Self-organization of hydrophobized polyzwitterions*

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Several series of copolymers of different geometry were synthesized from zwitterionic surfactant monomers and polar non-ionic comonomers. Bulk properties were investigated by d.s.c. and X-ray scattering. The copolymers were amorphous, but exhibited superstructures up to high comonomer contents. Solubility of the copolymers was determined as a function of geometry and composition. From the results, a main chain spacer model has been derived. All water-soluble copolymers exhibited characteristic features of classical polysoaps, as shown by surface tension measurements and by solubilization of pyrene. But gradual differences depending on the polymer geometry were observed for the solubilization sites.

(Keywords: copolymer; spacer group; micelle)

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 polysoap[5], as they may combine the behaviour of ionic and non-ionic polysoaps advantageously[1,2].

However, as shown for several series of isomeric monomers, the water-solubility of polymers obtained from reactive surfactants bearing a vinyl group is controlled by their molecular geometry[1] (*Figure 1*). If the surfactant structure is bound to the polymer backbone via the end of the hydrophobic tail ('tail end' type, *Figure 1c*), the polymers are generally water-soluble, but insoluble in most organic solvents. In contrast, if the surfactant structure is bound to the polymer backbone via the hydrophilic head group ('head' type, *Figure 1a*), polymers are soluble in rather unpolar solvents such as ethanol or chloroform/methanol mixtures, but are insoluble in water. If the surfactant structure is bound to the polymer backbone via the front part of the hydrophobic tail ('mid-tail' type, *Figure 1b*), an intermediate solubility is observed[1].

This behaviour seems not to be restricted to zwitterionic polymers, but to be general for all polymerized surfactants based on vinyl monomers[6–10]. It may be rationalized by simple geometric considerations: to provide good amphiphilic properties, as observed for the monomers, all surfactant side chains have to be arranged at one side of the polymer backbone (*Figure 2a*). However, the C_2-repeat unit of a vinyl polymer backbone ($\sim$2.5 nm) is much shorter than the diameter of an alkyl chain ($\sim$5 nm), as well as of the hydrophilic head group. Hence, the 'amphiphilic' conformation cannot be realized efficiently. Instead, a brush-like conformation is preferred, with the terminal groups of the side chains outside (*Figures 2b,c*). Such a 'core–shell' conformation would easily account for the observed effects of polymer geometry on the solubility. This model implies that only vinyl homopolymers of the tail end type yield useful polysoaps, in agreement with the literature[1–13].

However, in tail end polysoaps there are indications that the emulsifying properties are restricted[2,11], presumably due to the 'immobilization' of the hydrophobic chains by the polymer backbone[12,13]. In polymers of the mid-tail and head types, the hydrophobic chains should be much more mobile and thus might be better suited for efficient solubilization[2]. But their insolubility in water prevents the comparison.

The spacer model[14] in polysoaps

To overcome these problems, and to combine water-solubility and solubilization power, we have investigated the effect of spacer groups in polymerized surfactants. As side-chain spacers (*Figure 3a*) such as oligoethyleneglycols were not successful[15], we have studied the effect of main chain spacers (*Figure 3b*), i.e. the effect of thinning the density of the surfactant side chains at the polymer backbone. The most convenient approach to such polymers with main chain spacer is the statistical copolymerization of surfactant monomers of the head or mid-tail type with polar comonomers[16].

Empirically, such copolymers have been successfully applied as polysoaps[17–19], including, for example, the widely used alternating copolymers of maleic anhydride and vinylethers[5]. The water-insolubility of fully alkylated poly(vinylpyridine)s, but the polysoap behaviour of partially alkylated ones[20,21] may be rationalized analogously. But systematic studies on the minimum and maximum length of the main chain spacer are scarce, and geometric effects of the surfactant side chains have not been considered yet.

As the minimum spacer length should also depend on the bulkiness of the head group, we have focused on zwitterionic polysoaps with the ammonio-propane-

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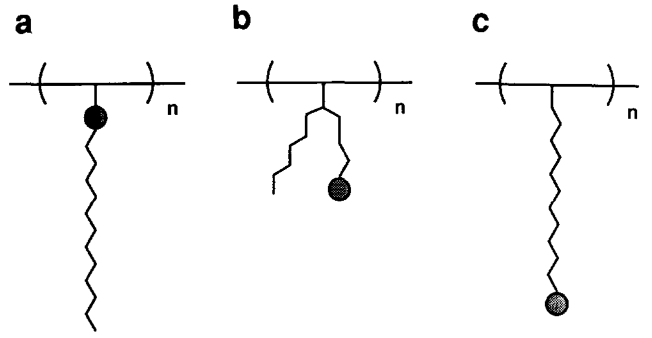


Figure 1 Scheme of geometries in polymerized surfactants: (a) head type; (b) mid-tail type; (c) tail end type

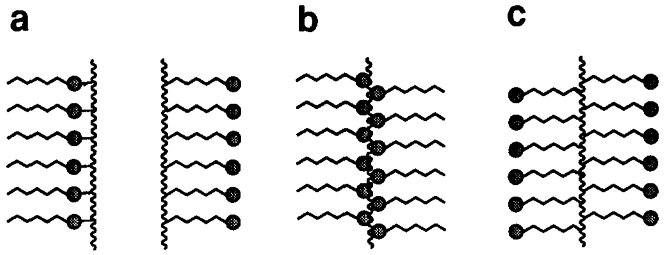


Figure 2 Scheme of conformations of polymerized surfactants: (a) amphiphilic conformations; (b) hydrophobic conformation; (c) hydrophilic conformation

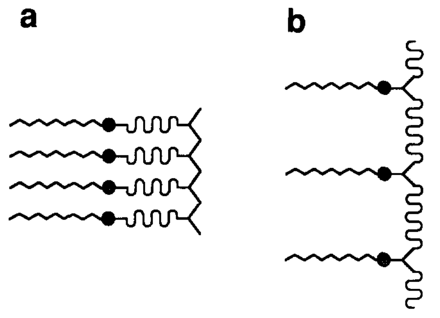


Figure 3 Scheme of spacer groups[14,16] in polymerized surfactants: (a) side chain spacer; (b) main chain spacer

sulphonate head group (sulphobetaine). One cationic analogue, monomer *1*, is used as reference to distinguish effects particular to polyzwitterions for general polysoap properties. One water-soluble polysoap homopolymer of the tail end type, poly-5, is also included for comparison. Only non-ionic or zwitterionic hydrophilic comonomers were used for the copolymerization with the surfactant monomers, in order to keep the charge neutrality of the individual polymer chains. Thus the potential advantages of zwitterionic polysoaps ae preserved. The comonomers *II–VI* differ in hydrophilicity, size and H-bonding capability. Furthermore, only monomer pairs with identical polymerizable moieties were used, in order to approach ideal copolymerization, and thus to minimize the chemical heterogeneity of the copolymers obtained. The monomer pairs chosen and the copolymers synthesized with their notations are shown in *Table 1*. Surfactants *1–3* represent head type monomers, surfactant *4* mid-tail type monomers, and surfactant *5* tail end type monomers. Surfactants *3–5* are isomers, i.e. they have identical hydrophilic, hydrophobic and polymerizable moieties, but different geometries.

EXPERIMENTAL

Materials

All solvents used were distilled prior to use, or were analytical grade. Acetonitrile was dried over 3 Å molecular sieves. Tetrahydrofuran (THF) was distilled over potassium. 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). Melting points were uncorrected.

Monomers

2-Methacryloylethyl trimethyl ammonium bromide *I* (cholinmethacrylate) was a gift from B. Schlarb. Commercially available comonomers *II*, *III*, *IV* and *V* were purified prior to use: *N*,*N*-dimethyl-*N*-2-methacryloylethyl-3-ammonio propane sulphonate *II* (Raschig) was recrystallized from ethanol. Hydroxyethylmethacrylate *III* (Fluka) was distilled under reduced pressure. *N*,*N*-dimethylacrylamide *IV* (Fluka) was purified by filtration through a column of neutral Al_2O_3 (Merck, activity 1). Acrylamide *V* (Merck) was recrystallized from $CHCl_3$.

N-(*trishydroxymethyl*)*methyl-acrylamid* VI. As a modification to the original procedure[22], 24.2 g (0.2 mol) of dried (trishydroxymethyl)aminomethane was suspended in 200 ml anhydrous CH_3CN. While cooling with ice and stirring vigourously, a solution of 9 g (0.1 mol) acryloylchloride in 30 ml CH_3CN was added over 4 h. The mixture was allowed to reach room temperature, then filtered. The precipitate was refluxed in 400 ml CH_3CN adding 0.2 ml nitrobenzene, and filtered off hot. The combined filtrates were evaporated, yielding 12.6 g of crude product (m.p. 132°C). As small amounts of (trishydroxymethyl)methylammonium hydrochloride could not be removed by repeated recrystallization, the crude product was purified by flash chromatography (silicagel, eluent ethanol).

Yield: 9.9 g (57%) colourless crystals, m.p. 136°C (lit[22]. 131–133°C).

Elemental analysis ($C_7H_{13}NO_4$): calcd: C = 47.99%, H = 7.48%, N = 8.00%; found: C = 47.90%, H = 6.95%, N = 8.04%.

^1H n.m.r. (in D_2O): δ (in ppm) = 3.77 s (6H, $-C(CH_2-O-)_3$), 5.72 m (1H, $=CH-CON$), 6.25 m (1H, $CH=C-CON$ *cis*), 6.75–6.84 m (1H, $CH=C-CON$ *trans*).

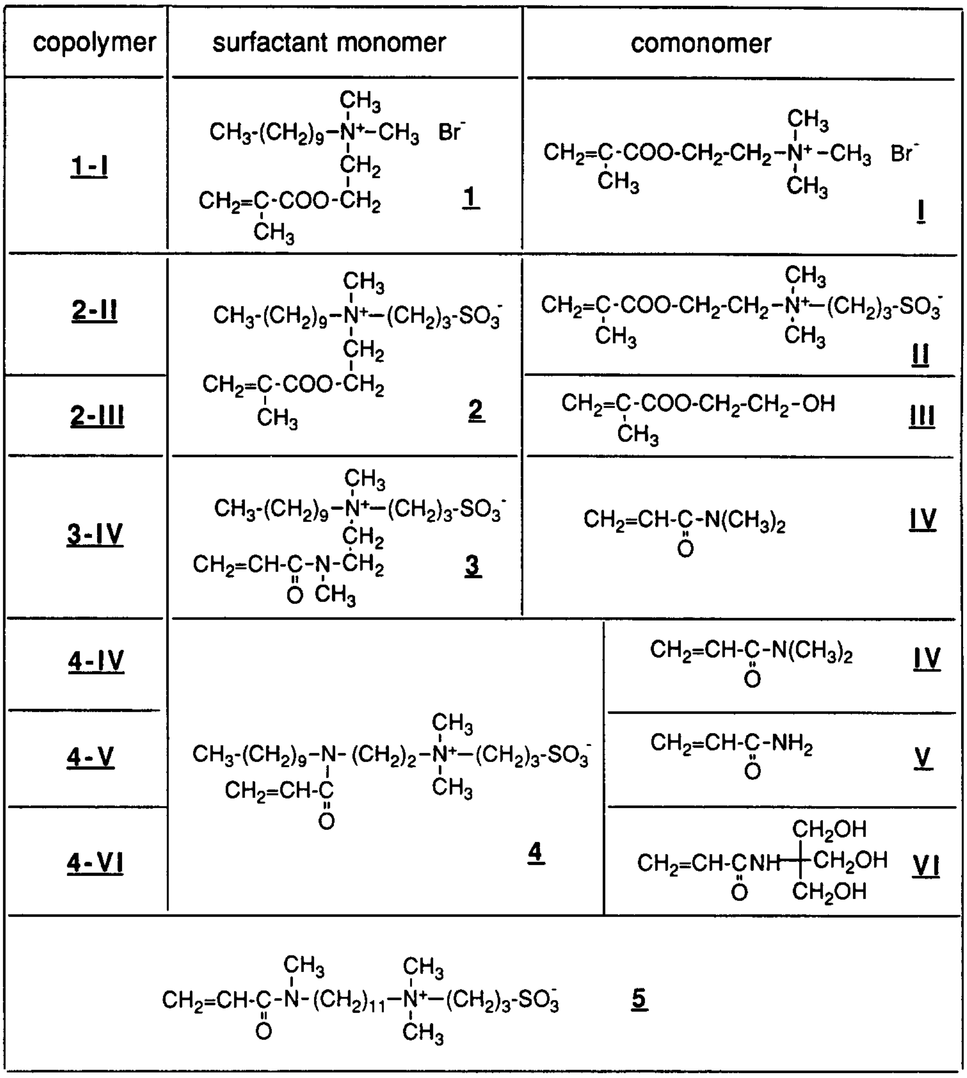
^{13}C n.m.r. (in D_2O): δ (in ppm) = 61.3 (CH_2-OH), 62.9 ($-NH-C$), 128.2 ($=CH-$), 131.0 ($CH_2=$), 169.5 ($-C=O$).

Surfactant monomers

Synthesis and characterization of the surfactant monomers *1–4* have been described elsewhere[1]. Monomer *5* was synthesized as follows.

11-Bromoundecanoic acid-N-*methyl amide*. 11-Bromoundecanoylchloride (103.7 g, 0.37 mol), prepared from undecanoic acid and $SOCl_2$ by a standard procedure[23],

Table 1 Monomer pairs used and copolymers synthesized



was dissolved in 250 ml anhydrous ether. The solution was slowly dropped into 82 ml (0.97 mol) of 11.85 M aqueous methylamine while cooling with ice. The mixture was filtered, the precipitate collected, washed with water and ether and dried *in vacuo*.

Yield: quantitative, colourless waxy crystals, m.p. 55°C.

*11-(Dimethylamino)undecanoic acid-*N*-methyl amide.* Crude 11-bromoundecanoic acid-*N*-methyl amide (18 g, 0.065 mol) was suspended in 40 ml (0.32 mol) of 7.9 M aqueous dimethylamine. After addition of 3 g (0.075 mol) NaOH in 70 ml ethanol, the mixture was refluxed for 7 days under nitrogen. The solvent was removed, the residue suspended in 200 ml dry acetone, the solution filtered, and the filtrate evaporated.

Yield: 9.7 g (60%) slightly yellow wax, m.p. 45°C.

*11-Methylaminoundecyl-*N,N*-dimethyl-1-amin.* Absolute THF (100 ml) was cautiously added to 3.2 g (0.084 mol) of $LiAlH_4$. While cooling, a solution of 24.7 g (0.1 mol) crude 11-(dimethylamino)undecanoic acid-*N*-methyl amide in 150 ml THF was added dropwise. When the addition was complete, the mixture was stirred for 30 min at 20°C, and refluxed for another 7 days under nitrogen. Then, 2 g ethyl acetate was added. The mixture was decomposed with 7.5 ml water while cooling and stirring, and allowed to settle overnight. The precipitate was removed by filtration, extracted twice with 200 ml boiling THF, and filtered again. The combined filtrates were evaporated, and the residue distilled *in vacuo*.

Yield: 7 g (30%) colourless oil, $n_D^{21} = 1.4519$.

^1H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 1.1–1.3 m (14H, $-(CH_2)_7-$), 1.35–1.5 m (4H, $-CH_2-C-N-$), 2.1–2.2 m (8H, $-CH_2-N(CH_3)_2$), 2.36 s (3H, $>N-CH_3$), 2.49 t (2H, $-CH_2-N<$ sec amine).

N*-Methyl,*N*-11-(dimethylamino)undecyl acrylamide.* 11-Methylaminoundecyl-1-amin (3 g, 0.013 mol) was dissolved in 50 ml anhydrous CH_2Cl_2. After adding 1.4 g powdered Na_2CO_3 and a few drops of nitrobenzene, 1.2 g (0.013 mol) of acryloylchloride (Merck, stabilized with 0.1% CuCl) in 50 ml anhydrous CH_2Cl_2 was added slowly, while stirring and cooling. The mixture was refluxed for an additional 3 h. The mixture was extracted twice with half-saturated aqueous Na_2CO_3. The organic phase was separated and dried over $MgSO_4$, yielding 2.8 g of crude product. Purification by chromatography on basic Al_2O_3 (Merck, activity 1, 70–230 mesh ASTM), eluent CH_2Cl_2.

Yield: 1.6 g (43%) slightly yellow viscous oil.

^1H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 1.1–1.3 m

(14H, $-(CH_2)_7-$), 1.3–1.6 m (2H, $-CH_2-C-N-$), 2.1–2.2 m (8H, $-CH_2-N(CH_3)_2$), 2.95 s/3.05 s (3H, $-CO-N(CH_3)$ *trans/cis* conformers), 3.2–3.45 m (2H, $-CON-CH_2-$ *trans/cis* conformers), 5.55–5.65 m (1H, $CH{=}C-CON-$ *trans*), 6.2–6.35 m (1H, $CH{=}C-CON-$ *cis*), 6.45–6.65 m (1H, $=CH-CON-$).

*3-*N*-(11-(*N'*-methylacrylamido)undecyl-*N,N*-dimethyl)-ammonio propane sulphonate* 5. *N*-methyl,*N*-11-(dimethylamino)undecyl acrylamide (1.5 g, 0.0053 mol), 0.64 g (0.0052 mol) propanesultone and two drops of nitrobenzene were refluxed in 40 ml anhydrous acetonitrile for 48 h under nitrogen. The solution was evaporated, extracted several times with diethylether and purified by flash chromatography on silicagel, eluent $CHCl_3/CH_3OH$, 4/1 by vol.

Yield: 1.3 g (60%) hygroscopic, waxy crystals, m.p. 51°C.

Elemental analysis ($C_{20}H_{40}N_2O_4S \times H_2O$): calcd: C = 56.84%, H = 10.02%, N = 6.29%, S = 7.54%; found: C = 56.57%, H = 9.98%, N = 6.59%, S = 7.71%.

^1H n.m.r. (400 MHz, D_2O): δ (in ppm) = 1.2–1.4 m (14H, $(CH_2)_7-$), 1.59 m (2H, $-CH_2-C-N-CO-$), 1.77 m (2H, $-CH_2-C-N^+-$), 2.22 m (2H, $N^+-C-CH_2-C-SO_3$), 2.97 m (3.6H, $-CH_2-SO_3$, $-CON(CH_3)$ *trans*), 3.05–3.12 m (7.4H, $-N^+-CH_3$, $-CON(CH_3)$ *cis*), 3.25–3.35 m (2H, $-CH_2N^+$), 3.35–3.5 m (4H, $-CON-CH_2-$, $-N^+-CH_2-C-C-SO_3$), 5.77 m (1H, $CH{=}C-CON$ *trans*), 6.13 m (1H, $CH{=}C-CON-$ *cis*), 6.73 m (1H, $=CH-CON-$).

The complexity of the spectrum is due to the overlay of the amid *cis–trans* conformers (~55% *cis*, 45% *trans*).

Polymers

The preparation of homopolymers poly-1–poly-4 has been described previously[1]. Analogously, copolymers were obtained by free radical polymerization of 2 wt% ethanolic solutions of the chosen mixtures of surfactant monomer and comonomer. In the case of copolymers with hydroxyethylmethacrylate *III*, isopropanol was used as solvent instead of ethanol. The solutions were purged with nitrogen for 30 min, sealed and reacted for 12–18 h at 60°C, using 1–2 mol% azobis(isobutyronitrile) (AIBN) as initiator. The copolymers produced were worked up depending on their solubilities. Ethanol-insoluble polymers were repeatedly extracted with ethanol, filtered off and washed. Otherwise, the reaction mixtures were concentrated and precipitated into a large excess of dry acetone. Mixtures containing high fractions of *N,N*-dimethylacrylamide *IV* were precipitated into diethylether/acetone, 1/1 by vol. The precipitates were filtered off, or centrifuged, and washed. Finally, all polymers were dissolved or suspended in water, and lyophilized. The purified polymers were free of residual monomer according to thin layer chromatography, *FT*i.r. and ^1H n.m.r.

Methods

N.m.r. spectra were recorded on an Aspect 3000 spectrometer (400 MHz, Bruker). Sulphur content was analysed according to Schöniger[24] and Fritz and Yamamura[25]. Thermogravimetry was performed on a Perkin–Elmer TGS-2 thermogravimetric analyser, with a heating rate of 10°C min^{-1} in nitrogen. D.s.c. was performed with a Perkin–Elmer DSC2, with heating and cooling rates of 20°C min^{-1}. The glass transition temperature, T_g, was determined by the inflection point (mid-point) method from heating cycles[26]. X-ray scattering experiments were carried out with a Siemens Kristalloflex diffractometer, using the Ni-filtered Cu-Kα line ($\lambda = 0.1541$ nm). Surface tensions were measured with a Lauda tensiometer, at 25°C. Fluorescence spectra of pyrene were taken with a Spex spectrograph, exciting at 334 nm.

RESULTS AND DISCUSSION

Copolymer composition

The composition of the zwitterionic copolymers was analysed using elemental analysis, ^1H n.m.r. spectroscopy and *FT*i.r. spectroscopy. For the sulphobetaine homopolymers, elemental analysis is only reliable for sulphur, therefore copolymer compositions were calculated from sulphur contents. Determination by ^1H n.m.r. is rather inaccurate due to the complexity of the spectra, in particular when one component is strongly dominant in the copolymer. Analysis by *FT*i.r. spectra is restricted to copolymers whose parent homopolymers have characteristic isolated and narrow bands.

As shown in *Table 2*, the compositions derived by the different analytical techniques are in good agreement. The compositions of the monomer feeds and of the resulting purified copolymers compare rather well. Even at intermediate conversions, and at monomer feeds containing a large surplus of the hydrophilic comonomers, the copolymer compositions correspond roughly to the composition of the monomer feed. Accordingly, the goal of ideal copolymerization, and thus low chemical heterogeneity of the copolymers prepared, is realized at least in good approximation. Only in the case of copolymers *4-VIa* and *4-VIb*, where a tertiary acrylamide is copolymerized with a secondary one, could the raw copolymer obtained be split into two fractions of slightly different composition (*Table 2*).

Thermal properties

The homopolymers[1] and copolymers are colourless, brittle and hygroscopic solids. When stored under ambient conditions ~5% water is taken up, and up to ~10% in the case of the copolymers with *II*. The bound water is reversibly removed by prolonged exposure *in vacuo*, or heating to 100–120°C in dry nitrogen. Thermogravimetry under nitrogen shows decomposition starting at ~180°C for the poly(methacrylate)s, and at ~200°C for the poly(acrylamide)s, thus corresponding to standard acrylic polymers.

As reported previously[1], no thermal transition can be detected by d.s.c. for the dry homopolymers between −70°C and 180°C. The same is true for the copolymer series *2-II* with zwitterionic comonomers, for series *4-V* and *4-VI* with strongly H-bonding comonomers, and the cationic series *1-I*. In contrast, some of the copolymers with hydroxyethyl methacrylate *II* and dimethylacrylamide *IV* show a T_g which shifts to lower temperatures with increasing comonomer content (*Table 3*). The T_g values of the pure homopolymers poly-III and poly-IV compare well with the literature[27,28]. The decrease of T_g with increasing comonomer content is illustrated for the copolymer series *3-IV* in Figure 4. The endothermal onset at 470 K for poly-3 is not significant, since thermal decomposition is starting. Accordingly, the various

Table 2 Composition of the zwitterionic copolymers, determined by elemental analysis, ^1H n.m.r. and *FT*i.r. spectroscopy

					Mole fraction surfactant monomer incorporated in copolymer		
Copolymer	Surfactant monomer	Copolymer	Mole fraction surfactant monomer in monomer feed	Yield (%)	Elemental analysis	N.m.r.	*FT*i.r.
1-Ib	1	I	0.33	74	0.40	0.4	0.44^a
1-Ic	1	I	0.17	80	0.17	0.15	0.18^a
1-Id	1	I	0.09	77	0.10	0.1	0.08^a
2-IIb	2	II	0.34	72	0.31		0.40^a
2-IIc	2	II	0.18	79	0.22		0.20^a
2-IId	2	II	0.09	55	0.11		0.12^a
2-IIIb	2	III	0.34	68	0.41	0.4	0.37^a
2-IIId	2	III	0.09	42	0.14	0.15	0.17^a
3-IVa	3	IV	0.49	43	0.56	0.5	0.48^b
3-IVb	3	IV	0.33	42	0.39	0.4	0.34^b
3-IVc	3	IV	0.16	43	0.16	0.2	0.17^b
3-IVd	3	IV	0.09	80	0.09	0.1	0.08^b
4-IVa	4	IV	0.50	60	0.42	0.5	0.46^b
4-IVb	4	IV	0.33	52	0.33	0.4	0.45^b
4-IVc	4	IV	0.17	60	0.24	0.2	0.25^b
4-IVd	4	IV	0.09	31	0.12	0.1	0.08^b
4-Va	4	V	0.50	22	0.44	0.5	
4-Vb	4	V	0.33	28	0.32	0.35	
4-Vc	4	V	0.17	68	0.24	0.2	
4-Vd	4	V	0.09	67	0.13	0.1	
4-VIa	4	VI	0.33	50	0.29	0.4	0.42^c
4-VIb	4	VI	0.33	16	0.25	0.3	0.32^c
4-VIc	4	VI	0.16	79	0.18	0.15	0.17^c
4-VId	4	VI	0.09	76	0.09	0.1	0.08^c

I.r. bands used (in cm^{-1}): ^{a}2925/1730; ^{b}1640/1045; ^{c}2925/1045

Table 3 Glass transition temperatures, T_g, of some zwitterionic copolymers, determined by d.s.c.

Polymer	Mole fraction of surfactant monomer	T_g (°C)
Poly-2	1	–
2-IIIb	0.41	–
2-IIId	0.14	124
poly-III	0	107
poly-3	1	–
3-IVa	0.56	169
3-IVb	0.39	153
3-IVc	0.16	119
3-IVd	0.09	110
poly-IV	0	105
poly-4	1	–
4-IVa	0.42	180
4-IVb	0.33	167
4-IVc	0.24	124
4-IVd	0.12	111
poly-IV	0	105

sulphobetaine homopolymers should exhibit T_gs beyond their decomposition temperatures. By reducing the density of the ionic groups, or by distorting their packing, T_g is substantially lowered, as demonstrated before for related poly(sulphobetaine)s[29,30].

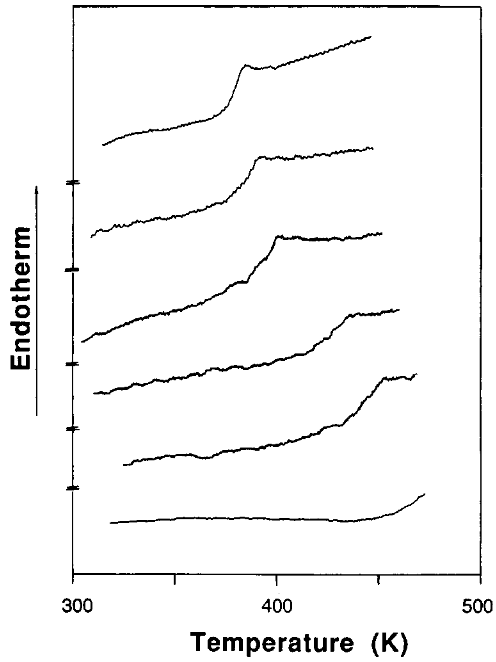


Figure 4 D.s.c. curves of the copolymer series *3-IV*: heating cycles. Top to bottom: poly-IV; *3-IVd*; *3-IVc*; *3-IVb*; *3-IVa*; poly-3

X-ray scattering

The sulphobetaine surfactant homopolymers were shown to be amorphous, but exhibited superstructures[1]. These were attributed to the presence of the surfactant side chains, with extended hydrophobic and ionic regions. The detailed structure of the diffraction pattern depends on the polymer geometry, as shown before. Poly-1–poly-4 produce the pattern characteristic of head and mid-tail type polymers, exhibiting one intense small angle peak at about 2.5°. Poly-5 shows a diffraction pattern characteristic of the tail end type polymers, exhibiting two peaks of medium intensity at 3.1° and 5.7°, with the latter being more intense (*Table 4*).

Powder diffractograms of the copolymers also show their non-crystalline nature. Bragg peaks, indicative of superstructures, are often found too. In all these cases, the general scattering pattern of the parent homopolymer of the head and mid-tail type is preserved, showing one intense small angle peak between 2.5° and 3.5° for 2θ, and an intense halo in the wide angle region aroung 19° (*Table 4*). Considering the d.s.c. data of *Table 3*, it is seen that some copolymers simultaneously exhibit a superstructure and a T_g, hence the two processes do not interfere with each other.

Comparing copolymers of a given series, the Bragg peak is found to lose intensity with increasing comonomer content, and finally vanishes, as shown in *Figure 5* for copolymer series *4-IV*. It is noteworthy that the Bragg peak is more easily lost for the methacrylate copolymers *1-I–2-III*. Furthermore, comparison of the isomeric series *3-IV* and *4-IV* suggests that the Bragg peaks are more easily lost for head type copolymers than for the mid-tail type. The position of the Bragg peak varies somewhat with changing comonomer content, but there is no simple correlation. A maximum for the *d*-spacing seems to exist at intermediate comonomer contents, in particular in the case of the methacrylate copolymer series, but this point needs further investigation.

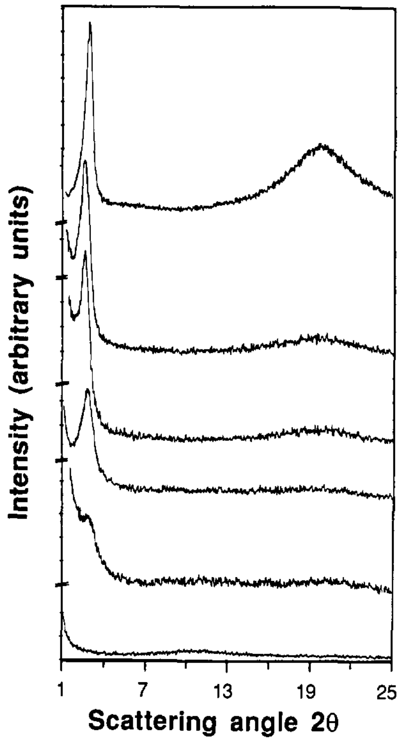


Figure 5 X-ray powder diffractograms of copolymer series *4-IV*. Top to bottom: poly-4; *4-IVa*; *4-IVb*; *4-IVc*; *4-IVd*; poly-IV

Table 4 X-ray scattering data of the zwitterionic copolymers at 300 K

Polymer	Mole fraction of surfactant monomer	Bragg peak[a]		Halo	
		2θ (degrees)	*d* (nm)	2θ (degrees)	*d* (nm)
poly-1	1	3.3	2.7	19.8	0.45
1-Ib	0.40	2.4	3.6	19.6	0.45
1-Ic	0.17	–	–	19.6	0.45
1-Id	0.10	–	–	19.6	0.45
poly-2	1	3.4	2.6	19.4	0.45
2-IIb	0.50	3.5	2.5	18.6	0.48
2-IIc	0.20	–	–	18.6	0.48
2-IId	0.12	–	–	18.5	0.48
2-IIIb	0.43	2.4	3.7	18.4	0.48
2-IIId	0.13	–	–	18.4	0.48
poly-2	1	3.3	2.7	19.8	0.45
2-IIIb	0.40	2.4	3.6	19.6	0.45
2-IIc	0.17	–	–	19.6	0.45
2-IId	0.10	–	–	19.6	0.45
poly-3	1	3.4	2.6	19.5	0.45
3-IVa	0.56	3.2	2.8	19.5	0.45
3-IVb	0.39	3.2	2.8	19.5	0.45
3-IVc	0.16	3.5	2.5	19.6	0.45
3-IVd	0.09	+			
poly-4	1	3.0	2.9	19.8	0.45
4-IVa	0.42	2.7	3.3	19.7	0.45
4-IVb	0.33	2.7	3.3	20.1	0.44
4-IVc	0.24	2.9	3.1	20.0	0.44
4-IVd	0.12	3.0	2.9	20.0	0.44
4-Va	0.44	2.8	3.2	19.7	0.45
4-Vb	0.32	2.9	3.1	19.8	0.45
4-Vc	0.24	3.2	2.8	19.8	0.45
4-Vd	0.09	3.3	2.7	19.7	0.45
4-VIa	0.29	2.7	3.3	19.4	0.46
4-VIb	0.25	2.9	3.1	19.0	0.47
4-VIc	0.18	2.9	3.0	19.0	0.47
4-VId	0.13	–	–	19.0	0.47
poly-5	1	3.1, 5.7	2.8, 1.5	19.8	0.45

[a] +, shoulder visible; –, no small angle peak observed

Solubility of polymers

The solubilities of the homopolymers in some standard solvents are listed in *Table 5*. The results show the characteristic geometry-controlled solubility of surfactant vinyl homopolymers: poly-1–poly-3 (head type) dissolve only in rather unpolar solvents, the isomeric poly-5 (tail end type) dissolves in water and formamide, and isomeric poly-4 (mid-tail type) shows an intermediate solubility behaviour[1].

All homopolymers of the 'spacer' comonomers chosen are water-soluble, with the known exception of poly-III[31] (the samples prepared here were insoluble in all solvents tested, presumably due to crosslinking[31]). But only the polycation poly-I and the tertiary polyacrylamide poly-IV are soluble in less polar solvents than formamide. In particular the latter, which lacks charges or strong H-bonding, has a broad range of possible solvents including $CHCl_3$.

The solubilities of the copolymers in some standard solvents are listed in *Table 6*. In agreement with the water-insolubility of their parent homopolymers (poly-2 and poly-III) the copolymer series *2-III* is water-insoluble at all compositions studied. As for the other copolymers,

Table 5 Solubility of zwitterionic and polar homopolymers in some standard solvents: +, soluble; −, insoluble

Polymer	H_2O	$HCONH_2$	CH_3OH	C_2H_5OH	CH_3OH/ $CHCl_3$ (1/1 by vol)	$CHCl_3$
poly-1[a]	−	−	+	+	+	+
poly-2[a]	−	−	−	+	+	−
poly-3[a]	−	−	−	+	+	−
poly-4[a]	−	+	+	+	+	−
poly-5	+	+	−	−	−	−
poly-I	+	+	+	−	+	−
poly-II	+	+	−	−	−	−
poly-III[b]	−			+		−
poly-IV	+	+	+	+	+	+
poly-V	+	+	−	−	−	−
poly-VI	+	+	−	−	−	−

[a] Data taken from ref. 1
[b] Data taken from ref. 31

Table 6 Solubility of zwitterionic and polar copolymers in some standard solvents: +, soluble; −, insoluble

Polymer	H_2O	2% aq. NaI	$HCONH_2$	CH_3OH	C_2H_5OH	CH_3OH/ $CHCl_3$ (1/1 by vol)	$CHCl_3$
1-Ib	+	−	+	+	+	+	−
1-Ic	+	−	+	+	+	+	−
1-Id	+	−	+	+	+	+	−
2-IIb	−	−	+	−	−	−	−
2-IIc	−	+	+	−	−	−	−
2-IId	−	+	+	−	−	−	−
2-IIIb	−	−	+	−	−	+	−
2-IIId	−	−	+	−	−	+	−
3-IVa	−	−	+	+	+	+	−
3-IVb	−	−	+	+	+	+	−
3-IVc	+	+	+	+	+	+	+
3-IVd	+	+	+	+	+	+	+
4-IVa	+	+	+	+	+	+	−
4-IVb	+	+	+	+	+	+	−
4-IVc	+	+	+	+	+	+	+
4-IVd	+	+	+	+	+	+	+
4-Va	−	+	+	+	−	+	−
4-Vb	−	+	+	+	−	+	−
4-Vc	−	+	+	−	−	−	−
4-Vd	−	+	+	−	−	−	−
4-VIa	−	+	+	−	−	−	−
4-VIb	+	+	+	−	−	−	−
4-VIc	+	+	+	−	−	−	−
4-VId	+	+	+	−	−	−	−

with increasing comonomer content they become soluble in increasingly polar solvents such as water, brine or formamide. This might have been expected from the solubilities of the homopolymers poly-I, poly-II and poly-IV–poly-VI (*Table 5*). However, a detailed examination reveals some important differences between the individual copolymers.

(i) Whereas the cationic copolymers *1-I*, representing the head type, become soluble in plain water, the analogous copolymer series *2-II* with sulphobetaine comonomer is not water-soluble. This can be attributed to strong attractive forces between the zwitterionic groups. However, at high comonomer contents series *2-II* becomes soluble in brine, whereas the cationic analogues *1-I* are not, demonstrating once more the salting-in of polyzwitterions, and salting-out of polycations[4,32–35]. The cationic series is soluble in aqueous media when the surfactant monomer content is reduced to about 0.4, whereas for the zwitterionic series *2-II* the surfactant content has to be considerably smaller, i.e. below 0.2 (*Tables 2* and *6*).

(ii) Also representing head type copolymers, series *3-IV*, which contains the tertiary acrylamide, is soluble in plain water when the surfactant content is reduced to 0.2 (*Tables 2* and *6*). No difference was observed between solubility in water and in brine. Most noteworthy, the improved solubility in water is paralleled by an improved solubility in $CHCl_3$.

(iii) Representing mid-tail type copolymers, series *4-IV*, which contains tertiary acrylamide, is soluble in plain water when the surfactant monomer content is reduced below 0.5, whereas series *4-V* with acrylamide is not water-soluble at all (*Tables 2* and *6*). However, both series are soluble in concentrated aqueous solutions of strongly interacting salts such as 2% aqueous NaI (2% aqueous NaCl is not a solvent for series *4-V*). Such behaviour corresponds to the high Krafft temperatures observed for low molecular weight zwitterionic surfactants, particularly when containing primary or secondary amide moieties[2]. Similar selective salting-in effects have been observed previously for zwitterionic polysoaps[4].

(iv) In contrast to series *4-IV* and *4-V* which are soluble in aqueous media at surfactant contents below 0.5, copolymer series *4-VI*, with the secondary acrylamide *VI*, is soluble in water only at surfactant contents smaller than 0.3.

(v) comparing the isomeric copolymer series *3-IV* of the head type and *4-IV* of the mid-tail type, the latter is water-soluble at higher surfactant monomer contents, i.e. at ~0.5 compared to 0.2. But both series become soluble in $CHCl_3$ at roughly the same content of comonomer *IV*.

Evaluating these differences, it is first of all obvious that zwitterionic comonomers such as *II*, or strongly H-bonding comonomers such as *V*, are poorly suited to achieve solubility of the zwitterionic copolymers in plain water, although they are useful in brine. The best performance is observed for the tertiary acrylamide *IV*.

Second, both analogous copolymer series of the head type, *2-II* and *3-IV*, start to become soluble in 2% aqueous NaI at about the same ratio of monomer surfactant to polar comonomer (i.e. about 1:4), despite the different hydrophilicities of the comonomers used. Similarly, comparing series *4-VI* and *4-IV*, which employ the identical surfactant monomer *4*, higher contents of the more hydrophilic comonomer *VI* are required to render the copolymers water-soluble, compared to the less hydrophilic comonomer *IV* (*Tables 2* and *6*). Therefore, the primary effect of the comonomer cannot be improved hydrophilicity. In contrast, copolymer series *3-IV* and *4-IV* are apparently more hydrophobic than their parent homopolymer(poly-4) as they are soluble in $CHCl_3$ at high comonomer contents. Still, they become more soluble in water with increasing comonomer content as well.

Accordingly, the effect of the comonomers is a steric rather than a polar one. The behaviour may be rationalized with the spacer model sketched in *Figure 3*, considering the comonomers as 'spacer' units. The incorporation of small comonomers provides the space required for the surfactant side chains to adapt an efficient amphiphilic conformation (*Figure 2a*), shielding the hydrophobic chains from contact with water molecules. Thus solubility in water is achieved.

This model also accounts for the polymer geometry effects observed. Mid-tail copolymers require less comonomer, i.e. shorter spacers, to become water-soluble than their head type isomers, because they need less space to adopt an optimized amphiphilic conformation, presenting their hydrophilic head groups at the outside. The model explains too, why roughly equivalent fractions of comonomer are needed to achieve solubility in aqueous media for such different systems as copolymers *2-II* and *3-IV*. For a given head group, i.e. the sulphobetaine, comparable spacer lengths are required to gain enough space to realize an amphiphilic conformation. Within this line, even the observed differences in water-solubility of the cationic and zwitterionic copolymer analogues *1-I* and *2-II* may be understood. They may reflect the larger size of the sulphobetaine head group, requiring a longer spacer to realize a sufficiently amphiphilic conformation.

The spacer model would explain most of the literature data on soluble polysoap copolymers as well. For example, the success of the classical polysoaps poly(maleate-*alt*-vinylether)[36–40] can be understood by the most advantageous combination of favourable geometry (mid-tail type), of small head group and of small spacer comonomer. On the other hand, the low maximum surfactant content of polysoap copolymers of the diallylammonium type[19] can be understood by the unfavourable combination of head type geometry, of bulky head group and of rigid, bulky spacer comonomer.

Surface activity

The comonomers *I–VI* are only barely surface active. In contrast, the surfactant monomers used are true surfactants, and as such they show a critical micelle concentration (CMC) (*Table 7*). Accordingly, the plot of surface tension *versus* the logarithm of concentration shows a continuous decrease, with a break point at the CMC, above which the surface tension stays constant (*Figures 6* and *7*). Because of the high Krafft temperature in water[2], the CMC of sulphobetaine *2* was determined in 0.1 M aqueous NaBr. Due to the salting-in of zwitterions, the value found should be slightly higher than expected in pure water. The CMC value of 0.69×10^{-2} mol l^{-1} is lower than that of its cationic analogue *1* (1.7×10^{-2} mol l^{-1}), indicating a lower hydrophilicity of the zwitterionic head group, in agreement with the literature[41]. Furthermore, comparing

Table 7 Critical micelle concentrations (CMC) of monomers *1–5* in water at 25°C

Monomer	CMC (g l^{-1})	CMC (mol l^{-1})	γ_{min} (mN m^{-1})
1	6.3 (5.0[b])	1.7×10^{-2}	34
2[a]	2.8	0.69×10^{-2}	35
3	5.7 (4.3[b])	1.4×10^{-2}	40
4	0.95(0.8[b])	0.24×10^{-2}	36
5	31	7.7×10^{-2}	35

[a] At 25°C in 0.1 M NaBr

[b] By pyrene label

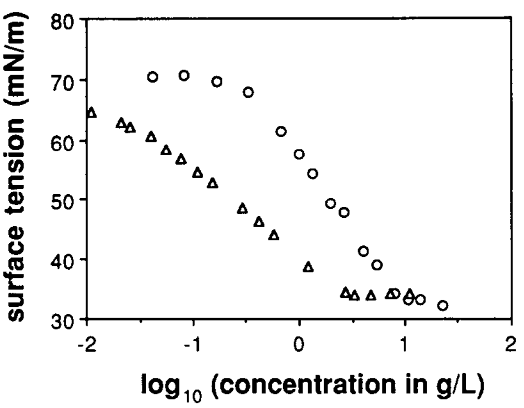


Figure 6 Surface activity of monomers *1* (○) in water and *2* (△) in 0.1 M aqueous NaBr at 25°C

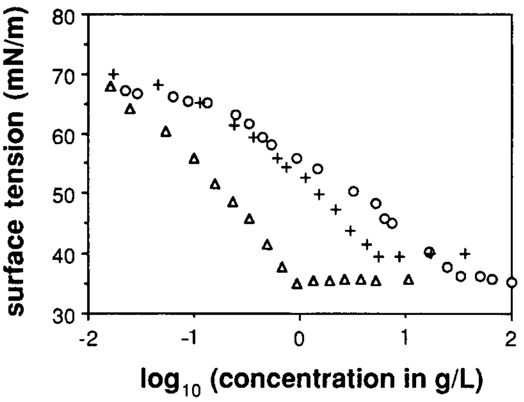


Figure 7 Surface activity of monomers *3* (+), *4* (△) and *5* (○) in water at 25°C

analogous sulphobetaine monomers, the CMC of the methacrylate *2* is only half the CMC of the acrylamide *3*, demonstrating the inherent hydrophilicity of the tertiary[42] acrylamide moiety.

The CMC values of *Table 7* compare well with those of related compounds, except for monomer *5* of the tail end type. Zwitterionic *5* shows a high CMC of 7.7×10^{-2} mol l^{-1} which is well above the CMCs of the head and mid-tail type isomers *3* and *4*. This result was unexpected, as for analogously built cationic and anionic acrylamides much lower CMCs of about 5×10^{-3} mol l^{-1} have been reported[7,43]. Also, for analogous acrylate and methacrylate sulphobetaine surfactants, tail end isomers have considerably lower CMCs than the head type isomers, in analogy to straight chain and branched chain surfactants[2]. The unusual behaviour of the isomeric acrylamides *3*–*5* is attributed to the combination of the weakly hydrophilic tertiary acrylamide with the moderately hydrophilic sulphobetaine head group[44], as discussed above. In the case of the tail end isomer *5*, the separated amide moiety competes successfully as hydrophilic head group with the sulphobetaine group, resulting in an unsymmetric bola amphiphile with high CMC. In contrast, in the head type monomer *3* and in the mid-tail monomer *4*, the acrylamide is attached close to the sulphobetaine moiety, thus enabling standard surfactant behaviour with a much lower CMC.

The surface activity of the water-soluble copolymers and of poly-5 is illustrated in *Figures 8–10*. All zwitterionic polymers show a moderate surface activity. However, the decrease occurs linearly, and no break point indicative of a CMC is visible. Such behaviour is characteristic of polysoaps[45]. Within a given copolymer series, there is no significant difference between samples of different surfactant monomer content (*Figures 8* and *9*). Also, copolymer series *4-IV* and *4-VI*, which contain different comonomers, behave nearly the same. There is also no significant difference between isomeric copolymers *3-IV* and *4-IV* of the head and mid-tail type, respectively (*Figures 8* and *9*), and between these copolymers and the tail end homopolymer poly-5. Hence, the moderate surface activity seems to be a characteristic feature of the sulphobetaine type polysoaps[2–4].

As for the zwitterionic copolymers, there is no indication of a CMC for the cationic copolymers *1-I* (*Figure 10*). But the cationic copolymers become increasingly surface active with increasing content of surfactant monomer. This behaviour corresponds to the increased surface activity of cationic polysoaps upon addition of salt[4,45]. Both phenomena may be explained by a decreased hydrophilicity of the polymers, due to enhanced amounts of hydrophobic chains, or due to the suppressed dissociation of the counterions, respectively.

Solubilization of pyrene

Polysoaps are characterized by their ability to solubilize hydrophobic molecules in water (hence the name)[5]. If the water-soluble homo- and copolymers prepared are indeed polysoaps, they must be capable of solubilization. This was investigated for the acrylamide-based polymers

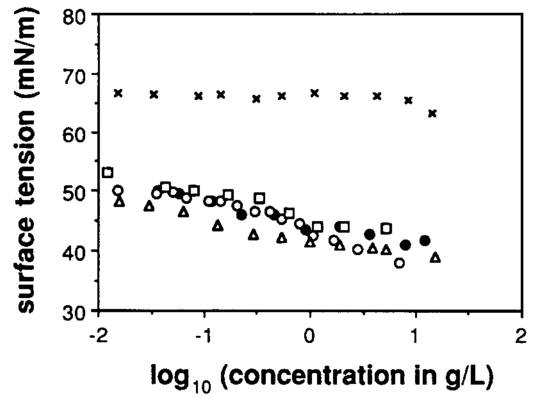


Figure 8 Surface activity of copolymer series *4-IV*. □, *4-IVa*; ●, *4-IVb*; △, *4-IVc*; ○, *4-IVd*; ×, poly-IV

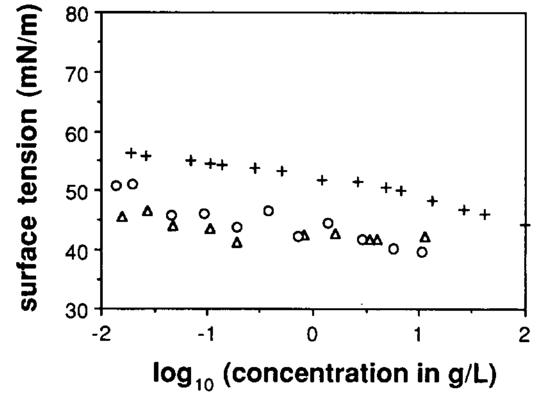


Figure 9 Surface activity of copolymer series *3-IV*. △, *3-IVc*; ○, *3-IVd*; +, poly-5

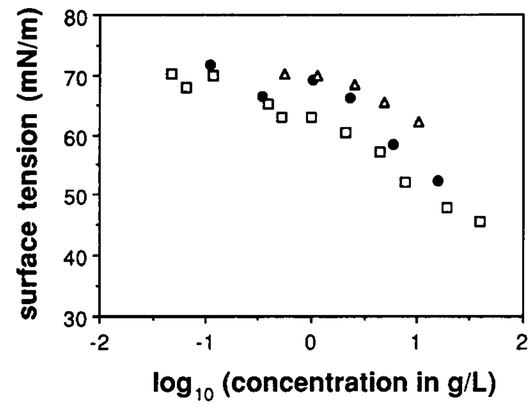


Figure 10 Surface activity of copolymer series *1-I*. □, *1-Ib*; ●, *1-Ic*; △, *1-Id*

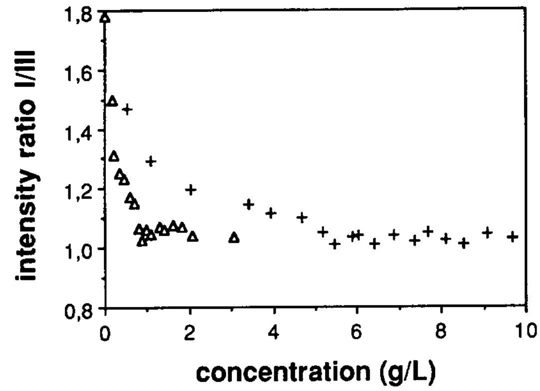


Figure 11 Intensity ratio of bands I and III of pyrene emission in aqueous solutions of monomers *3* (+) and *4* (△) at 25°C

using the hydrophobic dye pyrene. As the fine structure of its fluorescence spectrum probes the polarity of its local environment, pyrene allows study of the onset of formation of hydrophobic pockets in water, and their polar quality[46]. In general, the intensity ratio of the emission bands at 372 nm (band I) and at 383 nm (band III) is used in the so-called Py-scale[46,47].

Characteristically for low molecular weight surfactants, the intensity ratio I/III decreases with increasing concentration until the CMC is reached, to level in a final plateau; that is, efficient solubilization of pyrene depends on the presence of micelles. This is shown for monomers *3* and *4* in *Figure 11*. Starting at an intensity ratio I/III of 1.78 in pure water, the final ratio I/III reached by both monomers above the CMC is about 1, pointing to a rather hydrophobic environment in the micelles. The CMCs determined by this method are slightly lower than those obtained by surface tension measurements (*Table 7*).

For the solutions of all water-soluble polyacrylamides, the intensity ratio I/III is considerably lower than for water, but nearly constant in the concentration range studied (*Figures 12* and *13*). The results indicate the presence of hydrophobic pockets even at high dilution[39]. Accordingly, micelle formation is not observed, in agreement with the surface tension studies, but an intramolecular aggregation of the surfactant groups takes place. Such behaviour is characteristic of polysoaps[5].

Studying the intensity ratios I/III of the various polymers in more detail, within a given copolymer series, there is no significant difference. This implies that at least down to a surfactant content of 0.1, the copolymers still behave as polysoaps. However, changes of the intensity ratios between different polymer series are evident. For copolymers *3-IVc* and *3-IVd* the ratio is about 1.1, for copolymers *4-IVa–d* the ratio is about 1.2–1.3, and for poly-5 the ratio is about, 1.45 (*Figures 12* and *13*). This means that the hydrophobicity of the pyrene environment is highest in the polysoaps of the head type, and lowest in the tail end type. Furthermore, the ratio I/III is considerably higher for the polymers than for their parent surfactant monomers above the CMC. Even in the case of the copolymer series *3-IV* with the most hydrophobic environment of the polymers, the intensity ratio I/III is still slightly lower than for its monomer *4* above the CMC.

The differences between the polymers may be caused by different solubilization sites of pyrene. Possibly, an excluded volume effect prevents solubilization close to the polymer backbone. In the case of head type polymers, the dye is therefore solubilized in the region of the hydrophobic chains, whereas for the tail end polymers the dye is solubilized closer to the head group region. Alternatively, the behaviour may be explained by the restricted mobility of the alkyl segments close to the backbone. If only very mobile segments are capable of efficient solubilization, a more polar environment of pyrene would be found in the tail end polymer

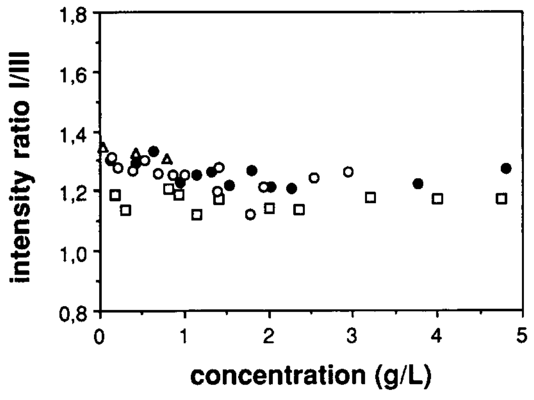


Figure 12 Intensity ratio of bands I and III of pyrene emission in aqueous solutions of copolymers *4-IV* at 25°C. □, *4-IVa*; ●, *4-IVb*; △, *4-IVc*; ○, 4-IVd

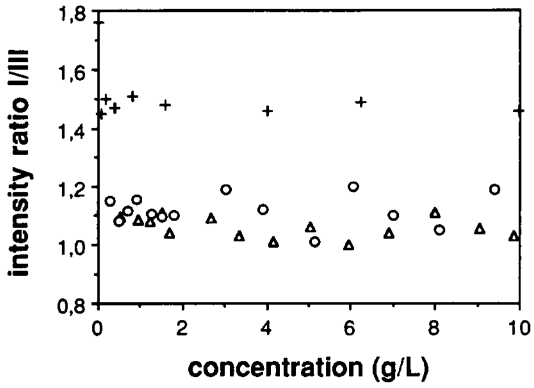


Figure 13 Intensity ratio of bands I and III of pyrene emission in aqueous solutions of copolymers *3-IV* and poly-5 at 25°C. △, *3-IVc*; ○, *3-IVd*; +, poly-5

again. This explanation would also account for the generally less hydrophobic environment of pyrene solubilized by the polysoaps than by low molecular weight surfactants[2,3,11]. But clearly, the phenomenon needs further investigation.

CONCLUSIONS

Several series of vinyl copolymers were synthesized from zwitterionic surfactant monomers and polar comonomers, modifying the properties of the zwitterionic homopolymers. Surfactant monomers with different positions of the polymerizable moiety were used to prepare amphiphilic polymers of different geometry. Choosing appropriate comonomers, the glass transitions of the copolymers are lowered with increasing comonomer content. Simultaneously, the characteristic superstructures in bulk are lost, but copolymers with both glass transitions and superstructures can be prepared.

The comonomer content influences the solubility characteristics too. This is partially due to changes of the overall polarity, but in addition the incorporated comonomer must be considered as a main chain spacer. Reducing the density of surfactant groups fixed at the polymer backbone, the spacer enables the surfactant moieties to adopt an amphiphilic conformation. Thus, water-soluble copolymers of all geometries — tail end, mid-tail and head type — are obtained. The minimum spacer lengths required increase with the bulkiness of the comonomer, with the size of the hydrophilic head group, and with the steric requirements of the polymer geometry, that is head type copolymers require longer spacers than mid-tail types. Using sulphobetaine head groups, the maximum acceptable surfactant monomer content is 40–50 mol% for mid-tail type copolymers, corresponding to an average minimum length of the repeat unit of C_4. For head type copolymers, it is only about 20 mol%, corresponding to an average minimum length of the repeat unit of C_{10}.

All water-soluble copolymers with surfactant monomer contents of 10–50 mol% behave like classical polysoaps, independent of their geometry. No CMCs are observed, and intramolecular aggregation is occurring. Nevertheless, all zwitterionic polysoaps show moderate surface activity, which seems to be a characteristic feature of the sulphobetaine polymers studied. The polymers are able to solubilize the hydrophobic fluorescent dye pyrene. The environment of the solubilization site depends on the geometry of the polysoap. It is most hydrophobic for the head type polysoaps, and least hydrophobic for the tail end polysoaps. It is unclear whether the different solubilization sites are linked to different solubilization capabilities of the polysoaps. Hence, it would be most interesting to see how quantitative studies compare with the qualitative studies performed here.

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