulfoxide moiety. In fact, the complex NMR spectra obtained for **6** (Fig. 3) reflect the presence of a mixture of two diastereomer pairs. According to the integration of the signals in the ^1H spectra, the ratio between the two diastereomers is 57:43, indicating a slight preference for the formation of one of the stereoisomers. So far, we have not been able to attribute the corresponding threo/erythro configurations to the signals. The effect of such mixtures of diastereomers on the surfactants properties, compared to the behaviour of the clean racemates, is hardly known up to now; at least, diastereomeric mixtures tend to reduce the Krafft temperature markedly.

Surfactant behaviour

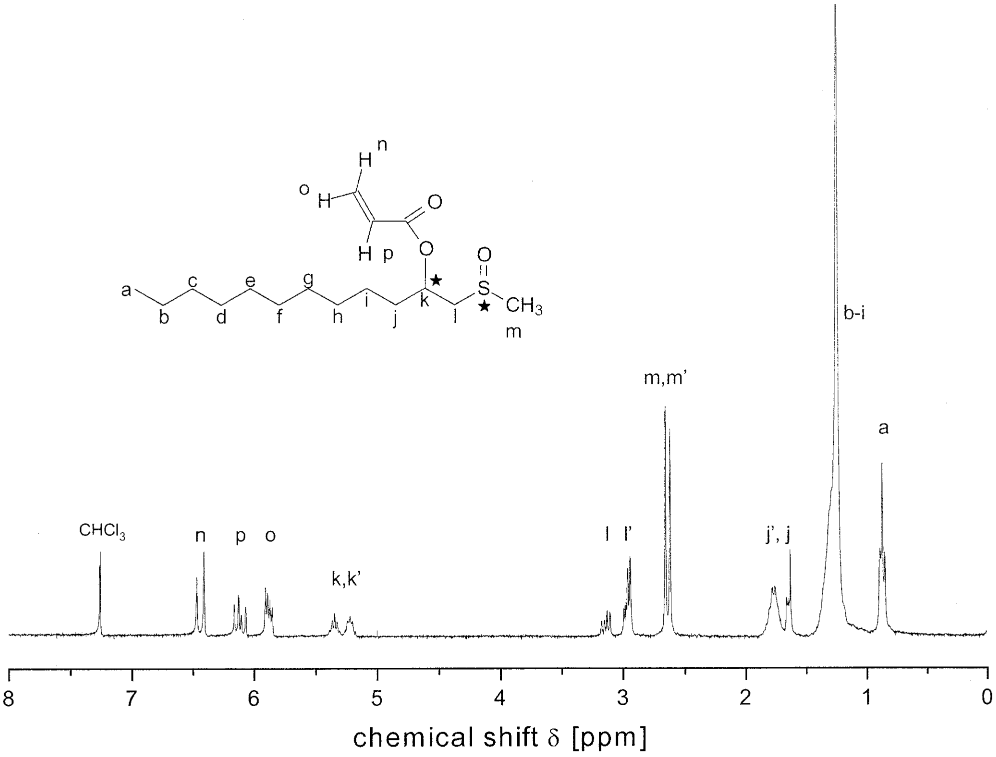
The sulfoxides **1**–**10** have only limited solubilities in water at ambient temperature. In some cases heating leads to a marked improvement in the solubility. This makes a marked difference to nonionic surfactants of the oligo(ethylene oxide) type. The compounds are surface-active, and the aqueous solutions obtained foam.

Crystals of sulfoxides **1**, **2**, **4**–**8**, and **10** placed between two microscope slides and brought into contact with water give rise to liquid-crystalline phases. The oily-streak textures observed between crossed polarisers suggest the formation of lamellar mesophases [31, 32]. For sulfoxides **3** and **9**, no lyotropic liquid-crystalline birefringent phases were found at ambient temperature.

The semilogarithmic plots of the surface tension versus surfactant concentration of the various amphiphilic sulfoxides are shown in Figs. 4 and 5. The discontinuities found in some of the resulting curves, from where on the surface tension stays virtually constant, were taken as the critical micellar concentration (cmc). These values, together with the surface tension at the cmc, are listed in Table 1. We noted that all the compounds gave notably turbid solutions when passing over the cmc, suggesting the presence of large, nonspherical micelles.

cmcs were found for compounds **1**, **2**, **6**, and **8**. The reference compound **1** has a cmc of about 1.3×10^{-4} mol/l, in good agreement with the literature

Fig. 3 ^1H NMR of monomer **6** in $CDCl_3$



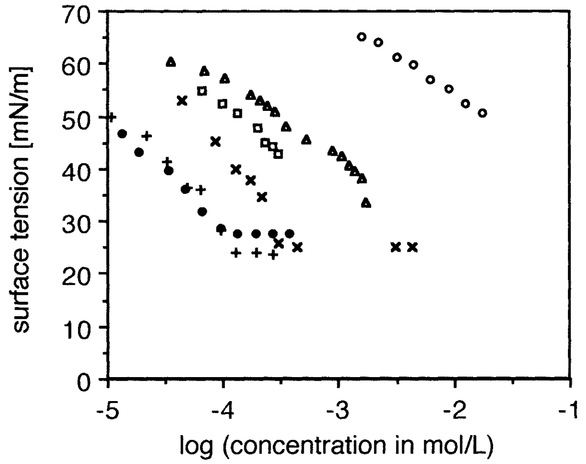


Fig. 4 Surface tension versus surfactant concentration of aqueous solutions of amphiphilic sulfoxides: **1** (+), **2** (×), **3** (○), **4** (△), **5** (□), **6** (●)

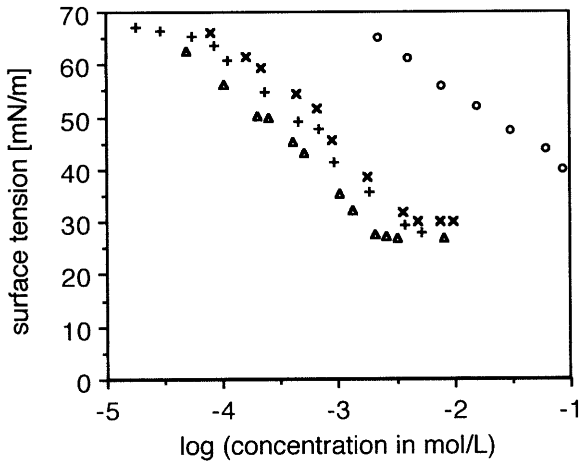


Fig. 5 Surface tension versus surfactant concentration of aqueous solutions of amphiphilic sulfoxides: **7** (+), **8** (×), **9** (○), **11** (△)

Table 1 Surfactant properties of sulfoxides **1**–**11** at 21 ± 1 °C in aqueous solution

Monomer	Solubility limit (g/l)	cmc (g/l)	cmc (mmol/l)	Surface tension at the cmc (mN/m)
1		0.025	0.13	24
2		0.081	0.35	25
3	> 5			50[a]
4	0.6			34[a]
5		0.1	43[a]	
6		0.032	0.11	28
7	1.4			28
8		1.1	3.8	30
9	> 30			40[b]
10	0.9			62[a]
11		0.50	2.1	27

[a] Surface tension at the limit of solubility

[b] Surface tension at 30g/l

[33]. Surfactant **1** induces a remarkably strong decrease in the surface tension down to about 24 mN/m. Compared to oligo(ethylene oxide) surfactants, the cmc of **1** compares well with that of 0.86×10^{-4} mol/l for dodecylheptaethylene glycol [34], demonstrating the efficiency of the methyl sulfoxide moiety as a nonionic, small volume hydrophilic group. Still, as indicated by the miscibility gap at higher concentrations [21], the balance between the sulfoxide and the dodecyl groups seems to be at the limit for water solubility. Within this line of reasoning, the low surface tensions obtained at the cmc of **1** may reflect low hydration of the methyl sulfoxide moiety owing to the low hydrophilicity (compared to charged groups): in combination with the inherent small molecular volume of this head group, the alkyl chains can be densely packed, thus reducing the surface tension most efficiently.

The surface tension of methyl-11-dodecenyl sulfoxide (**2**) at the cmc is again remarkably low, about 25 mN/m. The cmc of 3.5×10^{-4} mol/l is higher than for the saturated analogue **1**, but is very close to the cmc value of methyl undecyl sulfoxide [22], as could be expected from the higher polarity of alkenes compared to alkanes. Polymerisable sulfoxide **6** displays a cmc very similar to reference surfactant **1**, except for a slightly higher surface tension of 28 mN/m at the cmc. The latter can be attributed to the laterally anchored polymerisable moiety which interferes with the very efficient packing of the alkyl chains.

The surfactant behaviour of the amphiphilic sulfoxides was substantially modified when placing the acryloyl group at the end of the alkyl chain. This is clearly illustrated for sulfoxide **5**, which is a positional isomer of monomer **6**. A notable decrease in the surface tension of the aqueous solutions was observed only at considerably higher concentrations than for **6** (Figure 4), and the hypothetical cmc is higher than the solubility limit of about 0.1 g/l. A similar difference is found when comparing reference **1** with monomer **4**. However in the past, very close cmc values have been reported for polymerisable surfactants bearing an 11-acryloyloxyundecyl hydrophobic chain and their *n*-dodecyl analogues (Fig. 6, Table 2) [35, 36, 37, 38, 39]. Analogously for homologue **3** with the 8-acryloyloxyoctyl chain, the surface tension curve is shifted to much higher concentrations (Fig. 5) compared to *n*-nonyl methyl sulfoxide [22], and no cmc was observed.

The unexpected surfactant behaviour of monomers **3**–**5** cannot be attributed to an unfavourable hydrophilic–hydrophobic balance as such, as monomer **6**, which is isomeric to **5**, behaves "normally"; however, the distribution of the individual molecular fragments within the molecules, namely of the hydrophilic sulfoxide moiety, of the hydrophobic alkyl chain, and of the acryloyl residue of intermediate polarity seems to play a major role. For a surfactant, the sequence of the

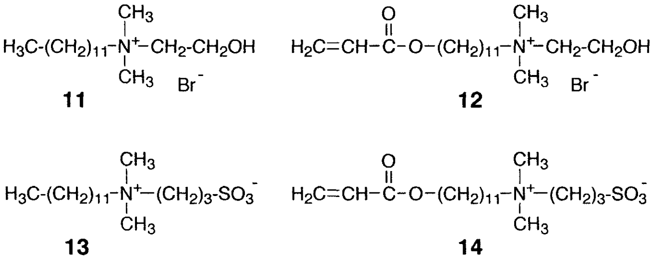


Fig. 6 Structure of polymerisable surfactants of the tail-end type bearing the acrylate moiety [35, 36], and their saturated analogues

Table 2 Surfactant behaviour of polymerisable surfactants bearing an 11-acryloyloxyundecyl hydrophobic chain and their *n*-dodecyl analogues, according to the literature [35–37]

Surfactant	Ref.	cmc (g/l)	cmc (mmol/l)	Surface tension at the cmc (mN/m)
11	[35]	4.9	15	38
12	[36]	2.4	5.9	40
13	[37]	1.1	3.2	36
14	[36]	1.5	3.8	41

functional fragments is most appropriate in isomer **6**, going from the most hydrophilic to the most hydrophobic one. This is not the case for its isomer **5**, nor for the homologues of the latter. Nevertheless, such reasoning should also apply in the case of monomers **12** and **14**, but these surfactants do not behave unusually with respect to cmc and surface activity [35–37].

We hypothesise that the unexpectedly poor surfactant performance of series **3**–**5** results from the combination of an unfavourable distribution of the individual hydrophilic, polar, and hydrophobic fragments within the molecules, together with a limited difference in the polarity of the sulfoxide group and the acrylic ester. This combination confers to the monomers a similarity to the so-called "bola surfactants", i.e., surfactants bearing a hydrophilic group at each end of the hydrophobic chain which are known for their low surface activity and high cmcs [1, 40, 41]. The two polar groups at the opposite ends of the alkyl chain are not of equal importance in polymerisable surfactants such as **4**, **12**, and **14**; however, the lower the relative hydrophilicity of the "primary" hydrophilic group, the more the behaviour ressembles that of bola surfactants. Consequently, the cmcs of monomers **4**, **12**, and **14** shift increasingly to higher values, relative to the ones of their simple alkyl analogues **1**, **11**, and **13** (Tables 1, 2).

In the context of the previous discussion, we explored whether we could increase the hydrophilicity of the nonionic head group somewhat while keeping its volume small. We therefore studied the effect of the addition of a $-CH_2OH$ fragment, thus replacing the methyl sulfoxide group by the 2-hydroxyethyl sulfoxide moiety, by the help of surfactant **11** (Fig. 5). Similar to the behaviour of the methyl sulfoxide analogue **2**, which exhibits a cmc very close to that of the saturated homologue with a hydrophobic chain reduced by one $-CH_2-$ fragment (see earlier), the cmc of **11** corresponds closely to that of decyl 2-hydroxyethyl sulfoxide [24]; however, this means that the additional $-CH_2OH$ fragment has a very small effect on the hydrophilicity only, if at all, an observation which corroborates previous reports on alkylsulphinyl alkanols [24].

We therefore added alternatively a tertiary amide group which is known to be rather hydrophilic [21, 42] to the sulfoxide moiety, thus obtaining surfactants **7**–**10**. Still, Figs. 4 and 5, and the data in Table 1 demonstrate, that the modified head groups do not confer a notably enhanced hydrophilicity to the surfactants in comparison to their methyl sulfoxide analogues. The solubilities of monomers **9** and **10** are nearly the same as for their analogues **3** and **4**. Also, Figs. 4 and 5 illustrate that the surface tension curves of compounds **3** and **9** are very close. However, the heterocycle seems to increase the Krafft temperature markedly, compared to the simple methyl sulfoxides, so surfactants **8**–**10** apparently do not provide an advantage over their structurally much simpler analogues **2**–**5**.

Conclusions

Compared to many other nonionic hydrophilic fragments, the sulfoxide group behaves as a strongly hydrophilic fragment of small volume, that can balance up to an acryloyloxyundecyl hydrophobic chain. Therefore, various types of true nonionic polymerisable surfactants ("surfmers") can be made, which are characterised by low cmcs and by strong reductions of the aqueous surface tension. In consequence, sulfoxide-based surfactant monomers are interesting alternatives to the hitherto mainly employed oligo(ethylene oxide) surfmers. Nevertheless, compared to ionic groups, the hydrophilicity is still limited. The low surface tensions typically found above the cmc are thus ascribed to a very dense packing of the alkyl chains in the soluble monolayer owing to the lower hydratation of the head group. Also, the incorporation of additional polar functional groups, such as an acrylate moiety, at the end of the hydrophobic chain, confers surfactant properties similar to those of bola amphiphiles to the monomers. The polymerisation of the sulfoxide surfmers and some characterisitics of the resulting amphiphilic polymers will be reported elsewhere.

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