Polymerizable and polymeric zwitterionic surfactants: 2. Surface activity and aggregation behaviour in aqueous systems

André Laschewsky* and **I. Zerbe**
Institut für Organische Chemie, Universität Mainz, Germany
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The surfactant properties of a series of permanently zwitterionic monomers and polymers were studied with respect to structural variations. A strong influence of the molecular geometry on solubility and aggregation behaviour was observed, in particular for the polymers. Whereas all monomers were water-soluble and true surfactants, the water solubility of the polymers was restricted to selected geometries. Water-soluble polymers showed the properties of classical polysoaps, i.e. low surface activity and solubilization power for hydrophobic solutes. In contrast, water-insoluble polymers formed stable monolayers at the air–water interface and could be deposited onto solid substrates by the Langmuir–Blodgett method.

(Keywords: polymerizable surfactants; micellar polymers; surface activity; micelles; monolayers)

INTRODUCTION

Many amphiphilic, water-soluble polymers are characterized by very low viscosities of their aqueous solutions and the ability to solubilize hydrophobic, water-insoluble compounds. This behaviour is explained by the aggregation of the hydrophobic groups of the polymers, as concluded in the pioneering work of Strauss[1,2]. Therefore such polymers are called 'micellar polymers' or 'polysoaps', in analogy to the self-organization of low molecular weight surfactants into micelles.

Although many polysoap systems have been reported[1–11], the nature of the polymeric aggregates formed is still a matter of discussion, and the relationship between polymeric micelles and micelles of standard surfactants[12–14] is not clear. Better understanding of the aggregates and the aggregation process is desirable, especially since polysoaps have found increasing use in science and in technology, ranging from enzyme models to additives in tertiary oil recovery.

Within the various types of polysoaps, fully zwitterionic ones[15] are of particular interest. Due to the high hydrophilicity of the ionic groups, but neutral electrical charge of the macromolecules, due to the equivalent number of anionic and cationic groups present, zwitterionic polysoaps may combine the advantages of ionic and non-ionic polysoap systems. The high, temperature-independent hydrophilicity, absence of lower critical solution temperatures, optional modification by added salt, low tendency to gelatinize and lack of polyelectrolyte effects. However, despite these potential opportunities, zwitterionic polysoaps have hardly been studied up to now, partly due to the often limited solubility of polymeric zwitterions[16,17].

To explore the potential of zwitterions, a series of reactive, zwitterionic surfactants[15], and the polysoaps therefrom were investigated, with respect to their surface activity and their aggregation behaviour in aqueous systems. A particular point of interest was the importance of the type and position of the polymer backbone in polysoaps (*Figure 1*). Positioning the polymer backbone at the end of the hydrophobic tail was favoured in the past for geometric reasons[18,19], however dynamic considerations favour the positioning of the polymer backbone close to the hydrophilic head[13,14]. *Table 1* lists the sulphobetaine surfactant monomers studied and some cationic analogues used for comparative studies.

EXPERIMENTAL

Materials

The synthesis and characterization of the surfactant monomers and polymers are described elsewhere[15]. Water used for the experiments was purified by a Milli-Q water purification system (resistance 18 MΩ).

Methods

Krafft temperatures were determined by a microscope (Ortholux, Leitz) equipped with a hot stage (Mettler FP52). The onset of solubility of a little crystal suspended in water was taken as the Krafft temperature. Surface tensions were measured with a Lauda tensiometer at 25°C, if not otherwise stated. Minimal areas per surfactant molecule were calculated from the Gibbs surface tension equation, using the approximations: $A = kT \times d\ln(c)/d\gamma$ for zwitterionic surfactants, and $A = 2kT \times d\ln(c)/d\gamma$ for the cationic surfactants respectively. A denotes the surface area per molecule, k the Boltzmann constant, T the temperature, c the surfactant concentration and γ the surface tension. Monolayer behaviour was investigated with a computer controlled film balance[20] on pure aqueous subphase. Fluorescence spectra were taken with a Spex fluorolog 112X spectrograph.Pyrene was excited at 310 nm and the change of the vibrational fine structure of the emission spectrum of pyrene, in particular the change of the relative intensities of the vibronic band I at 372 nm and of band III at 383 nm,

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* To whom correspondence should be addressed

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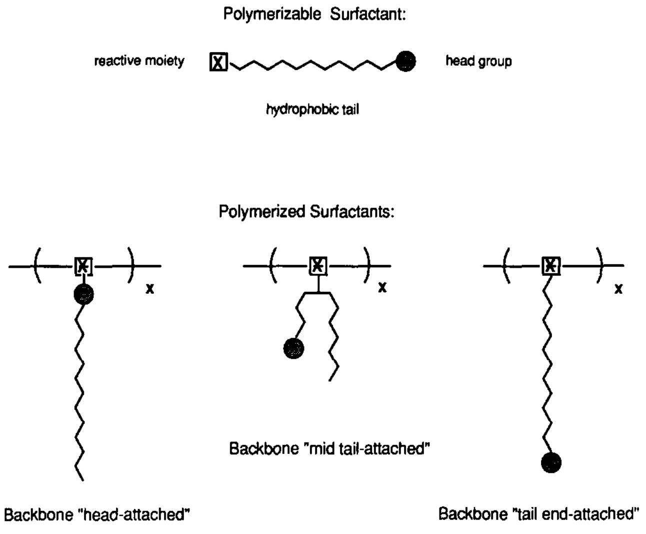


Figure 1 Scheme of the molecular architecture of polysoaps

was used to determine solubilization and the critical micelle concentration[21,22].

RESULTS AND DISCUSSION

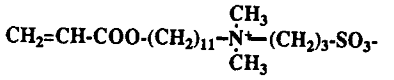
Surfactant properties of monomers

General behaviour. All the monomers **1–11** are water-soluble. Their aqueous solutions are foaming, show strongly reduced surface tensions and are capable of solubilizing water-insoluble dyes such as Sudan red. Highly concentrated aqueous solutions are birefringent but mobile, indicating the formation of anisotropic lyotropic mesophases. The textures of optical polarized micrographs point to hexagonal mesophases in the case of the zwitterionic surfactants **1–9**. In the case of the cationic monomer **10**, the textures of the mesophase point to a lamellar mesophase. All these properties demonstrate that the synthesized monomers are true surfactants[23,24].

Krafft temperatures. The lower temperature limit for micellar properties of surfactants is given by the Krafft temperature T_K, where the solubility curve meets the critical micelle concentration. Hence for good micellar performance, low values of T_K are desirable. *Table 2* lists the T_K values of the surfactants synthesized. The table illustrates the general tendency of the zwitterionic surfactants for high values of T_K, in agreement with the literature[23]. For comparison, no T_K could be detected for compounds **10** and **11**, the cationic analogues of the zwitterions **2** and **8**. Considering the strong attractive forces between the zwitterionic head groups and the general poor solubilities of zwitterionic compounds, these findings are not surprising.

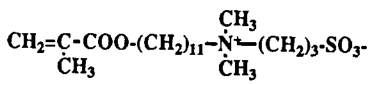
The T_K values of the various zwitterionic surfactants synthesized depend strongly on their molecular structure. Particular effects are: (a) the molecular geometry (compare isomers **1** and **7** or **2** and **8**); (b) the nature of the polymerizable unit (compare analogues such as **1** and **2** or **7–9**); (c) the nature of the zwitterionic head group; and (d) the presence of H-bonding groups (*Table 1*). High values of T_K are found for all the pyridino propanesulphonate monomers **3–5**, e.g. T_K of monomer **3** is higher by 16°C than the T_K of its ammonio propanesulphonate analogue **2**. This behaviour can be explained either by additional attractive forces of the aromatic moieties or alternatively by steric reasons. The bulkiness of the ammonio propanesulphonate group will prevent optimal packing of the ionic groups compared to pyridinio derivatives and thus should reduce the intermolecular attraction. The comparison of the ester **3** and its secondary amide analogue **4** reveals the additional increase of T_K by the presence of H-bonds[25]. Although the exchange of the ester groups by amide groups should render monomer **4** more hydrophilic than monomer **3** (ref. 23), T_K is increased by 26°C (*Table 2*). Thus strong H-bonding groups such as amides are a disadvantage in the tailoring of monomeric and probably even polymeric zwitterionic surfactants.

Table 1 Polymerizable zwitterionic surfactants investigated and cationic analogues



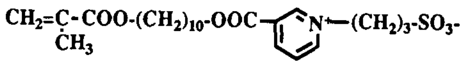
$CH_2{=}CH{-}COO{-}(CH_2)_{11}{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$

1



$CH_2{=}\underset{CH_3}{C}{-}COO{-}(CH_2)_{11}{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$

2



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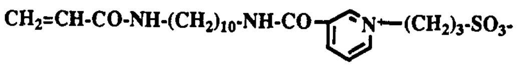

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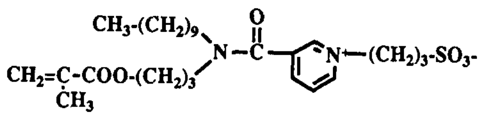

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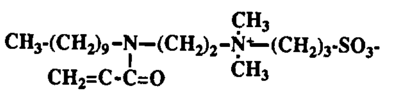
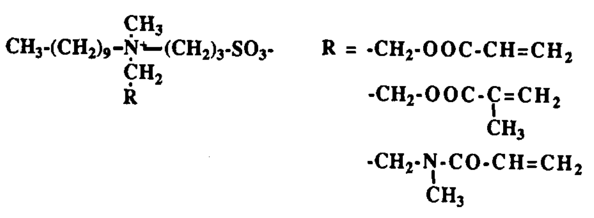


$CH_3{-}(CH_2)_9{-}\underset{CH_2=C-C=O}{N}{-}(CH_2)_2{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$

6

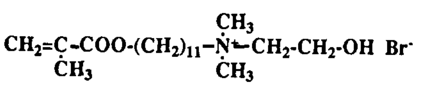


$CH_3{-}(CH_2)_9{-}\overset{CH_3}{\underset{\underset{R}{CH_2}}{N^+}}{-}(CH_2)_3{-}SO_3^-$

$R = -CH_2{-}OOC{-}CH{=}CH_2$ 7

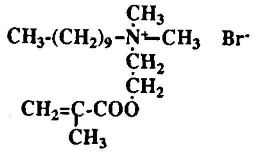
$-CH_2{-}OOC{-}\underset{CH_3}{C}{=}CH_2$ 8

$-CH_2{-}\underset{CH_3}{N}{-}CO{-}CH{=}CH_2$ 9



$CH_2{=}\underset{CH_3}{C}{-}COO{-}(CH_2)_{11}{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}CH_2{-}CH_2{-}OH\ Br^-$

10



$CH_3{-}(CH_2)_9{-}\overset{CH_3}{\underset{\begin{array}{c}CH_2\\CH_2\\CH_2=\underset{CH_3}{C}-COO\end{array}}{N^+}}{-}CH_3\ Br^-$

11

Table 2 Surfactant properties of the monomers

Monomer	T_K (°C)	CMC (g l^{-1})	CMC (mol l^{-1})	γ_{min} (mN m^{-1})	$A_{min}{}^a$ (nm^2 per molecule)
1	8	1.5	0.38×10^{-2}	41	0.44
2	16	0.81 (0.8^b)	0.20×10^{-2}	41	0.44
3	32				
4	58				
5	33				
6	<20	0.95 (1.1^b)	0.24×10^{-2}	36	0.45
7	34				
8	37	(4.6^c)			
9	<10	5.7	1.4×10^{-2}	40	0.57
10	<10	2.4 (1.5^b)	0.59×10^{-2}	40	0.55
11	<10	6.3 (5.0^b)	1.7×10^{-2}	34	0.68

[a] A_{min} = area per molecule at the water interface at CMC
[b] By pyrene label at 25°C
[c] By pyrene label at 40°C

Critical micelle concentrations of the monomers. Critical micelle concentrations (CMCs) were determined for all monomers with T_K below 25°C. The results are listed in *Table 2*. Characteristic surface tension measurements as used to determine CMCs are displayed in *Figures 2–5*. In the case of the cationic monomer **11**, the observed CMC agrees well with previously reported values[9,10]. In selected cases, the surface tension data were supplemented by studying fluorescence of pyrene in water independent of the surfactant concentration[21]. As the vibrational fine structure of pyrene emission depends on the polarity of the local environment (so-called Py-scale[22]), changes in the relative intensities of two sensitive bands, band I (~374 nm) and band III (~384 nm), are recorded indicating the transition from aqueous to micellar environment with increasing surfactant concentration[21,22]. Good agreement was found for the CMCs determined by surface tension measurements and by the pyrene probe (*Table 2*). The dye solubilization method to determine CMCs[24] was abandoned, as polymerization of the highly purified monomers may interfere with the long equilibration times required.

As a general feature, the zwitterionic surfactants exhibit lower CMCs than their cationic analogues, i.e. the sulphobetaine headgroup is less hydrophilic. Furthermore, the zwitterions occupy a smaller area per molecule at the gas–water interface at the CMC, i.e. they are more densely packed in the monolayer. This is exemplified by comparison of monomers **2** and **8** with monomers **10** and **11** in *Table 2*. Both observations can be rationalized by simple electrostatic effects: the cationic monomers are subject to charge repulsion, in contrast to the zwitterionic monomers, thus the tendency to aggregate and to pack density is lower. However, the surface tensions of the monomers at their CMC are virtually identical for zwitterionic and cationic analogues (*Figure 2*).

Characteristic differences are found for the surfactant behaviour of the various zwitterionic surfactants. The CMC values listed in *Table 2* depend notably on the molecular structure and geometry, ranging from 2×10^{-3} to 2×10^{-2} mol l^{-1}. The observed decrease of the CMC replacing the acrylate group in **1** by the methacrylate group in **2** reflects the well known decrease of the CMC with increasing hydrophobicity. But comparison of zwitterionic isomers (**2** and **8**, **6** and **9**) reveals that the position of the polymerizable moiety has a marked influence on the CMC too. Direct attachment at the hydrophilic head group increases both the CMC and the area occupied per molecule at the gas–water interface (*Table 2*, *Figure 3*). This observation can be explained by classifying the polymerizable moieties as hydrophobic

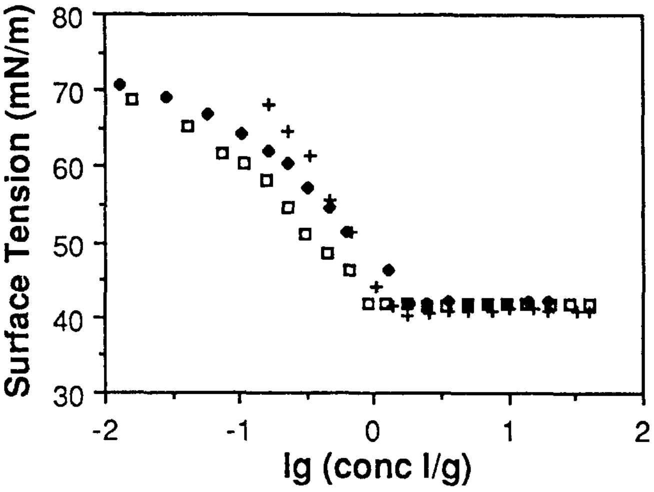


Figure 2 Surface activity of analogous monomers: ◆, monomer **1**; □, monomer **2**; +, monomer **10**

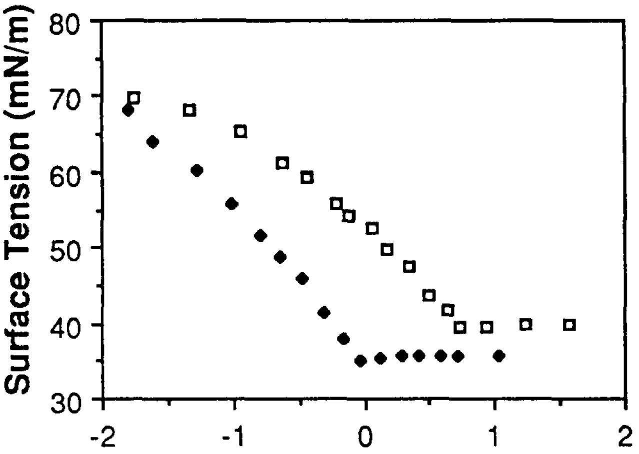


Figure 3 Surface activity of isomeric monomers: ◆, monomer **6**; □, monomer **9**

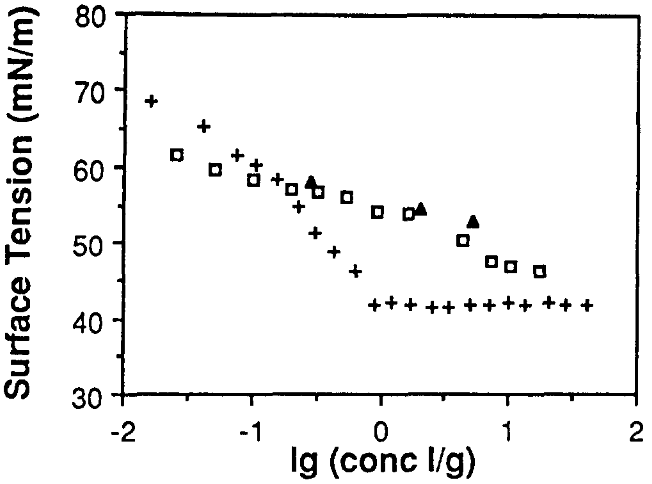


Figure 4 Surface activity of zwitterionic monomers and polysoaps: +, monomer **2**, $T = 25°C$; □, poly (**2**), $T = 25°C$, $M_n = 1 \times 10^4$; ▲, poly (**2**), $T = 40°C$, $M_n = 7 \times 10^5$

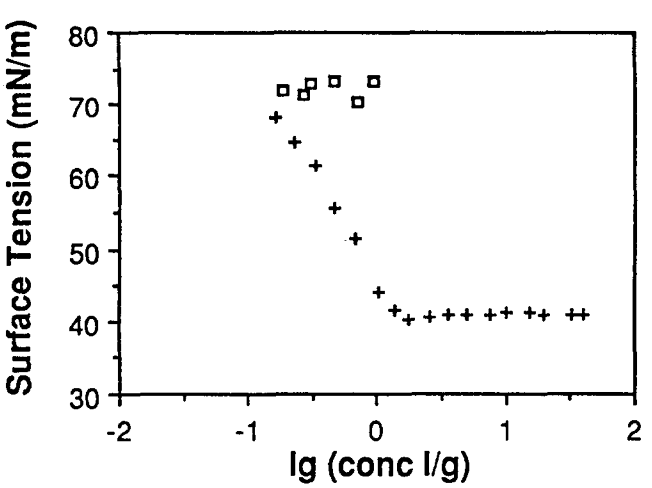


Figure 5 Surface activity of cationic monomers and polysoaps: +, monomer **10**, $T = 25°C$; □, poly (**10**), $T = 25°C$, $M_n > 10^6$

groups. The isomers with the polymerizable moiety attached at the head group hence represent 'branched surfactants', the lower CMC of which agrees well with the behaviour of unbranched and branched classical surfactant isomers[26].

As observed for zwitterionic and cationic analogues, the surface tensions of all zwitterionic monomers at their CMC are fairly uniform, in the range 35 to 41 mN m^{-1}. The values are comparable to that of the zwitterionic standard surfactant *N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-propanesulphonate[27]. There is no substantial difference between slightly modified analogues such as **1** and **2**, between isomers such as **6** and **9** and, as mentioned above, between zwitterionic and cationic analogues such as **2** and **10**.

Surfactant properties of polymers

Water-soluble polymers in aqueous solution. The polymers poly(**1**), poly(**2**) and poly(**10**), in which surfactant side chains are attached to the polymer backbone via the tail end, are water-soluble[15]. Thus they were studied with respect to their polysoap behaviour. Their surface activity and their solubilization of the hydrophobic probe pyrene is shown in *Figures 4–7*.

The plot of surface tension *versus* polymer concentration demonstrates the marked differences in surface activity of the polymers compared to the monomers (see *Figures 4* and *5*), in particular of the zwitterions **2** and poly(**2**). Although the polymer is slightly surface active at low concentrations, much higher concentrations than for the monomer are needed to obtain a substantial decrease of the surface tension. The surface tension decreases continuously in a nearly linear dependence on log[concentration], lacking a distinct break indicative of a CMC. The molecular weight of the polymer seems to be of minor or no importance. As shown in *Figure 2*, samples of poly(**2**), of number average molecular weight of 10000 and 500000, exhibit comparable surface activities. Comparisons between the cationic monomer **10** and its polymer are limited, since polymer solutions gelatinize at concentrations above 1 g l^{-1}. In contrast, the zwitterionic poly(**2**) still yields low viscous solutions at concentrations of 20 g l^{-1}, probably due to its electroneutral character thus preventing uncontrolled swelling and gelation. It is noteworthy that highly concentrated solutions of poly(**2**) and poly(**11**) are mobile and birefringent, pointing to the formation of polymeric,

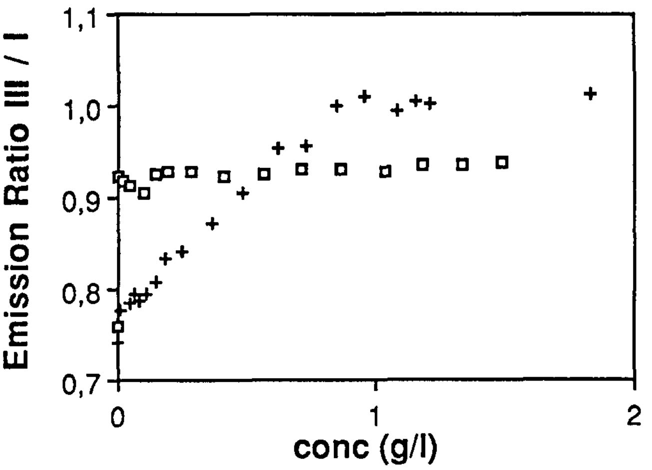


Figure 6 Solubilization of pyrene by zwitterionic monomers and polysoaps: +, monomer **2**, $T = 25°C$; □, poly(**2**), $T = 25°C$, $M_n = 1 \times 10^4$

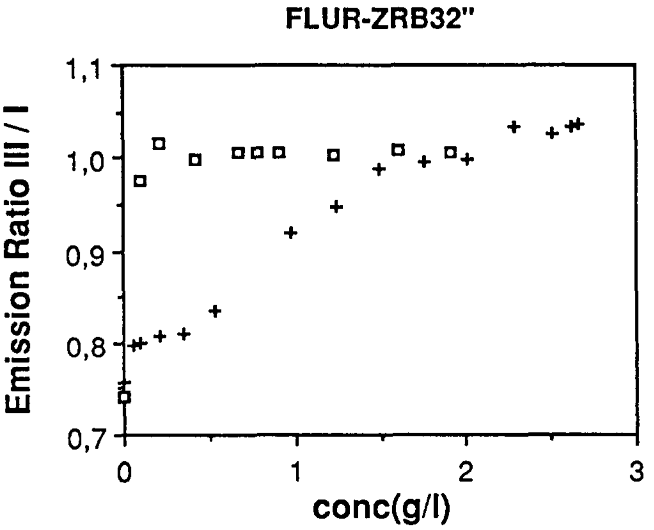


Figure 7 Solubilization of pyrene by cationic monomers and polysoaps: +, monomer **10**, $T = 25°C$; □, poly(**10**), $T = 25°C$, $M_n > 10^6$

lyotropic mesophases. Due to their unspecificity, the textures of the polarized micrographs do not yet enable a phase assignment.

Solubilization studies of pyrene by poly(**2**) and poly(**10**) (*Figures* 6 and 7) demonstrate a rather hydrophobic environment over the complete concentration range. In contrast to the monomers, no change of the emission spectra with increasing concentration, which would indicate the presence of a CMC, was observed[21]. The intensity ratios of bands III and I are constant, being much higher than for non-micellar solutions. Interestingly, however, the intensity ratios of 0.93 and 1.0 respectively for the solutions of poly(**2**) and poly(**10**) are significantly lower than for micellar solutions of the corresponding monomeric surfactants **2** and **10**, yielding ratios of 1.01 and 1.05. This indicates that the local environment is less hydrophobic (or more polar) in the polysoaps than in micelles of the analogous low molecular weight surfactants. Similar observations have been reported recently[28].

Both the results from surface tension studies and from pyrene fluorescence prove the classical polysoap behaviour of the water-soluble polymeric surfactants[1,2]. The lack of a CMC revealed by both methods demonstrates the concentration independent, and thus intramolecular aggregation of the polymers. In agreement, surface activity of the polymers is low, as the intramolecular aggregation minimizes interfacial accumulation of the polymeric surfactants. As postulated for polysoaps, the aggregates are able to solubilize hydrophobic solutes, such as pyrene. However, the low ratio of intensity of band III *versus* band I suggests that the solubilization in the polysoaps studied is not optimal. The local environment in the polysoaps is only partially hydrophobic. Presumably the attachment of the hydrophobic tails at the polymer backbone immobilizes the most flexible part[13] of the monomeric surfactants, decreasing the efficiency of pyrene solubilization. This result would imply that the widespread concept of polysoap architecture, i.e. attachment of the surfactant side chains to the polymer backbone via the end of the hydrophobic tail[18,19], is ambiguous: good water-solubility is counterbalanced by poor solubilization capability.

Monolayer behaviour of water-insoluble polymers. Whereas all zwitterionic monomers and their cationic analogues are true surfactants and thus water-soluble, the majority of the polymers are insoluble in water[15].

However, many of the water-insoluble surfactant polymers, such as poly(**6**)-poly(**9**) and poly(**11**) are soluble in chloroform/methanol mixtures. They can be spread at the air–water interface to study their surface activity in insoluble monolayer experiments[29]. These polymers, derived from water-soluble monomers, indeed form stable monolayers, of which the surface pressure *versus* area diagrams ('isotherms') are shown in *Figure 8*. Note that the polymeric monolayers could successfully be transferred onto solid supports by the Langmuir–Blodgett (LB) technique[29] to build LB films.

Although monolayers of amphiphilic vinyl polymers have increasingly been investigated in recent years[19], comparative studies of analogues have been restricted to the variation of the length of the hydrophilic tail or the nature of the polar head group. Systematic studies of analogous systems which are only distinguished by different polymer backbones are almost entirely absent.

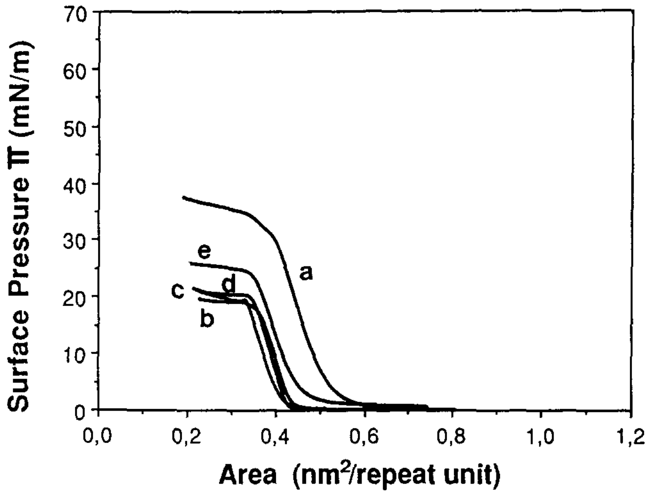


Figure 8 Spreading of water-insoluble polymerized surfactants on pure water, $T = 20°C$: a, poly (**6**); b, poly (**7**); c, poly (**8**); d, poly (**9**); e, poly (**11**)

Therefore the comparison of the polymerized surfactant analogues poly(**6**)–poly(**9**) and poly(**12**) is very instructive, with respect to different chemical structures of the backbone as well as to different position of the backbones.

The isotherms of the head attached polymers, poly(**7**)–poly(**9**) and poly(**12**), are very similar (*Figure 8*). The collapse areas of $\sim 0.35\,nm^2$ per repeat unit indicate a rather loose packing of the hydrocarbon chains. The collapse pressures of $\sim 20\,mN\,m^{-1}$ are rather low. Between 1 and 50°C, the spreading behaviour is independent of the temperature. All results point to a fluid-like state of the hydrophobic chains, agreeing well with their shortness from the standard monolayer point of view[29]. Interestingly, the different polymer backbones exert only a minor influence on the isotherms. Collapse areas and collapse pressures of the zwitterionic analogues poly(**7**)–poly(**9**) are virtually the same (*Figure 8b–d*). The zwitterionic surfactant structure obviously dominates. Only the collapse point becomes more distinct in the sequence polymethacrylate–poly(*N*-methylacrylamide)–poly(acrylate). This may indicate an improved self-organization, which is explained by the increasing flexibility of the polymer backbone.

The isotherms of the zwitterionic and cationic analogues poly(**8**) and poly(**12**) exhibit only small differences (*Figure 8*). The cationic polymer exhibits a slightly increased collapse area and a moderately enhanced collapse pressure of $\sim 25\,mN\,m^{-1}$.

Major differences in their spreading behaviour are found for polymers with different geometry, such as the isomeric poly(*N*-methylacrylamide)s poly(**6**) and poly(**9**). The isotherm of poly(**6**) in *Figure 8* demonstrates the much higher collapse pressure of $32\,mN\,m^{-1}$ compared to poly(**9**), and the slightly increased collapse area. The enhanced collapse pressure of poly(**6**) can be explained by its favourable polymer geometry. The attachment of the polymer backbone in the hydrophobic tail allows a better contact of the sulphobetaine groups with the water. This minimizes interactions of the hydrophobic chains with water and improves surface activity. At the same time, the surfactant structure is rigidly fixed in the polymer backbone, which may be responsible for the less efficient spreading and packing[19] of poly(**6**). This result underlines the importance of the position of the polymer backbone for self-organization of polymers in aqueous environments.

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