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Oligoethyleneoxide spacer groups in polymerizable surfactants

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Oligoethyleneoxide spacer groups in polymerizable surfactants

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Abstract: Cationic and zwitterionic polymerizable surfactants bearing tri- and tetraethyleneglycol spacer groups between the polymerizable moiety and the surfactant structure were prepared and polymerized. Monomers and polymers were investigated with respect to their aggregation behavior in aqueous systems and compared to analogous monomers and polymers lacking spacer groups. In the case of the monomeric surfactants, the spacer groups depress both the Krafft-temperature and the critical micelle concentration. The area occupied per molecule at the air-water interface is substantially enlarged by the spacers, whereas the depression of surface tension is nearly constant. Although the monomers with and without spacers are true surfactants, all the polymers are water-insoluble, but form monomolecular layers at the air-water interface. In analogy to the monomer behavior, the incorporation of the spacer groups increases the area occupied per repeat unit at the air-water interface substantially, but hardly affects the surface activity.

Key words: Polymerizable surfactant; polysoap; sulfobetain; spacer; micelle; monolayer

Introduction

Recently, we have reported on the synthesis and aqueous aggregation behavior of fully zwitterionic, polymerizable surfactants and the polymers derived therefrom [1]. Such polymers represent an unconventional, but interesting type of polysoaps [2], as they may combine the behavior of ionic and non-ionic polysoaps advantageously.

However, the watersolubility of polymers obtained from reactive surfactants bearing a vinyl group is controlled by their molecular geometry [1, 3, 4]. If the surfactant structure is bound to the polymer backbone via the end of the hydrophobic tail (Fig. 1a), the polymers are generally water-soluble. However, the emulsifying properties seem to be restricted due to the "immobilization" of the hydrophobic chains by the backbone [1, 5]. If the surfactant structure is bound to the polymer backbone via the hydrophilic head group (Fig. 1b), the hydrophobic chains should be much more mobile [6, 7] and thus be capable of efficient solubilization. Yet such polymers are generally water-insoluble.

To overcome these problems and to combine the water-solubility and solubilization powers, we have investigated the effect of oligoethyleneglycol spacer groups incorporated between the polymerizable moiety and the surfactant structure. Flexible side-chain spacer groups have been known to improve substantially the self-organization behavior of functional polymers, such as polymeric liquid crystals [3, 4, 8]. In particular, oligoethyleneglycol spacer groups have been shown to improve the self-organization of amphiphilic polymers with lipid-like structure in monolayers, Langmuir–Blodgett multilayers, and vesicles [9, 10].

Experimental part

Materials

All solvents used were analytical grade. Acetonitril and triethylamine were dried over molecular sieves 3 Å. All other solvents are dried by neutral Al_2O_3 (Merck, activity 1). Water used for the ionic and zwitterionic compounds was purified by a Milli Q water-purification system. Flash chromatography was performed on Silicagel (Baker, 230 mesh).
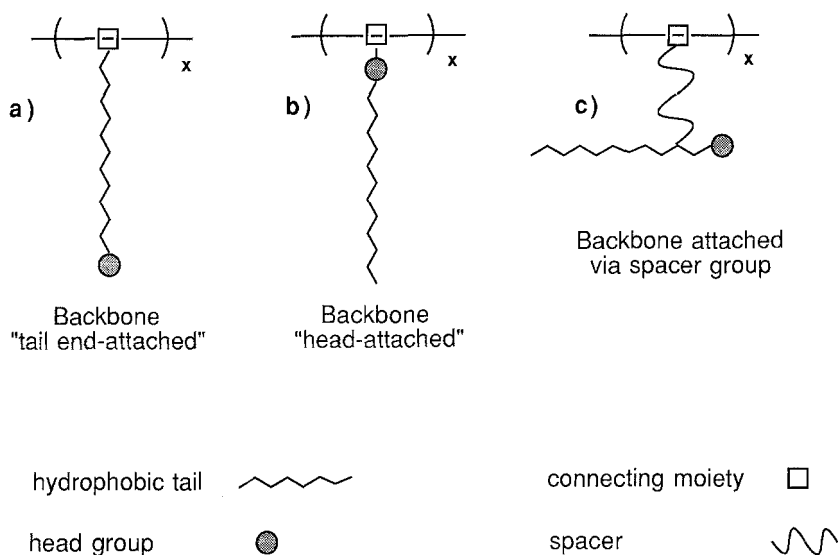
Polymerized Surfactants:

Fig. 1. Scheme of the molecular architecture of polymerizable surfactants, and of polysoaps: (a) "tail end attached" polysoap, b) "head attached" polysoap, c) polysoap with spacer

The synthesis of monomer N-decyl,N-(2-methacryloyloxy-ethyl),N,N-dimethyl ammonium bromide 1 [11, 12] and monomer 3-(N-decyl,N-(2-methacryloyloxyethyl),N-methyl) ammoniopropanesulfonate 3 has been described previously [1].

8-Iodo-3,6-dioxa-octan-1-ol (triethyleneglycol monoiodohydrin)

For 3 days, 33.6 g (0.2 mol) of triethyleneglycolmonochlorohydrin (Fluka) and 30 g of dry NaI were refluxed in 100 ml of dry acetone. The precipitate was filtered off and the solvent evaporated. The residue was dissolved in ether, filtered from insoluble parts, and evaporated. The crude product was used without further purification.

Yield: 43 g (83%) brownish, hygroscopic oil, n_D^{23} = 1.5232
^{1}H-NMR (200 MHz, CDCl$_3$): δ (in ppm) = 2.84 s (broad) (1.2H, –OH and H$_2$O), 3.24t (2H, –CH$_2$–I), 3.5–3.8m (10H, –O–(CH$_2$–CH$_2$–O)$_2$–CH$_2$–).

8-Iodo-3,6-dioxa-octyl methacrylate

Dissolved in 400 ml of dry ether were 39 g (0.15 mol) of 8-iodo-3,6-dioxa-octan-1-ol and 15.2 g (0.15 mol) of triethylamin.

While cooling with ice, 15.7 g (0.15 ml) of methycryloylchloride in 50 ml ether was added slowly. The mixture was stirred overnight; precipitate removed by filtration; and filtrate extracted with water, dried over MgSO$_4$, and evaporated. The crude product was free of starting material, according to TLC

(eluent ligroin/ethylacetate 10 v/1 v), and used without further purification.

Yield: 40.3 g (82%) yellow oil
^{1}H-NMR (200 MHz, CDCl$_3$): δ (in ppm) = 1.92s (3H, =C–CH$_3$), 3.22t (2H, –CH$_2$–I), 3.5–3.9m (8H, –CH$_2$–O–CH$_2$–CH$_2$–O–CH$_2$–), 4.28t (2H, –COO–CH$_2$–), 5.55m (1H, CH=C–COO– trans), 6.12m (1H, CH=C–COO– cis).

N-decyl-N-methyl-N-(8-methacryloyl-3,5-dioxa-octyl)amin

N-methyl-n-decylamin was prepared via alkylation and hydrolysis of the sulfonamide prepared from *p*-toluenesulfonylchloride and decylamin (Fluka) according to standard procedures [13–15]. For 3 days under N$_2$ 11.9 g (0.07 mol) of N-methyldecylamin, 23 g (0.07 mol) of 8-Iodo-3,6-dioxa-octyl methacrylate, and 1 ml nitrobenzene in 200 ml dry acetonitril were refluxed. The mixture was extracted with saturated aqueous NaCO$_3$, dried over MgSO$_4$, and evaporated. Purification was by flash chromatography (eluent CHCl$_3$/CH$_3$OH 20 v/1 v).

Yield: 12.7 g (49%) colorless oil, n_D^{25} = 1.4648

N-decyl-N,N-dimethyl-N-(8-methacryloyl-3,5-dioxaoctyl)ammonium iodide 2

Refluxed for 72 h under N$_2$ were 5.5 g (0.015 mol) of N-decyl-N-methyl-N-(8-methacryloyl-3,5-dioxaoctyl)amin, 2.4 g

(0.017 mol) of iodomethane, and 2 ml of nitrobenzene in 90 ml acetonitril. The solvent was removed in vacuo, and the crude product purified twice by flash chromatography (eluent $CHCl_3/CH_3OH$ 4 v/1 v and 7 v/1 v).

Yield: 3.2 g (42%) slightly yellow hygroscopic oil, $n_D^{25} = 1.5023$ solidifies slowly when stored in the refrigerator
Elemental analysis $(C_{22}H_{44}NO_4I)$:

Calculated: C = 51.46%, H = 8.64%, N = 2.73%,
I = 24.71%
Found: C = 50.79%, H = 8.73%, N = 2.86%,
I = 24.27%

^{1}H-NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0.83t (3H, $-CH_3$), 1.15–1.35m (14H, $-(CH_2)_7-$), 1.71m (2H, $-CH_2-C-N^+$) 1.89s (3H, $=C-CH_3$), 3.35s (6H, $-N^+-CH_3$), 3.5–4.0 m (12H, $-CH_2-N^+-(CH_2-CH_2-O)_2-CH_2-$), 4.24t (2H, $-CH_2-OOC-$), 5.56m (1H, CH=C-COO trans), 6.06m (1H, CH=C-COO cis)

3-(N-decyl-N-methyl-N-(8-methacryloyl-3,5-dioxaoctyl))ammoniopropanesulfonate 4

Refluxed for 72 h under N_2 were 10 g (0.027 mol) of N-decyl-N-methyl-N-(8-methacryloyl-3,5-dioxaoctyl)amin, 3.1 g (0.025 mol) of propanesultone, and 2 ml of nitrobenzene in 110 ml acetonitril. The solvent was removed in vacuo and the crude product purified twice by flash chromatography (eluent $CHCl_3/CH_3OH$ 4 v/1 v and 7 v/1 v)

Yield: 4.7g (35%) colorless, waxy, hygroscopic solid
Elemental analysis $(C_{24}H_{47}NO_7S \times H_2O)$

Calculated: C = 56.33%, H = 9.65%, N = 2.74%,
S = 6.27%
Found: C = 56.01%, H = 9.38%, N = 2.95%,
S = 6.18%

FD mass spectrum: signal at mass 494 (M^+)
^{1}H-NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0.83t (3H, $-CH_3$), 1.15–1.35m (14H, $-(CH_2)_7-$), 1.67m (2H, CH_2-C-N^+-), 1.90s (3H, $=C-CH_3$), 2.18m (2H, $N^+-C-CH_2-C-SO_3$), 2.84t (2H, $-CH_2-SO_3$), 3.12s (3H, $-N^+-CH_3$), 3.28m (2H, $-CH_2-N^+$), 3.5–4.0 m (12 H, $-CH_2-(O-CH_2-CH_2)_2-N^+-CH_2-C-C-SO_3$), 4.24t (2H, $-CH_2-OOC-$), 5.55m (1H, CH=C-COO trans), 6.07m (1H, CH=C-COO cis)

N-methyl, N-(vinyloxycarbonylmethyl)-1-aminodecane

To 18.2 g (0.106 mol) of N-methyl-decylamin and 1 ml nitrobenzene in 100 ml of dry acetonitril 17.5 g of vinyl-2-bromoacetate was added. This mixture was stirred at 60 °C for 48 h. The solvent was evaporated and the residue diluted by 200 ml diethylether, extracted with 2n NaOH, and dried over Na_2SO_4. After removal of the solvent, the product was purified by flash chromatography (eluent ethylacetate).

Yield: 2.6 g (10%) brownish, viscous oil

^{1}H-NMR (200 MHz, $CDCl_3$); δ (in ppm) = 0.85t (3H, $-CH_3$), 1.1–1.5m (16H, $-(CH_2)_8-$), 2.35s (3H, $-N-CH_3$), 2.45t (2H, $-CH_2-N<$), 3.3s (2H, $N-CH_2-COO$), 4.56m (1H, $-COO-C=CH$ trans), 4.86 m (1H, $-COO-C=CH$ cis), 7.26 m (1H, $-COO-CH=C$)

N-decyl,N-methyl,N-(vinyloxycarbonylmethyl)-3-ammoniopropane sulfonate 5

Refluxed in 15 ml of acetonitril for 72 h under N_2 were 1.44 g (5.6 mmol) of N-methyl,N-(vinyloxycarbonylmethyl)-1-aminodecane, 0.668 g (5.5 mmol) of propanesultone, and 3 drops of nitrobenzene. The product precipitated on cooling, and was repeatedly recrystallized from acetonitril.

Yield: 0.5 g (23%) colorless hygroscopic solid, m.p. 174 °C
Elemental analysis $(C_{18}H_{35}NO_5S \times H_2O)$:

Calculated: C = 54.66%, H = 9.43%, N = 3.54%,
S = 8.10%
Found: C = 55.58%, H = 10.29%, N = 3.65%,
S = 8.09%

^{1}H-NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0.85t (3H, $-CH_3$), 1.15–1.35 m (14H, $-(CH_2)_7-$), 1.69m (2H, CH_2-C-N^+-), 2.26m (2H, $N^+-C-CH_2-C-SO_3$), 2.90t (2H, $-CH_2-SO_3$), 3.39s (3H, $-N^+-CH_3$), 3.54m (2H, $-CH_2-N^+$), 3.90m (2H, $N^+-CH_2-C-C-SO_3$), 4.5–4.8m (3H, N^+-CH_2-COO-, $-COO-C=CH$ trans), 5.07m (1H, $-COO-C=CH$ cis), 7.16m (1H, $-COO-CH=C$)

N-(3-dimethylaminopropyl)-4-hexyloxybenzene-sulfonamide

To 36 g (0.2 mol) hexyloxybenzene in 80 ml $CHCl_3$, 45.5 g (0.39 mol) of chlorosulfonic acid was slowly added, keeping the temperature below -5 °C. The mixture was stirred for 3 h more, allowing it to reach room temperature. After dilution with 200 ml petrolether, the mixture was poured onto 200 g of ice and NaCl was added. The organic phase was separated, dried over Na_2SO_4, and evaporated. This process yielded 33.5 g (60%) of dark oil of crude 4-hexyloxybenzene-sulfonyl-chloride. These 33.5 g (0.12 mol) dissolved in 100 ml petrolether were added slowly to a stirred mixture of 12.4 g (0.12 mol) of 3-dimethylamino-propylamin (Fluka) placed on top of 80 ml of 10% aqueous NaOH at 20 °C. After 1 h, the resulting emulsion was neutralized by HCl. The organic phase was separated and evaporated. The residue was purified by flash chromatography (eluent: acetone).

Yield: 19 g (46%) colorless oil, $n_D^{24} = 1.5119$, which solidified in the refrigerator

^{1}H-NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0.86t (3H, $-CH_3$), 1.30m (4H, $-(CH_2)_2-$), 1.42m (2H, $-CH_2-C-C-O$), 1.55m (2H, $-CH_2-C-O-$), 1.75 m (2H, $N-C-CH_2-C-N<$), 2.13 s (6H, $-N-CH_3$), 2.26t (2H, $-CH_2-N<$), 2.97t (2H, $-CH_2-N-SO_2-$), 3.96t (2H, $-CH_2-O-$), 6.92d (2H, $-O-C=CH$), 7.71d (2H, $-SO_2-C=CH$)

N-(15-acryloyl-3-carboxy-4,7,10,13 tetraoxapentadecyl), N-(3-dimethylaminopropyl)-4-hexyloxybenzenesulfonamide

Refluxed for 4 days were 6.9 g (0.20 mol) of N-(3-dimethylaminopropyl)-4-hexyloxybenzene-sulfonamide, 7.1 g (0.023 mol) of tetraethyleneglycoldiacrylate, 0.12 g (0.003 mol) of NaOH, and 0.5 ml nitrobenzene in 100 ml dry acetonitril. The mixture was cooled, filtered, evaporated, and the crude product purified by flash chromatography (eluent: $CHCl_3/CH_3OH$ 10 v/1 v).

Yield: 3.8 g (30%) colorless oil, $n_D^{25} = 1.5011$

^{1}H-NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0.87t (3H, $-CH_3$), 1.25–1.55m (6H, $-(CH_2)_3-$), 1.65–1.85m (4H, $-CH_2-C-O-$, $N-C-CH_2-C-N<$), 2.19s (6H, $-N-CH_3$), 2.28t (2H, $-CH_2-N<$), 2.64t (2H, $-CH_2-COO-$), 3.11t (2H, $-CH_2-N-SO_2-$), 3.35t (2H, $-OOC-C-CH_2-N-SO_2-$), 3.65–3.75m (12H, $-CH_2-O-(CH_2-CH_2-O)_2-CH_2-$), 3.96t (2H, $-CH_2-O-Ar$), 4.25–4.35m (4H, $-CH_2-OOC-$), 5.82m (1 H, CH=C-COO– trans), 6.11m (1H, =CH-COO-), 6.39m (1H, CH=C-COO– cis), 6.90d (2H, $-O-C=CH$), 7.69d (2H, $-SO_2-C=CH$)

3-N,N-dimethyl,N-(3'-(N'-(15-acryloyl-3-carboxy-4,7,10,13 tetraoxapentadecyl)-(4-hexyloxy-benzenesulfonamido)propyl) ammonio propanesulfonate 6

Refluxed in 40 ml dry acetonitril under N_2 for 2 days were 3.8 g (5.9 mmol) of N-(15-acryloyl-3-carboxyl-4,7,10,13 tetraoxapentadecyl, N-(3-dimethylaminopropyl)-4-hexyloxy-benzenesulfonamide, 0.78 g (6.1 mmol) of propanesultone, and 1 ml nitrobenzene. The solvent is removed in vacuo, and the residue purified by flash chromatography (eluent: $CHCl_3/CH_3OH$ 4 v/1 v)

Yield: 3.2 g (71%) colorless, viscous oil, $n_D^{24} = 1.5138$

Elemental analysis ($C_{34}H_{58}N_2O_{13}S_2 \times H_2O$):

Calculated: C = 52.02%, H = 7.70%, N = 3.57%
Found: C = 51.56%, H = 7.80%, N = 3.74%

^{1}H-NMR (400 MHz, CD_3OD): δ (in ppm) = 0.97t (3H, $-CH_3$), 1.41m (4H, $-(CH_2)_2-$), 1.54m (2H, $-CH_2-C-C-O-Ar$), 1.85m (2H, $-CH_2-C-O-$), 2.15m (2H, $-SO_2-C-CH_2-C-N^+-$), 2.26 m (2H, $N^+-C-CH_2-C-SO_3$), 2.72t (2H, $-CH_2-COO-$), 2.93t (2H, $-CH_2-SO_3$), 3.17s (3H, $-N^+-CH_3$), 3.26t (2H, $-SO_2-N-CH_2-C-C-N^+$), 3.4–3.5m (4H, $-SO_2-N-C-C-CH_2-N^+$, $-SO_2-N-CH_2-C-COO$), 3.57m (2H, $N^+-CH_2-C-C-SO_3$), 3.68m (8H, $-O-(CH_2-CH_2-O)_2-$), 3.76m (4H, $-CH_2-O(C-C-O)_2-O-CH_2-$), 4.11t (2H, $-CH_2-O-Ar$), 4.25–4.35m (4H, $-CH_2-OOC-$), 5.94m (1 H, CH=C-COO– trans) 6.21m (1H, =CH-COO–) 6.44m (1H, CH=C-COO– cis), 7.15d (2H, $-O-C=CH$), 7.82d (2H, $-SO_2-C=CH$)

Polymerization of monomers

Polymers were obtained from monomers by free radical polymerization. Polymerizations of 1–4 and 6 were performed

in ethanolic solution as well as in aqueous, micellar solution. In the case of monomer 5, acetonitril was used as solvent. Monomer solutions of approximately 5% by weight in ethanol, or of 1–2% in water (or acetonitril), respectively, were purged with nitrogen for 30 min, sealed, and reacted for 12–18 h at 60 °C using 1–2 mol% azobis (isobutyronitril) AIBN as initiator.

When polymerized in water, the polymer precipitated at the bottom of the reaction vessel. It was extracted and washed several times with hot water and lyophilized. The dry polymers were dissolved in ethanol, filtered from the unsoluble parts, and precipitated into acetone. The precipitates were swollen with water, extracted and washed throughly with water, and lyophilized again.

Ethanolic reaction mixtures were filtered from the unsoluble parts and precipitated into acetone after removal of most of the solvent. The precipitates were swollen with water, extracted and washed thoroughly with water, and lyophilized.

On polymerization in acetonitril, poly(5) precipitated at the bottom of the reaction vessel. It was washed and extracted several times with hot acetonitril and dried.

The purified polymers were free of residual monomer, according to FT-IR, ^{1}H-NMR, and TLC.

Methods

NMR-spectra were recorded with an Aspect 3000 400 MHz-spectrometer (Bruker). Signals were attributed by comparison with model compounds and by double-resonance experiments. Thermogravimetry was performed on a Thermogravimetric Analyzer Type TGS-2 (Perkin-Elmer); the samples were heated under a nitrogen rate of 10 °C/min. Differential scanning calorimetry DSC was performed with a Perkin-Elmer DSC2. Heating rates of 5 °C/min to 40 °C/min were applied. Lyotropic liquid crystal were studied by a polarizing microscope (Ortholux, Leitz) equipped with a hot stage (Mettler FP52). Surface tensions were measured with a Lauda tensiometer at 25 °C. Monolayer behavior was investigated with a computer-controlled film balance [16] on pure aqueous subphase.

Results and discussion

Synthesis of surfactants containing spacer groups

The cationic ammonium salts and zwitterionic sulfobetaine surfactants studied are displayed in Fig. 2. Emphasis was placed on zwitterionic surfactants due to their special properties, such as missing polyelectrolyte effects [1]. The reaction scheme for the synthesis of monomers 2 and 4–6 is shown in Fig. 3.

Two types of surfactants containing oligoethyleneoxide spacer groups between the surfactant structure and the polymerizable group were synthesized. In monomers 2 and 4, the reactive methacrylate was attached via triethyleneglycol to the
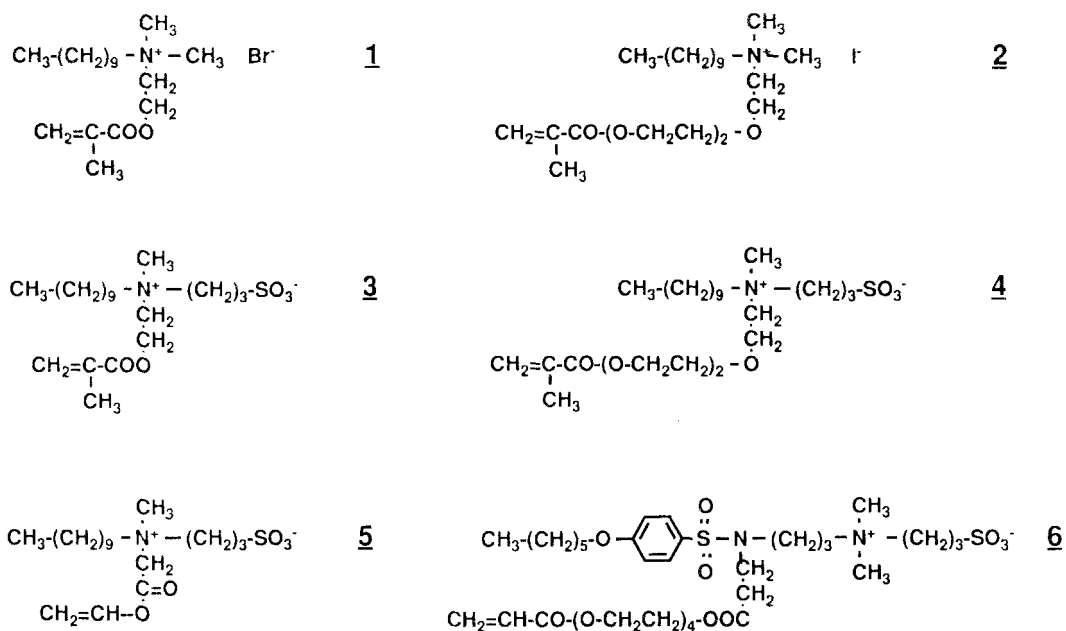
Fig. 2. Polymerizable surfactants investigated

quarternary ammonium group, i.e., it was bound to the head group of the surfactant. In monomer 6, the reactive acrylate was attached via tetraethyleneglycol to the sulfonamide moiety, i.e., it was bound to the front part of the hydrophobic tail. As this part is considered to be the least mobile one of surfactants in micelles [6, 7], such an architecture seems to be the most suitable for preserving maximal mobility of the surfactant structure in polymers. The complex ^{1}H-NMR spectrum of 6 is exhibited in Fig. 4.

Due to their analogous structure, surfactants 1–4 enabled comparative studies of cationic and zwitterionic analogs, and of spacer-free and spacer-containing analogs.

According to the model discussed in the introduction [1, 3, 4], the polymer of the sulfobetaine 5 is not expected to be watersoluble, because in this polymer the surfactant structure is attached to the polymer backbone via the head group (see Fig. 1b). However, we wanted to examine this compound, because recently the polymer of the analogous cationic surfactant was reported to be water soluble [5].

General properties of the monomers

By incorporation of oligoethyleneoxide groups, the melting points of 2 and 4 are strongly decreased

compared to their spacer-free analogs 1 and 3 . In fact, both spacer containing monomers exhibit a complicated melting behavior. Whereas 2 shows the existence of several crystal modifications in the DSC trace (Fig. 5) k_1 24 k_2 27 k_3 32 i, the spacer surfactant 4 is a thermotropic liquid crystal, showing birefringence and mobility in the polarizing microscope. DSC investigations reveal a complex behavior, pointing to the presence of several mesophases k 65 LC_1 72 LC_2 92 LC_3 104 i (Fig. 5). As 4 tends to undergo thermal polymerization in the temperature range of interest, a detailed study of the mesophases is missing yet.

The monomers 1–2 and 4–6 are well water soluble at 20 °C; only monomer 3 exhibits a Krafft-temperature of 37 °C; The high Krafft-temperature was attributed to special interactions of the methacrylate group with the sulfobetain structure [1]. Noteworthy is that such interactions are missing in case of the analogously built vinylester 5. The Krafft-temperature is depressed as well by incorporation of oligoethyleneoxide groups as exemplified by spacer surfactant 4, which is well water soluble at 20 °C, in contrast to its analog 3. Such a depression of the Krafft-temperature is analogous to the well documented one of anionic surfactants when oligoethyleneoxide groups are incorporated [17]. Highly concentrated aqueous solutions of 3–6, the zwitterionic surfactants are birefringent,

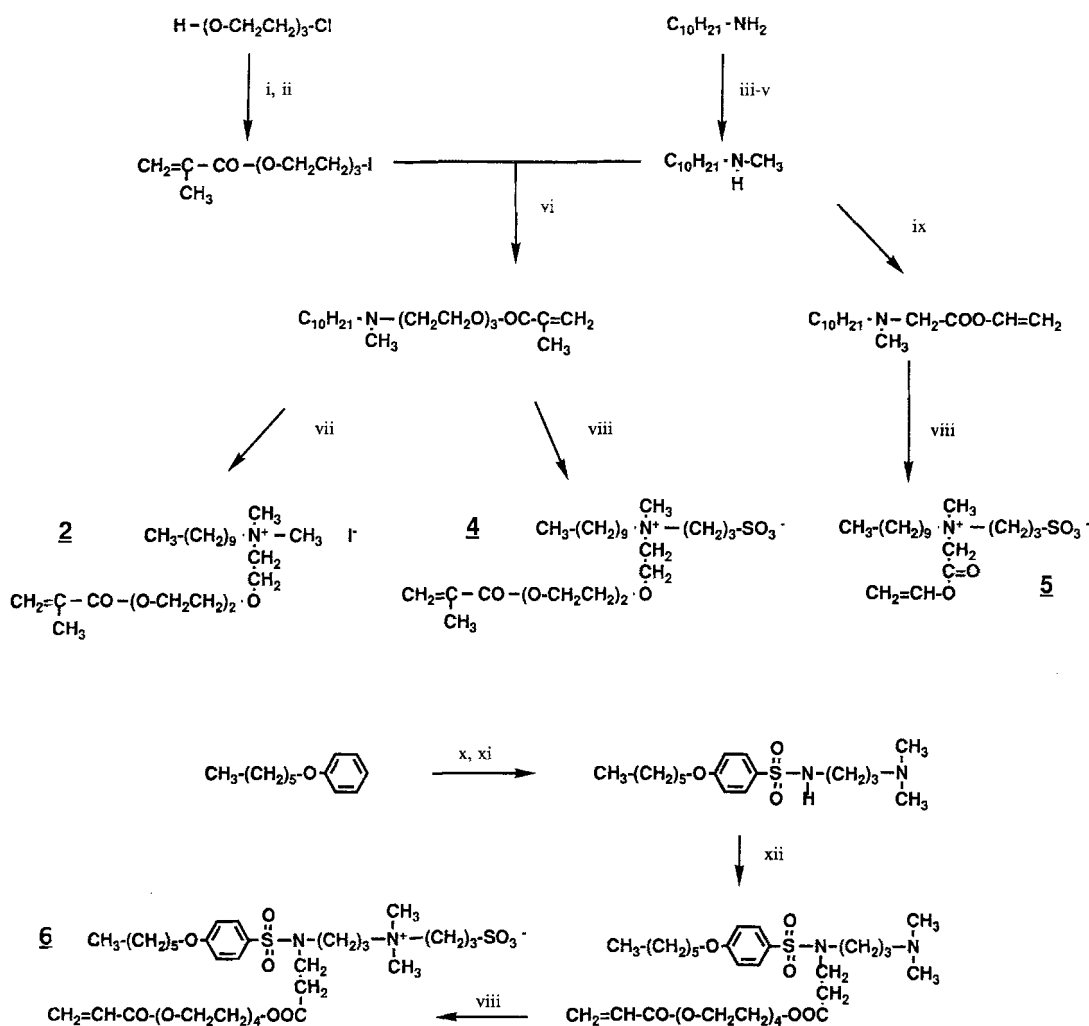Fig. 3. Schematic synthesis of the monomers synthesized: a) monomers based on N-methyl-decylamin, i) NaI/acetone, ii) CH₂=C(CH₃)–COCl + (C₂H₅)₃N, iii) TosCl + NaOH, iv) CH₃I + NaOH/EtOH, v) H₂SO₄/Δ, vi) CH₃CN/Δ, vii) CH₃I/CH₃CN, viii) propanesultone/CH₃CN, ix) BrCH₂COO–CH=CH₂/CH₃CN, b) monomer based on 4-hexyloxybenzenesulfonamide, x) SO₂Cl₂/CHCl₃, xi) H₂N–(CH₂)₃–N(CH₃)₂/NaOH, xii) CH₂=CH–COO–(CH₂–CH₂–O)₄ –OC–CH=CH₂ + NaOH/CH₃CN

indicating the formation of anisotropic lyotropic mesophases. The textures of polarized optical micrographs point to the presence of hexagonal mesophases, as found for many sulfobetaine surfactants [1, 18].

Critical micelle concentrations (CMC) of the monomers

CMCs were determined for the newly synthesized monomers 2 and 4–6 by surface tension measurements. The results are displayed in Figs. 6 and 7

and listed in Table 1, comparing them with the CMCs of the reference surfactants 1 and 3 .

The surface tensions of the monomers at their CMC are virtually identical for zwitterionic and cationic analogs, such as 2 and 4 (Fig. 6). However, as observed previously [1], the zwitterionic surfactants 3 and 4 exhibit lower CMCs than their cationic analogues 1 and 2. Accordingly, the cationic moiety is slightly more hydrophilic than the zwitterionic one.

The comparison of the spacer free surfactants 1 and 3 with the spacer containing analogs 2 and 4

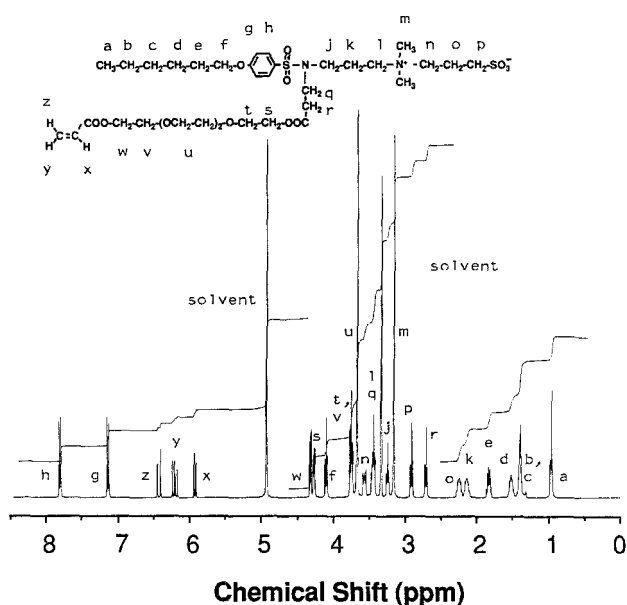Fig. 4. ¹H-NMR spectra of monomer 2 in CD₃OD at room temperature

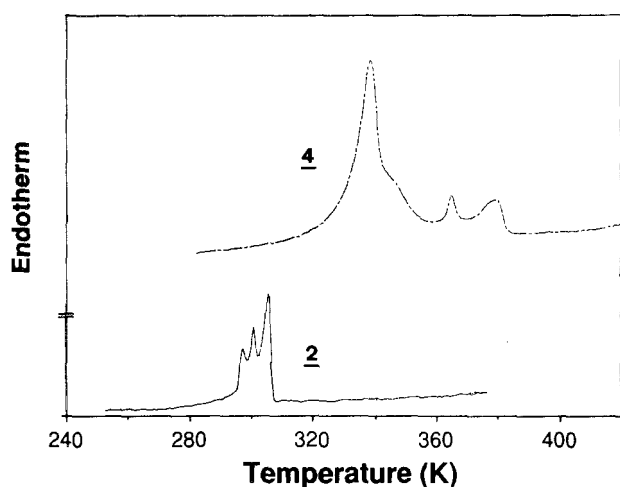Fig. 5. DSC trace of monomers 2 and 4 heating cycle. Heating rate 10 °C/min

reveals a decrease of the CMCs on incorporation of the triethyleneglycol spacer group (Fig. 6), as observed for oligoetheralkanesulfonates [17]. In fact, the poor hydrophilicity of oligoethyleneoxide end-capped by acrylate has been described before [19]. Additionally, the spacer containing monomers exhibit slightly decreased surface tensions at the CMC. This is in contrast to the behavior of oligo-
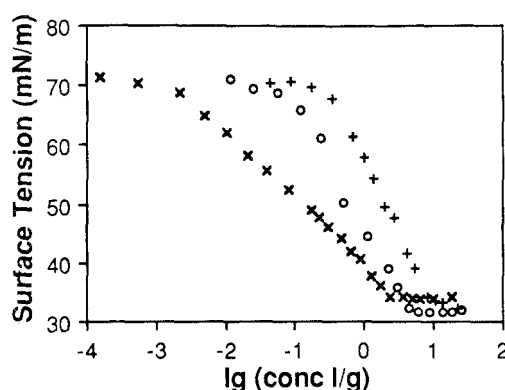

Fig. 6. Surface activity of monomers 1, 2 and 4 at 25 °C in water. + = 1, ○ = 2, × = 4

Table 1. Surfactant properties of the monomers at 25 °C. Values for monomers 1 and 3 taken from [1]

Monomer	T_K (°C)	CMC (g/l)	CMC (mol/l)	γ_{min} (mN/m)
1	< 10	6.3	1.7×10^{-2}	34
2	< 10	4.5	0.88×10^{-2}	32
3	37	4.6[a])	1.1×10^{-2}	
4	< 10	2.3	0.47×10^{-2}	34
5	< 20	3.4	0.94×10^{-2}	36
6	< 10	0.48	0.06×10^{-2}	37

T_K = Krafft-temperature, CMC = critical micelle concentration, γ_{min} = surface tension at CMC
[a]) by pyrene label at 40 °C

etheralkane-sulfonates [17], i.e., it is of great importance whether the oligoethyleneoxide group is incorporated between the hydrophobic chain and the hydrophilic head or whether both the hydrophobic tail and the oligoethyleneoxide group are attached to the hydrophilic head. For 2 and 4, the observations clearly indicate that the methacrylate end-capped triethyleneglycol group should be considered slightly hydrophobic and not hydrophilic.

Figure 7 shows the plot of surface tension vs the log of concentration for monomer 5. The slight minimum indicates the presence of a small amount of impurities. As the monomer has been carefully purified, the impurity may well be not inherent, but due to slow hydrolysis of the vinylester in the course of the measurements (see below). Comparing monomers 3 and 5, its CMC of 0.94×10^{-2} mol/l is very similar to the value of
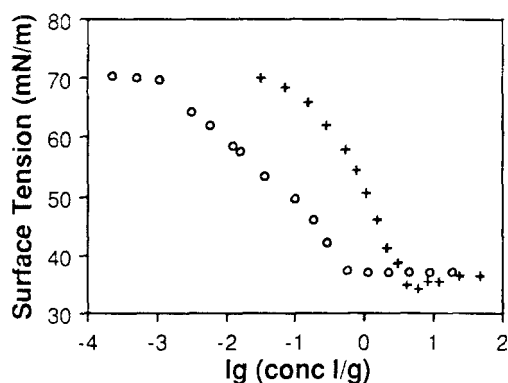
Fig. 7. Surface activity of monomers 5 and 6 at 25 °C in water.
+ = 5, O = 6

Chemical Shift in ppm

Fig. 8. ^{1}H-NMR spectra of vinylester 5 in D$_2$O demonstrating partial hydrolysis after 4 days storage at room temperature (ca 22 °C). Most prominent is the gradual decrease of the signals of the olefinic protons at 7.2 ppm and 5.1 ppm, protons next to the C=O group at x) 4.4 ppm, and protons of the N$^+$–CH$_3$ group at a) 3.3 ppm. The latter ones are replaced by new signals at z) 4.0 ppm and at b) 3.2 ppm of the resulting carboxylic acid. For full signal assignment of 5 see experimental section

monomer 3 (Table 1) and related sulfobetaine surfactants [1]. The same is true concerning the surface tension of 36 mN/m at the CMC [1]. Thus, despite of the strongly decreased Krafft-temperature, the replacement of the methacrylate by the vinylester moiety is only of minor importance for surface activity, because the basic zwitterionic structure dominates.

Figure 7 illustrates the micelle formation of the spacer-containing monomer 6. In agreement with the discussion above, the CMC of 6.3×10^{-4} mol/l of 6 is relatively low. Obviously, the end-capped tetraethyleneglycol behaves more like a second hydrophobic chain than a second hydrophilic head group. This interpretation accounts as well for the low surface tension of 37 mN/m at the CMC considering the shortness of the basic hydrophobic part.

Solvolytic stability of vinylester 5

Attempts to polymerize vinylester 5 in ethanol or water by AIBN were not successful. Although the vinylester signals vanish completely in the FT-IR and ^{1}H-NMR spectra, TLC indicates that only very little polymer, but mainly low molecular weight side products, are formed. The polymer could not be separated successfully from the major products. According to NMR and IR, the major side reaction in ethanol is transesterification, yielding the corresponding ethylester. The major side reaction in water is the ester hydrolysis (see Fig. 8). The half-life time of the ester in water is ca 8 days at room temperature (approximately 22 °C) and ca
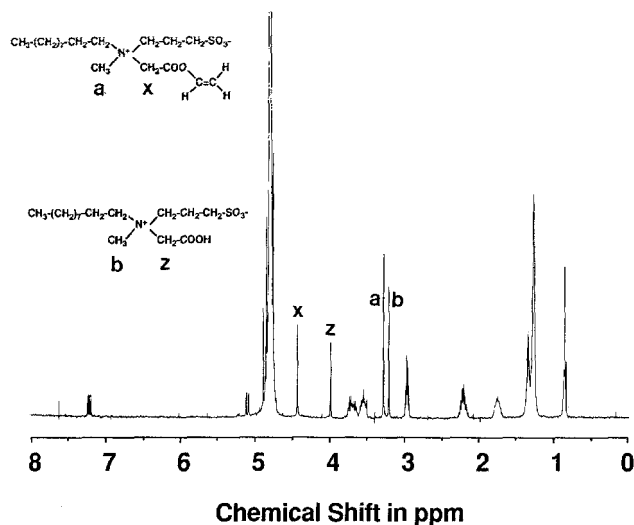
3 h at 65 °C. The facile solvolysis is attributed to the activation of the carbonyl group by the quarternary ammonium group in α-position. Thus, even for the little polymer formed, a copolymer structure based on 5 and vinylalcohol is probable. Such a "copolymer" formation may account for the reported water solubility of the analogous cationic polymer [5].

General properties of the polymers

All polymers are solids, which decompose above ca 200 °C. Only in the case of the cationic spacer polymer, a glass transition was found at 10 °C. Whereas the cationic poly(1) and poly(2) are well soluble in methanol, ethanol, chloroform, or chloroform/methanol mixtures, the zwitterionic polymers are only well soluble in ethanol or chloroform/methanol mixtures, but not in pure methanol or chloroform. The limited solubility of the zwitterionic polymers is in agreement with previous reports [1, 20, 21], and the type of useful solvents is in agreement with the molecular architecture of the polymers [1], i.e., the polymer backbone is attached to the hydrophilic head groups or to the

front part of the hydrophobic tail. Most important, however, is that even the spacers containing the polymers are insoluble in water. This includes the cationic poly(2). Thus, the insolubility in water cannot be attributed to the general poor solubility of zwitterionic polymers.

Monolayer behavior of the polymers

Due to their solubility in 10 v/1 v chloroform/methanol mixtures, the polymers can be spread at the air-water interface to study their surface activity in insoluble monolayer experiments. As reported previously [1], for poly(1) and poly(3) these polymers derived from water-soluble monomers indeed form stable insoluble monolayers, for which surface pressure-area diagrams ("isotherms") are displayed in Fig. 9.

The isotherms of the reference polymers without spacer groups poly(1) and poly(3) are very similar (Fig. 9a, c). In comparison, the cationic polymer exhibits only a slightly increased collapse area and a moderately enhanced collapse pressure of ca 25 mN/m. The collapse areas of ca 0.35 nm^2/repeat unit indicate a rather loose packing of the hydrocarbon chains. The collapse pressures of ca 20 mN/m–25 mN/m are rather low, compared to standard amphiphiles, such as stearic acid [22]. Between 1°C and 50 °C, the spreading behavior is independent of the temperature. These results were concluded to indicate a fluid-like state of the hydrophobic chains in the monolayer [1].

The isotherms of the polymers bearing spacer groups poly(2), poly(4), and poly(6) show marked differences. In particular, the collapse areas are substantially increased compared with the polymers without spacer groups. Such large areas per molecule of amphiphilic monomers and polymers bearing oligoethyleneoxide spacer groups have been previously reported in the expanded phase of insoluble monolayers [9, 10] (but not in the condensed phase), supporting the conclusion that the hydrophobic chains of the polymers are in a fluid-like state. In contrast to the packing of the monolayers, the collapse pressures do not change much on incorporating the spacers. Only slight increases are observed, thus paralleling the effect of the spacer groups onto the surface activity of the monomers (see Table 1).

As observed for the reference polymers poly(1) and poly(3), the isotherms of the cationic and
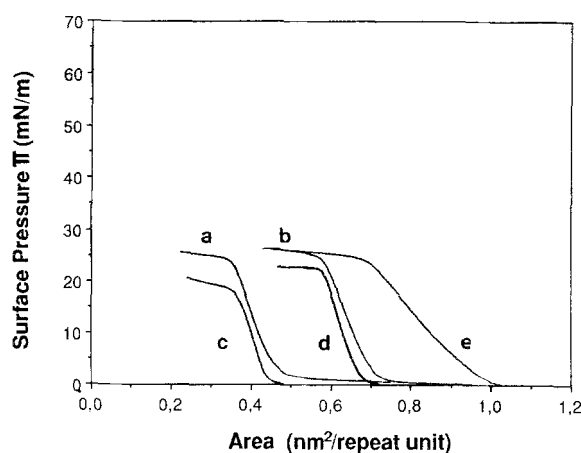

Fig. 9. Surface pressure-area diagrams of polymers poly(1), poly (4), and poly (6) at 20 °C. Pure aqueous subphase, pH = 5.8. a) poly(1), b) poly(2), c) poly(3), d) poly(4), e) poly(6)

zwitterionic analogs poly(2) and poly(4) bearing spacer groups are very similar (Fig. 9b, d). Here too, the cationic polymer exhibits only a slightly increased collapse area and a moderately enhanced collapse pressure. Noteworthy is that these slight differences in surface activity correspond to the ones observed for the monomer pair (Table 1, Fig. 6). Nevertheless, the nature of the head group, whether cationic ammonium salt or zwitterionic sulfobetain, is of minor importance only for the monolayer behavior. Polymer architecture [1] (see Fig. 1), hydrophobic chain length [23], and the presence of spacer groups seem to be the dominating factors.

Conclusions

The incorporation of oligoethyleneoxide groups as flexible side-chain spacers into polymerizable surfactants has a marked influence on their aggregation behavior in aqueous systems. Although the spacers behave as slightly hydrophobic components, the effective depression of the melting temperatures and Krafft-temperatures T_K of the monomers makes the spacers useful components in the design of surfactants, all the more so as the surface activity is hardly modified. This is particularly true for sulfobetaine surfactants, which often suffer from their notoriously high values of T_K [1, 18]. However, although the concept of side-chain spacers is very successful for polymeric liquid

crystals or polymeric mono- and multilayers, it seems not to be appropriate to provide polysoaps derived from single-chain surfactants having attached a polymerizable moiety to their hydrophilic head.

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