



Universität Potsdam

Peter Anton, Peter Köberle, André Laschewsky

Recent developments in the field of micellar polymers

first published in:

Die Makromolekulare Chemie, 194 (1993) S. 1-27, ISSN 0025-116X
DOI 10.1002/macp.1993.021940101

Postprint published at the Institutional Repository of Potsdam University:

In: Postprints der Universität Potsdam

Mathematisch-Naturwissenschaftliche Reihe ; 90

<http://opus.kobv.de/ubp/volltexte/2008/1726/>

<http://nbn-resolving.de/urn:nbn:de:kobv:517-opus-17263>

Postprints der Universität Potsdam

Mathematisch-Naturwissenschaftliche Reihe ; 90

Recent developments in the field of micellar polymers

*Peter Anton, Peter Köberle, André Laschewsky**^{a)}

Institut für Organische Chemie, Universität Mainz, Johann-Joachim-Becher Weg 18–20,
D-6500 Mainz, Germany

(Received: June 16, 1992; revised manuscript of August 25, 1992)

SUMMARY:

This article describes recent achievements in the field of micellar polymers, or “polysoaps”. Taking advantage of zwitterionic model polymers, systematic variations of the molecular architecture have provided an improved understanding of the relationship between the molecular structure of the polymers and their key properties such as surface activity and solubilization capacity. Useful rules are established, which take into account much of the previous data in the literature.

Introduction

Micellar polymers

The importance of water-soluble polymers is increasingly growing, equally for technical applications, for biological/medical purposes, and for environmental aspects. Still, the aqueous-solution properties are not well understood yet, in particular when charged polymers are involved.

A particularly interesting class of water-soluble polymers are the “micellar polymers” or “polysoaps”^{1–3)}. Known since the early 1950ies, but neglected for a while — e.g. in favour of polymeric vesicles⁴⁾ — polysoaps experience a revival in recent years. Capable of self-organization due to hydrophobic interactions, but still isotropically soluble, they stand right between classical, homogeneously dissolved polymers and extensively self-organized but phase-separated systems, such as monolayers and vesicles of polymeric lipids⁴⁾. Towards both extremes there are gradual transitions: Towards the homogeneously dissolved polymers we find water-soluble polymers modified by a small number of hydrophobic groups acting as thickeners due to intermolecular aggregations⁵⁾; towards monolayers and vesicles we find polymeric lyotropic liquid crystals due to superstructures created from surfactant aggregates^{4, 6, 7)}.

Polysoaps can be visualized as a large number of surfactant structures linked by a polymer backbone (Fig. 1). Aqueous solutions of such polymers are characterized by unusually low viscosities, and by high solubilization capacities^{1, 8–13)}. These

^{a)} New address: Université Catholique de Louvain, Département de Chimie, Place L. Pasteur 1,
B-1348 Louvain-la-Neuve (Belgium).

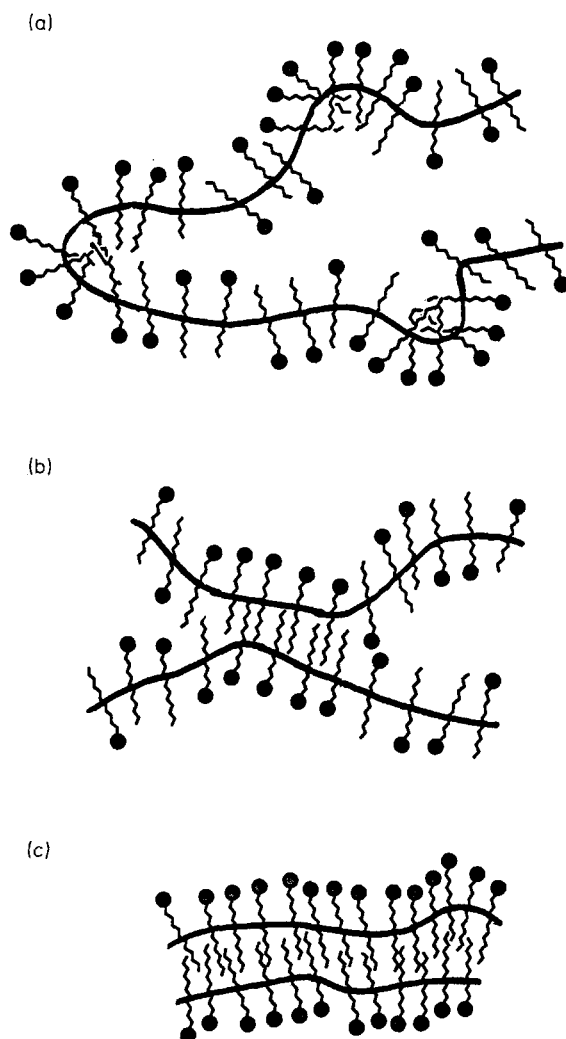


Fig. 1. Models of
"polymeric micelles"
formed by polysoaps
(a) "local micelle",
(b) "regional micelle",
(c) "molecular micelle"

properties are attributed to the aggregation of the surfactant side chains providing hydrophobic microdomains in isotropic aqueous solution. Such a behaviour resembles the micelle formation of low-molecular-weight surfactants in water. Hence, the names "polysoaps" or "micellar polymers" were coined¹⁾, and the hydrophobic aggregates formed in polysoaps are referred to as "polymeric micelles".

A particular feature of polysoaps seems to be their intramolecular hydrophobic aggregation³⁾ (Fig. 1) which is explained by the close proximity of the surfactant side chains within one macromolecule. Due to the intramolecular aggregation, an equivalent to the "critical micelle concentration" (cmc) of low-molecular-weight surfactants is generally missing³⁾. This makes a major difference to low-molecular-weight sur-

factants and amphiphilic block copolymers which both aggregate *intermolecularly* (behaving in many respects like “oversize” surfactants, the latter often being called “macrosurfactants”^{14, 15}). Occasionally, there are reports on cmc’s of polymers which from their molecular structure could be classified as polysoaps^{16–20}. But apparently in these cases, low oligomers^{18–20} or chemically ill-characterized (and thus disputable) structures^{16, 17} are involved, which makes it difficult to decide whether the reported cmc’s are real.

“Polymeric micelles”

Keeping in mind that the structure of standard micelles is still a matter of discussion^{21–26}, the structure of “polymeric micelles” is even more subject to discussion. Two major models have been proposed which will be referred to here as “local micelle” and “molecular micelle”, respectively (see Fig. 1 (a) and (c)).

Originating in the pioneering work of Strauss, the “local micelle” assumes the aggregation of a limited number of neighbouring surfactant side chains^{2, 11, 27, 28}. The model is independent of the number-average degree of polymerization \bar{X}_n allowing a gradual transition from fully to partially aggregated macromolecules². In analogy to standard micelles²¹, a fast exchange between aggregated surfactant fragments and “free unimers” could occur. The model requires a high flexibility of the polymer backbone, to enable an efficient clustering of the surfactant fragments. As steric problems will arise nevertheless, polysoaps would be expected to exhibit more hydrophobic contacts than analogous low-molecular-weight surfactants. Therefore, the hydrophilic-hydrophobic balance (HLB) of polysoaps should be more on the hydrophilic side.

The model of the “molecular micelle” (Fig. 1 (c)) assumes the intramolecular aggregation of virtually all surfactant side chains of a given macromolecule into one aggregate^{7, 29–31}. This model was widely spread due to the work of Elias, and has been treated theoretically recently^{32, 33}. With all surfactant fragments aggregated, the model omits the exchange between aggregated surfactant fragments and “free unimers”. As the aggregation number will depend in the degree of polymerization \bar{X}_n , the shape of the “micelles” might be controlled by \bar{X}_n . E.g., above a critical value, geometric restrictions will prevent the formation of spherical micelles⁷. Compared to the “local micelle”, the “molecular micelle” requires less flexibility of the polymer backbones. Thus, the HLB of polysoaps would be closer to the one of analogous low-molecular-weight surfactants.

A compromise model between these extremes is represented by the “regional micelle” (Fig. 1 (b)), assuming the aggregation of a few neighbouring surfactant side chains superposed by the aggregation of individual segments of the polymer. The resulting properties would be similar to the ones of the “local micelle”, except for the fact that the severe geometric restrictions imposed by the limited flexibility of the polymer backbone are circumvented by the more efficient regional aggregation. Too, this model would account for a gradual transition from intra- to intermolecular aggregation.

Because only few experimental data are available, up to now none of the polysoap models can be rejected. Fluorescence quenching and neutron scattering studies support

the “local micelle”^{34,35}), but theoretical treatments favour the “molecular micelle”³³). At least an analogue to the latter has been realized recently with some starburst polymers and hypercrosslinked polymers, replacing the self-organization of hydrophobic moieties by covalent bonding^{36,37}). Perhaps, there exists more than a single structure but several ones, depending on the molecular architecture of the polymers. Clearly, more experiments will be needed to resolve this problem.

Preparation of polysoaps

Polysoaps are accessible by several synthetic strategies three of which are most widely used (Fig. 2):

Method 1 uses the grafting of hydrophobic elements onto a hydrophilic or proto-hydrophilic backbone (Fig. 2a). This method was applied originally^{1,10,12,38,39}), e.g. in the preparation of partially quarternized poly(vinylpyridines). It is still used frequently up to now^{40–43}), as it is generally simple and enables the use of well-characterized parent polymers. This is advantageous if polymers of known, narrowly distributed molecular weights are desired. However, all problems typical for polymer-analogous reactions apply, and hence the detailed chemical structure of the polysoap prepared might be problematic. Some of the chemical problems are avoided by grafting full surfactant moieties to a preformed polymer backbone^{44,45}) (Fig. 2b). Nevertheless, the need of reactive moieties in the polymer backbone limits the possible variations of the method.

Method 2 uses the polymerization of prefabricated reactive surfactants^{19,20,46–56}) (Fig. 2c). Although often rather demanding from the viewpoint of synthetic work, the method is well suited for model studies as this strategy provides polymers with the chemically best defined structures (see also Fig. 4 and *Scheme 1* below).

Method 3 uses the copolymerization of hydrophilic and hydrophobic or amphiphilic monomers^{57–65}) (Fig. 2d, see also *Scheme 2* below). Like method 1, this preparation of polysoaps is fairly simple, and it is particularly adaptable to broad synthetic variations. But the chemical structure of the polysoaps obtained may be poorly defined, thus limiting its use for model studies.

All three strategies provided polysoaps in the past, but noteworthy produced a number of failures as well. E.g. poly(vinylpyridines) fully quaternized with long alkyl groups become water-insoluble^{66–68}), as do many prefabricated surfactants after polymerization^{49,50,64,69–78}). Obviously, there is little correlation between water-solubility and HLB, or the overall hydrophilicity of the polymers. These quite puzzling observations have initiated the studies about the optical molecular architecture of polysoaps.

Molecular architecture of polysoaps

The combination of polymer and surfactant structures in polysoaps produces a number of structural variables which can be modified. On the one hand, there are variations of the surfactant side chains, in particular the nature of the head group and the length and branching of the alkyl chain. Beyond these classical variations,

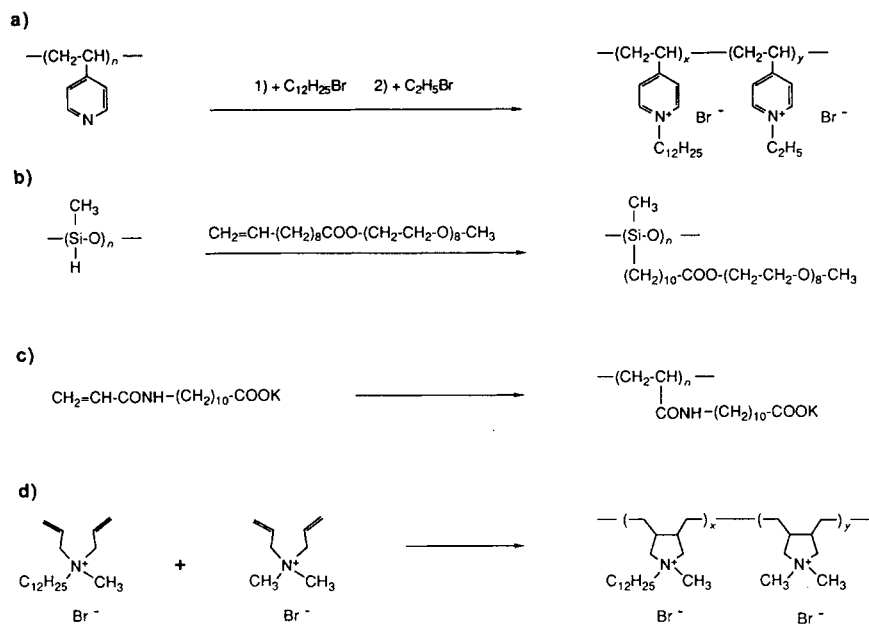


Fig. 2. Examples for synthetic routes to polysoaps: a) hydrophobization of preformed polymers^{1, 8)}; b) grafting of surfactant groups onto preformed polymers⁴⁴⁾; c) polymerization of reactive surfactants²⁹⁾; d) copolymerization of hydrophilic and hydrophobic monomers⁶⁴⁾

polysoaps offer on the other hand a number of possibilities characteristic for polymers which are unknown in classical surfactant chemistry. This broadens the synthetic scope considerably. E. g., the polymer structure can be varied with respect to the nature of the polymer backbone, the polymer geometry and the incorporation of flexible spacer groups (Fig. 3).

Variation of the polymer backbone will alter its hydrophilicity (and thus the HLB) and its flexibility. Further, the density of the surfactant side chains can be modified. The variation of the polymer geometry produces polysoaps with the backbone attached at different positions of the surfactant side chains, ranging from "frontal" attachment at the hydrophilic head group to "terminal" attachment at the end of the hydrophobic tail^{4, 6, 56)} (Fig. 4). As for the last variable, flexible spacer groups might improve the aggregation process as is known for a number of self-organized systems, such as side-chain liquid-crystalline polymers^{4, 79, 80)}, or polymeric amphiphiles^{4, 81-83)}.

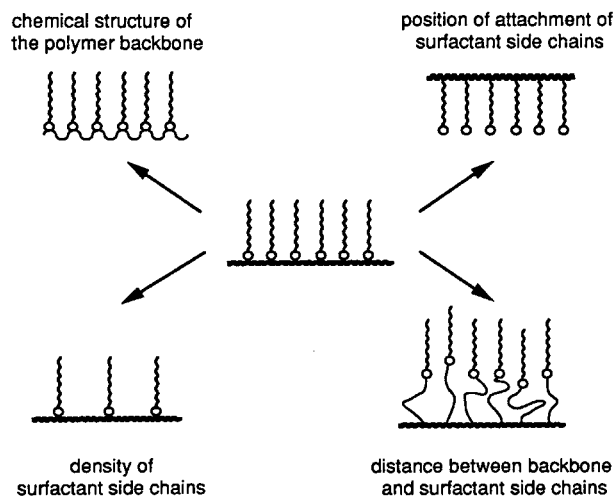


Fig. 3. Structural variations of polysoaps characteristic for polymers

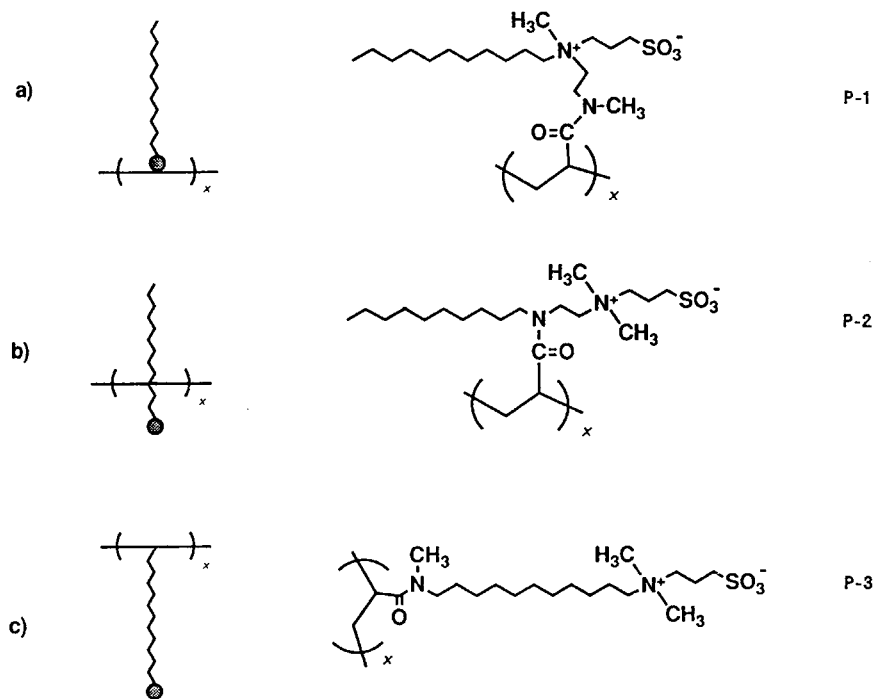


Fig. 4. Variations of polysoap geometry by attaching the polymer backbone at different positions of the surfactant groups, as illustrated by isomeric polyacrylamides **P-1**–**P-3**: a) “head” geometry, b) “mid-tail” geometry, c) “tail-end” geometry

Surfactant side chains

Up to now, systematic investigations were mostly restricted to the classical variations of the surfactant fragment, in particular of the length of the alkyl chains employed^{2, 12, 33, 35, 61, 72, 73, 84}). Although many types of head groups have been reported, including cationic, anionic, non-ionic and zwitterionic ones, systematic variations are scarce^{29, 44, 49, 85, 86}). In any case, the effects of such variations generally agree well with the known effect of similar variations on low-molecular-weight surfactants.

Specific deviations arise, when charged surfactant fragments are used: Such polysoaps behave as polyelectrolytes, with all implications^{7, 39, 52, 67, 84, 87, 88}), i. e., as the dissociation of the ionic groups varies with the concentration, meaningful concentration-dependent studies in water become difficult. This is best exemplified by viscosimetric studies (see Fig. 5). The problem may be overcome, by the addition of large amounts of salt, but ternary systems are created then. Further, some ionic polysoaps tend to precipitate in brine^{27, 89}).

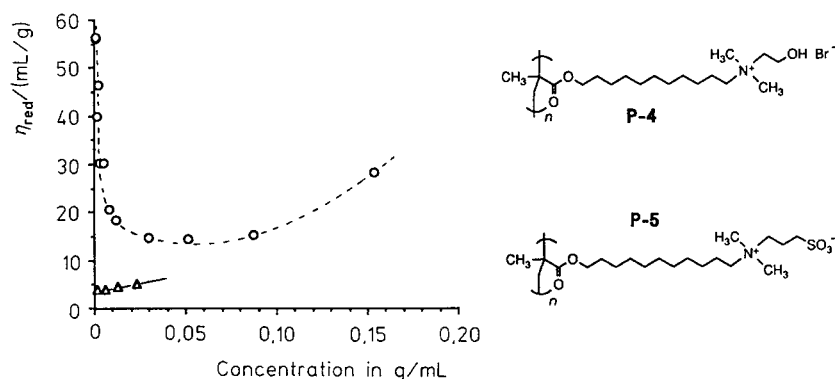
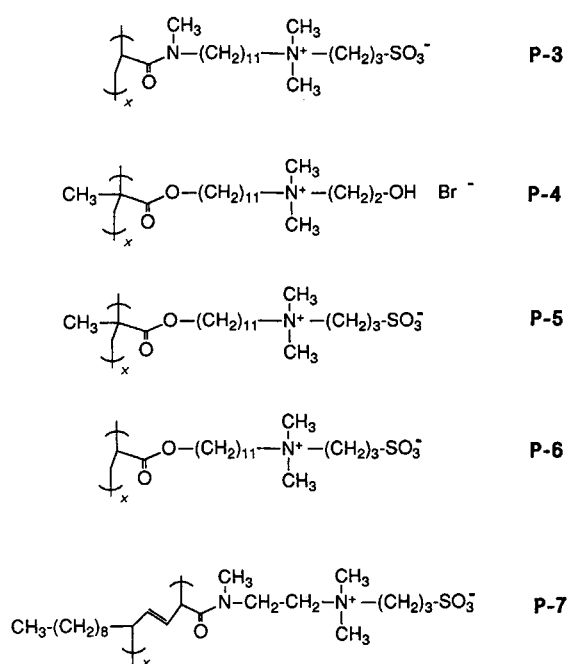


Fig. 5. Reduced viscosity of aqueous polysoap solutions at 20 °C⁹⁰). Cationic polymethacrylate **P-4** (○); analogous zwitterionic polymethacrylate **P-5** (△)

To avoid these complications, non-ionic^{6, 7, 54, 55, 86, 91}) and fully zwitterionic^{56, 78, 89}) polysoaps have been increasingly employed. Fig. 5 exemplifies for viscosity studies, how ionic polysoaps are advantageously replaced by zwitterionic ones, facilitating the interpretation of concentration-dependent studies. Whereas the viscosity of the cationic polysoap **P-4** exhibits the complex concentration dependence characteristic of polyelectrolytes, the viscosity of the analogous zwitterionic polysoap **P-5** increases linearly with concentration⁹⁰) as for an uncharged polymer.

Unfortunately, non-ionic and fully zwitterionic polysoaps have some inherent problems of their own. Non-ionic systems are prone to phase separation at elevated

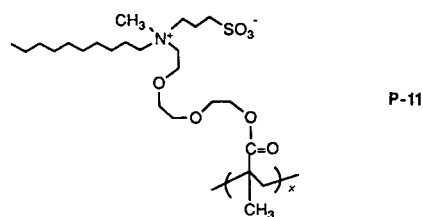
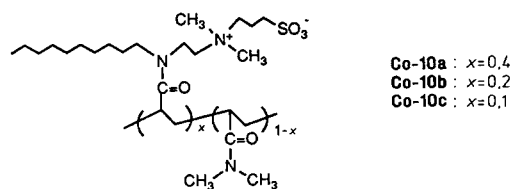
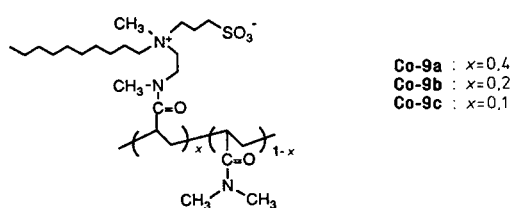
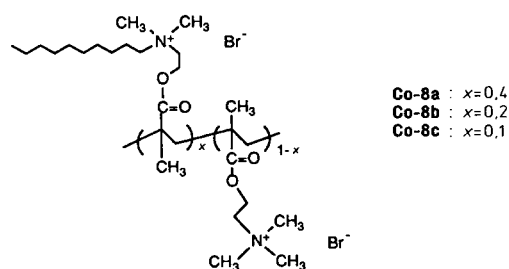
temperatures⁶⁾. Further, the most widely used non-ionic head groups are oligo(ethylene oxide)s which are very large in comparison to the appropriate hydrophobic moieties, thus yielding polymers with an unfavourable ratio of hydrophobic to hydrophilic domains. When sugars and related non-ionic moieties are used instead, strong hydrogen bonding causes solubility problems^{51,92,93)}. Similarly, zwitterionic polysoaps are often troubled by their inherent low solubility in pure water⁷⁸⁾, but by appropriate design these problems can be minimized. Hence, recent efforts have produced a number of zwitterionic polysoaps which are well suited for systematic studies^{56,65,94–96)} (see *Scheme 1* and *Scheme 2*).



Scheme 1: Examples of zwitterionic polysoaps prepared by radical polymerization of surfactant monomers

Steric requirements

Systematic variations of the structural variables characteristic for polymers have been addressed only recently, mostly focusing on geometrical aspects^{6,7,49,78,97)}. As polysoaps bear “directed” side chains having a hydrophilic “front part” and a hydrophobic “back side”, a major influence of the polymer geometry was expected. In such studies, isomeric vinylic surfactant monomers were polymerized to produce polymers in which the surfactant side chains are fixed to the backbone at different positions (Fig. 4). Most strikingly, only polymers with “tail-end” geometry (Fig. 4c)



Scheme 2: Examples for polysoaps containing spacer groups: polymers with “main-chain” spacers prepared by radical copolymerization of surfactant monomers and small, polar comonomers (**Co-8**–**Co-10**). Polymers with “side-chain” spacers prepared by radical polymerization of functionalized surfactant monomers (**P-11**)

are water-soluble and behave as polysoaps^{6, 78}). In contrast, the isomers with other geometries do not dissolve in water, although all the monomers are good surfactants. However, the water-insoluble polymers are soluble in less polar solvents, whereas the

water-soluble isomers are not^{49,78)}. Only very few exceptions to this behaviour have been reported up to now^{97–99)}. In the cases, the chemical integrity of the polymers prepared, their structure, or their polymeric nature can be questioned⁹⁵⁾.

Obviously, there is no simple correlation between solubility and overall hydrophilicity of vinylic polymerized surfactants, considering the sum of all fragments: In case of the poorly performing “head” geometry, apparently more hydrophilic polymers are less soluble in water than apparently more hydrophobic ones of the well performing “tail-end” geometry⁷⁸⁾. The opposite is true when organic solvents are used. More confusing, metastable aqueous solutions of “head” geometry polymers can be prepared by micellar polymerization of the monomers; this is true only for surfactant fragments with very long alkyl chains, i. e. for the least hydrophilic polymers within the series studied^{58, 73, 100)}.

All these observations can be explained by the high density of surfactant fragments on the polymer backbone^{65, 96)}: There is not enough space for an oriented alignment of the surfactant fragments, thus preventing an efficient “amphiphilic arrangement”, which is needed to minimize solvophobic contacts (Fig. 6(a)). Instead, a “hydrophobic arrangement” (Fig. 6(b)) or a “hydrophilic arrangement” (Fig. 6(c)) is favoured, in which only one type of functional group is exposed at the “shell” of the

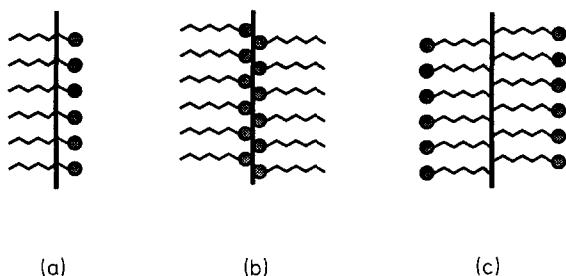


Fig. 6. Possible arrangements of polysoaps in solution (schematic)
(a) amphiphilic,
(b) hydrophobic,
(c) hydrophilic

polymer. The fragments of different polarity near the backbone are hidden in the polymer “core”. The metastable solutions reported occasionally for “head” geometry vinyl polymers^{58, 73, 100, 101)}, suggest that an “amphiphilic arrangement”— as poorly realizable it may be — still represents a local energy minimum, which can be frozen, if long alkyl chains are used. This agrees with the observations that many polymerized surfactants with “head” geometry form well-defined, stable insoluble monolayers at the air-water interface^{56, 68, 95)}. This form of self-organization requires an amphiphilic arrangement, but even a poorly realized one will suffice.

The steric problems described and the resulting behaviour should apply to all vinylic polymerized surfactants, independent of the structure of the “polymeric micelles” and of the resulting surface curvatures. Thus, vinylic surfactant homopolymers of other than “tail-end” geometry seem to be of little use as polysoaps. Even if the occasional exceptions reported are real, this rule is a most useful guideline for the tailoring of new polymers.

The use of spacer units

The geometrical constraints discussed for vinyl polymers are caused by the high density of surfactant side chains. Therefore, the problem can be overcome by appropriate dilution, which is achieved using so-called “main-chain” spacers”^{65, 96)} (Fig. 7(b)). Thus polysoaps of any geometry are accessible.

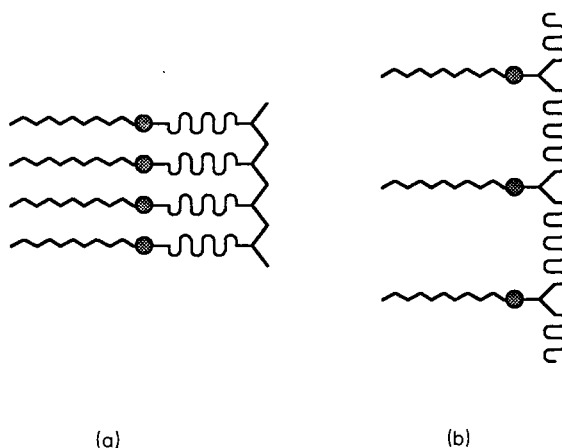


Fig. 7. Schematic representation of spacer groups in polysoaps:
(a) side-chain spacer,
(b) main-chain spacer

“Main-chain spacers” can be incorporated in various ways. Using homopolymerization of other than vinylic surfactant monomers, well defined spacer segments are produced in the backbone⁹⁶⁾. Polyaddition or polycondensation reactions could provide well defined spacer segments as well, but only few such systems (e.g. hydrophobized ionenes¹⁰²⁾) have been described. More conveniently, but generally in a less defined way, spacer segments are produced by copolymerization of amphiphilic monomers with polar comonomers without hydrophobic chains^{59–65)} (Fig. 2d). Also the classical approach to polysoaps, i.e. an incomplete hydrophobization of polar parent polymers (Fig. 2a), can be rationalized in terms of “main-chain spacers”: The unreacted units act as spacer segments. In agreement with the steric constraints, the spacer length required is longest for polysoaps of the “head” geometry, increasing with both the bulkiness of the surfactant fragment and of the main-chain spacer⁶⁵⁾. Whereas in the case of poly(sulfobetaines) the minimal spacer length for polysoaps of “head” geometry corresponds to a C_6 -repeating unit upwards, the minimal spacer length for polysoaps of “mid tail” geometry corresponds roughly to a C_4 -repeating unit⁹⁶⁾.

Considering the above discussion, the success of the most widely used polysoaps such as the copolymers poly[maleate-*alt*-(vinyl ether)] and poly(maleate-*alt*-alkene)^{31–35, 43, 84, 85, 103, 104)} having a C_4 -repeating unit, can be attributed to their advantageous combination of favourable “mid-tail” geometry, of small head group and of small spacer unit.

Alternatively to such “main-chain spacers”, so-called “side-chain spacers” can be employed^{4, 79, 82)} (Fig. 7(a)). They represent flexible units between polymer backbone

and surfactant fragment. An example of such a polymer with a “side-chain spacer” is **P-11** in *Scheme 2*. In contrast to other self-organized systems such as polymeric liquid crystals, “side-chain spacers” are much less effective for micellar polymers than “main-chain spacers”⁹⁵, presumably because the steric requirements in polysoaps are much more severe: The backbone may neither interfere with an efficient packing nor with the correct orientation of the side chains simultaneously. Thus, standard spacer lengths are insufficient, and polymers such as **P-11** are water-insoluble^{71, 95}. Obviously, “side-chain spacers” must be extensively long to provide water-solubility¹⁰⁵.

Properties of polysoaps in aqueous solution

Dynamic properties

Studies on the dynamics of polysoaps are rare. Micelles of low-molecular-weight surfactants are known to be dynamic structures of a limited, short lifetime only²¹. This problem has hardly been touched for polysoaps until now. More is known about the dynamics of the surfactant fragments within a “micelle”, where the various parts of surfactants are known to be subject to restrictions of mobility²¹. For low-molecular-weight surfactants, the “anchoring” of the hydrophilic head group at the micellar “surface” results in a decreasing mobility along the alkyl chain from its end towards the head group^{25, 106–108}. As the polymer backbone tends to immobilize the side-chain fragments close-by^{109, 110}, polysoaps of “tail-end” geometry show a dynamic profile of the surfactant fragments opposite to the one of the monomeric analogues. I. e., the end of the hydrophobic tails are the least mobile segments in the system^{111, 112}. This behaviour is also reflected in the nuclear magnetic resonance (NMR) spectra of vinylic polysoaps in solution, where the signals of protons in the proximity of the polymer backbone are virtually missing⁷⁸. However, the implications of this difference for the performance of polysoaps are not clear at present.

Viscosity

As mentioned before, the viscosity of aqueous polysoap solutions is characteristically low, up to high polymer contents (see Fig. 5). This behaviour was realized from the very beginning¹, and was considered to be a key feature distinguishing ionic polysoaps from standard polyelectrolytes^{12, 39, 67}. The unusually low viscosities were attributed to the intramolecular aggregation of the hydrophobic side chains, keeping the hydrodynamic radius small.

Noteworthy, this behaviour differs significantly from the one of slightly hydrophobized water-soluble polymers which act as thickeners^{5, 63, 113}. For them, intermolecular aggregation is assumed to cause substantial increases in viscosity. The border line between polysoaps and thickeners depends on the length of the hydrophobic chains chosen. The longer they are, the lower may be the content of hydrophobic chains, in order to produce polysoap characteristics. E. g. for poly(2-vinylpyridine), about 10% of derivatization with dodecyl chains, and about 20% of derivatization with octyl

chains are needed as a minimum to obtain polysoap behaviour¹²⁾. Similar numbers are obtained for other polysoap copolymers as well⁶⁵⁾. In analogy to the cmc of low-molecular-weight surfactants, this minimal content of hydrophobe, needed to enable the formation of intramolecular “polymeric micelles”, has been named “critical alkyl group content” (cac)^{39, 67)}.

Lyotropic liquid crystallinity

The formation of lyotropic liquid crystals (LC's) in water is considered to be an inherent property of low-molecular-weight surfactants¹¹⁴⁾. The temperature and concentration ranges of the LC phases are sometimes small, but nevertheless they are always found when carefully looked for. In case of the polysoaps, the standard situation is not clear. There are a number of reports on polymeric lyotropic LC's formed by polysoaps^{6, 7)}, particularly when polymerized surfactants are involved. E. g., polymers **P-4**–**P-6** of *Scheme 1* exhibit lyotropic LC phases in the concentrated regime¹¹⁵⁾. As for low-molecular-weight surfactants, the superstructures are most probably formed by micellar aggregates. However, for many polysoaps LC phases have not been observed yet, as for the copolymers shown in *Scheme 2*. Hence, the existence of lyotropic LC's might not be a general feature of polysoaps, in contrast to standard surfactants.

There is a second major difference to standard surfactants: Many virtually water-insoluble polymeric amphiphiles can be swollen, to yield polymeric lyotropic LC's even when the miscibility gap is broad. Such an unusual behaviour seems to be widespread for polymerized vinylic surfactants with side-chain spacers^{71, 115)}, such as polymer **P-11** in *Scheme 2*.

Aggregation behaviour in dilute and semidilute solution

Little is known so far about the aggregations taking place in “polymeric micelles” on a molecular basis. The few experimental studies available provide diverse results without a unified picture. This is partially due to the complexity of the phenomena involved and partially to the lack of straightforward analytical techniques.

From time-resolved fluorescence quenching (TRFQ) studies, rather small aggregation numbers of the hydrophobic side chains in “polymeric micelles” were concluded^{34, 104)}. Increasing with the length of the hydrophobic chains, they range from 15 to 60, being virtually independent of the degree of polymerization. As these values were well below the degrees of polymerization studied, these experiments point to the aggregation of the hydrophobic side chains into “local micelles” or “regional micelles” (Figs. 1(a) and (b)). Potentiometric titrations support this point of view, but the significance of the numbers obtained may be questioned because larger aggregation numbers were calculated for smaller hydrophobic chains²⁸⁾. Furthermore, other TRFQ experiments yield aggregation numbers of ca. 25 for the hydrophobic side chains in “polymeric micelles” which were equal to the degrees of polymerization employed³¹⁾. Although considered to support the idea of “molecular micelles” (Fig. 1(c)), these different results may be apparently contradictory only, due to the different degrees of polymerization employed: If they are in the range of the aggregation numbers, “local micelles” and “molecular micelles” would coincide.

Unfortunately, the TRFQ studies suffer from several assumptions made, which are difficult to verify. E.g., the percentage of aggregated versus not aggregated hydrophobic chains must be known, but is hardly available¹⁰⁴). The interpretation of TRFQ experiments is even more complicated by the observation that some polyelectrolytes show the presence of hydrophobic pockets with high aggregation numbers in TRFQ experiments¹¹⁶), although hydrophobic side chains are absent and polysoap characteristics are missing.

In contrast to the above studies, small-angle neutron scattering experiments yield aggregation numbers of polymeric micelles greater than the degree of polymerization³⁵). This suggests the overlap of intra- and intermolecular aggregation. In agreement, recent light-scattering data of nonionic polysoaps show additional intermolecular aggregation in dependence of the concentration and the degree of polymerization of the polysoaps¹¹⁷). Intermolecular aggregation in addition to intramolecular aggregation is deduced as well by recent electron microscopy studies. The micrographs visualize globular and threadlike structures of the polysoaps similar to giant micelles¹⁰¹). Unfortunately, the resolution of the micrographs does not allow an unambiguous distinction between “strings of beads” created from “local micelles” and extended cylindrical structures of real “molecular micelles”.

Surface activity

Despite its name, the surface activity of polysoaps has rarely been studied^{42, 56, 57, 61, 118}). Investigations are difficult because extensive equilibration times may be required^{118, 119}), due to slow diffusion¹²⁰) or perhaps due to conformational changes of the polysoap as proposed^{121, 122}).

Generally, polysoap solutions exhibit a continuous decrease of surface tension with increasing concentration, if they are surface active at all (Figs. 8–10). No cmc or a break point resembling a cmc is observed, in contrast to low-molecular-weight surfactants²¹) (Fig. 8). Although more studies would be needed to obtain a full picture, the data available suggest that for a given HLB, the surface activity tends to

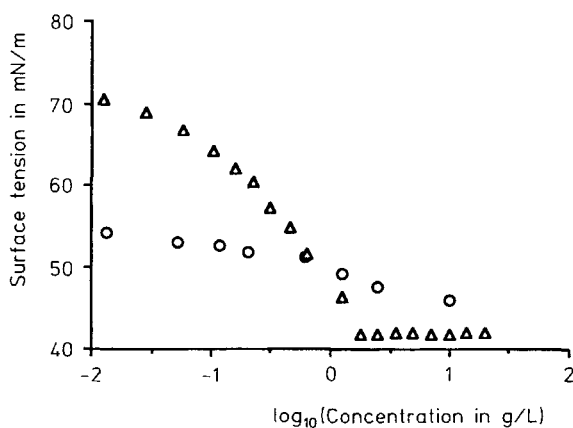


Fig. 8. Surface activity of surfactants and polysoaps in water at 25 °C, exemplified by zwitterionic acrylates. Surfactant monomer (Δ), polysoap P-6 (○)

Fig. 9. Surface activity of closely related polysoaps in dependence of their geometry in water at 25 °C. Cationic polysoap **P-4** ("tail-end" geometry) (Δ); cationic polysoap **Co-8a** ("head" geometry) (\bullet)

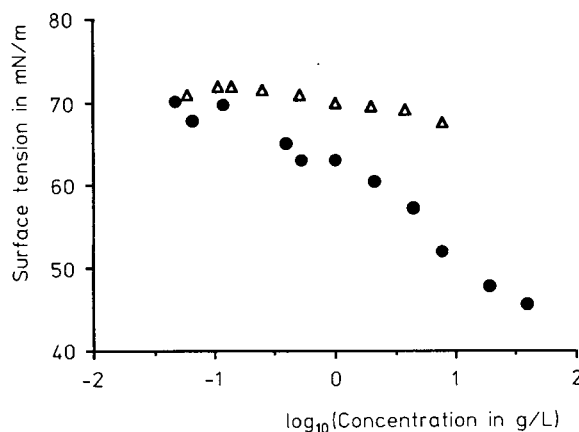
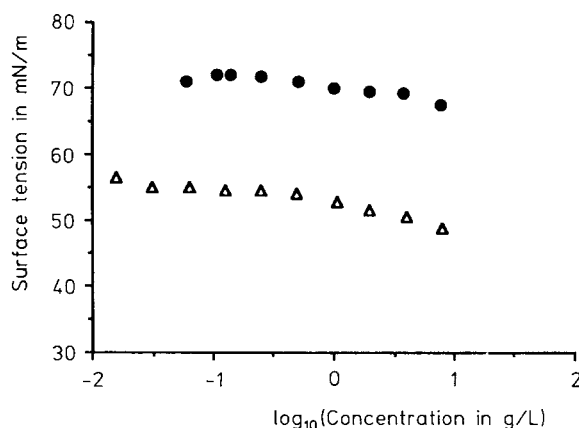


Fig. 10. Surface activity of analogous polysoaps with "tail-end" geometry in water at 25 °C. Cationic polymethacrylate **P-4** (\bullet); zwitterionic polymethacrylate **P-5** (Δ)



increase with the proximity of the backbone and the surfactant head group: The surface activities reported for polysoaps of the "tail-end" geometry are generally somewhat lower than for analogues of the "head" geometry (Fig. 9). Such a behaviour parallels the problems of the different geometries to realize an efficient amphiphilic arrangement in solution.

Comparing polysoaps of a given geometry, the data reported suggest that the more hydrophilic the surfactant head group, the lower is the surface activity. E. g. cationic polysoaps with "tail-end" geometry are slightly surface active only, whereas the zwitterionic analogues with lower HLB exhibit moderate surface activity (Fig.10).

Moderate surface activities are often observed for nonionic polysoaps, too¹²³. In analogy, the cationic polysoaps **Co-8** of "head geometry", prepared by copolymerization of a cationic monomer and a surfactant monomer, show increasing surface activity with increasing surfactant content (Fig. 11). The rule may serve as a useful guideline, even if it does not always hold true¹²⁴. It is consistent with the idea of intramolecular aggregation, and rationalizes as well the observed effects of added salt^{57,89}.

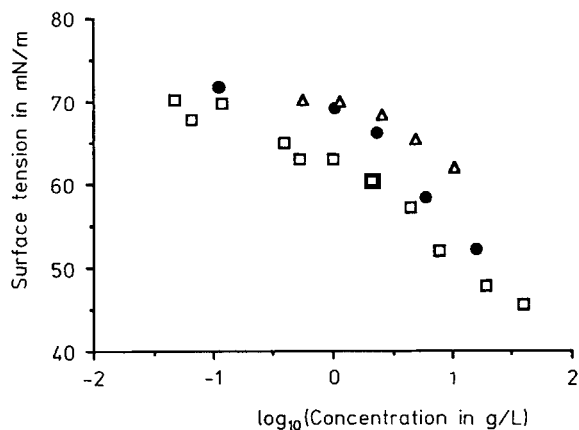


Fig. 11. Surface activity of cationic polysoap copolymers **Co-8** in dependence on their content of hydrophilic comonomer (cholin methacrylate) in water at 25 °C; **Co-8a**, 60 mol-% of hydrophilic comonomer (\square); **Co-8b**, 80 mol-% of hydrophilic comonomer (\bullet); **Co-8c**, 90 mol-% of hydrophilic comonomer (\triangle)

Depressing the dissociation of the charged head groups and hence reducing their hydrophilicity, added salt enhances the surface activity of cationic polysoaps. In contrast, the surface activity of zwitterionic polysoaps is diminished by added salt due to their anti-polyelectrolyte character¹²⁵⁾.

Solubilization

Solubilization as defined by Elworthy, Florence and MacFarlane is “the preparation of thermodynamically stable isotropic solutions of substances normally insoluble or slightly soluble in a given solvent by the introduction of an additional amphiphilic component or components”¹²⁶⁾. From practical aspects the capability of solubilization is one of the key properties of surfactants¹²⁷⁾. As efficient solubilization is bound to the presence of micelles, surfactant concentrations above the cmc are required¹²⁶⁾ (see Fig. 12). This causes inherent problems if dilute solutions are involved (e. g. for

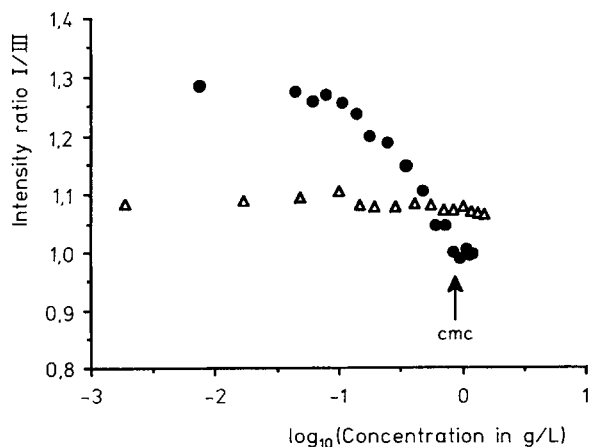


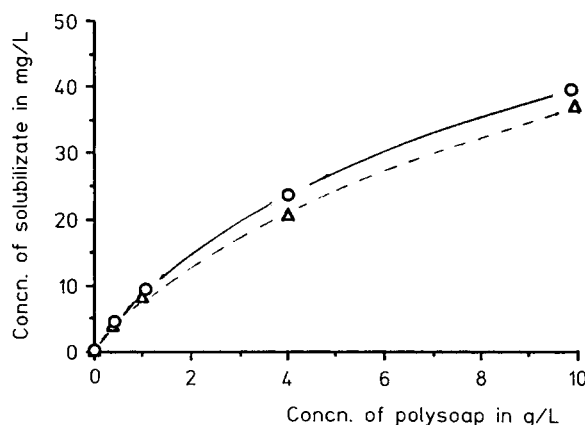
Fig. 12. Concentration-dependent solubilization of pyrene by polysoap **P-5** (\triangle) and its monomer (\bullet). Monitored is the change of the intensity ratio of fluorescence band I (372 nm) and band III (383 nm). A lower ratio I/III indicates a more hydrophobic environment of the pyrene label

reasons of the stability of biological solubilisates, of toxicology, or of waste-water treatment). Similarly, dilution of the surfactant solutions below the cmc will lead to a deposition of the solubilizates contained, a problem often encountered in rinsing processes.

This problem does not exist for polysoaps: Due to the intramolecular aggregation of the surfactant fragments, they are capable of solubilization at any concentration^{56, 85, 104} (see Fig. 12), the resulting solutions being stable against even extensive dilution. Thus, polysoaps may be the perfect match to standard surfactants for special applications. A promising field for example may be the use of polysoaps in emulsion polymerization processes^{128, 129} or as "switchable surfactants"¹²⁴.

Another interesting feature emerges from concentration-dependent solubilization studies. As illustrated in Fig. 13, the cationic and zwitterionic analogues **P-4** and **P-5** exhibit virtually identical concentration dependences of their solubilization capacity. This contrasts markedly with the differences in reduced viscosity observed in the same concentration range (Fig. 5), implying two important conclusions: First, even in the concentration range with polyelectrolyte behaviour, "polymeric micelles" are still

Fig. 13. Solubilization of azodye **S4** by the cationic polysoap **P-4** (○) and its zwitterionic analogue **P-5** (△) in dependence of polysoap concentration



present. Hence, the absolute values of the reduced viscosity rather than the shape of the curve are indicative of polysoap behaviour, a point often confused in the literature. Second, the observations go well along with modern polyelectrolyte theory which attributes the viscosity behaviour to the formation of supramolecular structures instead of to a "coil-to-rod" transition¹³⁰⁻¹³²; hence there is no contradiction between the high reduced viscosities observed and the presence of hydrophobic aggregates. Nevertheless, a considerable expansion of polyelectrolyte coils still occurs at low concentrations. Therefore in case of "molecular micelles" (Fig. 1 (c)), different concentration dependences would be expected for the polyelectrolyte **P-4** and the zwitterion **P-5** which are not observed. Accordingly, the solubilization experiments point to the presence of "local micelles" or "regional micelles" (Fig. 1 (a) and (b)).

The practical interest in the solubilization properties of polysoaps is reflected already in the initial studies of Strauss et al.^{1, 8-10}, who studied the solubilization of aliphatic

and aromatic hydrocarbons. Substantial solubilization capacities and aggregational changes were found. Despite these early attempts to study solubilization quantitatively, the majority of studies has been confirmed to qualitative investigations rather than quantitative ones: Usually the question is addressed, which environment is encountered by the solubilizates, thus drawing conclusions towards the nature of “polymeric micelles”, their size and the microdomains available for solubilization. Most of such experiments make use of solubilizing probes the spectral properties of which are sensitive to the environment of the chromophore¹³³⁾.

Fluorescence spectroscopy of pyrene derivatives proved to be a powerful technique for qualitative solubilization experiments by virtue of excimer formation and pyrene fluorescence fine structure^{134–136)}. The intensity ratio of the fluorescence bands I at 372 nm and III at 383 nm is a convenient measure for the hydrophobicity of the environment of the label.

As expected, the hydrophobicity of the “polymeric micelles” increases with the length of the alkyl chains incorporated¹⁰⁴⁾. Concerning the polymer geometry, structural variations of vinylic polysoap isomers suggest that the hydrophobicity of the “polymeric micelles” is highest for polysoap of “head” geometry and lowest for “tail-end” geometry⁶⁵⁾ (Fig. 14). These observations can be rationalized by a hydrophobicity profile of the respective polysoap structures: As the polymer backbone generally bears some polar groups, it has to be considered as a fragment of intermediate hydrophobicity partially interfering with the hydrophobicity profile of the parent surfactant side chain. The exact quality depends on the chemistry of the backbone chosen (Fig. 15).

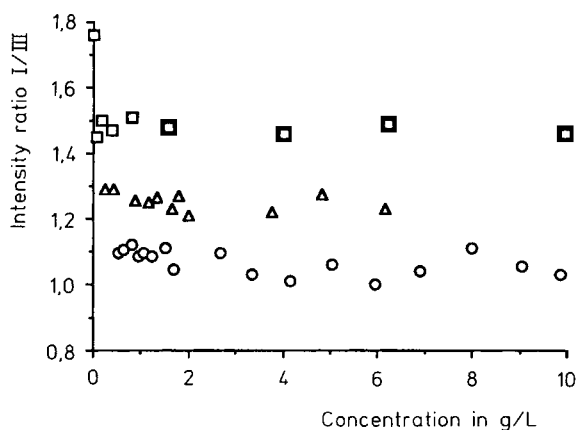


Fig. 14. Concentration-dependent solubilization of pyrene by polysoap **P-3** with “tail-end” geometry (\square), by the isomeric analogue **Co-10a** with “mid-tail” geometry (\triangle) and by the isomeric analogue **Co-9b** with “head” geometry (\circ). Monitored is the change of the intensity ratio of fluorescence band I (372 nm) and band III (383 nm) as in Fig. 12

Correlations between the molecular structure of surfactants and their absolute solubilization capacities are difficult to establish¹³⁷⁾. The capacities depend in a complex way on both the surfactant and the solubilize chosen, and are modified by additional factors such as pH or ionic strength¹²⁶⁾. Furthermore, the uptake of considerable amounts of solubilize may change the aggregate structure involved²¹⁾, thus rendering the interpretation of the studies even more complicated.

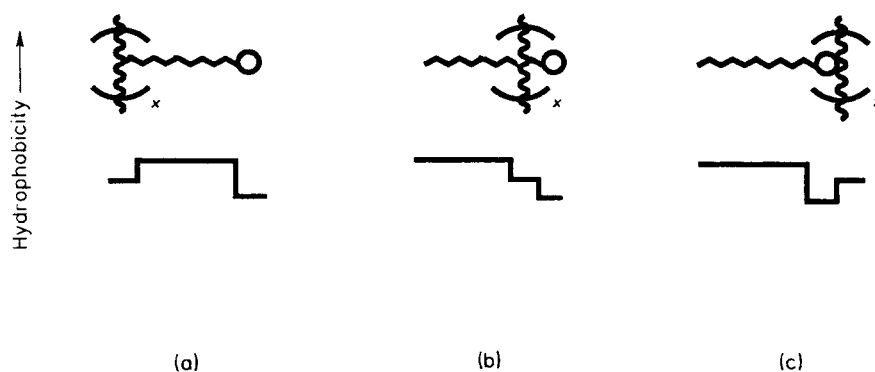
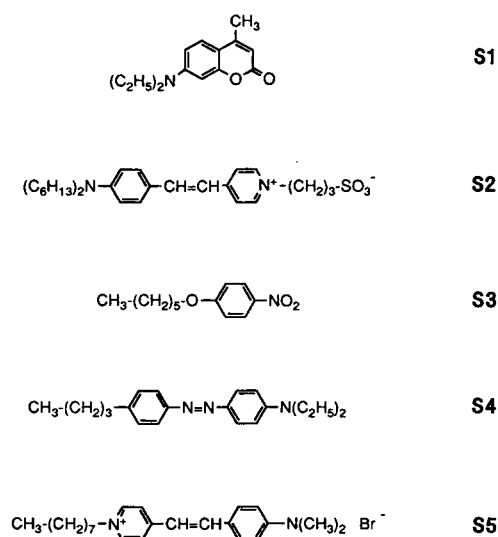


Fig. 15. Schematic polarity profile in the surfactant side chains of polysoaps: (a) “tail-end” geometry, (b) “mid-tail” geometry, (c) “head” geometry

A key question is, how the polymer fixation of surfactant groups influences the solubilization capacity. Hydrophobic dyes are conveniently used for such experiments (*Scheme 3*) as they enable quantification by ultraviolet-visible (UV/VIS) spectroscopy. Comparisons reveal that the solubilization capacity of polysoaps compares well with that of low-molecular-weight surfactants in general, although a detailed look produces a complex picture (Fig. 16): Simple polar solubilizes such as coumarin **S1** are equally efficiently solubilized by methacrylate polysoaps of “tail-end” geometry and by low-



Scheme 3: Hydrophobic and amphiphilic dyes used for solubilization experiments

molecular-weight analogues. Similar results have been obtained for diazepam (7-chloro-2,3-dihydro-1-methyl-5-phenyl-1*H*-benzodiazepin-2-one) and naphthalene previously¹³⁸. When more bulky, amphiphilic substrates such as the phenyl ether **S3** or the azodye **S4** are used, monomeric surfactants seem to solubilize somewhat more efficiently than polymeric analogues, but the differences are small. In selected cases, polymers may be even more efficient than monomers, as observed for isooctane¹⁾ or some hydrophobic dyes⁸⁵, such as the dye **S2**¹³⁷ (Fig. 16).

Solubilize:

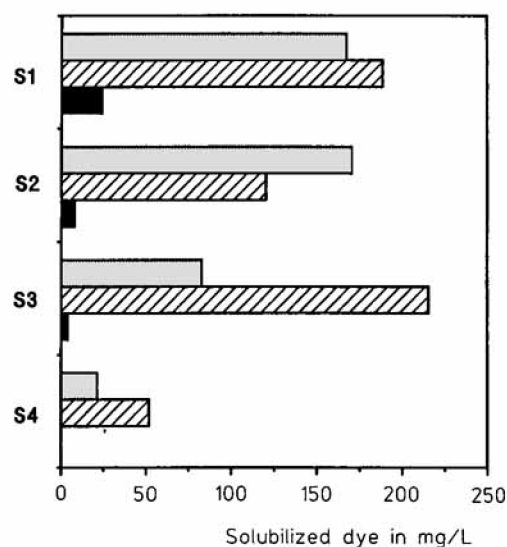


Fig. 16. Solubilization capacities of polysoap **P-5** and its low-molecular-weight surfactant analogue *N*-dodecyl-*N,N*-dimethyl 3-ammoniopropanesulfonate (DDAPS) for various hydrophobic dyes (4 g soap per litre): polysoap **P-5** (▨); surfactant analogue DDAPS (▧); pure water (reference) (■)

By comparing polysoaps of different structure, marked differences are found depending on the content of hydrophobe, the polymer geometry and the nature of the backbone. The nature of the headgroup becomes important when specific interactions with the solubilize take place. E. g., cationic polysoaps are better suited to solubilize the zwitterionic cyanine dye **S2** than their zwitterionic analogues, but are much less efficient in case of the cationic cyanine dye **S5**. Here, electrostatic attraction and repulsion, respectively, play a dominating role. However, if no such strong specific interactions occur, the solubilization capacities of the analogues are comparable, as exemplified by the azodye **S4** (Fig. 13) or the nitrophenol ether **S3** (Fig. 17).

The role of the content of hydrophobe seems rather straightforward: As the content of hydrophobic chains increases, the solubilization capacity increases as well. For some polysoap copolymers, this dependence can be approximated by a linear relationship (Fig. 18), but for others the solubilization capacity increases faster than the hydrophobe content does¹⁾. In any case, recalling that the polar comonomer content is needed as a "main-chain spacer", these findings imply the existence of an optimal spacer length for polysoaps: It must be long enough to provide water-solubility, but short enough to enhance the solubilization power.

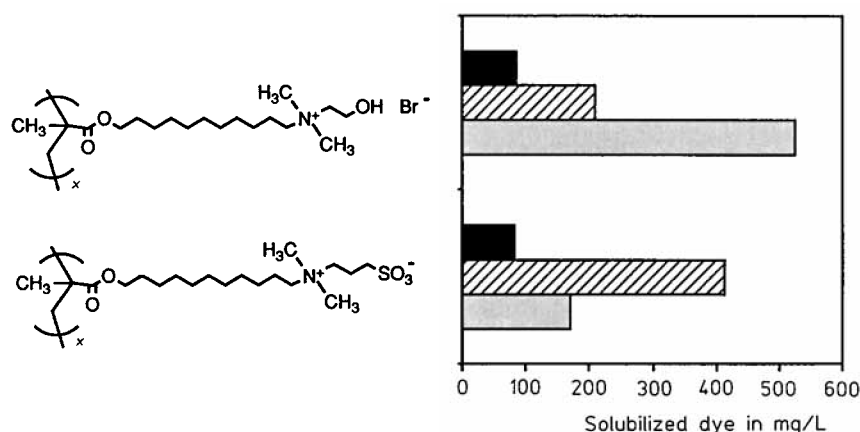


Fig. 17. Solubilization capacities of cationic polysoap **P-4** and its zwitterionic analogue **P-5** for various hydrophobic dyes (4 g soap per litre: uncharged dye **S3** (■); cationic dye **S5** (▨); zwitterionic dye **S2** (▤))

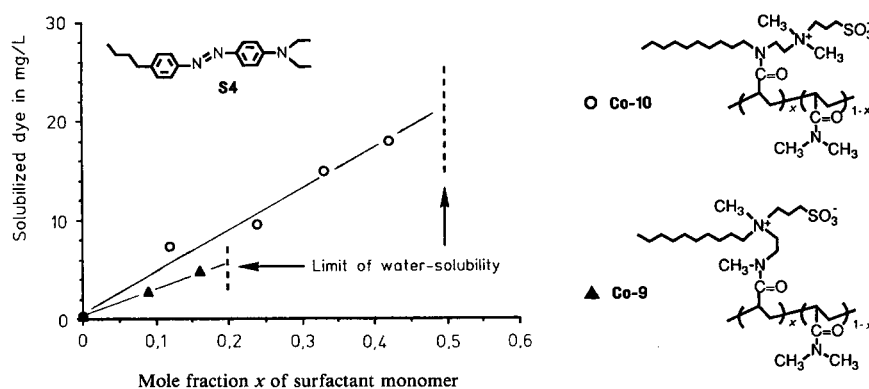


Fig. 18. Solubilization capacity of isomeric polysoap copolymers **Co-9** ("head" geometry) and **Co-10** ("mid-tail" geometry) in dependence of the mole fraction x of surfactant monomer incorporated (4 g soap per litre)

The effects of polymer geometry and the nature of the backbone are interdependent. Comparing "isomeric" polysoaps based on poly(*N*-methylacrylamide), polysoaps of "mid-tail" geometry solubilize best, in particular when the spacers are kept short as for **Co-10a** and **P-7** (Fig. 19). Second in solubilization power is the "head isomer" **Co-9b** in spite of the long spacer required which reduces the capacity as shown above. The "tail-end" isomer **P-3** is surprisingly inefficient. Noteworthy, the sequence of solubilization capacity is "mid-tail" > "head" > "tail-end" geometry and does not parallel the sequence of hydrophobicity probed by pyrene, which is "head" > "mid-tail" > "tail-end".

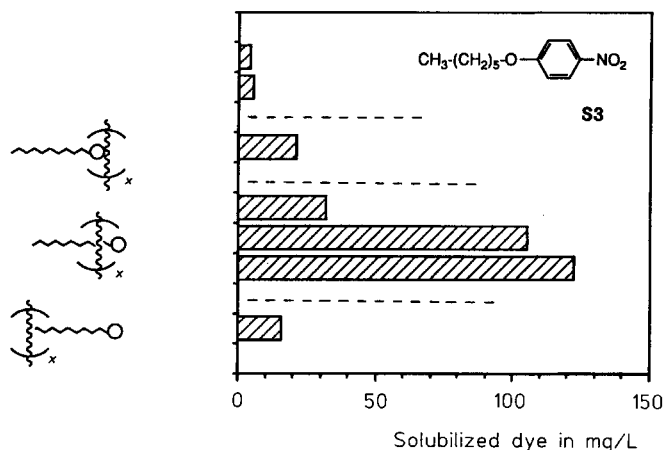


Fig. 19. Solubilization capacity of closely related poly(*N*-methylacrylamide) polysoaps for the hydrophobic dye **S3** in dependence of their polysoap geometry (4 g soap per litre). From top to bottom: pure water and poly(*N,N*-dimethylacrylamide) (both as references); copolymer **Co-9b** with "head" geometry; the "isomeric" copolymer **Co-10b**, copolymer **C-10a** and polymer **P-7** with "mid-tail" geometry; polymer **P-3** with "tail-end" geometry

Such a comparison of geometrical "isomers" with respect to their solubilization capacity should not be overestimated, as it does not do full justice to the problem addressed. Considering Fig. 15, only a hydrophobic backbone will provide a good hydrophobic interior of the polymeric "micelles" for polysoaps with "tail-end" geometry. Indeed, as illustrated for a series of polysoap analogues in Fig. 20, the capacity of "tail-end" polysoaps increases sharply in the series polyacrylamide **P-3** < polyacrylate **P-6** < polymethacrylate **P-5**, i. e. with increasing hydrophobicity of the polymer backbone.

According to the same picture, polysoaps of "mid-tail" geometry would not be expected to be very sensitive to backbone polarity, in agreement with the comparable solubilization capacity of **P-7** and **Co-10a** (Fig. 19). Polysoaps with "head" geometry should advantageously have a hydrophilic backbone (Fig. 15c). As polysoaps with "head" geometry require anyhow rather polar backbones to be water-soluble, such ranking is difficult to verify, however. But for sure, the above results show that an appropriate comparison uses "optimized" polysoaps of different geometry instead of "isomeric" ones. If done so, it appears that differences in solubilization capacity are gradual only. More polar solubilizates such as the coumarin dye **S1** which can be assumed to reside close to the "micellar surface" are more efficiently solubilized by polysoaps with "tail-end" geometry. In contrast, solubilizates of amphiphilic structure such as the phenyl ether **S3** are more efficiently solubilized by polysoaps of "mid-tail" geometry (Fig. 21).

The differences observed may be due to the respective positions of the polymer backbones, which occupy space needed to accommodate the solubilizate. Most

Fig. 20. Solubilization capacities of analogous zwitterionic polysoaps with “tail-end” geometry for azodye **S4** in dependence of the polymer backbone chosen (4 g per litre). The hydrophobicity of the backbone increases from top to bottom: polyacrylamide **P-3** < polyacrylate **P-6** < polymethacrylate **P-5**

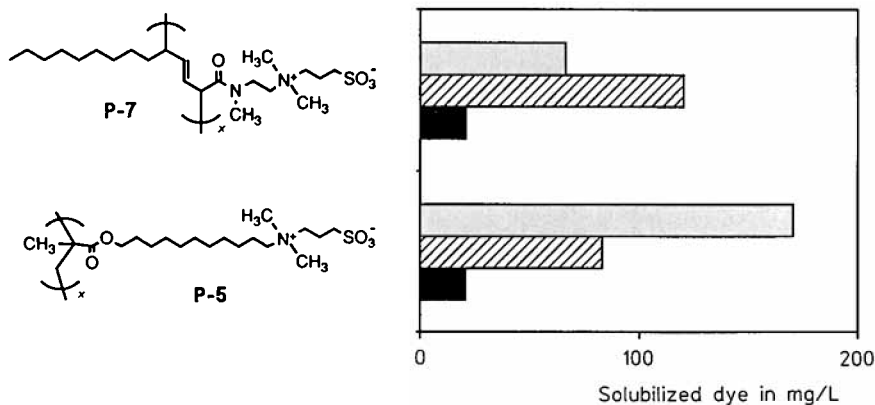
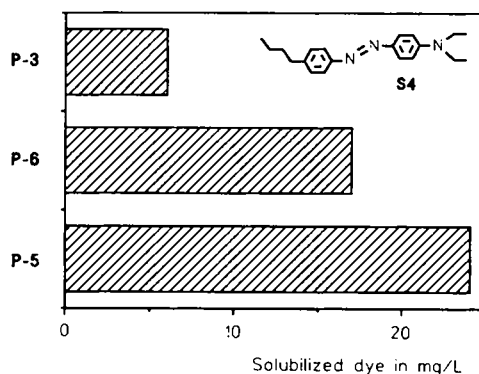


Fig. 21. Solubilization capacity of two analogous “optimized” polysoaps **P-7** with “mid-tail” and **P-5** with “tail-end” geometry for various hydrophobic dyes (4 g soap per litre): coumarin **S1** (□); nitrophenyl ether **S3** (▨); azodye **S4** (■)

noteworthy, the results imply that “the optimal polysoap” structure does not exist, but the systems to be chosen advantageously depend on the problem addressed.

In the above comparisons, polysoaps with “head” geometry always emerge as less efficient solubilizing agents. Nevertheless, the capacities observed are still fair, and therefore such polysoaps are still suited for solubilization. In spite of their inferior solubilization capacity, “head”-type polysoaps may — for practical purposes — even prove to be the solubilizing agent of choice if optimal solubilization is not essential, particularly when keeping the ease of their synthesis in mind.

Conclusions

Micellar polymers are intriguing substances from the scientific and practical point of view. Clearly, many problems are still awaiting more research. E.g., the detailed

nature of the aggregates formed is still an open question. Further, as systematic structural investigations have just started, many novel aspects of polysoap systems are expected from future work. Nevertheless, some general relationships between the molecular architecture and key properties in aqueous solutions such as surface activity and solubilization power can be established, covering most of the present data. These relationships will provide useful guidelines for the synthesis of new types of polysoaps.

- ¹⁾ U. P. Strauss, E. G. Jackson, *J. Polym. Sci.* **5**, 649 (1951)
- ²⁾ U. P. Strauss, "Hydrophobic Polyelectrolytes" in: *"Polymers in Aqueous Media"*, J. E. Glass, Ed., *Advances in Chemistry Series* No. 223, 317 pp, Am. Chem. Soc., Washington DC 1989
- ³⁾ E. A. Bekturov, Z. Kh. Bakauova, *"Synthetic Water-Soluble Polymers in Solution"*, 178 pp, Hütthig & Wepf, Basel 1986
- ⁴⁾ H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **100**, 117 (1988)
- ⁵⁾ B. Magny, I. Iliopoulos, R. Audebert, *Polym. Commun.* **32**, 456 (1991)
- ⁶⁾ H. Finkelmann, G. Rehage, *Adv. Polym. Sci.* **60/61**, 99 (1984)
- ⁷⁾ H. Finkelmann, E. Jahns "Association and Liquid Crystalline Phases of Polymers in Solution", in: *"Polymer Association Structures"*, M. A. El-Nokaly, Ed., 1 pp, *ACS Symp. Ser.* **384**, Am. Chem. Soc., Washington DC 1989
- ⁸⁾ E. G. Jackson, U. P. Strauss, *J. Polym. Sci.* **5**, 473 (1951)
- ⁹⁾ L. H. Layton, E. G. Jackson, U. P. Strauss, *J. Polym. Sci.* **9**, 295 (1952)
- ¹⁰⁾ U. P. Strauss, N. L. Gersfeld, *J. Phys. Chem.* **58**, 747 (1954)
- ¹¹⁾ T. Nakagawa, H. Inoue, *Kolloid Z. Z. Polym.* **195**, 93 (1964)
- ¹²⁾ H. Inoue, *Kolloid Z. Z. Polym.* **195**, 102 (1964)
- ¹³⁾ H. Inoue, *Kolloid Z. Z. Polym.* **196**, 1 (1964)
- ¹⁴⁾ I. R. Schmolka, *J. Am. Oil Chem. Soc.* **59**, 110 (1977)
- ¹⁵⁾ R. I. Hancock, "Macromolecular Surfactants", in: *"Surfactants"*, T. F. Tadros, Ed., 287 pp, Academic Press, New York 1984
- ¹⁶⁾ Yu. V. Tanchuk, G. S. Pop, *Colloid J. USSR (Engl. Transl.)* **40**, 1024 (1978)
- ¹⁷⁾ Y. Morishima, T. Kobayashi, S. Nazakura, *Polym. J.* **21**, 267 (1989)
- ¹⁸⁾ Y. Barakat, T. S. Gendy, A. I. Mohammed, A. F. M. Youssef, *Br. Polym. J.* **21**, 383 (1989)
- ¹⁹⁾ K. Arai, S. Miyahara, *Makromol. Chem.* **191**, 2647 (1990)
- ²⁰⁾ K. Arai, S. Miyahara, T. Okabe, *Makromol. Chem.* **192**, 2183 (1991)
- ²¹⁾ Y. Chevalier, T. Zemb, *Rep. Prog. Phys.* **53**, 279 (1990)
- ²²⁾ F. M. Menger, *Acc. Chem. Res.* **12**, 111 (1979)
- ²³⁾ P. Fromherz, *Ber. Bunsen-Ges. Phys. Chem.* **85**, 891 (1981)
- ²⁴⁾ K. A. Dill, P. J. Flory, *Proc. Natl. Acad. Sci. U. S. A.* **77**, 3115 (1980)
- ²⁵⁾ D. W. R. Gruen, *Prog. Colloid Polym. Sci.* **70**, 6 (1985)
- ²⁶⁾ B. Cabane, R. Duplessix, T. Zemb, *J. Phys.* **46**, 2161 (1985)
- ²⁷⁾ P. L. Dubin, U. P. Strauss, "Hypercoiling in Hydrophobic Polyacids" in: *"Polyelectrolytes and Their Applications"* A. Rembaum and E. Sélégny, Eds., 3 ff, D. Reidel, Dordrecht 1975
- ²⁸⁾ a) U. P. Strauss, B. W. Barbieri, *Macromolecules* **15**, 1347 (1982)
b) B. W. Barbieri, U. P. Strauss, *ibid.* **18**, 411 (1985)
- ²⁹⁾ U. Kammer, H.-G. Elias, *Kolloid Z. Z. Polym.* **250**, 344 (1972)
- ³⁰⁾ K. Nagai, H.-G. Elias, *Makromol. Chem.* **188**, 1095 (1987)
- ³¹⁾ D. Y. Chu, J. K. Thomas, *Macromolecules* **20**, 2133 (1987)
b) D. Y. Chen, J. K. Thomas, *ibid.* **24**, 2212 (1991)
- ³²⁾ E. Hamad, S. Qutubuddin, *Macromolecules* **23**, 4185 (1990)
- ³³⁾ E. Hamad, S. Qutubuddin, *J. Chem. Phys.* **96**, 6222 (1992)
- ³⁴⁾ J. L. Hsu, U. P. Strauss, *J. Phys. Chem.* **91**, 6238 (1987)
- ³⁵⁾ a) L. B. Shih, E. Y. Shen, S. H. Chen, *Macromolecules* **21**, 1387 (1988)
b) L. B. Shih, D. H. Mauer, C. J. Verbrugge, C. F. Wu, S. L. Chang, S. H. Chen, *ibid.* **21**, 3235 (1988)

- 36) N. J. Turro, J. K. Barton, D. A. Tomalia, *Acc. Chem. Res.* **24**, 332 (1991)
- 37) G. R. Newcome, C. N. Moorefield, G. R. Baker, M. J. Saunders, S. H. Grossmann, *Angew. Chem.* **103**, 1207 (1991)
- 38) A. I. Medalia, H. H. Freedman, S. Sinha, *J. Polym. Sci.* **40**, 15 (1959)
- 39) D. Woermann, F. T. Wall, *J. Phys. Chem.* **64**, 581 (1960)
- 40) H. Hidaka, T. Onai, M. Murata, K. Fujiwara, M. Takai, M. Moriya, *J. Colloid Interface Sci.* **119**, 565 (1987)
- 41) C. Luca, E. Avram, I. Petrariu, *J. Macromol. Sci., Chem.* **A25**, 345 (1988)
- 42) T. Seo, S. Take, K. Miwa, K. Hamada, T. Iijima, *Macromolecules* **24**, 4255 (1991)
- 43) C. L. McCormick, C. E. Hoyle, M. D. Clark, *Polymer* **33**, 243 (1992)
- 44) H. Finkelmann, B. Lühmann, G. Rehage, *Colloid Polym. Sci.* **260**, 56 (1982)
- 45) B. Lühmann, H. Finkelmann, G. Rehage, *Angew. Makromol. Chem.* **123/124**, 217 (1984)
- 46) H. H. Freedman, J. P. Mason, A. I. Medalia, *J. Org. Chem.* **23**, 76 (1958)
- 47) C. E. Larrabee jr., E. D. Sprague, *J. Polym. Sci., Polym. Lett. Ed.* **17**, 749 (1979)
- 48) S. Hamid, D. C. Sherrington, *J. Chem. Soc., Chem. Commun.* **1986**, 936 (1986)
- 49) S. Hamid, D. C. Sherrington, *Polymer* **28**, 325, 332 (1987)
- 50) C. M. Paleos, S. Voliotis, G. Margomenou-Leonidopoulou, P. Dais, *J. Polym. Sci., Polym. Chem. Ed.* **18**, 3463 (1980)
- 51) H. Finkelmann, M. Schafheutle, *Colloid Polym. Sci.* **264**, 786 (1986)
- 52) K. W. Yeoh, C. H. Chew, L. M. Gan, L. L. Koh, *J. Macromol. Sci., Chem.* **A27**, 63 (1990)
- 53) V. Egorov, *Makromol. Chem., Macromol. Symp.* **31**, 157 (1990)
- 54) J. Klein, M. Kunz, J. Kowalczyk, *Makromol. Chem.* **191**, 517 (1990)
- 55) B. Boyer, G. Lamaty, J. M. Moussamou-Missima, A. A. Pavia, B. Pucci, J. P. Roque, *Tetrahedron Lett.* **32**, 1191 (1991)
- 56) A. Laschewsky, I. Zerbe, *Polymer* **32**, 2081 (1991)
- 57) H. E. Jorgensen, U. P. Strauss, *J. Phys. Chem.* **65**, 1873 (1961)
- 58) J. C. Salamone, P. Taylor, B. Snider, S. C. Israel, *J. Polym. Sci., Polym. Chem. Ed.* **13**, 161 (1975)
- 59) D. N. Schulz, J. J. Kaladas, J. J. Maurer, J. Bock, S. J. Pace, W. W. Schulz, *Polymer* **28**, 2110 (1987)
- 60) Fed. Rep. Ger. 3 636 429 (1987) invs.: H. J. Kock, H. Finkelmann, C. Meier; *Chem. Abstr.* **107**, 238937p (1987)
- 61) R. J. Weinert I. Piirma, *J. Appl. Polym. Sci.* **38**, 1295 (1989)
- 62) C. H. Do, G. B. Butler, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **30**(2), 352 (1989)
- 63) D. G. Pfeiffer, *Polymer* **31**, 2353 (1990)
- 64) Y. J. Yang, J. F. B. N. Engberts, *J. Org. Chem.* **56**, 4300 (1991)
- 65) P. Köberle, A. Laschewsky, D. v. d. Boogaard, *Polymer* **33**, 4029 (1992)
- 66) U. P. Strauss, S. J. Assony, E. G. Jackson, L. H. Layton, *J. Polym. Sci.* **9**, 509 (1952)
- 67) U. P. Strauss, N. L. Gershfeld, E. H. Crook, *J. Phys. Chem.* **60**, 577 (1956)
- 68) M. Plaisance, L. Ter-Minassian-Saraga, *J. Colloid Interface Sci.* **59**, 113 (1977)
- 69) J. C. Salamone, S. C. Israel, P. Taylor, B. Snider, *J. Polym. Sci., Polym. Symp.* **45**, 65 (1974)
- 70) R. Griffith, Thesis, Mainz (Germany) 1986
- 71) E. Jahns, H. Finkelmann, *Colloid Polym. Sci.* **265**, 304 (1987)
- 72) K. Nagai, Y. Ohishi, H. Inaba, S. Kudo, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 1121 (1985)
- 73) K. Nagai, Y. Ohishi, *J. Polym. Sci., Part A: Polym. Chem.* **25**, 1 (1987)
- 74) C. M. Paleos, A. Malliaris, *J. Macromol. Sci., Rev. Macromol. Chem.* **C28**, 403 (1988)
- 75) A. León, L. Gargallo, D. Radic, A. Horta, *Polymer* **32**, 761 (1991)
- 76) T. R. Fang, X. B. Zhu, *Polym. Bull. (Berlin)* **25**, 467 (1991)
- 77) K. Naitoh, Y. Ishii, K. Tsujii, *J. Phys. Chem.* **95**, 7915 (1991)
- 78) A. Laschewsky, I. Zerbe, *Polymer* **32**, 2070 (1991)
- 79) H. Finkelmann, G. Rehage, *Adv. Polym. Sci.* **60/61**, 99 (1984)
- 80) V. Percec, C. Pugh, in: "Side Chain Liquid Crystals", C. B. McArdle, Ed., 30 pp, Blackie and Son, Glasgow 1989
- 81) R. Elbert, A. Laschewsky, H. Ringsdorf, *J. Am. Chem. Soc.* **107**, 4134 (1985)
- 82) A. Laschewsky, H. Ringsdorf, G. Schmidt, J. Schneider, *J. Am. Chem. Soc.* **109**, 788 (1987)

- 83) F. Embs, D. Funhoff, A. Laschewsky, U. Licht, H. Ohst, W. Prass, H. Ringsdorf, G. Wegner, R. Wehrmann, *Adv. Mater.* **3**, 25 (1991)
- 84) E. Pefferkorn, A. Schmitt, R. Varoqui, *C. R. Acad. Sci.* **C267**, 349 (1968)
- 85) K. Ito, H. Ono, Y. Yamashita, *J. Colloid Sci.* **19**, 28 (1964)
- 86) B. Lühmann, H. Finkelmann, *Colloid Polym. Sci.* **265**, 506 (1987)
- 87) K. W. Yeoh, C. H. Chew, L. M. Gan, L. L. Koh, *Polym. Bull. (Berlin)* **22**, 123 (1989)
- 88) K. T. Wang, I. Iliopoulos, R. Audebert, *Polym. Bull. (Berlin)* **20**, 577 (1988)
- 89) P. Köberle, A. Laschewsky, T. D. Lomax, *Makromol. Chem., Rapid Commun.* **12**, 427 (1991)
- 90) P. Lange, A. Laschewsky, B. A. Wolf, unpublished
- 91) R. Löffler, H. Finkelmann, *Makromol. Chem., Rapid Commun.* **11**, 321 (1990)
- 92) D. A. Frankel, D. F. O'Brien, *J. Am. Chem. Soc.* **113**, 7436 (1991)
- 93) J. H. Fuhrhop, R. Blumtritt, C. Lehmann, P. Luger, *J. Am. Chem. Soc.* **113**, 7437 (1991)
- 94) P. Anton, A. Laschewsky, *Makromol. Chem., Rapid Commun.* **12**, 189 (1991)
- 95) A. Laschewsky, *Colloid Polym. Sci.* **269**, 785 (1991)
- 96) P. Anton, A. Laschewsky, *Makromol. Chem.*, in press
- 97) C. M. Paleos, G. Margomenou-Leonidopoulou, A. Malliaris, *Mol. Cryst. Liq. Cryst.* **161**, 385 (1988)
- 98) C. M. Paleos, P. Dais, A. Malliaris, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 3383 (1984)
- 99) C. M. Paleos, A. Malliaris, P. Dais, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **28** (2), 434 (1987)
- 100) a) D. Cochlin, R. Zana, F. Candau, *Polymer International*, in press
b) D. Chocin, Ph. D. Thesis, Strasbourg (France) 1991
- 101) D. Cochlin, F. Candau, R. Zana, Y. Talmon, *Macromolecules* **25**, 4220 (1992)
- 102) A. J. Sanessa, W. Cullen, P. Ander, *Macromolecules* **13**, 195 (1980)
- 103) P. L. Dubin, U. P. Strauss, *J. Phys. Chem.* **74**, 2842 (1970)
- 104) a) W. Binana-Limbelé, R. Zana, *Macromolecules* **20**, 1331 (1987)
b) W. Binana-Limbelé, R. Zana, *ibid.* **23**, 2731 (1990)
- 105) K. Ito, K. Tanaka, H. Tanaka, G. Imai, S. Kawaguchi, S. Itsuno, *Macromolecules* **24**, 2348 (1991)
- 106) M. Jansson, P. Li, P. Stilbs, *J. Phys. Chem.* **91**, 5279 (1987)
- 107) P. Li, M. Jansson, P. Stilbs, *J. Colloid Interface Sci.* **142**, 593 (1991)
- 108) R. Bacaloglu, A. Blasko, C. A. Bunton, G. Cerichelli, A. Shirazi, *Langmuir* **7**, 1107 (1991)
- 109) R. Ebelhäuser, H. W. Spiess, *Makromol. Chem.* **188**, 2935 (1987)
- 110) T. Fahmy, J. Wesser, H. W. Spiess, *Angew. Makromol. Chem.* **166/167**, 39 (1989)
- 111) B. Durairaj, F. D. Blum, *Langmuir* **5**, 370 (1989)
- 112) R. J. Gambogi, F. D. Blum, *J. Colloid Interface Sci.* **140**, 525 (1990)
- 113) Y. X. Zhang, A. H. Da, G. B. Butler, T. E. Hogen-Esch, *J. Polym. Sci., Part A: Polym. Chem.* **30**, 1383 (1992)
- 114) R. G. Laughlin, "Solvation and Structural Requirements of Surfactant Hydrophilic Groups", in: "Advances in Liquid Crystals", G. H. Brown, Ed., Vol. 3, 41 pp, Academic Press, New York 1978
- 115) G. Brezezinski, A. Laschewsky, unpublished
- 116) T. Miyashita, Y. Arito, M. Matsuda, *Macromolecules* **24**, 872 (1991)
- 117) W. Richtering, R. Löffler, W. Burchard, *Macromolecules* **25**, 3642 (1992)
- 118) Y. Morishima, S. Nozakura, *J. Polym. Sci., Polym. Symp.* **74**, 1 (1986)
- 119) G. S. Pop, Yu. V. Tanchuk, *Ukr. Khim. Zh.* **45**, 991 (1979)
- 120) W. Nitsch, W. Kremnitz, G. Schwyer, *Ber. Bunsen-Ges. Phys. Chem.* **91**, 218 (1987)
- 121) T. Okubo, *J. Colloid Interface Sci.* **125**, 386 (1988)
- 122) T. Michel, personal communication
- 123) K. Kamide, M. Saito, T. Akedo, *Polymer International* **27**, 35 (1992)
- 124) P. Anton, J. Heinze, A. Laschewsky, *Langmuir*, in press
- 125) J. C. Salamone, W. C. Rice, "Polyampholytes" in: "Encyclopedia of Polymer Science and Technology", J. I. Kroschwitz, Ed., 2nd edition, Vol. 11, 514 pp, Wiley-Interscience, New York 1988

- ¹²⁶⁾ P. H. Elworthy, A. T. Florence, C.B. MacFarlane, “*Solubilization by Surface-Active Agents*”, 68 ff., Chapman and Hall, London 1968
- ¹²⁷⁾ “*Surfactants in Consumer Products*”, J. Falbe, Ed., Springer, Heidelberg 1987
- ¹²⁸⁾ Y. J. Yang, J. B. F. N. Engberts, *Eur. Polym. J.* **28**, 881 (1992)
- ¹²⁹⁾ A. Laschewsky, T. D. Lomax, unpublished
- ¹³⁰⁾ S. Förster, M. Schmidt, M. Antonietti, *Polymer* **31**, 781 (1990)
- ¹³¹⁾ M. Schmidt, *Macromolecules* **24**, 5361 (1991)
- ¹³²⁾ S. Förster, M. Schmidt, M. Antonietti, *J. Phys. Chem.* **96**, 4008 (1992)
- ¹³³⁾ F. Grieser, C. J. Drummond, *J. Phys. Chem.* **92**, 5580 (1988)
- ¹³⁴⁾ K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **99**, 2039 (1977)
- ¹³⁵⁾ D. C. Dong, M. A. Winnik, *Can. J. Chem.* **62**, 2560 (1984)
- ¹³⁶⁾ K. W. Street, jr, W. E. Acree, jr, *Analyst (London)* **111**, 1197 (1986)
- ¹³⁷⁾ P. Anton, A. Laschewsky, to be published
- ¹³⁸⁾ M. Kiefer, *Dissertation*, Universität Freiburg (Germany) 1990