Peter Anton, André Laschewsky

Zwitterionic polysoaps with reduced density of surfactant side groups

first published in:
Die Makromolekulare Chemie 194 , (1993) S. 601-624, ISSN 0025-116X
DOI 10.1002/macp.1993.021940221

Zwitterionic polysoaps with reduced density of surfactant side groups

*Peter Anton, André Laschewsky**[a]

Institut für Organische Chemie, Universität Mainz,
Johann-Joachim-Becher Weg 18–20, D-W6500 Mainz, Germany

(Received: May 19,1992; revised manuscript of June 10, 1992)

SUMMARY:

Several zwitterionic polymers were prepared by radical homopolymerization of surfactant monomers which bear diallyl, diene or vinylcyclopropane moieties. These polymer systems were complemented by alternating copolymers of appropriate zwitterionic vinyl compounds. Thus, polymers with reduced (as compared with simple vinylic homopolymers, or statistical copolymers) and well defined density of surfactant side groups are obtained. The solubilities found for these polymers are dominated by polymer geometry rather than by the balance of hydrophilic and hydrophobic fragments, thus corroborating a "main-chain spacer" model proposed recently. All water-soluble polymers exhibit characteristic features of classical polysoaps, as shown by surface tension measurements and by solubilization of hydrophobic dyes. In contrast, the water-insoluble copolymers are capable to form stable monolayers at the air-water interface.

Introduction

Recently, we have reported on fully zwitterionic, polymerizable surfactants, and the polymers derived therefrom[1–4]. Such polymers represent an unconventional but interesting type of micellar polymers ("polysoaps"[5,6]), as they may combine advantageously the behaviour of ionic and non-ionic polysoaps[1,3,7].

Unfortunately, the synthesis of such zwitterionic polysoaps is not straightforward. Due to the preferred solubility of zwitterions in protic solvents[8], radical polymerization is the method of choice. But in the case of simple vinyl polymers, the solubility of polymerized surfactants is controlled by their molecular geometry rather than by the hydrophilic-hydrophobic balance[1–4,7]. This phenomenon is not restricted to polyzwitterions but seems to be a general one: Water-soluble vinylic polysoaps are obtained only if the surfactant structure is bound to the polymer backbone via the end of the hydrophobic tail ("tail-end" type, Fig. 1 c)[9]. However, in such "tail-end" polysoaps, there are indications that the solubilization capacity is restricted[1,10], presumably due to the "immobilization" of the hydrophobic chains by the polymer backbone[11–13]. As the hydrophobic chains are much more mobile in polymers of the "mid-tail" and "head" types (Fig. 1 a and b), they should be better suited for efficient solubilization. But their insolubility in water has prevented the direct comparison of isomeric vinyl polymers of different geometry.

To overcome these problems, i.e. to combine water-solubility and solubilization power, the effect of spacer groups in polymerized surfactants was studied[4,7]. Whereas

[a] Dépt. de Chimie, Université Catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium.

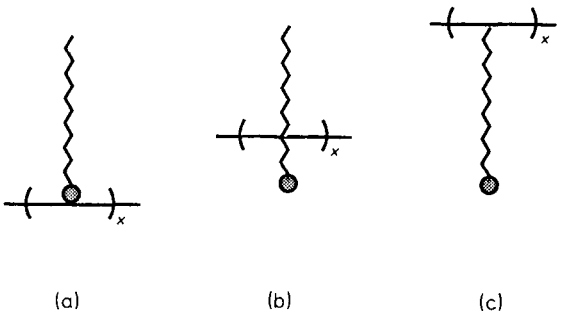


Fig. 1. Schematic geometry of polymerized surfactants:
(a) "head-type",
(b) "mid-tail type",
(c) "tail-end type"

side-chain spacers (Fig. 2a) such as oligo(ethylene glycol)s are of limited use only, as they have to be very long to be sufficient[7, 14, 15], main-chain spacers (Fig. 2b) are very effective, i.e., if the density of the surfactant side chains at the polymer backbone is sufficiently reduced, polysoaps of any geometry (Fig. 1) can be prepared[7].

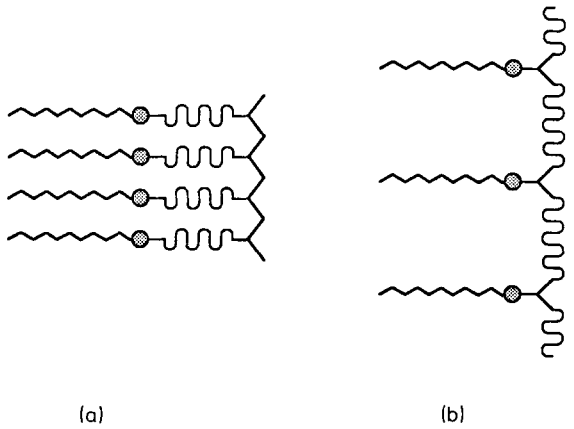
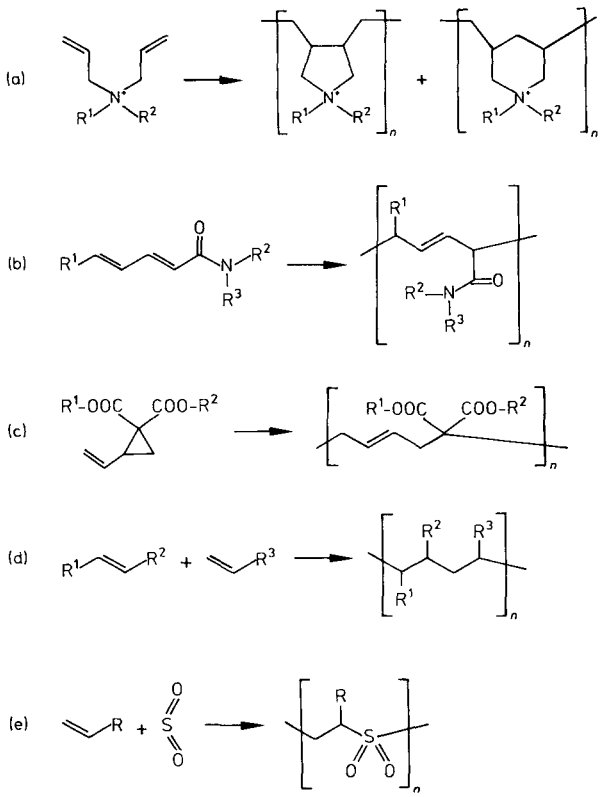


Fig. 2. Scheme of spacer groups in polymerized surfactants:
(a) side-chain spacer,
(b) main-chain spacer

The most convenient approaches to such polymers with "main-chain spacer" are the statistical copolymerization of surfactant monomers with polar comonomers, or polymer-analogous reactions of preformed polymers, respectively[16]. However, both methods produce polymers, the chemical structures of which are rather ill-defined. For a better insight in the structure-properties relationship of micellar polymers, more defined structures are desirable. Therefore, zwitterionic monomers are synthesized, the radical polymerization of which should yield polymers with a longer repeating unit than the standard C_2-unit (see *Scheme 1*). These monomers and polymers are studied with respect to their solubility and their self-organization in aqueous systems.

Scheme 1: Polymers with reduced density of side chains prepared by radical-initiated polymerization: (a) diallylammonium salts, (b) dienoyl monomers, (c) vinylcyclopropanes, (d) alternating polymers of complementary vinyl monomers, (e) aliphatic polysulfones



Experimental part

Methods

NMR-spectra were recorded with a Bruker 200 MHz and a Bruker 400 MHz. Fourier-transform infrared (FT-IR) spectra were recorded from KBr pellets with a spectrometer 5DXC (Nicolet). UV/VIS spectra were recorded with a spectrometer Lambda-5 (Perkin-Elmer). Thermogravimetry was performed on a Perkin-Elmer analyzer TGS-2 under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC2. With both methods, a heating rate of 10 °C/min was applied. Mesophases and Krafft-temperatures were determined with a polarization microscope (Ortholux, Leitz), equipped with a hot stage (FP52, Mettler). The onset of solubility of a little crystal suspended in water was taken as Krafft-temperature. Surface tensions were measured at 25 °C according to de Nouy, using a semi-automatic tensiometer TE 1C/2 (Lauda). The monolayer behaviour was investigated with a computer-controlled film balance [17], on a pure aqueous subphase.

Materials

General: All solvents used were of analytical grade. Acetonitrile, *N,N*-dimethylformamide (DMF), formamide, dimethylsulfoxide (DMSO) and triethylamine were dried over molecular sieves 3 Å. Tetrahydrofuran (THF) was distilled over potassium metal. All other solvents were dried by passing through a short column of neutral Al_2O_3 (Merck, activity 1). Water used for the ionic and zwitterionic compounds was purified by a Milli Q water purification system (resistance 18 MΩ). Flash chromatography was performed on silicagel (Baker, 230 mesh).

Monomers

N-Methylmaleimide (**10**) (Aldrich), dimethyl maleate (**11**) (Fluka) and fumaronitrile (**12**) (Fluka) were recrystallized or distilled prior to use. Octadecyl vinyl ether (BASF AG) and *N*-methyl-*N*-vinylformamide (**13**) (C. Erdelen) were gifts. The synthesis of monomer **9** has been described elsewhere[18].

N,N-Diallyldecylamine

8,2 g (0,084 mol) of diallylamine and 9,3 g (0,042 mol) of 1-bromodecane are refluxed in 100 mL of ethanol for 60 h. After evaporation of the solvent, the residue is treated with 100 mL of 2 M KOH, and extracted with diethyl ether. Distillation in vacuo yields 8,5 g (85%) of a colourless liquid (b.p. (0,1 mbar): 80 °C, refractive index at 20 °C n_D^{20} = 1,4526).

^{1}H NMR (400 MHz, $CDCl_3$): 0,85 (t, 3H, CH_3—), 1,26 (m, 14H, —$(CH_2)_7$—), 1,45 (m, 2H, —CH_2—C—N<), 2,38 (t, 2H, —CH_2—N<), 3,08 (d, 4H, >N—CH_2—C=), 5,13 (m, 4H, —C=CH_2), 5,86 (m, 2H, —CH=C).

3-(*N,N*-Diallyl-*N*-decyl)ammoniopropanesulfonate (**1**)

8,0 g (0,034 mol) of *N,N*-diallyldecylamine and 3,91 g (0,032 mol) of 1,3-propanesultone are refluxed in 120 mL of dry acetonitrile for 72 h under N_2. After evaporation of the solvent, the residue is purified by flash-chromatography (eluent: $CHCl_3/CH_3OH$ mixture (volume ratio changing from 20/1 to 1/1). Yield 3,5 g (29%) of a colourless wax, m.p. 84 °C.

$C_{19}H_{37}NO_3S$, (359,36)	Calc.	C 63,45	H 10,38	N 3,90	S 8,92
	Found	C 62,04	H 10,26	N 3,82	S 9,17

^{1}H NMR (400 MHz, $CDCl_3$): 0,85 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,73 (m, 2H, —CH_2—C—N^+), 2,2–2,35 (m, 3,5 H, N^+—C—CH_2—C—SO_3^- + x H_2O), 2,87 (t, 2H, —CH_2—SO_3^-), 3,08 (m, 2H, —CH_2—N^+), 3,61 (m, 2H, —N^+—CH_2—C—C—SO_3^-), 3,94 (m, 4H, N^+—CH_2—C=), 5,70 (m, 4H, —C=CH_2), 5,98 (m, 2H, —CH=C).

N-Decyl-*N*-2-(dimethylamino)ethylpenta-2,4-dienamide

3,5 g (15,3 mmol) of *N*-[2-(dimethylamino)ethyl]decylamine[18], 3,6 g (36 mmol) of triethylamine and 0,5 mL of nitrobenzene are suspended in 5 mL of dry CH_2Cl_2 at 25 °C. 1,5 g (15,3 mmol) of penta-2,4-dienoic acid and 4,7 g (18 mmol) of 2-chloro-*N*-methylpyridinium chloride are added successively[19]. The mixture warms up slightly and turns brown. After 18 h of stirring, all components are dissolved. The mixture is diluted with 20 mL of CH_2Cl_2, extracted with 1 M NaOH, dried over $MgSO_4$, and the solvent is removed at 25 °C under reduced pressure. The residual oil is purified by flash-chromatography (eluent: methanol), to yield 3,2 g (67%) of a brownish oil which solidifies in the refrigerator. According to the ^{1}H NMR, the product is approximately a 1 : 1 mixture of the trans- and cis isomers.

^{1}H NMR (200 MHz, $CDCl_3$), 0,85 (t, 3H, —CH_3), 1,25 (m, 14H, —$(CH_2)_7$—), 1,53 (m, 2H, CH_2—C—NCO—), 2,25 (m, 6H, —$N(CH_3)_2$), 2,35–2,65 (m, 2H, —CH_2—N<), 3,2–3,6 (m, 4H, (—$CH_2)_2$—NCO), 5,35–5,6 (m, 2H, CH_2=C), 6,1–6,6 (m, 2,5H, =CH—C=CH—CON—, —CH=C—CON— cis), 7,2–7,35 (m, ?H/$CHCl_3$ signal superposed, —CH=C—CON— trans).

3-{*N*-[2-(*N*-Decyl-*N*-*trans,trans*-penta-2,4-dienoyl)aminoethyl]-*N,N*-dimethyl}ammoniopropanesulfonate (**2**)

3,15 g (10 mmol) of *N*-decyl-*N*-2-(dimethylamino)ethylpenta-2,4-dienamide, 1,22 g (10 mmol) of 1,3-propanesultone and 1 mL of nitrobenzene in 50 mL of acetonitrile are refluxed under N_2 for 3 days. On cooling, a brown mass is formed which is extracted with diethyl ether. After flash-chromatography (eluent: ethanol, gradually changing to methanol), 0,75 g (17%) of colourless crystals are obtained (monomer tends to polymerize upon storage, polymerization in bulk above 80 °C).

$C_{22}H_{42}N_2O_4S$ (430,65)	Calc.	C 61,37	H 9,83	N 6,50	S 7,45
	Found	C 60,11	H 10,00	N 6,24	S 8,02

^{1}H NMR (400 MHz, D_2O): 0,80 (t, 3H, $-CH_3$), 1,21 (m, 14H, $-(CH_2)_7-$), 1,55 (m, 2H, $CH_2-C-NCO-$), 2,22 (m, 2H, $N^+-C-CH_2-C-SO_3^-$), 2,91 (t, 2H, $-CH_2-SO_3^-$), 3,17 (m, 6H, $-N^+(CH_3)_2$), 3,4–3,6 (m, 6H, $(-CH_2)_2-NCO$), $-N^+-CH_2-C-C-SO_3^-$), 3,81 (m, 2H, $-NCO-C-CH_2-N^+$), 5,38 (d, 1H, $-CH=C-C=C-CON-$ cis), 5,66 (m, 1H, $CH=C-C=C-CON-$ trans), 6,3–6,5 (m, 2H, $=CH-C=CH-CON-$), 7,17 (m, 1H, $-CH=C-CON-$ trans).

trans,trans-(*N*-2-Dimethylaminoethyl)-*N*-methyl)tetradeca-2,4-dienamide

In analogy to *N*-decyl-*N*-2-(dimethylamino)ethylpenta-2,4-dienamide above, 2,5 g (24 mmol) of *N,N,N'*-trimethylethylenediamine, 5,4 g (15,3 mmol) of tetradeca-2,4-dienoic acid[20] and 8,5 g (39 mmol) of 2-fluoro-*N*-methylpyridinium toluene-4-sulfonate are reacted[19]. Purification by flash-chromatography (eluent: acetone) yields 1,5 g (20%) of slightly yellowish oil, refractive index at 24 °C n_D^{24} = 1,4979.

^{1}H NMR (200 MHz, $CDCl_3$): 0,85 (t, 3H, CH_3-), 1,15–1,45 (m, 14H, $-(CH_2)_7-$), 2,12 (m, 2H, $-CH_2-C=$), 2,23 (m, 6H, $-N(CH_3)_2$), 2,42 (t, 2H, $-CH_2-N\langle$), 3,01, 3,08 (s, s, 3H, $-CON-CH_3$), 3,45–3,60 (m, 2H, $-CON-CH_2-$), 5,9–6,3 (m, 3H, $-CH=CH-C=CH-CON\langle$), 7,1–7,3 (m, ?H/superposed by $CHCl_3$ signal, $-CH=C-CON\langle$); superposition of the cis- and trans-amide conformers.

3-{*N*-[2-(*N-trans,trans*-Tetradeca-2,4-dienoyl-*N*-methyl)aminoethyl]-*N,N*-dimethylammonio}propanesulfonate (**3**)

A mixture of 0,93 g (3 mmol) of *trans,trans*-(*N*-2-dimethylaminoethyl-*N*-methyl)tetradeca-2,4-dienamide, 0,36 g (3 mmol) of 1,3-propanesultone and 0,5 mL of nitrobenzene in 20 mL of acetonitrile is refluxed under N_2 for 3 days. On cooling, the product crystallizes from the mixture. Extensive recrystallization yields 1,0 g (80%) of a colourless, hygroscopic, liquid-crystalline wax: see Tab. 1. (Polymerization in bulk above 120 °C, monomer tends to polymerize upon storage).

$C_{22}H_{42}N_2O_4S$ (430,65)	Calc.	C 61,37	H 9,83	N 6,50	S 7,45
	Found	C 55,38	H 9,14	N 5,48	S 7,38

^{1}H NMR (400 MHz, D_2O): 0,86 (t, 3H, $-CH_3$), 1,26 (m, 14H, $-(CH_2)_7-$), 1,39 (2H, $-CH_2-C-C=$), 2,05–2,35 (m, 4H, $-CH_2-C=$, $N^+-C-CH_2-C-SO_3^-$), 2,91 (t, 2H, $-CH_2-SO_3^-$), 3,1–3,2 (m, 9H, $-CON-CH_3$, $-N^+(CH_3)_2$), 3,4–3,6 (m, 4H, $-CH_2-N^+-CH_2-$), 3,85 (m, 2H, $-CON-CH_2-$), 6,1–6,3 (m, 2H, $-CH=CH-$), 6,34 (d, 1H, $=CH-CON\langle$), 7,12 (m, 1H, $-CH=C-CON\langle$).

N-Methyl-*N'*-(tetradeca-2,4-dienoyl)piperazine

2,5 g (25 mmol) of *N*-methylpiperazine and 2,5 g (25 mmol) of tetradeca-2,4-dienoic acid are reacted in 140 mL of CH_2Cl_2 using 0,2 g of 4-dimethylaminopyridine and 5,4 g (26 mmol) of di-

cyclohexylcarbodiimide[21]. Purification by flash-chromatography (eluent: $CHCl_3/CH_3OH$ (volume ratio 10/1) yields 1,2 g (16%) of yellowish oil.

^1H NMR (400 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,23 (m, 14H, $—(CH_2)_7—$), 2,11 (m, 2H, $—CH_2—C=$), 2,27 (m, 3H, $>N—CH_3$), 2,37 (m, 4H, $—CH_2—N—$), 3,5–3,7 (m, 4H, $—CON—CH_2—$), 6,0–6,25 (m, 3H, —CH=CH—C=CH—CON<), 7,22 (m, ?H/superposed by $CHCl_3$ signal, —CH=C—CON<).

3-[*N*-(*trans,trans*-Tetradeca-2,4-dienoyl)-*N'*-methylpiperazinio]propanesulfonate (**4**)

The monomer is prepared and purified as described for **3**, starting from 1,2 g (3,9 mmol) *trans,trans*-tetradeca-2,4-dienoyl-*N'*-methylpiperazide and 0,49 g (3,9 mmol) of 1,3-propanesultone. Yield: 0,8 g (62%) colourless, hygroscopic crystals (polymerization in bulk above 180 °C).

$C_{22}H_{40}N_2O_4S$ (428,65)	Calc.	C 61,65	H 9,41	N 6,53	S 7,48
	Found	C 59,12	H 9,27	N 6,59	S 7,42

Field desorption (FD)-mass spectrum: Peaks at 429 and 430 $(M)^+$, $(M + 1)^+$.

^1H NMR (400 MHz, CD_3OD): 0,94 (t, 3H, $—CH_3$), 1,33 (m, 14H, $—(CH_2)_7—$), 1,49 (2H, $—CH_2—C—C=$), 2,15–2,35 (m, 4H, $—CH_2—C=$, $N^+—C—CH_2—C—SO_3^-$), 2,94 (t, 2H, $—CH_2—SO_3^-$), 3,26 (m, 3H, $N^+—CH_3$), 3,58 (m, 4H, $—CON—CH_2—$), 3,73 (m, 2H, $N^+—CH_2—C—C—SO_3^-$), 3,9–4,2 (m, 4H, $—CON—C—CH_2—N^+$), 6,23 (m, 1H, —CH=C—C=C—CON<), 6,35 (m, 1H, —C=CH—C=C—CON<), 6,53 (d, 1H, —CH—CON<), 7,29 (m, 1H, —CH=C—CON<).

Decyl 2-(dimethylamino)ethyl malonate

31,6 g (0,2 mol) of 1-decanol in 50 mL of dry diethyl ether are slowly added over 2 h to an ice-cold solution of 28,22 g (0,2 mol) of freshly distilled malonyl dichloride in diethyl ether. After stirring the mixture for 14 h at 25 °C, and refluxing it for 2,5 h, the mixture is cooled again with ice. 35,6 g (0,4 mol) of 2-(dimethylamino)ethanol in diethyl ether (100 mL) are added dropwise. After stirring for 12 h more at 25 °C, the precipitate is recovered, treated with 10 wt.-% aqueous Na_2CO_3, and extracted with diethyl ether. The organic phase is separated, dried over $MgSO_4$ and evaporated under reduced pressure. Yield: 9,1 g (15%) yellowish oil, refractive index at 28 °C $n_D^{28} = 1{,}4461$.

^1H NMR (200 MHz, $CDCl_3$): 0,85 (t, 3H, CH_3—), 1,27 (m, 14H, $—(CH_2)_7—$), 1,62 (m, 2H, $—CH_2—C—OOC—$), 2,25 (s, 6H, $—N(CH_3)_2$), 2,55 (t, 2H, $—CH_2—N<$), 3,37 (s, 2H, $—OOC—CH_2—COO—$), 4,10 (t, 2H, $—CH_2—OOC—$), 4,24 (t, 2H, $—COO—CH_2—C—N<$).

1-Decyloxycarbonyl-1-[2-(dimethylamino)ethoxycarbonyl]-2-vinylcyclopropane

In variation of ref.[22], 9,1 g (29 mmol) of decyl 2-(dimethylamino)ethyl malonate and 0,5 mL of nitrobenzene are dissolved in 100 mL of absolute tetrahydrofuran (abs THF) at 25 °C. 6,52 g (58 mmol) of potassium *tert*-butylate are added in small portions, whereupon the mixture warms up gently and turns brownish. The mixture is heated to 60 °C for 30 min, before 6,2 g (29 mmol) of 1,4-dibromobut-2-ene in 100 mL of abs THF are slowly added. After 2 h more at 60 °C and stirring overnight at room temperature, the mixture is decanted, passed over basic Al_2O_3, and the solvent removed under reduced pressure. The residue is dissolved in CH_2Cl_2, extracted with 5 wt.-% of aq. Na_2CO_3, dried over $MgSO_4$ and evaporated. 2 g of crude product are obtained which still contain some starting material. Full separation is tedious and requires repeated purifications by flash-chromatography (eluent $CHCl_3/CH_3OH$ (volume ratio 75/1), to yield a faintly orange oil.

^{1}H NMR (200 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,26 (m, 14H, —$(CH_2)_7$—), 1,45–1,75 (m, —CH_2—C—OOC—, (—OOC)$_2$C—CH_2), 2,21 (s, 6H, —$N(CH_3)_2$), 2,53 (m, 3H, —CH_2—N<, CH—C=C), 4,0–4,3 (m, 4H, —CH_2—OOC—C—COO—CH_2—), 5,05–5,55 (m, 3H, —CH=CH_2).

1-Decyloxycarbonyl-1-[*N,N*-dimethyl-*N*-(3-sulfonatopropyl)-2-ammonioethoxycarbonyl]-2-vinylcyclopropane (**5**)

The monomer is prepared and purified as described for **3**, starting from 350 mg (0,95 mmol) of pure 1-decyloxycarbonyl-1-[2-(dimethylamino)ethoxycarbonyl]-2-vinylcyclopropane and 112 mg (0,92 mmol) of 1,3-propanesultone. Yield: 120 mg (25%) colourless, hygroscopic crystals of complex phase behaviour (liquid-crystalline): k_1 131 k_2 135 LC_1 170 d (see footnote Tab. 1).

$C_{24}H_{43}NO_7S$ (489,67)	Calc.	C 58,87	H 8,85	N 2,86	S 6,55
	Found	C 58,52	H 8,74	N 2,76	S 6,61

Fast atom bombardment (FAB) mass spectrum: Peaks at 490 and 512 $(M + 1)^+$, $(M + 23)^+$.

^{1}H NMR (400 MHz, CD_3OD) 0,94 (t, 3H, CH_3—), 1,34 (m, 14H, —$(CH_2)_7$—), 1,6–1,9 (m, 4H, —CH_2—C—OOC—, (—OOC)$_2$C—CH_2), 2,27 (m, 2H, N^+—C—CH_2—C—SO_3^-), 2,68 (m, 1H, CH—C=C), 2,91 (t, 2H, —CH_2—SO_3^-), 3,23 (m, 6H, —$N^+(CH_3)_2$), 3,66 (m, 2H, —N^+—CH_2—C—C—SO_3^-), 3,79 (m, 2H, —COO—C—CH_2—N^+), 4,05–4,25 (m, 2H, —CH_2—OOC—), 4,6–4,75 (m, 2H, —COO—CH_2—C—N^+), 5,19 (m, 1H, >C—C=CH trans), 5,38 (m, 1H, >C—C=CH cis), 5,54 (m, 1H, >C—CH=C); complex spectrum due to superposition of two diastereomeric pairs (2 chiral carbon atoms in cyclopropane).

N-Decyl-*N*-methyl-2-(vinyloxy)ethylamine

20 g (0,093 mol) of *N*-decyl-*N*-methyl-2-aminoethanol [18] and 0,56 g of mercury(II) acetate are refluxed for 11 days in 40,2 g (0,56 mol) of ethyl vinyl ether under N_2. The mixture is passed over a short column filled with basic Al_2O_3, diluted with dry diethyl ether, and 0,66 g (0,017 mol) of $LiAlH_4$ are added cautiously. When the production of hydrogen gas has finished, the mixture is passed once more over a short column filled with basic Al_2O_3. Evaporation of the solvent yields 11,3 g (45%) of a slightly yellowish oil, refractive index at 23 °C n_D^{23} = 1,4461.

^{1}H NMR (400 MHz, $CDCl_3$): 0,85 (t, 3H, CH_3—), 1,24 (m, 14H, —$(CH_2)_7$—), 1,43 (m, 2H, —CH_2—C—N<), 2,25 (s, 3H, CH_3—N<), 2,26 (t, 2H, —CH_2—N<), 3,12 (t, 2H, >N—CH_2—C—O—), 3,75 (t, 2H, —CH_2—O—), 3,95 (m, 1H, —O—C=CH trans), 4,15 (m, 1H, —O—C=CH cis), 6,45 (m, 1H, —O—CH=).

3-[*N*-Decyl-*N*-methyl-*N*-2-(vinyloxy)ethyl]ammoniopropanesulfonate (**6**)

9,45 g (0,039 mol) of *N*-decyl-*N*-methyl-2-(vinyloxy)ethylamine, 4,64 g (0,039 mol) of 1,3-propanesultone and 1 mL of nitrobenzene are stirred in 90 mL of dry acetonitrile for 36 h under N_2 at 90 °C bath temperature. On cooling, a colourless precipitate is formed, which is recovered and repeatedly recrystallized from acetonitrile. Yield: 6,9 g (50%) of colourless, hygroscopic crystals of m.p. 161 °C.

$C_{18}H_{37}NO_4S$ (363,56)	Calc.	C 59,47	H 10,26	N 3,85	S 8,82
	Found	C 58,73	H 10,00	N 3,99	S 8,89

^{1}H NMR (400 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,70 (m, 2H, —CH_2—C—N^+), 2,21 (m, 2H, N^+—C—CH_2—C—SO_3^-), 2,85 (t, 2H, —CH_2—SO_3^-), 3,16 (s, 3H, —N^+—CH_3), 3,27 (m, 2H, —CH_2—N^+), 3,6–3,9 (m, 4H,

—O—C—CH_2—N^+—CH_2—C—C—SO_3^-), 4,05–4,25 (m, 3H, —CH_2—O—, —O—C=CH trans), 4,31 (m, 1H, —O—C=CH cis), 6,37 (m, 1H, —O—CH=).

Mixture of decyl 2-(dimethylamino)ethyl fumarate and decyl 2-(dimethylamino)ethyl maleate

5,0 g (19,5 mmol) of crude monodecyl maleate (prepared from decanol and maleic anhydride) are reacted in CH_2Cl_2 with 1,74 g (19,5 mmol) of 2-(dimethylamino)ethanol, using 4,4 g (21,4 mmol) of dicyclohexylcarbodiimide and 0,2 g of 4-dimethylaminopyridine[21]. Purification by flash-chromatography (eluent: acetone) yields 3,0 g (45%) of slightly yellow oil, refractive index at 20 °C, n_D^{20} = 1,4600.

According to ^{1}H NMR spectra, the product is an approx. 2 : 1-mixture of the isomeric fumarate and maleate. Partial isomerization is obviously induced by the aminoalcohol, as other esterification techniques yield isomeric mixtures as well (e. g. activation of the monoester by oxalyl chloride, or by 2-chloro-*N*-methylpyridinium chloride/triethylamine[19], or by *p*-toluenesulfonyl chloride/K_2CO_3/phase transfer catalysis[23]).

^{1}H NMR (90 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,70 (m, 2H, —CH_2—C—OOC—), 2,27 (m, 6H, —$N(CH_3)_2$), 2,58 (t, 2H, —CH_2—N<), 4,0–4,35 (m, 4H, —CH_2—OOC—), 6,21 (s, (2/3)H, —OOC—CH=CH—COO— cis), 6,83 (s, (4/3)H, —OOC—CH=CH—COO— trans).

3-{*N*-2-[2-(Decyloxycarbonyl)vinylcarbonyloxy]ethyl-*N*,*N*-dimethylammonio}propanesulfonate (mixutre of trans and cis isomers) (7)

The monomer is prepared and purified as described for **6**, starting from 2,88 g (8,8 mmol) of the mixture of decyl 2-(dimethylamino)ethyl fumarate and decyl 2-(dimethylamino)ethyl maleate with 1,07 g (8,8 mmol) of 1,3-propanesultone. Yield: 2,7 g (68%) of colourless, hygroscopic crystals. Complex phase behaviour (liquid-crystalline), see Tab. 1.

According to ^{1}H NMR and ^{13}C NMR, the product is a mixture of the isomeric fumarate and maleate. In D_2O the ratio of fumarate/maleate was calculated to be approx. 5 : 1 from the integration of the ^{1}H NMR spectrum, in $CDCl_3$ to be approx. 10 : 1.

$C_{21}H_{39}NO_7S$ (449,61)	Calc.	C 56,11	H 8,74	N 3,12	S 7,13
	Found	C 55,52	H 8,60	N 3,24	S 7,18

FD-mass spectrum: Peaks at 450,6 $(M + 1)^+$, 472,7 $(M + Na)^+$.

^{1}H NMR (400 MHz, $CDCl_3$): 0,83 (t, 3H, CH_3—), 1,24 (m, 14H, —$(CH_2)_7$—), 1,64 (m, 2H, —CH_2—C—OOC—), 2,21 (m, 2H, N^+—C—CH_2—C—SO_3^-), 2,86 (t, 2H, —CH_2—SO_3^-), 3,21 (m, 6H, —$N^+(CH_3)_2$), 3,73 (m, 4H, —N^+—CH_2—C—C—SO_3^-), 3,82 (m, 2H, —COO—C—CH_2—N^+), 4,05–4,20 (m, 2H, —CH_2—OOC—), 4,67 (m, 2H, —COO—CH_2—C—N^+), 6,19, 6,42 (d, d, 2 · 0,1H, —OOC—CH=CH—COO— cis), 6,75–6,9 (1,8H, —OOC—CH=CH—COO— trans).

N-Allyldecylamine

45,7 g (0,8 mol) of allylamine and 44,2 g (0,2 mol) of 1-bromodecane are refluxed for 12 h. During the reaction the mixture separates into two phases. After evaporation of the excess allylamine, the residue is extracted with 1 M aqueous NaOH, dried over $MgSO_4$, and distilled in vacuo. Yield: 31,5 g (80%) of colourless liquid, b. p. (0,5 mbar): 105–107 °C, refractive index at 22 °C n_D^{22} = 1,4428.

^{1}H NMR (200 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,42 (m, 2H, —CH_2—C—N<), 2,56 (t, 2H, —CH_2—N<), 3,20 (d, 2H, >N—CH_2—C=), 5,0–5,2 (m, 2H, —C=CH_2), 5,88 (m, 1H, —CH=C).

N-Allyl-*N*-decyl-2-bromoacetamide

23,6 g (0,15 mol) of freshly distilled bromoacetyl chloride are dissolved in 100 mL of CH_2Cl_2. While cooling with ice and purging with N_2, 29,6 g (0,15 mol) of *N*-allyldecylamine in 200 mL of CH_2Cl_2 are added over 2 h. After additional 5 h of stirring at 25 °C, the mixture is passed over neutral Al_2O_3, and the solvent is evaporated. The crude product can be used without further purification. Yield: 47,4 g (80%) of yellowish wax.

N-Allyl-*N*-decyl-2-(dimethylamino)acetamide

5 g (15,7 mmol) of *N*-allyl-*N*-decyl-2-bromoacetamide in 80 mL of ethanol are added to a mixture of 20 mL of 7,9 M (160 mmol) aq. dimethylamine and 20 mL of ethanol. After refluxing for 18 h under N_2, the volatile components are removed in vacuo. The residue is dissolved in diethyl ether, extracted with 1 M NaOH, dried over $MgSO_4$ and evaporated, to yield 3,1 g (70%) yellowish oil.

^{1}H NMR (200 MHz, $CDCl_3$): 0,84 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,49 (m, 2H, —CH_2—C—N<), 2,25 (m, 6H, —$N(CH_3)_2$), 3,06 (m, 2H, >N—CO—CH_2—N<), 3,2–3,35 (m, 2H, —CH_2—N—CO—), 3,9–4,1 (m, 2H, N—CH_2—C=C), 5,0–5,25 (m, 2H, —C=CH_2), 5,65–6,0 (m, 1H, —CH=C); superposition of the cis- and trans amide conformers.

3-[*N*-(*N*-Allyl-*N*-decylaminocarbonylmethyl)-*N*,*N*-dimethylammonio]propanesulfonate (**8**)

The monomer is prepared and purified as described for **6**, starting from 3,12 g (11 mmol) of *N*-allyl-*N*-decyl-2-(dimethylamino)acetamide and 1,34 g (11 mmol) of 1,3-propanesultone. Yield: 2,0 g (47%) colourless, hygroscopic crystals. Complex phase behaviour (liquid-crystalline), see Tab. 1).

$C_{20}H_{40}N_2O_4S$ (404,62)	Calc.	C 59,37	H 9,96	N 6,92	S 7,92
	Found	C 58,55	H 9,68	N 6,74	S 7,93

FD-mass spectrum: Peaks at 405 $(M + 1)^+$, 427 $(M + Na)^+$.

^{1}H NMR (400 MHz, $CDCl_3$): 0,87 (t, 3H, CH_3—), 1,25 (m, 14H, —$(CH_2)_7$—), 1,48 (m, 2H, —CH_2—C—N—CO—), 2,20 (m, 2H, N^+—C—CH_2—C—SO_3^-), 2,85 (t, 2H, —CH_2—SO_3^-), 3,27 (m, 2H, —CH_2—N—CO—), 3,37 (m, 6H, —N^+—CH_3), 3,9–4,05 (m, 4H, —N^+—CH_2—C—C—SO_3^-, —CO—N—CH_2—C=C), 4,40–4,45 (m, 2H, >N—CO—CH_2—N^+), 5,1–5,3 (m, 2H, —C=CH_2), 5,65–5,95 (m, 1H, —CH=C); superposition of the cis- and trans amide conformers.

Initiators

2,2'-Azodiisobutyronitrile (AIBN) recrystallized from diethyl ether, was used as standard initiator. *N*,*N*'-bis(2-hydroxyethyl)-2,2'-azodiisobutyramide "VO86" and the double hydrochloride of *N*,*N*'-dibenzyl-2,2'-azodiisobutyramidine) "VA552", which were used occasionally (see text), were gifts from Wako Fine Chemicals.

Polymer syntheses

Homo- and copolymers were prepared by radical-initiated polymerization, using thermal initiators in water and in ethanol. Procedures and purification of the polymers have been described previously [18]. If not stated otherwise, the samples investigated are prepared using ca. 1 mol-% of AIBN as initiator in a 5 wt.-% solution of the monomers in ethanol.

The polymer poly(**1**) was obtained by UV-irradiation of an ice-cooled 0,25 wt.-% aqueous solution (concentration > critical micelle concentration (CMC)) in presence of 1 mol-% of

AIBN. Precipitating during the reaction, the polymer is recovered, washed, extracted subsequently with hot water and $CHCl_3$, and dried.

Copolymerization of **8** and SO_2 was performed in 0,2 wt.-% aqueous solution (concentration > CMC), as well as in liquid SO_2, as described elsewhere[2, 24, 25].

All purified polymers were free of monomer according to ^1H NMR, FT-IR and thin layer chromatography. Sulfur analysis of the homopolymers according to Schöniger[26] and Fritz[27] gave correct values.

Results and discussion

Monomers

Polymerizable moieties investigated

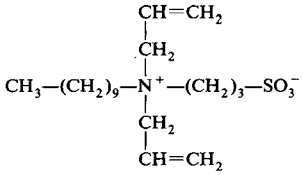
The monomeric surfactants were newly synthesized (except for monomer **9**[18]) and are displayed in *Scheme 2.* They all bear the zwitterionic ammoniopropanesulfonate head group. Diallyl compound **1** is suited for a cyclopolymerization yielding polymers with a C_4-repeating unit containing a pyrrolidine or a piperidine ring[28, 29]. Butadienoyl derivatives **2**–**4** are suited for a 1,4-homopolymerization[30, 31], yielding a C_4-repeating unit as well. The vinylcyclopropane **5** is accessible to a ring-opening homopolymerization, leading to a C_5-repeating unit[32, 33]. Monomers **6**–**8** are suited for alternating copolymerizations: Using electron-poor comonomers, or electron-rich comonomers, respectively, **6** and **7** should yield polymers with defined C_4-repeating units. Monomer **8** is suited for the copolymerization with SO_2 to give an aliphatic polysulfone[2, 34]. Due to the long C—S bonds, the length of the repeating unit of the latter corresponds roughly to a C_4-repeating unit. The acrylamide **9** and its homopolymer are used for reference.

Monomers **1** and **6** have the polymerizable moiety attached to the ammonium moiety of the hydrophilic head group of the surfactant structure ("head"-type, see Fig. 1 a). Monomers **2**–**5** and **7**–**9** have the polymerizable moiety attached in the front part of the hydrophobic chain, thus belonging to the "mid-tail" type geometry (Fig. 1 b). Noteworthy, monomers **4** and **6** are racemic mixtures due to the chiral nitrogen of the ammonium moiety. Monomer **5** is a diastereomeric mixture due to the two asymmetric carbon atoms in the cyclopropane ring; an ^1H NMR spectrum is shown in Fig. 3. Monomer **7** is an approximately 9/1 mixture of the trans and cis isomers.

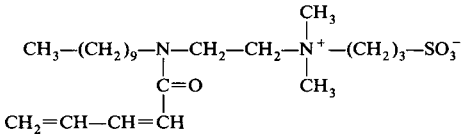
Thermal phase behaviour of the monomers

The often complex phase behaviour of monomers **1**–**9** is listed in Tab. 1. Many of the monomers exhibit thermotropic liquid-crystalline phases, as is evident from their differential thermal calorimetry (DSC) traces (Fig. 4) and from polarization microscopy. Thermotropic mesophases of amphiphiles, and in particular of zwitterionic ones, have been known for long[35], but the accumulation in case of the polymerizable sulfobetaines is noteworthy. Detailed studies of the mesophases have been omitted, due to the thermal decomposition of most monomers in the temperature range of interest. Generally, mesophases seem to be favoured by less symmetrical structures.

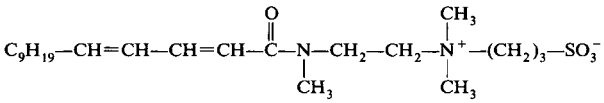
Scheme 2:



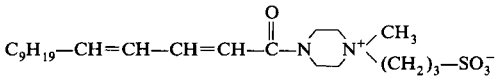
1



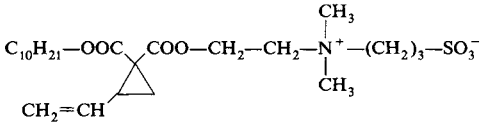
2



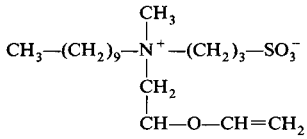
3



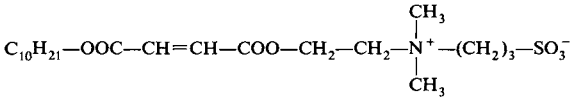
4



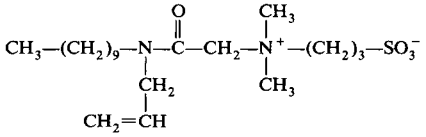
5



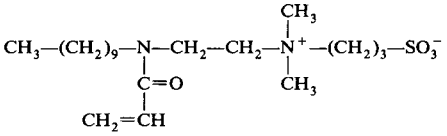
6



7



8



9

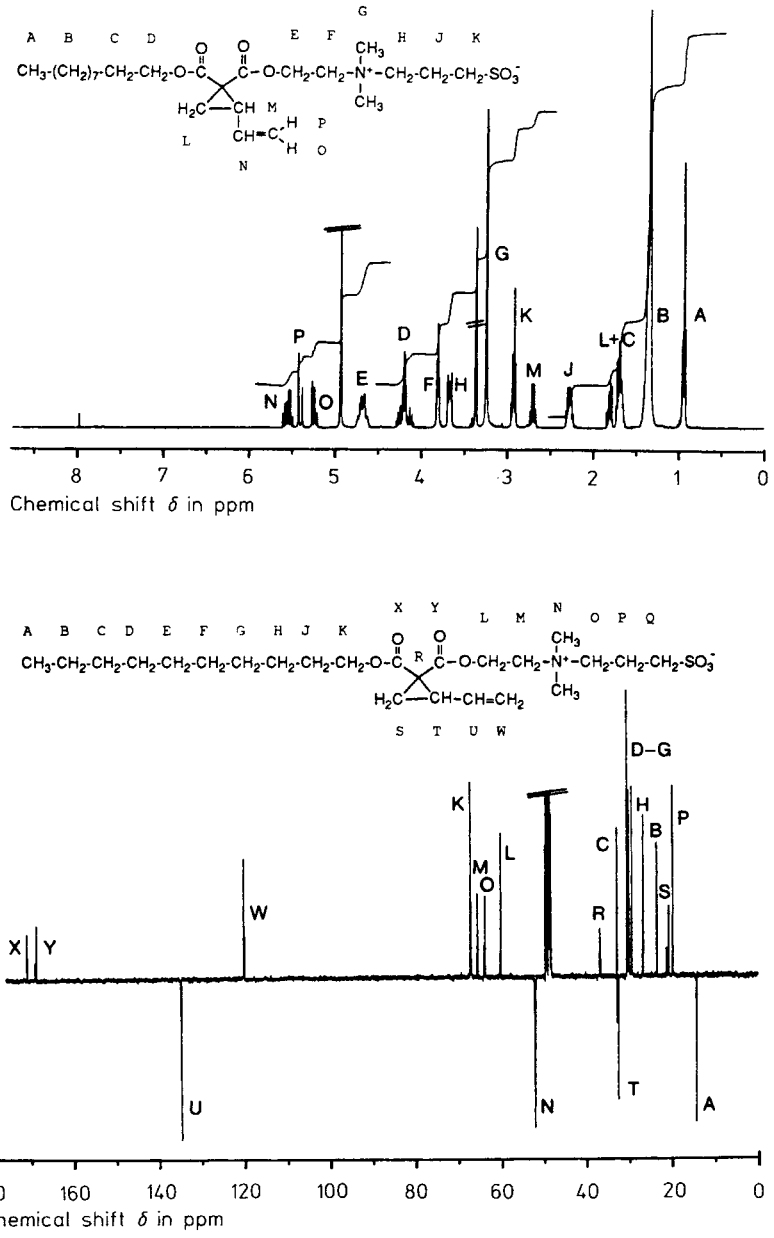


Fig. 3. ^{1}H NMR and ^{13}C NMR spectra (spin-echo) of vinylcyclopropane **5** in CD_3OD. (Signals marked // are signals from the solvent)

Tab. 1. Phase behaviour of sulfobetaine monomers **1–9** studied

Surfactant monomer	Start of thermal decomposition at (°C)	Phase transition[a] temperatures in °C
1	210	k 84 i
2	210	k 80 d
3	210	LC_1 114 LC_2 120 d
4	210	k 180 d
5	170	k_1 129 k_2 135 i
6	170	k 161 i
7	180	k_1 100 k_2 174 LC_1 (191 LC_2 207 i)
8	190	k_1 39 k_2 59 k_3 150 LC 168 i
9	210	k 158 LC 168 i

[a] k = crystalline; LC = liquid-crystalline; i = isotropic; d = decomposition.

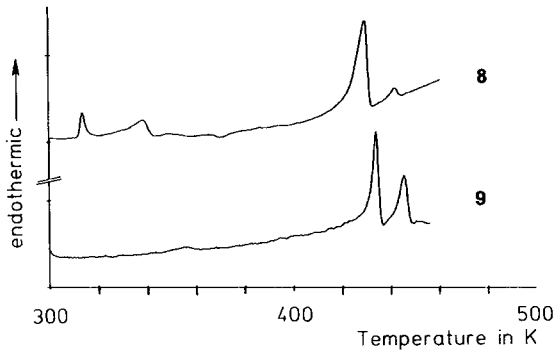


Fig. 4. Differential scanning calorimetry traces of monomers **8** (top) and **9** (bottom), 1st heating cycle

Micellar properties

Monomers **1–3** and **6–9** are water-soluble at 20 °C showing characteristic surfactant properties, e. g. strongly foaming aqueous solutions, and the formation of lyotropic liquid crystals in the concentrated regime. Their fan-shaped textures point to the presence of hexagonal phases, as described previously[1–4]. Monomer **4** has a Krafft-temperature T_K of 47 °C (Tab. 2). The much higher value for T_K of the alicyclic **4** compared to its aliphatic analogue **3** is attributed to the cyclic head group, which presumably enables a better packing of the monomer, in agreement with the increased melting point (Tab. 1). In case of monomer **5**, the high value of T_K = 50 °C is attributed to the ester moiety in β-position, a behaviour which has been discussed for sulfobetaine surfactants previously[1]. The high T_K may result from a specific interaction in the ammonium group and the ester moiety[1,36,37]. Accordingly, a high value of T_K would be expected for monomer **7** as well, but the mixture of trans- and cis-isomer apparently depresses melting point and Krafft-temperature sufficiently to render the monomer water-soluble at room temperature.

Tab. 2. Krafft temperatures (T_K), critical micelle concentrations (CMC) and surface tension at CMC (γ_{CMC}) of monomers **1–9**

Monomer	T_K/°C	CMC		γ_{CMC} mN/m
		(in g/L)	(in mmol/L)	
1	<5	7,1	20	39
2	<20	0,67	1,6	31
3	<20	0,14	0,32	32
4	47			
5	50			
6	<20	3,4	9,4	36
7	<20	0,15	0,33	36
8	<5	1,0	2,5	35
9	<5	0,95	2,4	36

The critical micelle concentrations (CMC) of the monomers are listed in Tab. 2. The values compare well with those of similar sulfobetaine surfactant monomers[1-4]. Within the monomer series, the differences observed are easily rationalized. The "head-type" monomers **1** and **6** have lower CMC than the "mid-tail type" monomers, corresponding to their more "branched" structures. Also, comparing the isomeric dienes **2** and **3**, the "branched" isomer **2** exhibits the higher CMC, as would be expected from standard surfactants. Diene **3** exhibits a lower CMC than its vinyl analogue **9**, in agreement with the increased hydrophobicity, whereas the positional isomers **8** and **9** have nearly identical CMC.

Polymers

Homopolymers prepared

Diallylammonium compounds are known to cyclopolymerize readily[28,29]. But in case of the sulfobetaine **1**, polymerization could not be initiated thermally by AIBN. Polymers were only obtained when the polymerization reaction was performed at low temperatures, i. e. cooling with ice. This may point to a low ceiling temperature, perhaps due to the two bulky substituents. In the IR-spectrum of the polymer, the olefinic signals at 3082 cm^{-1}, 994 cm^{-1} and 956 cm^{-1} of the monomer are missing. In the ^{13}C NMR spectrum in solution, only the carbon atoms far away from the polymer backbone give well resolved, intense signals (Fig. 5b). Characteristically, signals of carbons in the polymer backbone or close to it are missing, or are severely broadened. This behaviour seems to be a characteristic feature of many polymerized surfactants[18], pointing to an immobilization of the fragments attached to the polymer backbone. However, the ^{13}C NMR spectrum in bulk provides well resolved signals of all polymer fragments (Fig. 5). Considering the literature data[29], the positions of the backbone signals point to the dominating formation of five-membered rings. This agrees well with recent studies on polymers of cationic analogues of **1**[38,39].

Dienes **2** and **3** were polymerized thermally using AIBN as initiator, isotropically dissolved in ethanol, as well as under micellar conditions in water. The polymers

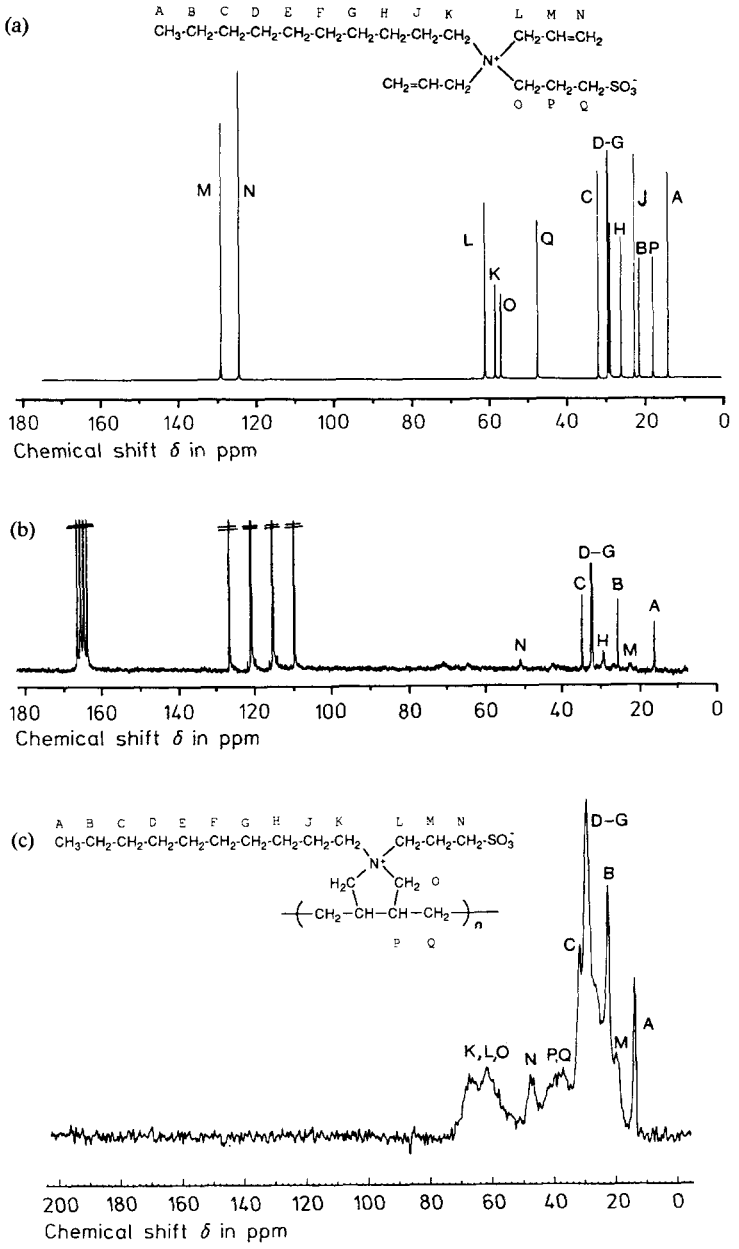


Fig. 5. ^{13}C NMR spectra of: (a) diallyl monomer **1** in D_2O, (b) poly(**1**) in CF_3COOH and (c) poly(**1**) in bulk. (Signals marked with // are signals from the solvent)

obtained by both methods show identical IR-, NMR- and UV-spectra. Diene **4** which does not dissolve notably in water below 50 °C was polymerized only in ethanol. In contrast to dienes **2** and **3**, insoluble polymers were always obtained. The reasons are not clear, but crosslinking side reactions have to be assumed.

To clarify whether the radical polymerization of the dienoyl monomers proceeds via a 1,4- or a 3,4-addition mechanism, the structure of the polymers formed was analyzed by IR-, NMR- and UV-spectroscopy: In the IR-spectra of the polymers, the twin signals at 1650 cm^{-1} and 1620 cm^{-1} (amide I conjugated and in plane (i.p.) ν(C=C)) of the monomers are replaced by a single new signal at 1635 cm^{-1} (amide I, not conjugated) which is found as well in the homopolymer of acrylamide **9**. Further, the signal patterns in the 1000–900 cm^{-1} region of the =CH out of plane (o.o.p.) are changed upon polymerization: Three weak signals at ca. 1000 cm^{-1}, 970–950 cm^{-1} and 920–900 cm^{-1} are replaced by two equally weak signals at ca. 980 cm^{-1} and 920 cm^{-1}. New signals at 800–650 cm^{-1} pointing to newly formed cis double bonds are missing. These observed changes correspond to the ones observed for trans-1,4-polysorbates prepared by group transfer polymerization[40,41].

After polymerization, the ^1H NMR signals of the dienoyl groups have disappeared in the spectra of poly(**2**) and poly(**3**), demonstrating their full conversion (Fig. 6). However, the spectra lack new signals in the 5–6 ppm region which would be expected for a newly formed double bond. These observations are in agreement with previous studies on polymers of long-chain derivatives of sorbic acid (hexa-2,4-dienoic acid)[42]. Also, the ^{13}C NMR spectra in solution lack any signal indicative of double bonds or carbonyl moieties. These findings parallel the missing signals of polymer fragments close to the backbone discussed above for poly(**1**). Hence, no detailed structural information could be gathered from the NMR-spectra.

UV-spectra of monomers **2**–**4** in water or methanol show absorbance maxima of the conjugated amide moieties at 256 nm, 269 nm and 267 nm, respectively. Upon polymerization, the absorbance maxima shift considerably to lower wavelengths, i.e. 205 nm and lower. This corresponds to the UV-spectrum of the analogous polyacrylamide poly(**9**) in methanol, the monomer of which exhibits an absorbance maximum at 234 nm. Therefore the UV-spectra verify the absence of conjugated double bonds in the polymers obtained, in agreement with the IR-spectra. Thus, taking the various spectral data into account, a 3,4-polymerization mechanism can be excluded. At least predominantly, the polymers formed are trans-1,4-polydienes.

The vinylcyclopropane **5** could not be polymerized using AIBN as initiator, neither in ethanol nor in acetonitrile, nor using 2,2′-azobis[*N*-(2-hydroxyethyl)isobutyramide] in water. Difficulties in the polymerization of vinylcyclopropanes with bulky substituents have been mentioned before[43]. Polymer was only obtained using 2,2′-azobis-(*N*-benzylisobutyramidine) dihydrochloride in water under micellar conditions. Since poly(**5**), which precipitates from the solution, is insoluble in all solvents tested, crosslinking has to be assumed, as reported for some vinylcyclopropanes in the past[44]. The FT-IR spectrum of the polymer exhibits only changes in the spectral regions characteristic for olefins: The monomer signals at 990 cm^{-1} (R—CH=CH_2), o.o.p., 1,2 wagging), 960 cm^{-1} and 928 cm^{-1} (=CH_2 o.o.p. wagging) disappear, whereas a new signal at 969 cm^{-1} emerges, pointing to a trans R—CH=CH—R′

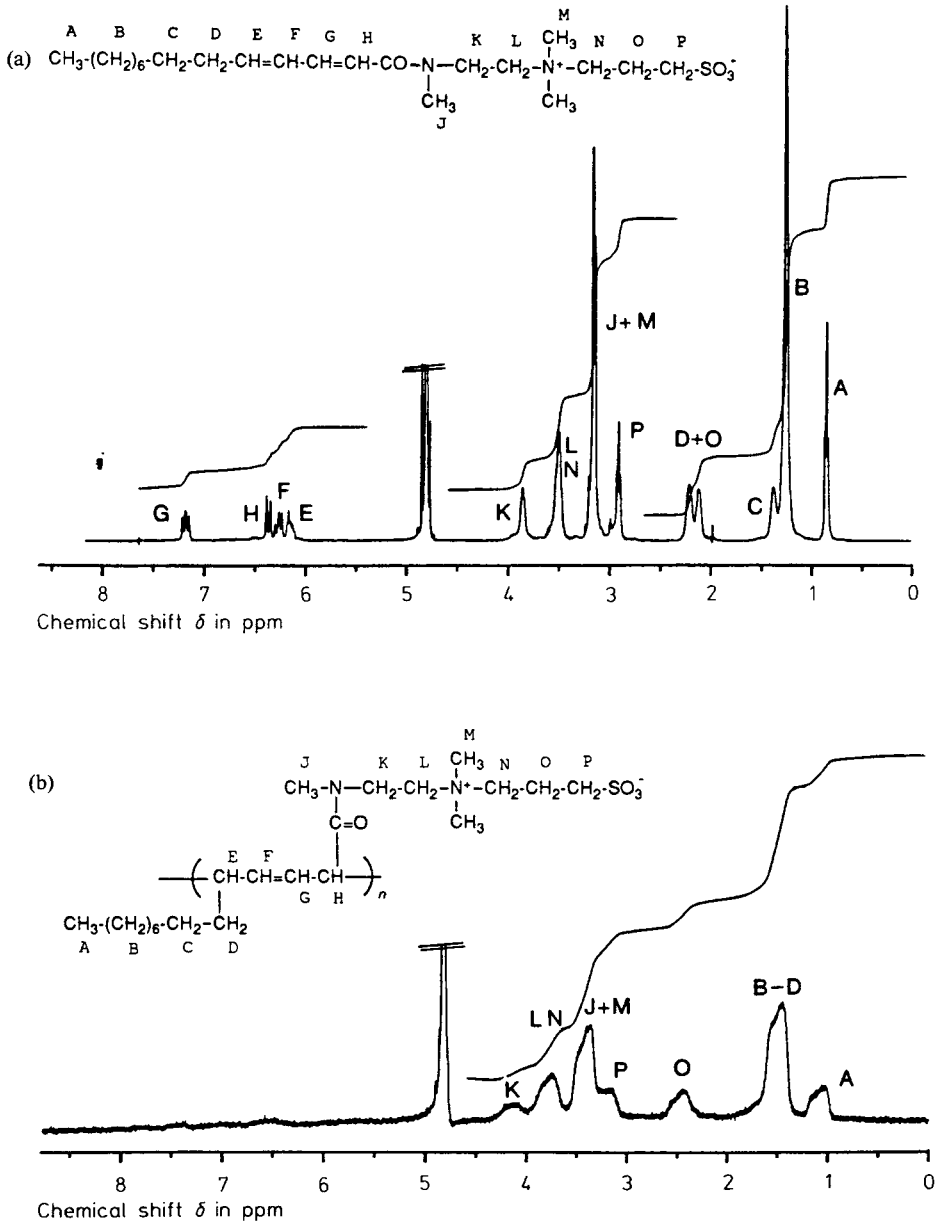


Fig. 6. ^{1}H NMR spectrum of diene **3** in D_2O: (a) monomer, (b) polymer. (Signals marked with // are signals from the solvent)

moiety (o. o. p., 1,2 wagging). These changes are paralleled by the change of the signals of the olefinic C—H stretching modes: The bands at 3087 cm and 3013 cm

(R—CH=CH_2, i.p. ν_{as} and ν_s) disappear, while the band at 3030 cm^{-1} (=CH—, i.p. ν) is retained. These data agree well with the ones reported for the 1,5-polymerization of vinylcyclopropanes by ring-opening, producing a trans R—CH=CH—R′ moiety in the polymer backbone[44,45]. Perhaps, this double bond, or the allylic CH-moieties are responsible for the crosslinking observed.

Molecular weights of the zwitterionic polymers could not be determined satisfactorily. Gel-permeation chromatography studies failed due to adsorption of the polymers onto the column material. Hence, end-group analysis was applied, for a minimal estimate of the molar masses obtained. CN-groups of the initiator AIBN could neither be detected in ^{13}C NMR spectra (no signal at δ = 115–125 ppm) nor in the FT-IR-spectra (no signal at ν = 2260–2240 cm^{-1} (ν, —CN)) of the polymers. As in control experiments 5 mol-% of CN-groups could still be seen easily, the number-average degree of polymerization $\bar{P}_n$ has to exceed 20.

Copolymers prepared

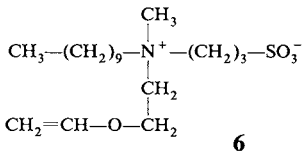
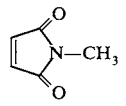
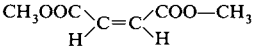
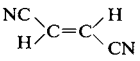
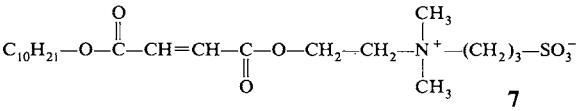
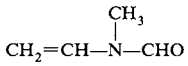
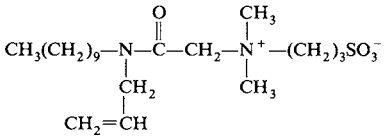
The monomer pairs used to prepare copolymers are listed in *Scheme 3.* The vinylether **6** could be polymerized successfully with *N*-methylmaleimide (**10**) and dimethyl maleate (**11**), to yield the corresponding copolymers copoly(**6**/**10**) and copoly(**6**/**11**). Similarly, monomer **7** and *N*-methyl-*N*-vinylformamide (**13**) were copolymerized to produce copolymer copoly(**7**/**13**).

However, all attempts to prepare a copolymer of **6** and fumaronitrile **12** failed, although octadecyl vinyl ether and fumaronitrile **12** could be copolymerized easily. Perhaps, steric requirements are too high for the rather bulky sulfobetaine vinyl ether **6**.

In case of the allylamide **8**, copolymers copoly(**8**/**14**) with SO_2 could be prepared, but yields are low, even when the copolymerization is performed at low temperatures[24,25]. Because comparable problems were encountered with a related zwitterionic allyl ether previously, but not with zwitterionic terminal olefins[2], the problems may be connected with the allylic group.

IR-spectra of the copolymers show qualitatively, that both monomers are incorporated: The characteristic sulfonate bands at $\nu \approx$ 1200 cm^{-1} and $\nu \approx$ 1045 cm^{-1} are present in all copolymers. For copolymers copoly(**6**/**10**), copoly(**6**/**11**) and copoly(**7**/**13**) additional bands at ν = 1774 cm^{-1} and 1698 cm^{-1} (imide C=O), ν = 1734 cm^{-1} (ester C=O) and ν = 1168 cm^{-1} (amide C=O) appear. In agreement, the ^1H NMR spectra of the copolymers illustrate that both monomers are incorporated at a substantial level (Fig. 7). Unfortunately, the integration of the ^1H NMR spectra is not accurate enough to enable an exact compositional analysis of the copolymers. But elemental analysis of the copolymers indicates that equimolar amounts of both monomers are incorporated (Tab. 3). Because the polymer yields are moderate or low, these results strongly support a strictly alternating structure, as would be expected from the pairs of polymerizable moieties employed[34].

Scheme 3:

Copolymer	Surfactant monomer	Comonomer
copoly(**6**/**10**)	 **6**	 **10**
copoly(**6**/**11**)		 **11**
copoly(**6**/**12**)		 **12**
copoly(**7**/**13**)	 **7**	 **13**
copoly(**8**/**14**)	 **8**	SO_2 **14**

Tab. 3. Yield and composition of copolymers prepared

Copolymer	Surfactant monomer	Comonomer	x_1 [a]	Yield in %	X_1 [b]
copoly(**6**/**10**)	**6**	**10**	0,5	20	0,49
copoly(**6**/**11**)	**6**	**11**	0,5	18	0,52
copoly(**6**/**12**)	**6**	**12**	0,5	—	—
copoly(**7**/**13**)	**7**	**13**	0,5	22	0,50
copoly(**8**/**14**)	**8**	**14** (SO_2)	—	4	0,46

[a] x_1 = Mole fraction of surfactant monomer in monomer feed.
[b] X_1 = Mole fraction of surfactant monomer in copolymer, determined by means of elemental analysis.

Solubility of polymers

The solubilities of the polymers in some standard solvents are listed in Tab. 4. Characteristically for polysulfobetaines, all polymers are insoluble in aprotic or weakly protic solvents, such as tetrahydrofuran, ethyl acetate, acetone, *N,N*-dimethylformamide, dimethyl sulfoxide or $CHCl_3$, but soluble in protic, fluorinated solvents[8,18,46] such as CF_3COOH, neglecting the obviously crosslinked samples of poly(**4**) and

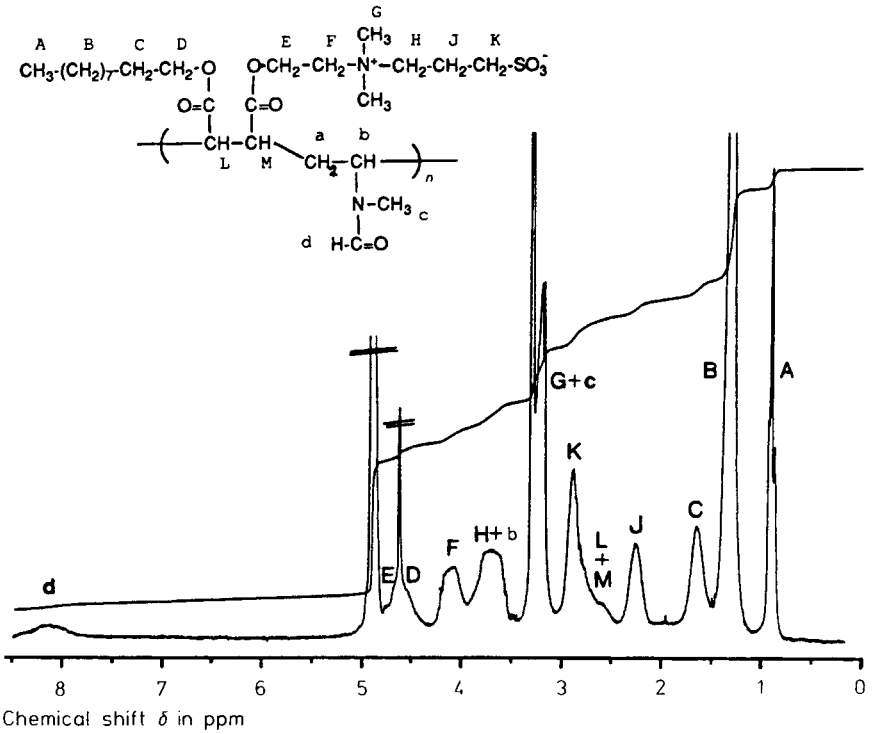


Fig. 7. ^{1}H NMR spectrum of copolymer copoly(**7**/**13**) in hot D_2O. (Signals marked with // are signals from the solvent)

poly(**5**). Looking at the solubilities in more detail, it becomes evident, that all the polymers of "head-type" geometry are insoluble in water. Whereas the copolymers copoly(**6**/**10**) and copoly(**6**/**11**) dissolve in polar aprotic solvents such as formamide, methanol or ethanol, homopolymer poly(**1**), which contains a rather stiff polymer backbone, does not. The situation is different in case of the polymers with "mid-tail" geometry. Having repeating units of C_4 or equivalent length, they are soluble at least in hot water. Most remarkably, the polydienoylamide poly(**2**) (although less hydrophilic from the structural point of view) is soluble in water, in contrast to its polyacrylamide analogue poly(**9**), which is not[18].

These results can be rationalized by a geometrical model proposed recently[1,7]: In vinyl homopolymers, the high density of surfactant side groups blocks their amphiphilic character, due to the mismatch of the diameter of the hydrocarbon chains ($\geq$0,5 nm) and the length of the C_2-repeating unit ($\leq$0,25 nm). Instead of an "amphiphilic" conformation with hydrophilic and hydrophobic ends (Fig. 8a), only a "bottle-brush" conformation can be easily realized (Figs. 8b, c), thus making the end groups of the side chains control the solubility.

I. e., polymerized vinylic surfactants of the "head type" are soluble only in rather unpolar solvents (Fig. 8b), whereas polymerized vinylic surfactants of the "tail-end

Tab. 4. Solubilities in some standard solvents of the polymers prepared[a]

Polymer	Solvent						
	H_2O	$HCONH_2$	CF_3COOH	CH_3OH	C_2H_5OH	$CH_3OH/CHCl_3$[b]	$CHCl_3$
head-type							
poly(**1**)	−	−	+	−	−	−	−
copoly(**6/10**)	−	+	+	+	+	+	−
copoly(**6/11**)	−	+	+	+	+	+	−
mid-tail type							
poly(**2**)	$+^h$	+	+	+	+	+	−
poly(**3**)	+	+	+	+	+	+	−
poly(**4**)[c]	−	−	−	−	−	−	−
poly(**5**)[c]	−	−	−	−	−	−	−
copoly(**7/13**)	$+^h$	+	+	+	+	+	−
copoly(**8/14**)	+	+	+	+	+	+	−
poly(**9**)	−	+	+	+	+	+	−

[a] +: soluble; $+^h$: hot soluble; −: insoluble.
[b] Vol. ratio 1/1.
[c] Crosslinked.

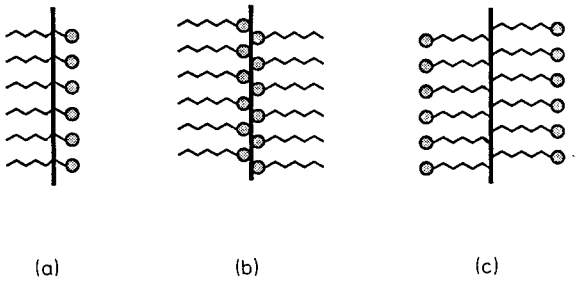


Fig. 8. Ideal conformations of polymerized surfactants:
(a) amphiphilic conformation,
(b) hydrophobic conformation,
(c) hydrophilic conformation

type" are soluble only in water or very polar solvents (Fig. 8c), with little regard to the overall hydrophilic-hydrophobic balance.

The steric problems can be overcome by thinning the density of the side groups, corresponding to the concept of the "main-chain spacers" (Fig. 2b)[7]. In case of sulfobetaines, it was exemplified by statistical copolymers that a C_4/C_5-repeating unit on average is sufficient for copolymers of the "mid-tail type" geometry[7]. However, copolymers of "head-type" geometry require longer average repeating units ($>C_6/C_8$), because the geometric constraints are more severe. Now, the data of Tab. 4 match well with these observations: A defined C_4-repeating unit is indeed sufficient for polymeric surfactants of the "mid-tail type" geometry to provide water-solubility. But it is too short for polymeric surfactants of the "head-type" geometry. Thus, the behaviour of the polymers with a well-defined reduced density of the surfactant side groups corroborates the recent estimation of the minimal length of main-chain spacers in statistical copolymers.

Self-organization of the polymers in aqueous media

Polymers poly(**3**) and copoly(**8/14**) are soluble in water at room temperature. The surface activities correspond to those of other zwitterionic polysoaps[1-3,7]: Both polymers show a slightly increased depression of surface tension γ at low concentrations, but a much lower depression of γ at moderate and high concentrations, compared to their monomers. Further, the depression of γ with increasing concentration exhibits neither a break nor a plateau value indicative of a CMC (Fig. 9). The missing CMC is characteristic for polysoaps, and has been attributed to intramolecular aggregation of the hydrophobic groups in the polymers[6,47].

Both poly(**3**) and copoly(**8/14**) are capable of solubilizing hydrophobic dyes, such as 4-(4-butylphenylazo)-*N,N*-diethylaniline. Solubilization occurs even at concentrations much below the CMC of their monomers, thus supporting the model of intramolecular aggregation of the hydrophobic groups.

Copolymers copoly(**6/10**) and copoly(**6/11**) of the "head-type" geometry are water-insoluble, but soluble in $CH_3OH/CHCl_3$ mixtures which allows spreading experiments[48,49]. Indeed, these polymers form stable insoluble monolayers at the air-water interface (Fig. 10), as reported for some polymerized sulfobetaine surfactants of the "head-type" geometry before[1,4], despite the very hydrophilic head-groups and the very short alkyl chains. In comparison to the analogous vinylic homopolymers[1], the collapse pressures and the collapse areas are increased, and the collapse points are better defined. These improvements agree well with the effect of main-chain spacers on the spreading behaviour of standard amphiphilic polymers with long alkyl chains[50-53]. I.e., although not sufficiently to achieve solubility in water, even short main-chain spacers improve the self-organization behaviour of "head-type" polymerized surfactants.

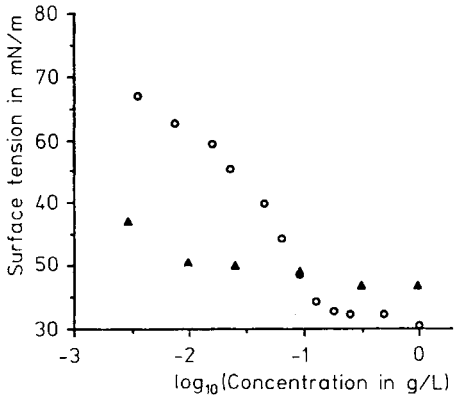


Fig. 9.

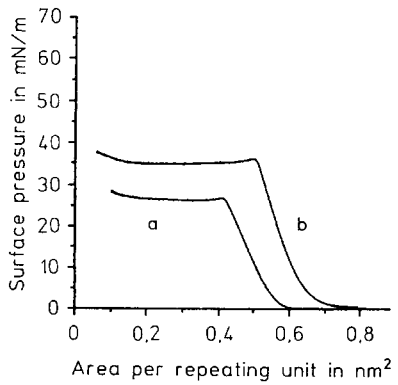


Fig. 10.

Fig. 9. Surface activity of diene **3** (○) and its polymer (△) in pure water, at 25 °C

Fig. 10. Surface pressure versus area diagrams of copolymers copoly(**6/10**) (a) and copoly(**6/11**) (b) at 20 °C (subphase: pure water)

Conclusions

The general geometric requirements for the solubility of polysoaps in water, derived from studies of statistical copolymers, has been corroborated by polymers with well defined reduced density of surfactant side groups. In case of polymers of the "mid-tail" type, a C_4-repeating unit is enough to provide solubility in water, and thus polysoap characteristics. Polymers of "head-type" geometry require longer spacers. Therefore, at medium spacer lengths, they may serve as amphiphilic polymers for the preparation of mono- and multilayers with unusually high contents of hydrophilic groups.

[1] A. Laschewsky, I. Zerbe, *Polymer* **32**, 2081 (1991)
[2] P. Anton, A. Laschewsky, *Makromol. Chem., Rapid Commun.* **12**, 189 (1991)
[3] P. Köberle, A. Laschewsky, T. D. Lomax, *Makromol. Chem., Rapid Commun.* **12**, 427 (1991)
[4] A. Laschewsky, *Colloid Polym. Sci.* **269**, 785 (1991)
[5] U. P. Strauss, "Hydrophobic Polyelectrolytes", in: *"Polymers in Aqueous Media"*, J. E. Glass, Ed., Advances in Chemistry Series No. 223, *Am. Chem. Soc.*, Washington DC, 1989, pp. 317
[6] E. A. Bekturov, Z. Kh. Bakauova, *"Synthetic Water-Soluble Polymers in Solution"*, Hüthig & Wepf, Basel 1986, pp. 178
[7] P. Köberle, A. Laschewsky, D. v. d. Boogaard, *Polymer* **33**, 4029 (1992)
[8] J. C. Salamone, W. C. Rice, "Polyampholytes", in: *Encyclopedia of Polymer Science and Technology"*, 2nd edition, J. I. Kroschwitz, Ed., Vol. 11, 514 pp, Wiley-Interscience, New York 1988, vol. 11, pp. 514
[9] H. Finkelmann, E. Jahns, "Association and Liquid Crystalline Phases of Polymers in Solution", in: *"Polymer Association Structures"*, M. A. El-Nokaly, Ed., *ACS Symp. Ser.* **384**, 1 (1989)
[10] C. M. Paleos, G. Margomenou-Leonidopoulou, A. Malliaris, *Mol. Cryst. Liq. Cryst.* **161**, 385 (1988)
[11] R. Ebelhäuser, H. W. Spieß, *Makromol. Chem.* **188**, 2935 (1987)
[12] T. Fahmy, J. Wesser, H. W. Spieß, *Angew. Makromol. Chem.* **166/167**, 39 (1989)
[13] R. J. Gambogi, F. D. Blum, *J. Colloid Interface Sci.* **140**, 525 (1990)
[14] E. Jahns, H. Finkelmann, *Colloid Polym. Sci.* **265**, 304 (1987)
[15] K. Ito, K. Tanaka, H. Tanaka, G. Imai, S. Kawaguchi, S. Itsuno, *Macromolecules* **24**, 2348 (1991)
[16] A. Laschewsky, *Colloid Polym. Sci.* **269**, 785 (1991) and P. Köberle, A. Laschewsky, D. v. d. Boogaard, *Polymer* **33**, 4029 (1992) and references therein
[17] O. Albrecht, *Thin Solid Films* **99**, 227 (1983)
[18] A. Laschewsky, I. Zerbe, *Polymer* **32**, 2070 (1991)
[19] K. Saigo, M. Usui, K. Kikuchi, E. Schimada, T. Mukaiyama, *Bull. Chem. Soc., Jpn.* **50**, 1863 (1977)
[20] H. Ringsdorf, H. Schupp, *J. Macromol. Sci., Chem.* **A15**, 1015 (1981)
[21] B. Neises, W. Steglich, *Angew. Chem.* **90**, 556 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 522 (1978)
[22] R. W. Kierstead, R. P. Linstead, B. C. L. Weedon, *J. Chem. Soc.* **1952**, 3610 (1952)
[23] Z. M. Jászay, I. Petneházy, L. Töke, *Synthesis* **1989**, 745 (1989)
[24] D. Braun, R. P. Herr, N. Arnold, *Makromol. Chem., Rapid Commun.* **8**, 359 (1987)
[25] Z. Florjanczyk, E. Zygadlo, *Polymer* **32**, 2853 (1991)
[26] W. Schöniger, *Mikrochim. Acta* **1956**, 869 (1956)
[27] J. S. Fritz, S. S. Yamamura, *Analyt. Chem.* **27**, 1461 (1955)
[28] G. B. Butler, R. J. Angelo, *J. Am. Chem. Soc.* **79**, 3128 (1957)
[29] J. E. Lancaster, L. Baccei, H. P. Panzer, *J. Polym. Sci., Polym. Lett. Ed.* **14**, 549 (1976)

[30] A. Matsumoto, A. Horie, T. Otsu, *Makromol. Chem., Rapid Commun.* **12**, 681 (1991)
[31] E. Tsuchida, E. Hasegawa, N. Kimura, M. Hatashita, C. Makino, *Macromolecules* **25**, 207 (1992)
[32] W. J. Bailey, "Ring-opening Polymerization", in: *"Comprehensive Polymer Science"*, G. Allen, Ed., Pergamon Press, Oxford, UK 1989, Vol. 3, pp. 283
[33] H. K. Hall, jr., L. G. Snow, "Ring-opening Polymerizations via Carbon-Carbon σ-Bond Cleavage", in: *"Ring-opening Polymerization"*, K. J. Ivin and T. Saegusa, Eds., Elsevier, London 1984, Vol. 1, pp. 83
[34] G. M. Cowie, Ed., *"Alternating Copolymers"*, Plenum Press, New York 1985
[35] D. Demus, H. Demus, H. Zaschke, *"Flüssige Kristalle in Tabellen"*, Bd. 1 and 2, VEB Verlag für Grundstoffchemie, Leipzig 1974/1984
[36] H. Ringsdorf, D. Thunig, *Makromol. Chem.* **178**, 2205 (1977)
[37] S. K. Abid, S. M. Hamid, D. C. Sherrington, *J. Colloid Interface Sci.* **120**, 245 (1987)
[38] Y. J. Yang, J. F. B. N. Engberts, *J. Org. Chem.* **56**, 4300 (1991)
[39] C. H. Do, G. B. Butler, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **30**(2), 352 (1989)
[40] W. R. Hertler, T. V. Rajan Babu, D. W. Overnall, G. S. Reddy, D. S. Sogah, *J. Am. Chem. Soc.* **110**, 5841 (1988)
[41] A. Laschewsky, M. D. Ward, *Polymer* **32**, 146 (1991)
[42] A. Laschewsky, H. Ringsdorf, *Macromolecules* **21**, 1936 (1988)
[43] T. Endo, M. Watanabe, K. Suga, T. Yokozawa, *Makromol. Chem.* **190**, 691 (1989)
[44] I. Cho, K. D. Ahn, *J. Polym. Sci., Polym. Chem. Ed.* **17**, 3169 (1979)
[45] T. Endo, K. Suga, *J. Polym. Sci., Part A: Polym. Chem.* **27**, 1831 (1989)
[46] V. M. Monroy Soto, J. C. Galin, *Polymer* **25**, 121 (1984)
[47] H. E. Jorgensen, U. P. Strauss, *J. Phys. Chem.* **65**, 1873 (1961)
[48] G. L. Gaines, jr., *"Insoluble Monolayers at the Liquid-Gas Interfaces"*, Interscience Publishers, New York 1966
[49] G. L. Gaines, jr., *Langmuir* **7**, 834 (1991)
[50] P. Hodge, E. Khoshdel, R. H. Tredgold, A. J. Vickers, C. S. Winter, *Br. Polym. J.* **17**, 368 (1985)
[51] W. Frey, J. Schneider, H. Ringsdorf, E. Sackmann, *Macromolecules* **20**, 1312 (1987)
[52] M. B. Biddle, J. B. Lando, H. Ringsdorf, G. Schmidt, J. Schneider, *Colloid Polym. Sci.* **266**, 806 (1988)
[53] T. L. Penner, J. S. Schildkraut, H. Ringsdorf, A. Schuster, *Macromolecules* **24**, 1041 (1991)